Preparation, Structure, and Properties of a Mixed-Valent $Ni^{II}Ni^{III}$ Amine-Selenolate Complex

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Dedicated to Prof. Dr. Bernt Krebs on the occasion of his 60th birthday

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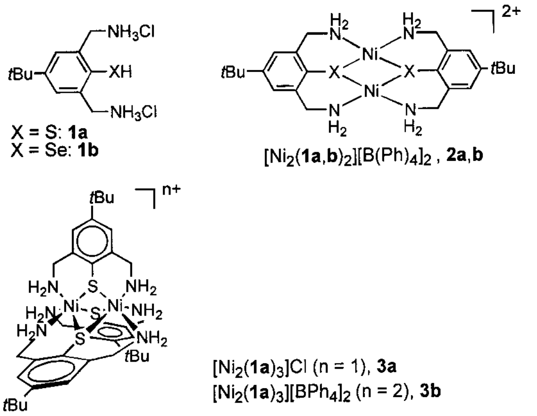
Two dinuclear nickel amine-selenolate complexes of the tridentate amine-selenolate ligand, 4-*tert*-butyl-2,6-di-(aminomethyl)selenophenol (**1b**), have been synthesized and their properties characterized. The green complex $[Ni^{II}_2(\mathbf{1b})_3]Cl$ (**4a**) is readily prepared from **1b**, $NiCl_2 \cdot 6\,H_2O$, and NaOMe in methanol or by reaction of coordinatively unsaturated $[Ni^{II}_2(\mathbf{1b})_2][BPh_4]_2$ (**2b**) with another one equivalent of **1b** in the presence of triethylamine. The face-sharing, bioctahedral structure of **4a** is derived from UV/Vis spectroscopy, cyclic voltammetry, and single-crystal X-ray diffraction of its oxidation product, $[Ni^{II}Ni^{III}(\mathbf{1b})_3]^{2+}$. The dication was prepared by air-oxidation of **4a** in MeOH and isolated as the dark-brown BPh_4^- salt, $[Ni^{II}Ni^{III}(\mathbf{1b})_3][BPh_4]_2 \cdot CH_3OH$ (**4b**). Mixed-valent complex **4b** consists of a dinuclear, face-sharing bioctahedral dication with a central $N_3Ni^{II}(\mu_2\text{-}SeR)_3Ni^{III}N_3$ core and well-separated tetraphenylborate anions. Distortions from D_{3h} symmetry suggest that **4b** is a trapped-valence compound in the solid-state. On the CV time scale complex **4a** undergoes two reversible one-electron oxidations at $E^1_{1/2} = -0.15$ and at $E^2_{1/2} = +0.29$ V vs SCE, affording **4b** and the thermally not stable trication $[Ni^{III}_2(\mathbf{1b})_3]^{3+}$, respectively. The EPR spectrum of a powdered sample of **4b** reveals an $S = {}^3/_2$ ground state of the mixed-valent $Ni^{II}Ni^{III}$ complex.

Introduction

In contrast to the considerable chemistry of nickel thiolate complexes,[1] the coordination chemistry of nickel selenolate complexes has been less extensively developed.[2] The majority of the structurally characterized complexes contain divalent, four-coordinate nickel with planar[3] or tetrahedral coordination environments.[4] Recently, higher coordination numbers have been realized by partial selenolate ligand replacement through multidentate N-based colligands.[5][6] Structurally characterized selenolate complexes of trivalent[7] and quadrivalent[8] nickel are known as well, most of them with unsaturated selenolate ligands, as for instance with benzene-1,2-diselenol.[9] However, attempts to prepare nickel(III) complexes of monodentate aliphatic or aromatic selenolate ligands have not yet been successful.

