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Antiproliferative Activity and Electrochemical Oxygen Evolution by Ni(II) Complexes of N'-(aroyl)-hydrazine Carbodithioates

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Contents

1. Materials and methods

Commercial reagents were used without further purification and all experiments were carried out in an open atmosphere. methyl-4-methylbenzoate (Sigma Aldrich), Isonicotinic acid hydrazide (Sigma Aldrich), methylsalicylate (Sigma Aldrich), CS_2 (SD Fine Chemicals, India), and KOH (Qualigens) were used as received. Ethyl iodide was procured from CDH Chemicals, India. All the solvents were purchased from Merk Chemicals, India, and used after purification. The carbon, hydrogen, and nitrogen contents were estimated on a Carlo Erba 1108 model microanalyzer. Magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using $Hg[Co(NCS)_4]$ as the calibrant. Electronic spectra were recorded on a SHIMADZU 1700 UV-Vis spectrophotometer. Infrared spectra were recorded in the 4000-400 cm^{-1} region as KBr pellets on a PerkinElmer Spectrum Version 10.4.3 3100 FT-IR spectrophotometers. Thermogravimetric analysis (TG-DTA) of complexes **1, 2,** and **3** were done using a Perkin Elmer-STA 6000 thermal analyzer, TA Instruments with a heating rate of 5ºC min^{-1}. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a JEOL AL 300 FT-NMR spectrometer using TMS as an internal reference.

1.1 Cell culture

Human erythromyeloma cells K562 were procured from American Type Culture Collection (ATCC), Manassas, USA, and was maintained in RPMI 1640 (Invitrogen, Carlsbad, CA) with supplements including 10% fetal bovine serum (Hyclone, Logan, UT), 100 U/ml penicillin and 100 μg/ml streptomycin (Invitrogen, Carlsbad, CA), henceforth considered as a complete medium.

1.2 Cytotoxicity assay

The lytic activity of the metal salts, ligands, and their complexes **1**, **2,** and **3** against the K562 cells was measured by cytotoxicity assay (CytoTox 96 cytotoxicity assay kit, Promega, USA).[1] Tumor cells (5×10^3) were co-cultured in the presence of increasing concentrations (50-150 μM) of the indicated materials in a 96 well culture dish. The tumor cells were incubated for 18 hours at 37˚C, with 5% CO_2. Specific lysis (percentage of cytotoxicity) was ascertained from the undermentioned formula:

$$\%\ Cytotoxicity = \frac{(Experimental\ -\ Effector\ Spontaneous\ -\ Target\ Spontaneous)}{(Target\ Maximum\ -\ Target\ Spontaneous)} \times 100$$

1.3 Cell growth inhibition assay

Growth inhibitory potential of metal salts, ligands, and their complexes **1**, **2,** and **3** against the K562 cells was studied by MTT assay. Tumor target cells (5×10^3 cells /well) in a 96 well culture dish were treated with serial concentrations (10, 25, 50, and 100 μM) of the indicated compounds. Following incubation at 37°C, 5% CO_2, for 48 hours, the proliferation of the tumor cells was assessed by MTT assay using CellTiter 96 kit (Promega, USA). The measurement of absorbance (OD values) was made at 570 nm in a plate reader (BioTek, USA).[2] Percent inhibition of the tumor cells was calculated using the mentioned formula:

$$\%\ Growth\ Inhibition\ = [1 - \frac{Experimental\ OD570}{Target\ OD570}] \times 100$$

The Experimental OD indicates the values of the tumor cells in the presence of indicated compounds and the Target OD indicates the corresponding values of the tumor cells alone, cultured in medium only.

1.4 Statistical analysis

Unpaired student's t-test or one-way ANOVA followed by Tukey's post hoc test was performed while comparing between the groups. Each experiment was performed in triplicate and the data were presented as mean ± SD (standard deviation). Differences were considered significant for p-value < 0.05. *<0.05, **<0.01 and ***<0.001.

1.5 Electrochemical water oxidation

KOH was purchased from Merk, India. Nafion (5 % solution in lower alcohols, Nf) and RuO_2 (99.9 %) were purchased from Sigma-Aldrich, India. All electrochemical measurements were performed using electrochemical workstation CHI-660C (CH Instruments, USA). Three electrode-one compartment system was used for the measurements. Surface modified glassy carbon (GC) electrode of area 0.07 cm^2, Hg/HgO (20% KOH), and platinum wire was used as the working, reference, and counter electrodes, respectively. Surface modification of GC electrodes was achieved by the drop-casting approach. A suspension of the respective complex (1 mM) and 0.1 % Nf was prepared in methanol. The suspension (5 μL) was drop-cast on vertically mounted clean and dry GC electrodes and allowed to dry to get the working electrode (GC/Nf/Complex **1**, **2**, and **3**). Unless otherwise stated, the term overpotential in this manuscript implies overpotential required to drive a geometrical current density of 10 $mAcm^{-2}$.

For the calculation of turnover frequency (TOF), first, the charge is calculated by integrating the reduction peak area of the respective complex. Relation between the charge and the number of moles of active sites is given by equation 1,

$$N = \frac{Charge}{F \times Scan\ rate} \quad \ldots 1$$

where N is the number of moles of active sites and F is Faraday constant. Further, the TOF value is calculated using equation 2.

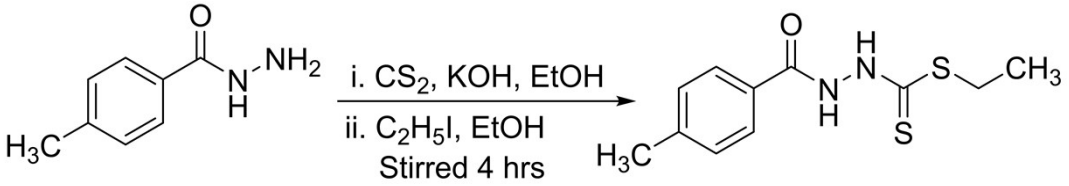
$$TOF = \frac{J}{4nF} \quad \ldots 2$$

Where J is the geometrical current density obtained from the linear sweep voltammetry (LSV).

