itatively, the off-rates for the gases appear much faster than in the dpm systems, and this could be of value in gas separation technology.[12] The H_2S reaction at 1 atm and 20 °C, as in the dpm system,[13] is complete in minutes.

syn-**1** in $CHCl_3$ isomerizes very slowly to the anti form ($t_{1/2} \sim 15$ days). Within the A-frame products of **1**, however, the syn species are preferred; thus, the μ-Se and -SeO derivatives of *anti*-**1** spontaneously convert to the syn forms.[14] Of note, the syn form of an A-frame species, in a boat conformation with both Me groups pseudoequatorial, allows for minimum steric interactions (just the two methine hydrogens) for the bridged moiety.

The synthesis of *syn*-**1** from *anti*-**1** is clearly based on preferred formation of the *syn*-μ-CO species.

Experimental Section

The sources of the materials, syntheses of the precursor complexes, and instrumentation used have been described earlier.[3,6,8]

***syn*-1 and Derivatives.** What proved to be a 2:1 mixture of *anti*- and *syn*-**1** was prepared as described in ref 3 to the stage of precipitation by addition of Et_2O. This mixture (1.07 g, 1 mmol) was dissolved in 25 mL of CH_2Cl_2 and the solution exposed to ~140 atm CO for 60 h at −20 °C without stirring. The CO was then released and the solution volume reduced to 5 mL by evacuation; addition of 20 mL of Et_2O precipitated yellow crystals (0.81 g) that contained a syn–anti mixture in about a 4:1 ratio by ^{1}H NMR. Dissolution in 3 mL of $CHCl_3$ and reprecipitation by addition of 10 mL of MeOH gave 0.33 g of a material with 95% syn content.

The syntheses of the *syn*-μ-S and -Se complexes and oxidation of these to the monooxo derivatives by using *t*-BuOOH follow the procedures described in refs 7 and 8 for the dpm analogues. For convenience, mixtures of *anti*- and *syn*-**1** were generally used as precursors, but the pure syn products were readily isolated from the $CHCl_3$/MeOH reprecipitation procedure described above. All the isolated complexes gave satisfactory elemental analyses. The *syn*-μ-O species, formed in situ at −50 °C by using *m*-chloroperbenzoic acid,[8] remained sufficiently stable at ~20 °C to record the ^{1}H NMR spectrum at this temperature, while the *anti*-μ-O species[14] decomposed above −25 °C.

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Synthesis, Structure, and Properties of Potassium Bis(L-cysteinato-*N*,*S*)nickelate(II) Sesquihydrate

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Introduction

The existence of Ni–S ligation at the Ni site(s) of the [NiFeS] hydrogenases,[1-4] as demonstrated by recent spectroscopic studies,[5-7] has raised new interest in the structure and coordination chemistry of monomeric nickel complexes with S-containing ligands. Model studies have indicated that the unusual redox properties of the nickel site arise from the presence of soft thiolato S atoms in the first coordination sphere of nickel.[8-10] Structural and spectroscopic parameters of the cysteinato complexes of nickel therefore deserve special attention. Despite earlier reports,[11-16] precise structural information on such complexes is yet unavailable. As part of our systematic analogue studies,[10,17,18] we report here the synthesis and structure of potassium bis(L-cysteinato-*N*,*S*)nickelate(II) sesquihydrate (**1**). Synthetic procedures that yield impure samples of this complex have been published by other groups. The present procedures allow isolation of pure material. The ^{1}H and ^{13}C spectra of **1** are also discussed.

Experimental Section

Preparation of Compounds. L-Cysteine and L-cysteine ethyl ester hydrochloride were purchased from Aldrich Chemical Co. In the following preparations, all operations were performed under a pure dinitrogen atmosphere.