Recently we have reported the synthesis, solution- and solid-state structures of dinuclear nickel complexes **2a**,**b** of amine-thiolate and -selenolate ligands **1a**,**b**.[10] In contrast to many other $N_2Ni(\mu_2\text{-}SR)_2NiN_2$ type complexes, the amine-thiolate complex **2a** was shown to readily react with another one equivalent of **1a** to afford the dinuclear, face-sharing bioctahedral complex **3a**. Furthermore, complex **3a** could be reversibly oxidized to afford the mixed-valent dication $[Ni^{II}Ni^{III}(\mathbf{1a})_3]^{2+}$ in **3b** with distinct localized Ni^{III} ($S = {}^1/_2$) and Ni^{II} ions ($S = 1$).[11] Such dinuclear, face-sharing octahedral complexes have attracted considerable attention in regards to their electronic structures.[12,13]



X = S: **1a**
X = Se: **1b**

$[Ni_2(\mathbf{1a,b})_2][B(Ph)_4]_2$, **2a**,**b**

$[Ni_2(\mathbf{1a})_3]Cl$ (n = 1), **3a**
$[Ni_2(\mathbf{1a})_3][BPh_4]_2$ (n = 2), **3b**

Scheme 1. Structures of ligands and complexes **1a**,**b**, **2a**,**b**, and **3a**,**b**

We now present the synthesis, structural, spectral, and redox properties of the selenium analogs of **3a**,**b**.

Results and Discussion

Syntheses

The synthesis of amine-selenolate complexes **4a**,**b** is shown in Scheme 2. Analogously to the preparation of amine-thiolate complex **3a**, complex **4a** was obtained by reaction of **2b** with another one equivalent of **1b** in the presence of triethylamine. Alternatively, complex **4a** could also

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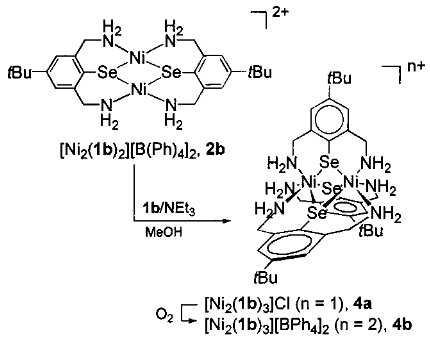

Scheme 2. Preparation of amine-selenolate complexes **4a**,**b**

be obtained by the direct reaction between **1b** and $Ni(ClO_4)_2 \cdot 6\ H_2O$ in a 3:2 molar ratio. The face-sharing, bioctahedral structure of **4a** is derived from UV/Vis spectroscopy, cyclic voltammetry, and single-crystal X-ray diffraction of its oxidation product **4b** (see below).

Complex **4a** is a pale-green, air-sensitive solid that is insoluble in most common organic solvents, but a suspension of **4a** in methanol, when exposed to air, produces a clear deep brown solution. From the resulting clear solution, upon addition of $NaBPh_4$, the dicationic salt $[Ni_2(\mathbf{1b})_3][BPh_4]_2 \cdot MeOH$ (**4b**) is obtained as black crystals.

Crystal Structure of 4b

The crystal structure determination of **4b** confirms the dinuclear structure and the mixed-valent nature of the $[Ni_2(\mathbf{1b})_3]^{2+}$ dication. The crystal structure consists of well-separated dications $[Ni_2(\mathbf{1b})_3]^{2+}$, BPh_4^- anions, and one methanol molecule of crystallization. Complex **4b** is isostructural with the amine-thiolate complex **3b**.[11] The molecular structure of the $[Ni_2(\mathbf{1b})_3]^{2+}$ dication is displayed in Figure 1 along with important bond lengths and angles.

