2992 *Inorg. Chem.* **1992**, *31*, 2992–2994

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Discrete Mononuclear Nickel(II) Selenolate Complexes: Syntheses, Structures, and Properties of $K_2[Ni(SeCH_2CH_2Se)_2]\cdot 2C_2H_5OH$ and $(Me_4N)_2[Ni(SeCH_2CH_2Se)_2]\cdot 1.2H_2O$

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Received February 10, 1991

Introduction

Recent spectroscopic investigations have revealed metal–selenium (M–Se) interactions in the active site of the [FeNiSe] hydrogenases.[1] Selenium has also been found in the enzymes formate dehydrogenase and glutathione peroxidase.[2] Very distinct differences between [FeNi] hydrogenases (enzymes containing Fe, Ni, and S) and [FeNiSe] hydrogenases are believed to arise from Se ligation to the nickel site of the enzyme,[1c,d] and thus a unique role for selenocysteine in this biological system has emerged. Such findings have instigated the study of metal–selenium chemistry, in much the same way as the extensive study of metal–sulfur chemistry was initiated subsequent to the discovery of metal–sulfur (M–S) interactions in the active sites of several biological systems.[3] Unlike M–S chemistry, M–Se chemistry remains relatively unexplored at present. To date, only a few reports on M–Se interactions have appeared in the literature.[4-17] In order to understand the systematic changes that occur in inorganic complexes or complicated biological systems when sulfur ligation to the metal center(s) is replaced by selenium ligation, it is necessary to investigate M–Se interactions analogous to known M–S interactions. In a previous account, as part of our synthetic analogue studies on the structure and properties of the nickel-containing active site of [FeNi] hydrogenases,[18] we have reported the syntheses, structures, and properties of complexes containing the planar NiS_4 chromophore.[18f] We now report the structures and properties of $K_2[Ni(SeCH_2CH_2Se)_2]\cdot 2C_2H_5OH$ (**1**) and $(Me_4N)_2[Ni(SeCH_2CH_2Se)_2]\cdot 1.2H_2O$ (**2**) and compare them with the sulfur analogues. The effect of the cation on $[Ni(SeCH_2CH_2Se)_2]^{2-}$ in complexes **1** and **2** is also discussed.

Experimental Section

Preparation of Compounds. Ethane-1,2-diselenol was synthesized by following a literature procedure[19] and then characterized by spectroscopic techniques.[20] Freshly distilled and degassed solvents were used for all preparations. Standard Schlenk line techniques were used under an atmosphere of pure and dry dinitrogen.

$K_2[Ni(SeCH_2CH_2Se)_2]\cdot 2C_2H_5OH$ (1). To a solution of 1.6 mmol of $K_2(SeCH_2CH_2Se)$ (obtained by mixing 0.30 g of ethane-1,2-diselenol and 0.18 g of KOH) in 20 mL of ethanol was added with stirring a solution of 0.077 g (0.32 mmol) of $NiCl_2\cdot 6H_2O$ in 5 mL of ethanol, and the dark brown solution thus obtained was stirred for 2 h. The reaction mixture was then filtered, and the filtrate was cooled for 12 h at 0 °C, whereupon green rhombus-shaped crystals were deposited. Combined yield: 88 mg (47%). Selected IR bands (KBr pellet, cm^{-1}): 3307 (br), 2966 (m), 1408 (m), 1270 (s), 1096 (s), 1020 (s), 867 (w), 797 (s). ^1H NMR (300 MHz, $(CD_3)_2SO$, 298 K), δ (ppm from TMS): 1.00–1.05 (t, CH_3 of EtOH), 2.12 (s, CH_2), 3.37–3.44 (q, CH_2 of EtOH). ^{13}C NMR (300 MHz, $(CD_3)_2SO$, 298 K), δ (ppm from TMS): 18.25 (EtOH), 24.23 (CH_2), 55.54 (EtOH). Anal. Calcd for $C_8H_{20}O_2K_2Se_4Ni$: C, 15.99; H, 3.35. Found: C, 15.46; H, 3.22.