$K_2[Ni(SCH_2CH(NH_2)COO)_2]\cdot 1.5H_2O$ (1). To a solution of dipotassium cysteinate ($KSCH_2CH(NH_2)COOK$), prepared from 0.61 g (5 mmol) of L-cysteine and 0.58 g (10.3 mmol) of KOH in 20 mL of ethanol, was added with stirring a solution of 0.29 g (1 mmol) of nickel nitrate hexahydrate in 5 mL of ethanol. The initial brown mixture turned cloudy and a flocculent green precipitate appeared within 10 min. After

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Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement Parameters for $K_2[Ni(SCH_2CH(NH_2)COO)_2]\cdot 1.5H_2O$ (**1**)

formula	$C_6H_{13}N_2O_{5.5}S_2K_2Ni$	β, deg	123.56 (3)
mol wt	402.2	*V*, Å^3	1361 (1)
T, K	130	*Z*	4
cryst syst	monoclinic	d_{calcd}, g cm^{-3}	1.963
space group	$P2_1$	abs coeff (μ), cm^{-1}	23.54
a, Å	17.055 (7)	R^a	0.0401
b, Å	6.424 (3)	$R_w{}^b$	0.0378
c, Å	14.905 (6)		

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

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

	x	*y*	*z*	U(eq)^a
K(1)	2623 (1)	1778 (1)	8601 (1)	20 (1)
K(2)	4589 (1)	8154 (4)	9103 (1)	17 (1)
K(3)	2106 (1)	2142 (4)	11166 (1)	19 (1)
K(4)	−412 (1)	3640 (4)	9064 (1)	16 (1)
Ni(1)	2736 (1)	5052 (4)	6219 (1)	13 (1)
S(1)	1610 (2)	2910 (5)	5942 (2)	18 (1)
S(2)	3877 (1)	7209 (5)	6582 (2)	16 (1)
N(1)	1952 (5)	7319 (13)	6071 (5)	15 (3)
N(2)	3555 (5)	2791 (13)	6399 (5)	17 (3)
O(1)	2658 (4)	7589 (10)	8192 (4)	21 (3)
O(2)	1586 (4)	5349 (11)	8053 (4)	21 (3)
O(3)	5280 (4)	4463 (10)	9078 (4)	17 (3)
O(4)	4116 (4)	2123 (10)	8456 (4)	20 (3)
C(1)	782 (5)	4850 (15)	5851 (6)	17 (4)
C(2)	1329 (5)	6778 (15)	6439 (6)	18 (4)
C(3)	1920 (5)	6513 (14)	7676 (6)	16 (4)
C(4)	4810 (5)	5299 (15)	6976 (6)	17 (4)
C(5)	4551 (6)	3276 (14)	7267 (6)	15 (4)
C(6)	4642 (6)	3296 (16)	8358 (7)	20 (4)
Ni(2)	2104 (1)	5248 (4)	13621 (1)	13 (1)
S(3)	1073 (2)	7625 (5)	13372 (2)	16 (1)
S(4)	3126 (2)	2882 (5)	13815 (2)	19 (1)
N(3)	1188 (5)	3186 (12)	13359 (5)	14 (3)
N(4)	3001 (5)	7325 (13)	13860 (5)	17 (3)
O(5)	625 (4)	2833 (10)	11298 (4)	18 (3)
O(6)	−552 (4)	5110 (11)	10714 (4)	18 (3)
O(7)	2316 (4)	7843 (11)	11744 (5)	25 (3)
O(8)	3364 (4)	5642 (11)	11815 (4)	23 (3)
C(7)	30 (6)	5976 (14)	12860 (7)	17 (4)
C(8)	200 (5)	3906 (14)	12512 (6)	17 (4)
C(9)	80 (5)	3937 (13)	11423 (6)	12 (4)
C(10)	4054 (6)	4613 (15)	13966 (7)	19 (4)
C(11)	3604 (5)	6721 (15)	13484 (6)	16 (4)
C(12)	3036 (5)	6713 (14)	12239 (6)	15 (4)
O(9)	1312 (4)	5295 (11)	9696 (4)	20 (3)
O(10)	3653 (4)	4908 (11)	10143 (4)	22 (3)
O(11)	2961 (4)	−95 (11)	10425 (4)	26 (3)