Both nickel ions are facially coordinated to three amine nitrogen atoms and three bridging selenolate selenium atoms of three amine-selenolate ligands. The N_3Se_3 octahedra around Ni(1) and Ni(2) are different, and consequently, the local symmetry of the $[Ni_2(\mathbf{1b})_3]^{2+}$ dication is distorted from D_{3h} symmetry. These distortions are manifested in three different Ni−Se distances at Ni(1) at 2.456(1), 2.427(1), and 2.533(1) Å and similarly at Ni(2) at 2.443(1), 2.391(1), and 2.529(1) Å. Likewise, the Ni−N distances at Ni(1) at 2.042(4), 2.102(4), and 2.061(4) Å and similarly at Ni(2) at 2.011(4), 2.107(4), and 2.087(4) Å are not equidistant. It is noted that the Ni−N and Ni−Se bond lengths appear to be shorter at Ni(2).

As expected, the average Ni−Se bond length at 2.463(1) Å is longer than the average Ni−S bond length in **3b** at 2.380(1) Å. The average Ni−N bond length, on the other hand, has decreased from 2.089(3) Å in **3b** to 2.068(4) Å in **4b**. Both, Ni−Se and Ni−N distances should be compared with Ni−Se and Ni−N distances of 2.440(3) and 2.063(5) Å, respectively, in $[Ni(terpy)(SeC_6H_2\text{-}2,4,6\text{-}Me_3)_2]$, which contains five-coordinate Ni^{II} in a distorted trigonal-bipyramidal coordination environment.[6] As a consequence of longer Ni−Se distances, the Ni(1)···Ni(2) separation in **4b** is 3.181(1) Å. The corresponding value in **3b** was determined to be 3.064(1) Å. In both compounds, however, wide Ni−S−Ni [mean 80.16(3)°] and Ni−Se−Ni angles [mean 80.48(3)°] preclude any attraction between the metal atoms.[14]

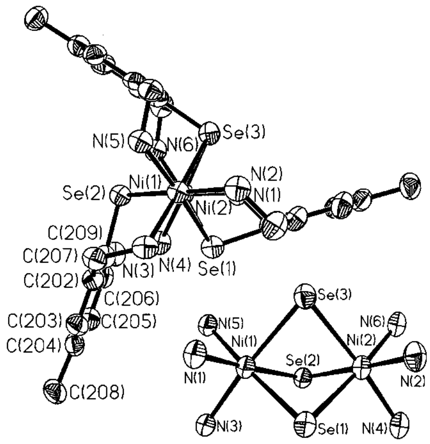

Figure 1. Molecular structure of the $[Ni^{II}Ni^{III}(\mathbf{1b})_3]^{2+}$ dication and the structure of the central $N_3Ni(\mu_2\text{-}SeR)_3NiN_3$ core in **4b** (50% probability thermal ellipsoids). Hydrogen atoms and *tert*-butyl methyl carbon atoms have been omitted for reasons of clarity. Selected bond lengths [A] and angles [°]: Ni(1)−N(1) 2.042(4), Ni(1)−N(3) 2.102(4), Ni(1)−N(5) 2.061(4), Ni(2)−N(2) 2.011(4), Ni(2)−N(4) 2.107(4), Ni(2)−N(6) 2.087(4), Ni(1)−Se(1) 2.456(1), Ni(1)−Se(2) 2.427(1), Ni(1)−Se(3) 2.533(1), Ni(2)−Se(1) 2.443(1), Ni(2)−Se(2) 2.391(1), Ni(2)−Se(3) 2.529(1); Ni(1)−Se(1)−Ni(2) 80.96, Ni(1)−Se(2)−Ni(2) 82.63(1), Ni(1)−Se(3)−Ni(2) 77.84(1), N−Ni−N 89.0(2)−92.7(2), Se−Ni−Se 80.40(3)−85.99(3), $N{-}Ni{-}Se_{cis}$ 91.4(1)−93.8(1), $N{-}Ni{-}Se_{trans}$ 172.1(1)−174.7(7), Ni−Se−Ni 77.84(1)−82.63(1)

