Electronic Supplementary Information (ESI)

Modulation of the electronic states and magnetic properties of nickel catecholdithiolene complex by oxidation-coupled deprotonation

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Simplified synthetic scheme and crystallographic parameters for the obtained crystals were described in the following Figure S1 and Table S1, respectively.

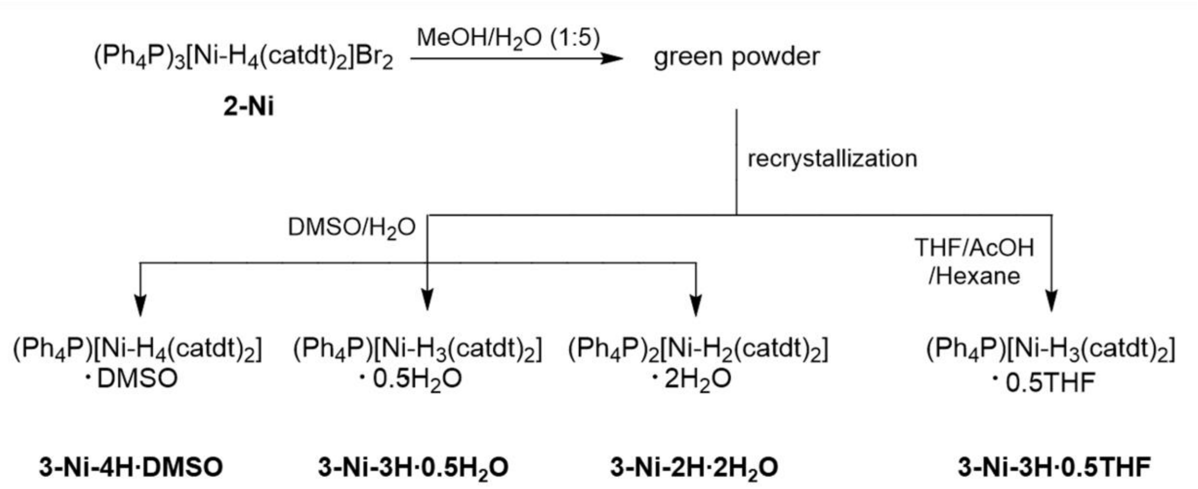

Fig. S1 Synthetic scheme of $(Ph_4P)[Ni\text{-}H_4(catdt)_2]\cdot DMSO$, **3-Ni-4H·DMSO**; $(Ph_4P)[Ni\text{-}H_3(catdt)_2]\cdot 0.5H_2O$, **3-Ni-3H·0.5$H_2O$**; $(Ph_4P)_2[Ni\text{-}H_2(catdt)_2]\cdot 2H_2O$, **3-Ni-2H·2$H_2O$**; and $(Ph_4P)[Ni\text{-}H_3(catdt)_2]\cdot 0.5THF$, **3-Ni-3H·0.5THF** using previously reported $(Ph_4P)_3[Ni\text{-}H_4(catdt)_2]Br_2$.[1]

Table S1. Crystallographic parameters for the crystals **3-Ni-4H·DMSO**, **3-Ni-3H·0.5H$_2$O**, **3-Ni-3H·0.5THF**, and **3-Ni-2H·2H$_2$O**.

	3-Ni-4H·DMSO	**3-Ni-3H·0.5H$_2$O**	**3-Ni-3H·0.5THF**	**3-Ni-2H·2H$_2$O**
formula	$C_{38}H_{34}NiO_5PS_5$	$C_{36}H_{29}NiO_5PS_4$	$C_{38}H_{31}NiO_{4.5}PS_4$	$C_{60}H_{46}NiO_6P_2S_4$
formula weight	820.66	759.51	777.55	1111.86
crystal system	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.188(2)	7.1612(5)	11.3377(2)	13.9446(3)
b (Å)	13.333(3)	16.3222(8)	12.8849(2)	12.5782(3)
c (Å)	13.7783)	28.1125(15)	13.4427(7)	17.5902(7)
α (deg.)	92.947(3)	90	80.666(1)	70.3620(10)
β (deg.)	99.616(4)	90.563(5)	69.189(1)	76.0230(10)
γ (deg.)	94.177(4)	90	69.799(1)	104.3310(10)
V (Å^3)	1836.5(8)	3285.8(3)	1720.99(10)	2631.12(14)
Z	2	4	2	2
T (K)	293	293	293	293
D_{calc} (g·cm^{-3})	1.484	1.535	1.502	1.403
λ (Å)	0.71073	0.71073	0.71073	0.99968
R_{int}	0.0218	0.0878	0.0163	0.0307
R_1 ($I>2.00\sigma(I)$)	0.0478	0.0890	0.0368	0.0386
wR_2 (All reflections)	0.1361	0.1475	0.0981	0.1074
GOF	1.065	1.108	1.032	0.740
CCDC	2065214	2065215	2065216	2065217

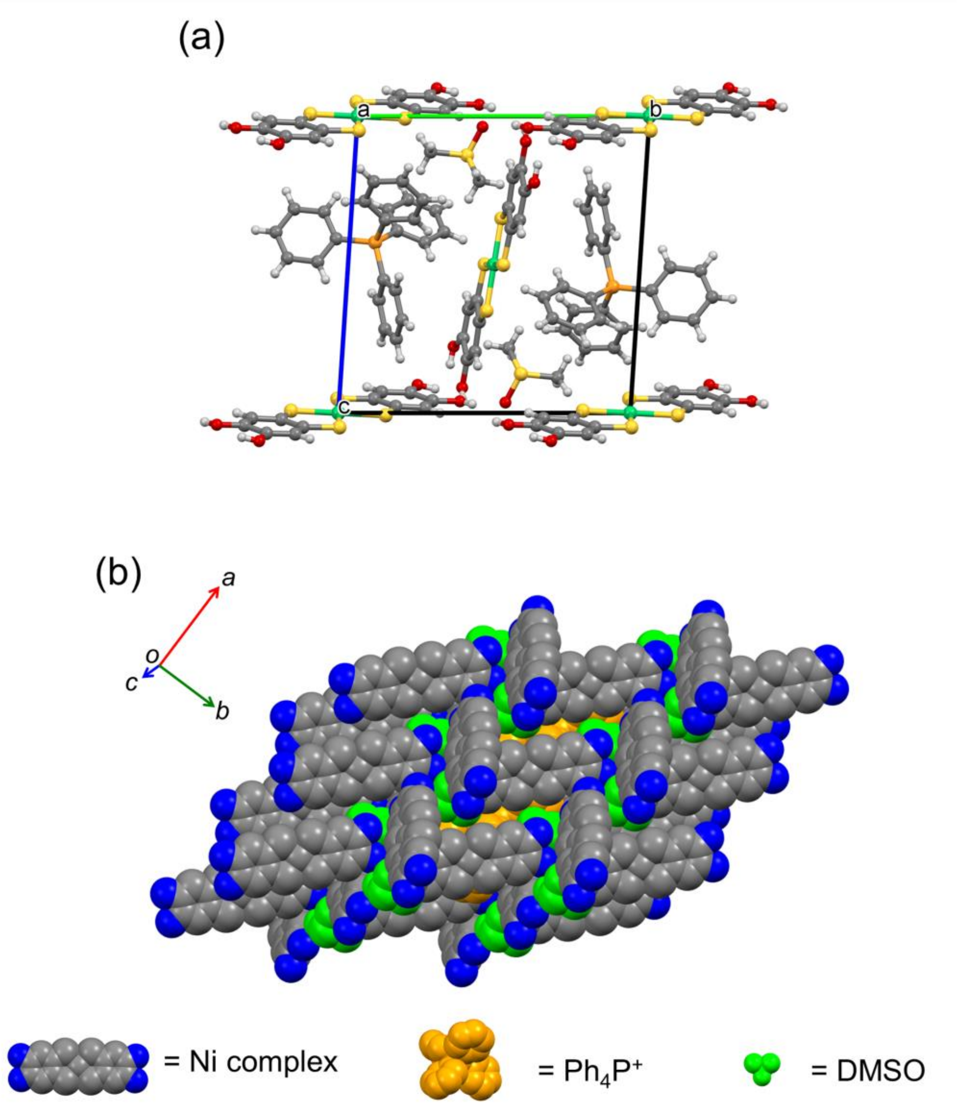

Fig. S2 Structure of the DMSO-containing crystal **3-Ni-4H·DMSO**. (a) Unit cell and (b) overview of the 3D framework structure (left), and the top view of the framework (right). Light green = Ni, yellow = S, orange = P, gray = C, red = O, and white = H.

