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Electronic Supporting Information (ESI) for the manuscript:

Multielectron oxidation in a ferromagnetically coupled dinickel(II) triple mesocate

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Materials

All chemicals were of reagent grade quality. They were purchased from commercial sources and used as received, except those for electrochemical measurements. The nBu$_4$NPF$_6$ salt was recrystallized twice from ethyl acetate/diethyl ether, dried at 80 °C under vacuum, and kept in an oven at 110 °C. Acetonitrile was purified by distillation from calcium hydride on activated 3 Å molecular sieves and stored under argon. Elemental analyses (C, H, N) were performed at Atlantic Microlab Inc (Norcross, GA, USA).

Preparations

***N,N′*-1,3-phenylenebis(pyrazine-2-carboxamidate) (H_2-L):** 1,3-phenylenediamine (4.4 g, 40 mmol) dissolved in pyridine (60 mL) was added dropwise into a solution of 2-pyrazinecarboxylic acid (10.0 g, 80 mmol) in pyridine (100 mL) under vigorous stirring. After addition of triphenyl phosphite (21.1 mL, 80 mmol), the reaction mixture was refluxed for 5 h. The white solid was collected by filtration after cooling, washed with pyridine and then with a small amount of acetone, and dried under vacuum (11.6 g, 90% yield). Anal.: calcd for $C_{16}H_{12}N_6O_2$ (320.1 g mol^{-1}): C, 60.00; H, 3.78; N, 26.24%. Found: C, 59.98; H, 3.82; N, 26.29%; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 ºC, TMS): δ = 7.35 (t, 1 H, H^6 of C$_6$H$_4$), 7.60 (dd, 2 H, H^5 and H^7 of C$_6$H$_4$), 8.54 (d, 1 H, H^4 of C$_6$H$_4$), 8.80 (dd, 2 H, H^2 and H^9 of C$_4$H$_3$N$_2$), 8.92 (d, 2 H, H^1 and H^{10} of C$_4$H$_3$N$_2$), 9.29 (d, 2 H, H^3 and H^8 of C$_4$H$_3$N$_2$), 10.73 (s, 2 H, 2 NH); IR (KBr): ν = 3305, 3256 (N–H), 1680, 1663 cm^{-1} (C=O), 1533 cm^{-1} (C=N).

K_2[Ni_2L_3] · 3MeOH · 3H_2O (1a): A methanolic solution (20 mL) of KOH (0.6 g, 15.0 mmol) was added to a suspension of H_2-L (1.60 g, 5.0 mmol) in 200 mL of methanol. Ni(NO$_3$)$_2$ · 6H$_2$O (0.97 g, 3.3 mmol) dissolved in methanol (50 mL) was then

added dropwise under stirring. The initial yellow reaction mixture was refluxed for 4 h to afford a final brown suspension. The resulting brown solid was collected after cooling to room temperature, washed with acetone and diethyl ether, and dried under vaccum (1.6 g, 75% yield). X-ray quality brown tiny prisms of **1a** were obtained after slow evaporation of mother liquors. Anal.: calcd for $C_{51}H_{48}Ni_2N_{18}K_2O_{12}$ (1300.69 g mol^{-1}): C, 47.10; H, 3.72; N, 19.38%. Found: C, 46.90; H, 3.66; N, 19.26%; IR (KBr): ν = 1603, 1567 cm^{-1} (C=O), 1470 cm^{-1} (C=N).

(nBu$_4$N)$_2$[Ni$_2$L$_3$] · 4MeOH (1b): A 1.0 M methanolic solution of nBu$_4$NOH (15.0 mL, 15.0 mmol) was added to a suspension of H_2-L (1.60 g, 5.0 mmol) in 200 mL of methanol. $Ni(NO_3)_2 \cdot 6H_2O$ (0.97 g, 3.3 mmol) dissolved in methanol (50 mL) was then added dropwise under stirring. The initial yellow reaction mixture was refluxed for 4 h to afford a final brown suspension. The resulting brown solid was collected after cooling to room temperature, washed with acetone and diethyl ether, and dried under vaccum (1.94 g, 70% yield). Anal.: calcd for $C_{84}H_{118}Ni_2N_{20}O_{10}$ (1682.8 g mol^{-1}): C, 59.86; H, 7.06; N, 16.62%. Found: C, 59.80; H, 7.10; N, 16.76%; IR (KBr): ν = 1606, 1569 cm^{-1} (C=O), 1470 cm^{-1} (C=N).

Physical techniques

^{1}H NMR spectra were recorded at room temperature on a Mercury 300 (300.1 MHz) spectrometer. Chemical shifts are reported in δ (ppm) *vs*. TMS. [D_6]DMSO was used as solvent and internal standard (δ = 2.50 ppm). FTIR spectra were recorded on a SHIMADZU IR Affintty-1spectrophotometer as KBr pellets.

X-ray crystallographic data collection and structure refinement

Single crystal X-ray diffraction data sets of **1a** was collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-K_α radiation

(λ = 0.71073 Å), Data were indexed, integrated and scaled using the SAINT and XPREP program.[1] The structure of **1a** was solved by direct methods and subsequent Fourier syntheses using the SHELXS97 program.[2] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares technique based on F^2 using the SHELXL97 program.[2] The hydrogen atoms of the ligand have been set on geometrical positions and refined with a riding model. Those of the water molecules were neither found nor set. Crystallographic data for the structure **1a** has been deposited at the Cambridge Crystallographic Data Centre with CCDC reference number 1045153. The final geometrical calculations and the graphical manipulations were carried out with the PLATON, WinGX and CRYSTAL MAKER programs, respectively.[3, 4, 5] Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for **1a**: $C_{51}H_{48}K_2N_{18}Ni_2O_{12}$, M = 1300.69, monoclinic, space group $P2_1/n$, with cell parameters a = 12.536(3), b = 28.635(6), c = 15.794(3) Å and β = 91.53(3)º, V = 5686.9(7) Å^3, T = 100(2) K, Z = 4, ρ_{calcd} = 1.524 g cm^{-3}, μ(Mo-Kα) = 0.889 mm^{-1}, 11146 unique reflections, and 7857 observed with $I > 2\sigma(I)$. Refinement of 770 parameters with anisotropic thermal parameters for all non-hydrogen atoms gave R_1 = 0.0746, wR_2 = 0.2133, and GOF = 1.069 ($I > 2\sigma(I)$).

Magnetic measurements

Variable-temperature (2.0–300 K) magnetic susceptibility measurements under an applied field of 10 kOe ($T \geq 50$ K) and 100 Oe ($T < 50$ K) and variable-field (0–7.0 T) magnetization measurements at 2.0 K were carried out on powdered samples of **1a** and

1 *SAINT and XPREP*, version 6.45, Bruker Analytical X-ray Systems, Madison, WI, 2003.
2 G. M. Sheldrick, *Acta Cryst. A,* 2008, **64**, 112.
3 A. L. Spek, *J. Appl. Cryst*., 2003, **36**, 7-13.
4 L.J. Farrugia, *J. Appl. Cryst.,* 1999, **32**, 837.
5 D. Palmer, *CRYSTAL MAKER,* Cambridge University Technical Services, Cambridge, 1996.

1b with a SQUID magnetometer. The experimental data were corrected for the diamagnetic contributions of the constituent atoms and the sample holder as well as for the temperature-independent paramagnetism (tip) of the Ni^{II} ion (100×10^{-6} cm^3 mol^{-1}).

$$\mathbf{H} = -J\,\mathbf{S_1} \cdot \mathbf{S_2} + D\,\Sigma_{i=1,2}\,\mathbf{S_{zi}}^2 + g\beta H\,\Sigma_{i=1,2}\,\mathbf{S_i} \qquad \text{(S1)}$$

Electrochemical measurements

The electrochemical studies were performed using a PAR 273A scanning potentiostat operating at a scan rate of 10–1000 mV s^{-1}. Cyclic voltammograms were carried out using 0.1 M nBu$_4$NPF$_6$ as supporting electrolyte and 1.0 mM of **1b** in acetonitrile. The working electrode was a glassy carbon disk (0.32 cm^2) that was polished with 1.0 μm diamond powder, sonicated, washed with absolute ethanol and acetone, and air dried. The reference electrode was $AgClO_4$/Ag separated from the test solution by a salt bridge containing the solvent/supporting electrolyte, with platinum as auxiliary electrode. All experiments were performed in standard electrochemical cells at 25 °C under argon. The investigated potential range was in the range of –2.00 to +1.80 V *vs*. SCE. The formal potentials were measured at a scan rate of 50, 100 and 200 mV s^{-1} and they were referred to the saturated calomel electrode (SCE). Ferrocene (Fc) was added as internal standard at the end of the measurements [$E(Fc^+/Fc)$ = +0.40 V *vs*. SCE (CH_3CN, 0.1 M nBu$_4$NPF$_6$, 25 °C)].[6]

Chemical oxidation procedures and spectroscopic measurements

The monooxidized species was obtained by addition of a 0.01 M acetonitrile solution of bromine (0.1 mL) to a 1.0 mM acetonitrile solution of **1b** (0.1 mL) at –40 °C. X-band EPR spectra (ν = 9.47 GHz) of frozen-matrix acetonitrile solutions were recorded under non-saturating conditions on a Bruker ER 200 D spectrometer

6 N. G. Connelly and W. E. Geiger, *Chem. Rev.,* 1996, **96**, 877.

equipped with a helium cryostat.

Computational details

Density functional (DF) calculations were carried out on the actual crystal structure and optimized geometries of **1a** in acetonitrile solution with the hybrid CAM-B3LYP method[7] combined with the "broken-symmetry" approach,[8] as implemented in the Gaussian 09 program.[9] The triple- and double-ζ quality basis sets proposed by Ahlrichs and co-workers[10] were used for the metal and non-metal atoms, respectively. Solvation effects were introduced using a polarizable continuum model (PCM), where the cavity is created via a series of overlapping spheres.[11] Negatively charged oxamate ligands are connected to the positive Ni(II) or Ni(III) ions. Thus, due to a large delocalization usually observed in DF calculations, these ligands can give a part of their electronic surplus inducing total or partial charge transfers in some cases.[12] The solvation effects included with the PC model avoid this fact stabilizing the electronic surplus just as it is done by the hydrogen bonds and other intermolecular contacts created with the surrounding molecules in the solid state. Similar calculations were also done on the optimized geometries of different oxidized species, being the geometry optimization started from the experimental conformation in **1a** and from adequately modified geometries to favour one kind of

7 A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648.

8 (*a*) E. Ruiz, J. Cano, S. Alvarez and P. Alemany, *J. Comput. Chem.,* 1999, **20**, 1391; (*b*) E. Ruiz, A. Rodriguez-Fortea, J. Cano, Alvarez and P. Alemany, *J. Comput. Chem.,* 2003, **24**, 982.

9 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision C.02* Gaussian, Inc., Wallingford CT, 2004.

10 (*a*) A. Schaefer, H. Horn and R. Ahlrichs, *J. Chem. Phys.,* 1992, **97**, 2571; (*b*) A. Schaefer, C. Huber and R. Ahlrichs, *J. Chem. Phys.,* 1994, **100**, 5829.

