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The First Structurally Characterized Dinuclear Nickel(II) Selenocyanate Compound: (μ-SeCN)$_2$[Ni(Medpt)(SeCN)]$_2$. Magnetic Behavior

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Introduction

Thiocyanate and selenocyanate ions can act as bridging ligands in dinuclear and 1-D nickel(II) compounds. Several structural examples of the two types of compound have been reported[1–8]: μ-thiocyanato and bis(μ-thiocyanato) 1-D compounds,[2–5] bis(μ-thiocyanato) dinuclear nickel(II) compounds,[6–8] and only one bis(μ-selenocyanato) 1-D compound.[1] No bis(μ-selenocyanato) dinuclear complexes have been structurally described. In this work, we present the synthesis and first structural study of one bis(μ-selenocyanato)nickel(II) dinuclear compound: (μ-SeCN)$_2$[Ni(Medpt)(SeCN)]$_2$, where **Medpt** = *N*,*N*-bis(3-aminopropyl)methylamine. We also describe the magnetic behavior of this new dinuclear compound which, like all reported bis(μ-seleno)- or bis(μ-thiocyanato)nickel(II) compounds is ferromagnetically coupled.

Experimental Section

Synthesis. (μ-SeCN)$_2$[Ni(Medpt)(SeCN)]$_2$ where **Medpt** = *N*,*N*-bis(3-aminopropyl)methylamine (**1**) was prepared by mixing 0.003 mol of nickel(II) nitrate hexahydrate, 0.003 mol of Medpt, and 0.006 mol of potassium selenocyanate in 75 mL of water. From this solution, protected from light, blue monocrystals suitable for X-ray determination of (μ-SeCN)$_2$[Ni(Medpt)(SeCN)]$_2$ were collected 2 weeks later. Analytical data were in agreement with the formula proposed.

Magnetic Measurements. Magnetic measurements were carried out with a Pendulum type magnetometer (MANICS DSM8) equipped with an Oxford CF 1200 S helium continuous-flow cryostat, working in the temperature range 300–4 K, and a Bruker B E15 electromagnet. The magnetic field was approximately 15 000 G. Calibration of the instrument was made by a magnetization measurement of a standard ferrite. Diamagnetic corrections were estimated from Pascal's tables.

EPR measurements were performed with a Bruker ES200 spectrometer at X-band frequency, working with an Oxford helium liquid cryostat for variable temperatures.

X-ray Crystallography. A prismatic blue crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections ($16 < \theta < 21°$) and refined by least-squares methods. Intensities were recorded with graphite-monochromatized Mo Kα radiation. A total of 4124 reflections were collected in the range $2 < \theta < 30°$, 1993 of which were assumed as observed, applying the conditions $I > 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls; no significant intensity decay was observed. The crystallographic data, conditions used for the intensity data collection, and some features of the structure refinement and listed in Table I. Lorentz–polarization and absorption corrections were made. The structure was solved by a Patterson synthesis, using the SHELXS computer program,[9] and refined by full-matrix least-squares methods, with the SHELX76 computer program.[10] The function minimized was $\Sigma w \| F_o| - |F_c\|^2$, where $w = (\sigma^2(F_o) + 0.0031|F_o|^2)^{-1}$; f, f', and f'' were taken from ref 11. Maximum shift/esd = 0.1, and maximum and minimum peaks in final difference synthesis were 0.4 and –0.3 e Å^{-3}, respectively. Final atomic coordinates are given in Table II.

Table I. Crystallographic Data for (μ-SeCN)$_2$[Ni(Medpt)(SeCN)]$_2$

chem formula	$C_{18}H_{38}N_{10}Ni_2Se_2$
a, Å	9.351(2)
b, Å	13.847(3)
c, Å	11.744(2)
β, deg	90.69(2)
V, Å^3	1520.5(9)
Z	2
fw	413.98
space group	$P2_1/n$
T, °C	25
λ(Mo Kα), Å	0.710 69
d_{calc}, g cm^{-3}	1.799
μ(Mo Kα), cm^{-1}	64.07
R^a	0.051
$R_w{}^b$	0.051

^{a} $R(F_o) = \Sigma\| F_o| - |F_c\|/\Sigma|F_o|$. ^{b} $R_w(F_o) = \Sigma w\| F_o| - |F_c\|/\Sigma|F_o|$.