2. Preparation of Ligands

2.1 N'-(4-Methyl-benzoyl)hydrazinecarbodithioic acid ethyl ester (H_2mbhce)

N'-(4-Methyl-benzoyl) hydrazinecarbodithioic acid ethyl ester (H_2mbhce) was synthesized by a mixture of methyl-4-methylbenzoate (2.84 mL, 20 mmol) and hydrazine hydrate (1.0 mL, 20 mmol) in absolute ethanol and refluxed for 6 h. The white precipitate obtained upon cooling was filtered off, washed thoroughly with hot water. The above precipitate was dissolved in an alcoholic solution of KOH (1.12 g, 20 mmol) and carbon disulfide (1.2 mL, 20 mmol) was added dropwise in ice-cold conditions. After 20 min of stirring, a white precipitate was obtained which was filtered off washed with ether, and dried in *vacuo*. Further, the precipitate was dissolved in absolute ethanol kept on an ice bath and ethyl iodide (1.28 mL, 16 mmol) was added. After 8 h of continuous stirring at room temperature, a colorless solution was obtained which was filtered off and kept overnight and acidified with dilute acetic acid (50%). White crystalline solid was obtained which was filtered off, wash with hot water, and recrystallized in absolute ethanol.

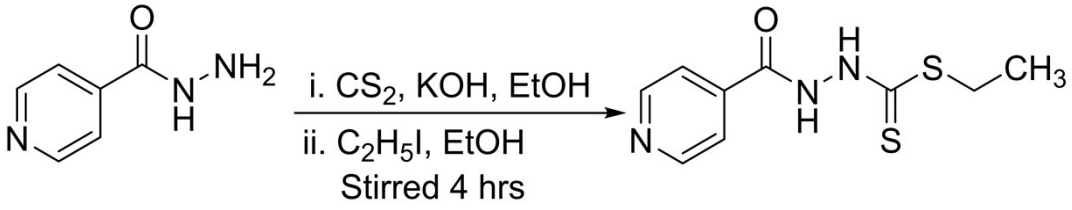


Scheme 1. Preparation of H_2mbhce

Yield: 58%; m.p. 83 ^{o}C. Anal. Found (%): C = 52.20, H = 5.70, N = 10.90. Anal. Calcd (%):51.96.26, H = 5.51, N = 11.02 for $C_{11}H_{14}N_2OS_2$ (254.00) IR (ν cm^{-1}, KBr): ν(NH) 3261, 3139; ν(C=O) 1645; ν(N–N) 1052; ν(C=S) 963. ^{1}H NMR (DMSO-d6; δ ppm): 11.19 & 10.62 (2NH), 8.05–7.39 (m, 4H, aromatic ring), 3.26 (s, Ar-CH_3), 1.51 (q, CH_2), 1.38 (t, CH_3). ^{13}C NMR (DMSO-d6; δ ppm): 203.1 (C=S), 165.2 (C=O), 119.8–143.3 (aromatic carbons), 28.4 (CH_3 carbon), 21.0 & 13.7 (S-CH_2 & CH_3). UV-vis (λ_{max}, DMSO, nm) 281 and 320.

2.2 N'-(pyridine-4-carbonyl)hydrazinecarbodithioic acid ethyl ester (H_2pchce)

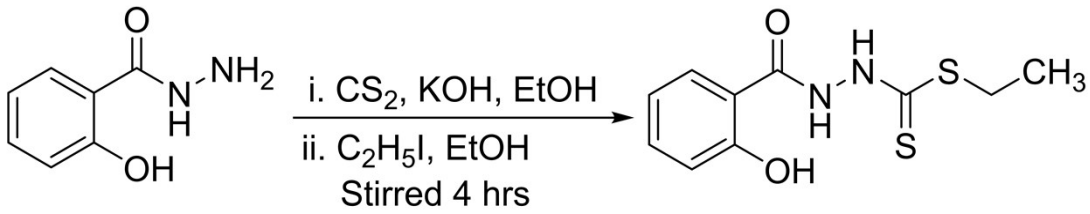
The ligand N'-(pyridine-4-carbonyl)hydrazine carbodithioic acid ethyl ester (H_2pchce) was prepared by literature method.[3]



Scheme 2. Preparation of H_2pchce

2.3 N'-(2-Hydroxy-benzoyl)hydrazinecarbodithioic acid ethyl ester (H_2hbhce)

N'-(2-Hydroxy-benzoyl)-hydrazinecarbodithioic acid ethyl ester (H_2hbhce) was synthesized by a refluxing methylsalicylate (2.59 mL, 20 mmol) and hydrazine hydrate (1.0 mL, 20 mmol) in absolute ethanol for 5 h. The white precipitate obtained upon cooling was filtered off, washed thoroughly with water, and finally with ether and recrystallized from ethanol. The above precipitate was dissolved in an alcoholic solution of KOH (1.12 g, 20 mmol) and carbon disulfide (1.2 mL, 20 mmol) was added dropwise in ice-cold conditions. After 25 minutes of stirring, a white precipitate was obtained which was filtered off, washed with ether, and dried in *vacuo*. Further, the white solid was dissolved in absolute ethanol and ethyl iodide (1.44 mL, 18 mmol) was added. After 8 h of continuous stirring at room temperature, a clear solution was obtained which was filtered off and kept overnight at room temperature in an open atmosphere and acidified with dilute acetic acid (50%) white solid precipitate was obtained, which was filtered off, washed with hot water and recrystallize in absolute ethanol.