11 (*a*) M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comp. Chem.,* 2003, **24**, 669; (*b*) J. Tomasi, B. Mennucci and E. Cances, *J. Mol. Struct.-Theochem.,* 1999, **464**, 211.

12 D. Visinescu, L. M. Toma, J. Cano, O. Fabelo, C. Ruiz-Pérez, A. Labrador, F. Lloret, M. Julve, *Dlaton Trans.,* 2010, **39**, 5028.

electronic configuration. In all cases, a different guess wave-function was imposed in each case. Calculations without solvation effects were also done and similar results to the previous ones were found (see Table S7).

Calculations of the *zfs* parameters were performed with the version 3.0 of the ORCA program system [Neese, F. WIREs Computational Molecular Science 2012, 2, 73] from CAS calculations by including contributions from triplet (20 states) and singlet states (20 states) in $Ni^{II}Zn^{II}$ models generated from electron promotion between *d* orbitals, which corresponds to the full active space built from only the five *d* orbitals of the d^8 nickel(II) ion. A Ahlrichs' TZVP[10] and the auxiliary TZV/C correlation fitting [Eichkorn, K.; Treutler, O.; Ohm, H.; Haser, M.; Ahlrichs, R. Chem.Phys. Lett, 1995, 240, 283; Eichkorn, K.; Treutler, O.; Ohm, H.; Haser, M.; Ahlrichs, R. Chem.Phys. Lett, 1995, 242, 652; Eichkorn,K.;Weigend,F.;Treutler,O.;Ahlrichs,R. Theor. Chem. Acc., 1997, 97, 119] basis sets and tight SCF criteria were used in all cases.

Table S1. Atomic Cartesian coordinates (x, y, z) in angstroms for model including K^I ions used in theoretical calculations and that was built from experimental crystal structure of **1a**.

Atom	x	y	z
Ni	0.000000	3.450198	0.001546
Ni	0.000001	–3.450197	–0.001544
K	1.594293	–0.175625	5.007614
K	–5.379210	–0.269445	–0.691144
K	4.783491	–0.089429	–2.022181
N	1.267345	4.694081	1.108266
N	3.162422	5.949407	2.710030
N	0.052200	2.452759	1.844234
N	1.252359	–4.655506	1.162512
N	3.231912	–5.740655	2.790125
N	–0.035338	–2.427343	1.824804
N	0.370534	4.514720	–1.772028
N	0.416601	–4.178067	8.635022
N	–7.731591	–6.865551	–2.198754
N	1.046086	5.611783	–4.222939
N	1.349179	–5.363053	6.312731
N	1.650801	2.425375	–0.775918
N	–7.891614	–3.262045	0.865557
N	1.189155	–1.759548	9.377043
N	0.366517	–4.469776	–1.832292
N	–10.659556	3.015793	–0.933317
N	–1.578783	4.518280	7.578182
N	–10.368526	3.544676	–3.663330
N	0.801673	–5.220572	–4.490179
N	–1.287755	5.047162	4.848159
N	1.640276	–2.417100	–0.762937
N	–8.975817	1.428314	0.341214
N	0.104965	2.930800	8.852705
N	–1.720208	4.519765	0.590285
N	9.397064	–3.775548	–0.263058
N	–4.148627	5.434320	1.584868
N	7.219648	–5.089632	0.857160
N	–1.527464	2.380244	–0.914891
N	9.129395	–1.827135	–1.998639
N	–1.705893	–4.582977	0.515456
N	7.393516	5.037803	–1.347713
N	–4.216749	–5.635903	1.174499
N	4.703652	5.574237	–0.778252
N	–1.485745	–2.443696	–1.020710
N	8.101725	2.843676	–2.639623
N	–8.660452	–5.679362	0.127015

O	1.438479	2.256166	3.692430
O	0.988368	–2.406003	3.885794
O	2.734850	2.071194	–2.809462
O	–6.887754	–2.904215	–1.208128
O	2.193020	–1.401717	7.303365
O	2.897918	–2.107748	–2.682916
O	–7.656987	1.194420	–1.548146
O	1.423789	2.696918	6.963353
O	–3.818890	1.990771	–0.757527
O	6.806851	–1.940449	–1.856840
O	–3.773505	–2.310972	–1.279011
O	5.903762	2.179156	–2.852988
O	4.825169	–0.548527	–4.776490
O	–5.405951	–0.121087	–3.479693
O	3.674823	1.381403	5.031804
C	1.783256	5.881319	0.775855
C	2.720199	6.500196	1.588040
C	2.630436	4.753700	3.042185
C	1.667029	4.124693	2.256691
C	1.029009	2.816516	2.648788
C	–0.638773	1.232383	2.133132
C	–2.008528	1.258435	2.418682
C	–2.714436	0.064944	2.533246
C	–2.075180	–1.168049	2.362483
C	–0.707463	–1.195876	2.100843
C	0.000000	0.000000	2.020191
C	0.791552	–2.856616	2.736437
C	1.556611	–4.108759	2.343036
C	2.549778	–4.636083	3.139161
C	2.874606	–6.311431	1.647580
C	1.893992	–5.783622	0.835107
C	–0.231033	5.609459	–2.224260
C	–9.002313	–6.924683	–0.196883
C	0.078458	–5.422197	8.314606
C	0.116608	6.159966	–3.444773
C	–8.526032	–7.516354	–1.353015
C	0.554741	–6.013867	7.158483
C	–7.414280	–5.610776	–1.873453
C	1.629646	4.502663	–3.764396
C	1.666490	–4.108291	6.638037
C	6.098863	–0.726247	–5.251389
C	–4.197543	0.280798	–3.987257
C	4.883232	1.783285	4.524240
C	1.301909	3.953007	–2.553385
C	–7.870843	–5.016574	–0.726916
C	1.209926	–3.514090	7.784573
C	1.968125	2.688258	–2.040647
C	–7.508117	–3.586707	–0.366062
C	1.572650	–2.084222	8.145426

C	2.207668	1.217612	–0.262834
C	–7.622879	–1.911570	1.234448
C	1.457891	–0.409084	9.745936
C	3.134413	1.213980	0.785889
C	–6.733189	–1.586184	2.264613
C	2.347585	–0.083698	10.776109
C	3.569830	0.007874	1.304812
C	–6.582576	–0.263618	2.641011
C	2.498194	1.238867	11.152499
C	3.105734	–1.203301	0.817175
C	–7.297555	0.752711	2.027813
C	1.783219	2.255198	10.539309
C	2.196234	–1.217957	–0.242275
C	–8.174344	0.447676	0.984740
C	0.906425	1.950162	9.496230
C	1.761375	–0.013490	–0.775854
C	–8.324593	–0.874814	0.593589
C	0.756182	0.627673	9.105087
C	2.025671	–2.697961	–1.984195
C	–8.647047	1.650339	–0.908399
C	0.433727	3.152828	7.603096
C	1.295638	–3.864790	–2.587434
C	–9.610048	2.551915	–1.628209
C	–0.529279	4.054401	6.883280
C	–9.478792	2.807383	–2.990729
C	1.497282	–4.234389	–3.914719
C	–0.398023	4.309881	5.520758
C	–0.121424	–5.795200	–3.740909
C	–11.405353	3.979826	–2.970980
C	–2.324584	5.482312	5.540507
C	–0.360139	–5.430150	–2.420251
C	–11.573668	3.719797	–1.615082
C	–2.492893	5.222284	6.896416
C	–1.804035	5.628665	1.320833
C	9.552088	–4.787327	0.587028
C	–3.010273	6.075177	1.811003
C	8.468851	–5.432968	1.138759
C	–4.051815	4.318708	0.842342
C	7.075943	–4.069788	–0.005732
C	–2.850306	3.868236	0.332495
C	8.153942	–3.423551	–0.577402
C	–2.748580	2.630786	–0.512719
C	7.989299	–2.295992	–1.555926
C	–1.338629	1.194013	–1.681007
C	9.060053	–0.721079	–2.893956
C	–0.892270	1.227202	–3.002992
C	9.519144	–0.800978	–4.209568
C	–0.677319	0.032268	–3.704276
C	9.472522	0.326487	–5.041752

C	–0.876921	–1.197415	–3.067023
C	8.997276	1.544222	–4.542449
C	–1.312181	–1.227278	–1.738866
C	8.549660	1.624033	–3.220479
C	–1.565974	–0.038885	–1.076164
C	8.557433	0.490017	–2.426870
C	–2.718821	–2.829941	–0.826489
C	6.811371	2.965994	–2.474070
C	–2.851493	–4.039082	0.046509
C	6.402998	4.204840	–1.739055
C	–4.085875	–4.569082	0.381395
C	5.077723	4.481738	–1.449650
C	–3.080211	–6.151845	1.629900
C	5.691710	6.376614	–0.397162
C	–1.848472	–5.644467	1.308731
C	7.009218	6.122561	–0.675416
H	1.510415	6.296971	–0.009774
H	3.050128	7.331382	1.337350
H	2.918087	4.336504	3.822084
H	–2.447940	2.071906	2.530604
H	–3.623348	0.086056	2.727030
H	–2.557701	–1.961300	2.423576
H	0.919555	–0.023960	1.887921
H	2.756199	–4.212544	3.942418
H	3.299476	–7.095167	1.385561
H	1.673776	–6.219557	0.044316
H	–0.896000	6.013578	–1.714111
H	–9.567444	–7.407022	0.363230
H	–0.486670	–5.904534	8.874727
H	–0.311210	6.935635	–3.729393
H	–8.767614	–8.394254	–1.544437
H	0.313160	–6.891768	6.967061
H	–6.864503	–5.125073	–2.445535
H	2.280538	4.090540	–4.285869
H	2.216267	–3.622586	6.065955
H	3.454844	2.017068	1.131082
H	–6.247005	–2.254839	2.692772
H	2.833774	–0.752355	11.204255
H	4.189132	0.012736	1.997040
H	–5.986318	–0.054186	3.321713
H	3.094465	1.448300	11.833207
H	3.399053	–2.003389	1.193464
H	–7.193671	1.634611	2.309303
H	1.887104	3.137109	10.820799
H	1.163127	–0.019374	–1.487390
H	–8.900314	–1.080729	–0.106677
H	0.180459	0.421758	8.404820
H	–8.749411	2.453955	–3.447206
H	2.135786	–3.780909	–4.416676

H	0.331363	3.956442	5.064292
H	–0.634688	–6.477197	–4.112792
H	–12.052361	4.485442	–3.409808
H	–2.971587	5.987933	5.101689
H	–1.034027	–5.857033	–1.939100
H	–12.331388	4.037325	–1.175895
H	–3.250619	5.539811	7.335596
H	–1.030211	6.110620	1.504619
H	10.411152	–5.062263	0.813476
H	–3.027258	6.855169	2.318177
H	8.618911	–6.136098	1.729530
H	–4.823643	3.832104	0.664507
H	6.217728	–3.789264	–0.226821
H	–0.735275	2.044869	–3.419348
H	9.858735	–1.604504	–4.534556
H	–0.720092	–1.991488	–3.524725
H	8.979830	2.297479	–5.087364
H	–1.894293	–0.063538	–0.206998
H	8.220984	0.537545	–1.561777
H	–4.853893	–4.166677	0.042979
H	4.422356	3.884049	–1.731699
H	–3.122319	–6.892575	2.193417
H	5.479369	7.147407	0.081159
H	–1.088658	–6.053045	1.656481
H	7.655107	6.725451	–0.384672
H	6.596890	0.089340	–5.141710
H	–3.532479	–0.386718	–3.793982
H	5.548304	1.115767	4.717512
H	6.528000	–1.429594	–4.761460
H	–3.941205	1.111708	–3.583801
H	5.139579	2.614193	4.927693
H	–4.270114	0.392217	–4.937931
H	6.064686	–0.955770	–6.182844
H	4.810658	1.894704	3.573565
H	4.329407	–1.395554	–4.938572
H	3.785588	1.288778	6.016397
H	–6.074902	0.571865	–3.728292
H	–0.384496	0.056983	–4.584799
H	9.757466	0.264646	–5.925309

Table S2. Atomic Cartesian coordinates (x, y, z) in angstroms for model excluding K^I ions used in theoretical calculations and that was built from experimental crystal structure of **1a**.