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

Table III. Selected Bond Distances and Angles for **1**

	Bond Lengths (Å)		
Ni(1)–S(1)	2.209 (4)	Ni(1)–S(2)	2.199 (3)
Ni(1)–N(1)	1.906 (9)	Ni(1)–N(2)	1.928 (9)
S(1)–C(1)	1.832 (10)	S(2)–C(4)	1.830 (10)
N(1)–C(2)	1.481 (15)	N(2)–C(5)	1.492 (9)
O(1)–K(1A)	2.767 (7)	O(3)–K(2B)	2.729 (7)
O(4)–K(2B)	3.110 (6)	Ni(2)–S(3)	2.199 (4)
K(1)–S(1)	3.413 (3)	K(2)–S(2)	3.304 (4)
Ni(2)–S(4)	2.209 (4)	Ni(2)–N(3)	1.916 (8)
Ni(2)–N(4)	1.910 (9)	S(3)–C(7)	1.836 (9)
S(3)–K(4B)	3.218 (4)	S(4)–C(10)	1.834 (11)
N(3)–C(8)	1.514 (9)	N(4)–C(11)	1.470 (15)
	Bond Angles (deg)		
S(1)–Ni(1)–S(2)	177.0 (1)	S(1)–Ni(1)–Ni(1)	88.4 (3)
S(2)–Ni(1)–N(1)	90.9 (3)	S(1)–Ni(1)–N(2)	92.6 (3)
S(2)–Ni(1)–N(2)	88.1 (3)	N(1)–Ni(1)–N(2)	178.6 (2)
K(1)–S(1)–Ni(1)	94.9 (1)	K(1)–S(1)–C(1)	96.1 (3)
Ni(1)–S(1)–C(1)	98.3 (3)	K(2)–S(2)–Ni(1)	96.6 (1)
K(2)–S(2)–C(4)	92.9 (3)	Ni(1)–S(2)–C(4)	98.7 (3)
Ni(1)–N(1)–C(2)	112.3 (6)	Ni(1)–N(2)–C(5)	110.7 (6)
O(1)–C(3)–O(2)	127.3 (8)	O(1)–C(3)–C(2)	116.2 (9)
O(2)–C(3)–C(2)	116.4 (7)	O(3)–C(6)–O(4)	126.7 (10)
O(3)–C(6)–C(5)	115.8 (9)	O(4)–C(6)–C(5)	117.4 (7)
S(3)–Ni(2)–S(4)	178.01 (1)	S(3)–Ni(2)–N(3)	87.7 (3)
S(4)–Ni(2)–N(3)	92.7 (3)	S(3)–Ni(2)–N(4)	91.7 (3)
S(4)–Ni(2)–N(4)	87.8 (3)	N(3)–Ni(2)–N(4)	179.0 (3)
Ni(2)–S(3)–C(7)	99.8 (3)	Ni(2)–S(3)–K(4B)	94.6 (1)
C(7)–S(3)–K(4B)	89.6 (3)	K(3)–S(4)–Ni(2)	94.9 (1)
Ni(2)–S(4)–C(10)	99.4 (3)	Ni(2)–N(4)–C(11)	113.7 (6)
N(3)–C(8)–C(7)	108.6 (6)	N(3)–C(8)–C(9)	109.0 (8)
O(5)–C(9)–O(6)	124.8 (9)	O(5)–C(9)–C(8)	118.4 (6)
O(6)–C(9)–C(8)	116.9 (9)	N(4)–C(11)–C(10)	109.2 (8)
N(4)–C(11)–C(12)	110.6 (6)	O(7)–C(12)–O(8)	125.7 (7)
O(7)–C(12)–C(11)	117.6 (9)	O(8)–C(12)–C(11)	116.6 (7)