Scheme 3. Preparation of H_2hbhce

Yield: 74%; m.p. 90 °C. Anal. found: C = 46.81, H = 4.70, N = 10.88 (%) Anal. calc for $C_{10}H_{12}N_2O_2S_2$ (256.00) C = 46.85, H = 4.72, N = 10.93. IR (ν cm^{-1}, KBr): ν(OH) 3301, ν(NH) 3220, 3105; ν(C=O) 1621; ν(N–N) 1051; ν(C=S) 968. ^{1}H NMR (DMSO-d6; δ ppm): 11.63 (NH), 7.95–6.77 (m, 4H, aromatic protons), 1.27 (q, CH_2), 1.14 (t, CH_3). ^{13}C NMR (DMSO-d6; δ ppm): 203.36 (C=S), 164.33 (C=O), 114.98–134.98 (aromatic ring carbons), 29.09-14.24 (S-CH_2-CH_3). UV-vis (λ_{max}, DMSO, nm) 251, 288 and 320.

2.4 Discussion of ^{1}H and ^{13}C NMR spectra of ligands

The ^{1}H NMR spectrum of H_2mbhce shows two peaks at δ 11.19 and 10.62 ppm for the amide and thioamide protons, respectively. The peaks at 1.38 and 1.24 ppm are attributable to CH_2 and CH_3 protons respectively. The benzylic protons are observed at 3.26 ppm and aromatic protons appear as multiplets between δ 8.05–7.39 ppm. The ^{13}C NMR spectrum of H_2mbhce shows two peaks at δ 203.1 and 165.2 ppm attributes to the >C=S and >C=O, carbons, respectively. The peaks for >CH_2 and -CH_3 carbons are observed at δ 21.0 and 13.7 ppm. The phenyl ring carbons are seen in 119.8–143.3 ppm range. The methyl carbon attached with the phenyl ring appears at 28.4 ppm. The ^{1}H NMR spectrum of H_2hbhce shows two signals at δ 11.63 and 10.05 ppm due to phenolic (OH) and hydrazine (NH) protons, respectively. The signals for methylene and methyl protons are observed at 1.27 and 1.44 ppm, respectively. Phenyl ring protons appear in the δ 7.95–6.77 ppm range. The ^{13}C NMR spectrum of H_2hbhce displays two signals at δ 203.36 and 164.33 ppm are because of the >C=S and >C=O carbons, respectively. The peaks for >CH_2 and -CH_3 carbons are observed at δ 29.0 and 14.2 ppm. The phenyl ring carbons are observed in the 114.98–134.98 ppm range.

3. Crystallographic Appendix

3.1 X-ray crystallography

X-ray diffraction measurements of complexes **1, 2,** and **3** were performed on an Oxford Gemini diffractometer equipped with a CrysAlis CCD software package using a graphite mono-chromated Mo Kα (λ=0.71073 Å) radiation source at 293 (for **1**)/ 299 (for **2**)/ 298 K (for **3**). Multi-scan absorption correction was applied to the X-ray data collection for all the complexes. The structures were solved by direct methods (SHELXL-2013) and refined by full-matrix least-square on F^2 (SHELXL) using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in the calculated position and refined with a riding model.[4] The MERCURY package and ORTEP-3 for Windows program were used for generating molecular graphics. [5,6]

Supplementary Table 1. Crystallographic data for complexes **1**, **2** and **3**

Parameters	**Complex 1**	**Complex 2**	**Complex 3**
Empirical formula	$C_{32}H_{36}N_6NiO_2S_4$ $[Ni(Hmbhce)_2(py)_2]$	$C_{34}H_{33}N_7\ NiO_4S_2$ $[Ni(pchce)(o\text{-phen})_2]\cdot CH_3OH\cdot 2H_2O$	$C_{143}H_{119}C_{l21}N_{24}Ni_4O_{12}\ S_8$ $4[Ni(hbhce)(o\text{-phen})_2]\cdot 7CHCl_3\cdot 4H_2O$
Formula weight	723.60	726.50	3601.38
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P 21/c
T (K)	293(2)	299(2)	298(2)
λ, Cu-Kα (Å)/ Mo-Kα (Å)	0.71073	0.71073	0.71073
a (Å)	8.8513(9)	10.8202(9)	17.1272(12)
b (Å)	9.9415(10)	12.6519(12)	20.0705(13)
c (Å)	10.9782(10)	12.8207(15)	11.5195(9)
α (º)	68.212(9)	104.095(9)	90
β (º)	89.716(8)	96.477(8)	96.170(7)
γ(º)	74.358(9)	95.991(7)	90
V, (Å^3)	858.90(16)	1675.5(3)	3936.9(5)
Z	1	2	1

ρ_{calcd} (g/cm^3)	1.399	1.440	1.519
μ (mm^{-1})	0.847	0.754	1.000
F(000)	378.0	756	1838
Crystal size (mm^3)	0.25 x 0.18 x 0.15	0.25 x 0.18 x 0.11	0.26 x 0.19 x 0.15
θ range for data collections (º)	3.593 to 29.471	2.028 to 28.929	3.001 to 29.083
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -14 ≤ l ≤ 15	-6 ≤ h ≤ 14, -16 ≤ k ≤ 16, -16 ≤ l ≤ 17	-18 ≤ h ≤ 22, -16 ≤ k ≤ 27, -14 ≤ l ≤ 1
No. of reflections collected	12689	13193	21378
No. of independent reflections (R_{int})	4773	7516	8758
No. of data/restrains/parameters	4773 / 0 / 209	7516 / 6 / 451	8758 / 61 / 513
Goodness-of-fit on F^2	1.039	1.063	0.872
$R_1{}^a$, w$R_2{}^b$ [(I>2σ(I)]	0.0377, 0.0924	0.0501, 0.1320	0.0805, 0.1732
$R_1{}^a$, w$R_2{}^b$ (all data)	0.0492, 0.1017	0.0646, 0.1416	0.2124, 0.2041
Largest difference in peak /hole (e.Å^{-3})	0.459, -0.348	1.088, -0.547	0.846, -0.514