Atom	x	y	z
Ni	0.000000	–3.450200	0.001535
Ni	0.000000	3.450200	–0.001535
N	–1.267344	–4.694087	1.108251
N	–3.162429	–5.949417	2.710016
N	–0.052203	–2.452765	1.844225
N	–1.252366	4.655513	1.162519
N	–3.231928	5.740654	2.790136
N	0.035337	2.427344	1.824812
N	–0.370531	–4.514727	–1.772042
N	–1.046081	–5.611779	–4.222956
N	–1.650799	–2.425380	–0.775921
N	–0.366520	4.469783	–1.832283
N	–0.801667	5.220583	–4.490167
N	–1.640283	2.417104	–0.762930
N	1.720212	–4.519763	0.590275
N	4.148637	–5.434329	1.584860
N	1.527465	–2.380244	–0.914897
N	1.705888	4.582984	0.515464
N	4.216753	5.635917	1.174519
N	1.485751	2.443703	–1.020701
O	–1.438485	–2.256174	3.692423
O	–0.988373	2.405999	3.885804
O	–2.734853	–2.071194	–2.809469
O	–2.897920	2.107753	–2.682914
O	3.818898	–1.990772	–0.757533
O	3.773515	2.310977	–1.279000
C	–1.783263	–5.881330	0.775841
C	–2.720206	–6.500208	1.588027
C	–2.630443	–4.753710	3.042172
C	–1.667030	–4.124702	2.256682
C	–1.029011	–2.816530	2.648782
C	0.638775	–1.232390	2.133129
C	2.008535	–1.258436	2.418676
C	2.714441	–0.064952	2.533248
C	2.075179	1.168046	2.362489
C	0.707458	1.195875	2.100851
C	0.000000	0.000000	2.020197
C	–0.791558	2.856618	2.736447
C	–1.556620	4.108764	2.343048
C	–2.549786	4.636084	3.139172
C	–2.874613	6.311438	1.647592
C	–1.893999	5.783625	0.835121
C	0.231038	–5.609466	–2.224274
C	–0.116604	–6.159969	–3.444785

C	–1.629645	–4.502665	–3.764405
C	–1.301907	–3.953006	–2.553392
C	–1.968128	–2.688255	–2.040654
C	–2.207673	–1.217613	–0.262840
C	–3.134418	–1.213981	0.785882
C	–3.569835	–0.007876	1.304808
C	–3.105745	1.203296	0.817177
C	–2.196244	1.217957	–0.242277
C	–1.761378	0.013492	–0.775852
C	–2.025672	2.697963	–1.984191
C	–1.295638	3.864792	–2.587425
C	–1.497285	4.234394	–3.914716
C	0.121428	5.795209	–3.740900
C	0.360142	5.430158	–2.420243
C	1.804038	–5.628675	1.320819
C	3.010280	–6.075179	1.810992
C	4.051826	–4.318712	0.842332
C	2.850310	–3.868236	0.332486
C	2.748588	–2.630788	–0.512724
C	1.338634	–1.194005	–1.681013
C	0.892270	–1.227201	–3.002991
C	0.677323	–0.032265	–3.704273
C	0.876928	1.197419	–3.067020
C	1.312189	1.227283	–1.738859
C	1.565978	0.038884	–1.076166
C	2.718822	2.829950	–0.826481
C	2.851499	4.039091	0.046522
C	4.085882	4.569094	0.381411
C	3.080219	6.151855	1.629912
C	1.848469	5.644476	1.308749
H	–1.510419	–6.296983	–0.009789
H	–3.050134	–7.331392	1.337337
H	–2.918098	–4.336513	3.822073
H	2.447941	–2.071913	2.530604
H	3.623354	–0.086062	2.727031
H	2.557708	1.961301	2.423582
H	–0.919560	0.023953	1.887922
H	–2.756206	4.212543	3.942433
H	–3.299489	7.095172	1.385574
H	–1.673778	6.219563	0.044332
H	0.896007	–6.013585	–1.714131
H	0.311215	–6.935636	–3.729412
H	–2.280540	–4.090535	–4.285881
H	–3.454854	–2.017077	1.131079
H	–4.189147	–0.012743	1.997042
H	–3.399064	2.003385	1.193471
H	–1.163128	0.019375	–1.487386
H	–2.135792	3.780917	–4.416667
H	0.634688	6.477213	–4.112783

H	1.034024	5.857044	–1.939087
H	1.030213	–6.110628	1.504607
H	3.027268	–6.855173	2.318164
H	4.823660	–3.832106	0.664502
H	0.735280	–2.044868	–3.419354
H	0.720096	1.991494	–3.524720
H	1.894300	0.063537	–0.206997
H	4.853903	4.166682	0.042988
H	3.122324	6.892585	2.193432
H	1.088660	6.053049	1.656497
H	0.382493	–0.057366	–4.584389
Ni	0.000000	–3.450200	0.001535
Ni	0.000000	3.450200	–0.001535
N	–1.267344	–4.694087	1.108251
N	–3.162429	–5.949417	2.710016
N	–0.052203	–2.452765	1.844225
N	–1.252366	4.655513	1.162519
N	–3.231928	5.740654	2.790136
N	0.035337	2.427344	1.824812
N	–0.370531	–4.514727	–1.772042
N	–1.046081	–5.611779	–4.222956
N	–1.650799	–2.425380	–0.775921
N	–0.366520	4.469783	–1.832283
N	–0.801667	5.220583	–4.490167
N	–1.640283	2.417104	–0.762930
N	1.720212	–4.519763	0.590275
N	4.148637	–5.434329	1.584860
N	1.527465	–2.380244	–0.914897
N	1.705888	4.582984	0.515464
N	4.216753	5.635917	1.174519
N	1.485751	2.443703	–1.020701
O	–1.438485	–2.256174	3.692423
O	–0.988373	2.405999	3.885804
O	–2.734853	–2.071194	–2.809469
O	–2.897920	2.107753	–2.682914
O	3.818898	–1.990772	–0.757533
O	3.773515	2.310977	–1.279000
C	–1.783263	–5.881330	0.775841
C	–2.720206	–6.500208	1.588027
C	–2.630443	–4.753710	3.042172
C	–1.667030	–4.124702	2.256682
C	–1.029011	–2.816530	2.648782
C	0.638775	–1.232390	2.133129
C	2.008535	–1.258436	2.418676
C	2.714441	–0.064952	2.533248
C	2.075179	1.168046	2.362489
C	0.707458	1.195875	2.100851
C	0.000000	0.000000	2.020197
C	–0.791558	2.856618	2.736447

C	–1.556620	4.108764	2.343048
C	–2.549786	4.636084	3.139172
C	–2.874613	6.311438	1.647592
C	–1.893999	5.783625	0.835121
C	0.231038	–5.609466	–2.224274
C	–0.116604	–6.159969	–3.444785
C	–1.629645	–4.502665	–3.764405
C	–1.301907	–3.953006	–2.553392
C	–1.968128	–2.688255	–2.040654
C	–2.207673	–1.217613	–0.262840
C	–3.134418	–1.213981	0.785882
C	–3.569835	–0.007876	1.304808
C	–3.105745	1.203296	0.817177
C	–2.196244	1.217957	–0.242277
C	–1.761378	0.013492	–0.775852
C	–2.025672	2.697963	–1.984191
C	–1.295638	3.864792	–2.587425
C	–1.497285	4.234394	–3.914716
C	0.121428	5.795209	–3.740900
C	0.360142	5.430158	–2.420243
C	1.804038	–5.628675	1.320819
C	3.010280	–6.075179	1.810992
C	4.051826	–4.318712	0.842332
C	2.850310	–3.868236	0.332486
C	2.748588	–2.630788	–0.512724
C	1.338634	–1.194005	–1.681013
C	0.892270	–1.227201	–3.002991
C	0.677323	–0.032265	–3.704273
C	0.876928	1.197419	–3.067020
C	1.312189	1.227283	–1.738859
C	1.565978	0.038884	–1.076166
C	2.718822	2.829950	–0.826481
C	2.851499	4.039091	0.046522
C	4.085882	4.569094	0.381411
C	3.080219	6.151855	1.629912
C	1.848469	5.644476	1.308749
H	–1.510419	–6.296983	–0.009789
H	–3.050134	–7.331392	1.337337
H	–2.918098	–4.336513	3.822073
H	2.447941	–2.071913	2.530604
H	3.623354	–0.086062	2.727031
H	2.557708	1.961301	2.423582
H	–0.919560	0.023953	1.887922
H	–2.756206	4.212543	3.942433
H	–3.299489	7.095172	1.385574
H	–1.673778	6.219563	0.044332
H	0.896007	–6.013585	–1.714131
H	0.311215	–6.935636	–3.729412
H	–2.280540	–4.090535	–4.285881

H	–3.454854	–2.017077	1.131079
H	–4.189147	–0.012743	1.997042
H	–3.399064	2.003385	1.193471
H	–1.163128	0.019375	–1.487386
H	–2.135792	3.780917	–4.416667
H	0.634688	6.477213	–4.112783
H	1.034024	5.857044	–1.939087
H	1.030213	–6.110628	1.504607
H	3.027268	–6.855173	2.318164
H	4.823660	–3.832106	0.664502
H	0.735280	–2.044868	–3.419354
H	0.720096	1.991494	–3.524720
H	1.894300	0.063537	–0.206997
H	4.853903	4.166682	0.042988
H	3.122324	6.892585	2.193432
H	1.088660	6.053049	1.656497
H	0.382493	–0.057366	–4.584389

Table S3. Atomic Cartesian coordinates (x, y, z) in angstroms for optimized model excluding K^I ions and that was built from experimental crystal structure of **1a**.

