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## Coordination Modes of Polydentate Ligands. 3. Five-Coordinate Complexes of $\text{Co}^{2+}$ , $\text{Cu}^{2+}$ , and $\text{Ni}^{2+}$ Containing a Tridentate Thioether-Alkoxy Ligand<sup>1</sup>

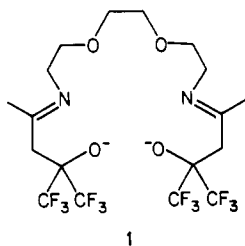
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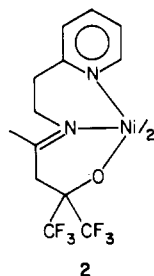
A study has been made of the application of the dianion of the fluorinated alcohol-thioether 2,2'-[thiobis(methylene)]bis-[1,1,1,3,3,3-hexafluoro-2-propanol],  $[\text{HO}(\text{CF}_3)_2\text{CH}_2]_2\text{S}$ , as a tridentate, dinegative, ligand. Stable, neutral, complexes are formed with  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$  from nitrogen-containing coligands, and five-coordination is favored. A complete structural determination has been carried out on the complex  $\text{Co}[\text{OC}(\text{CF}_3)_2\text{CH}_2]_2\text{S}(\text{C}_5\text{H}_5\text{N})_2$ . The crystals are monoclinic, space group  $C2/c$ , with  $a = 26.24$  (1) Å,  $b = 16.565$  (9) Å,  $c = 10.998$  (6) Å,  $\beta = 104.50$  (4)°, and  $Z = 8$ . The  $\text{Co}^{2+}$  ion is five-coordinate in trigonal-bipyramidal geometry, with the alkoxy-thioether ligand adopting a facial configuration, the sulfur atom being in the apical position. These complexes show no tendency to increase the coordination number of the metal to 6 by solvation, an effect attributed to the bulk of the fluorinated alkoxy groups.

### Introduction

In previous parts of this series, we have reported synthetic and structural studies on complexes of polydentate ligands in which one or two fluorinated alkoxy groups,  $-\text{C}(\text{CF}_3)_2\text{O}^-$ , are combined with other nitrogen- or oxygen-containing donor sites. The coordination number of the metal ion in such complexes is influenced by a number of factors, including the geometry of the ligand and the nature of the metal. For example, the potentially hexadentate ligand **1** gives a neutral, six-coordinate complex of cobalt(II), with highly distorted octahedral geometry, but the nickel(II) analogue is four-coordinate, with the two ethereal oxygen atoms not bonding to the metal.<sup>3</sup>



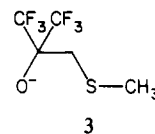
A six-coordinate nickel complex may be produced by the use of two tridentate uninegative ligands, as in **2**.<sup>4</sup>



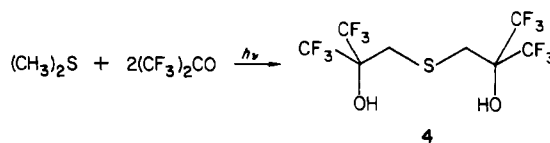
However, the coordination around the metal is very sensitive to changes in the nature of the donor groups or in chelate ring size, and four- or five-coordination is more commonly found in complexes of this type. Our experience has generally suggested that the bulk of the  $-\text{C}(\text{CF}_3)_2\text{O}^-$  group disfavors coordination numbers above 5.<sup>5</sup>

In our previous studies, we reported the synthesis of polydentate ligands in which the fluorinated alkoxy group is combined with other "hard" donor sites, containing oxygen or nitrogen. It is clearly of interest to extend these studies to potential ligands in

which the second donor site is "soft" in character, and we have recently made compounds in which the  $-\text{C}(\text{CF}_3)_2\text{O}^-$  donor is combined with groups containing thioether<sup>6</sup> or diarylphosphino<sup>7</sup> functions. The simplest example of the former class of compounds is ligand **3**, which we have found to form stable complexes with palladium(II) and platinum(II).<sup>6</sup>



However, the synthesis of the fluorinated diol **4** has been reported,<sup>8</sup> and this compound is clearly of potential application as a tridentate, dinegative, ligand.



In this paper, we report the successful application of **4** (in its diionized form) as a tridentate ligand, giving stable, neutral, complexes of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$ . By the use of neutral, nitrogen-containing coligands, five-coordinate complexes are formed, and the facial mode of coordination of ligand **4** has been established by a complete structural determination on a cobalt(II) derivative.