$^aR_1 = \Sigma||F_o| - |Fc||\Sigma|F_o|$;

$^bR_2 = [\Sigma w\,(|F^2_o| - |F^2_c|)^2/\Sigma w|F^2_o|^2]^{1/2}$

Supplementary Table 2. Selected interatomic distances and angles for $[Ni(Hmbhce)_2(py)_2]$ (**1**)

Bond length (Å)		Bond angle (º)	
Ni-O(1)	2.0339(13)	O(1)-Ni-N(3)	90.08(6)
Ni-N(3)	2.1091(17)	O(1)-Ni-N(3)i	89.92(6)
Ni-N(2)	2.1282(15)	O(1)-Ni-N(2)	79.05(6)
S(2)-C(9)	1.769(2)	N(3)i-Ni-N(2)i	88.77(6)
S(2)-C(10)	1.796(2)	N(3)-Ni-N(2)i	91.23(6)
S(1)-C(9)	1.694(2)	O(1)i-Ni-N(2)	100.95(6)
O(1)-C(8)	1.257(2)	N(3)-Ni-N(2)	88.77(6)
N(2)-N(1)	1.386(2)	N(1)-N(2)-Ni	106.31(11)
N(3)-C(16)	1.331(3)	C(8)-O(1)-Ni	114.15(12)
N(1)-C(8)	1.317(2)	N(3)i-Ni-N(2)	91.23(6)

Supplementary Table 3. Intramolecular interactions [Å and º] for $[Ni(Hmbhce)_2(py)_2]$ (**1**)

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(16)-H(16)...O(1)	0.93	2.59	3.060(3)	111.9
C(12)-H(12)...O(1)i	0.93	2.62	3.078(3)	110.6
N(1)-H(1N1)...S(1)	0.82(3)	2.34(3)	2.8363(18))	119(2)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1

Supplementary Table 4. Interatomic distances and angles for $[Ni(pchce)(o\text{-phen})_2]\bullet CH_3OH\bullet H_2O$ (**2**)

Bond length (Å)		Bond angle (º)	
Ni-O(1)	2.034(2)	O(1)-Ni-N(1)	78.74(9)
Ni-N(1)	2.079(3)	O(1)-Ni-N(7)	91.17(9)
Ni-N(7)	2.102(2)	N(1)-Ni-N(7)	95.95(10)
Ni-N(4)	2.107(2)	O(1)-Ni-N(4)	94.99(9)
Ni-N(5)	2.138(3)	N(7)-Ni-N(4)	168.33(10)
Ni-N(5)	2.138(3)	O(1)-Ni-N(6)	169.27(9)
S(1)-C(7)	1.684(3)	N(7)-Ni-N(6)	79.31(10)
S(2)-C(7)	1.803(3)	N(4)-Ni-N(6)	93.57(10)
S(2)-C(8)	1.804(4)	N(4)-Ni-N(5)	78.48(10)
O(1)-C(6)	1.293(3)	N(6)-Ni-N(5)	87.75(10)
N(1)-N(2)	1.399(4)	C(7)-S(2)-C(8)	104.00(19)
N(2)-C(6)	1.312(4)	C(6)-O(1)-Ni	110.51(18)
N(1)-C(7)	1.324(4)	C(10)-N(4)-Ni	127.9(2)

Supplementary Table 5. Intermolecular interactions [Å and º] for [Ni(pchce)(*o*-phen)$_2$]•CH_3OH•H_2O (**2**)

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(8)-H(8A)...S(1)	0.97	2.63	3.148(4)	113.9
C(19)-H(19A)...N(7)	0.93	2.69	3.222(4)	117.1
C(22)-H(22A)...S(1)#1	0.93	2.86	3.709(4)	152.1
C(31)-H(31A)...O(1)	0.93	2.62	3.136(4)	115.4
O(1W)-H(1W1)...N(3)	0.82(2)	2.13(3)	2.944(5)	172(9)
O(1W)-H(1W2)...O(1S)#2	0.83(2)	2.07(4	2.857(8)	158(10)
O(2W)-H(2W1)...O(1W)#3	0.828(19)	2.12(3)	2.887(7)	155(6)
O(2W)-H(2W2)...S(2)	0.83(2)	2.73(4)	3.506(5)	157(7)
O(2W)-H(2W2)...N(2)	0.83(2)	2.51(4)	3.197(7)	141(7)
O(1S)-H(1S)...O(2W)	0.82	1.88	2.701(6)	174.5

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+2,-z+1 #2 -x+1,-y+1,-z+2 #3 x+1,y,z

Supplementary Table 6. Selected interatomic distances and angles for [Ni(hbhce)(*o*-phen)$_2$]•1.75$CHCl_3$•H_2O (**3**)

