Electronic Supplementary Information

Ion-pairing assemblies of heteroporphyrin-based π -electronic cation with various counteranions

Masaki Fujita, Yohei Haketa, Hiroki Tanaka, Nobuhiro Yasuda and Hiromitsu Maeda*

Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, Kusatsu 525–8577, Japan, Fax: +81 77 561 2659; Tel: +81 77 561 5969; E-mail: maedahir@ph.ritsumei.ac.jp and Diffraction and Scattering Division, Japan Synchrotron Radiation Research Institute, Sayo 679–5198, Japan

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1. Synthetic procedures and spectroscopic data

General procedures. Starting materials were purchased from FUJIFILM Wako Pure Chemical Industries Ltd., Nacalai Tesque Inc., Tokyo Chemical Industry Co., Ltd., and Sigma-Aldrich Co., and were used without further purification unless otherwise stated. 5,10,15,20-Tetraphenyl-21-thiaporphyrin 1[S1] and the NiII complex 1ni⁺ as a Cl⁻ ion pair (1ni⁺-Cl⁻)^[S2] were prepared according to the literature procedures. NMR spectra used in the characterization of products were recorded on a JEOL ECA-600 600 MHz spectrometer. All NMR spectra were referenced to solvent. UV-visible spectra were recorded on a Hitachi U-3500 spectrometer. Highresolution (HR) electrospray ionization mass spectrometry (ESI-MS) was recorded on a BRUKER microTOF using ESI-TOF method. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was recorded on a Shimadzu Axima-CFRplus. TLC analyses were carried out on aluminum sheets coated with silica gel 60 (Merck Column chromatography was performed on 5554). Sumitomo alumina KCG-1525 and Wakogel C-300.

Ni^Ⅱ of 5,10,15,20-tetraphenyl-21complex thiaporphyrin as a BF_4^- ion pair, $1ni^+-BF_4^-$. To a MeOH solution (3 mL) of $1ni^+$ -Cl⁻ (28.0 mg, 38.6 μ mol) was added AgBF₄ (13.0 mg, 66.8 µmol), and the reaction mixture was stirred at r.t. for 15 min, followed by filtration and evaporation to dryness. The residue was purified by silica gel column chromatography (Wakogel C-300; eluent: 5% MeOH/CH2Cl2) and was recrystallized from CH₂Cl₂/*n*-hexane to afford $1ni^+$ -BF₄⁻ (13.12 mg, 16.9 µmol, 44%) as a brown solid. $R_f = 0.17 (5\%)$ MeOH/CH₂Cl₂). The signals in ¹H NMR (600 MHz, CDCl₃, 20 °C), observed at 9.75, 7.49, 7.47, 7.46, and 6.05 ppm, were too broad to discuss in detail due to the paramagnetic Ni^{II}, whereas the signals in ${}^{13}C{}^{1}H$ NMR (151 MHz, CDCl₃, 20 °C) were not detected. UV/vis (CH₂Cl₂, $\lambda_{max}[nm]$ (ϵ , 10⁵ M⁻¹cm⁻¹)): 289 (0.21), 347 (0.17), 432 (0.89), 530 (0.090), 700 (0.027). HRMS (ESI-TOF) m/z: $[M - BF_4]^+$ Calcd for C44H₂₈N₃SNi 688.1352; Found 688.1352. MALDI-TOF-MS: m/z (% intensity): (negative) 87.0 (100). Calcd for BF4: ([M -C44H28N3SNi]-): 87.00.



Ni^{II} complex of 5,10,15,20-tetraphenyl-21thiaporphyrin as a PF₆⁻ ion pair, $1ni^+$ -PF₆⁻. To a MeOH solution (3 mL) of $1ni^+$ -Cl⁻ (28.9 mg, 40.0 µmol) was added AgPF₆ (20.2 mg, 79.9 µmol) and the reaction mixture was stirred at r.t. for 15 min, followed by filtration

and evaporation to dryness. The residue was purified by silica gel column chromatography (Wakogel C-300; eluent: 5% MeOH/CH₂Cl₂) and was recrystallized from CH_2Cl_2/n -hexane to afford $1ni^+$ -PF₆ (22.3 mg, 26.7 µmol, 67%) as a brown solid. $R_f = 0.33$ (5% MeOH/CH₂Cl₂). The signals in ¹H NMR (600 MHz, CDCl₃, 20 °C), observed at 9.96 (s, 2H, β-CH), 9.04–8.89 (β-CH), 8.24 (d, 4H, Ph-H), 8.09 (d, 4H, Ph-H), and 7.93–7.79 (m, 4H, Ph-H) ppm, were too broad to discuss in detail, whereas the signals in ¹³C{¹H} NMR (151 MHz, CDCl₃, 20 °C) were not fully detected. UV/vis (CH₂Cl₂, λ_{max} [nm] (ϵ , 10⁵ M⁻¹cm⁻¹)): 289 (0.22), 347 (0.20), 432 (0.88), 554 (0.095), 688 (0.029). HRMS (ESI-TOF) m/z: $[M - F_6P]^+$ Calcd for C44H28N3SNi 688.1352; Found 688.1352. [M -C₄₄H₂₈N₃SNi]⁻ Calcd for F₆P 144.9647; Found 144.9647. This compound was further characterized by singlecrystal X-ray analysis.



Ni^Ⅱ complex 5,10,15,20-tetraphenyl-21of thiaporphyrin as a $B(C_6F_5)_4^-$ ion pair, $1ni^+-B(C_6F_5)_4^-$. To a MeOH solution (10 mL) of **1ni**⁺-Cl⁻ (31.7 mg, 43.7 µmol) was added Li⁺ salt of tetrakis(pentafluorophenyl)borate (LiB(C_6F_5)₄) (30.5 mg, 44.5 µmol) and the reaction mixture was stirred at r.t. for 1 h, followed by filtration and evaporation to dryness. The residue was purified by silica gel column C-300; chromatography (Wakogel eluent: 5% MeOH/CH₂Cl₂) and was recrystallized from acetone/nhexane to afford 1ni⁺-B(C₆F₅)₄⁻ (46.0 mg, 33.6 µmol, 77%) as a purple solid. $R_f = 0.70 (5\% \text{ MeOH/CH}_2\text{Cl}_2).$ The signals in ¹H NMR (600 MHz, CDCl₃, 20 °C), observed at 9.88 (s, 2H, β-CH), 9.00 (s, 4H, β-CH), 8.90 (s, 2H, β-CH), 8.15–8.13 (m, 4H, Ph-H), 8.07– 8.05 (m, 4H, Ph-H), 7.91-7.85 (m, Ph-H), and 7.81-7.79 (m, 4H, Ph-H) ppm, were too broad to discuss in detail, whereas the signals in ¹³C{¹H} NMR (151 MHz, CDCl₃, 20 °C) were not fully detected. UV/vis (CH₂Cl₂, $\lambda_{max}[nm]$ (ϵ , 10⁵ M⁻¹cm⁻¹)): 290 (0.22), 431 (1.1), 527 (0.10), 717 (0.026). HRMS (ESI-TOF) m/z: [M - $C_{24}BF_{20}$]⁺ Calcd for $C_{44}H_{28}N_3SN_i$ 688.1352; Found $688.1352. \ [M - C_{44}H_{28}N_3SNi]^- \ Calcd \ for \ C_{24}BF_{20}$ 678.9783; Found 678.9783. This compound was further characterized by single-crystal X-ray analysis.



Ni^Ⅱ complex of 5,10,15,20-tetraphenyl-21thiaporphyrin as a PCCp⁻ ion pair, 1ni⁺-PCCp⁻. To a MeOH solution (3 mL) of $1ni^+$ -Cl⁻ (9.49 mg, 13.1 μ mol) added sodium pentacyanocyclopentadienide was $(NaPCCp)^{[S3]}$ (2.48 mg, 13.0 $\mu mol)$ and the reaction mixture was stirred at r.t. for 1 h, followed by filtration and evaporation to dryness. The residue was purified by silica gel column chromatography (Wakogel C-300; eluent: 5% MeOH/CH2Cl2) and was recrystallized from CH₂Cl₂/n-hexane to afford 1ni⁺-PCCp⁻ (7.05 mg, 8.01 µmol, 61%) as a purple solid. $R_f = 0.68 (5\%)$ MeOH/CH₂Cl₂). ¹H NMR (600 MHz, CDCl₃, 20 °C): δ (ppm) 11.42 (s, 2H, β-CH), 10.13 (s, 2H, β-CH), 10.02 (s, 2H, β -CH), 8.45 (s, 2H, β -CH), 8.23 (d, J = 7.2 Hz, 4H, Ph-H), 8.16 (d, *J* = 6.6 Hz, 4H, Ph-H), 8.01 (t, *J* = 7.2 Hz, 4H, Ph-H), 7.90 (t, J = 7.2 Hz, 4H, Ph-H), 7.81 (t, J = 8.4 Hz, 4H, Ph-H) (the signals in ${}^{13}C{}^{1}H$ NMR (151 MHz, CDCl₃, 20 °C) were not fully detected). UV/vis (CH₂Cl₂, $\lambda_{max}[nm]$ (ϵ , 10⁵ M⁻¹cm⁻¹)): 292 (0.35), 431 (1.2), 526

(0.12), 715 (0.031). HRMS (ESI-TOF) m/z: [M – $C_{10}N_5$]⁺ Calcd for $C_{44}H_{28}N_3SNi$ 688.1352; Found 688.1352. [M – $C_{44}H_{28}N_3SNi$]⁻) Calcd for $C_{10}N_5$ 190.0157; Found 190.0157. This compound was further characterized by single-crystal X-ray analysis.



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- [S2] (a) C. E. Stilts, M. I. Nelen, D. G. Hilmey, S. R. Davies, S. O. Gollnick, A. R. Oseroff, S. L. Gibson, R. Hilf and M. R. Detty, J. Med. Chem., 2000, 43, 2403–2410; (b) D. G. Hilmey, M. Abe, M. I. Nelen, C. E. Stilts, G. A. Baker, S. N. Baker, F. V. Bright, S. R. Davies, S. O. Gollnick, A. R. Oseroff, S. L. Gibson, R. Hilf and M. R. Detty, J. Med. Chem., 2002, 45, 449–461.
- [S3] (a) O. W. Webster, J. Am. Chem. Soc., 1965, 87, 1820–1821; (b) T. Sakai, S. Seo, J. Matsuoka and Y. Mori, J. Org. Chem., 2013, 78, 10978–10985.







2. X-ray crystallographic data

Method for single-crystal X-ray analysis. Crystallographic data are summarized in Table S1. A single crystal of $1ni^+-Cl_{tri}$ was obtained by vapor diffusion of *n*-hexane into a CHCl₃ solution. The data crystal was a brown prism of approximate dimensions 0.30 mm \times 0.20 mm \times 0.20 mm. A single crystal of 1ni⁺-Cl⁻_{ortho} was obtained by vapor diffusion of *n*-pentane into a THF solution in the presence of 1,3-bis(3,4-diethylpyrrol-2-yl)-1,3-propanedione BF₂ complex^[S4] **2b** (1 equiv). The data crystal was a purple plate of approximate dimensions 0.240 mm \times 0.100 mm \times 0.056 mm. A single crystal of $1ni^+$ -PF₆⁻ was obtained by vapor diffusion of *n*-pentane into a CH₂Cl₂ solution. The data crystal was a brown prism of approximate dimensions 0.350 mm \times 0.152 mm \times 0.110 mm. A single crystal of **1ni**⁺- $B(C_6F_5)_4$ was obtained by vapor diffusion of *n*-hexane into a chlorobenzene solution. The data crystal was a brown block of approximate dimensions $0.02 \text{ mm} \times 0.02 \text{ mm} \times 0.01 \text{ mm}$. A single crystal of $1ni^+$ -PCCp⁻ was obtained by vapor diffusion of n-hexane into a CH₂Cl₂ solution. The data crystal was a brown plate of approximate dimensions 0.10 mm \times 0.10 mm \times 0.08 mm. A single crystal of **1ni**⁺-**2a** · Cl⁻ was obtained by vapor diffusion of *n*-hexane into a CH₂Cl₂ solution of $1ni^+$ -Cl⁻ and 1,3-di(pyrrol-2-yl)-1,3-propanedione BF₂ complex^[S5] 2a in the 1:1 ratio. The data crystal was a brown plate of approximate dimensions $0.30 \text{ mm} \times 0.30 \text{ mm} \times 0.10 \text{ mm}$. A single crystal of $1 \text{ni}^+ 2 \text{b} \cdot \text{Cl}^-$ was obtained by vapor diffusion of *n*-hexane into a CCl₄ solution of $1ni^+$ -Cl⁻ and 2b in the 1:1 ratio. The data crystal was a brown block of approximate dimensions 0.100 mm \times 0.050 mm \times 0.030 mm. A single crystal of 1ni⁺-2c Cl⁻ was obtained by vapor diffusion of *n*-hexane into a CHCl₃ solution of 1ni⁺-Cl⁻ and 1,3-bis(3,4-difluoropyrrol-2-yl)-1,3-propanedione BF₂ complex^[S6] 2c in the 1:1 ratio. The data crystal was a purple block of approximate dimensions 0.05 mm \times 0.03 mm \times 0.03 mm. The data of 1ni⁺-Cl⁻tri, 1ni⁺-PCCp⁻, and 1ni⁺-2a[•]Cl⁻ were collected at 90 K on a Bruker D8 Venture diffractometer with MoK α radiation ($\lambda = 0.71073$ Å) focused by multilayer confocal mirror, whereas those of 1ni⁺-Cl⁻ ortho, 1ni⁺-PF₆⁻, and 1ni⁺-2b·Cl⁻ were collected at 100 K on a DECTRIS PILATUS3 CdTe 1M diffractometer with Si (311) monochromated synchrotron radiation ($\lambda = 0.4125$, 0.4125, and 0.4127 Å, respectively) at BL02B1 (SPring-8).^[S7] The data of $1ni^+-B(C_6F_5)_4^-$ and $1ni^+-2c\cdot Cl^-$ were collected at 90 K on a Dectris EIGER X 1M diffractometer with Si (111) monochromated synchrotron radiation ($\lambda = 0.81106$ and 0.81063 Å, respectively) at BL40XU (SPring-8).^[S8] All the structures were solved by dual-space method. The structures were refined by a full-matrix least-squares method by using a SHELXL 2014^[S9] (Yadokari-XG).^[S10] In each structure, the non-hydrogen atoms were refined anisotropically. CIF files (CCDC-2167300–2167307) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Table S1 Crystallographic details.