The individual bond lengths and angles within the three amine-selenolate ligands show no unusual features ruling out the possibility of a ligand-centered oxidation of **4a** with one of the ligands being coordinated as a selenyl radical in **4b**. A metal-centered rather than a ligand-centered oxidation is also supported by infrared spectroscopy. From the apparent distortions from D_{3h} symmetry complex **4b** appears to be a trapped-valence $Ni^{II}Ni^{III}$ compound with distinct localized Ni^{II} and Ni^{III} sites (Class I in Robin and Day′s classification of mixed-valent species).[15] A delocalized species would be expected to have structurally identical nickel sites.[16] The greater extent of distortion in Ni−N and Ni−Se distances at Ni(2) may be due to a Jahn−Teller distortion, which is expected for an octahedral Ni^{III} ion with low-spin d^7 electronic configuration. Thus, Ni(2) is presumably a Ni^{III} ion.

Infrared and UV/Vis Spectra of 4a, b

The most characteristic features in the infrared spectrum of **4a** are two strong absorptions at 3328 and 3250 cm^{-1}. These bands are assigned to $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ stretching vibrations of the RNH_2 groups.[17] In the infrared spectrum of **4b**, the $\nu(NH_2)$ stretching frequencies are shifted by ca. 20 cm^{-1} to lower wavenumbers. This further supports the metal-centered oxidation of **4a** and the ground state of

4b, since the decrease in Ni−N bond lengths upon passing from $Ni^{II}-NH_2$ to $Ni^{III}-NH_2$ is expected to give a more polarized $Ni^{III}N-H$ bond, causing a weakening of the N−H bonds. Furthermore, the increase in the number of $\nu(NH_2)$ stretching vibrations from two in **4a** to five in **4b** nicely corroborates with the notion of distinct localized Ni^{II} and Ni^{III} oxidation states in the mixed-valent compound **4b**.

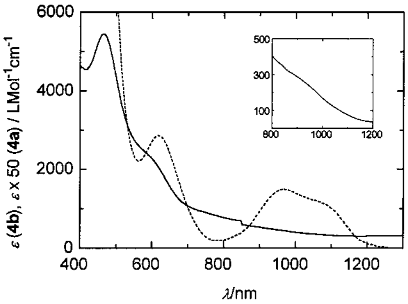

Figure 2. UV/Vis spectra of **4a** (···) and **4b** (—) in DMF at 295 K. The inset displays the spectrum of **4b** in the 800-to-1200 nm region

The pale-green complex **4a** exhibits typical weak d-d transitions of octahedral nickel(II) (d^8) in the 500 to 1200 nm region (Figure 2). Compared to the thiolate complex **3a**, the ligand field transitions ν_2 ($^3A_{2g} \rightarrow {}^3T_{1g}$) at 617 nm and ν_1 ($^3A_{2g} \rightarrow {}^3T_{2g}$) at 966 and 1065 nm (splitting due to lower symmetry) are shifted by 24 and 44 nm to lower energies, consistent with a weaker ligand field strength of the amine-selenolate ligand. The electronic spectrum of **4b** is dominated by two intense, spin-allowed charge transfer (CT) transitions at 465 and 604 nm. Similar intense absorptions were observed for complex **3b** at 473 and 580 nm. Other than the two intense CT bands, the UV/Vis spectrum of **4b** reveals no further characteristic features.

Electrochemistry

The cyclic voltammogram of **4a** in DMF solution reveals two one-electron oxidation waves at $E^1_{1/2} = -0.15$ V and $E^2_{1/2} = +0.29$ V vs SCE both closely approaching the characteristics of reversible charge transfer processes; that of **4b** using the same experimental conditions is identical to that of **4a** (Figure 3).