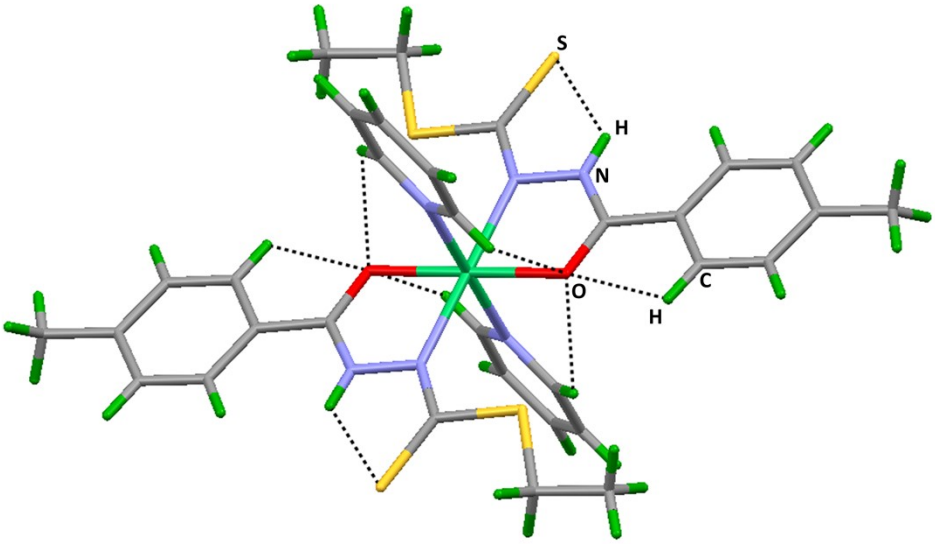
Bond length (Å)		Bond angle (º)	
Ni-O(1)	2.052(4)	O(1)-Ni-N(1)	79.37(16)
Ni-N(1)	2.080(5)	O(1)-Ni-N(3)	91.21(17)
Ni-N(4)	2.083(5)	N(1)-Ni-N(4)	101.33(18)
Ni-N(6)	2.084(4)	O(1)-Ni-N(4)	170.15(16)
Ni-N(3)	2.106(5)	O(1)-Ni-N(6)	95.11(16)
Ni-N(5)	2.109(5)	N(1)-Ni-N(6)	95.39(18)
S(1)-C(8)	1.701(6)	N(4)-Ni-N(6)	94.60(18)
S(2)-C(9A)	1.744(18)	O(1)-Ni-N(3)	91.21(17)
S(2)-C(8)	1.782(6)	N(1)-Ni-N(3)	93.78(18)
S(2)-C(9)	1.84(5)	N(4)-Ni-N(3)	78.94(19)
O(1)-C(7)	1.280(6)	N(6)-Ni-N(3)	169.68(19)
N(1)-C(8)	1.308(7)	O(1)-Ni-N(5)	91.55(16)
N(1)-N(2)	1.406(6)	N(1)-Ni-N(5)	168.90(17)
N(2)-C(7)	1.321(7)	N(4)-Ni-N(5)	88.72(18)
C(1S)-Cl(3S)	1.735(4)	N(6)-Ni-N(5)	78.94(19)
C(1S)-Cl(2S)	1.735(4)	N(3)-Ni-N(5)	92.76(18)
C(1S)-Cl(1S)	1.743(4)	C(7)-O(1)-Ni	109.4(3)
O(2)-C(1)	1.335(7)	C(7)-N(2)-N(1)	113.8(5)

Supplementary Table 7. Intra and Intermolecular interactions [Å and º] for [Ni(hbhce)(*o*-phen)$_2$]•1.75$CHCl_3$•H_2O (**3**)

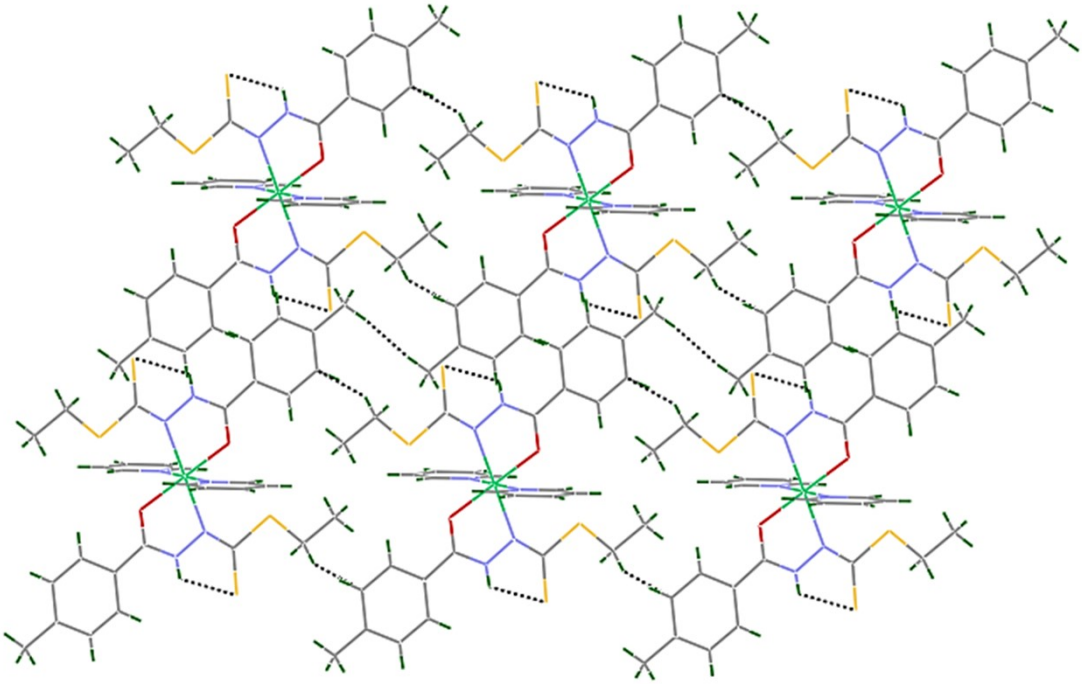
D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(2)-H(2)...S(2)	0.82	2.73	3.415(5)	141.5
O(2)-H(2)...N(2)	0.82	1.81	2.536(6)	145.9
C(9)-H(9A)...Cl(1S)	0.97	2.89	3.63(4)	134.4
C(9)-H(9B)...S(1)	0.97	2.56	3.19(2)	122.8
C(10)-H(10B)...Cl(4S)	0.96	2.39	3.08(3)	128.3
C(11)-H(11A)...O(1)	0.93	2.62	3.139(8)	115.6
C(24)-H(24A)...O(2)#3	0.93	2.48	3.387(8)	165.3
C(1S)-H(1S)...O(2)#4	0.98	2.23	3.160(7)	157.5
O(1W)-H(1W2)...Cl(4S)	0.85	2.41	2.863(8)	114.0
O(1W)-H(1W1)...Cl(5S)	0.90	2.34	3.073(8)	138.7
O(1W)-H(1W1)...Cl(6S)	0.90	1.86	2.584(8)	136.3
O(1W)-H(1W2)...Cl(4S)	0.85	2.41	2.863(8)	114.0