fermulaCalla,NSCNCAIIa- CHG,NSCN-CAII- CHEN,NSCN-CAII		$1ni^+-Cl_{tri}^-$	1ni ⁺ -Cl ⁻ ortho	1ni+-PF6-	$1ni^+-B(C_6F_5)_4^-$	1ni ⁺ -PCCp ⁻
fpr990.45970.2104 2.21441.06109.47crystal stem0.30 x 0.20 x 0.200.210 x 0.100 x 0.102 x 0.1020.102 x 0.10	formula	C44H28N3SClNi·C6H14· CHCl3	$C_{44}H_{28}N_3SClNi\cdot C_4H_8O$	C44H28N3SNi · PF6 · 2CH2Cl2	C44H28N3SNi·C24BF20· C6H5Cl	$\begin{array}{c} C_{44}H_{28}N_3SNi\cdot C_{10}N_5\cdot\\ 2CH_2Cl_2\end{array}$
crysnl size, and crysnl system0.30 × 0.20 × 0.200.30 × 0.20 × 0.200.40 × 0.01 × 0.010.00 × 0.00 × 0.010.10 × 0.01 × 0.01segre group segre groupPT (mo.2)PT (mo.6)PT (mo.6)PT (mo.7)1.32112(3)1.3334(1.2)a.A1.2837(3)2.3185(4)1.0517(1)1.51908(4)1.5374(1.4)1.5374(1.4)b.A1.7347(3)2.3185(4)1.023(1)6.3908(2)9.2334(1.4)1.5374(1.4)c.A1.7347(3)2.318(1.4)1.923(3)6.3908(2)9.2334(1.4)1.5374(1.4)c.A1.7347(3)9.149(1.4)1.923(3)6.3908(2)9.2334(1.4)1.5374(1.4)c.A7.814(3)9.149(1.4)9.0438(6)8.23(3)9.23(4.4)9.23(3.4)c.A7.814(3)9.149(1.4)9.245(1.4)9.23(3.4)9.23(3.4)9.23(3.4)c.A7.814(3)9.161(1.4)1.536(1.4)9.23(3.4)9.15(1.4)9.23(3.4)c.A7.814(3)9.161(1.4)1.536(1.4)1.62(7)1.53(1.4)9.23(1.4)c.A9.751.53(1.4)1.62(1.4)1.53(1.4)1.62(7)1.53(1.4)c.A9.051.53(1.4)1.53(1.4)1.53(1.4)1.53(1.4)1.53(1.4)c.A9.051.53(1.4)1.53(1.4)1.53(1.4)1.53(1.4)1.53(1.4)c.A9.051.53(1.4)1.53(1.4)1.53(1.4)1.53(1.4)1.53(1.4)c.A9.051.53(1.4)1.53(1.4)1.53(1.4)1.53(1.4)1.53(1.4)c.A9.153(1.4)	fw	930.45	797.02	1004.28	1481.06	1049.46
cryptal systeminditioninditioninditioninditioninditionspace graph// funo 21// funo 21// funo 21// funo 21// funo 21space graph// funo 21// funo 21// funo 21// funo 21// funo 21s, A1.2371(0)2.18(4)// funo 21// funo 21// funo 21// funo 21c, A8.237(2)2.18(4)// funo 21// funo 21// funo 21// funo 21// funo 21c, A8.237(2)8.24(3)// funo 21// funo 21// funo 21// funo 21// funo 21g, A6.538(3)7.64(2)// funo 21// funo 21// funo 21// funo 21// funo 21g, A6.538(3)7.64(2)// funo 21// funo 21// funo 21// funo 21// funo 21g, A0.7571.64(2)// funo 21// funo 21// funo 21// funo 21// funo 21g, G,	crystal size, mm	$0.30 \times 0.20 \times 0.20$	$0.240 \times 0.100 \times 0.056$	$0.350 \times 0.152 \times 0.110$	$0.02 \times 0.02 \times 0.01$	$0.10\times0.10\times0.08$
space groupPí (m. 2)Píce (m. 6)Pí (m. 2)Pí (m. 2)a. Å15.8(%)14.8(%)13.71(3)15.211(2)13.945(1)b. Å12.327(1)21.8(%)16.031(1)15.702(4)13.74(4)c. Å13.347(5)21.8(%)16.031(1)16.702(4)40.75(2)a. %13.84(3)996.338(2)92.20(4)j. **8.82(3)994.503(2)92.20(4)j. **8.42(3)0.212(2)92.30(4)92.30(4)j. *24.8(3)90.445(6)24.5(3)92.3(4)j. A. 10.20124.8(3)90.400.404(4)0.51(1)92.7(7)j. A. 10.20124.8(3)96.71.53(2)1.45(7)j. A. 10.301100(2)0.0210.712*0.712*j. m. 10.756*0.164*0.202*0.712*0.712*j. m. 6. 10.371.5313.5361.641.5110.710*j. a. 6. 10.3110.755*1.5310.5310.5161.511j. a. 6. 10.3210.3910.412*0.61310.6111.12*j. a. 6. 10.3210.3910.6140.6630.8111.15*j. a. 6. 10.3210.3910.6410.6611.5*1.5*j. a. 6. 10.3210.3930.5*0.115*1.5*1.5*j. j. a. 10.3010.102*0.5*1.5*1.5*1.5*j. j. j	crystal system	triclinic	orthorhombic	monoclinic	triclinic	triclinic
a, Å18389(9)14.84(3)13.77(3)13.2112(3)15.934(12)b, Å12.257(10)23.185(4)16.057(19)15.906(4)15.374(14)c, Å17.3475(2)20.185(4)19.021(5)15.024(4)20.457(5)a, "a80.827(5)9042.96(2)72.20(3)g, "a66.538(5)90074.502(2)89.60(3)y, "a66.538(5)90074.502(2)69.239(4)y, "a66.538(5)1400156.6416.39422.67(7)p, au, gen?13.761400156.6416.39422.67(7)p, au, gen?13.761400123.01301.51(1)72.97(7)mm"0.756710400.02290(2)90(2)mo fordina350721.930123.013151172.97no dreifina55366183.9313.6434.54y, (1 > 2,17)0.1620.3120.41250.81100.71073*mo fordina5530.6140.66730.8110.71073*with (2 > 2,01)0.1280.3910.14250.81100.611y, (2 > 2,01)0.1280.3910.16090.6671.492formulaCall-SNSCINi- CLISNSCINi- CLISNSCINi- CLISNSCINi- 	space group	<i>P</i> 1 (no. 2)	<i>Pbca</i> (no. 61)	$P2_1/c$ (no. 14)	<i>P</i> 1 (no. 2)	<i>P</i> 1 (no. 2)
b.Åi2573(0)21.85(4)16.057(7)15.996(4)15.374(1)c.Å30.477(1)521.49(4)90423(5)16.7024(4)24.075(2)β.*80.82(3)90.4090.485(6)87.227(2)88.6(3)β.*24.54(3)90.4090.485(6)87.227(2)89.86(3)β.*24.54(3)554(2)204.85(6)87.227(2)89.86(3)β.ab24.54(2)204.81204.81205.14(4)472.627(7)β.ab24.5420.4420.4420.4772.627(7)β.ab105710.61102.010.05(1)472.627(7)μ.man*0.756*10.62102.220.72.490.22μ.on ofraige effit10.756*10.6210.2290.27winables15373536183113167297winables55363.510.0740.816*145μ.(γ-2.07)0.1020.910.764140.61142.61μ.(γ-2.07)0.103*0.910.764144.930.116*μ.(γ-2.07)0.103*0.910.141.94149.14149.14μ.(γ-2.07)0.103*0.910.141.94149.14μ.(γ-2.07)0.103*0.910.141.94149.14μ.(γ-2.07)10.34.741.304.75149.14149.14μ.(γ-2.07)10.34.741.304.75149.14149.14μ.(γ-2.07)10.34.751.320.141.41.14149.14μ.(γ-2.07)10.34.741.320.141	a, Å	11.8089(9)	14.864(3)	13.771(3)	13.2112(3)	13.9345(12)
c, Å17.3475(15)21.949(4)9.023(5)16.7024(4)24.075(2)a, a'90.827(3)9062.95(2)75.20(4)g, a'75.40(3)90.481(2)90.425(3)85.6(1)y, k'65.35(3)909074.503(2)69.239(4)y, k'25.85(3)75.6(2)40.94.8(2)3001.55(14)475.2(7)y, k'13.7616.001.55616.911.475y, k'0.020.0290(2)90(2)90(2)y, mm ⁻¹ 0.756*/10.940.202*/90(2)90(2)no, of unique cellus350712.53012.53015.117297no, of unique cellus537855795710.9422350no, of unique cellus53764120.07640.07630.0173*kt (J > 2.01)0.1020.03910.07640.06730.0181*kt (J > 2.01)0.1020.99380.16000.16631.049GOF1.043.41.0451.0601.0661.049fromulaC, HashNSCIN* C, LabeNSOPF L, 2.86(2), C.1.C, HasNSCIN* C, LabeNSOPF C, LabeNSOPF L, 2.86(1), C.1.1.262(1)1.263(1)reystal size, mi0.03.4.0.030.05 × 0.03 × 0.030.051.365(1)1.475fromula10.4000.05 × 0.03 × 0.031.253(1)1.253(1)1.253(1)reystal size, mi10.000 × 0.05 × 0.03 × 0.031.253(1)1.253(1)1.253(1)reystal size, mi13.06(0)12.354(1)1	b. Å	12.2573(10)	23.185(4)	16.0517(19)	15.9096(4)	15.3744(14)
a**80.827(3)909062.35(2)79.220(4) β^* 75.40(3)9090.885(6)7.227(2)89.86(1) γ^* 66.58(7)9090.885(6)7.227(2)89.82(3) γ^* 245.8(3)7564(2)4204.8(12)300.55(14)4726.2(7) β_{max} 1.3761.4001.5861.6391.475 Z 28424 $7.K$ 90(2)100(2)100(2)90(2)90(2) μ mur10.756*0.164*0.202*0.752*0.731*no. of enfins350721530123001351177297no. of unique refins15737858796571094232350variabes553530.3910.07640.6730.0811 $k_1(r > 2.a(f))$ 0.1280.4125*0.4125*0.4125*0.01773* $k_1(r > 2.a(f))$ 0.1280.3910.37640.66730.0811 $w^* e(r > 2.a(f))$ 0.5120.9980.16461.775 $formula$ 1.942.1.9451.9641.775 $egree groupPT (max, PT (m$	c. Å	17.3475(15)	21.949(4)	19.023(3)	16.7024(4)	24.075(2)
β° 78.40079094.485(6)87.27(2)89.86(3) γ° 6538(3)90904.502(3)6239(4) j, λ^{3} 245.8(3)756(2)424.8(2)16394736.2(7) $j, habs ger1^{30}$ 1.7001.4001.5801.6391.4175 $j, mars0.7020.02(2)0.02(2)0.02(2)0.02(2)0.02(2)j, mm^{1}0.7560.1640.202 +0.07520.731*no of unique refla37072.53366181311345a, f(1 > 20/f)0.7107*0.4125*0.8106*0.7107*no funique refla0.707*0.4125*0.8106*0.6173k_{1}^{*}(1 > 20/f)0.1280.3910.07640.16430.1707*k_{2}^{*}(1 > 20/f)0.1280.3910.1640.1750.1643k_{3}^{*}(1 > 20/f)0.1280.3910.06740.16430.175e_{3}^{*}(1 > 20/f)0.1280.3910.06740.16430.175e_{3}^{*}(1 > 20/f)0.1280.3910.06740.16430.175e_{3}^{*}(1 > 20/f)0.2580.1690.16430.175e_{3}^{*}(1 > 20/f)0.3910.0510.0510.16430.175e_{3}^{*}(1 > 20/f)0.3910.0510.16430.1750.1643e_{3}^{*}(1 > 20/f)0.3910.0510.16430.1750.1643e_{3}^{*}(1 > 20/f)0.3910.0510.16430.16430.1643e_{3}^$	a,°	80.827(3)	90	90	62.936(2)	79.220(4)
μ μ μ(AC)(AC)(AC)(AC)(AC)μ.da gem32245 8(3)7564(2)4204.8(12)3001.5(14)47.62(7)μ.da gem31.3761.4001.5861.6391.475Z28424T.K.90(3)100(2)100(2)90(2)90(2)μ.mm ⁴ 0.756*0.102.1100(2)90(2)90(2)no. of refins350721593013301151177297no. of unique refins157785870.65710442323013.55330.7640.8106*0.71073*variables57370.4125*0.4125*0.8106*0.073k. (1 > 2 \La (1))0.10280.03910.07640.06730.0811k. (1 > 2 \La (1))0.1281.6851.6061.4751.475formulaCallan/SCIN* Call	ß.°	78.140(3)	90	90.485(6)	87.227(2)	89.861(3)
$r, Å^3$ 2448.037564(2)4204.8(12)3001.55(14)4226.2(7) ρ_{Abce} gem³1.3761.400.1.5861.639.1.475. Z 28424 T, K 90(2)100(2)90(2)90(2)90(2) μ mm²0.756°0.164°0.202°0.732°0.731° $no. of enling55070.164°0.202°0.194232350no. of enling55375336618831345x (1 > Z\alpha)0.4125°0.8106°0.7107°0.811winbles5530.330.6110.06730.0611winbles5530.330.6120.1166°0.7107°winbles5530.330.6110.06730.0811winbles0.5120.09380.18000.14630.175GOF1.0431.0851.0601.0661.049winblesCarl-SNSCNi$	r, v. °	66.538(3)	90	90	74.503(2)	69.239(4)
no. of cells phalagem"1.4001.56 (a)1.6391.475 (b)Z28424T.K90(2)100(2)100(2)90(2)90(2) μ mm ⁻¹ 0.756*0.164*0.202*0.732*0.731*no. of reflns350772159301233013151177297no. of nuique reflns157378879657104232350 λ_A 0.71073*0.4125*0.4125*0.81106*0.71073* λ_1 0.1280.09310.07640.66730.0811 $w_2(r > 2o(r))$ 0.1280.09310.07640.66730.0811 $w_2(r > 2o(r))$ 0.1280.09310.07640.41630.1775 GOF 1.0481.0601.4060.17750.419 $fromulanir -2n-C1nir -2n-C1nir -2n-C1nir -2n-C1formulaCall-BNSCINirCall-BNSOFFCall-BNSOFFCall-BNSOFFVeystal size, mm0.30 × 0.0100.005 × 0.05 × 0.03 × 0.$	V. Å ³	2245.8(3)	7564(2)	4204.8(12)	3001.55(14)	4726.2(7)
panageminlatelatelatelatelateZ28424T.K90(2)100(2)90(2)90(2)90(2)µmm ⁻¹ 0.756*0.164*0.202*0.732*0.731*no. of unigue153772159302123013151177297no. of unigue1537785870.661831345xaibles53536412*0.8110*0.713*kÅ0.10280.3910.6740.8110*0.713*k/(2-2cf))0.10280.3910.6740.06730.8811k% (2-2cf)0.9280.18000.4430.1775GOF1.0431.0851.661.4630.1775formulaCall-BaNSCIN: Call-BINSO-F2*DCCall-BaNSCIN: Call-BINSO-F2*DC1.492fw1.88.451.99451.664.911.257fw1088.451.99450-12*2C14 Call-BINSO-F2*D151.412NSCIN: 	$\rho_{\rm relad}$ g cm ⁻³	1 376	1 400	1 586	1 639	1 475
I I	7	2	8	4	2	4
r, km^{-1} 0.02 0.002 0.002 0.020^{-1} 0.02^{-1} <td>TK</td> <td>2 90(2)</td> <td>100(2)</td> <td>100(2)</td> <td>2 90(2)</td> <td>90(2)</td>	TK	2 90(2)	100(2)	100(2)	2 90(2)	90(2)
μ mm6.1506.1646.1646.1646.1646.1746.174mo. of unique reflus15737215930123013151177297mo. of unique reflus5535336618831345 λ, \dot{A} 0.71073"0.4125 h 0.4125 h 0.8110 h 0.7073" $k_1 (J > 2a(J))$ 0.0280.0930.14630.1775 GOT 1.0431.0851.0601.0661.049 $wR_2 (J > 2a(J))$ 0.25120.09380.18000.14630.1775 GOT 1.0431.0851.0601.0661.049formulaCall-BNSOCIN: C.HBNNO.0FF: L.258CH-LC:Call-BNSOCIN: C.HBNNO.0FF: C.HBNNO.0FF: C.HBNNO.0FF: C.HBNNO.0FF: 	1, K	90(2) 0.756 <i>ª</i>	0.164^{b}	0.202^{b}	0 732 ^b	0.731 a