Table II. Final Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2) and Their Estimated Standard Deviations for (μ-SeCN)$_2$[Ni(Medpt)(SeCN)]$_2$

atom	x/a	y/b	z/c	$B_{eq}{}^a$
Ni	4936(10)	–20066(10)	–5446(7)	3.50(5)
Se(1)	212(11)	6304(9)	22716(7)	4.79(5)
Se(2)	3296(14)	–43525(11)	–37431(9)	6.40(6)
N(1)	2638(7)	–1750(6)	–800(6)	3.66(34)
N(2)	966(8)	–3177(6)	605(6)	4.25(37)
N(3)	–1739(7)	–2116(6)	–416(6)	3.87(34)
N(4)	499(7)	–992(6)	710(6)	3.62(34)
N(5)	325(8)	–2972(6)	–1856(7)	4.57(40)
C(1)	3493(11)	–2529(9)	–976(9)	5.04(52)
C(2)	3506(8)	–3306(6)	19(6)	2.73(33)
C(3)	2180(7)	–3761(5)	237(5)	1.87(27)
C(4)	–277(10)	–3792(8)	636(9)	5.08(54)
C(5)	–1968(7)	–3309(5)	903(5)	1.51(24)
C(6)	–2437(13)	–3152(11)	–39(11)	7.38(76)
C(7)	1275(14)	–2788(10)	1746(11)	7.19(74)
C(8)	363(8)	–358(6)	1288(6)	2.28(29)
C(9)	453(9)	–3508(7)	–2588(7)	3.40(38)

^{a} $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Results and Discussion

Description of the Structure. The structure of (μ-SeCN)$_2$[Ni(Medpt)(SeCN)]$_2$ consists of discrete [{Ni(Medpt)(SeCN)$_2$}$_2$] entities. The two nickel(II) atoms are bridged by two selenocyanate ions in an end-to-end fashion, the other two selenocyanate groups acting as terminal ligands. No hydrogen bonds between the dinuclear entities are present. The dimeric compound is shown in Figure 1. The main bond lengths and angles are gathered in Table III. Each nickel atom is octahedrally coordinated by the three N atoms of the Medpt ligand, one N atom of one nonshared selenocyanate group, one N atom of one bridging selenocyanate group, and one Se atom of the other bridging selenocyanate group. The three N atoms of the Medpt ligand, the N atom of the nonbridging selenocyanato group, and the nickel atom are in the same plane. The Ni–Se–C and Ni–N–C angles in the bridge are respectively 94.7(3) and 169.2(6)°. The Ni–N(4) and Ni–Se(1)

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Table III. Selected Bond Lengths (Å) and Angles (deg) for $(\mu\text{-SeCN})_2[\text{Ni(Medpt)(SeCN)}]_2$

N(1)–Ni	2.062(7)	N(5)–Ni	2.044(9)
N(2)–Ni	2.152(8)	Se(1)I–Ni	2.820(3)
N(3)–Ni	2.100(7)	C(8)–Se(1)	1.822(8)
N(4)–Ni	2.036(8)	C(9)–Se(2)	1.794(9)
N(2)–Ni–N(1)	91.6(3)	Se(1)I–Ni–N(1)	86.4(2)
N(3)–Ni–N(1)	173.8(3)	Se(1)I–Ni–N(2)	172.8(2)
N(3)–Ni–N(2)	95.6(3)	Se(1)I–Ni–N(3)	86.5(2)
N(4)–Ni–N(1)	89.6(3)	Se(1)I–Ni–N(4)	93.0(2)
N(4)–Ni–N(2)	93.8(3)	Se(1)I–Ni–N(5)	83.6(2)
N(4)–Ni–N(3)	89.5(3)	N(4)–C(8)–Se(1)	175.6(7)
N(5)–Ni–N(1)	94.0(3)	N(5)–C(9)–Se(2)	170.3(8)
N(5)–Ni–N(2)	89.6(3)	C(8)–N(4)–Ni	169.2(6)
N(5)–Ni–N(3)	89.5(3)	C(8)–Se(1)I–Ni	94.7(3)
N(5)–Ni–N(4)	175.0(3)		