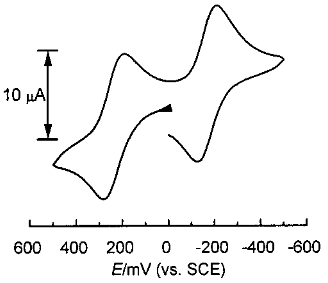

Figure 3. Cyclic voltammogram of **4b** in DMF at 295 K. Experimental conditions: [**4b**] ca. 1×10^{-3} M, 0.1 M [nBu_4N][PF_6], Pt disk working electrode, Ag wire reference electrode, scan rate = 200 $mV\cdot s^{-1}$

At all scan rates (50−500 $mV\cdot s^{-1}$), the ratio i_{pc}/i_{pa}, $i_p/\nu^{1/2}$ is independent of scan rate, and $\Delta E^1_p = 85$ mV and $\Delta E^2_p = 79$ mV (at 100 $mV\cdot s^{-1}$) increase slightly with scan rate. Controlled-potential coulometry of **4a** in DMF at an applied potential of 0.0 V vs SCE consumed $n = 0.96 \pm 2$ e^-/complex. The brown solution contains the $[Ni_2(\mathbf{1b})_3]^{2+}$ dication as shown by UV/Vis spectroscopy. Rereduction at −0.45 V vs SCE reforms the pale-green complex **4a**. Accordingly, the respective one-electron-transfer processes are assigned to Eqs. 1a, b producing the mixed-valent complex **4b** and subsequently the thermally instable dinickel(III) selenolate species.

$$[Ni^{III}Ni^{III}(\mathbf{1b})_3]^{3+} + e^- \rightleftharpoons [Ni^{III}Ni^{II}(\mathbf{1b})_3]^{2+} \quad E^2_{1/2} \tag{1a}$$

$$[Ni^{III}Ni^{II}(\mathbf{1b})_3]^{2+} + e^- \rightleftharpoons [Ni^{II}Ni^{II}(\mathbf{1b})_3]^{1+} \quad E^1_{1/2} \tag{1b}$$

$$[Ni^{III}Ni^{III}(\mathbf{1b})_3]^{3+} + [Ni^{II}Ni^{II}(\mathbf{1b})_3]^{1+} \rightleftharpoons [Ni^{III}Ni^{II}(\mathbf{1b})_3]^{2+} \quad K_{com}$$

From the redox potentials $E^x_{1/2}$ the comproportionation constant K_{com} is calculated to be 1.1×10^7, which is slightly smaller than the corresponding constant determined for **3b** (1.4×10^8). Relative to the amine-thiolate complexes **3a**,**b**, the $Ni^{III/II}$ redox potentials of the amine-selenolate complexes **4a**,**b** are cathodically shifted by 0.18 V and 0.13 V, respectively.

EPR Spectroscopy

The mixed-valent nature of **4b** is further confirmed by EPR-Spectroscopy. The EPR spectrum of a powdered sample of **4b** at 77 K exhibits a rhombic signal with three resonances at 1230, 2210, and 3350 G, indicating an $S = {}^3/_2$ ground state. Closer inspection reveals a further resonance at 1080 G, which is also present in the single-crystal EPR spectra. This resonance is tentatively assigned to the $M_s = -{}^3/_2$ to $M_s = +{}^3/_2$ transition, which is forbidden in axial environments, but gains intensity by the rhombic distortion. Unfortunately, hyperfine coupling to nitrogen atoms (^{14}N) could not be observed.

Thus, mixed-valent complex **4b** exhibits an $S = {}^3/_2$ ground state, which is most likely attained by an intramolecular ferromagnetic exchange interaction between a low-spin Ni^{III} ion ($S = {}^1/_2$) and a Ni^{II} ion ($S = 1$). It is interesting to note that an intramolecular ferromagnetic exchange interaction between adjacent Ni^{III} and Ni^{II} ions has also been observed in the trinuclear $Co^{III}Ni^{III}Ni^{II}$ complex $[LCo^{III}Ni^{III}Ni^{II}L][PF_6]_2$ [L = 1,4,7-tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane], which contains a central $N_3Co^{III}(\mu_2\text{-}SR)_3Ni^{III}(\mu_2\text{-}SR)_3Ni^{II}N_3$ core with three face-sharing octahedra.[12] We anticipate a more detailed study of the electronic spin systems of **3b** and **4b** by magnetic susceptibility measurements.