### Experimental Section

**General Information.** Infrared spectra were recorded on a Beckman 4250 spectrophotometer, visible-UV spectra on a Cary 118 spectrometer, and mass spectra on a Varian-MAT 311 instrument. Microanalysis was performed by Guelph Analytical Laboratories, Guelph, Ontario; all analytical data are in Table I. Solution molecular weights were determined by Malissa-Reuter Laboratories.

Diol **4** was prepared by the irradiation of hexafluoroacetone with dimethyl sulfide in Pyrex glass tubes as described by Mir and Shreeve.<sup>8</sup>

**Synthesis of Complexes.** The same general method was used for the preparation of each of the complexes **5-12**. The anhydrous metal chloride  $\text{MCl}_2$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Cu}$ ) was dissolved in ethanol, and an equimolar amount of diol **4** added; no sign of reaction occurred at this stage. The nitrogen-containing coligand was then added in the appropriate molar ratio (1:1 for tetramethylethylenediamine or bipyridyl; 2:1 for pyridine) followed by dropwise addition of the stoichiometric amount of KOH in ethanol (2:1 molar ratio). Color changes and the precipitation of KCl occurred during the addition of base. The solution was filtered and solvent removed by rotary evaporation; then the residue was extracted with  $\text{CH}_2\text{Cl}_2$  and the solution filtered and evaporated. The resulting solid

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(2) (a) University of Western Ontario. (b) University of Windsor.

(3) Konefal, E.; Loeb, S. J.; Stephan, D. W.; Willis, C. J. *Inorg. Chem.* **1984**, *23*, 538.

(4) Loeb, S. J.; Stephan, D. W.; Willis, C. J. *Inorg. Chem.* **1984**, *23*, 1509.

(5) Relevant earlier work is reviewed in ref 3.

(6) Boéré, R. T.; Willis, C. J. Abstracts, 10th International Symposium on Fluorine Chemistry, Vancouver, B.C., 1982; *J. Fluorine Chem.* **1982**, *21*, 18.

(7) Boéré, R. T.; Montgomery, C. D.; Willis, C. J., unpublished work.

(8) Mir, Q.-C.; Shreeve, J. M. *Inorg. Chem.* **1980**, *19*, 1510.

Table I. Analytical Data

no.	compd	formula	% C		% H		% N		mp, °C
			calcd	found	calcd	found	calcd	found	
5	Co(O-S-O)(TMED) <sup>a</sup>	C <sub>14</sub> H <sub>20</sub> CoF <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S	29.64	29.68	3.55	3.60	4.94	4.96	96-98
6	Co(O-S-O)(py) <sub>2</sub> <sup>b</sup>	C <sub>18</sub> H <sub>14</sub> CoF <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S	35.48	35.52	2.32	2.00	4.60	4.76	173
7	Co(O-S-O)(bpy) <sup>c</sup>	C <sub>18</sub> H <sub>12</sub> CoF <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S	35.60	35.64	1.99	1.98	4.61	4.59	270 dec
8	Ni(O-S-O)(TMED)	C <sub>14</sub> H <sub>20</sub> F <sub>12</sub> N <sub>2</sub> NiO <sub>2</sub> S	29.65	29.60	3.56	3.20	4.94	4.86	80-85
9	Ni(O-S-O)(py) <sub>2</sub>	C <sub>18</sub> H <sub>14</sub> F <sub>12</sub> N <sub>2</sub> NiO <sub>2</sub> S	35.50	35.00	2.33	2.36	4.60	4.38	102-104
10	Cu(O-S-O)(TMED)	C <sub>14</sub> H <sub>20</sub> CuF <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S	29.40	29.53	3.53	3.76	4.90	4.65	70-75
11	Cu(O-S-O)(py) <sub>2</sub>	C <sub>18</sub> H <sub>14</sub> CuF <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S	35.22	35.17	2.30	2.34	4.56	4.51	108-110
12	Cu(O-S-O)(bpy)	C <sub>18</sub> H <sub>12</sub> CuF <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S	35.33	35.33	1.98	2.41	4.58	4.60	205

<sup>a</sup> TMED = *N,N,N',N'*-tetramethylethylenediamine. <sup>b</sup> py = pyridine. <sup>c</sup> bpy = bipyridyl.