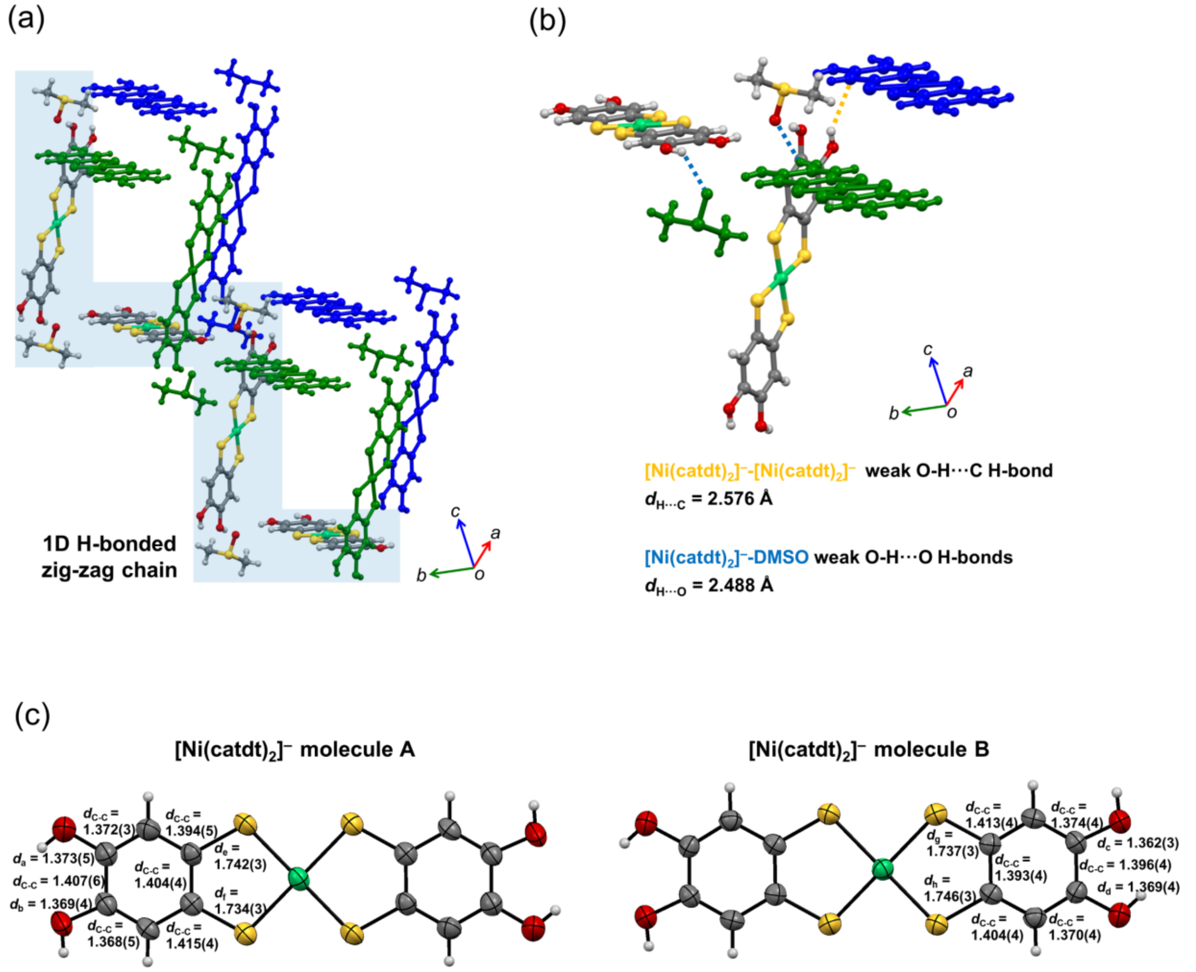

Fig. S3 Details of the H-bonded structure and molecular structure in **3-Ni-4H·DMSO**. (a) The 1D H-bonded zig-zag chains in the 3D framework structure. Blue and green molecules belong to different 1D chains, respectively. (b) Weak intermolecular H-bonds on a node of the framework structure. (c) The molecular structures and bond lengths of crystallographically half-independent nickel complexes. Here, $d_{C–C}$ indicates the C–C bond lengths, and d_a~d_h correspond to the C–O or C–S bond described in Table 1 in the main text.

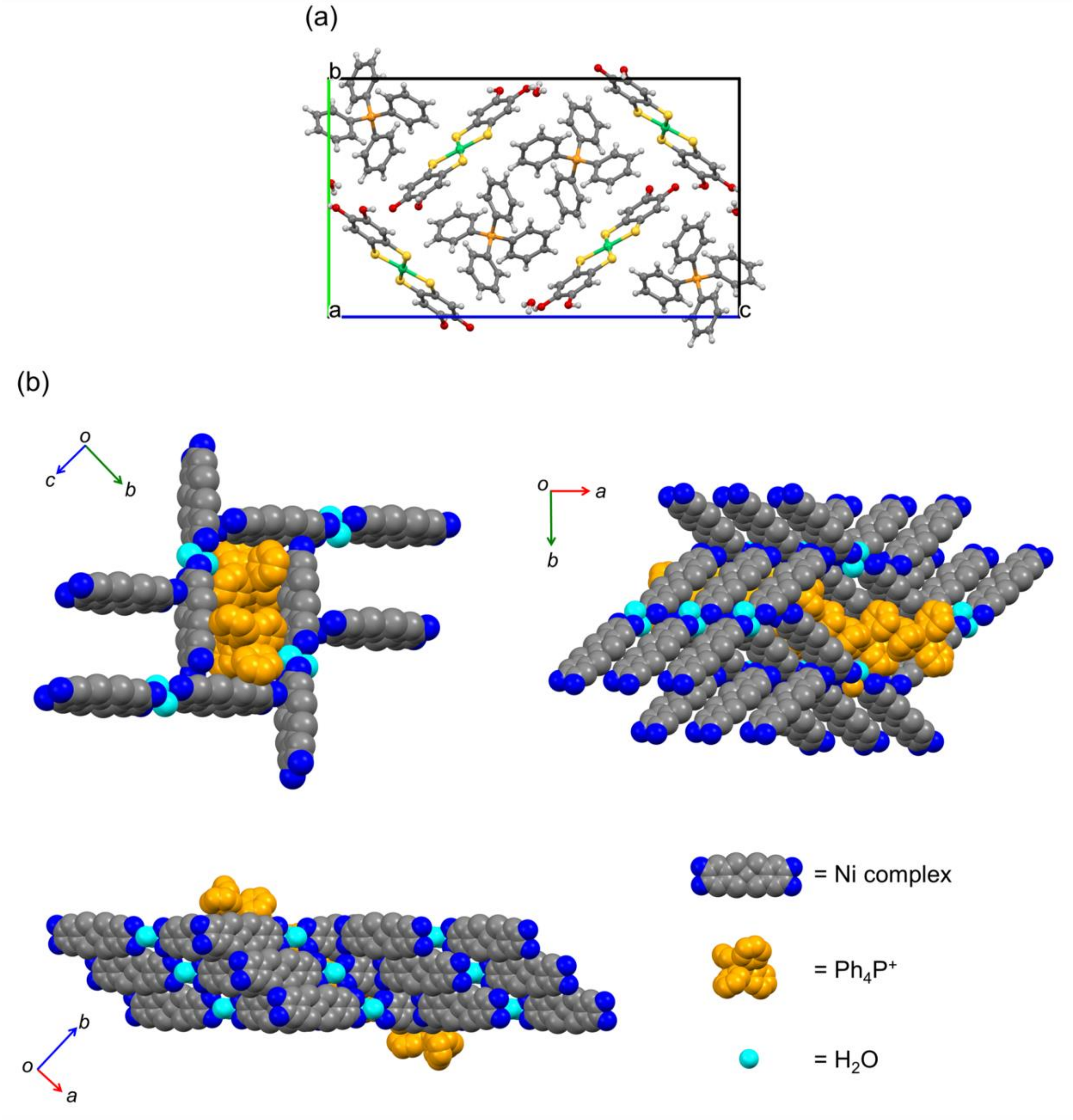

Fig. S4 Structure of the H_2O-containing crystal **3-Ni-3H·0.5H_2O**. (a) Unit cell and (b) overview of the 3D framework structure viewed along each axis. In (a), light green = Ni, yellow = S, orange = P, gray = C, red = O, and white = H.