Atom	x	y	z
Ni	–0.002638	–3.364575	0.022825
Ni	–0.005181	3.327646	–0.047242
N	–1.387213	–4.598383	1.148465
N	–3.215061	–5.769909	2.884017
N	0.032003	–2.433081	1.877179
N	–1.389129	4.584785	1.052190
N	–3.213091	5.795745	2.764598
N	0.031112	2.436218	1.826438
N	–0.276504	–4.630716	–1.714584
N	–0.865604	–5.859376	–4.137108
N	–1.637666	–2.464529	–0.886022
N	–0.280287	4.556604	–1.811292
N	–0.870263	5.732579	–4.259478
N	–1.639736	2.407346	–0.936477
N	1.652601	–4.596910	0.676460
N	4.058114	–5.788925	1.394124
N	1.589758	–2.463876	–0.958087
N	1.650010	4.575107	0.579815
N	4.055677	5.782290	1.271452
N	1.587416	2.407190	–1.008748
O	–0.784642	–2.645222	4.079130
O	–0.781603	2.697329	4.024617
O	–3.147065	–2.733639	–2.677746
O	–3.149056	2.636698	–2.733765
O	3.896015	–2.722215	–1.377706
O	3.893430	2.657473	–1.434350
C	–2.167930	–5.617097	0.740343
C	–3.084464	–6.200998	1.612102
C	–2.441094	–4.747481	3.279707
C	–1.520095	–4.144602	2.408003
C	–0.688240	–2.976692	2.859697
C	0.738071	–1.218138	2.124837
C	2.111276	–1.209073	2.413206
C	2.785566	0.009360	2.550663
C	2.110840	1.224408	2.387949
C	0.737603	1.226975	2.099493
C	0.063428	0.003149	2.000524
C	–0.687312	3.001584	2.797945
C	–1.519764	4.159341	2.321826
C	–2.438812	4.782038	3.181571
C	–3.084817	6.198151	1.483094
C	–2.170233	5.594403	0.622861
C	0.477906	–5.648699	–2.170955
C	0.181245	–6.261103	–3.386631
C	–1.606022	–4.837393	–3.680546

C	–1.311546	–4.205610	–2.461657
C	–2.130086	–3.037863	–1.985357
C	–2.217819	–1.246721	–0.419729
C	–3.160892	–1.230204	0.619089
C	–3.631668	–0.008461	1.112600
C	–3.161637	1.203168	0.594085
C	–2.218676	1.198939	–0.444917
C	–1.780851	–0.029151	–0.957674
C	–2.132512	2.956664	–2.047869
C	–1.315014	4.114751	–2.548973
C	–1.610002	4.720132	–3.781094
C	0.176321	6.151086	–3.517830
C	0.473378	5.565158	–2.289272
C	1.682923	–5.593092	1.581958
C	2.890813	–6.187173	1.941330
C	4.020468	–4.787896	0.501021
C	2.810916	–4.173933	0.138362
C	2.793243	–3.025217	–0.831523
C	1.460880	–1.258955	–1.711991
C	1.024840	–1.266951	–3.045600
C	0.816891	–0.057140	–3.717267
C	1.023151	1.166525	–3.070658
C	1.459373	1.186663	–1.737263
C	1.699394	–0.029368	–1.084260
C	2.790715	2.971613	–0.894396
C	2.808283	4.140720	0.050789
C	4.017892	4.762308	0.400080
C	2.888427	6.192253	1.810037
C	1.680500	5.590588	1.463637
H	–2.055244	–5.955324	–0.290350
H	–3.725208	–7.025394	1.290151
H	–2.522186	–4.365864	4.297713
H	2.645342	–2.156741	2.512574
H	3.858728	0.011762	2.763564
H	2.644576	2.174137	2.467591
H	–1.001484	0.000673	1.781091
H	–2.518065	4.423369	4.208032
H	–3.725779	7.015465	1.143993
H	–2.059328	5.909409	–0.415340
H	1.322293	–5.964089	–1.557045
H	0.789005	–7.085147	–3.767946
H	–2.456088	–4.478903	–4.261426
H	–3.508871	–2.174578	1.043737
H	–4.358132	–0.000284	1.930622
H	–3.510080	2.155892	0.999226
H	–1.054443	–0.037254	–1.766556
H	–2.459864	4.348750	–4.354116
H	0.783500	6.967170	–3.916775
H	1.317437	5.894146	–1.682047

H	0.733180	–5.904553	2.018221
H	2.927581	–6.993394	2.677846
H	4.943637	–4.432734	0.042554
H	0.835768	–2.220923	–3.543020
H	0.832646	2.109827	–3.587494
H	2.040146	–0.018522	–0.051733
H	4.941004	4.397372	–0.050769
H	2.925262	7.014149	2.529019
H	0.730889	5.911529	1.893296
H	0.464670	–0.068036	–4.753020
Ni	–0.002638	–3.364575	0.022825
Ni	–0.005181	3.327646	–0.047242
N	–1.387213	–4.598383	1.148465
N	–3.215061	–5.769909	2.884017
N	0.032003	–2.433081	1.877179
N	–1.389129	4.584785	1.052190
N	–3.213091	5.795745	2.764598
N	0.031112	2.436218	1.826438
N	–0.276504	–4.630716	–1.714584
N	–0.865604	–5.859376	–4.137108
N	–1.637666	–2.464529	–0.886022
N	–0.280287	4.556604	–1.811292
N	–0.870263	5.732579	–4.259478
N	–1.639736	2.407346	–0.936477
N	1.652601	–4.596910	0.676460
N	4.058114	–5.788925	1.394124
N	1.589758	–2.463876	–0.958087
N	1.650010	4.575107	0.579815
N	4.055677	5.782290	1.271452
N	1.587416	2.407190	–1.008748
O	–0.784642	–2.645222	4.079130
O	–0.781603	2.697329	4.024617
O	–3.147065	–2.733639	–2.677746
O	–3.149056	2.636698	–2.733765
O	3.896015	–2.722215	–1.377706
O	3.893430	2.657473	–1.434350
C	–2.167930	–5.617097	0.740343
C	–3.084464	–6.200998	1.612102
C	–2.441094	–4.747481	3.279707
C	–1.520095	–4.144602	2.408003
C	–0.688240	–2.976692	2.859697
C	0.738071	–1.218138	2.124837
C	2.111276	–1.209073	2.413206
C	2.785566	0.009360	2.550663
C	2.110840	1.224408	2.387949
C	0.737603	1.226975	2.099493
C	0.063428	0.003149	2.000524
C	–0.687312	3.001584	2.797945
C	–1.519764	4.159341	2.321826

C	–2.438812	4.782038	3.181571
C	–3.084817	6.198151	1.483094
C	–2.170233	5.594403	0.622861
C	0.477906	–5.648699	–2.170955
C	0.181245	–6.261103	–3.386631
C	–1.606022	–4.837393	–3.680546
C	–1.311546	–4.205610	–2.461657
C	–2.130086	–3.037863	–1.985357
C	–2.217819	–1.246721	–0.419729
C	–3.160892	–1.230204	0.619089
C	–3.631668	–0.008461	1.112600
C	–3.161637	1.203168	0.594085
C	–2.218676	1.198939	–0.444917
C	–1.780851	–0.029151	–0.957674
C	–2.132512	2.956664	–2.047869
C	–1.315014	4.114751	–2.548973
C	–1.610002	4.720132	–3.781094
C	0.176321	6.151086	–3.517830
C	0.473378	5.565158	–2.289272
C	1.682923	–5.593092	1.581958
C	2.890813	–6.187173	1.941330
C	4.020468	–4.787896	0.501021
C	2.810916	–4.173933	0.138362
C	2.793243	–3.025217	–0.831523
C	1.460880	–1.258955	–1.711991
C	1.024840	–1.266951	–3.045600
C	0.816891	–0.057140	–3.717267
C	1.023151	1.166525	–3.070658
C	1.459373	1.186663	–1.737263
C	1.699394	–0.029368	–1.084260
C	2.790715	2.971613	–0.894396
C	2.808283	4.140720	0.050789
C	4.017892	4.762308	0.400080
C	2.888427	6.192253	1.810037
C	1.680500	5.590588	1.463637
H	–2.055244	–5.955324	–0.290350
H	–3.725208	–7.025394	1.290151
H	–2.522186	–4.365864	4.297713
H	2.645342	–2.156741	2.512574
H	3.858728	0.011762	2.763564
H	2.644576	2.174137	2.467591
H	–1.001484	0.000673	1.781091
H	–2.518065	4.423369	4.208032
H	–3.725779	7.015465	1.143993
H	–2.059328	5.909409	–0.415340
H	1.322293	–5.964089	–1.557045
H	0.789005	–7.085147	–3.767946
H	–2.456088	–4.478903	–4.261426
H	–3.508871	–2.174578	1.043737

H	–4.358132	–0.000284	1.930622
H	–3.510080	2.155892	0.999226
H	–1.054443	–0.037254	–1.766556
H	–2.459864	4.348750	–4.354116
H	0.783500	6.967170	–3.916775
H	1.317437	5.894146	–1.682047
H	0.733180	–5.904553	2.018221
H	2.927581	–6.993394	2.677846
H	4.943637	–4.432734	0.042554
H	0.835768	–2.220923	–3.543020
H	0.832646	2.109827	–3.587494
H	2.040146	–0.018522	–0.051733
H	4.941004	4.397372	–0.050769
H	2.925262	7.014149	2.529019
H	0.730889	5.911529	1.893296
H	0.464670	–0.068036	–4.753020

Table S4. Atomic Cartesian coordinates (x, y, z) in angstroms for optimized model excluding K^{I} ions of oxidized Ni^{III}_2 species.

Atom	x	y	z
Ni	0.011926	–3.431158	–0.017208
Ni	0.054278	3.388191	–0.057977
N	–1.420953	–4.617121	1.101103
N	–3.337986	–5.598614	2.838991
N	0.042000	–2.439733	1.647340
N	–1.364182	4.605532	1.046070
N	–3.272658	5.627904	2.769667
N	0.071773	2.416493	1.618602
N	–0.235349	–4.577615	–1.609453
N	–0.829154	–5.883144	–3.977361
N	–1.478069	–2.452053	–0.768492
N	–0.179082	4.519731	–1.663677
N	–0.756061	5.803840	–4.047500
N	–1.449998	2.421481	–0.796469
N	1.552384	–4.478706	0.636137
N	3.886895	–5.757932	1.399871
N	1.535002	–2.456242	–1.059075
N	1.605337	4.426203	0.583710
N	3.954920	5.685855	1.333766
N	1.564407	2.383197	–1.086734
O	–0.932996	–2.285365	3.751197
O	–0.908276	2.297275	3.722426
O	–2.901404	–2.453980	–2.615218
O	–2.874949	2.421135	–2.641942
O	3.866082	–2.539868	–1.282871
O	3.896268	2.436857	–1.310975
C	–2.165665	–5.681404	0.756956
C	–3.134241	–6.171534	1.639658
C	–2.590347	–4.532616	3.173726
C	–1.626653	–4.032873	2.296110
C	–0.798546	–2.837202	2.627329
C	0.788327	–1.236826	1.843360
C	2.167894	–1.240558	2.095814
C	2.851416	–0.025155	2.230040
C	2.182887	1.196837	2.081262
C	0.803308	1.207020	1.829035
C	0.116914	–0.011103	1.775446
C	–0.765561	2.834749	2.592549
C	–1.579016	4.036342	2.246734
C	–2.538275	4.556794	3.117129
C	–3.059789	6.185803	1.564841
C	–2.095273	5.675083	0.689387
C	0.473679	–5.657737	–1.983217
C	0.165585	–6.310561	–3.181117
C	–1.529963	–4.802360	–3.595925