Table II. Visible Absorption Spectra

no.	compd	solvent	$\nu_{\max}$ , cm <sup>-1</sup> ( $\epsilon$ )
5	Co(O-S-O)(TMED)	C <sub>2</sub> H <sub>5</sub> OH	16 450 (62), 17 090 (64), 19 760 (63), 21 140 (54)
6	Co(O-S-O)(py) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	16 530 (83), 17 090 (79), 19 920 (212)
		C <sub>5</sub> H <sub>5</sub> N	16 580 (80), 17 240 (84), 20 080 (258)
7	Co(O-S-O)(bpy)	CH <sub>2</sub> Cl <sub>2</sub>	16 580 (14), 17 180 (16), 22 170 (72)
8	Ni(O-S-O)(TMED)	CHCl <sub>3</sub>	13 420 (27), 20 000 (20), 23 810 (64)
9	Ni(O-S-O)(py) <sub>2</sub>	CHCl <sub>3</sub>	13 890 (21), 20 620 (sh), 24 210 (84)
		C <sub>5</sub> H <sub>5</sub> N	13 950 (31), 21 010 (sh), 23 470 (132)
10	Cu(O-S-O)(TMED)	C <sub>2</sub> H <sub>5</sub> OH	15 580 (225)
11	Cu(O-S-O)(py) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	15 240 (325)
		C <sub>5</sub> H <sub>5</sub> N	14 880 (390)
12	Cu(O-S-O)(bpy)	CH <sub>2</sub> Cl <sub>2</sub>	13 890 (168)

was then recrystallized to give the following complexes, where (O-S-O) represents the diionized form of ligand 4: Co(O-S-O)(TMED) (5), purple crystals from ethanol; Co(O-S-O)(py)<sub>2</sub> (6), purple crystals from ethanol containing ~1% pyridine; Co(O-S-O)(bpy) (7), green crystals from dichloromethane; Ni(O-S-O)(TMED) (8), olive green crystals from ethanol; Ni(O-S-O)(py)<sub>2</sub> (9) olive green crystals from benzene/hexane; Cu(O-S-O)(TMED) (10), blue crystals from ethanol; Cu(O-S-O)(py)<sub>2</sub> (11), blue crystals from ethanol containing ~1% pyridine; Cu(O-S-O)(bpy) (12), blue crystals from dichloromethane/hexane.

The eight complexes were characterized by elemental analysis (Table I). Infrared spectra showed sharp absorptions characteristic of the O-S-O ligand at about 705, 750-760 (d), 980, and 1014 cm<sup>-1</sup>, together with strong C-F absorptions in the region 1150-1220 cm<sup>-1</sup>. Visible spectra are given in Table II. Room-temperature magnetic moments for the Co<sup>2+</sup> complexes were in the range 3.6-4.4  $\mu_B$ , while the Ni<sup>2+</sup> complexes were 2.2-2.5  $\mu_B$ ; both are slightly low for high-spin five-coordinate ions. The 300 K magnetic moments of the Cu<sup>2+</sup> complexes appeared to be significantly reduced, and this is being further investigated.

Mass spectra suggested that some rearrangement of the complexes was occurring in the instrument, since in all cases peaks were observed at mass numbers corresponding to some species containing two metal atoms. A number of significant peaks for each compound are shown in Table III; there were in addition other peaks corresponding to the loss of F<sup>-</sup>, CF<sub>3</sub><sup>-</sup>, (CF<sub>3</sub>)<sub>2</sub>O<sup>-</sup>, and other fragments generally found in complexes of this type. The ion corresponding to the expected mononuclear complex was observed in most cases, although sometimes in low intensity. A common peak was that corresponding to M<sub>2</sub>(O-S-O)<sub>2</sub>, that is, the product of dimerization after the loss of the nitrogen coligand, but occasionally a dimer of the complete complex appeared to be present.

In view of this unexpected result, solution molecular weights (osmometric in chloroform) were determined for three of the complexes, but no evidence for association was found: Co(O-S-O)(py)<sub>2</sub> (6) calcd 609.3, found 452 and 463; Ni(O-S-O)(py)<sub>2</sub> (9) calcd 609.0, found 483 and 493; Cu(O-S-O)(py)<sub>2</sub> (11) calcd 611.9, found 515 and 529.

We therefore assume that the anomalously high molecular weights obtained from the mass spectral data are an artefact of the technique produced by rearrangement on heating in the instrument.

### Structure Determination

**X-ray Data Collection and Reduction.** Crystallization performed by slow evaporation from ethanol containing ~1% of pyridine yielded purple blocks of Co(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>[OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>]<sub>2</sub>S (6).