1 h of stirring, 10 mL of water was added to the reaction mixture and it was warmed to 50 °C to obtain a clear red-brown solution. This solution was allowed to cool slowly to 5 °C and then stored at 5 °C for 24 h. The pink crystals thus obtained were collected by filtration and dried under partial vacuum. Yield: 250 mg (67%). Selected IR bands (KBr pellet, cm^{-1}): 3475 (s, br), 3295 (s), 3150 (s), 2915 (m), 2865 (m), 1600 (s), 1545 (s), 1472 (s), 1400 (s), 1337 (s), 1250 (m), 1160 (s), 1115 (s), 1054 (m), 912 (m), 857 (s), 810 (s), 575 (m), 531 (m). Anal. Calcd for $C_6H_{13}N_2O_{5.5}S_2K_2Ni$: C, 17.90; H, 3.26; N, 6.96. Found: C, 17.63, H, 3.17; N, 6.52.

Complex **1** has also been synthesized from nickel salts and excess (>5 equiv) L-cysteine ethyl ester in alkaline methanol. In such attempts, the metal ion promoted base hydrolysis of the ester produces the L-cysteinate ligand in situ and allows formation of **1** in good yield.

A solution of 0.58 g (2 mmol) of nickel nitrate in 20 mL of methanol was added with stirring to a solution of potassium ethyl cysteinate (prepared from 1.86 g (10 mmol) of L-cysteine ethyl ester hydrochloride and 1.68 g (30 mmol) of KOH in 100 mL of 5:1 (v/v) methanol:water mixture), upon which a red solution resulted. A green flocculent precipitate appeared after 1 h. At this time, more water was added and the mixture was warmed to ~50 °C, resulting in a clear red solution, which was then cooled slowly to 0 °C and stored at 0 °C for 24 h. A batch of 670 mg (90%) of pink needles was obtained.

$[Ni(SCH_2CH(NH_2)COOC_2H_5)_2]$ (2). This "bis" complex of L-cysteine ethyl ester has been reported previously.[19] However, we discovered that the product, synthesized by following the published procedure, is often not pure and leaves a residue when dissolved in solvents such as DMF, methanol, and pyridine (solvents mentioned in the reported work). Here, we report a synthesis of **2** that produces an analytically pure compound, which dissolves smoothly in the solvents mentioned above.

A solution of 0.31 g (1.05 mmol) of nickel nitrate hexahydrate in 10 mL of acetonitrile was slowly added to a solution of L-cysteine ethyl ester (prepared from 1 g (5.4 mmol) of L-cysteine ethyl ester hydrochloride and 0.43 g (10.8 mmol) of NaOH in 50 mL of a 4:1 (v/v) acetonitrile:water mixture), upon which a dark red solution was obtained. After 1 h of stirring at room temperature, this was stored at 5 °C for 24 h. The fine green needles that deposited during this period were collected by filtration and dried in vacuo. Yield: 200 mg (57%). Selected IR bands (KBr pellet, cm^{-1}): 3280 (s), 3164 (m), 3045 (s), 2974 (m), 1715 (vs, ν_{CO}), 1582 (m), 1465 (m), 1375 (m), 1322 (m), 1234 (s), 1215 (s), 1090 (s), 1020 (m), 860 (m), 720 (m), 670 (m), 495 (w). NMR (pyridine-d_5, 298 K, 300 MHz, ppm from TMS): ^{1}H NMR δ 4.79 (br, NH), 4.07 (q, $-CH_2CH_3$), 3.84 (br, $-SCH_2-$), 2.75 (m, $-CH-$), 1.03 (t, $-CH_2CH_3$); ^{13}C NMR δ 14.13 ($-CH_2CH_3$), 31.0 ($-CH-$), 61.26 ($-CH_2CH_3$), 65.21 ($-SCH_2-$), 172.09 ($-CO-$). Anal. Calcd for $C_{10}H_{20}N_2O_4S_2Ni$: C, 33.83, H, 5.67; N, 7.89. Found: C, 33.64; H, 5.72; N, 7.82.