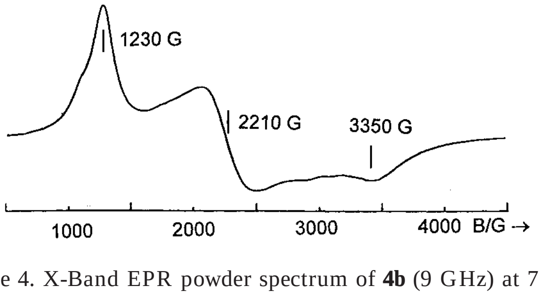

Figure 4. X-Band EPR powder spectrum of **4b** (9 GHz) at 78 K

In the present study it was shown that the coordinatively unsaturated amine-selenolate complex **2b**, upon reaction with **1b**, forms the dinuclear, face-sharing bioctahedral complex **4a** with a central $N_3Ni^{II}(\mu_2\text{-}SeR)_3Ni^{II}N_3$ core. Similarly to the electrochemical properties of isostructural amine-thiolate complex **3a**, complex **4a** undergoes an electrochemically and chemically reversible one-electron oxidation to produce a stable $Ni^{II}Ni^{III}$ amine-selenolate complex. Hence, the amine-chalcogenolate ligands **1a**,**b** both allow for the preparation of discrete dinuclear complexes and the stabilization of unusual nickel oxidation states. Further studies will focus on the isolation of the analogous tellurolate derivatives.

Experimental Section

Materials and Methods: Compounds **1b** and $[Ni_2(\mathbf{1b})_2][BPh_4]_2 \cdot CH_3OH \cdot CH_3CN$[10a] were prepared as previously described. All reactions were carried out under dry nitrogen with standard Schlenk techniques. Solvents were predried over molecular sieves and freshly distilled from appropriate drying agents. − CHN Analyses were determined with a Perkin-Elmer Elemental Analyzer 240. − IR spectra were recorded on a Bruker IFS25 spectrophotometer as KBr pellets. − Electronic spectra were recorded on a Jasco V-570 UV/VIS/NIR spectrometer. − Cyclic voltammetry measurements were carried out at 25°C with an EG&G Princeton Applied Research Potentiostat/Galvanostat Model 263 A. The cell contained a Pt working electrode, a Pt wire auxiliary electrode, and an Ag wire as reference electrode. Concentration of solutions were 0.1 M in supporting electrolyte (nBu$_4$NPF$_6$) and ca 1×10^{-3} M in sample. Ferrocenium/ferrocene was used as internal standard. All potentials were converted to the SCE reference. − EPR spectra were recorded by a conventional Varian X-band spectrometer with 100 kHz modulation.

$[Ni_2(1b)_3][Cl] \cdot EtOH$ (4a). − Method A: To a solution of $[Ni_2(\mathbf{1b})_2][BPh_4]_2 \cdot CH_3OH \cdot CH_3CN$ (137 mg, 0.100 mmol) in acetonitrile (5 mL) was added a solution of **1b** (34 mg, 0.10 mmol) in methanol (2 mL). Addition of 3 drops of NEt_3 initiated the precipitation of a pale-green solid, which was isolated by filtration, washed with methanol (2 mL) and ether (1 mL). The solid was recrystallized from ethanol. Yield: 62 mg (62%). − UV/Vis (DMF): λ_{max} (ε) = 617 (203), 966 (150), 1065 nm (137 $M^{-1}cm^{-1}$). − IR (KBr): $\tilde{\nu}$ = 3328s (NH_2), 3250s cm^{-1} (NH_2). − CV (DMF, 295 K, 0.1 M nBu$_4$NPF$_6$, E [V] vs SCE): $E^1_{1/2} = -0.15$ V, $E^2_{1/2} = +0.29$ V. − $C_{36}H_{57}N_6Se_3Ni_2Cl \cdot EtOH$ (1009.67): calcd. C 45.20, H 6.29, N 8.32; found C 44.83, H 5.87, N 7.94.