Table I. Summary of Crystal Data and Intensity Collection and Structure Refinement Parameters for $K_2[Ni(SeCH_2CH_2Se)_2]\cdot 2C_2H_5OH$ (**1**) and $[N(CH_3)_4]_2[[Ni(SeCH_2CH_2Se)_2]\cdot 1.2H_2O$ (**2**)

	complex **1**	complex **2**
formula (mol wt)	$C_8H_{20}O_2Se_4K_2Ni$ (601.0)	$C_{12}H_{34.4}N_2O_{1.2}Se_4Ni$ (600.54)
T, K	130	130
cryst system	monoclinic	orthorhombic
space group	$P2_1/c$	*Pbcn*
a, Å	9.904 (3)	8.255 (3)
b, Å	11.746 (5)	15.800 (6)
c, Å	7.793 (2)	15.996 (6)
β, deg	98.53 (2)	
V, Å^3	896.5 (5)	2086.3 (13)
Z	2	4
d_{calcd}, g cm^{-3}	2.23 (1)	1.91 (1)
abs coeff, μ, cm^{-1}	88.8	72.19
R^a	6.56	5.10
$R_w{}^b$	7.11	4.82

$^a R = (\sum||F_o| - |F_c||)/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o{}^2|]^{1/2}$.

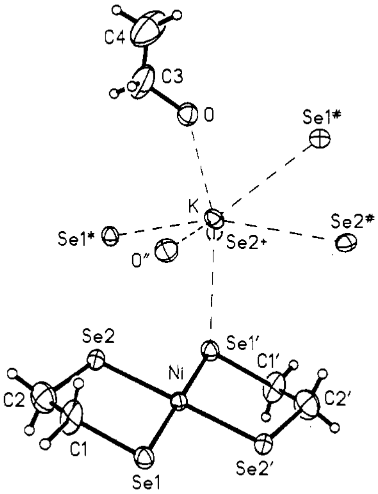

Figure 1. Thermal ellipsoid plot at the 50% probability level of complex **1** showing the structure of the anion and interaction of one K^+ cation with Se atoms of the neighboring anions as well as ethanol molecules of crystallization. Hydrogen atoms are given an arbitrary size. Symbols on the figure correspond as follows to the symmetry codes given in the footnote to Table III: single prime (i); double prime (ii); asterisk (iii); number sign (iv); plus sign (v).

$(Me_4N)_2[Ni(SeCH_2CH_2Se)_2]\cdot 1.2H_2O$ (2). A solution of $(Me_4N)_2(SeCH_2CH_2Se)$ was prepared by the addition of 0.83 g (4.6 mmol) of $Me_4NOH\cdot 5H_2O$ to 0.43 g (2.3 mmol) of ethane-1,2-diselenol in 20 mL of ethanol. To it was added with stirring a solution of 0.11 g (0.46 mmol) of $NiCl_2\cdot 6H_2O$ in 10 mL of ethanol. The resulting dark brown solution was stirred for 2 h and then filtered. The filtrate was cooled for 12 h at 0 °C, whereupon a light brown microcrystalline material was precipitated. This compound was redissolved in the mother liquor, and the

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Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3) for Complexes **1** and **2**

	x	*y*	*z*	*U*(eq)[a]
		Complex **1**		
Ni	0	0	0	20 (1)
Se(1)	1093 (1)	−381 (1)	−2352 (1)	26 (1)
Se(2)	1724 (1)	−845 (1)	1885 (1)	26 (1)
K	357 (2)	2143 (2)	5617 (2)	27 (1)
O	2175 (7)	3149 (5)	8226 (8)	34 (2)
C(1)	2951 (10)	−756 (10)	−1214 (14)	44 (4)
C(2)	2948 (13)	−1474 (11)	366 (15)	51 (4)
C(3)	3589 (12)	3010 (13)	9007 (17)	64 (5)
C(4)	4045 (16)	3748 (16)	10357 (21)	92 (7)
		Complex **2**		
Ni	0	1332 (1)	2500	20 (1)
Se(1)	1265 (1)	2345 (1)	1696 (1)	28 (1)
Se(2)	1244 (1)	316 (1)	1678 (1)	27 (1)
N(1)	6111 (8)	1453 (4)	761 (4)	30 (2)
C(1)	581 (18)	−701 (6)	2237 (7)	94 (6)
C(2)	244 (16)	3409 (5)	2072 (5)	54 (4)
C(3)	6040 (14)	2279 (7)	1148 (7)	65 (5)
C(4)	6029 (13)	772 (7)	1419 (5)	51 (4)
C(5)	7657 (12)	1377 (6)	282 (5)	48 (3)
C(6)	4715 (10)	1373 (6)	186 (5)	35 (3)
O	1371 (14)	9241 (7)	4592 (6)	45 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

solution was cooled for 2 days at 5 °C, whereupon dark brown needles were obtained. Combined yield: 99 mg (37%). Selected IR bands (KBr pellets, cm^{-1}): 3330 (br), 2995 (s), 1472 (s), 1437 (m), 1402 (s), 1250 (m), 950 (s), 803 (m). ^{1}H NMR (300 MHz, $(CD_3)_2SO$, 298 K), δ (ppm from TMS): 2.13 (s, CH$_2$), 3.25 (s, Me$_4$N). ^{13}C NMR (300 MHz, $(CD_3)_2SO$, 298 K), δ (ppm from TMS): 24.54 (CH$_2$), 55.59 (Me$_4$N). Anal. Calcd for $C_{12}H_{34.4}O_{1.2}N_2Se_4Ni$: C, 24.00; H, 5.77; N, 4.67. Found: C, 24.28; H, 5.56; N, 4.90.