no. of runna no. of unique reflus no. of unique reflus to of unique reflus 	μ,	0.750	0.104	122201	0.752	77207
no. of unique reins15/3 /85/ /90 /109423230 $yariables$ 535361831345 $\lambda, \dot{\Lambda}$ 0.71073 /*0.4125 h 0.81106 h 0.71073 /* $k_1(z > 2cl)$)0.10280.03910.07640.06730.0811 $wR_2(z > 2cl)$)0.1280.09880.16000.14630.1775 GOF 1.0431.0851.0601.0661.049formulaCall-BN/SCIN: C_1H4BN/SCIN: C_1H5DN/SCIN: C_1H5DN/SCIN: C_1H5DN/SCIN: C_1H5DN/SCIN: C_1H5DN/SCIN: C_1H5DN/SCIN: C_1H5DN/SCIN: C_	no. of refins	350//	213930	123301	31311	22250
Variabes5535536018551345 $\dot{\lambda}$ Å0.71073"0.4125^h0.4125^h0.81106^h0.71073" \dot{k} ($l > 2c(l)$)0.10280.03910.07640.66730.0811 wR_2 ($l > 2c(l)$)0.25120.09380.18000.14630.1775 OOF 1.0431.0851.0601.0661.049Ini*-2a CI-Ini*-2b CI-Ini*-2c CI-formulaCaH2NSCRNi: CaH3NSCRNI: CaH3NSCRNI: CaH3NSCRNI: CAH3NS	no. of unique refins	15/3/	8387	9657	10942	32350
λ, Λ 0.71073^{-4} 0.4125^{-5} 0.4125^{-5} 0.81106^{-7} 0.71073^{-5} $R_1(I > 2\sigma(I))$ 0.1028 0.0391 0.0764 0.0673 0.0811 $w_i; (I > 2\sigma(I))$ 0.2512 0.03938 0.1800 0.1463 0.1775 GOF 1.043 1.085 1.060 1.066 1.049 $Ini^-2a C \Gamma$ $Ini^+2b C \Gamma$ $Ini^+2c C \Gamma$ formula $C_{aH_S}NSCNi;$ $C_{1H_S}NSO_2F_2CC14C_{aH_S}NSCNi;C_{1H_S}NSO_2F_2'C14C_{aH_S}NSO_2F_2'CC14C_{aH_S}NSO_2F_2'C14C_{aH_S}NSO_2F_2'C14C_{aH_S}NSO_2F_$	variables	553 0.51052.4	533 0.4105h	001	883	1345
$X_1(I \geq 2\alpha(I))$ 0.1028 0.0391 0.0764 0.0673 0.0871 $wR_2(I \geq 2\alpha(I))$ 0.2512 0.0938 0.1800 0.1463 0.1775 GOF 1.043 1.085 1.060 1.066 1.049 GOF 1.043 1.085 1.060 1.066 1.049 OOF 1.043 0.057 Cult Cult Cult Cult Cult Cult Description Des	λ, Α	0.71073*	0.4125	0.4125	0.81106 *	0.71073*
why $(t > 2a(t))$ 0.2512 0.0938 0.1800 0.1463 0.1475 GOF 1.043 1.085 1.060 1.066 1.049 GOF 1.043 1.085 1.060 1.066 1.049 Imi*2a CI- Imi*2b CI: Imi*2c CI- 1.066 1.049 formula CutHaBN_OD,Fr. CuHaBNSO,Fr. CuHaBNSO,Fr. CuHaBNSO,Fr. CuHaBNSO,Fr. CuHaBNSO,Fr. CuHaBNSO,Fr. CuHaBNSO,Fr. 1.258CHyclic CatHaSNSCNi: CuHaBNSO,Fr. H2O CutHaBNSO,Fr. CuHaBNSO,Fr. H2O CutHaBNSO,Fr. CuHaBNSO,Fr. H2O CutHaBNSO,Fr. CuHaBNSO,Fr. H2O CutHaBNSO,Fr. CuHaBNSO,Fr. H2O CutHaBNSO,Fr. CuHaBNSO,Fr. H2O CutHaBNSO,Fr. CuHaBNSO,Fr. H2O CutHaBNSO,Fr. CuHaBNSO,Fr. H2O CutHaBNSO,Fr. CuHaBNSO,Fr. H2O CutHaBNSO,Fr. H2O CutHaBNSO,Fr. H2O <th< td=""><td>$R_1 (I > 2\sigma(I))$</td><td>0.1028</td><td>0.0391</td><td>0.0764</td><td>0.06/3</td><td>0.0811</td></th<>	$R_1 (I > 2\sigma(I))$	0.1028	0.0391	0.0764	0.06/3	0.0811
COP 1.043 1.085 1.060 1.066 1.049 Ini*-2a-C1 Ini*-2b C1 Ini*-2c C1* Ini*	$wR_2 (I \ge 2\sigma(I))$	0.2512	0.0938	0.1800	0.1463	0.1775
InitialIni	GOF	1.043	1.085	1.060	1.066	1.049
formula $C_{nH}_{BNS}SCINi-C_{nH}_{BBNO}SF2-CL1C_{nH}_{BNSO}SCINi-C_{nH}_{BSNO}SF2-CL1C_{nH}_{BSNO}SCINi-C_{nH}_{BSNO}SF2-CL1fw1083.451394.751064.91crystal size, mm0.30 × 0.30 × 0.100.100 × 0.050 × 0.030.05 × 0.03 × 0.03crystal systemtriclinicmonoclinictriclinicspace groupP^{T} (no.2)P_{21/c} (no.14)P^{T} (no.2)a, Å13.066(3)12.96(2)13.2407(4)c, A15.987(4)27.519(15)14.7731(5)a, ^{\circ}15.987(4)02.088(18)84.024(3)\beta^{\circ}9.484(8)102.088(18)84.024(3)\beta^{\circ}9.330(8)9081.561(3)\beta^{\circ}9.333.5(10)5967(7)2363.86(13)\beta_{ades} genr31.4201.5531.496Z42T, K90(2)0.902q, mn^{-1}0.668×0.109b^{\circ}no. of mingue reflms17002131879no. of unique reflms170021531a_{Ades}1702816a_{Adas}0.7173*816a_{Adas}0.7173*816a_{Adas}0.71073*0.4127b^{\circ}a_{Adas}1.6020.902a_{Adas}0.703*0.902a_{Adas}0.703*0.9167b^{\circ}a_{Adas}0.703*0.9167b^{\circ}a_{Adas}0.703*0.9167b^{\circ}a_{Adas}0.703*0.9167b^{\circ}a_{Adas}0.70$						
fw1083.451394.751064.91crystal size, mm $.03 \times 0.30 \times 0.10$ $.010 \times 0.050 \times 0.03$ $.005 \times 0.03 \times 0.03$ crystal systemticlinicmonoclinicticlinicspace group P^{T} (no. 2) $P_{2/c}$ (no.14) P^{T} (no. 2) $a, Å$ 13.06(3) $12.962(9)$ $12.3536(4)$ $b, Å$ 13.295(3)17.107(12) $13.2407(4)$ $c, Å$ 13.95(3) $27.519(15)$ $14.7731(5)$ $a, °$ 13.935(9)90 $83.126(3)$ $a, °$ 91.848(8)90.2088(18) $84.02(3)$ $g, °$ 92.340(8)90.2088(18) $84.02(3)$ $g, °$ 93.510(1) $967(7)$ $2363.8(13)$ P_{Aads} 92.533.5(10) $967(7)$ $2363.8(13)$ P_{Aads} 92.102 1002 902 1002 $f, Å^3$ 91.92 1032 81.5613 r_{Aads} 92.102 1002 902 1002 f, K 902 1002 902 1002 g, mm^{-1} 1668^a 1019^b 8833 $no. of unique refin17021187918843no. of unique refin1703^a81692i_AÅ0.717^a81692i_AÅ0.717^a0.167^b0.8163^bi_AAA0.173^a0.167^b0.102^bi_AAA0.1073^a0.167^b0.102^b$		1ni⁺-2a·Cl⁻	1ni⁺-2b·Cl⁻	1ni⁺-2c·Cl⁻		
erystal size, mm $0.30 \times 0.30 \times 0.101$ $0.100 \times 0.050 \times 0.030$ $0.05 \times 0.03 \times 0.03$ crystal systemtriclinicmonoclinictriclinicspace group P_1^{-} (no. 2) P_1^{-} (no. 1) P_1^{-} (no. 2) a, \tilde{A} 13.066(3)12.962(9)12.3536(4) b, \tilde{A} 13.295(3)17.107(12)13.2407(4) c, \tilde{A} 15.987(4)27.519(15)14.7731(5) a, \circ 13.359(9)9083.126(3) a, \circ 91.484(8)10.088(18)84.02(3) g, \circ 92.340(8)9081.561(3) Y, \tilde{A}^3 23.51(1)5967(7)236.86(13) P_{akde} gcm ⁻³ 14.40.55314.90 Z 9023.85(13)14.90 μ mm ⁻¹ 0.668 ^a 0.109 ^b 0.834 ^b no. of reflns37.9613.187918843no. of reflns17.0210.5184.58variables67781.6692 $\lambda_{i} \tilde{A}$ 0.1073 ^a 0.4127 ^b 0.8163 ^b $\lambda_{i} (1 > 2\alpha(f))$ 0.9630.10670.8163 ^b	formula	1ni⁺-2a ·Cl ⁻ C ₄₄ H ₂₈ N ₃ SClNi ⁻ C ₁₁ H ₉ BN ₂ O ₂ F ₂ ⁻ 1.258CH ₂ Cl ₂	$\begin{array}{c} {\bf 1ni^{+}\text{-}2b \cdot Cl^{-}} \\ C_{44}H_{28}N_{3}SClNi \cdot \\ C_{19}H_{25}BN_{2}O_{2}F_{2} \cdot 2CCl_{4} \end{array}$	1ni⁺-2c ·Cl ⁻ C ₄₄ H ₂₈ N ₃ SClNi· C ₁₁ H ₅ BN ₂ O ₂ F ₆ ·H ₂ O		
crystal systemtriclinicmonoclinictriclinicspace group $P\bar{1}$ (no.2) $P_{1/c}$ (no.14) $P\bar{1}$ (no.2) a, \bar{A} 13.066(3)12.962(9)12.3536(4) b, \bar{A} 13.295(3)17.107(12)13.2407(4) c, \bar{A} 15.987(4)27.519(15)14.7731(5) $a, °$ 13.935(9)9083.126(3) $\beta, °$ 91.484(8)102.088(18)84.024(3) $\gamma, °$ 92.340(8)9081.561(3) $\gamma, Å^3$ 253.5(10)5967(7)2363.86(13) $\rho_{abd,} gcm^{-3}$ 1.4201.5531.496 Z 242 T, K 90(2)100(2)90(2) μ, mm^{-1} 0.668 "0.190 b0.834 bno. of enfins3739613187918843no. of unique refins17602105318458variables677816692 λ, \tilde{A} 0.7107 "0.4127 b0.81063 b $\mu, (1 > 2\alpha(T))$ 0.9630.10670.519	formula	1ni⁺-2a ·Cl ⁻ C ₄₄ H ₂₈ N ₃ SClNi· C ₁₁ H ₉ BN ₂ O ₂ F ₂ · 1.258CH ₂ Cl ₂ 1083.45	Ini*-2b·Cl- C44H28N3SCINi· C19H25BN2O2F2·2CCl4 1394.75	1ni⁺-2c ·Cl ⁻ C ₄₄ H ₂₈ N ₃ SClNi· C ₁₁ H ₃ BN ₂ O ₂ F ₆ ·H ₂ O 1064.91		
space group $P\bar{1}$ (no. 2) $P_{21/c}$ (no. 14) $P\bar{1}$ (no. 2) a, \bar{A} 13.066(3)12.962(9)12.3536(4) b, \bar{A} 13.295(3)17.107(12)13.2407(4) c, \bar{A} 15.987(4)27.519(15)14.7731(5) a, \circ 113.935(9)9083.126(3) β, \circ 91.484(8)102.088(18)84.024(3) γ, \bar{A}^{3} 2533.5(10)5967(7)2363.86(13) $\rho_{alcd,} gcm^{-3}$ 1.4205531496 Z 1100(2)90(2) μ, mm^{-1} 0.668 a 0.190 b 0.834 b no. of reflns3739613187918843no. of unique reflns17602105318458variables677816692 λ, \bar{A} 0.7107 a 0.4127 b 0.8160 b $R_1(I > 2\sigma(I))$ 0.9630.10670.8019	formula fw crystal size, mm	$\begin{array}{c} \textbf{1ni}^{+}\textbf{-2a}\cdot Cl^{-} \\ \hline \\ C_{44}H_{28}N_3SClNi^{-} \\ C_{11}H_9BN_2O_2F_2^{-} \\ 1.258CH_2Cl_2 \\ 1083.45 \\ 0.30\times0.30\times0.10 \end{array}$	$\begin{array}{c} 1ni^+ -2b \cdot Cl^- \\ C_{44}H_{28}N_3SClNi \cdot \\ C_{19}H_{25}BN_2O_2F_2 \cdot 2CCl_4 \\ 1394.75 \\ 0.100 \times 0.050 \times 0.030 \end{array}$	$\begin{array}{c} \textbf{1ni}^{+}\textbf{-2c}\cdot\text{Cl}^{-} \\ \hline C_{44}H_{28}N_{3}SClNi\cdot \\ C_{11}H_{5}BN_{2}O_{2}F_{6}\cdotH_{2}O \\ \hline 1064.91 \\ 0.05\times0.03\times0.03 \end{array}$		
a , Å13.06(3)12.96(29)12.3536(4) b , Å13.295(3)17.107(12)13.2407(4) c , Å15.987(4)27.519(15)14.7731(5) a , °113.935(9)9083.126(3) β , °91.484(8)102.088(18)84.024(3) γ , Å23.30(8)9081.561(3) γ , Å'253.5(10)5967(7)2363.86(13) ρ_{alcd} , gcm ⁻³ 1.4205957(7)2363.86(13) ρ_{alcd} , gcm ⁻³ 1.4201.5531.496 Z 9990(2)90(2) μ , mm ⁻¹ 0.668 a 0.190 b 0.834 b no. of reflns3739613187918843no. of unique reflns17602105318458variables677816692 λ , Å0.7107 a 0.4127 b 0.81063 b $k_1(I > 2\sigma(I))$ 0.9630.10670.519	formula fw crystal size, mm crystal system	$\begin{array}{c} {\bf 1ni^{+}-2a \cdot Cl^{-}} \\ \hline \\ C_{44}H_{28}N_{3}SClNi \cdot \\ C_{11}H_{9}BN_{2}O_{2}F_{2} \cdot \\ 1.258CH_{2}Cl_{2} \\ 1083.45 \\ 0.30 \times 0.30 \times 0.10 \\ triclinic \end{array}$	$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	Ini ⁺ -2c·Cl ⁻ C ₄₄ H ₂₈ N ₃ SClNi· C ₁₁ H ₃ BN ₂ O ₂ F ₆ ·H ₂ O 1064.91 0.05 × 0.03 × 0.03 triclinic		
b, Å13.295(3)17.107(12)13.2407(4)c, Å15.987(4)27.519(15)14.7731(5) α , °113.935(9)9083.126(3) β , °91.484(8)102.088(18)84.024(3) γ , °92.340(8)9081.561(3) γ , Å'2533.5(10)5967(7)2363.86(13) $\rho_{alcd,}$ gem ⁻³ 1.4201.5531.496Z242T, K90(2)100(2)90(2) μ , mm ⁻¹ 0.668 a0.190 b0.834 bno. of reflns3739613187918843no. of unique reflns17602105318458variables677816692 λ , Å0.7107 a'0.10670.81063 b $R_1(I > 2\sigma(I))$ 0.9650.10670.519	formula fw crystal size, mm crystal system space group	$\begin{array}{c} {\bf 1ni^{+}-2a \cdot Cl^{-}} \\ \hline \\ C_{44}H_{28}N_{3}SClNi \cdot \\ C_{11}H_{9}BN_{2}O_{2}F_{2} \cdot \\ 1.258CH_{2}Cl_{2} \\ 1083.45 \\ 0.30 \times 0.30 \times 0.10 \\ triclinic \\ P\bar{1} \ (no. 2) \end{array}$	$1ni^+ -2b \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{19}H_{25}BN_2O_2F_2 \cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P2_1/c$ (no.14)	$\begin{array}{c} \mathbf{1ni^{+}-2c\cdot Cl^{-}} \\ C_{44}H_{28}N_{3}SClNi\cdot \\ C_{11}H_{3}BN_{2}O_{2}F_{6}\cdot H_{2}O \\ 1064.91 \\ 0.05\times0.03\times0.03 \\ triclinic \\ P\bar{1} \ (no. 2) \end{array}$		