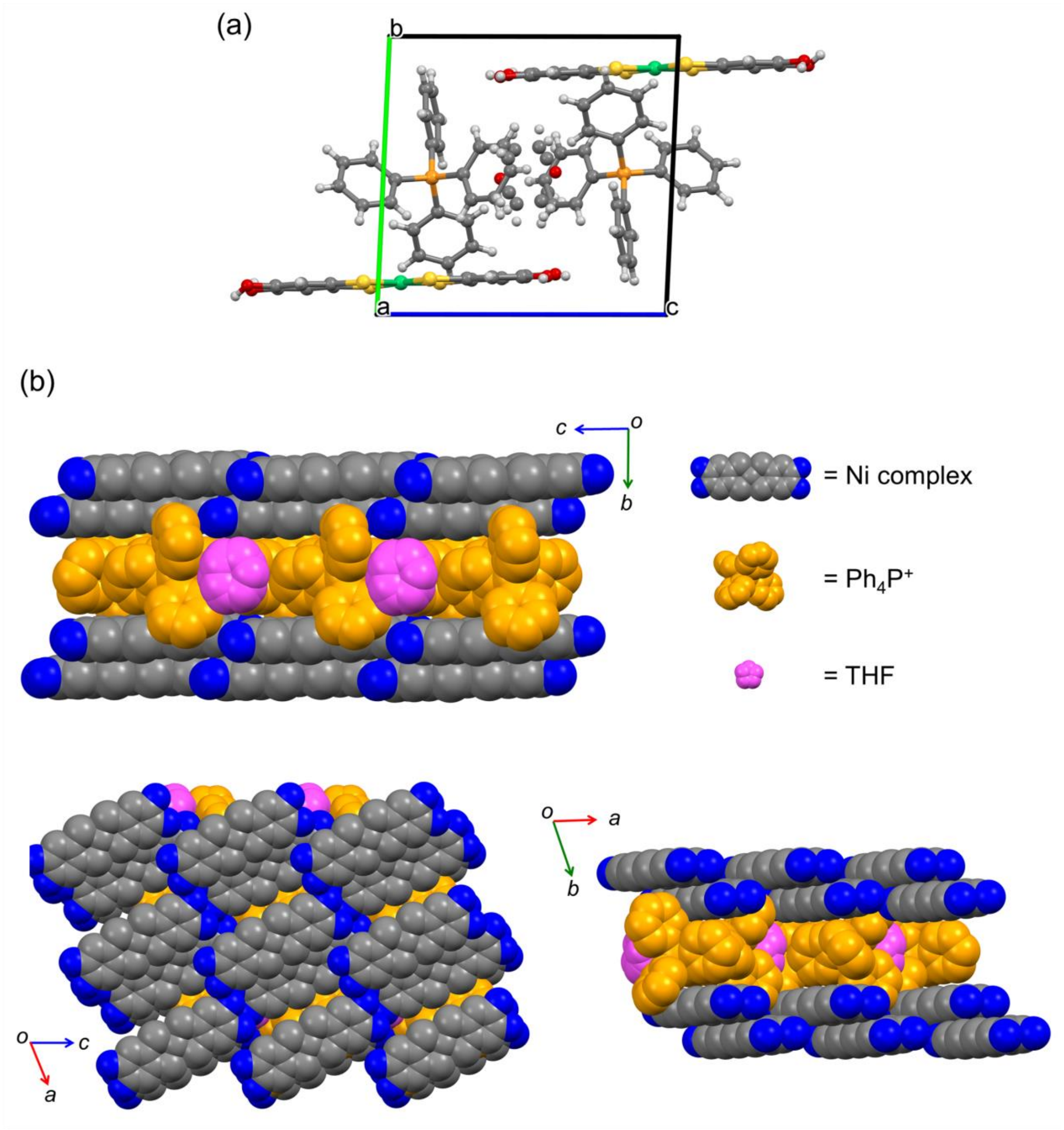

Fig. S5 Structure of the THF-containing crystal, **3-Ni-3H·0.5THF**. (a) Unit cell and (b) overview of the 2D sheet structure viewed along each axis. In (a), light green = Ni, yellow = S, orange = P, gray = C, red = O, and white = H.

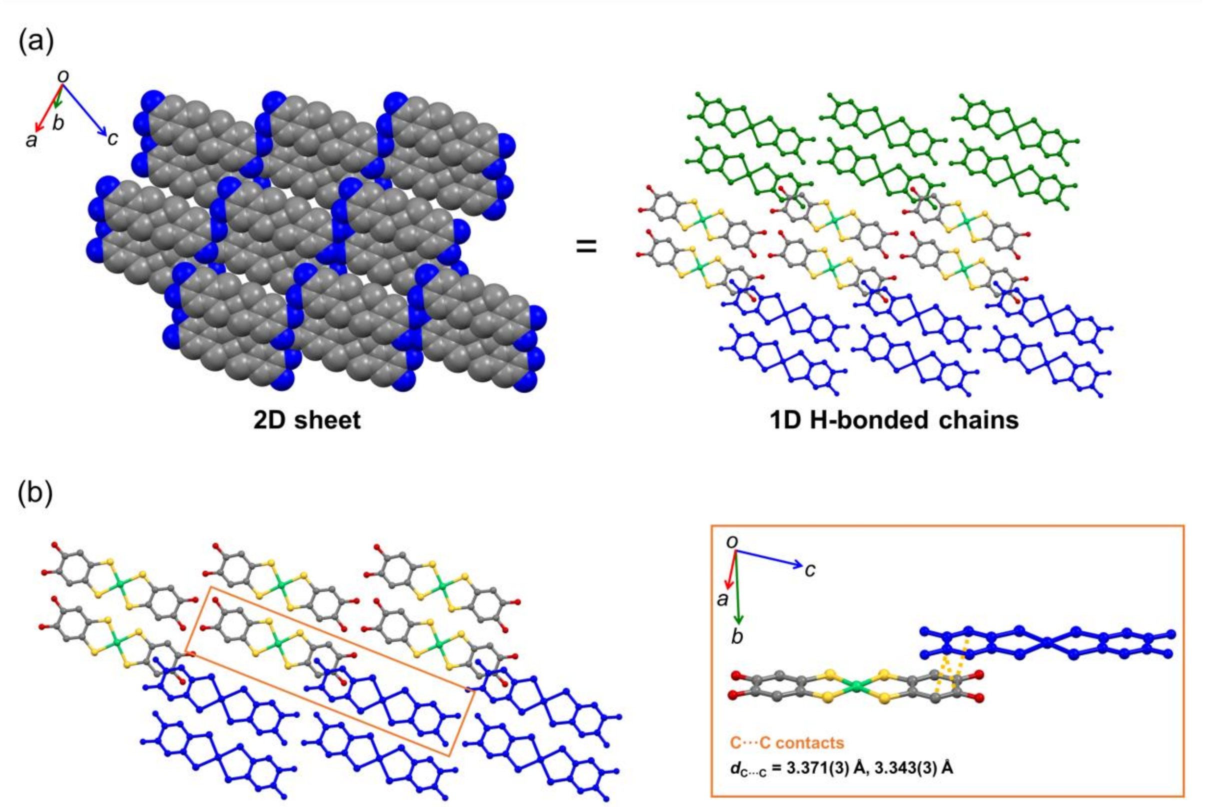

Fig. S6 (a) Correspondence between the 2D sheet structure and 1D H-bonded chains of **3-Ni-3H·0.5THF**. (b) Neighboring 1D H-bonded chains. Colored nickel complexes belong to the same 1D H-bonded chain (left) and π-π interactions (C···C contacts) between nickel complexes belonging to each chain (right). The orange box focuses on the two nickel complexes belonging to different 1D H-bonded chains.