Physical Measurements. Absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were monitored with a Perkin-Elmer 1600 FTIR spectrometer. NMR spectra were recorded on a General Electric 300-MHz GN-300 instrument. Elemental analyses were completed by Atlantic Microlab Inc., Atlanta, GA.

Table III. Selected Bond Lengths (Å) and Angles (deg)[a]

	Complex **1**		
Se(1)–Ni	2.307 (1)	Se(1)–C(1)	1.970 (9)
Se(2)–Ni	2.305 (1)	Se(2)–C(2)	1.961 (13)
K–O	2.773 (6)	K–Se(1)^{iii}	3.388 (2)
K–Se(1)^{i}	3.426 (2)	K–Se(1)^{iv}	3.596 (3)
K–Se(2)^{v}	3.399 (3)	K–Se(2)^{iv}	3.528 (2)
K–O^{ii}	2.797 (7)	O–C(3)	1.451 (13)
C(1)–C(2)	1.492 (17)	C(3)–C(4)	1.386 (21)
Ni–Se(1)–C(1)	101.7 (3)	Ni–Se(1)–K^{iii}	96.2 (1)
C(1)–Se(1)–K^{iii}	121.9 (3)	Ni–Se(1)–K^{i}	120.9 (1)
C(1)–Se(1)–K^{i}	117.4 (3)	K^{iii}–Se(1)–K^{i}	98.3 (1)
Ni–Se(2)–C(2)	104.1 (3)	Ni–Se(2)–K^{v}	95.9 (1)
C(2)–Se(2)–K^{v}	131.2 (4)	Se(1)–Ni–Se(2)	91.9 (1)
Se(1)–Ni–Se(1)^{i}	180.0 (1)	Se(2)–Ni–Se(1)^{i}	88.1 (1)
Se(1)–Ni–Se(2)^{i}	88.1 (1)	Se(2)–Ni–Se(2)^{i}	180.0 (1)
Se(1)^{i}–Ni–Se(2)^{i}	91.9 (1)	O–K–Se(1)^{iii}	87.6 (1)
O–K–Se(1)^{i}	163.2 (2)	Se(1)^{iii}–K–Se(1)^{i}	81.7 (1)
O–K–Se(1)^{iv}	68.4 (1)	Se(1)^{iii}–K–Se(1)^{iv}	127.0 (1)
O–K–Se(2)^{i}	98.9 (2)	Se(1)^{iv}–K–Se(2)^{v}	80.6 (1)
Se(1)^{i}–K–Se(2)^{iv}	81.3 (1)	Se(2)^{v}–K–Se(2)^{iv}	105.2 (1)
O–K–O^{ii}	97.4 (2)	Se(1)^{iii}–K–O^{ii}	95.1 (1)
Se(1)^{i}–K–O^{ii}	70.8 (1)	K–O–C(3)	137.8 (7)
Se(1)–C(1)–C(2)	112.5 (8)	O–C(3)–C(4)	115.7 (12)
	Complex **2**		
Ni–Se(1)	2.305 (2)	Ni–Se(2)	2.315 (2)
Se(1)–C(2)	1.975 (9)	Se(2)–C(1)	1.919 (11)
N(1)–C(3)	1.446 (12)	N(1)–C(4)	1.507 (11)
N(1)–C(5)	1.493 (12)	N(1)–C(6)	1.480 (11)
C(1)–C(1)^{i}	1.275 (27)	C(2)–C(2)^{i}	1.428 (18)
Se(1)–Ni–Se(2)	87.9 (1)	Se(1)–Ni–Se(1)^{vi}	92.0 (1)
Se(2)–Ni–Se(1)^{vi}	179.2 (1)	Se(2)–Ni–Se(2)^{vi}	92.2 (1)
Ni–Se(1)–C(2)	103.2 (3)	Ni–Se(2)–C(1)	100.9 (4)
C(3)–N(1)–C(4)	110.1 (7)	C(3)–N(1)–C(5)	109.1 (7)
C(4)–N(1)–C(5)	109.8 (7)	C(3)–N(1)–C(6)	108.2 (7)
C(4)–N(1)–C(6)	109.8 (7)	C(5)–N(1)–C(6)	109.9 (6)
Se(2)–C(1)–C(1)^{vi}	121.5 (5)	Se(1)–C(2)–C(2)^{vi}	114.4 (4)

[a] Symmetry codes: (i) $-x, -y, -z$; (ii) $x, {}^1/_2 - y, -{}^1/_2 + z$; (iii) $x, y, 1 + z$; (iv) $-x, {}^1/_2 + y, {}^1/_2 - z$; (v) $-x, -y, 1 - z$; (vi) $-x, y, {}^1/_2 - z$.