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

X-ray Data Collection, Structure Solution, and Refinement. Pink/green dichroic needles were obtained from an aqueous solution of **1** following cooling at 4 °C for 3 days. Diffraction experiments were performed on a Siemens R3m/V machine equipped with graphite monochromator and a modified LT-1 low-temperature apparatus. Mo Kα 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 (SHELXTL PLUS (VMS)). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were

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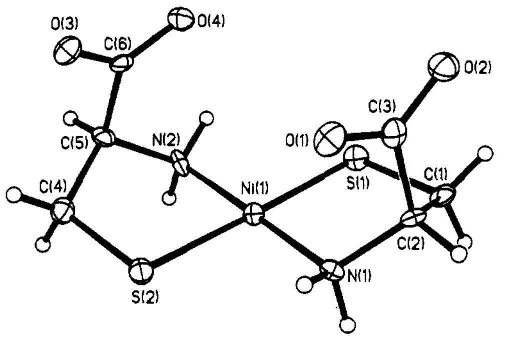

Figure 1. Thermal ellipsoid plot at the 50% probability level of one of the two anions of **1** in the asymmetric unit. Hydrogen atoms are given an arbitrary size.

included at calculated positions, and a riding model was used with fixed isotropic thermal parameters. A total of 2305 reflections with $F > 4.0\sigma(F)$ were used in the refinement (full-matrix least squares), and the data were corrected for absorption effects by the use of the program XABS.[20]

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

Results and Discussion

Two groups have isolated the complex anion bis(L-cysteinato)nickelate(II) as the lithium (purple-brown)[11] and the potassium (brown)[13] salt from aqueous solutions. Though satisfactory elemental analyses were provided for both compounds, we found that the product or products obtained from aqueous solution are invariably impure and leave variable amounts of residue when redissolved in different solvents. It is important to note that, in the previously reported procedures,[11,13] the L-cysteinate ligand was generated in the presence of excess nickel ion by the addition of LiOH or KOH to a 1:2 nickel salt:L-cysteine mixture in water. Since multinuclear complexes with bridging cysteinate ligands (i.e., $[Ni_2L_3]^{2-}$ or $[Ni_3L_4]^{2-}$) are formed at low ligand:metal ratios,[11,12,21] it is quite probable that, in previous attempts, such species were formed during the early stages of mixing and contaminated the final product. In the present work, two steps were taken to avoid the formation of multinuclear complexes. First, an excess (5 equiv) of L-cysteinate was used, and second, the mode of addition was reversed (i.e., metal to ligand). These two steps ensured a large excess of ligand during the entire period of mixing.[22] Even so, a small amount of green precipitate[23] was noticed in the reaction mixture in ethanol. However, addition of water and heating resulted in a clear red-brown solution from which **1** crystallized in high yield.

Structure of $K_2[Ni(SCH_2CH(NH_2)COO)_2]\cdot 1.5H_2O$ (1). The crystal structure consists of K^+ ions, two independent but very similar types of anions (there are two of each type in the asymmetric unit), and water molecules. The K^+ ions are surrounded by five or six oxygen atoms (distance range 2.657 (2)–2.823 (2) Å) from the carboxylate groups of L-cysteinate and the water molecules. In addition, each K^+ ion has an S atom within bonding range (average distance 3.3 Å). The two types of anions are also connected through the water molecule represented by O(11). A computer-generated thermal ellipsoid plot of one of the two essentially similar anions is shown in Figure 1. Plots of the two anions with their closest interatomic contacts and disposition of the K^+ ions are shown in Figures S1 and S2 (supplementary material).