Symmetry transformations used to generate equivalent atoms: #1 -x+2, y+1/2, -z-1/2 #2 x, -y+1/2, z-1/2 #3 x, y, z-1 #4 -x+2, -y+1, -z

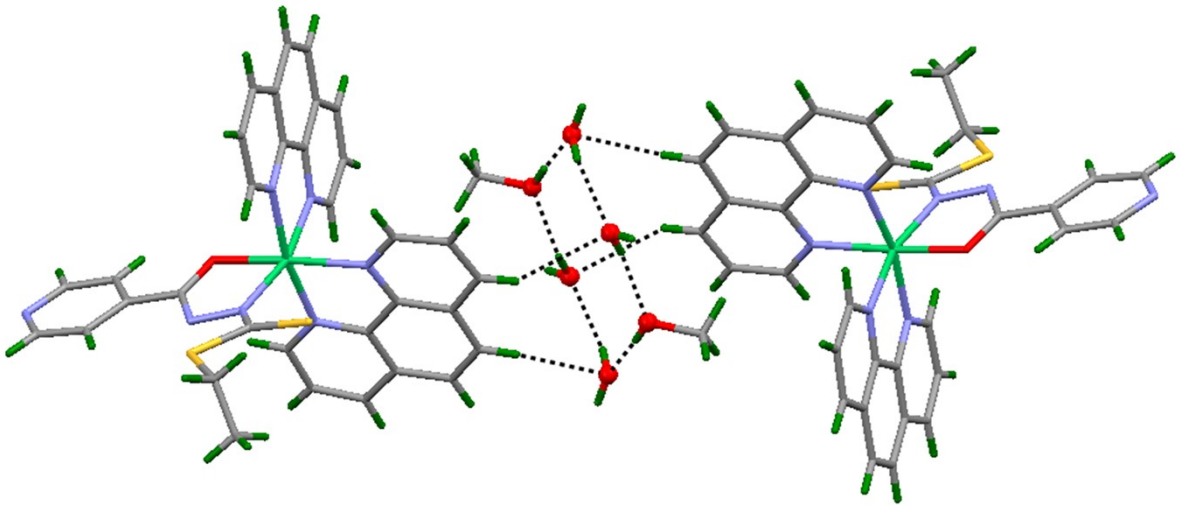
4. H-Bonding interaction Figures



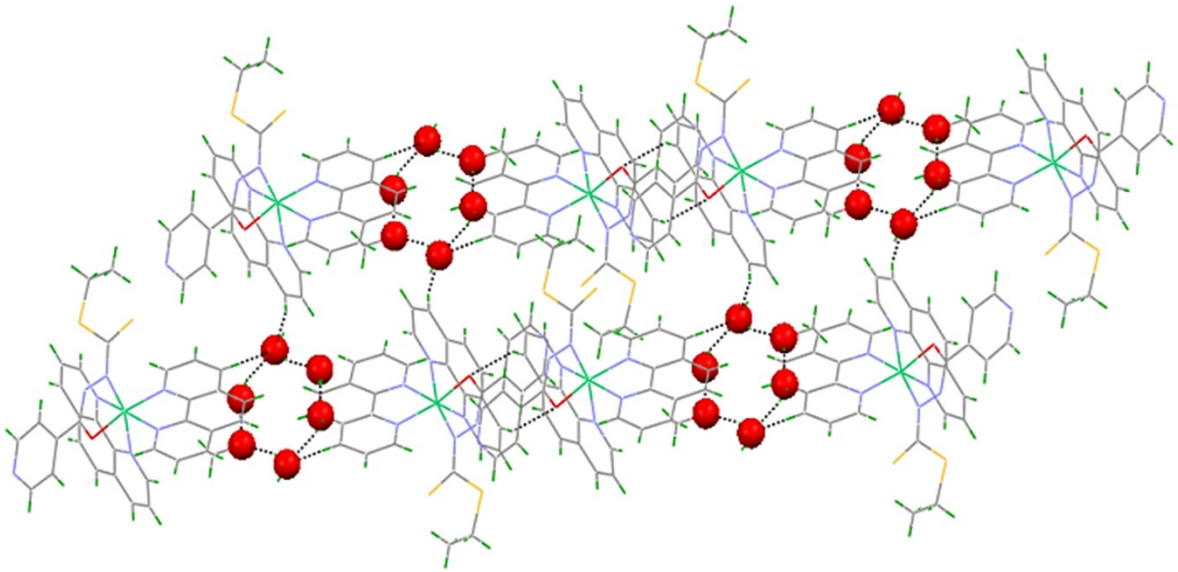
SF 1 A. Showing intramolecular N-H···S and C-H···O hydrogen bonding interactions in complex **1**