Method B: To a solution of $Ni(ClO_4)_2 \cdot 6\,H_2O$ (244 mg, 0.67 mmol) and the hydrochloride salt of the ligand **1b** (344 mg, 1.00 mmol) in ethanol (10 mL) was added a solution of triethylamine (303 mg, 3.00 mmol) in ethanol (3 mL). The mixture was stirred for 30 min at 20°C during which time a pale-green microcrystalline of **4a** formed which was filtered off, washed with ethanol and ether, and dried in vacuum. Yield: 240 mg (72%).

$[Ni_2(1b)_3][BPh_4]_2 \cdot MeOH$ (4b): A suspension of **4a** (101 mg, 0.100 mmol) in methanol (30 mL) was stirred for 6h in the presence of air to ensure complete oxidation of **4a**. To the resulting brown solution was added dropwise a solution of $NaBPh_4$ (0.20 g, 0.58 mmol) in methanol (2 mL). The solution was filtered and was allowed to stand for 2d at room temperature during which time **4b** precipitated as black crystals. Yield: 86 mg (54%). − IR (KBr): $\tilde{\nu}$ = 3302 m, 3289 w, 3268 w, 3242 s, 3229 s cm^{-1} (NH_2). − UV/Vis (DMF): λ_{max} (ε) = 350 (8710), 399 (4644), 465 (4978), 604 nm (1554 $M^{-1}cm^{-1}$). − CV (DMF, 295 K, 0.1 M nBu$_4$NPF$_6$, E [V] vs SCE): $E^1_{1/2} = -0.15$ V, $E^2_{1/2} = +0.29$ V. − $C_{85}H_{101}B_2N_6Ni_2OSe_3$ (1598.66): calcd. C 63.86, H 6.37, N 5.26; found C 63.83, H, 6.22, N 5.11.

Crystal-Structure Determination: Black crystals of **4b** suitable for single-crystal X-ray determination were obtained by the procedure described above. Crystal data and refinement details for **4b** ($C_{85}H_{101}B_2N_6Ni_2OSe_3$, M_r 1598.66): crystal size $0.52 \times 0.44 \times 0.32$ mm^3, STOE IPDS diffractometer, T = 193(2) K, monoclinic, space group $P2_1/c$, a = 23.552(5), b = 19.384(4), c = 16.701(3) Å, β = 105.79(3)° , V = 7507(3) Å^3, Z = 4, ρ_{calcd} = 1.41 g·cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 2.007 mm^{-1}, $2\theta_{max}$ = 48.6°, 63669 reflections collected, 11924 unique reflections (R_{int} = 0.1051), 8926 observed reflections [$I > 2\sigma(I)$]. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-86)[18] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93). All non-hydrogen atoms were refined anisotropically except the methyl carbon atoms of one disordered *tert*-butyl group. An isotropic split-atom model was applied for the disordered methyl carbon and oxygen atoms. The multiplicities of the respective orientations C(210)−C(212)/C(213)−C(215) were refined as follows: 0.73(1)/0.27(1). Hydrogen atoms were placed at calculated positions and were refined using a riding model with isotropic thermal parameters fixed at 1.2 times the equivalent isotropic U of the atom to which they were bonded. Final residuals: $R1$, $wR2$ [$F_o > 4\sigma(F_o)$]: 0.0446, 0.0963, $R1$, $wR2$ (all data): 0.0701, 0.1137, goodness-of-fit on F^2: 1.05, residual electron density: 0.58/ −0.62 e·Å^{-3}. The quality of the structure could not be improved with an absorption correction. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102536 (**4b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 (1223) 336-033; E-mail: deposit@cam.ac.uk].

Acknowledgments

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