Table III. Significant Mass Spectral Peaks

compd	mass no. <sup>a</sup>	assgnt
5	1134 (m) <sup>b</sup>	Co <sub>2</sub> (O-S-O) <sub>2</sub> (TMED) <sub>2</sub>
	902 (w)	Co <sub>2</sub> (O-S-O) <sub>2</sub>
6	[567] <sup>c</sup>	Co(O-S-O)(TMED)
	981 (w)	Co <sub>2</sub> (O-S-O) <sub>2</sub> (py)
7	902 (m)	Co <sub>2</sub> (O-S-O) <sub>2</sub>
	[609]	Co(O-S-O)(py) <sub>2</sub>
8	902 (w)	Co <sub>2</sub> (O-S-O) <sub>2</sub>
	607 (s)	Co(O-S-O)(bpy)
9	831 (w)	Ni <sub>2</sub> (O-S-O) <sub>2</sub> less CF <sub>3</sub>
	566 (s)	Ni(O-S-O)(TMED)
10	900 (m)	Ni <sub>2</sub> (O-S-O) <sub>2</sub>
	608 (w)	Ni(O-S-O)(py) <sub>2</sub>
11	910 (w)	Cu <sub>2</sub> (O-S-O) <sub>2</sub>
	571 (s)	Cu(O-S-O)(TMED)
12	910 (m)	Cu <sub>2</sub> (O-S-O) <sub>2</sub>
	534 (s)	Cu(O-S-O)(py)
	910 (w)	Cu <sub>2</sub> (O-S-O) <sub>2</sub>
	611 (m)	Cu(O-S-O)(bpy)

<sup>a</sup> For <sup>59</sup>Co, <sup>58</sup>Ni, or <sup>63</sup>Cu isotopes. <sup>b</sup> Relative intensities: s = strong; m = medium; w = weak. <sup>c</sup> A number in parentheses represents a species not observed in the spectrum.

Table IV. Summary of Crystal Data, Intensity Collection, and Structure Refinement for Co(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>[OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>]<sub>2</sub>S (6)

formula	C <sub>18</sub> H <sub>14</sub> CoF <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S
mol wt	609.28
<i>a</i> , Å	26.24 (1)
<i>b</i> , Å	16.565 (9)
<i>c</i> , Å	10.998 (6)
$\beta$ , deg	104.50 (4)
cryst syst	monoclinic
space group	C2/c
<i>V</i> , Å <sup>3</sup>	4628 (4)
<i>d</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.75
<i>Z</i>	8
cryst faces	{001} {100} {010}
cryst dims, mm	0.19 × 0.52 × 0.21
abs coeff ( $\mu$ ), cm <sup>-1</sup>	8.72
radiation	Mo K $\alpha$ ( $\lambda = 0.71069$ Å)
scan speed, deg/min	2.0-5.0 ( $\theta/2\theta$ scan)
scan range, deg	1.0 below K $\alpha_1$ to 1.1 above K $\alpha_2$
bkgd/scan time ratio	0.5
data collcd	2 $\theta$ of 4.5-50°; $\pm h, +k, +l$
total no. of data collcd	3041
no. of unique data ( $F_o^2 > 3\sigma(F_o^2)$ )	1797
no. of variables	335 (2 blocks)
<i>R</i> , %	4.35
<i>R</i> <sub>w</sub> , %	4.84

Diffraction experiments were carried out at 25 °C on a Syntex P2<sub>1</sub> four-circle diffractometer with graphite-monochromatized Mo K $\alpha$  radiation. On the basis of the observed extinctions, the compound crystallized in the monoclinic space group C2/c or Cc. C2/c was confirmed by structure solution and refinement. The final lattice parameters were obtained from 15 machine-centered reflections. The data ( $\pm h, +k, +l$ ) were collected in two shells ( $4.5 \geq 2\theta \geq 35$ ,  $35 \geq 2\theta \geq 50^\circ$ ). Machine parameters, crystal data, and data collection parameters are summarized in Table IV.