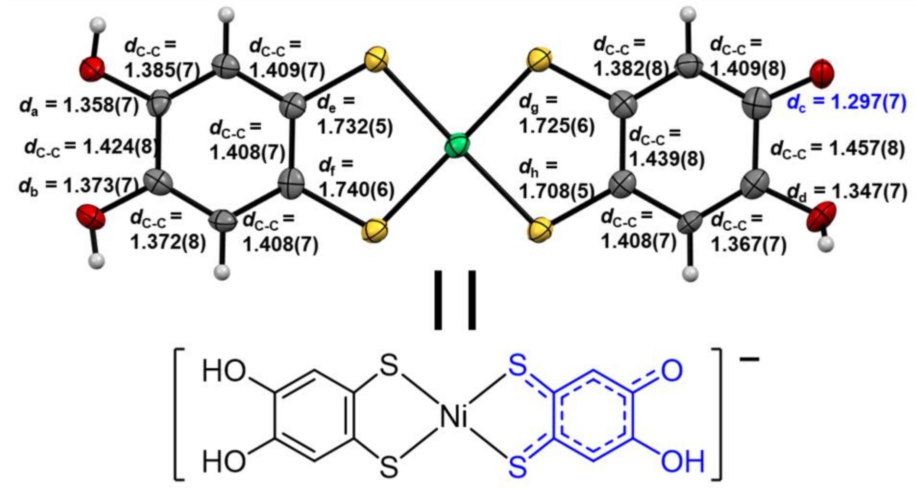

Fig. S7 The molecular structures and bond lengths of crystallographically independent nickel complex in **3-Ni-3H·0.5H$_2$O**.

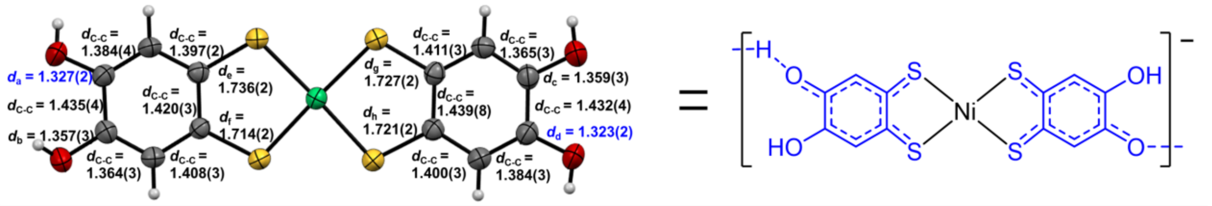

Fig. S8 The molecular structures and bond lengths of crystallographically independent nickel complex in **3-Ni-3H·0.5THF**.

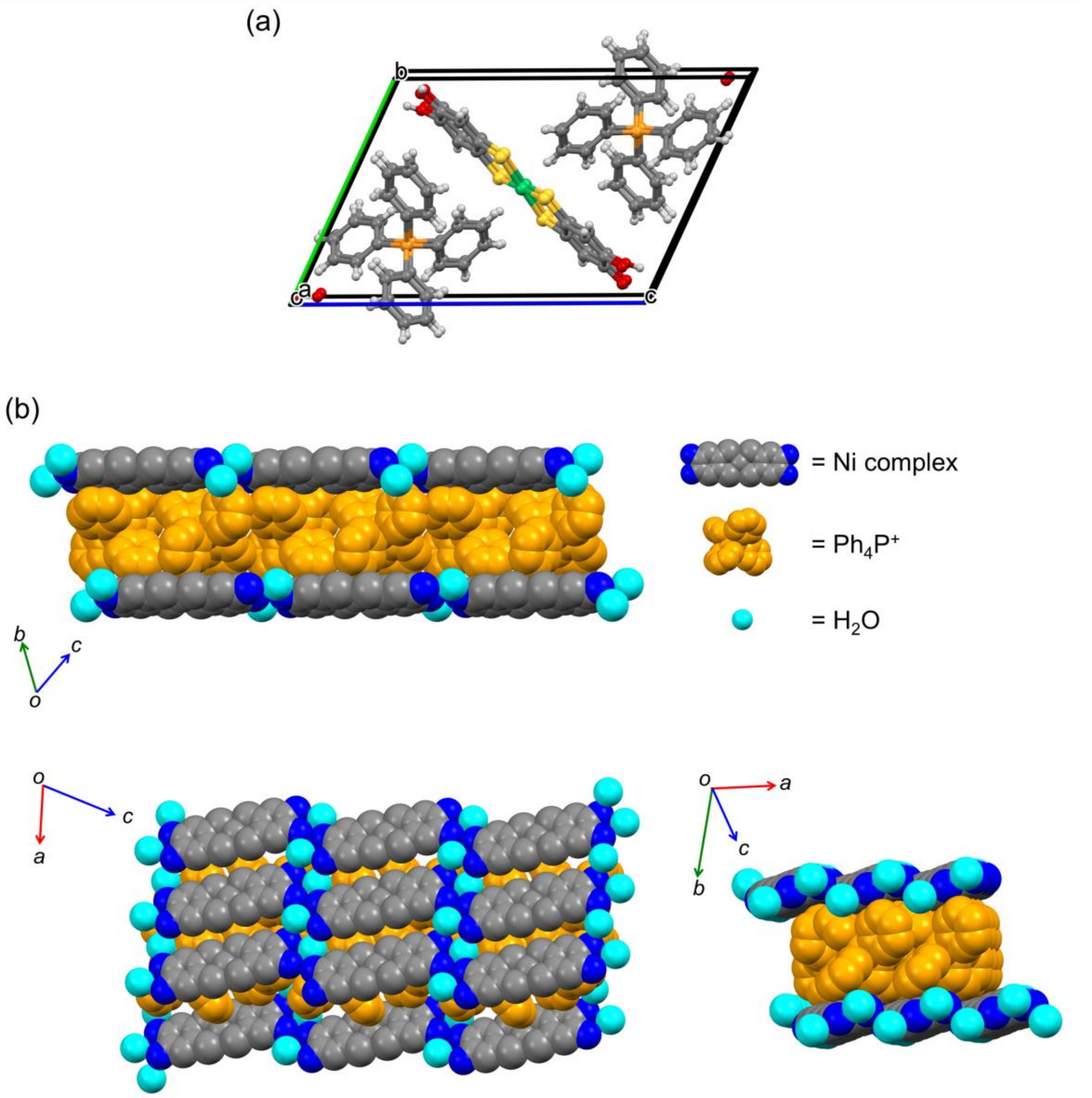

Fig. S9 Structure of the water-containing crystal, **3-Ni-2H·2H$_2$O**. (a) Unit cell and (b) the 2D H-bonded sheet structure viewed along each axis.

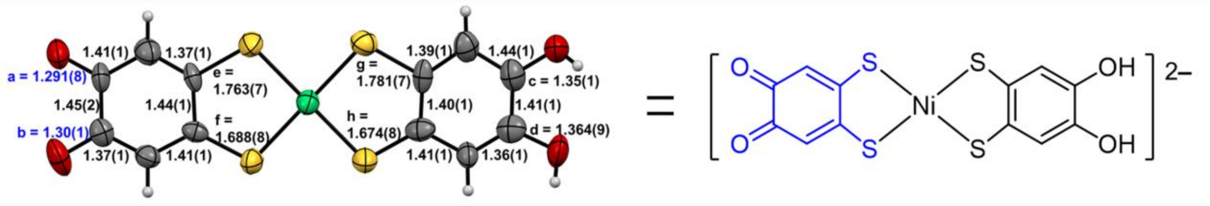

Fig. S10 Molecular structure, bond lengths (Å) and the possible chemical structure of the nickel complex in **3-Ni-2H·2H$_2$O**.