$c, Å$ 15.987(4)27.519(15)14.7731(5) $a, °$ 113.935(9)9083.126(3) $\beta, °$ 91.484(8)102.088(18)84.024(3) $\gamma, °$ 92.340(8)9081.561(3) $V, Å^3$ 253.5(10)5967(7)2363.86(13) ρ_{abcd}, gem^{-3} 1.4201.5531.496 Z 242 T, K 90(2)100(2)90(2) μ, mm^{-1} 0.668 $°$ 0.190 b 0.834 b no. of reflns3739613187918843no. of unique reflns17602105318458variables677816692 $\lambda, Å$ 0.90630.10670.81063 b $R_1(I > 2\sigma(I))$ 0.90630.0050.1073 a	formula fw crystal size, mm crystal system space group <i>a</i> , Å	$\begin{array}{c} {\bf 1ni^+-2a\cdot Cl^-} \\ \hline \\ C_{44}H_{28}N_3SCINi\cdot \\ C_{11}H_9BN_2O_2F_2\cdot \\ 1.258CH_2Cl_2 \\ 1083.45 \\ 0.30\times 0.30\times 0.10 \\ triclinic \\ P\overline{1} \ (no.\ 2) \\ 13.066(3) \end{array}$	$1ni^+-2b\cdot Cl^ C_{44}H_{28}N_3SCINi\cdot$ $C_{19}H_{25}BN_2O_2F_2\cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P2_1/c$ (no.14) 12.962(9)	$\begin{array}{c} \mathbf{1ni^{+}-2c\cdot Cl^{-}} \\ C_{44}H_{28}N_{3}SClNi\cdot \\ C_{11}H_{5}BN_{2}O_{2}F_{6}\cdot H_{2}O \\ 1064.91 \\ 0.05\times0.03\times0.03 \\ triclinic \\ P\overline{1} \ (no.\ 2) \\ 12.3536(4) \end{array}$		
α , °113.935(9)9083.126(3) β , °91.484(8)102.088(18)84.024(3) γ , °92.340(8)9081.561(3) $V, Å^3$ 2533.5(10)5967(7)2363.86(13) $\rho_{alcd,} gcm^{-3}$ 1.4201.5531.496 Z 242 T, K 90(2)100(2)90(2) μ, mm^{-1} 0.668 °0.190 °0.834 °no. of reflns37361.3187918843no. of unique reflns17602105318458variables677816692 $\lambda, Å$ 0.90630.10670.81063 ° $R_1(I > 2\sigma(I))$ 0.9630.10670.1072 °	formula fw crystal size, mm crystal system space group <i>a</i> , Å <i>b</i> , Å	$1ni^+-2a \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{11}H_9BN_2O_2F_2$ $1.258CH_2Cl_2$ 1083.45 $0.30 \times 0.30 \times 0.10$ triclinic $P\overline{1}$ (no. 2) $13.066(3)$ $13.295(3)$	$1ni^+ -2b \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{19}H_{25}BN_2O_2F_2 \cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P2_1/c$ (no.14) 12.962(9) 17.107(12)	$\begin{array}{c} \mathbf{Ini^{+}-2c\cdot Cl^{-}} \\ C_{44}H_{28}N_{3}SCINi \\ C_{11}H_{5}BN_{2}O_{2}F_{6}\cdot H_{2}O \\ 1064.91 \\ 0.05 \times 0.03 \times 0.03 \\ triclinic \\ P\overline{1} \ (no. 2) \\ 12.3536(4) \\ 13.2407(4) \end{array}$		
β °91.484(8)102.088(18)84.024(3) γ °92.340(8)9081.561(3) $V, Å^3$ 2533.5(10)5967(7)2363.86(13) $\rho_{raled, gcm^{-3}}$ 1.4201.5531.496 Z 242 T, K 90(2)100(2)90(2) μ mm^{-1}0.668 a 0.190 b 0.834 b no. of reflns3739613187918843no. of unique reflns17602105318458variables677816692 $\lambda, Å$ 0.71073 a 0.4127 b 0.81063 b $R_1(I > 2\sigma(I))$ 0.99630.10670.511	formula fw crystal size, mm crystal system space group <i>a</i> , Å <i>b</i> , Å <i>c</i> , Å	$\begin{array}{c} 1ni^{+}-2a \cdot Cl^{-} \\ C_{44}H_{28}N_3SCINi \cdot \\ C_{11}H_9BN_2O_2F_2 \cdot \\ 1.258CH_2Cl_2 \\ 1083.45 \\ 0.30 \times 0.30 \times 0.10 \\ triclinic \\ P\overline{1} \ (no. 2) \\ 13.066(3) \\ 13.295(3) \\ 15.987(4) \end{array}$	$1ni^+-2b \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{19}H_{25}BN_2O_2F_2 \cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P2_{1/c}$ (no.14) 12.962(9) 17.107(12) 27.519(15)	$\begin{array}{c} \mathbf{Ini}^{+}-\mathbf{2c}\cdot\mathrm{Cl}^{-} \\ C_{44}H_{28}N_{3}\mathrm{SCINi}\cdot \\ C_{11}H_{5}\mathrm{BN}_{2}O_{2}F_{6}\cdot\mathrm{H}_{2}\mathrm{O} \\ 1064.91 \\ 0.05\times0.03\times0.03 \\ \mathrm{triclinic} \\ P\overline{1} (\mathrm{no.}\ 2) \\ 12.3536(4) \\ 13.2407(4) \\ 14.7731(5) \end{array}$		
χ° 92.340(8)9081.561(3) $V, Å^3$ 2533.5(10)5967(7)2363.86(13) ρ_{alod}, gcm^{-3} 1.4201.5531.496 Z 242 T, K 90(2)100(2)90(2) μ, mm^{-1} 0.668 a 0.190 b 0.834 b no. of reflns3739613187918843no. of unique reflns17602105318458variables677816692 $\lambda, Å$ 0.71073 a 0.4127 b 0.81063 b $R_1(I > 2\sigma(I))$ 0.09630.10670.0519	formula fw crystal size, mm crystal system space group <i>a</i> , Å <i>b</i> , Å <i>c</i> , Å <i>a</i> , °	$Ini^+ - 2a \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{11}H_9BN_2O_2F_2$ $1.258CH_2Cl_2$ 1083.45 $0.30 \times 0.30 \times 0.10$ triclinic $P\bar{1}$ (no. 2) $13.066(3)$ $13.295(3)$ $15.987(4)$ $113.935(9)$	$\begin{array}{c} \mathbf{1ni}^{+}-\mathbf{2b}\cdot \mathrm{Cl}^{-}\\ \hline C_{44}H_{28}N_3\mathrm{SCINi}\cdot\\ C_{19}H_{25}\mathrm{BN}_2\mathrm{O}_2\mathrm{F}_2\cdot 2\mathrm{CCl}_4\\ \hline 1394.75\\ 0.100\times0.050\times0.030\\ \mathrm{monoclinic}\\ P2_{1/c}\ (\mathrm{no.14})\\ 12.962(9)\\ 17.107(12)\\ 27.519(15)\\ 90 \end{array}$	$\begin{array}{c} \mathbf{1ni^{+}-2c\cdot Cl^{-}} \\ C_{44}H_{28}N_{3}SCINi\cdot \\ C_{11}H_{3}BN_{2}O_{2}F_{6}\cdot H_{2}O \\ \hline 1064.91 \\ 0.05 \times 0.03 \times 0.03 \\ triclinic \\ P\bar{1} (no. 2) \\ 12.3536(4) \\ 13.2407(4) \\ 14.7731(5) \\ 83.126(3) \end{array}$		
$V, Å^3$ 2533.5(10)5967(7)2363.86(13) ρ_{calcd}, gcm^{-3} 1.4201.5531.496 Z 242 T, K 90(2)100(2)90(2) μ, mm^{-1} 0.668 a0.190 b0.834 bno. of reflns3739613187918843no. of unique reflns17602105318458variables677816692 $\lambda, Å$ 0.71073 a0.4127 b0.81063 b $R_1(I > 2\sigma(I))$ 0.09630.10670.0519	formula fw crystal size, mm crystal system space group a, Å b, Å c, Å a, \circ β, \circ	$ni^+-2a \cdot Cl^ C_{44}H_{28}N_3SClNi \cdot$ $C_{11}H_9BN_2O_2F_2 \cdot$ $1.258CH_2Cl_2$ 1083.45 $0.30 \times 0.30 \times 0.10$ triclinic $P\overline{1}$ (no. 2) $13.066(3)$ $15.987(4)$ $113.935(9)$ $91.484(8)$	$\begin{array}{c} {\bf 1ni^{+}-2b\cdot Cl^{-}}\\ \hline C_{44}H_{28}N_{3}SCINi^{+}\\ C_{19}H_{25}BN_{2}O_{2}F_{2}\cdot 2CCl_{4}\\ \hline 1394.75\\ 0.100\times 0.050\times 0.030\\ monoclinic\\ P2_{1/c}\ (no.14)\\ 12.962(9)\\ 17.107(12)\\ 27.519(15)\\ 90\\ 102.088(18)\\ \end{array}$	$\begin{array}{c} \mathbf{1ni^{+}-2c\cdot Cl^{-}} \\ \hline \\ C_{44}H_{28}N_{3}SClNi^{\cdot} \\ C_{11}H_{3}BN_{2}O_{2}F_{6}\cdot H_{2}O \\ \hline \\ 1064.91 \\ 0.05 \times 0.03 \times 0.03 \\ triclinic \\ P\overline{1} (no. 2) \\ 12.3536(4) \\ 13.2407(4) \\ 14.7731(5) \\ 83.126(3) \\ 84.024(3) \end{array}$		
ρ_{calcd}, gcm^{-3} 1.4201.5531.496Z242T, K90(2)100(2)90(2) μ, mm^{-1} 0.668 a0.190 b0.834 bno. of reflns3739613187918843no. of unique reflns17602105318458variables677816692 λ, \dot{A} 0.71073 a0.4127 b0.81063 b $R_1(I > 2\sigma(I))$ 0.09630.10670.0519	formula fw crystal size, mm crystal system space group a, Å b, Å c, Å a, \circ β, \circ γ, \circ	$ni^+-2a \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{11}H_{9}BN_2O_2F_2 \cdot$ $1.258CH_2Cl_2$ 1083.45 $0.30 \times 0.30 \times 0.10$ triclinic $P\overline{1}$ (no. 2) $13.066(3)$ $13.295(3)$ $15.987(4)$ $113.935(9)$ $91.484(8)$ $92.340(8)$	$Ini^+ -2b \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{19}H_{25}BN_2O_2F_2 \cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P2_1/c$ (no.14) 12.962(9) 17.107(12) 27.519(15) 90 102.088(18) 90	$\begin{array}{c} \mathbf{Ini^{+}-2c\cdot Cl^{-}} \\ C_{44}H_{28}N_{3}SClNi\cdot \\ C_{11}H_{3}BN_{2}O_{2}F_{6}\cdot H_{2}O \\ \hline 1064.91 \\ 0.05\times0.03\times0.03 \\ triclinic \\ P\overline{1} (no. 2) \\ 12.3536(4) \\ 13.2407(4) \\ 14.7731(5) \\ 83.126(3) \\ 84.024(3) \\ 81.561(3) \end{array}$		
Z242T, K90(2)100(2)90(2) μ mm ⁻¹ 0.668 a0.190 b0.834 bno. of reflns3739613187918843no. of unique reflns17602105318458variables677816692 λ, \dot{A} 0.71073 a0.4127 b0.81063 b $R_1(I > 2\sigma(I))$ 0.9630.10670.0519	formula fw crystal size, mm crystal system space group a, Å b, Å c, Å a, \circ β, \circ γ, \circ $V, Å^3$	$Ini^+ - 2a \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{11}H_9BN_2O_2F_2 \cdot$ $1.258CH_4Cl_2$ 1083.45 $0.30 \times 0.30 \times 0.10$ triclinic $P\overline{1}$ (no. 2) $13.066(3)$ $13.295(3)$ $15.987(4)$ $113.935(9)$ $91.484(8)$ $92.340(8)$ $2533.5(10)$	$Ini^+ -2b \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{19}H_{25}BN_2O_2F_2 \cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P_{21/c}$ (no.14) 12.962(9) 17.107(12) 27.519(15) 90 102.088(18) 90 5967(7)	$\begin{array}{c} \mathbf{Ini^{+}-2c\cdot Cl^{-}} \\ C_{44}H_{28}N_{3}SClNi\cdot \\ C_{11}H_{3}BN_{2}O_{2}F_{6}\cdot H_{2}O \\ \hline 1064.91 \\ 0.05 \times 0.03 \times 0.03 \\ triclinic \\ P\overline{1} (no. 2) \\ 12.3536(4) \\ 13.2407(4) \\ 14.7731(5) \\ 83.126(3) \\ 84.024(3) \\ 81.561(3) \\ 2363.86(13) \end{array}$		
T, K 90(2)100(2)90(2) μ, mm^{-1} 0.668 a0.190 b0.834 bno. of reflns3739613187918843no. of unique reflns17602105318458variables677816692 $\lambda, Å$ 0.71073 a0.4127 b0.81063 b $R_1 (I > 2\sigma(I))$ 0.09630.10670.0519	formula fw crystal size, mm crystal system space group a, Å b, Å c, Å a, \circ β, \circ γ, \circ $V, Å^3$ ρ_{aled}, gcm^{-3}	$Ini^+ -2a \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{11}H_9BN_2O_2F_2 \cdot$ $1.258CH_2Cl_2$ 1083.45 $0.30 \times 0.30 \times 0.10$ triclinic $P\overline{1}$ (no. 2) $13.066(3)$ $13.295(3)$ $15.987(4)$ $113.935(9)$ $91.484(8)$ $92.340(8)$ $2533.5(10)$ 1.420	$1ni^+ -2b \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{19}H_{25}BN_2O_2F_2 \cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P2_{1/c}$ (no.14) 12.962(9) 17.107(12) 27.519(15) 90 102.088(18) 90 5967(7) 1.553	$\begin{array}{c} \mathbf{1ni^{+}-2c\cdot Cl^{-}} \\ C_{44}H_{28}N_{3}SCINi\cdot \\ C_{11}H_{5}BN_{2}O_{2}F_{6}\cdot H_{2}O \\ \hline 1064.91 \\ 0.05 \times 0.03 \times 0.03 \\ triclinic \\ P\overline{1} (no. 2) \\ 12.3536(4) \\ 13.2407(4) \\ 14.7731(5) \\ 83.126(3) \\ 84.024(3) \\ 81.561(3) \\ 2363.86(13) \\ 1.496 \end{array}$		
μ , mm ⁻¹ 0.668 a0.190 b0.834 bno. of reflns3739613187918843no. of unique reflns17602105318458variables677816692 λ , Å0.71073 a0.4127 b0.81063 b R_1 ($I > 2\sigma(I)$)0.09630.10670.0519	formula fw crystal size, mm crystal system space group a, Å b, Å c, Å a, \circ β, \circ γ, \circ $V, Å^3$ ρ_{ealed}, gcm^{-3} Z	$\begin{array}{c} \mathbf{1ni^{+}-2a \cdot Cl^{-}} \\ \hline \\ C_{44}H_{28}N_3SCINi \cdot \\ C_{11}H_9BN_2O_2F_2 \cdot \\ 1.258CH_2Cl_2 \\ \hline \\ 1083.45 \\ \hline \\ 0.30 \times 0.30 \times 0.10 \\ triclinic \\ P\overline{1} (no. 2) \\ \hline \\ 13.066(3) \\ \hline \\ 13.295(3) \\ \hline \\ 15.987(4) \\ \hline \\ 113.935(9) \\ 91.484(8) \\ 92.340(8) \\ 2533.5(10) \\ \hline \\ 1.420 \\ 2 \end{array}$	$1ni^+-2b\cdot Cl^ C_{44}H_{28}N_3SCINi\cdot$ $C_{19}H_{25}BN_2O_2F_2\cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P2_{1/c}$ (no.14) 12.962(9) 17.107(12) 27.519(15) 90 5967(7) 1.553 4	$\begin{array}{c} \mathbf{1ni^{+}-2c\cdot Cl^{-}} \\ C_{44}H_{28}N_{3}SCINi\cdot \\ C_{11}H_{5}BN_{2}O_{2}F_{6}\cdot H_{2}O \\ \hline 1064.91 \\ 0.05 \times 0.03 \times 0.03 \\ triclinic \\ P\overline{1} (no. 2) \\ 12.3536(4) \\ 13.2407(4) \\ 14.7731(5) \\ 83.126(3) \\ 84.024(3) \\ 81.561(3) \\ 2363.86(13) \\ 1.496 \\ 2 \end{array}$		