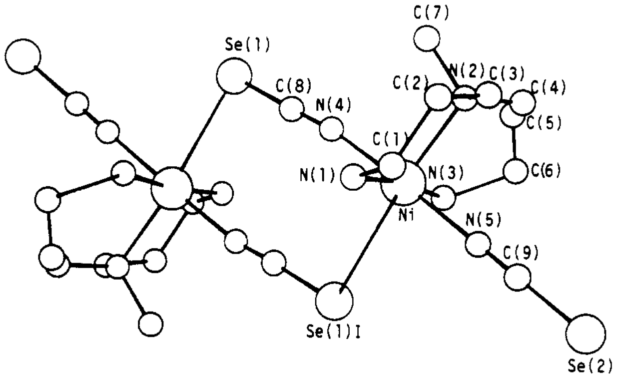

Figure 1. Atom-labeling scheme for $(\mu\text{-SeCN})_2[\text{Ni(Medpt)(SeCN)}]_2$.

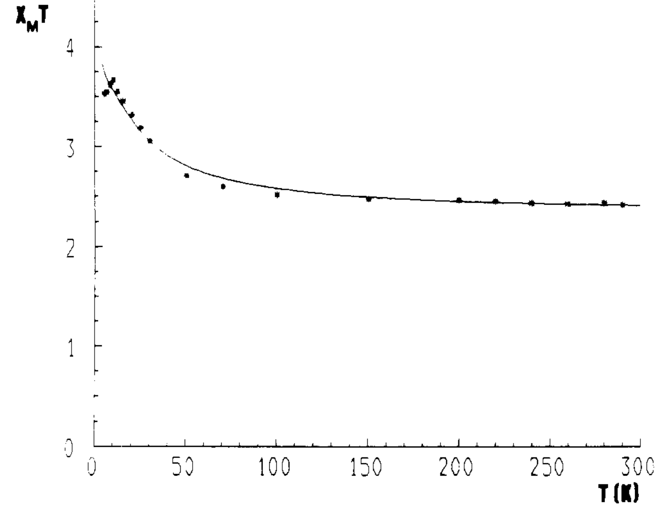

Figure 2. Magnetic susceptibility plots of a polycrystalline sample of $(\mu\text{-SeCN})_2[\text{Ni(Medpt)(SeCN)}]_2$. Units for $\chi_M T$ are cm^3 K mol^{-1}. The solid line shows the best fit of the Ginsberg equation (see text).

distances are respectively 2.036(8) and 2.820(3) Å. The Ni–Ni distance is 5.779(3) Å. For comparative purposes, in the 1-D compound *catena*-$(\text{SeCN})_2[\text{Ni(tmen)}]$,[1] where tmen is *N,N,N′,N′*-tetramethylethylenediamine, the Ni–N(bridge) and Ni–Se distances are 2.020(6) and 2.678(1) Å, respectively, and the Ni–Se–C and Ni–N–C angles in the bridge are respectively 99.2(2) and 168.9(5)°.