Magnetic properties of 3-Ni-4H·DMSO

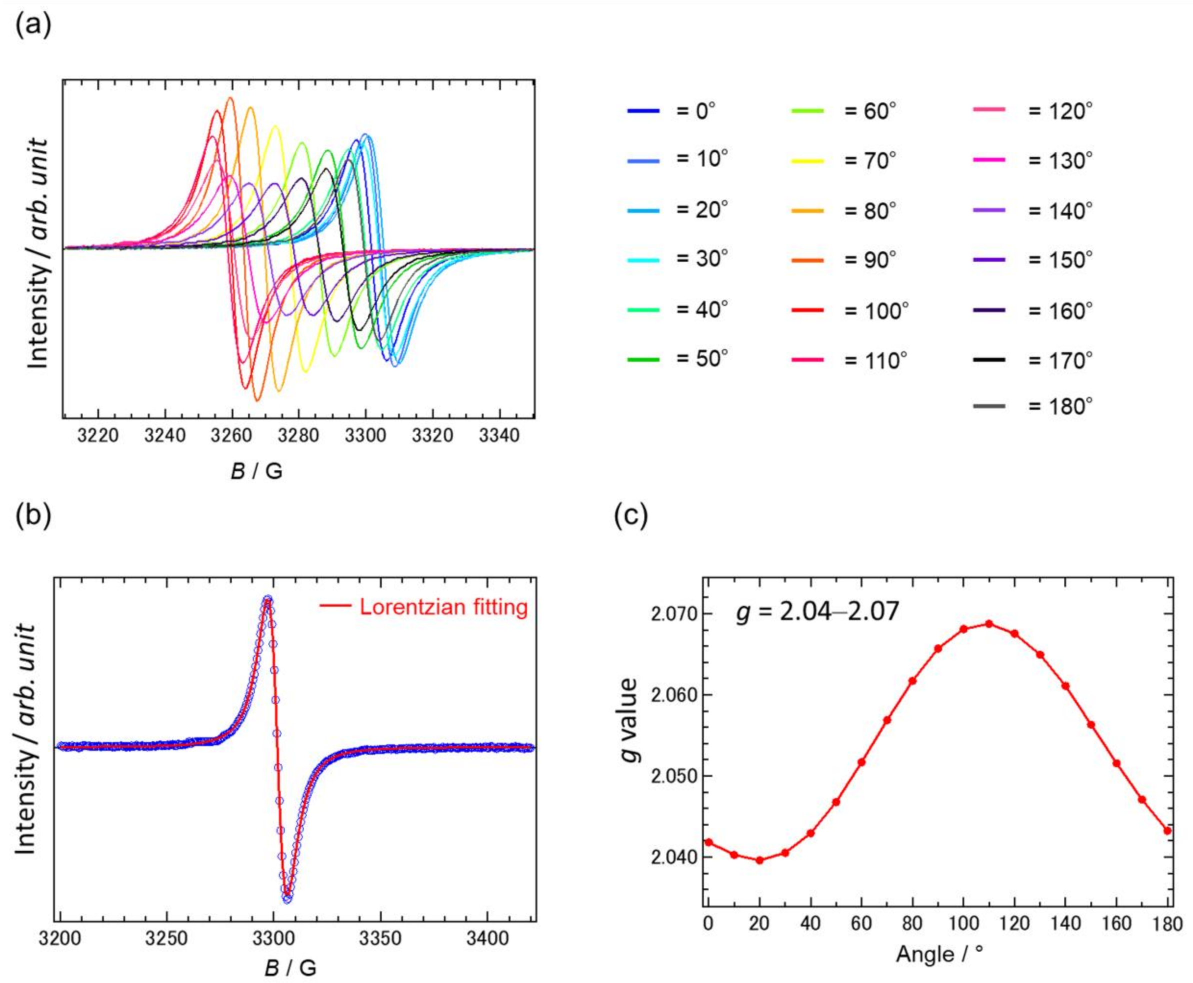

Fig. S11 (a) ESR signals measured under the magnetic field rotated around the *a* axis of **3-Ni-4H·DMSO** single crystal. (b) Lorentzian fitting of the ESR signal at 0 degrees in (a). (c) Angle dependence of the *g* value estimated from the Lorentzian fitting for the measurements.

The temperature dependence of the magnetic susceptibility of **3-Ni-4H·DMSO** was shown in Fig. S12. The Curie constant obtained by the fitting (0.382 emu K mol^{-1}) gives the *g* value to be 2.016 in the case of *S* = 1/2. This value is similar to that obtained from ESR measurement, rather than that of organic radicals (2.003).

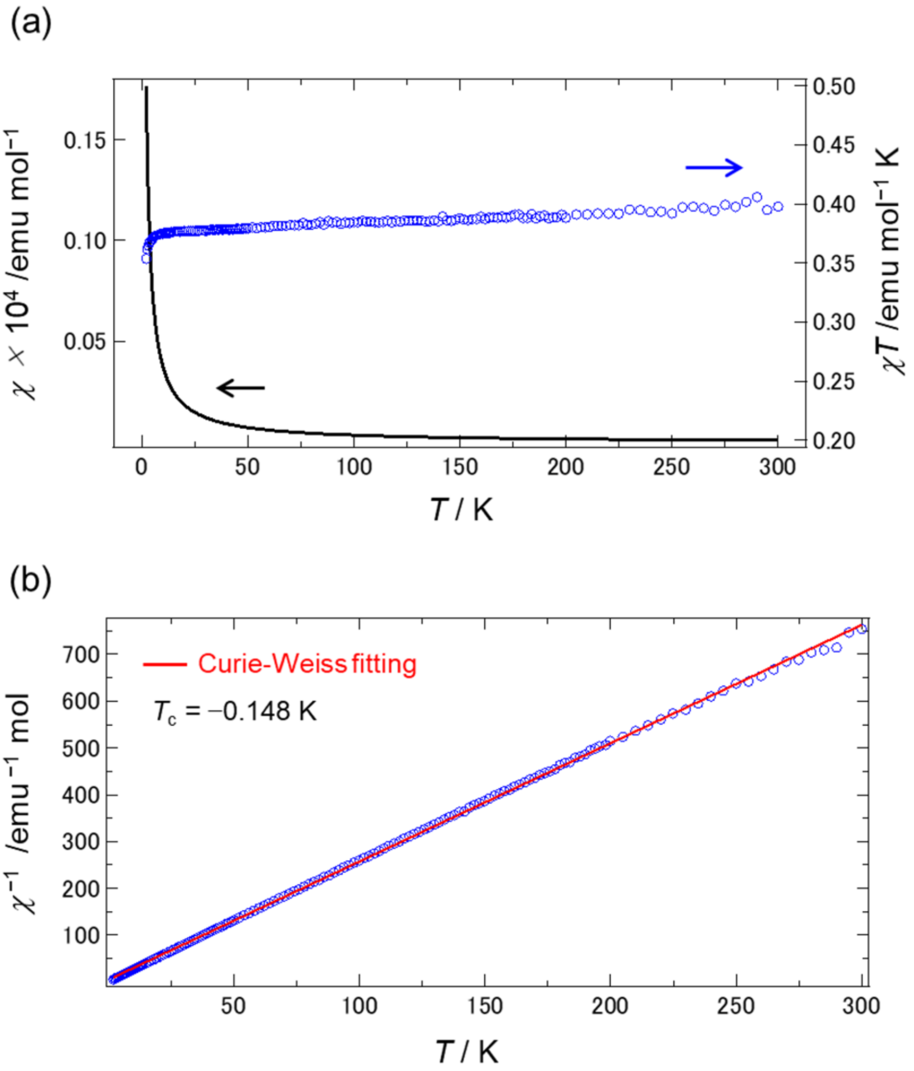

Fig. S12. Temperature dependences on the magnetic susceptibility of **3-Ni-4H·DMSO** polycrystals. (a) χ–T plot (black solid line) together with χT–T plot (blue circles). (b) χ^{-1}–T plot (blue circles) and Curie-Weiss fitting (red solid line).