X-ray Data Collection and Structure Solution and Refinement. Crystals for X-ray analysis were obtained by cooling the ethanolic solutions of the respective complexes. Diffraction experiments were performed on a Siemens R3m/V machine equipped with a graphite monochromator and a modified LT-1 low-temperature apparatus. Mo Kα (λ = 0.71069 Å) radiation was employed. No significant decay of intensity of two standard reflections recorded after every 198 reflections was observed. The structure was solved by direct methods.[21,22] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions, and a riding model was used with fixed isotropic thermal parameters. A total of 1678 and 1471 reflections with $F > 4.0\sigma(F)$ were used in the refinement (full-matrix least squares) for complexes **1** and **2**, respectively. The data were corrected for absorption effects by the use of the program XABS.[23]

Machine parameters, crystal data, and data collection parameters are summarized in Table I. Positional coordinates are included in Table II, while selected bond distances and angles are listed in Table III. The rest of the crystallographic data have been submitted as supplementary material.

Results and Discussion

The K$^+$ and Me$_4$N$^+$ salts (**1** and **2**, respectively) of the selenolato complex $[Ni(SeCH_2CH_2Se)_2]^{2-}$ are obtained in reactions of $NiCl_2 \cdot 6H_2O$ with excess ligand (Ni:ligand = 1:5) in anhydrous ethanol. The presence of a small amount of water in the reaction

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(20) Selected IR bands (Nujol mull, cm^{-1}): 2296 (w), 1237 (w), 1167 (s), 1096 (w), 720 (w). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K), δ (ppm from TMS): 2.90 (t, CH$_2$), −0.27 (m, SeH) (integration ratio 2:1). ^{13}C NMR (300 MHz, CDCl$_3$, 298 K), δ (ppm from TMS): 21.05 (CH$_2$).

(21) SHELXTL, version 5.1, installed on a Data General Eclipse computer; SHELXTL PLUS, installed on a MicroVAX 3200 computer.

(22) Neutral-atom scattering factors and corrections for anomalous dispersion were taken from: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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medium leads to formation of a product with different spectroscopic properties.[24] Quite in contrast, the sulfur analogue of this complex, namely $[Ni(SCH_2CH_2S)_2]^{2-}$, was successfully synthesized in aqueous medium.[18f] This clearly demonstrates the different reactivity of the selenolato complexes as compared to the thiolato complexes of bivalent nickel. It is interesting to note that the K^+ and Me_4N^+ complexes exhibit different colors in the solid state. In solution, their spectroscopic properties are identical however.

Structure of $K_2[Ni(SeCH_2CH_2Se)_2]\cdot 2C_2H_5OH$ (1). The crystal structure of **1** consists of K^+ ions, the $[Ni(SeCH_2CH_2Se)_2]^{2-}$ anion, and ethanol molecules. Each K^+ ion is in close contact with at least four Se atoms (distances ranging from 3.399 (3) to 3.596 (3) Å) from the neighboring anions as well as two O atoms from the ethanol molecules in the crystal lattice. Similar interactions have been observed in crystals of $K_2[Ni(SC(CH_3)_2CH(NH_2)COO)_2]\cdot 4H_2O$[18a] and $K_2[Ni(SCH_2CH(NH_2)COO)_2]\cdot 1.5H_2O$,[18b] wherein the potassium ions stay in close proximity to the S atoms coordinated to nickel. Also, there is strong K^+–oxygen interaction (K^+–O(av) = 2.77 Å) in the latter two complexes. The coordination geometry of nickel in the $[Ni(SeCH_2CH_2Se)_2]^{2-}$ anion is square planar, with an average Ni–Se bond length of 2.305 (3) Å. This compares well with the Ni–Se distances reported for square planar $NiSe_4$ cores in $(TMSF)_2[Ni(tds)_2]$[9] (tds = bis(trifluoromethyl)ethylenediselenolate, Ni–Se(av) = 2.255 Å) and $[(C_4H_9)_4N]_2[Ni(bds)_2]$[10] (bds = *o*-benzenediselenolate, Ni–Se(av) = 2.259 Å). The Ni–Se bonds in $[Ni(SeCH_2CH_2Se)_2]^{2-}$ are on the average 0.11 Å longer than the Ni–S bonds in the $[Ni(SCH_2CH_2S)_2]^{2-}$ anion.[18f] The same difference of 0.11 Å is observed between M–Se and M–S bonds in $[M(QPh)_4]^{2-}$ where Q = Se or S and M = Fe, Zn, or Cd.[5,8] A higher degree in the covalency in the M–Se bonds has been predicted on the basis of the latter data, and the Ni–Se bonds appear to be no exception.