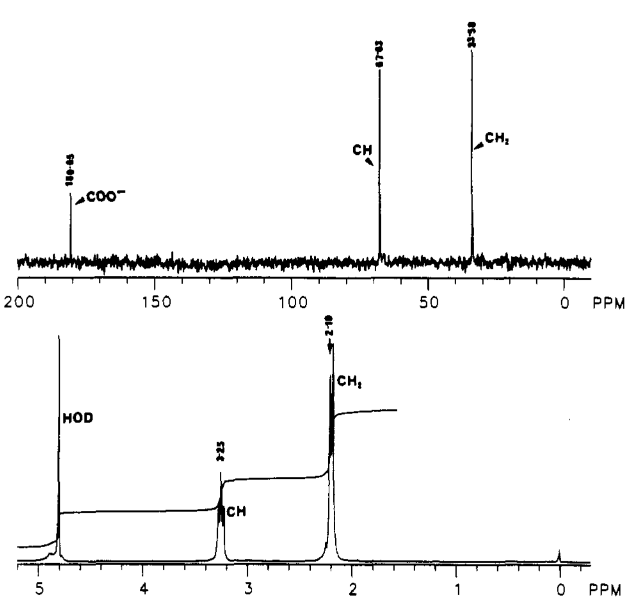

Figure 2. ^{13}C (top trace) and ^1H (bottom trace) NMR spectra (300 MHz, 293 K) in **1** in D_2O. The chemical shift values from TSP are indicated.

The coordination geometry around nickel is square planar with the two thiolato S and two amine N atoms of the two L-cysteinate ligands bonded to the metal center (Figure 1). The average Ni(II)–S and Ni(II)–N distances (2.204 (4) and 1.915 (8) Å) compare well with those observed in the nickel(II) complexes of 2-aminoethanethiol[24] and *N,N*-dimethyl-β-mercaptoethylamine.[25] The most unusual feature of the coordination sphere of nickel in **1** is the occurrence of the two carboxylate groups of the two L-cysteinate ligands on the same side of the mean coordination plane. Presumably, this type of disposition of the carboxylate groups facilitates both coordination to K^+ ions and H-bonding in the crystal lattice. A similar arrangement of carboxylate groups of penicillamine ligands has been noted in a tetranuclear heterometallic anion $[Au^I_2Ni^{II}_2(SC(CH_3)_2CH(NH_2)COO)_4]^{2-}$, a species in which the carboxylate groups are also not involved in coordination.[26] This behavior of the unligated carboxylate groups in square-planar complexes therefore appears to be independent of whether the two bidentate N,S-donating ligands are trans (present work) or cis[26] to each other.

In the two crystallographically independent anions of **1**, the various bond angles (Table III) as well as the conformations of the chelate rings are quite normal.[24-26] Also, the torsion angles are typical for five-membered chelate rings with N,S-donating ligands.

Properties. The fact that the IR spectrum of **1** exhibits no band in the region 2600–2500 cm^{-1} suggests coordination of the ligand as a thiolate. Also, the antisymmetric and the symmetric ν_{COO^-} at 1600 and 1400 cm^{-1} provide evidence of the presence of uncoordinated carboxylate groups in **1**. The results agree with previous reports.[11,13]

Shown in Figure 2 are the ^1H and ^{13}C NMR spectra of **1** in D_2O. All three ^{13}C resonances of L-cysteinate (27.58, 58.60, and 175.21 ppm from TSP; solvent D_2O; pD = 11) shift downfield upon coordination to nickel. Assignments of the NMR peaks rely on area integration as well as APT data.[27] That the monomeric structure of **1**, as shown in Figure 1, is retained in aqueous solution is indicated by the clean and simple NMR spectra of the complex.

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[21] Perrin, D. D.; Sayce, I. G. *J. Chem. Soc. A* **1968**, 53.

[22] Polymeric S-bridged products are conveniently avoided by the presence of excess ligand during the period of mixing. See refs 10a and 17.

[23] It is interesting to note that, in previous work,[12,21] a green coloration was observed at a low ligand:nickel ratio in aqueous solution.

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Supplementary Material Available: Computer-generated drawings of the two crystallographically independent anions of **1** showing the closest interatomic contacts and water molecules (Figures S1 and S2), a complete list of crystal data (Table I continued), and tables of bond distances and bond angles (Tables S1 and S2), anisotropic displacement coefficients (Table S3), and H atom coordinates (Table S4) for **1** (9 pages); a table of observed and calculated structure factors for **1** (10 pages). Ordering information is given on any current masthead page.