Differential Fourier map and calculation model for 3-Ni-3H·0.5THF

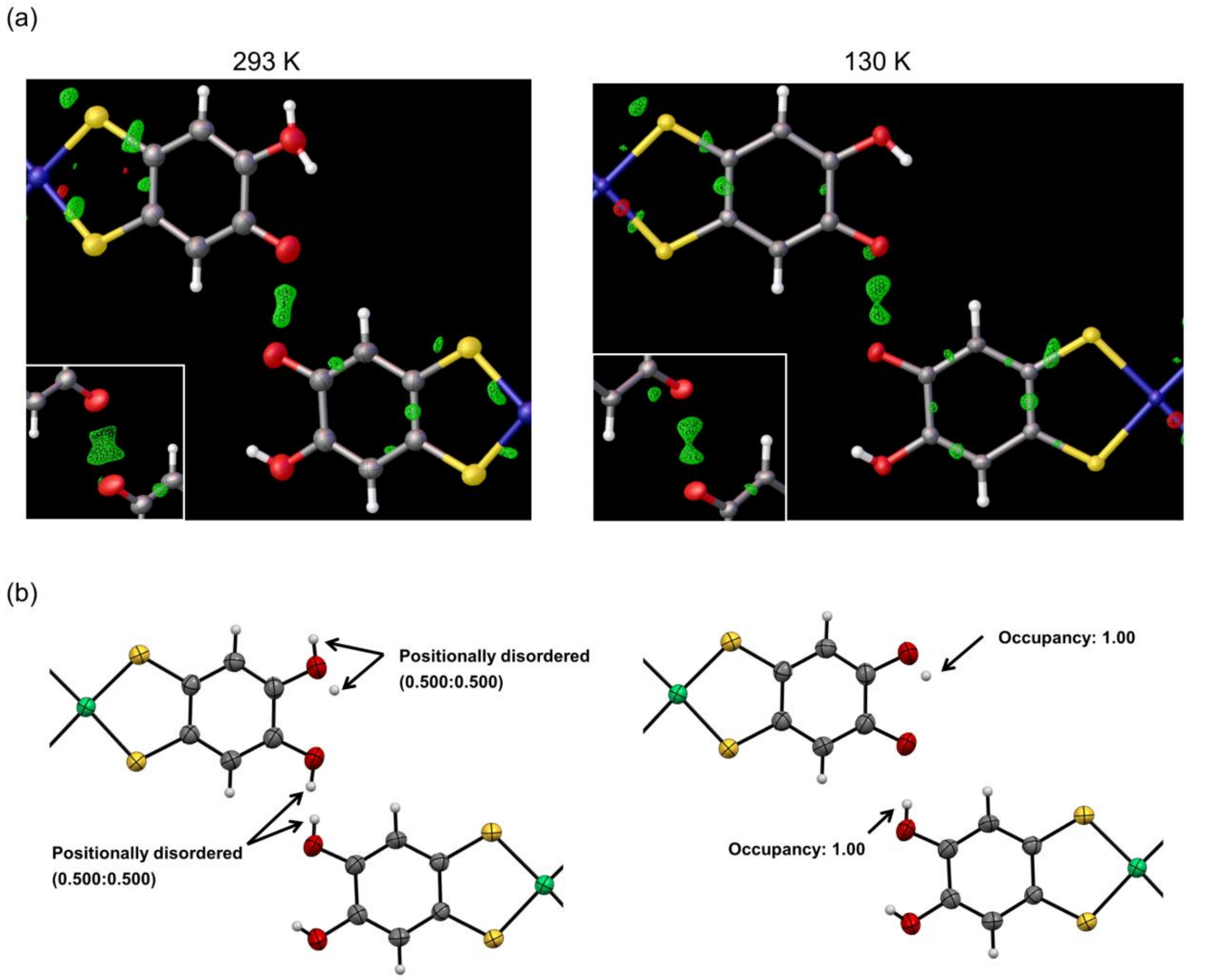

Fig. S13 (a) Differential Fourier maps around the short H-bond between hydroxy groups of nickel complex calculated from single-crystal XRD data. The threshold value of the differential Fourier surface is 0.300 electrons/Å^3 a 293 K and 0.400 electron/Å^3 at 130 K, respectively. The inset figures show enlarged views of the short [O–H···O] H-bonding part. These figures were visualized by the Olex2 software. (b) Positional disorder of the protons in the short H-bond part considered in the structural analysis (left) and structural model used on the DFT calculation of **3-Ni-3H·0.5THF** (right).

Compositions and structures of crystals with neutral nickel complex

The chemical formulas of two crystals having neutral nickel complex are $(Ph_4P)_2$[Ni-H_4(catdt)$_2$]Br_2·DMF (DMF: *N,N*-dimethylformamide); **3-Ni-4H·DMF**, and $(Ph_4P)_2$[Ni-H_3(catdt)$_2$]$_2$[Ni-H_4(catdt)$_2$]·solv.; **3-Ni-3,4H·solv**, respectively. The SQUEEZE equipped in the PLATON program[2–4] was used to remove disordered crystal solvent molecules in the latter crystal. The recrystallizations were performed by liquid-liquid diffusion method of DMF and Et_2O (~1:3) using **2-Ni** for **3-Ni-4H·DMF** (under atmosphere) and of Acetone/Acetic acid/Hexane (~10:1:30) solution for using the resulting green powder prepared from **2-Ni** for **3-Ni-3,4H·solv** (under argon).

Table S2. The crystallographic data for the crystals consisting of neutral non-deprotonated nickel complex, [Ni-H_4(catdt)$_2$].

crystals	**3-Ni-4H·DMF**	**3-Ni-3,4H·solv**
formula	$C_{114}H_{102}Br_4N_2NiO_8P_4S_4$	$C_{42}H_{31}Ni_{1.5}O_6PS_6$
formula weight	2258.44	952.13
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.4401(18)	10.770(5)
b (Å)	14.660(3)	13.090(6)
c (Å)	21.242(4)	15.722(7)
α (deg)	92.947(3)	71.015(14)
β (deg)	83.678(7)	84.98(2)
γ (deg)	77.178(6)	87.58(2)
V (Å^3)	77.841(6)	2087.6(17)
Z	1	2
T (K)	293	293
D_{calc} (g· cm^{-3})	1.341	1.515
λ (Å)	0.71073	0.71073
R_{int}	0.0259	0.0880
R_1 (I>2.00σ(I))	0.0641	0.1176
wR_2 (All reflections)	0.2082	0.3965
GOF	1.060	1.013
CCDC	2065218	2065219