Table V. Positional Parameters<sup>a</sup>

atom	x	y	z	atom	x	y	z
Co	1123 (2) <sup>b</sup>	2494 (1)	1149 (1)	F(1)	2010 (2)	3996 (3)	5286 (4)
S	787 (1)	2204 (1)	3094 (2)	F(2)	2356 (2)	3251 (3)	4122 (5)
O(1)	1491 (2)	3345 (2)	2174 (3)	F(3)	2174 (2)	4468 (3)	3619 (5)
O(2)	1253 (2)	1357 (2)	1228 (3)	F(4)	583 (2)	4005 (3)	2734 (5)
N(1)	398 (2)	2826 (3)	-20 (4)	F(5)	1057 (2)	4571 (3)	4351 (5)
N(2)	1551 (2)	2677 (2)	-208 (4)	F(6)	1163 (2)	4852 (3)	2565 (5)
C(1)	1456 (2)	3549 (5)	3343 (5)	F(7)	673 (2)	38 (3)	470 (5)
C(2)	1994 (3)	3829 (5)	4094 (8)	F(8)	634 (2)	-288 (3)	2309 (5)
C(3)	1066 (3)	4256 (5)	3263 (8)	F(9)	263 (2)	788 (3)	1421 (4)
C(4)	1289 (3)	2838 (4)	4092 (5)	F(10)	1684 (2)	-220 (3)	1449 (5)
C(5)	1114 (4)	1230 (4)	3331 (6)	F(11)	1660 (2)	-203 (3)	3427 (5)
C(6)	1174 (2)	844 (3)	2114 (5)	F(12)	2092 (2)	653 (4)	2707 (5)
C(7)	696 (3)	323 (5)	1568 (8)				
C(8)	1670 (4)	269 (5)	2437 (8)	C(21)	1631 (2)	2078 (4)	-937 (5)
C(11)	280 (3)	3607 (4)	-251 (6)	C(22)	1943 (3)	2151 (4)	-1775 (6)
C(12)	-179 (3)	3844 (5)	-1034 (7)	C(23)	2179 (3)	2869 (5)	-1885 (6)
C(13)	-546 (3)	3278 (7)	-1623 (6)	C(24)	2091 (3)	3492 (4)	-1152 (7)
C(14)	-427 (3)	2498 (6)	-1399 (7)	C(25)	1785 (2)	3368 (4)	-333 (5)
C(15)	48 (3)	2287 (4)	-593 (6)				

<sup>a</sup> Multiplied by 10<sup>4</sup>. <sup>b</sup> Estimated standard deviations are shown in parentheses.

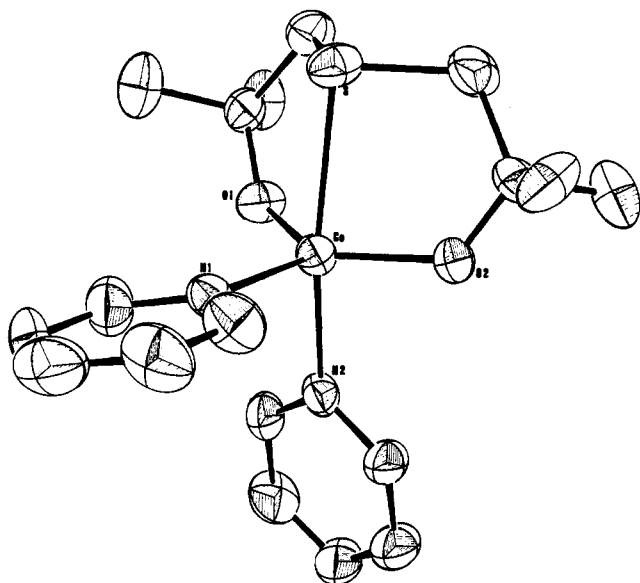


Figure 1.

Three standard reflections were recorded every 200 reflections; their intensities showed no statistically significant change over the duration of data collection. The absorption coefficient was 8.72 cm<sup>-1</sup>; thus, no absorption correction of the data was warranted. The data were processed with the SHELX-76 package.<sup>9</sup> A total of 1797 reflections having  $F_o^2 > 3\sigma(F_o^2)$  were used in the refinement.

**Structure Solution and Refinement.** Atomic scattering factors were taken from the tabulation of Cromer and Waber.<sup>10</sup> The cobalt position was located from a Patterson calculation, and all other non-hydrogen atoms were located from difference Fourier calculations. Full-matrix least-squares refinement techniques on  $F$  were employed. The function  $\sum w(|F_o| - |F_c|)^2$  was minimized, where the weight  $w$  is defined by  $4F_o^2/\sigma(F_o^2)$  and  $F_o$  and  $F_c$  are observed and calculated structure factor amplitudes. Refinement, where all non-hydrogen atoms were assigned isotopic temperature factors, yielded