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Ordering of Ligand Strengths for a Series of Dithiolate Ligands Attached to Platinum(II)

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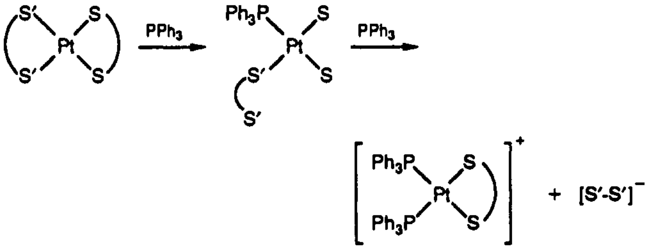
Pioneering work on the reactions of the bis(dithiolate)platinum(II) complexes $Pt(S\text{-}S)_2$ with monodentate group 15 donor ligands was done by Stephenson[1] and Fackler[2] and their coworkers. However, this work did not discriminate between the ligating powers of either the various dithiolates or the various group 15 ligands because the reaction sequences were very similar in all cases. More recently, we have established a consistent order of coordinating power for a series of group 15 and mixed group 15/group 16 donor bidentate ligands by investigating their reactions with $Pt(S_2P\{OEt\}_2)_2$[3] ($Pt(dtp)_2$), $Pt(S_2CNEt_2)_2$[4] ($Pt(dtc)_2$), and $Pt(S_2CO^nPr)_2$[5] ($Pt(xan)_2$). Evidence was also obtained from these studies that dithiocarbamate is a stronger ligand than dithiophosphate and xanthate.

In this note, we establish an order of relative ligating strengths for a number of dithiolates at platinum(II). The method is based upon the discovery that mixing two different dithiolates gives the mixed platinum dithiolate. With use of the work of Stephenson and Fackler, these were then reacted with PPh_3, and multinuclear magnetic resonance studies clearly reveal which dithiolate is displaced in the competitive situation



to give the $[(PPh_3)_2Pt(S\text{-}S)]^+$ complexes, which can be identified by their known NMR spectra.[6]

All NMR data are given in Table I.[7] Figure 1a is the platinum-195 NMR spectrum at −30 °C observed 1 week after mixing equimolar quantities of $Pt(dtp)_2$ and $Pt(xan)_2$ in dichloromethane. The triplet and the singlet are due to the starting materials, and the doublet is due to Pt(dtp)(xan). The relative proportions of the species are very close to 1:4:1, which shows that the mixed species is favored. Figure 1b is the platinum-195 NMR spectrum after the addition of an equimolar quantity of PPh_3 (i.e. PPh_3:total Pt = 1:1) to the solution at −30 °C. The spectrum is observed at low temperature to prevent intramolecular exchange between the bidentate and monodentate dithiolate ligands.[1] The spectrum consists of a weak doublet assigned to $(PPh_3)Pt(\eta^1\text{-xan})(\eta^2\text{-xan})$,[6] arising from the $Pt(xan)_2$ in the solution, and a doublet of doublets, which is clearly assignable to a species containing the phosphine and a coordinated dtp ligand. The coupling constant to the phosphorus of the dtp ligand is markedly reduced from the value in the starting materials and is consistent with monodentate coordination of the dtp ligand.[3,6] The complex in solution is therefore identified as $(PPh_3)Pt(\eta^1\text{-dtp})(\eta^2\text{-xan})$. Addition of a second equimolar quantity of PPh_3 produces the spectrum shown in Figure 1c. The main signal is a triplet, which is identified[6] as being due to $[(PPh_3)_2Pt(\eta^2\text{-xan})]^+$, and the weak triplet is assigned to $(PPh_3)_2Pt(S_2CO)$ formed by dealkylation of the coordinated xanthate ligand.[1] Confirmation of this reaction scheme is obtained from the phosphorus-31 NMR spectra, particularly with the appearance of a signal due to free $[dtp]^-$ after the reaction with 2 molar equiv of PPh_3. Thus these reactions show that in an even competition, *n*-propyl xanthate has a stronger coordinating power than diethyl dithiophosphate.