C	–1.232267	–4.142024	–2.405166
C	–1.958005	–2.933329	–1.939084
C	–2.037044	–1.229559	–0.280280
C	–3.033955	–1.215443	0.705459
C	–3.526207	0.007696	1.177668
C	–3.020536	1.219634	0.691028
C	–2.023299	1.211133	–0.294492
C	–1.574681	–0.014768	–0.799409
C	–1.924402	2.895428	–1.972359
C	–1.182303	4.088151	–2.453583
C	–1.471389	4.737523	–3.652490
C	0.244631	6.227589	–3.256787
C	0.544411	5.585332	–2.051037
C	1.515892	–5.483329	1.532849
C	2.698416	–6.122958	1.912150
C	3.913798	–4.749689	0.514199
C	2.742595	–4.094082	0.127142
C	2.756901	–2.941602	–0.825579
C	1.394305	–1.262297	–1.821178
C	0.880794	–1.263707	–3.127813
C	0.649210	–0.046496	–3.782478
C	0.895450	1.175123	–3.141473
C	1.409308	1.182303	–1.834999
C	1.699199	–0.038354	–1.215026
C	2.791929	2.857063	–0.858790
C	2.791139	4.021255	0.079938
C	3.969988	4.667348	0.459642
C	2.770755	6.070971	1.841223
C	1.580564	5.441723	1.468456
H	–1.993177	–6.147551	–0.213172
H	–3.746883	–7.034714	1.374703
H	–2.748005	–4.057827	4.142370
H	2.703664	–2.185414	2.196135
H	3.924028	–0.030523	2.436328
H	2.730266	2.136226	2.169590
H	–0.961764	–0.004961	1.691253
H	–2.703208	4.094305	4.090476
H	–3.661752	7.053293	1.289677
H	–1.914685	6.129280	–0.284857
H	1.276497	–6.010546	–1.340466
H	0.732480	–7.188463	–3.493760
H	–2.339542	–4.439800	–4.230247
H	–3.425957	–2.155511	1.097223
H	–4.307087	0.016529	1.941383
H	–3.402451	2.168460	1.071409
H	–0.839847	–0.023635	–1.595290
H	–2.285912	4.377993	–4.282194
H	0.823170	7.093855	–3.580350
H	1.352113	5.935023	–1.412748

H	0.554252	–5.781585	1.942383
H	2.679000	–6.938755	2.635952
H	4.867734	–4.432955	0.092377
H	0.656791	–2.210490	–3.623290
H	0.682449	2.118881	–3.647451
H	2.118661	–0.035282	–0.214615
H	4.920188	4.334454	0.041830
H	2.760990	6.895206	2.555598
H	0.622642	5.757110	1.873819
H	0.249809	–0.049779	–4.799820
Ni	0.011926	–3.431158	–0.017208
Ni	0.054278	3.388191	–0.057977
N	–1.420953	–4.617121	1.101103
N	–3.337986	–5.598614	2.838991
N	0.042000	–2.439733	1.647340
N	–1.364182	4.605532	1.046070
N	–3.272658	5.627904	2.769667
N	0.071773	2.416493	1.618602
N	–0.235349	–4.577615	–1.609453
N	–0.829154	–5.883144	–3.977361
N	–1.478069	–2.452053	–0.768492
N	–0.179082	4.519731	–1.663677
N	–0.756061	5.803840	–4.047500
N	–1.449998	2.421481	–0.796469
N	1.552384	–4.478706	0.636137
N	3.886895	–5.757932	1.399871
N	1.535002	–2.456242	–1.059075
N	1.605337	4.426203	0.583710
N	3.954920	5.685855	1.333766
N	1.564407	2.383197	–1.086734
O	–0.932996	–2.285365	3.751197
O	–0.908276	2.297275	3.722426
O	–2.901404	–2.453980	–2.615218
O	–2.874949	2.421135	–2.641942
O	3.866082	–2.539868	–1.282871
O	3.896268	2.436857	–1.310975
C	–2.165665	–5.681404	0.756956
C	–3.134241	–6.171534	1.639658
C	–2.590347	–4.532616	3.173726
C	–1.626653	–4.032873	2.296110
C	–0.798546	–2.837202	2.627329
C	0.788327	–1.236826	1.843360
C	2.167894	–1.240558	2.095814
C	2.851416	–0.025155	2.230040
C	2.182887	1.196837	2.081262
C	0.803308	1.207020	1.829035
C	0.116914	–0.011103	1.775446
C	–0.765561	2.834749	2.592549
C	–1.579016	4.036342	2.246734

C	–2.538275	4.556794	3.117129
C	–3.059789	6.185803	1.564841
C	–2.095273	5.675083	0.689387
C	0.473679	–5.657737	–1.983217
C	0.165585	–6.310561	–3.181117
C	–1.529963	–4.802360	–3.595925
C	–1.232267	–4.142024	–2.405166
C	–1.958005	–2.933329	–1.939084
C	–2.037044	–1.229559	–0.280280
C	–3.033955	–1.215443	0.705459
C	–3.526207	0.007696	1.177668
C	–3.020536	1.219634	0.691028
C	–2.023299	1.211133	–0.294492
C	–1.574681	–0.014768	–0.799409
C	–1.924402	2.895428	–1.972359
C	–1.182303	4.088151	–2.453583
C	–1.471389	4.737523	–3.652490
C	0.244631	6.227589	–3.256787
C	0.544411	5.585332	–2.051037
C	1.515892	–5.483329	1.532849
C	2.698416	–6.122958	1.912150
C	3.913798	–4.749689	0.514199
C	2.742595	–4.094082	0.127142
C	2.756901	–2.941602	–0.825579
C	1.394305	–1.262297	–1.821178
C	0.880794	–1.263707	–3.127813
C	0.649210	–0.046496	–3.782478
C	0.895450	1.175123	–3.141473
C	1.409308	1.182303	–1.834999
C	1.699199	–0.038354	–1.215026
C	2.791929	2.857063	–0.858790
C	2.791139	4.021255	0.079938
C	3.969988	4.667348	0.459642
C	2.770755	6.070971	1.841223
C	1.580564	5.441723	1.468456
H	–1.993177	–6.147551	–0.213172
H	–3.746883	–7.034714	1.374703
H	–2.748005	–4.057827	4.142370
H	2.703664	–2.185414	2.196135
H	3.924028	–0.030523	2.436328
H	2.730266	2.136226	2.169590
H	–0.961764	–0.004961	1.691253
H	–2.703208	4.094305	4.090476
H	–3.661752	7.053293	1.289677
H	–1.914685	6.129280	–0.284857
H	1.276497	–6.010546	–1.340466
H	0.732480	–7.188463	–3.493760
H	–2.339542	–4.439800	–4.230247
H	–3.425957	–2.155511	1.097223

H	–4.307087	0.016529	1.941383
H	–3.402451	2.168460	1.071409
H	–0.839847	–0.023635	–1.595290
H	–2.285912	4.377993	–4.282194
H	0.823170	7.093855	–3.580350
H	1.352113	5.935023	–1.412748
H	0.554252	–5.781585	1.942383
H	2.679000	–6.938755	2.635952
H	4.867734	–4.432955	0.092377
H	0.656791	–2.210490	–3.623290
H	0.682449	2.118881	–3.647451
H	2.118661	–0.035282	–0.214615
H	4.920188	4.334454	0.041830
H	2.760990	6.895206	2.555598
H	0.622642	5.757110	1.873819
H	0.249809	–0.049779	–4.799820

Table S5. Atomic Cartesian coordinates (x, y, z) in angstroms for optimized model excluding K^{I} ions of most stable configuration of oxidized $\{Ni^{II}L^{\bullet}\}_2$ species.

Atom	x	y	z
Ni	–0.071863	–3.493717	–0.067386
Ni	–0.043517	3.473072	–0.015012
N	–1.366209	–4.586784	1.086978
N	–3.075906	–5.770838	2.916439
N	0.101911	–2.424798	1.699536
N	–1.389910	4.612288	1.115076
N	–3.128230	5.817270	2.904764
N	0.029773	2.444345	1.757748
N	–0.367477	–4.646280	–1.796123
N	–0.955794	–5.858716	–4.218314
N	–1.648777	–2.466510	–0.950439
N	–0.357395	4.551852	–1.797696
N	–0.678894	5.571661	–4.358609
N	–1.756541	2.392409	–0.930045
N	1.597404	–4.624435	0.590744
N	3.970527	–5.610787	1.635317
N	1.521331	–2.458459	–1.020991
N	1.608642	4.601966	0.533849
N	4.036801	5.734553	1.247458
N	1.461995	2.413038	–1.010175
O	–0.700556	–2.479713	3.895916
O	–0.776495	2.522083	3.955214
O	–2.976488	–2.447246	–2.875267
O	–2.562477	2.058433	–3.084015
O	3.786143	–2.104822	–0.660271
O	3.793380	2.304435	–1.123316
C	–2.132650	–5.631828	0.725172
C	–2.994268	–6.223961	1.652283
C	–2.310287	–4.724105	3.267524
C	–1.449041	–4.119045	2.348506
C	–0.624754	–2.924444	2.712611
C	0.808842	–1.207671	1.956669
C	2.160862	–1.183654	2.334148
C	2.807684	0.046094	2.521639
C	2.126980	1.257443	2.344364
C	0.768760	1.246705	1.987223
C	0.132828	0.010940	1.817754
C	–0.688659	2.951536	2.764839
C	–1.500166	4.152068	2.378380
C	–2.374920	4.768116	3.276995
C	–3.021182	6.261250	1.639203
C	–2.144880	5.657804	0.732966
C	0.324788	–5.723920	–2.205389
C	0.024068	–6.331766	–3.427932

C	–1.638947	–4.776788	–3.806135
C	–1.345024	–4.159265	–2.588272
C	–2.072414	–2.931889	–2.132846
C	–2.187424	–1.255615	–0.455383
C	–3.003527	–1.239750	0.700633
C	–3.404656	–0.023822	1.290291
C	–2.966743	1.185187	0.771712
C	–2.197726	1.195403	–0.432407
C	–1.870030	–0.040636	–1.055353
C	–1.848655	2.688564	–2.271527
C	–1.146907	3.928811	–2.695768
C	–1.304109	4.441501	–3.984782
C	0.102748	6.191688	–3.459397
C	0.271768	5.679296	–2.167532
C	1.605946	–5.757360	1.311815
C	2.807205	–6.251942	1.834274
C	3.956251	–4.476754	0.912819
C	2.763391	–3.981172	0.384957
C	2.734309	–2.742708	–0.435071
C	1.315040	–1.263547	–1.677117
C	0.762520	–1.282987	–2.988876
C	0.591447	–0.088781	–3.672056
C	0.861836	1.140519	–3.036592
C	1.327163	1.184797	–1.707914
C	1.628243	–0.021616	–1.070538
C	2.707403	2.835654	–0.744583
C	2.768534	4.065977	0.103460
C	3.988690	4.642871	0.465833
C	2.875143	6.260677	1.676048
C	1.648839	5.694056	1.319101
H	–2.059029	–5.997049	–0.298268
H	–3.621538	–7.071204	1.370717
H	–2.368284	–4.341163	4.286405
H	2.701052	–2.118965	2.490932
H	3.861807	0.058902	2.810600
H	2.642407	2.209074	2.488853
H	–0.919709	–0.003788	1.569760
H	–2.455240	4.393008	4.297242
H	–3.639746	7.109285	1.340828
H	–2.050480	6.012859	–0.292920
H	1.116684	–6.102130	–1.559978
H	0.579554	–7.206721	–3.769383
H	–2.431641	–4.377701	–4.439114
H	–3.307247	–2.188961	1.145004
H	–4.030743	–0.040584	2.184070
H	–3.225719	2.134271	1.240359
H	–1.303465	–0.036160	–1.981072
H	–1.939652	3.929435	–4.707964
H	0.605620	7.110331	–3.765617