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 11.77\%$$

The pyridine and methylene hydrogen atom positions were calculated. C-H bond lengths of 1.08 Å were assumed, and

Table VI. Selected Bond Distances and Angles<sup>a</sup>

Distances			
Co-S	2.553 (2)	N(1)-C(11)	1.339 (9)
Co-O(1)	1.911 (4)	N(1)-C(15)	1.323 (8)
Co-O(2)	1.911 (4)	C(11)-C(12)	1.35 (1)
Co-N(1)	2.087 (4)	C(12)-C(13)	1.38 (1)
Co-N(2)	2.102 (5)	C(13)-C(14)	1.34 (1)
O(1)-C(1)	1.354 (7)	C(14)-C(15)	1.383 (9)
C(1)-C(2)	1.519 (9)	N(2)-C(21)	1.323 (8)
C(1)-C(3)	1.54 (1)	N(2)-C(25)	1.322 (8)
C(1)-C(4)	1.560 (9)	C(21)-C(22)	1.38 (1)
C(4)-S	1.824 (6)	C(22)-C(23)	1.36 (1)
C(5)-S	1.815 (7)	C(23)-C(24)	1.36 (1)
C(5)-C(6)	1.527 (9)	C(24)-C(25)	1.36 (1)
C(6)-C(7)	1.52 (1)		
C(6)-C(8)	1.58 (1)		
C(6)-O(2)	1.349 (7)		

Angles			
S-Co-O(1)	82.8 (1)	Co-O(1)-C(1)	126.9 (4)
S-Co-O(2)	82.7 (1)	O(1)-C(1)-C(2)	108.6 (6)
S-Co-N(1)	96.6 (1)	O(1)-C(1)-C(3)	109.6 (5)
S-Co-N(2)	168.2 (1)	O(1)-C(1)-C(4)	114.1 (5)
O(1)-Co-O(2)	129.9 (2)	C(1)-C(4)-S	111.9 (4)
O(1)-Co-N(1)	114.7 (2)	C(4)-S-C(5)	100.4 (3)
O(1)-Co-N(2)	91.8 (2)	S-C(5)-C(6)	113.3 (4)
O(2)-Co-N(1)	114.2 (2)	C(5)-C(6)-O(2)	115.9 (5)
O(2)-Co-N(2)	93.0 (2)	C(5)-C(6)-C(7)	109.3 (6)
N(1)-Co-N(2)	95.2 (2)	C(5)-C(6)-C(8)	108.4 (5)
C(6)-O(2)-Co	126.6 (4)	Co-N(1)-C(11)	120.2 (4)
Co-S-C(4)	92.7 (2)	Co-N(1)-C(15)	122.2 (4)
Co-S-C(5)	92.2 (3)	Co-N(2)-C(21)	121.0 (4)
N(1)-C(11)-C(12)	121.8 (6)	Co-N(2)-C(25)	122.9 (4)
C(11)-C(12)-C(13)	120.5 (8)	N(2)-C(21)-C(22)	123.1 (8)
C(12)-C(13)-C(14)	117.7 (7)	C(21)-C(22)-C(23)	119.6 (7)
C(13)-C(14)-C(15)	119.6 (7)	C(22)-C(23)-C(24)	117.5 (7)
C(14)-C(15)-N(1)	118.6 (6)	C(23)-C(24)-C(25)	119.4 (7)
C(15)-N(1)-C(11)	117.6 (5)	C(24)-C(25)-N(2)	124.3 (6)
		C(25)-N(2)-C(21)	116.0 (5)

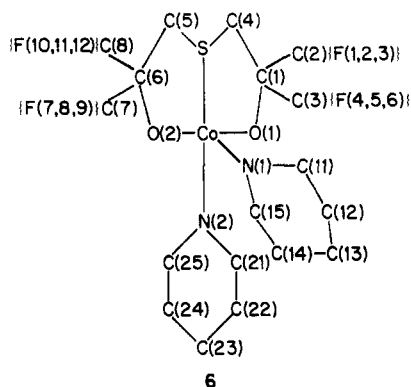
<sup>a</sup> Bond lengths in Å; angles in deg.

hydrogen atom temperature factors were fixed at 1.2× the isotopic temperature factor of the bonded carbon atom. In the final cycles of block-diagonal refinement, all of the non-hydrogen atoms were described anisotropically, and the hydrogen atom contributions were included but not refined. The maximum shift/σ on a parameter was 0.006. This gave  $R_1 = 4.35\%$  and  $R_2 = \{\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2\}^{1/2} = 4.84\%$ . The following data for compound 6 are reported: atomic positional parameters (Table V); selected interatomic positions and angles (Table VI); temperature factors (Table S-I); hydrogen atom coordinates and temperature factors (Table S-II); interatomic distances and angles associated with the CF<sub>3</sub> groups (Table S-III); values of  $10|F_o|$  and  $10|F_c|$  (Table S-IV).