no. of reflns3739613187918843no. of unique reflns17602105318458variables677816692 $\lambda, Å$ 0.71073 a0.4127 b0.81063 b $R_1 (I > 2 \sigma(I))$ 0.09630.10670.0519	formula fw crystal size, mm crystal system space group a, Å b, Å c, Å α, \circ β, \circ γ, \circ $V, Å^3$ ρ_{enled}, gcm^{-3} Z T, K	$Ini^+ - 2a \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{11}H_9BN_2O_2F_2 \cdot$ $1.258CH_2Cl_2$ 1083.45 $0.30 \times 0.30 \times 0.10$ triclinic $P\overline{1}$ (no. 2) $13.066(3)$ $13.295(3)$ $15.987(4)$ $113.935(9)$ $91.484(8)$ $92.340(8)$ $2533.5(10)$ 1.420 2 $90(2)$	$1ni^+-2b\cdot Cl^ C_{44}H_{28}N_3SCINi\cdot$ $C_{19}H_{25}BN_2O_2F_2\cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P2_{1/c}$ (no.14) 12.962(9) 17.107(12) 27.519(15) 90 5967(7) 1.553 4 100(2)	$\begin{array}{c} \mathbf{1ni^{+}-2c\cdot Cl^{-}} \\ C_{44}H_{28}N_{3}SCINi\cdot \\ C_{11}H_{3}BN_{2}O_{2}F_{6}\cdot H_{2}O \\ \hline 1064.91 \\ 0.05 \times 0.03 \times 0.03 \\ triclinic \\ P\overline{1} (no. 2) \\ 12.3536(4) \\ 13.2407(4) \\ 14.7731(5) \\ 83.126(3) \\ 84.024(3) \\ 81.561(3) \\ 2363.86(13) \\ 1.496 \\ 2 \\ 90(2) \end{array}$		
no. of unique reflns17602105318458variables677816692 $\lambda, Å$ 0.71073 a0.4127 b0.81063 b $R_1 (I > 2 \sigma(I))$ 0.09630.10670.0519	formula fw crystal size, mm crystal system space group a, Å b, Å c, Å a, \circ β, \circ γ, \circ $V, Å^3$ ρ_{calcd}, gcm^{-3} Z T, K μ, mm^{-1}	Ini ⁺ -2a·Cl ⁻ $C_{44}H_{28}N_3SCINi$ · $C_{11}H_5BN_2O_2F_2$ · $1.258CH_2Cl_2$ 1083.45 $0.30 \times 0.30 \times 0.10$ triclinic $P\overline{1}$ (no. 2) $13.066(3)$ $13.295(3)$ $15.987(4)$ $113.935(9)$ $91.484(8)$ $92.340(8)$ $2533.5(10)$ 1.420 2 $90(2)$ 0.668^a	$1ni^+-2b\cdot Cl^ C_{44}H_{28}N_3SCINi\cdot$ $C_{19}H_{25}BN_2O_2F_2\cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P2_{1/c}$ (no.14) 12.962(9) 17.107(12) 27.519(15) 90 5967(7) 1.553 4 100(2) 0.190^b	$\begin{array}{c} \mathbf{1ni^{+}-2c} \cdot \mathrm{Cl^{-}} \\ \hline \\ C_{44}H_{28}N_{3}\mathrm{SCINi^{\cdot}} \\ C_{11}H_{3}BN_{2}O_{2}F_{6}\cdot H_{2}\mathrm{O} \\ \hline \\ 1064.91 \\ 0.05 \times 0.03 \times 0.03 \\ \text{triclinic} \\ P\overline{1} & (no. 2) \\ 12.3536(4) \\ 13.2407(4) \\ 14.7731(5) \\ 83.126(3) \\ 84.024(3) \\ 81.561(3) \\ 2363.86(13) \\ 1.496 \\ 2 \\ 90(2) \\ 0.834^{b} \end{array}$		
variables677816692 $\lambda, Å$ 0.71073 a0.4127 b0.81063 b $R_1 (I > 2 \sigma(I))$ 0.09630.10670.0519D (I > 2 (I))0.2260.2050.1067	formula fw crystal size, mm crystal system space group a, Å b, Å c, Å a, \circ β, \circ γ, \circ γ, \circ $\gamma, \langle \Lambda^3 \rangle$ ρ_{calcd}, gcm^{-3} Z T, K μ, mm^{-1} no. of reflns	$Ini^+ -2a \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{11}H_9BN_2O_2F_2 \cdot$ $1.258CH_4Cl_2$ 1083.45 $0.30 \times 0.30 \times 0.10$ triclinic $P\overline{1}$ (no. 2) $13.066(3)$ $13.295(3)$ $15.987(4)$ $113.935(9)$ $91.484(8)$ $92.340(8)$ $2533.5(10)$ 1.420 2 $90(2)$ 0.668^a 37396	$1ni^+-2b\cdot Cl^ C_{44}H_{28}N_3SCINi\cdot$ $C_{19}H_{25}BN_2O_2F_2\cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P2_{1/c}$ (no.14) 12.962(9) 17.107(12) 27.519(15) 90 5967(7) 1.553 4 100(2) 0.190^b 131879	$\begin{array}{c} \mathbf{1ni^{+}-2c\cdot Cl^{-}} \\ \hline \\ C_{44}H_{28}N_{3}SCINi \\ C_{11}H_{3}BN_{2}O_{2}F_{6}\cdot H_{2}O \\ \hline \\ 1064.91 \\ 0.05 \times 0.03 \times 0.03 \\ triclinic \\ P\bar{1} (no. 2) \\ 12.3536(4) \\ 13.2407(4) \\ 14.7731(5) \\ 83.126(3) \\ 84.024(3) \\ 81.561(3) \\ 2363.86(13) \\ 1.496 \\ 2 \\ 90(2) \\ 0.834^{b} \\ 18843 \end{array}$		
λ , Å 0.71073^a 0.4127^b 0.81063^b R_1 ($I > 2\sigma(I)$) 0.0963 0.1067 0.0519 P_1 ($I > 2\sigma(I)$) 0.226 0.3205 0.1067	formula fw crystal size, mm crystal system space group a, Å b, Å c, Å a, \circ β, \circ γ, \circ $V, Å^3$ $\rho_{\text{calcd, gcm}^{-3}}$ Z T, K μ, mm^{-1} no. of reflns no. of unique reflns	$Ini^+ -2a \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{11}H_0BN_2O_2F_2 \cdot$ $1.258CH_2Cl_2$ 1083.45 $0.30 \times 0.30 \times 0.10$ triclinic $P\overline{1}$ (no. 2) $13.066(3)$ $13.295(3)$ $15.987(4)$ $113.935(9)$ $91.484(8)$ $92.340(8)$ $2533.5(10)$ 1.420 2 $90(2)$ 0.668^a 37396	$1ni^+ -2b \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{19}H_{22}BN_2O_2F_2 \cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P_{21/c}$ (no.14) 12.962(9) 17.107(12) 27.519(15) 90 5967(7) 1.553 4 100(2) 0.190^b 131879 10531	$\begin{array}{c} \mathbf{1ni^{+}-2c\cdot Cl^{-}} \\ \hline C_{44}H_{28}N_{3}SCINi \\ \hline C_{11}H_{3}BN_{2}O_{2}F_{6}\cdot H_{2}O \\ \hline 1064.91 \\ 0.05 \times 0.03 \times 0.03 \\ triclinic \\ P\overline{1} (no. 2) \\ 12.3536(4) \\ 13.2407(4) \\ 14.7731(5) \\ 83.126(3) \\ 84.024(3) \\ 81.561(3) \\ 2363.86(13) \\ 1.496 \\ 2 \\ 90(2) \\ 0.834^{b} \\ 18843 \\ 8458 \end{array}$		
$R_1 (I > 2\sigma(I))$ 0.0963 0.1067 0.0519	formula fw crystal size, mm crystal system space group a, Å b, Å c, Å a, \circ β, \circ γ, \circ $V, Å^3$ $\rho_{alcd,} gcm^{-3}$ Z T, K μ, mm^{-1} no. of reflns no. of unique reflns variables	$lni^+-2a \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{11}H_9BN_2O_2F_2$ $1.258CH_2Cl_2$ 1083.45 $0.30 \times 0.30 \times 0.10$ triclinic $P\overline{1}$ (no. 2) $13.066(3)$ $13.295(3)$ $15.987(4)$ $113.935(9)$ $91.484(8)$ $22.340(8)$ $2533.5(10)$ 1.420 2 $90(2)$ 0.668^a 37396 17602 677	$1ni^+ -2b \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{19}H_{25}BN_2O_2F_2 \cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P2_{1/c}$ (no.14) 12.962(9) 17.107(12) 27.519(15) 90 5967(7) 1.553 4 100(2) 0.190 b 131879 10531 816	$\begin{array}{c} \mathbf{1ni}^{+} - \mathbf{2c} \cdot \mathbf{Cl}^{-} \\ \hline \mathbf{C}_{44} \mathbf{H}_{28} \mathbf{N}_{3} \mathbf{SClNi} \\ \hline \mathbf{C}_{11} \mathbf{H}_{5} \mathbf{BN}_{2} \mathbf{O}_{2} \mathbf{F}_{6} \cdot \mathbf{H}_{2} \mathbf{O} \\ \hline 1064.91 \\ \hline 0.05 \times 0.03 \times 0.03 \\ \hline \mathbf{triclinic} \\ P\overline{1} (\mathbf{no. 2}) \\ \hline \mathbf{12.3536(4)} \\ \hline \mathbf{13.2407(4)} \\ \hline \mathbf{14.7731(5)} \\ \hline \mathbf{83.126(3)} \\ \hline \mathbf{84.024(3)} \\ \hline \mathbf{81.561(3)} \\ \hline \mathbf{2363.86(13)} \\ \hline 1.496 \\ 2 \\ \hline \mathbf{90(2)} \\ \hline 0.834 \ ^{b} \\ \hline 18843 \\ \hline 8458 \\ 692 \end{array}$		
	formula fw crystal size, mm crystal system space group a, Å b, Å c, Å a, \circ β, \circ γ, \circ $V, Å^3$ ρ_{ealed}, gcm^{-3} Z T, K μ, mm^{-1} no. of reflns no. of unique reflns variables $\lambda, Å$	$1ni^+ -2a \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{11}H_9BN_2O_2F_2$ $1.258CH_2Cl_2$ 1083.45 $0.30 \times 0.30 \times 0.10$ triclinic $P\overline{1}$ (no. 2) $13.066(3)$ $13.295(3)$ $15.987(4)$ $113.935(9)$ $91.484(8)$ $92.340(8)$ $2533.5(10)$ 1.420 2 $90(2)$ 0.668^a 37396 17602 677 0.71073^a	$1ni^+-2b\cdot Cl^ C_{44}H_{28}N_3SCINi\cdot$ $C_{19}H_{25}BN_2O_2F_2\cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P2_{1/c}$ (no.14) 12.962(9) 17.107(12) 27.519(15) 90 5967(7) 1.553 4 100(2) 0.190 ^b 131879 10531 816 0.4127 ^b	$\begin{array}{c} \mathbf{Ini}^{+}-\mathbf{2c}\cdot\mathbf{Cl}^{-} \\ \hline \\ \mathbf{C}_{44}\mathbf{H}_{28}\mathbf{N}_{3}\mathbf{SCINi} \\ \mathbf{C}_{11}\mathbf{H}_{5}\mathbf{B}\mathbf{N}_{2}\mathbf{O}_{2}\mathbf{F}_{6}\cdot\mathbf{H}_{2}\mathbf{O} \\ \hline 1064.91 \\ 0.05 \times 0.03 \times 0.03 \\ \text{triclinic} \\ \hline \\ P\overline{1} (no. 2) \\ 12.3536(4) \\ 13.2407(4) \\ 14.7731(5) \\ 83.126(3) \\ 84.024(3) \\ 81.561(3) \\ 2363.86(13) \\ 1.496 \\ 2 \\ 90(2) \\ 0.834^{b} \\ 18843 \\ 8458 \\ 692 \\ 0.81063^{b} \end{array}$		
$w_{K_2}(I \ge 2\sigma(I))$ 0.2626 0.3905 0.1183	formula fw crystal size, mm crystal system space group a, Å b, Å c, Å a, \circ β, \circ γ, \circ $V, Å^3$ $\rho_{\text{caled}}, \text{gcm}^{-3}$ Z T, K μ, mm^{-1} no. of reflns no. of unique reflns variables $\lambda, Å$ $R_1 (I > 2 \sigma(I))$	$Ini^+ - 2a \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{11}H_{9}BN_2O_2F_2 \cdot$ $1.258CH_2Cl_2$ 1083.45 $0.30 \times 0.30 \times 0.10$ triclinic $P\overline{1}$ (no. 2) $13.066(3)$ $13.295(3)$ $15.987(4)$ $113.935(9)$ $91.484(8)$ $92.340(8)$ $2533.5(10)$ 1.420 2 $90(2)$ 0.668^a 37396 17602 677 0.71073^a 0.0963	$1ni^+-2b\cdot Cl^ C_{44}H_{28}N_3SCINi\cdot$ $C_{19}H_{25}BN_2O_2F_2\cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P2_{1/c}$ (no.14) 12.962(9) 17.107(12) 27.519(15) 90 5967(7) 1.553 4 100(2) 0.190^b 131879 10531 816 0.4127^b 0.1067	$\begin{array}{c} \mathbf{Ini}^{+}-\mathbf{2c}\cdot \mathrm{Cl}^{-} \\ \mathbf{C}_{44}\mathbf{H}_{28}\mathbf{N}_{3}\mathrm{SCINi} \\ \mathbf{C}_{11}\mathbf{H}_{5}\mathbf{B}\mathbf{N}_{2}O_{2}\mathbf{F}_{6}\cdot\mathbf{H}_{2}\mathbf{O} \\ 1064.91 \\ 0.05 \times 0.03 \times 0.03 \\ \mathrm{triclinic} \\ P\overline{1} (no. 2) \\ 12.3536(4) \\ 13.2407(4) \\ 14.7731(5) \\ 83.126(3) \\ 84.024(3) \\ 81.561(3) \\ 2363.86(13) \\ 1.496 \\ 2 \\ 90(2) \\ 0.834^{b} \\ 18843 \\ 8458 \\ 692 \\ 0.81063^{b} \\ 0.0519 \end{array}$		
GOF 1.016 1.997 1.127	formula fw crystal size, mm crystal system space group a, Å b, Å c, Å a, \circ β, \circ γ, \circ $V, Å^3$ ρ -caled, gcm ⁻³ Z T, K μ , mm ⁻¹ no. of reflns no. of unique reflns variables $\lambda, Å$ $R_1 (I > 2 \sigma(I))$ $wR_2 (I > 2 \sigma(I))$	$lni^+ - 2a \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{11}H_{9}BN_2O_2F_2$ $1.258CH_2Cl_2$ 1083.45 $0.30 \times 0.30 \times 0.10$ triclinic $P\overline{1}$ (no. 2) $13.066(3)$ $13.295(3)$ $15.987(4)$ $113.935(9)$ $91.484(8)$ $92.340(8)$ $2533.5(10)$ 1.420 2 $90(2)$ 0.668^a 37396 17602 677 0.71073^a 0.0963 0.2626	$1ni^+-2b \cdot Cl^ C_{44}H_{28}N_3SCINi\cdot$ $C_{19}H_{25}BN_2O_2F_2\cdot 2CCl_4$ 1394.75 $0.100 \times 0.050 \times 0.030$ monoclinic $P2_1/c$ (no.14) 12.962(9) 17.107(12) 27.519(15) 90 5967(7) 1.553 4 100(2) 0.190^b 131879 10531 816 0.4127^b 0.1067 0.3905	$1ni^+ -2c \cdot Cl^ C_{44}H_{28}N_3SCINi \cdot$ $C_{11}H_3BN_2O_2F_6 \cdot H_2O$ 1064.91 $0.05 \times 0.03 \times 0.03$ triclinic $P\bar{1}$ (no. 2) $12.3536(4)$ $13.2407(4)$ $14.7731(5)$ $83.126(3)$ $84.024(3)$ $81.561(3)$ $2363.86(13)$ 1.496 2 $90(2)$ 0.834^b 18843 8458 692 0.81063^b 0.0519 0.1183		