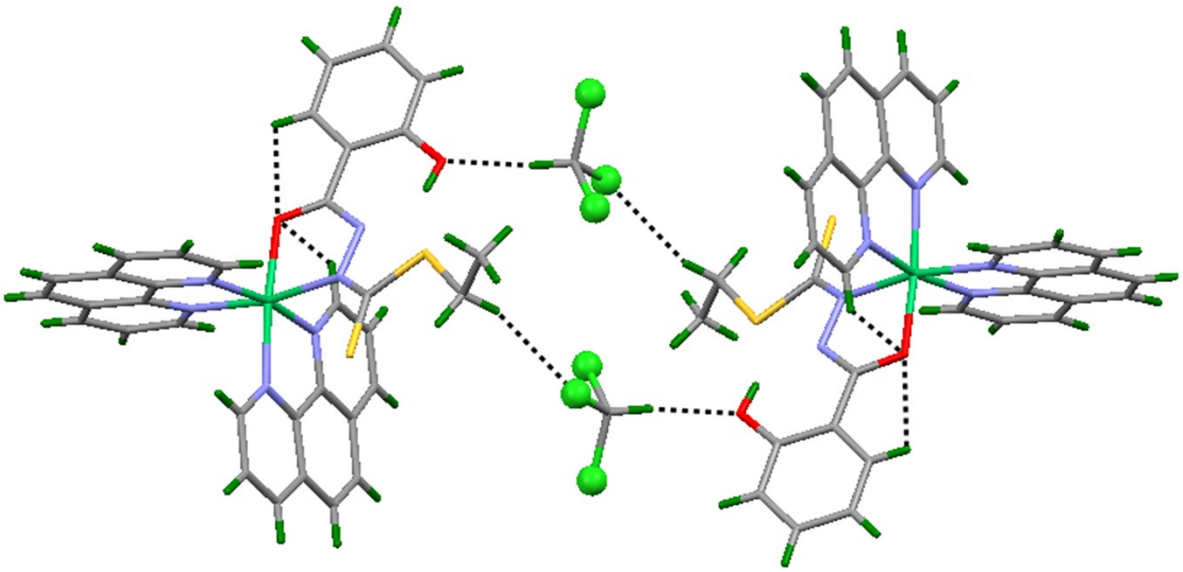
SF 1 B. Intramolecular N-H···S and weak intermolecular H···H interactions help to stabilise supramolecular architecture in complex **1**



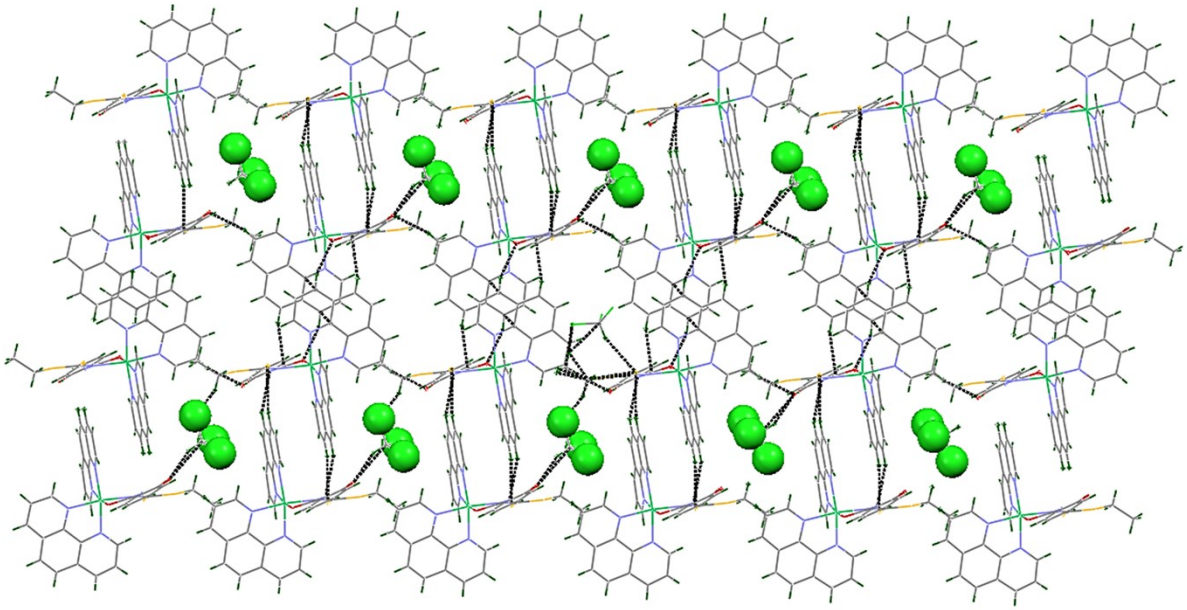
SF 2 A. Intermolecular C-H···O and O-H···O hydrogen bonding interactions present in complex **2** (oxygen atoms of CH_3OH and water molecules are shown in ball and stick model)