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**Structure Description.** An ORTEP view of the structure of the cobalt complex **6** is shown as Figure 1. The atom-numbering scheme is shown in the line diagram



The cobalt(II) ion is in essentially regular trigonal-bipyramidal coordination. The apical sulfur atom makes angles of 82.8 (1), 82.7 (1), and 96.6 (1) $^\circ$  with the three equatorial atoms O(1), O(2), and N(1), respectively. The bite angle between the two alkoxy oxygen donors is 129.9 $^\circ$ , marginally greater than an ideal 120 $^\circ$ , and the equatorial pyridine molecule lies almost in the plane and equidistant from the oxygen atoms. The second pyridine molecule occupies an apical position with its plane approximately parallel to the O—O axis of ligand **4**. The S—Co—N(2) axis of the molecule is slightly distorted from linearity [168.2 (1) $^\circ$  at Co] by displacement of the apical pyridine molecule toward ligand **4** and away from the equatorial pyridine molecule [ $\angle$ N(1)—Co—N(2) = 95.2 (2) $^\circ$ ].

Bond lengths from the ligands to cobalt are consistent with those previously reported. The two Co—O bonds are identical at 1.911 (4) Å, marginally shorter than those in the six-coordinate Co<sup>2+</sup> alkoxy complex we have studied previously.<sup>3</sup> It is difficult to compare the Co—S bond length of 2.553 (2) Å with previous values, as there are few structural reports on thioether complexes of cobalt, but 2.29 Å has been found in a six-coordinate complex of Co(ClO<sub>4</sub>)<sub>2</sub> with 2,5-dithiahexane.<sup>11</sup> In a six-coordinate Co<sup>2+</sup> complex of the tridentate ligand 1,4,7-trithianonane, the Co—S distances are in the range 2.24–2.37 Å.<sup>12</sup> Our slightly longer Co—S bond length in **6** may be associated with the apical position of the donor atom in the complex; there is a barely significant ( $\Delta/\sigma = 2.3$ ) difference in the Co—N bond lengths for apical pyridine, 2.102 (5) Å, and equatorial pyridine, 2.087 (4) Å.

The closest nonbonded contact between molecules is 2.422 Å between F(3) and H(24), and there is no evidence of any appreciable interaction between molecules in the crystal lattice.

## Results and Discussion

Although thioethers, R<sub>2</sub>S, are relatively poor ligands, their biological significance has ensured their transition-metal complexes of considerable attention, and a thorough discussion of this work has been given by Murray and Hartley.<sup>13</sup> They conclude that the neutral R<sub>2</sub>S ligand is both a weak  $\sigma$  donor and a weak  $\pi$  acceptor and that the stability of thioether complexes is significantly reduced by repulsion between the second nonbonding electron pair on sulfur and filled d orbitals on the metal atom. Consistent with this, stable complexes of monodentate thioethers are not generally found; the majority of those reported are formed by ligands in which there are either two such donor sites present or a combination of a thioether with some other donor species. A consequence of the weak interaction of the thioether with the metal ion is that the latter retains considerable electrophilic character. For example, structural studies on complexes of 2,5-dithiahexane (DTH) have shown that the very weakly coordinating ClO<sub>4</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup> ions are bonded to the metal, giving trans six-coordinate complexes, in the compounds [Co(DTH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.<sup>11</sup>

[Cu(DTH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>,<sup>14</sup> and [Cu(DTH)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>.<sup>15</sup>

Our previous studies have demonstrated that a combination of one fluorinated alkoxy donor and one thioether produces a ligand that gives more stable complexes with the softer second- and third-row transition elements. It seemed likely, however, that the combination of two fluorinated alkoxy groups with one thioether would shift the overall preference of the ligand in favor of the formation of complexes with the harder first-row transition metals, and that has proved to be the case. We find that molecule **4**, in the diionized form, acts as a tridentate ligand, giving stable complexes with Co<sup>2+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup>, whereas we have not been able to isolate well-characterized complexes with heavier elements such as Pd<sup>2+</sup> or Pt<sup>2+</sup>.