H	0.909447	6.176622	–1.438107
H	0.661691	–6.276013	1.473889
H	2.824533	–7.173991	2.417476
H	4.895748	–3.949024	0.745273
H	0.534179	–2.241086	–3.455062
H	0.708622	2.075481	–3.577439
H	2.074658	–0.004452	–0.080544
H	4.921157	4.201817	0.113564
H	2.918220	7.146167	2.312249
H	0.705729	6.117856	1.662196
H	0.222843	–0.093816	–4.699435
Ni	–0.071863	–3.493717	–0.067386
Ni	–0.043517	3.473072	–0.015012
N	–1.366209	–4.586784	1.086978
N	–3.075906	–5.770838	2.916439
N	0.101911	–2.424798	1.699536
N	–1.389910	4.612288	1.115076
N	–3.128230	5.817270	2.904764
N	0.029773	2.444345	1.757748
N	–0.367477	–4.646280	–1.796123
N	–0.955794	–5.858716	–4.218314
N	–1.648777	–2.466510	–0.950439
N	–0.357395	4.551852	–1.797696
N	–0.678894	5.571661	–4.358609
N	–1.756541	2.392409	–0.930045
N	1.597404	–4.624435	0.590744
N	3.970527	–5.610787	1.635317
N	1.521331	–2.458459	–1.020991
N	1.608642	4.601966	0.533849
N	4.036801	5.734553	1.247458
N	1.461995	2.413038	–1.010175
O	–0.700556	–2.479713	3.895916
O	–0.776495	2.522083	3.955214
O	–2.976488	–2.447246	–2.875267
O	–2.562477	2.058433	–3.084015
O	3.786143	–2.104822	–0.660271
O	3.793380	2.304435	–1.123316
C	–2.132650	–5.631828	0.725172
C	–2.994268	–6.223961	1.652283
C	–2.310287	–4.724105	3.267524
C	–1.449041	–4.119045	2.348506
C	–0.624754	–2.924444	2.712611
C	0.808842	–1.207671	1.956669
C	2.160862	–1.183654	2.334148
C	2.807684	0.046094	2.521639
C	2.126980	1.257443	2.344364
C	0.768760	1.246705	1.987223
C	0.132828	0.010940	1.817754
C	–0.688659	2.951536	2.764839

C	–1.500166	4.152068	2.378380
C	–2.374920	4.768116	3.276995
C	–3.021182	6.261250	1.639203
C	–2.144880	5.657804	0.732966
C	0.324788	–5.723920	–2.205389
C	0.024068	–6.331766	–3.427932
C	–1.638947	–4.776788	–3.806135
C	–1.345024	–4.159265	–2.588272
C	–2.072414	–2.931889	–2.132846
C	–2.187424	–1.255615	–0.455383
C	–3.003527	–1.239750	0.700633
C	–3.404656	–0.023822	1.290291
C	–2.966743	1.185187	0.771712
C	–2.197726	1.195403	–0.432407
C	–1.870030	–0.040636	–1.055353
C	–1.848655	2.688564	–2.271527
C	–1.146907	3.928811	–2.695768
C	–1.304109	4.441501	–3.984782
C	0.102748	6.191688	–3.459397
C	0.271768	5.679296	–2.167532
C	1.605946	–5.757360	1.311815
C	2.807205	–6.251942	1.834274
C	3.956251	–4.476754	0.912819
C	2.763391	–3.981172	0.384957
C	2.734309	–2.742708	–0.435071
C	1.315040	–1.263547	–1.677117
C	0.762520	–1.282987	–2.988876
C	0.591447	–0.088781	–3.672056
C	0.861836	1.140519	–3.036592
C	1.327163	1.184797	–1.707914
C	1.628243	–0.021616	–1.070538
C	2.707403	2.835654	–0.744583
C	2.768534	4.065977	0.103460
C	3.988690	4.642871	0.465833
C	2.875143	6.260677	1.676048
C	1.648839	5.694056	1.319101
H	–2.059029	–5.997049	–0.298268
H	–3.621538	–7.071204	1.370717
H	–2.368284	–4.341163	4.286405
H	2.701052	–2.118965	2.490932
H	3.861807	0.058902	2.810600
H	2.642407	2.209074	2.488853
H	–0.919709	–0.003788	1.569760
H	–2.455240	4.393008	4.297242
H	–3.639746	7.109285	1.340828
H	–2.050480	6.012859	–0.292920
H	1.116684	–6.102130	–1.559978
H	0.579554	–7.206721	–3.769383
H	–2.431641	–4.377701	–4.439114

H	–3.307247	–2.188961	1.145004
H	–4.030743	–0.040584	2.184070
H	–3.225719	2.134271	1.240359
H	–1.303465	–0.036160	–1.981072
H	–1.939652	3.929435	–4.707964
H	0.605620	7.110331	–3.765617
H	0.909447	6.176622	–1.438107
H	0.661691	–6.276013	1.473889
H	2.824533	–7.173991	2.417476
H	4.895748	–3.949024	0.745273
H	0.534179	–2.241086	–3.455062
H	0.708622	2.075481	–3.577439
H	2.074658	–0.004452	–0.080544
H	4.921157	4.201817	0.113564
H	2.918220	7.146167	2.312249
H	0.705729	6.117856	1.662196
H	0.222843	–0.093816	–4.699435

Table S6. Atomic Cartesian coordinates (x, y, z) in angstroms for optimized model excluding K^I ions of the oxidized $\{Ni^{II}Ni^{III}LL^{\bullet}\}$ species.

Atom	x	y	z
Ni	0.017390	–3.439684	0.092691
Ni	0.100231	3.467875	–0.022449
N	–1.340361	–4.495414	1.098460
N	–3.244706	–5.728435	2.690171
N	0.067474	–2.416999	1.929113
N	–1.304965	4.591850	1.138354
N	–3.398393	5.626226	2.642501
N	0.085812	2.408285	1.922259
N	–0.201502	–4.665953	–1.669717
N	–0.717681	–5.714860	–4.177429
N	–1.423274	–2.473263	–0.740759
N	–0.313646	4.565624	–1.753642
N	–1.037015	5.665493	–4.193155
N	–1.554537	2.396409	–0.754454
N	1.518962	–4.537281	0.729763
N	3.859617	–5.844340	1.418297
N	1.419085	–2.467056	–0.846348
N	1.765203	4.616241	0.504071
N	4.188362	5.867431	0.996176
N	1.588780	2.401948	–0.977807
O	–1.094339	–2.365116	3.959938
O	–1.386455	2.106072	3.702384
O	–2.767667	–2.393301	–2.634493
O	–2.987276	2.343403	–2.603663
O	3.720888	–2.546805	–1.225834
O	3.887620	2.469118	–1.423589
C	–2.033494	–5.553755	0.636675
C	–2.991352	–6.170167	1.446166
C	–2.552244	–4.670079	3.140886
C	–1.591860	–4.042013	2.345319
C	–0.832929	–2.846801	2.821970
C	0.758280	–1.209151	2.164011
C	2.165792	–1.181970	2.279125
C	2.866067	0.041985	2.296545
C	2.184634	1.238543	2.141679
C	0.755516	1.232590	2.121687
C	0.059592	–0.003241	2.210371
C	–1.029640	2.724815	2.676329
C	–1.727500	3.969042	2.258385
C	–2.780009	4.490845	3.012667
C	–2.974475	6.243980	1.528160
C	–1.920101	5.725543	0.766000
C	0.484610	–5.733482	–2.111262
C	0.220717	–6.257076	–3.381515

C	–1.398688	–4.646619	–3.727587
C	–1.135215	–4.112179	–2.465284
C	–1.851527	–2.912290	–1.945729
C	–1.999921	–1.272084	–0.218186
C	–2.974094	–1.297385	0.793192
C	–3.508284	–0.093908	1.264552
C	–3.068370	1.137592	0.757040
C	–2.089618	1.174760	–0.248119
C	–1.604410	–0.040787	–0.751189
C	–2.036790	2.837608	–1.921829
C	–1.330585	4.041193	–2.465891
C	–1.690781	4.603043	–3.694588
C	–0.019267	6.178715	–3.477384
C	0.348427	5.628165	–2.247508
C	1.490222	–5.563896	1.598295
C	2.678660	–6.217784	1.939500
C	3.878443	–4.812761	0.557938
C	2.702294	–4.149199	0.212404
C	2.664331	–2.977532	–0.700830
C	1.288553	–1.267714	–1.620939
C	0.896112	–1.289448	–2.967031
C	0.755361	–0.081152	–3.660973
C	0.995118	1.147837	–3.030526
C	1.402128	1.179918	–1.687633
C	1.567825	–0.038138	–1.014872
C	2.820460	2.913623	–0.899425
C	2.903774	4.146058	–0.047778
C	4.120940	4.785158	0.201794
C	3.050151	6.322033	1.551149
C	1.825413	5.695161	1.305380
H	–1.826073	–5.915125	–0.367161
H	–3.555844	–7.028850	1.080395
H	–2.746658	–4.292900	4.144959
H	2.713267	–2.124586	2.329145
H	3.954327	0.038749	2.378167
H	2.710209	2.191315	2.086105
H	–1.027241	–0.009817	2.187091
H	–3.116159	3.983320	3.917488
H	–3.477173	7.166135	1.232031
H	–1.575664	6.224046	–0.139088
H	1.235853	–6.177615	–1.458683
H	0.770473	–7.122464	–3.754783
H	–2.160754	–4.197003	–4.364562
H	–3.327079	–2.249384	1.191589
H	–4.276735	–0.112900	2.041127
H	–3.498554	2.069040	1.129596
H	–0.913722	–0.018388	–1.584869
H	–2.514935	4.172611	–4.263115
H	0.510969	7.040043	–3.886988