^{*a*} The values under the Mo-K α radiation. ^{*b*} The values under the synchrotron radiation.



Fig. S5 Ortep drawing of single-crystal X-ray structure (top and side views) of $1ni^+$ -Cl⁻tri as a pseudopolymorph of $1ni^+$ -Cl⁻ in the previous study.^[S1] Disordered structures are represented by black and white bonds for major and minor structures, respectively, in the ratio of 74 : 16 : 6 : 4 for the porphyrin inner atoms (according to the existence of sulfur). Thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted for clarity.



Fig. S6 Ortep drawing of single-crystal X-ray structure (top and side views) of $1ni^+$ -Cl⁻ortho</sup> as a pseudopolymorph of $1ni^+$ -Cl⁻ in the previous study.^[S1] Thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted for clarity.



Fig. S7 Ortep drawing of single-crystal X-ray structure (top and side view) of $1ni^+$ -PF₆⁻. Disordered structures are represented by black and white bonds for major and minor structures, respectively, in the ratios of 58 : 32 : 10 and 75 : 25 for the porphyrin inner atoms (according to the existence of sulfur) and a phenyl group, respectively. Thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted for clarity.



Fig. S8 Ortep drawing of single-crystal X-ray structure (top and side view) of $1ni^+-B(C_6F_5)_4^-$. Disordered structures are represented by black and white bonds for major and minor structures, respectively, in the ratios of 61 : 39 and 55 : 45 for the porphyrin inner atoms (according to the existence of sulfur) and a phenyl group, respectively. Thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted for clarity.



Fig. S9 Ortep drawing of single-crystal X-ray structure (top and side views) of $1ni^+$ -PCCp⁻. Disordered structures are represented by black and white bonds for major and minor structures, respectively, in the ratio of 72 : 28 for the porphyrin inner atoms (according to the existence of sulfur). Thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted for clarity.



Fig. S10 Ortep drawing of single-crystal X-ray structure (top and side views) of $1ni^+-2a \cdot Cl^-$. Disordered structures are represented by black and white bonds for major and minor structures, respectively, in the ratio of 88 : 12 for the porphyrin inner atoms (according to the existence of sulfur). Thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted for clarity.



Fig. S11 Ortep drawing of single-crystal X-ray structure (top and side views) of $1ni^+-2b \cdot Cl^-$. Thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted for clarity.



Fig. S12 Ortep drawing of single-crystal X-ray structure (top and side views) of $1ni^+-2c \cdot Cl^-$. Disordered structures are represented by black and white bonds for major and minor structures, respectively, in the ratio of 80 : 20 for the porphyrin inner atoms (according to the existence of sulfur) and chlorine, respectively. Thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted for clarity.



Fig. S13 Packing diagram (stacking assembly) of **1ni**⁺-Cl^{-tri} as (a) a top view and (b) a side view from the arrow shown in (a), (c) top views of the dimers as (i) major (74%) and (ii) second major (16%) structures (Fig. S5), and (d) side view of the major dimer. The stacking distances between two **1ni**⁺ (core 25 atoms) and the Ni…Ni distances in the column are 3.93/5.96 and 4.84/10.64 Å, respectively. The Ni–Cl distance is 2.27 Å and the angle of the line through Ni and Cl⁻ to the core porphyrin plane (25 atoms) is 70.7°. The S…N distance in two stacking **1ni**⁺ units is 3.33 Å and the dihedral angle between the thiophene plane and the core porphyrin plane (25 atoms) is 24.9°. Mean-plane deviation of the **1ni**⁺ core part (25 atoms) and τ_4 value^[S11] are 0.20 Å and 0.36, respectively. Atom color code: brown, pink, blue, orange, green, and light gray refer to carbon, hydrogen, nitrogen, sulfur, chlorine, and nickel, respectively. Solvent molecules are omitted for clarity.



Fig. S14 (a) Packing diagram (stacking assembly) of $1ni^+$ -Cl⁻_{ortho} as (i) a view along *c* axis and (ii) another view, (b) top view of the dimer, and (c) side view of the dimer. The stacking distances between two $1ni^+$ (core 25 atoms) and the Ni…Ni distances are 4.01 and 5.43 Å, respectively. The Ni–Cl distance is 2.29 Å and the dihedral angle of the line through Ni and Cl⁻ to the core porphyrin plane (25 atoms) is 71.0°. The dihedral angle between the thiophene plane and the core porphyrin plane (25 atoms) is 30.8°. Mean-plane deviation of the $1ni^+$ core part (25 atoms) and τ_4 value^[S11] are 0.30 Å and 0.36, respectively. Atom color code: brown, pink, blue, orange, green, and light gray refer to carbon, hydrogen, nitrogen, sulfur, chlorine, and nickel, respectively. Solvent molecules are omitted for clarity.



Fig. S15 Packing diagram (stacking assembly) of $1ni^+$ -PF₆⁻ as (a) a top view and (b) a side view from the arrow shown in (a), (c) top views of the dimers as (i) major (58%) and (ii) second major (32%) structures (Fig. S7), and (d) side view of the dimer. The stacking distances between two $1ni^+$ (core 25 atoms) and the Ni…Ni distances in the column are 3.69/4.01 and 4.78/10.48 Å, respectively. The S…N distance in two stacking $1ni^+$ units is 3.26 Å and the dihedral angle between the thiophene plane and the core porphyrin plane (25 atoms) is 24.6°. Mean-plane deviation of the $1ni^+$ core part (25 atoms) and τ_4 value^[S11] are 0.30 Å and 0.10, respectively. Atom color code: brown, pink, yellow green, blue, light orange, orange, and light gray refer to carbon, hydrogen, fluorine, nitrogen, phosphorus, sulfur, and nickel, respectively. Solvent molecules are omitted for clarity.



Fig. S16 (a) Packing diagram (stacking assembly) of $1ni^+$ -B(C₆F₅)₄⁻ as (a) a top view and (b) a side view, (c) top views of the dimers as (i) major (61%) and (ii) minor (39%) structures (Fig. S8), and (d) side view of the dimer. The distances between two $1ni^+$ (core 25 atoms) and the Ni…Ni distances are 3.77/5.43/8.51 and 4.95/13.67/11.80 Å, respectively. The S…N distance in two $1ni^+$ units in the column is 3.30 Å and the dihedral angle between the thiophene plane and the core porphyrin plane (core 25 atoms) is 22.0°. Mean-plane deviation of the $1ni^+$ core part (25 atoms) and z_4 value^[S11] are 0.21 Å and 0.10, respectively. Atom color code: brown, pink, yellow, blue, yellow green, orange, and light gray refer to carbon, hydrogen, boron, nitrogen, fluorine, sulfur, and nickel, respectively. Solvent molecules are omitted for clarity.