We have carried out similar studies with other pairs of dithiolates and have established the following order of ligating strengths:

$$[S_2CNEt_2]^- > [S_2CO^nPr]^- > [S_2P(OEt)_2]^- > [S_2PPh_2]^-$$

Another series of experiments was performed to substantiate this sequence. We have previously established[3-5] that $Ph_2PCH_2CH_2PPh_2$ (dpe) is the most strongly bound of all the group 15 bidentate ligands so that it effectively blocks two coordination sites at Pt(II) and allows a different type of competition reaction between different dithiolates. Reaction of $[Pt(dpe)_2]^{2+}$ with $Pt(S\text{-}S)_2$ gives $[(dpe)Pt(S\text{-}S)]^+$ quantitatively. These species were then reacted in dichloromethane solution at room temperature for a week with a different free dithiolate ion in the form of the salt $[PPh_3Bz][S\text{-}S]$,[8] and the results confirmed the order of ligand strengths given above. For example, addition of $[PPh_3Bz][xan]$ to $[(dpe)Pt(dtc)]^+$ gave no reaction, but $[PPh_3Bz][dtc]$ reacted with $[(dpe)Pt(xan)]^+$ to give $[(dpe)Pt(dtc)]^+$.

This second set of experiments allows the series of dithiolates studied to be extended. If reactions between dpe and $Pt(dtp)_2$ and $Pt(xan)_2$ are carried out at room temperature, the first formed products are $[(dpe)Pt(S\text{-}S)]^+$ and free $[S\text{-}S]^-$, which interact to give $(dpe)Pt(S_2P\{O\}\{OEt\})$ and $(dpe)Pt(S_2CO)$ and the appropriate dithiolate ester.[3,5] These dealkylated dithiolates are very strongly

Table I Phosphorus-31 and Platinum-195 NMR Data in Dichloromethane Solution[a]

compd	$\delta(^{31}P)$	$\delta(^{195}Pt)$	$^1J_{Pt,P}$, Hz	$^2J_{Pt,P}$, Hz	temp, °C
$Pt(xan)_2$		−4210 (s)			25
$Pt(dtp)_2$	99.9 (s)	−3985 (t)		445	25
$Pt(dtc)_2$		−3835 (s)			25
$Pt(S_2PPh_2)_2$	96.8 (s)	−3055 (t)		360	25
Pt(xan)(dtp)	102.8 (s)	−4110 (d)		415	25
Pt(xan)(dtc)		−4030 (s)			25
$Pt(xan)(S_2PPh_2)$	102.0 (s)	−3655 (d)		325	25
Pt(dtp)(dtc)	103.3 (s)	−3925 (d)		380	25
$Pt(dtp)(S_2PPh_2)$	99.2 (s), 97.5 (s)	−3520 (dd)		455, 365	25
$Pt(dtc)(S_2PPh_2)$	97.3 (s)	−3445 (d)		294	25
$(PPh_3)Pt(\eta^1\text{-dtp})(\eta^2\text{-xan})$	94.0 (s), 13.0 (s)	−4510 (dd)	3615	125	−30
$(PPh_3)Pt(\eta^1\text{-}S_2PPh_2)(\eta^2\text{-xan})$	86.0 (s), 12.0 (s)	−4515 (dd)	3650	88	−30
$(PPh_3)Pt(\eta^1\text{-}S_2PPh_2)(\eta^2\text{-dtp})$	97.3 (s), 85.7 (s), 13.5 (s)	−4485 (ddd)	3765	335, 120	−30
$(PPh_3)Pt(\eta^1\text{-xan})(\eta^2\text{-dtc})$	13.8 (s)	−4315 (d)	3580		−30
$(PPh_3)Pt(\eta^1\text{-dtp})(\eta^2\text{-dtc})$	97.2 (s), 14.0 (s)	−4325 (dd)	3505	117	−30
$(PPh_3)Pt(\eta^1\text{-}S_2PPh_2)(\eta^2\text{-dtc})$	85.1 (s), 13.4 (s)	−4345 (dd)	3530	99	−30

[a] Key: s = singlet; d = doublet; dd = doublet of doublets; ddd = doublet of doublet of doublets; t = triplet.

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