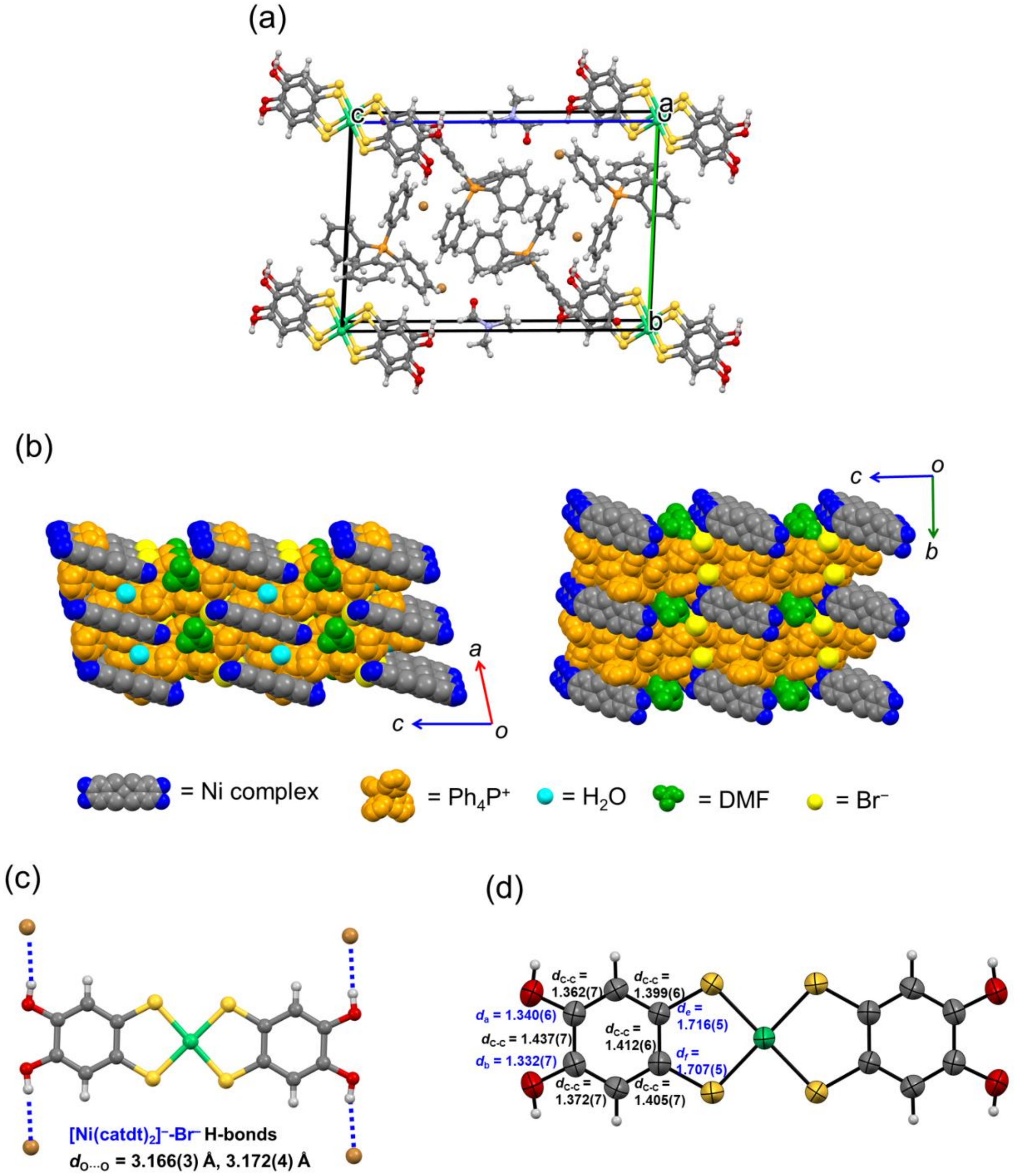

Fig. S14 Structure of the neutral nickel complex crystal **3-Ni-4H·DMF**. (a) Unit cell and (b) overview of the assembled structure viewed along *a* and *b* axis. (c) H-bonding manner around the nickel complex. (d) Molecular structure and bond lengths of the nickel complex. In (a), (c), and (d), light green = Ni, blown = Br, yellow = S, orange = P, blue = N, gray = C, red = O, white = H.

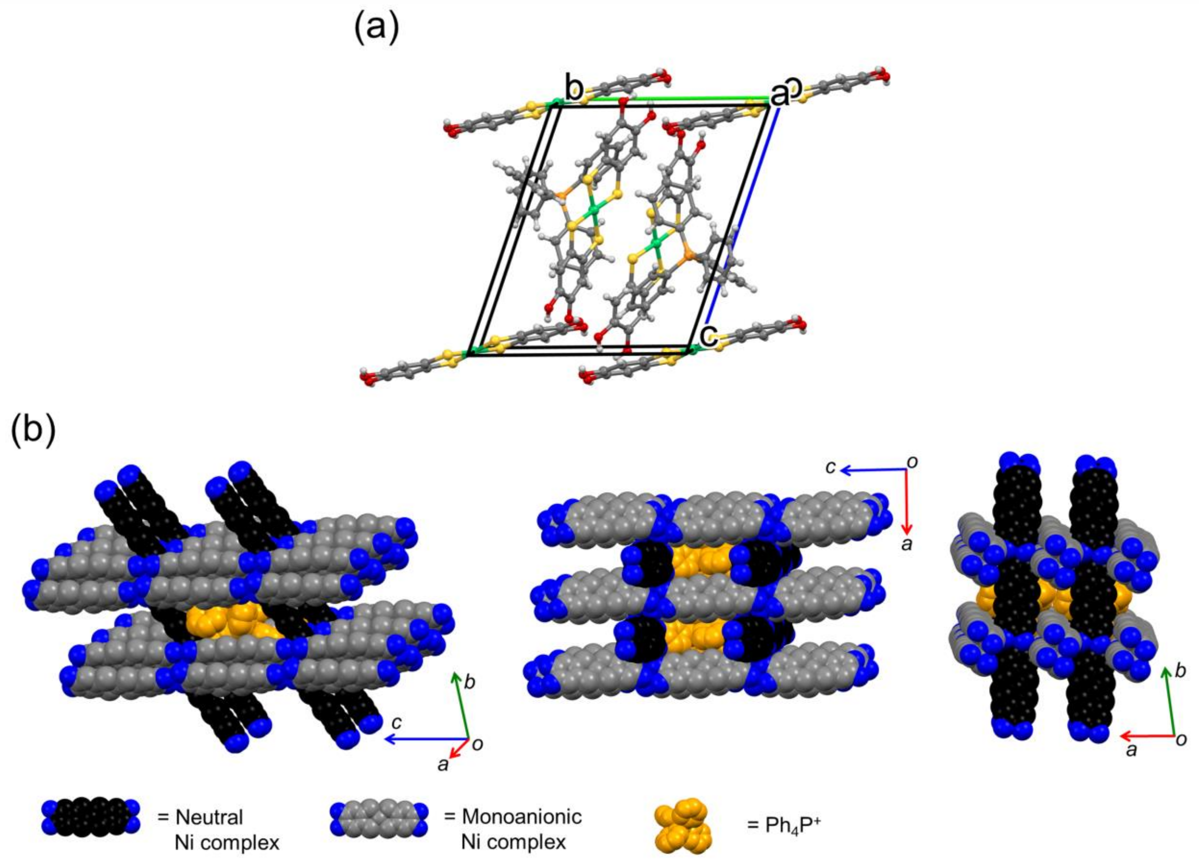

Fig. S15 Structure of the neutral nickel complex crystal **3-Ni-3,4H·solv**. (a) Unit cell and (b) overview of the 3D framework structure viewed along *a* and *b* axis. Black molecules show neutral non-deprotonated nickel complex and gray molecules indicate monoanionic one-deprotonated nickel complex. In (a), light green = Ni, yellow = S, orange = P, gray = C, red = O, white = H.