H	1.170069	6.039558	–1.661963
H	0.536721	–5.869977	2.021462
H	2.667830	–7.052636	2.641479
H	4.828649	–4.491050	0.130304
H	0.702241	–2.239438	–3.467400
H	0.862196	2.084174	–3.576351
H	1.901750	–0.023440	0.013899
H	5.035555	4.401585	–0.250395
H	3.111509	7.197493	2.199713
H	0.898297	6.057630	1.748866
H	0.443956	–0.096661	–4.708388
Ni	0.017390	–3.439684	0.092691
Ni	0.100231	3.467875	–0.022449
N	–1.340361	–4.495414	1.098460
N	–3.244706	–5.728435	2.690171
N	0.067474	–2.416999	1.929113
N	–1.304965	4.591850	1.138354
N	–3.398393	5.626226	2.642501
N	0.085812	2.408285	1.922259
N	–0.201502	–4.665953	–1.669717
N	–0.717681	–5.714860	–4.177429
N	–1.423274	–2.473263	–0.740759
N	–0.313646	4.565624	–1.753642
N	–1.037015	5.665493	–4.193155
N	–1.554537	2.396409	–0.754454
N	1.518962	–4.537281	0.729763
N	3.859617	–5.844340	1.418297
N	1.419085	–2.467056	–0.846348
N	1.765203	4.616241	0.504071
N	4.188362	5.867431	0.996176
N	1.588780	2.401948	–0.977807
O	–1.094339	–2.365116	3.959938
O	–1.386455	2.106072	3.702384
O	–2.767667	–2.393301	–2.634493
O	–2.987276	2.343403	–2.603663
O	3.720888	–2.546805	–1.225834
O	3.887620	2.469118	–1.423589
C	–2.033494	–5.553755	0.636675
C	–2.991352	–6.170167	1.446166
C	–2.552244	–4.670079	3.140886
C	–1.591860	–4.042013	2.345319
C	–0.832929	–2.846801	2.821970
C	0.758280	–1.209151	2.164011
C	2.165792	–1.181970	2.279125
C	2.866067	0.041985	2.296545
C	2.184634	1.238543	2.141679
C	0.755516	1.232590	2.121687
C	0.059592	–0.003241	2.210371
C	–1.029640	2.724815	2.676329

C	–1.727500	3.969042	2.258385
C	–2.780009	4.490845	3.012667
C	–2.974475	6.243980	1.528160
C	–1.920101	5.725543	0.766000
C	0.484610	–5.733482	–2.111262
C	0.220717	–6.257076	–3.381515
C	–1.398688	–4.646619	–3.727587
C	–1.135215	–4.112179	–2.465284
C	–1.851527	–2.912290	–1.945729
C	–1.999921	–1.272084	–0.218186
C	–2.974094	–1.297385	0.793192
C	–3.508284	–0.093908	1.264552
C	–3.068370	1.137592	0.757040
C	–2.089618	1.174760	–0.248119
C	–1.604410	–0.040787	–0.751189
C	–2.036790	2.837608	–1.921829
C	–1.330585	4.041193	–2.465891
C	–1.690781	4.603043	–3.694588
C	–0.019267	6.178715	–3.477384
C	0.348427	5.628165	–2.247508
C	1.490222	–5.563896	1.598295
C	2.678660	–6.217784	1.939500
C	3.878443	–4.812761	0.557938
C	2.702294	–4.149199	0.212404
C	2.664331	–2.977532	–0.700830
C	1.288553	–1.267714	–1.620939
C	0.896112	–1.289448	–2.967031
C	0.755361	–0.081152	–3.660973
C	0.995118	1.147837	–3.030526
C	1.402128	1.179918	–1.687633
C	1.567825	–0.038138	–1.014872
C	2.820460	2.913623	–0.899425
C	2.903774	4.146058	–0.047778
C	4.120940	4.785158	0.201794
C	3.050151	6.322033	1.551149
C	1.825413	5.695161	1.305380
H	–1.826073	–5.915125	–0.367161
H	–3.555844	–7.028850	1.080395
H	–2.746658	–4.292900	4.144959
H	2.713267	–2.124586	2.329145
H	3.954327	0.038749	2.378167
H	2.710209	2.191315	2.086105
H	–1.027241	–0.009817	2.187091
H	–3.116159	3.983320	3.917488
H	–3.477173	7.166135	1.232031
H	–1.575664	6.224046	–0.139088
H	1.235853	–6.177615	–1.458683
H	0.770473	–7.122464	–3.754783
H	–2.160754	–4.197003	–4.364562

H	–3.327079	–2.249384	1.191589
H	–4.276735	–0.112900	2.041127
H	–3.498554	2.069040	1.129596
H	–0.913722	–0.018388	–1.584869
H	–2.514935	4.172611	–4.263115
H	0.510969	7.040043	–3.886988
H	1.170069	6.039558	–1.661963
H	0.536721	–5.869977	2.021462
H	2.667830	–7.052636	2.641479
H	4.828649	–4.491050	0.130304
H	0.702241	–2.239438	–3.467400
H	0.862196	2.084174	–3.576351
H	1.901750	–0.023440	0.013899
H	5.035555	4.401585	–0.250395
H	3.111509	7.197493	2.199713
H	0.898297	6.057630	1.748866
H	0.443956	–0.096661	–4.708388

Table S7. Magnetic coupling constants (J, in cm^{-1}) calculated in gaseous and solvated phases on the fragment models including (Model **I**) and excluding (Model **II**) the K^+ ions and their surroundings.

Phase	**I**	**II**[a]
	Experimental	**Experimental / Optimized**
Solvated	3.9	3.9 / 4.2
Gaseous	4.1	4.2 / 3.9

[a] J values on the experimental and optimized geometries are given for **II**.

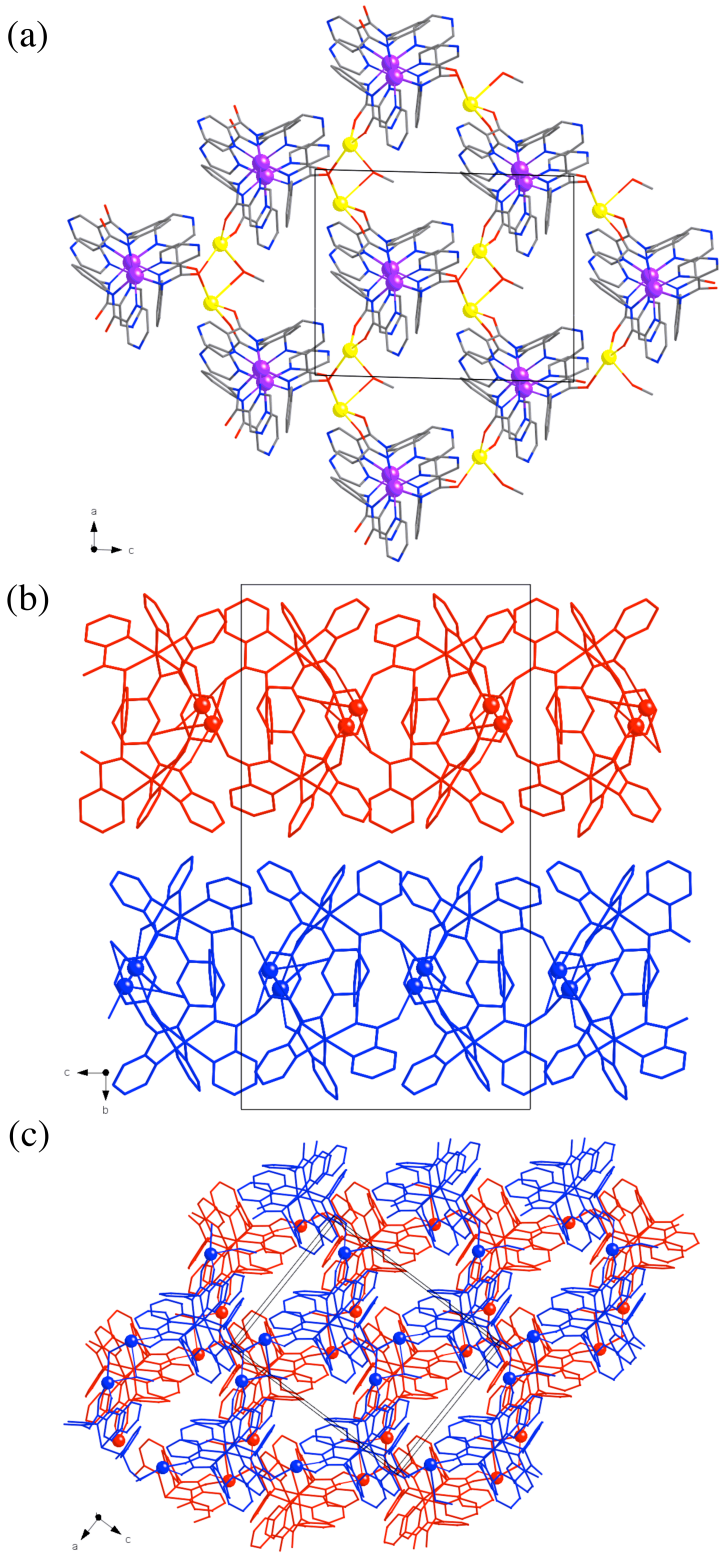

Fig. S1 (a) Projection view of a layer of potassium-bonded anionic dinickel units of **1a** along the crystallographic *b* axis. (b) and (c) Crystal packing view of **1a** along the crystallographic *a* and *b* axis respectively (hydrogen atoms and crystallization water molecules have been omitted for clarity).

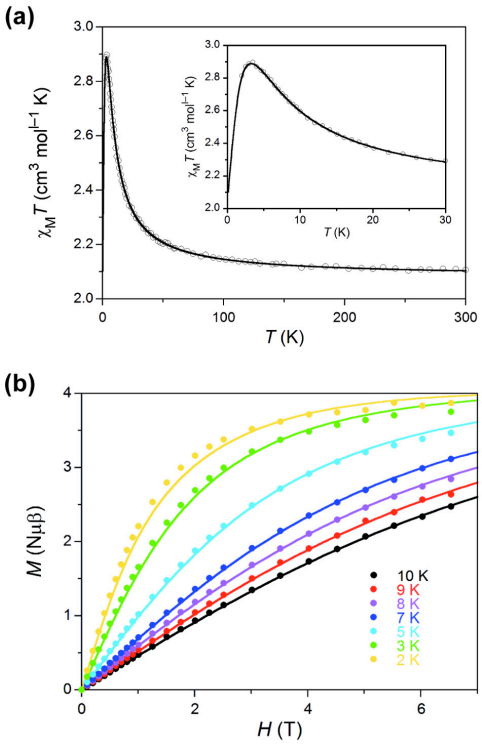

Fig. S2 Experimental (○) temperature dependence of $\chi_M T$ (a) and field dependence of the magnetisation (b), M, for **1a**. The solid lines correspond to the best-fit curves (see text).