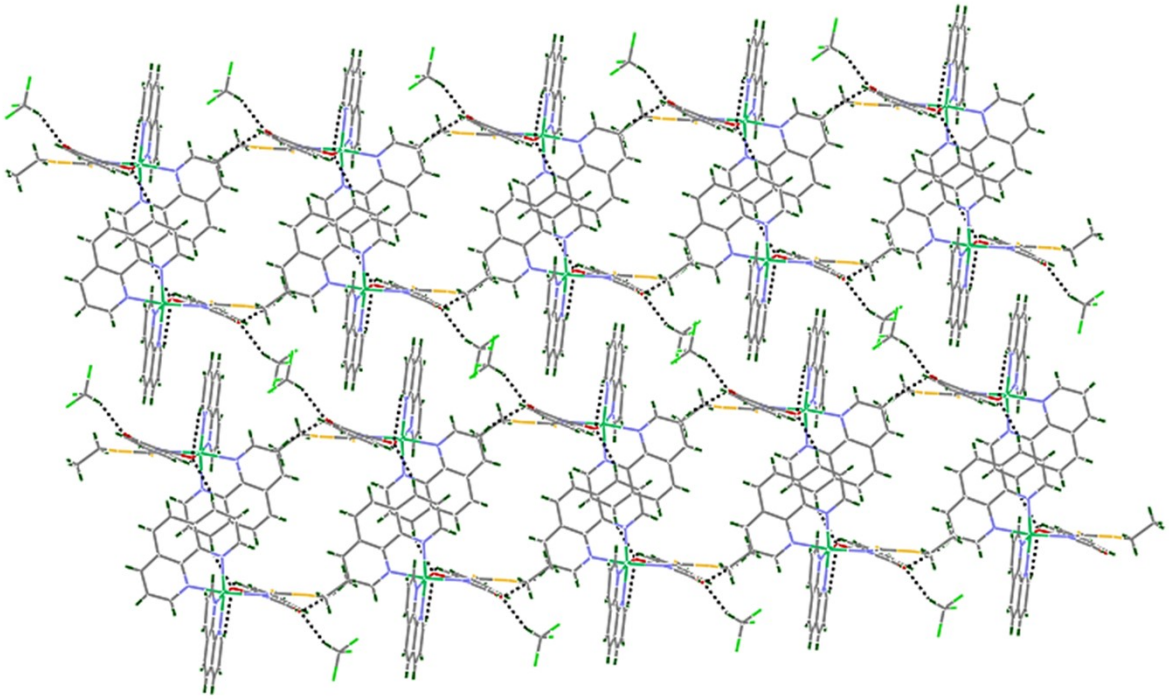
SF 2 B. Intermolecular C-H···O and O-H···O hydrogen bonding present in complex **2** leading a supramolecular framework *via* water and methanol molecules (oxygen atoms of CH_3OH and water molecules are shown in ball and stick model)



SF 3 A. Intermolecular C-H···Cl and inter/intramolecular C-H···O interactions in complex **3** (Chlorine atoms of $CHCl_3$ molecules are shown in ball and stick model)

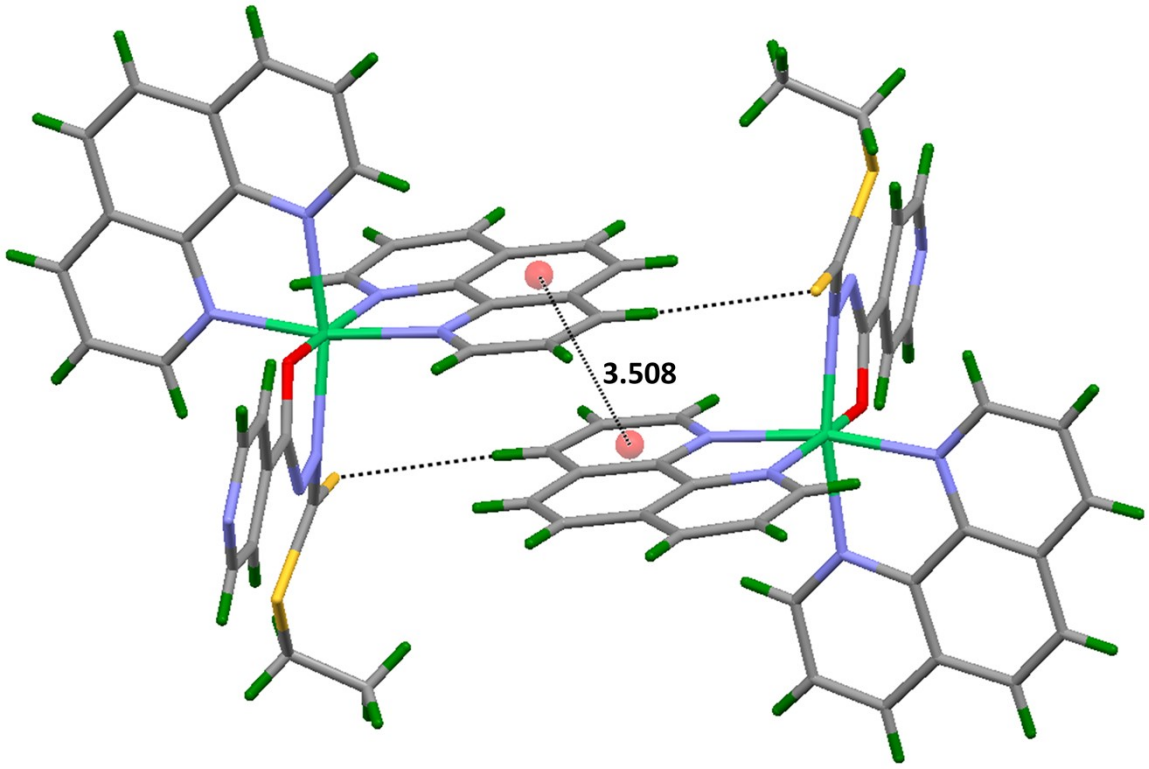


SF 3 B. Showing intermolecular C-H···Cl interactions in complex **3** leading a supramolecular framework (Chlorine atoms of $CHCl_3$ molecules are shown in ball and stick model)



SF 4. Showing C-H···O intermolecular interactions in complex **3** leading a supramolecular framework (CH of chloroform molecules and oxygen atom of hydroxyl group)

5. π– π Interaction figure



SF 5. Showing π···π stacking interactions in complex **2**

6. References

1. S. K. Hira, K. Ramesh, U. Gupta, K. Mitra, N. Misra, B. Ray and P. P. Manna, *ACS Appl. Mater.* Interfaces 2015, **7**, 20021-20033.
2. S. K. Hira, A. K. Mishra, B. Ray and P. P. Manna, *PLoS One* 2014, **9**, e94309.
3. N. K. Singh, M. K. Bharty, S. K. Kushawaha, U. P. Singh and P. Tyagi, *Polyhedron*, 2010, **29**, 1902-1909.
4. G. M. Sheldrick, *Acta Cryst. A,* 2008, **64**, 112.
5. I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C.F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr Sect B,* 2002, **58**, 389.
6. J. J. L. Farrugia, *Appl Crystallogr,* 1997, **30**, 565.