Interaction of the Ni atom with the ethanolic O atoms is, at best, only a very weak electrostatic one. The shortest Ni···O distance of 3.75 Å occurs at a 35.7° tip from the normal to the $NiSe_4$ plane, and the Ni···O–C angle is 140.2°.

Structure of $(Me_4N)_2[Ni(SeCH_2CH_2Se)_2]\cdot 1.2H_2O$ (2). The crystal structure of this salt consists of discrete Me_4N^+ and $[Ni(SeCH_2CH_2Se)_2]^{2-}$ ions as well as water molecules of crystallization.[25] As expected, the structure of the anion is identical to that observed in **1**. The major difference is the absence of any interaction between the cations and the complex anions in the solid state (the distances between the methyl hydrogens and Se atoms are over 3 Å). Also, the packing of the Me_4N^+ cations above and below the $NiSe_4$ plane precludes any Ni···O electrostatic interaction; the shortest contact is 4.87 Å.

Properties. Crystals of **1** and **2** are very sensitive to oxygen and exhibit different colors. The potassium salt of the $[Ni(SeCH_2CH_2Se)_2]^{2-}$ anion is *green*, while the Me_4N^+ salt is *dark brown*. However, both salts dissolve in solvents like DMSO, to give the same greenish-brown solution. The electronic spectrum of $[Ni(SeCH_2CH_2)_2]^{2-}$ in DMSO consists of bands with maxima [nm (ϵ, $M^{-1}\ cm^{-1}$)] at 690 (90), 520 (125), 344 (sh, 10000), and 308 (12000) when recorded within minutes after dissolution. The solution turn progressively orange-brown and exhibits increasingly higher molar extinction coefficients in the high-energy bands, indicating conversion to other species. At present, no attempt has been made to identify these products. The difference in color in the solid state could arise from the extent of interaction between the $[Ni(SeCH_2CH_2Se)_2]^{2-}$ anion and the countercations. Both compounds decompose rapidly in polar solvents such as ethanol in the absence of excess ligand.

The ^1H and ^{13}C NMR spectra of **1** and **2** have been recorded in $(CD_3)_2SO$. The CH_2 groups of the ligand resonate at ~2 (^1H) and ~24 (^{13}C) ppm in both complexes. The Me_4N^+ group of **2** exhibits peaks at 3.25 (^1H) and 55.59 (^{13}C) ppm. The clean NMR spectra of these complexes confirm the stability of the complexes in DMSO during the period of spectroscopic measurements.

Acknowledgment. Financial support of a grant from the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supplementary Material Available: A computer-generated drawing of the anion of **2** (Figure S1), computer-generated packing diagrams for **1** and **2**, a complete list of crystal data (Table S1), and tables of bond angles for **1** (Table S2), anisotropic displacement coefficients for **1** and **2** (Tables S3 and S4), and H atom coordinates and isotropic displacement coefficients for **1** and **2** (Tables S5 and S6) (6 pages); tables of observed and calculated structure factors for **1** and **2** (Tables S7 and S8) (17 pages). Ordering information is given on any current masthead page.

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[24] The solvent ratio used was H_2O:EtOH = 1:15 (v/v). The brown crystalline compound was identified as K_2Se_3 (Se–Se = 2.379 Å; K–Se(av) = 3.448 Å; Se–Se–Se = 102.2°). The compound is bright green in dimethyl sulfoxide and exhibits electronic absorption band maxima at 600 and 410 nm.

[25] The oxygen atom in compound **2** was clearly not at fully occupancy in the early stages of structure solution. However, it was well-behaved when allowed to refine with both the thermal parameters and occupancy as variables. The equivalent isotropic thermal parameter was 0.045 (4) $Å^2$ in the final cycle of refinement, and that was near the average for the structure. The occupancy converged to 0.59 (2) and was reported as 0.60 (or 1.2 for the formula stated).