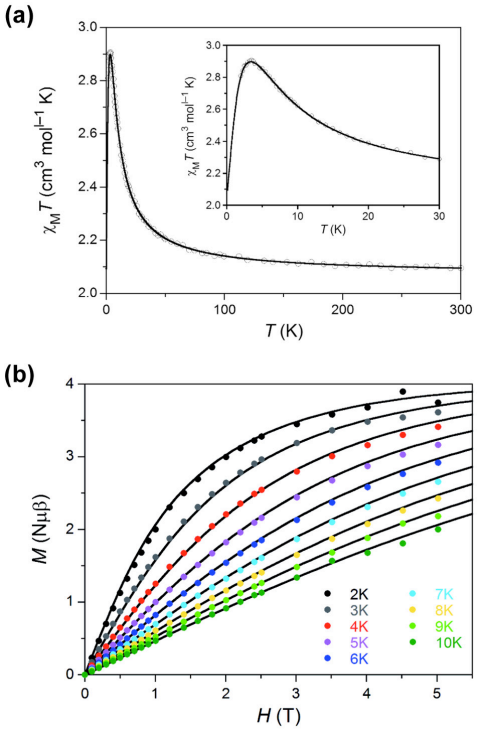

Fig. S3 Experimental (○) temperature dependence of $\chi_M T$ (a) and field dependence of the magnetisation (b), M, for **1b**. The solid lines correspond to the best-fit curves (see text).

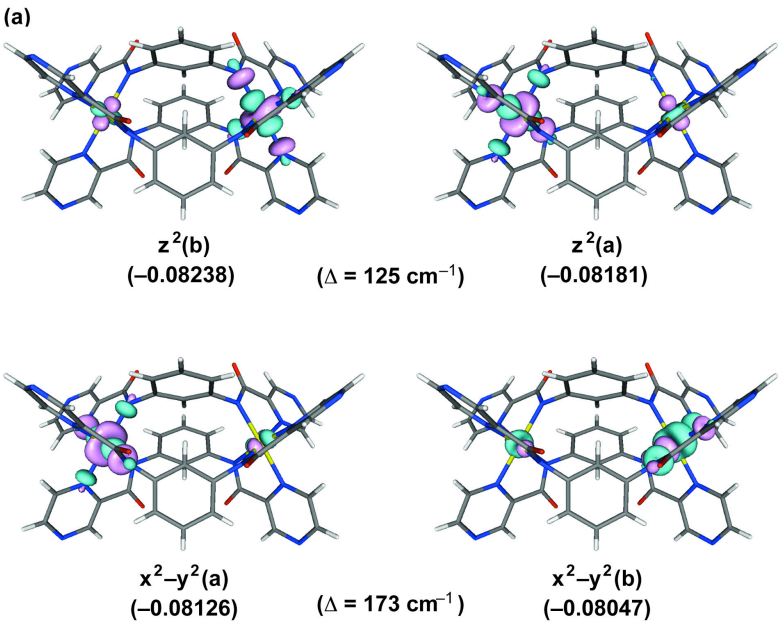

Fig. S4 Perspective views of the calculated e_g (z^2, x^2–y^2)-type natural orbitals corresponding to SOMOs (single-occupied molecular orbitals) for the ground quintet spin configuration of **1a**. The calculated MO energies (in a.u.) given in parentheses are calculated using frozen natural orbitals. The isodensity surface corresponds to a value of 0.04 e bohr^{-3} in (a) and 0.01 e bohr^{-3} in the magnification shown in (b). Δ (in cm^{-1}) is the energy gap between two equivalent SOMOs.

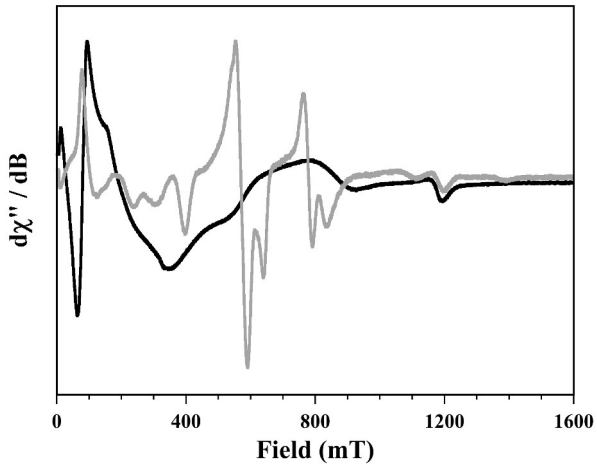

Fig. S5 Q-band EPR spectrum at 8 K of **1b** in acetonitrile solution (black line) and in solid (grey line).

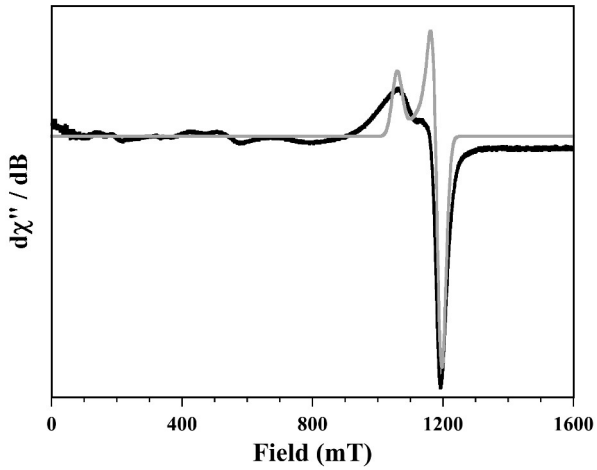

Fig. S6 Q-band EPR spectrum at 8 K of oxidized form of **1b** in acetonitrile solution (black solid line). Simulation for a Ni^{III} ion with $g_1 = 2.05$, $g_2 = 2.07$ and $g_3 = 2.20$ is shown in grey solid line.

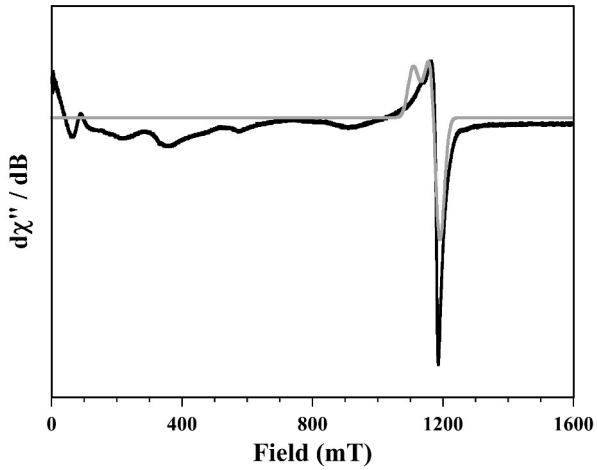

Fig. S7 Q-band EPR spectrum at 8 K of oxidized form of **1b** in solid (black solid line). Simulation for a Ni^{III} ion with $g_1 = 2.05$, $g_2 = 2.05$ and $g_3 = 2.30$ is shown in grey solid line.

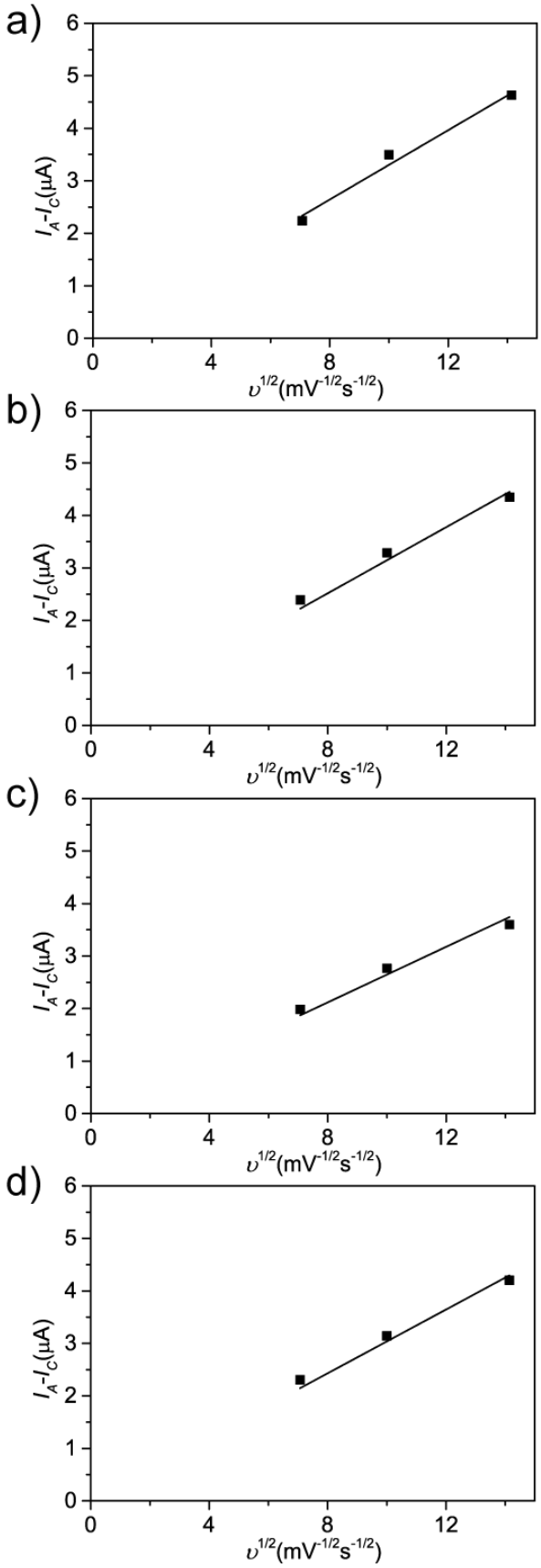

Fig. S8 Peak current *vs* the square root of the scan rate (50, 100 and 200 mV s^{-1}) for the a) first, b) second, c) third and d) fourth redox waves of **1b**.

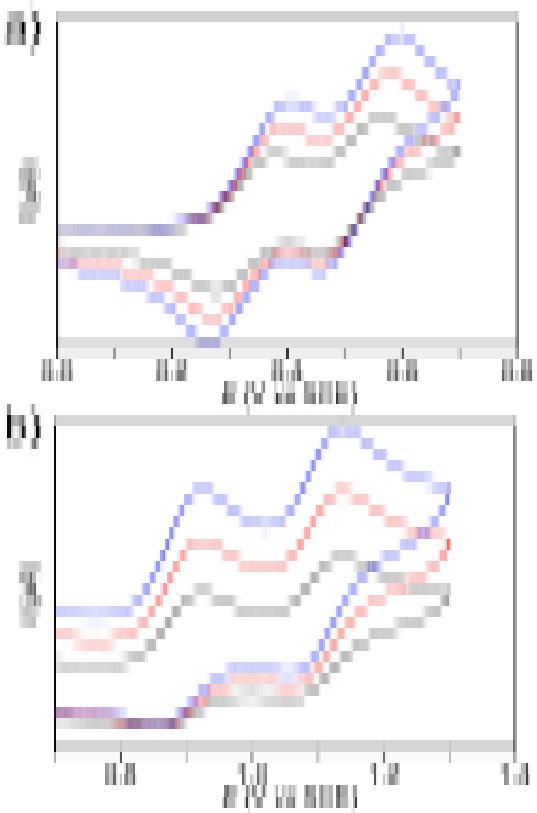

Fig. S9 CVs of **1b** in acetonitrile (0.1 M *n*-Bu_4NPF_6, 25 ˚C) measured at scan rates of 50 (black line), 100 (red line) and 200 mV s^{-1} (blue line).