Magnetic Results. The magnetic susceptibility data $\chi_M T$ *vs* T for $(\mu\text{-SeCN})_2[\text{Ni(Medpt)(SeCN)}]_2$ are plotted in Figure 2. The $\chi_M T$ value is approximately constant (1.2 cm^3 mol^{-1} K) in the range 290–70 K but from 60 K increases slightly, reaching a maximum of 1.83 cm^3 mol^{-1} K at 10 K. This behavior indicates a ferromagnetically coupled dinuclear compound. The susceptibility data were fitted by the expression of Ginsberg et al.[6] for a magnetically isotropic nickel(II) dimer. The parameters obtained were J = 8.8 cm^{-1}, g = 2.15, D = 1.5 cm^{-1}, and $z'J'$ = 0.11 cm^{-1}. The J values found for the related bis(μ-selenocyanato) complexes not X-ray structurally characterized $[\{\text{Ni(terpy)(NCSe)}_2\}_2]$,[7] where terpy is 2,2′:6′,2″-terpyridine, and $[\{\text{Ni(tren)(NCSe)}_2\}_2][\text{BPh}_4]_2$,[12] where tren is 2,2′,2″-triaminotriethylamine, are 10.1 and 1.6 cm^{-1}, respectively. All the structural and magnetically studied dinuclear bis(μ-thiocyanato)nickel(II) complexes are also ferromagnetically coupled, with lower J values of 4.5[6] and 4.9[7] cm^{-1}. The difference in the J values between the dinuclear SCN$^-$ and SeCN$^-$ complexes structurally characterized may be analyzed according to the Ginsberg model:[6] effectively, apply the Goodenough–Kanamow rules,[13] for angles Ni–S(Se)–C of 90° and Ni–N–C of 180°, strict orthogonality will be found, giving the strongest ferromagnetic complexes. In our case, the angles are 94.7 and 169.1°, respectively and, as can be seen in Table IV, they are the closest to the idealized values indicated by Ginsberg.

Table IV. Structural and Magnetic Parameters for Octahedrally Coordinated dipseudohalide- (NCY-) Bridged Nickel(II) Dimers[a] (NCY = NCS, NCSe)

compound	Ni–Y–C, deg	C–N–Ni, deg	J, cm^{-1}	ref
$[\{\text{Ni(en)}_2(\text{NCS}))_2]\text{I}_2$	100	167	4.5	6
$[\{\text{Ni(terpy)(NCS)}_2\}_2]$	100.8	159	4.9	7
$[\{\text{Ni(Medpt)(NCSe)}_2\}_2]$	94.7	169.2	8.8	*b*

[a] en = ethylenamine; terpy = 2,2′:6′,2″-terpyridine. [b] This work.

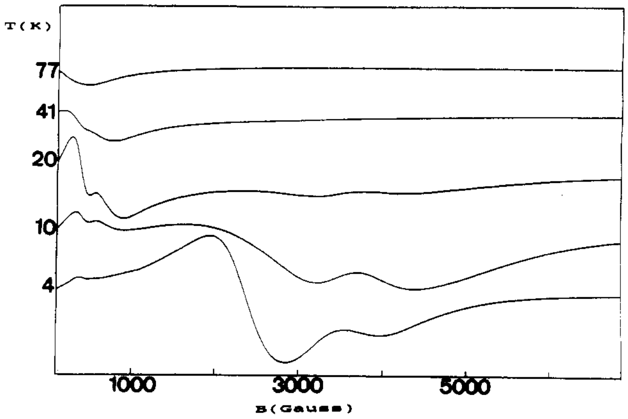

Figure 3. Variable-temperature EPR measurements (X-band) of a polycrystalline sample of $(\mu\text{-SeCN})_2[\text{Ni(Medpt)(SeCN)}]_2$.

Electron Spin Resonance. The ESR spectra of polycrystalline samples of the new complex recorded at variable temperature from 77 to 4.2 K are shown in Figure 3. Focusing our attention on the spectrum at 4 K, we observe a strong and broad band centered at 2380 G, together with a weak band at 470 G and another large one at 3950 G. Taking into account the magnetic results, at 4 K only the ground state of the dinuclear Ni(II) complex (S = 2) is populated. With an increase in temperature, the strong band and the large one centered at 2380 and 3959 G, respectively, diminish and, instead, the weak band centered at 470 G increases in intensity and a new band centered at 890 G appears. At 20 K, the bands in this low-field zone predominate. These low-field bands are similar to those reported by Rojo et al.[7] and Holman et al.[14] for related dinuclear nickel(II) complexes. After 20 K, the intensity of all the absorbed bands decreases with increasing temperature. Above 100 K, the signals disappear.

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Supplementary Material Available: A textual presentation of the experimental crystallographic work and tables giving crystal data and details of the structure determination, anisotropic thermal parameters, and bond angles and distances for $(\mu\text{-SeCN})_2[\text{Ni(Medpt)(SeCN)}]_2$ (4 pages). Ordering information is given on any current masthead page.

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