Fig. S17 Packing diagram (stacking assembly) of $1ni^+$ -PCCp⁻ as (a) a top view and (b) a side view from the arrow shown in (a), (c) top views of the dimers as (i) major (72%) and (ii) minor (28%) structures (Fig. S9), and (d) side view of the dimer. The distances between two $1ni^+$, that between $1ni^+$ and PCCp⁻, that between two PCCp⁻ (core 25 atoms), and the Ni···Ni distances in the column are 3.82/2.64/4.15, 3.40, 3.39, and 4.75/13.01/11.64 Å, respectively. The S···N distances in two stacking $1ni^+$ units are 3.26 and 3.33 Å and the dihedral angle between the thiophene plane and the core porphyrin plane (core 25 atoms) is 24.5° . Mean-plane deviation of the $1ni^+$ core part (25 atoms) and τ_4 value^[S11] are 0.30 Å and 0.11, respectively. Atom color code: brown, pink, blue, orange, and light gray refer to carbon, hydrogen, nitrogen, sulfur, and nickel, respectively. Solvent molecules are omitted for clarity.



Fig. S18 Packing diagram (stacking assembly) of $1ni^+2a \cdot Cl^-$ as (a) a top view and (b) a side view from the arrow shown in (a), (c) enlarged view of the packing structure, and (d) top and side views of the enlarged pair. The distances between two $1ni^+-Cl^-$ (core 25 atoms), that between two 2a, and the Ni…Ni distances in the column are 4.06/11.40, 3.47, and 6.19/13.07 Å, respectively. Pyrrole NH of 2a interacts with the F unit of another 2a with an N(–H)…F distance of 2.93 Å. Pyrrole NH, bridging CH, and pyrrole- β -CH interact with Cl^- with the N/C(–H)…Cl⁻ distances of 3.26, 3.52, and 3.79 Å, respectively. The Ni–Cl⁻ distance is 2.28 Å and the dihedral angle between the line through Ni and Cl⁻ to the core porphyrin plane (25 atoms) is 73.6°. The dihedral angle between the thiophene plane and the core porphyrin plane (core 25 atoms) is 25.5°. Mean-plane deviation of the $1ni^+$ core part (25 atoms) and τ_4 value^[S11] are 0.20 Å and 0.33, respectively. Atom color code: brown, pink, yellow, blue, red, yellow green, orange, green, and light gray refer to carbon, hydrogen, boron, nitrogen, oxygen, fluorine, sulfur, chlorine, and nickel, respectively. Solvent molecules are omitted for clarity.



Fig. S19 Packing diagram (stacking assembly) of $1ni^+2b \cdot Cl^-$ as (a) a top view and (b) a side view from the arrow shown in (a), (c) enlarged view of the packing structure, and (d) top and side views of the enlarged pair. The stacking distance between two $1ni^+-Cl^-$ (core 25 atoms) and the Ni…Ni distance in the column are 3.90 and 5.39 Å, respectively. Two pyrrole NH and bridging CH interact with Cl^- with the N/C(-H)…Cl⁻ distances of 3.16/3.37 and 3.44 Å, respectively. The Ni–Cl⁻ distance is 2.27 Å and the angle of the line through Ni and Cl⁻ to the core porphyrin plane (25 atoms) is 72.0°. The S…N distance in two stacking $1ni^+-Cl^-$ units is 3.42 Å and the dihedral angle between the thiophene plane and the core porphyrin plane (core 25 atoms) is 27.9°. Mean-plane deviation of the $1ni^+$ core part (25 atoms) and τ_4 value^[S11] are 0.22 Å and 0.33, respectively. Atom color code: brown, pink, yellow, blue, red, yellow green, orange, green, and light gray refer to carbon, hydrogen, boron, nitrogen, oxygen, fluorine, sulfur, chlorine, and nickel, respectively. Solvent molecules are omitted for clarity.



Fig. S20 Packing diagram (stacking assembly) of $1ni^+2c \cdot Cl^-$ as (a) a top view and (b) a side view from the arrow shown in (a), (c) top views of the dimers as (i) major (80%) and (ii) minor (20%) structures (Fig. S12), and (d) the enlarged structure. The stacking distance between two $1ni^+-Cl^-$ (core 25 atoms), that between $1ni^+-Cl^-$ and 2c, and the Ni \cdots Ni distances in the column are 3.82, 3.35, and 5.70/13.37 Å, respectively. Two pyrrole- α -CH interacts with Cl⁻ with the C(-H) \cdots Cl⁻ distances of 3.41/3.85 Å, respectively. Pyrrole NH interacts with F with the N(-H) \cdots F distance of 2.86 Å. The Ni–Cl⁻ distance is 2.32 Å and the angle of the line through Ni and Cl⁻ to the core porphyrin plane (25 atoms) is 72.6°. The S \cdots N distance in two stacking $1ni^+$ -Cl⁻ units is 3.29 Å and the dihedral angle between the thiophene plane and the core porphyrin plane (core 25 atoms) is 25.1°. Mean-plane deviation of the $1ni^+$ core part (25 atoms) and τ_4 value[^{S11]} are 0.21 Å and 0.34, respectively. Atom color code: brown, pink, yellow, blue, red, yellow green, orange, green, and light gray refer to carbon, hydrogen, boron, nitrogen, oxygen, fluorine, sulfur, chlorine, and nickel, respectively. Solvent molecules are omitted for clarity.



Fig. S21 Hirshfeld surface^[S12] of **1ni**⁺ in the crystal structure of **1ni**⁺-PF₆⁻ (a major disordered structure) mapped over (a) shape-index property and (b) curvedness property: (i) only surface and (ii) surface with a ball-and-stick model of the neighboring **1ni**⁺. Shape index is a qualitative measure of shape and is sensitive to subtle changes in surface shape, particularly in a flat region by differing by sign represent complementary bumps (blue) and hollows (red), whereas curvedness is a function of the root-mean-square curvature of the surface, and maps of curvedness typically show large regions of green (relatively flat) separated by dark blue edges (large positive curvature). The flat region on the curvedness surface suggested the characteristic mapping pattern for stacking in dimeric **1ni**⁺. Atom color code: brown, pink, blue, orange, and light gray refer to carbon, hydrogen, nitrogen, sulfur, and nickel, respectively.



Fig. S22 Hirshfeld surface^[S12] of **1ni**⁺ in the crystal structure of **1ni**⁺-B(C₆F₅)₄⁻ (a major disordered structure) mapped over (a) shape-index property and (b) curvedness property: (i) only surface and (ii) surface with a ball-and-stick model of the neighboring **1ni**⁺. Shape index is a qualitative measure of shape and is sensitive to subtle changes in surface shape, particularly in a flat region by differing by sign represent complementary bumps (blue) and hollows (red), whereas curvedness is a function of the root-mean-square curvature of the surface, and maps of curvedness typically show large regions of green (relatively flat) separated by dark blue edges (large positive curvature). The flat region on the curvedness surface suggested the characteristic mapping pattern for stacking in dimeric **1ni**⁺. Atom color code: brown, pink, blue, orange, and light gray refer to carbon, hydrogen, nitrogen, sulfur, and nickel, respectively.



Fig. S23 Hirshfeld surface^[S12] of $1ni^+$ in the crystal structure of $1ni^+$ -PCCp⁻ (a major disordered structure) mapped over (a) shape-index property and (b) curvedness property: (i) only surface and (ii) surface with a ball-and-stick model of the neighboring $1ni^+$. Shape index is a qualitative measure of shape and is sensitive to subtle changes in surface shape, particularly in a flat region by differing by sign represent complementary bumps (blue) and hollows (red), whereas curvedness is a function of the root-mean-square curvature of the surface, and maps of curvedness typically show large regions of green (relatively flat) separated by dark blue edges (large positive curvature). The flat region on the curvedness surface suggested the characteristic mapping pattern for stacking in dimeric $1ni^+$. Atom color code: brown, pink, blue, orange, and light gray refer to carbon, hydrogen, nitrogen, sulfur, and nickel, respectively.



Fig. S24 Hirshfeld surface^[S12] of **1ni**⁺ in the crystal structure of **1ni**⁺-PCCp⁻ (a major disordered structure) mapped over (a) shape-index property and (b) curvedness property: (i) only surface and (ii) surface with a ball-and-stick model of the neighboring PCCp⁻. Shape index is a qualitative measure of shape and is sensitive to subtle changes in surface shape, particularly in a flat region by differing by sign represent complementary bumps (blue) and hollows (red), whereas curvedness is a function of the root-mean-square curvature of the surface, and maps of curvedness typically show large regions of green (relatively flat) separated by dark blue edges (large positive curvature). The surfaces of **1ni**⁺ showed the red and blue triangles arranged in bow-tie shapes (indicated by a white arrow in (a)) on the shape-index surface and flat region (indicated by red dashed area in (b)) on the curvedness surface, indicating the characteristic mapping pattern for ⁱπ-ⁱπ stacking.^[S13] Atom color code: brown and blue refer to carbon and nitrogen, respectively.



Fig. S25 Hirshfeld surface^[S12] of $1ni^+$ -Cl⁻ in the crystal structure of $1ni^+$ -2a·Cl⁻ mapped over (a) shape-index property and (b) curvedness property: (i) only surface and (ii) surface with a ball-and-stick model of the neighboring $1ni^+$ -Cl⁻. Shape index is a qualitative measure of shape and is sensitive to subtle changes in surface shape, particularly in a flat region by differing by sign represent complementary bumps (blue) and hollows (red), whereas curvedness is a function of the root-mean-square curvature of the surface, and maps of curvedness typically show large regions of green (relatively flat) separated by dark blue edges (large positive curvature). The flat region on the curvedness surface suggested the characteristic mapping pattern for stacking in dimeric $1ni^+$. Atom color code: brown, pink, blue, orange, green, and light gray refer to carbon, hydrogen, nitrogen, sulfur, chlorine, and nickel, respectively.



Fig. S26 Hirshfeld surface^[S12] of $1ni^+$ -Cl⁻ in the crystal structure of $1ni^+$ -2a·Cl⁻ mapped over (a) shape-index property and (b) curvedness property: (i) only surface and (ii) surface with a ball-and-stick model of the neighboring 2a. Shape index is a qualitative measure of shape and is sensitive to subtle changes in surface shape, particularly in a flat region by differing by sign represent complementary bumps (blue) and hollows (red), whereas curvedness is a function of the rootmean-square curvature of the surface, and maps of curvedness typically show large regions of green (relatively flat) separated by dark blue edges (large positive curvature). Atom color code: brown, pink, yellow, blue, red, and yellow green refer to carbon, hydrogen, boron, nitrogen, oxygen, and fluorine, respectively.



Fig. S27 Hirshfeld surface^[S12] of $1ni^+$ in the crystal structure of $1ni^+2b\cdot Cl^-$ mapped over (a) shape-index property and (b) curvedness property: (i) only surface and (ii) surface with a ball-and-stick model of the neighboring $1ni^+-Cl^-$. Shape index is a qualitative measure of shape and is sensitive to subtle changes in surface shape, particularly in a flat region by differing by sign represent complementary bumps (blue) and hollows (red), whereas curvedness is a function of the root-mean-square curvature of the surface, and maps of curvedness typically show large regions of green (relatively flat) separated by dark blue edges (large positive curvature). The flat region on the curvedness surface suggested the characteristic mapping pattern for stacking in dimeric $1ni^+$. Atom color code: brown, pink, blue, orange, green, and light gray refer to carbon, hydrogen, nitrogen, sulfur, chlorine, and nickel, respectively.



Fig. S28 Hirshfeld surface^[S12] of $1ni^+$ in the crystal structure of $1ni^+2b \cdot Cl^-$ mapped over (a) shape-index property and (b) curvedness property: (i) only surface and (ii) surface with a ball-and-stick model of the neighboring 2b. Shape index is a qualitative measure of shape and is sensitive to subtle changes in surface shape, particularly in a flat region by differing by sign represent complementary bumps (blue) and hollows (red), whereas curvedness is a function of the root-mean-square curvature of the surface, and maps of curvedness typically show large regions of green (relatively flat) separated by dark blue edges (large positive curvature). Atom color code: brown, pink, yellow, blue, red, and yellow green refer to carbon, hydrogen, boron, nitrogen, oxygen, and fluorine, respectively.



Fig. S29 Hirshfeld surface^[S12] of $1ni^+$ in the crystal structure of $1ni^+2c\cdot Cl^-$ mapped over (a) shape-index property and (b) curvedness property: (i) only surface and (ii) surface with a ball-and-stick model of the neighboring $1ni^+-Cl^-$. Shape index is a qualitative measure of shape and is sensitive to subtle changes in surface shape, particularly in a flat region by differing by sign represent complementary bumps (blue) and hollows (red), whereas curvedness is a function of the root-mean-square curvature of the surface, and maps of curvedness typically show large regions of green (relatively flat) separated by dark blue edges (large positive curvature). The flat region on the curvedness surface suggested the characteristic mapping pattern for stacking in dimeric $1ni^+$. Atom color code: brown, pink, blue, orange, green, and light gray refer to carbon, hydrogen, nitrogen, sulfur, chlorine, and nickel, respectively.



Fig. S30 Hirshfeld surface^[S12] of $1ni^+$ in the crystal structure of $1ni^+2c\cdot Cl^-$ mapped over (a) shape-index property and (b) curvedness property: (i) only surface and (ii) surface with a ball-and-stick model of the neighboring $1ni^+-Cl^-$. Shape index is a qualitative measure of shape and is sensitive to subtle changes in surface shape, particularly in a flat region by differing by sign represent complementary bumps (blue) and hollows (red), whereas curvedness is a function of the root-mean-square curvature of the surface, and maps of curvedness typically show large regions of green (relatively flat) separated by dark blue edges (large positive curvature). The surfaces of $1ni^+$ showed the red and blue triangles arranged in bow-tie shapes (indicated by a white arrow in (a)) on the shape-index surface and flat region (indicated by red dashed area in (b)) on the curvedness surface, suggesting the characteristic mapping pattern for stacking between $1ni^+$ and 2c. Atom color code: brown, pink, yellow, blue, red, and yellow green refer to carbon, hydrogen, boron, nitrogen, oxygen, and fluorine, respectively.

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3. Theoretical studies

DFT calculations. DFT calculations were carried out using *Gaussian 16* program.^[S14]



Fig. S31 Optimized structures of (a) $1ni^+$, (b) $1ni^+$ -Cl⁻, (c) $1ni^+$ -BF₄⁻, (d) $1ni^+$ -PF₆⁻, (e) $1ni^+$ -B(C₆F₅)₄⁻, and (f) $1ni^+$ -PCCp⁻ at PCM-B3LYP/6-31+G(d,p)(CH₂Cl₂) except for (e) at PCM-B3LYP/6-31+G(d,p)(CH₂Cl₂)//PCM-B3LYP/6-31G(d,p)(CH₂Cl₂). Crystal structures (Fig. S13,15–17) were used for the initial structures for the optimizations except for $1ni^+$ -BF₄⁻, whose initial structure was prepared based on the geometry of $1ni^+$ -PF₆⁻.