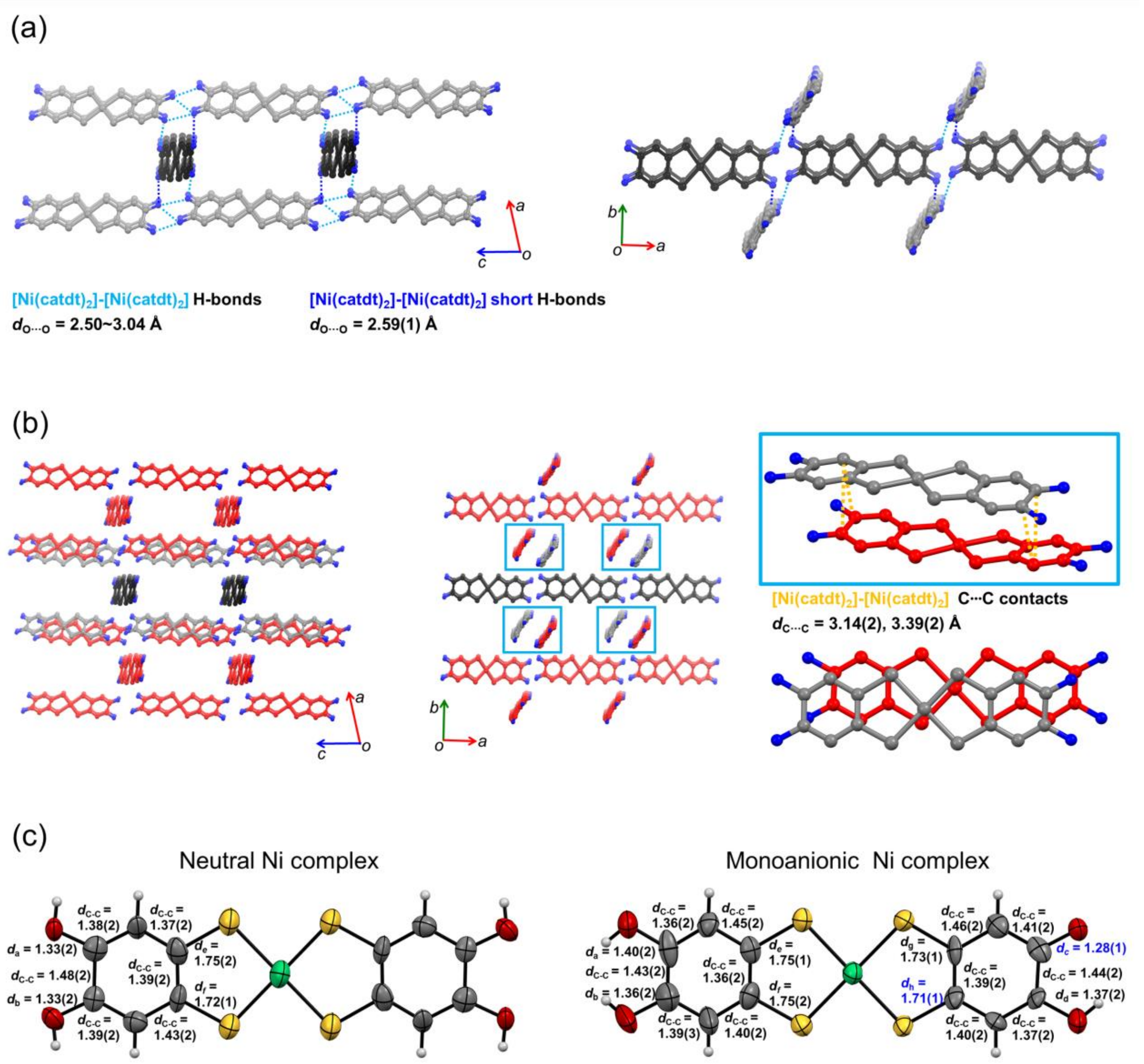

Fig. S16 Details of the H-bonded structure and the molecular structures in **3-Ni-3,4H·solv**. (a) 2D H-bonded framework structure based on the nickel complexes. There is short [O–H···O] H-bonds between the deprotonated hydroxy group and the non-deprotonated hydroxy group of the nickel complexes. Black molecules show neutral non-deprotonated nickel complex and gray molecules indicate monoanionic one-deprotonated nickel complex. (b) Stacking manner of the 2D H-bonded frameworks and C···C contacts (π-π interactions) between the nickel complexes belonging to different 2D H-bonded framework. The grey/black and red molecules show the nickel complexes belonging to individual neighboring 2D H-boned frameworks. (c) Molecular structures and bond lengths of the nickel complexes. Neutral nickel complex is crystallographically half-molecules independent whereas monoanionic nickel complex is crystallographically one-molecule independent.

^{1}H-NMR spectrum of the green powder obtained from 2-Ni

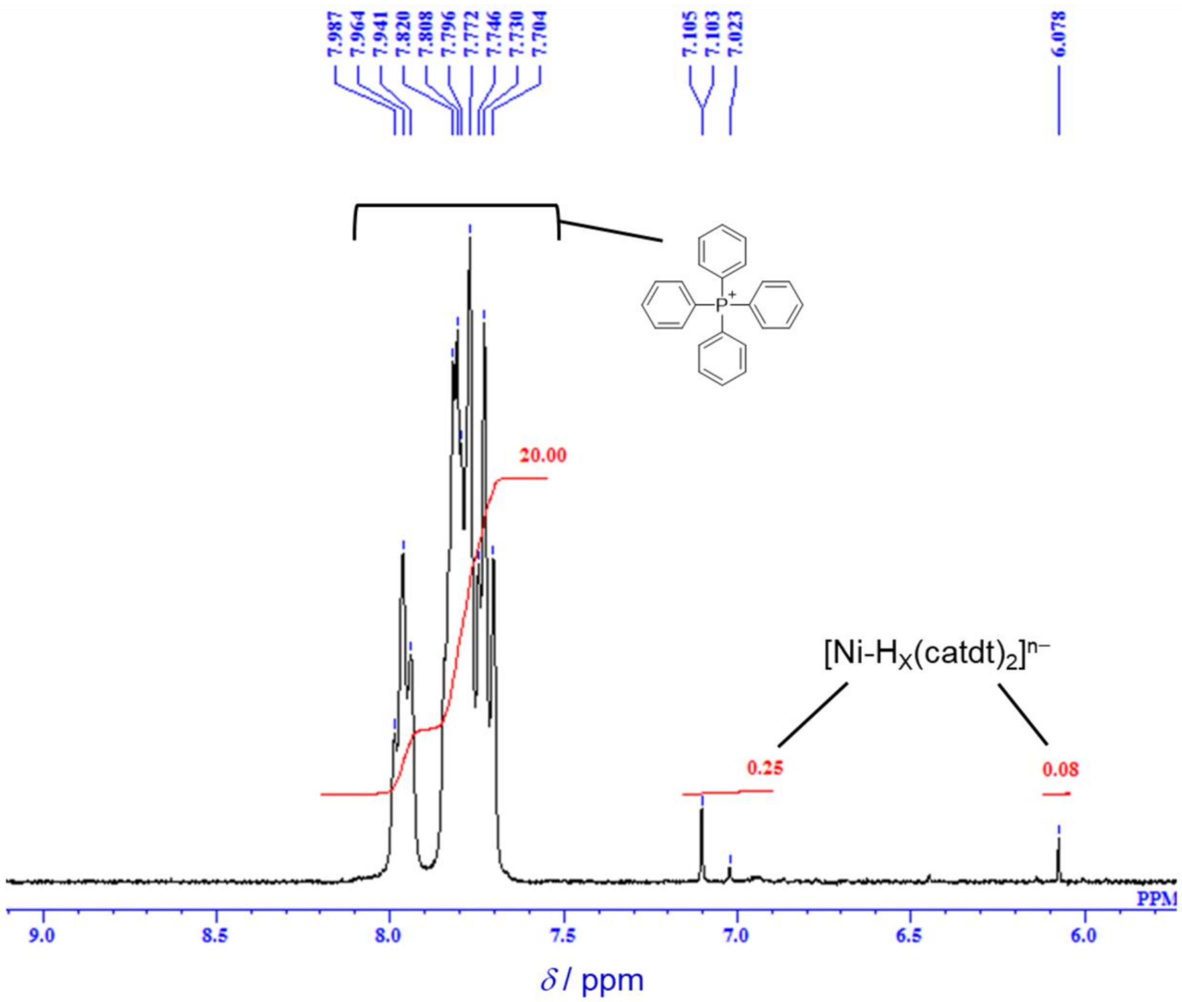

Fig. S17 ^{1}H NMR spectrum of the green powder prepared from **2-Ni** (300 MHz, DMSO-d_6). Multiplets at 7.65–8.10 ppm were attributed to protons of Ph_4P^+ cations. Singlets at 6.08, 7.02, and 7.10 ppm should be derived from the minor oxidized species of the nickel complex **[1−/4H]**, **[1−/3H]**, and/or **[2−/2H]**, which are in a closed-shell state and thus NMR active.

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