Fig. S32 Molecular orbitals (HOMO/LUMO) of 1ni⁺ estimated at PCM-B3LYP/6-31+G(d,p)(CH₂Cl₂).



Fig. S33 Molecular orbitals (HOMO/LUMO) of 1ni⁺-Cl⁻ estimated at PCM-B3LYP/6-31+G(d,p)(CH₂Cl₂).



Fig. S34 TD-DFT-based UV/vis absorption stick spectrum of $1ni^+$ with the transitions correlated with molecular orbitals estimated at PCM-B3LYP/6-31+G(d,p)(CH₂Cl₂).

Fig. S35 TD-DFT-based UV/vis absorption stick spectrum of $1ni^+$ -Cl⁻ with the transitions correlated with molecular orbitals estimated at PCM-B3LYP/6-31+G(d,p)(CH₂Cl₂). Theoretical study showed a small band with the maximum at 476 nm, which was not seen in anion-free $1ni^+$ (Fig. S34) and may be characteristic to the Cl⁻-coordination state.

Fig. S36 NICS values $(ppm)^{[S15]}$ of (a) $1ni^+$ and (b) $1ni^+-Cl^-$ based on the optimized structures at PCM-B3LYP/6-31+G(d,p)(CH₂Cl₂) (Fig. S31). The aromaticity of $1ni^+-Cl^-$ is comparable to that of $1ni^+$ although the details were not discussed from the broad ¹H NMR signals of $1ni^+-Cl^-$ due to the paramagnetic property.

Fig. S37 Anisotropy of the induced current density $(ACID)^{[S16]}$ of (a) $1ni^+$ and (b) $1ni^+-Cl^-$ (top and side views) at isosurface value of $\delta = 0.015$ based on the optimized structures (Fig. S31) at PCM-B3LYP/6-31+G(d,p)(CH₂Cl₂). Current density vectors are plotted on to the ACID isosurface based on the vector of the magnetic field (H_0) which is orthogonal with respect to the molecule. The theoretical results were consistent with the NICS values (Fig. S36).

Fig. S38 Electrostatic potential (ESP) mapping (top and side views, $\delta = 0.01$) of (a) $1ni^+$ -Cl⁻tri, (b) $1ni^+$ -PF6⁻, (c) $1ni^+$ -B(C6F5)4⁻, and (d) $1ni^+$ -PCCp⁻ in the single-crystal X-ray structures (Fig. S13,15–17) calculated at B3LYP/6-31+G(d,p) for C, H, B, N, F, P, S, and Cl and B3LYP/LanL2DZ for Ni.

Fig. S39 Single-crystal X-ray structure of $1ni^+$ -PF₆⁻ for the EDA calculations (Table S2): (a) top view of charge-by-charge structure and (b) side view of shaded part in (a). The labels (c1,2 and a1) correspond to the fragments shown in Table S2.

Table S2 Energies between selected fragments in $1ni^+$ -PF₆⁻ (Fig. S39) estimated by EDA calculations based on an FMO2-MP2 using mixed basis sets including NOSeC-V-TZP with MCP for Ni and NOSeC-V-DZP with MCP for the other atoms.^[S17–19]

fragments	total interaction energy	electrostatic interaction	dispersion interaction	exchange repulsion	charge-transfer interaction
	(E_{tot})	energy (E_{es})	energy (E_{disp})	interaction energy (Eex)	energy $(E_{ct + mix})$
	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)
c1-c2	-160.909	0.585	-202.705	68.376	-27.165
c1-a1	-74.524	-57.149	-17.176	2.076	-2.274

Fig. S40 Single-crystal X-ray structure of $1ni^+$ -B(C₆F₅)₄⁻ for the EDA calculations (Table S3): (a) top view of charge-bycharge structure and (b) side view of shaded part in (a). The labels (c1,2 and a1) correspond to the fragments shown in Table S3.

Table S3 Energies between selected fragments in $1ni^+$ -B(C₆F₅)₄⁻ (Fig. S40) estimated by EDA calculations based on an FMO2-MP2 using mixed basis sets including NOSeC-V-TZP with MCP for Ni and NOSeC-V-DZP with MCP for the other atoms.^[S17-19]

fragments	total interaction energy (E_{tot})	electrostatic interaction energy (<i>E</i> _{es})	dispersion interaction energy (Edisp)	exchange repulsion interaction energy (E_{ex})	charge-transfer interaction energy $(E_{\text{ct+mix}})$
	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)
c1-c2	-139.397	12.078	-178.494	45.088	-18.069
c1-a1	-77.894	-39.681	-40.777	6.197	-3.634

Fig. S41 Single-crystal X-ray structure of $1ni^+$ -PCCp⁻ for the EDA calculations (Table S4): (a) top view of charge-bycharge structure and (b) side view of shaded part in (a). The labels (c1,2 and a1,2) correspond to the fragments shown in Table S4.

Table S4 Energies between selected fragments in **1ni**⁺-PCCp⁻ (Fig. S41) estimated by EDA calculations based on an FMO2-MP2 using mixed basis sets including NOSeC-V-TZP with MCP for Ni and NOSeC-V-DZP with MCP for the other atoms.^[S17–19]

fragments	total interaction energy	electrostatic interaction	dispersion interaction	exchange repulsion	charge-transfer interaction
	(E_{tot})	energy (E_{es})	energy (E_{disp})	interaction energy (E_{ex})	energy $(E_{ct + mix})$
	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)
c1-c2	-145.015	14.676	-185.254	42.901	-17.338
c2-a1	-163.833	-61.142	-115.234	22.515	-9.972
a1-a2	-0.379	45.185	-52.509	10.815	-3.870

Cartesian coordination of optimized structures

Cartesian Coordination of 1ni⁺

-2425.2657623 hartree

H.33.1395536108.15.0036693587.8.4034294974 H,34.1972122927,16.8122291573,9.7474729621 C,19.4329552759,15.8879527997,3.9540824968 C,19.0795124479,16.6662728706,2.847126063 C.19.9984305651.17.578549484.2.3183343044 H,18.7267436608,15.1738450038,4.3673358227 H,18.0955198313,16.5623707933,2.39952221 H,19.7300792898,18.1890719496,1.4611901461 C,32.6342537556,15.9566692876,8.5287001487 H,30.1480320563,13.5085965964,0.4853024588 H,29.1205882535,14.2275946598,2.620845093 H,30.9290841131,15.3672210179,7.3524057058 C,28.5742199621,16.3284734331,-0.5961748307 C,29.35414396,15.1684656886,-0.644919796 H 28 4221295575 16 9221808998 -1 4927383182 H.29.8071211329.14.8551917599.-1.5808981017 C,24.5534999102,18.3084561062,9.1235411933 C,23.8399255695,18.3895858002,10.4290559929 C.24.1068184859.19.4490494674.11.315083799 C,23.4552428483,19.5225989591,12.547946322 C,22.5401513914,18.5318135336,12.9188491455 C,22.2755288963,17.4687441503,12.0486910259 C,22.916963303,17.3986482817,10.8106489286 C,23.8083436652,18.1680091271,7.9199021368 C,22.3944365215,18.4346632947,7.8844828352 C.21.9519091233.18.1109441235.6.6405649543 C,23.0886550835,17.6202357965,5.9050152995

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Ni.26.0721229263.17.4257784804.5.9129722765
S,26.8248268551,18.570048217,7.6366175575
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Cartesian Coordination of 1ni⁺-Cl⁻ -2885 6408336 hartree

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Cartesian Coordination of $1ni^+\text{-}BF_4^-$

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-2849.9207917 hartree
H,-0.82174837,15.5235462679,1.8909363527
H,2.923177627,15.8098976477,14.8305040434
H.4.0556688567.15.3648539452.16.9868243476
H.0.2485459186,15.7190987213,4.1162974025
C,0.0197144662,14.0243064127,6.232024118
C,-0.6275005347,13.902106131,4.8882561818
C,-0.3959320466,14.8721360809,3.898478366
C,-1.0011764166,14.7614694295,2.6438639326
C.-1.8337321895.13.6736716582.2.3603466242
C,-2.0615724621,12.7006749749,3.3388514523
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C,-0.7932033583,14.273680466,7.3457123389
C,-2.2139166975,14.4886338825,7.2442573495
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 $\begin{array}{l} F_{2}-2.1482463859, 8.5061700756, 8.283677652\\ F_{3}-1.8431412346, 10.2020888787, 6.7459915157\\ F_{3}-2.2781300674, 10.7114108178, 8.9571213167\\ F_{3}-3.9406013938, 9.8094546809, 7.6306734596\\ B_{3}-2.5540474953, 9.8059193797, 7.9043237839\\ \end{array}$

Cartesian Coordination of 1ni⁺-PF₆⁻

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C,-5.0685484961,0.8311190969,0.0125300302 C,-3.6759389303,1.1882203745,-0.0703285242 C -3.2160118871.2.5054204905.0.0663300563 C,-4.209537205,3.5813047571,0.3748132891 C.-4.8661325262.3.6148352669.1.6163678195 C,-5.7840417057,4.6281724745,1.9051225001 C,-6.0658645639,5.6135506125,0.9534188483 C,-5.4198286101,5.5851153712,-0.2867428247 C,-4.492551113,4.5794740319,-0.5724456086 C.-1.8685165956,2.8714182816,-0.0592942981 C.-1.354275185.4.1984907924.0.1779838917 C,-0.0272563861,4.1684623313,-0.1260689357 C,0.2745874303,2.8238161069,-0.5530633927 C,-1.6219852102,-4.145915971,-0.1494059172 C,-2.2601369666,-2.9206090848,-0.4579712427 H.-7.1538215256.-5.8866472006.1.8000018548 H,-6.4650932078,-3.9300188605,3.176106352 H.-4.7962757569.-2.3237877509.2.305124586 H,-6.0123582783,-1.1506582837,0.016199365 H,-5.8866327477,1.5312736497,0.0859552597 H.-1.9333845619.5.0340731248.0.5410266738 H.0.6878824451.4.974309207.-0.0597430421 H,-2.1353553824,-4.9445859704,0.3709660259 H,-4.6465138787,2.8543413938,2.3599848317 H.-6.2769586728.4.6467664615.2.8727045106 H,-6.7823477332,6.3984921737,1.1770141081 H,-5.6352854467,6.3449807924,-1.0322340298 H,-3.9937569999,4.5604359767,-1.5371382708 N,-0.8528040609,2.0441519667,-0.4731257674 N,-2.8938691713,0.0548936877,-0.2141446011 Ni,-0.9436230081,0.140979689,-0.6907141613 S.-1.1546605004.-1.9313656807.-1.401820331

Cartesian Coordination of 1ni⁺-B(C₆F₅)₄⁻ -5361.3663366 hartree

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C,7.5722383704,-14.9779767834,-28.7915821051
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F,5.7809807947,-15.9464702834,-30.008832984
F,4.2919081481,-16.0726116409,-27.7094317892
C,7.6495672277,-14.9427144511,-23.6179478007
C,7.7654023529,-14.4356644979,-22.3193483457
C,7.7227911775,-15.2085025257,-21.1655969917
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C,7.5145432364,-16.3326249669,-23.6668010238
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C,10.1495652574,-12.5814933843,-24.2544408579
C,11.5182601885,-12.5040168413,-23.993494448
C,11.7720595495,-14.6990998936,-24.8995127356
C,10.4000737313,-14.7402584344,-25.1184406911
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B,7.8800439883,-13.937287966,-24.924292758
C,7.3836409033,-14.5828579509,-26.3685164269
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Cartesian Coordination of 1ni⁺-PCCp⁻

-3080.1949264 hartree

H,0.5486854562,7.235609839,1.9562871629 H,-1.0108605299,8.833349979,0.8550021342 C,0.0365670193,-6.8922728789,0.038130353 C,0.507236203,-7.5395445688,-1.1088078111 C,0.7987296541,-6.7943011304,-2.2560403052 H.-0.1851921042,-7.462793164,0.9352443777 H,0.6476931994,-8.6164963104,-1.1082507889 H,1.1623817462,-7.2897853273,-3.151544929 C,-0.0991188309,6.8992154426,1.152281218 C,2.4265408548,-1.531016158,3.4303980564 C,3.2295675307,-2.6944534353,3.5165711793 C,1.0084094302,-1.4975449047,3.3849192113 C,0.1465886696,-2.6207532589,3.4103548474 C,0.6040685792,-0.139657407,3.3034761567 C,-0.7307362696,0.3285174338,3.2437435752 C,1.7722531979,0.6660907346,3.295577849 C,1.8069810674,2.0792005701,3.2135983639 C,2.8985356421,-0.1938781676,3.3759829244 C,4.2547503774,0.2131020655,3.4002142293 H,7.1556223413,2.0809687945,-0.4348505654

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4. Properties of π -electronic cations

Fig. S42 Summarized ¹H NMR spectra of **1ni**⁺-X⁻ (X⁻ = Cl⁻, BF₄⁻, PF₆⁻, B(C₆F₅)₄⁻, PCCp⁻) in CDCl₃ (600 MHz, 20 °C) (Fig. S1–4). The broad signals for **1ni**⁺-Cl⁻ in the wide range from 66 to –31 ppm were derived from the paramagnetic Ni^{II} by Cl⁻ coordination.^[S20] The differences in **1ni**⁺-X⁻ (X⁻ = BF₄⁻, PF₆⁻, B(C₆F₅)₄⁻, PCCp⁻) are related with the interactions between the anions and **1ni**⁺ in solution. The details on the solution-state ion pairing will be examined and reported elsewhere.

Fig. S43 (a) UV/vis absorption spectra with (b) enlarged version for $1ni^+$ -X⁻ (X⁻ = Cl⁻, BF₄⁻, PF₆⁻, B(C₆F₅)₄⁻, PCCp⁻) in CH₂Cl₂ (1 × 10⁻⁵ M for $1ni^+$ -Cl⁻, $1ni^+$ -BF₄⁻, and $1ni^+$ -PF₆⁻ and 8×10^{-6} M for $1ni^+$ -B(C₆F₅)₄⁻ and $1ni^+$ -PCCp⁻). The spectrum of $1ni^+$ -BF₄⁻ is similar to that of $1ni^+$ -Cl⁻ except for the Soret band, whereas $1ni^+$ -PF₆⁻, $1ni^+$ -B(C₆F₅)₄⁻, and $1ni^+$ -PCCp⁻ have similar Soret and Q bands. The absence of axial Cl⁻ coordination resulted in the blue-shifted Soret band at 432 nm for $1ni^+$ -PF₆⁻ and at 431 nm for $1ni^+$ B(C₆F₅)₄⁻ and $1ni^+$ -PCCp⁻ compared to that of $1ni^+$ -Cl⁻ at 471 nm.

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