For complexes of any tridentate ligand, two points of interest arise: the mode of attachment (facial or meridional) and the preferred total coordination number of the metal. Structural studies have been reported on a number of complexes containing neutral, tridentate, thioether ligands with the donor sequences N—S—N or N—S—S, and the coordination is generally found to be facial,<sup>16–19</sup> although a distorted meridional arrangement has also been reported.<sup>20</sup> The thiodiacetate ligand, S(CH<sub>2</sub>COO<sup>-</sup>)<sub>2</sub>, which is closely comparable to the diionized form of ligand **4**, is known to coordinate facially in a six-coordinate Cu<sup>2+</sup> complex.<sup>21</sup>

In the present study, we have been able to prepare neutral complexes by combining ligand **4** with divalent metals in a 1:1 molar ratio. Remaining coordination sites on the metal were filled by neutral ligands, and in the absence of other donors, hydrates were formed for Co<sup>2+</sup> and Cu<sup>2+</sup>. These were of uncertain stoichiometry, and better results were achieved by the use of organic, nitrogen-containing bases as coligands with **4**. With all three of the metals studied, stable complexes were given by the use of pyridine or *N,N,N',N'*-tetramethylethylenediamine, while bipyridyl was suitable for use with Co<sup>2+</sup> and Cu<sup>2+</sup>. Stoichiometry of each complex corresponded to five-coordination at the metal, with the donor set (O—S—O)(N,N) and visible spectra, in cases where a clear distinction was possible, were in agreement with this. The spectra of the nickel complexes (Table II) were the most definitive; five-coordination may be recognized by comparison with our previous studies<sup>22</sup> or with results on other well-characterized systems.<sup>23</sup>

No increase in the coordination number of the metal ion by solvation was apparent when each of the complexes was dissolved in strong donor solvents such as pyridine. The complexes **6**, **9**, and **11**, in which pyridine was the coligand, gave substantially the same spectra as they did in nondonor solvents. With the remaining complexes, the spectra approximated those of the pyridine complexes, suggesting that some ligand exchange was occurring. This result is entirely consistent with our past experience with complexes in which two —C(CF<sub>3</sub>)<sub>2</sub>O<sup>-</sup> groups are present; steric hindrance reduces solvation at the metal to five- rather than six-coordination.<sup>22</sup>

A complete structural determination on Co(O—S—O)<sub>2</sub>(py)<sub>2</sub> (**6**) confirmed five-coordination in a trigonal-bipyramidal geometry at the metal and showed the facial mode of coordination of the alkoxy—thioether ligand (Figure 1). The sulfur atom occupies an apical position in the structure, and its pyramidal geometry is consistent with the use of one out of the two nonbonding pairs

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for coordination to the metal ion. Clearly, the steric preferences of sulfur in a ligand of this type are incompatible with the donor sites occupying three positions coplanar with a metal atom, as would be required for meridional coordination, for coordination around one square-planar center, or for a tetradentate mode of coordination in which the sulfur atom is bridging between two square-planar centers as found in  $\text{Pt}_2\text{Cl}_4(\mu\text{-SEt}_2)_2$ .<sup>24</sup>

We conclude that the diol **4** is a useful tridentate ligand for the preparation of complexes of first-row transition metals, requiring a facial mode of coordination that provides favorable geometry at the central sulfur atom. The total coordination

number of the resulting complex is limited to 5 by the bulk of the ligand.

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**Supplementary Material Available:** Tables of temperature factors (Table S-I), hydrogen atom coordinates and temperature factors (Table S-II), interatomic distances and angles associated with the  $\text{CF}_3$  groups (Table S-III), and  $10|F_o|$  and  $10|F_c|$  (Table S-IV) (14 pages). Ordering information is given on any current masthead page.

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## Synthesis, Characterization, and Photobehavior of *cis*- and *trans*-Diammine(1,4,8,11-tetraazacyclotetradecane)chromium(III) and Some Related Compounds<sup>1</sup>

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The Cr(III) complexes *cis*- and *trans*-Cr(cyclam)( $\text{NH}_3$ )<sub>2</sub><sup>3+</sup>, where cyclam is the macrocyclic tetraamine 1,4,8,11-tetraazacyclotetradecane, have been synthesized by the reaction of liquid ammonia with the corresponding bis(nitrato)-Cr(III) species. The photophysical and photochemical behaviors of these compounds have been examined in some detail. Both isomers exhibit strong <sup>2</sup>E<sub>g</sub> → <sup>4</sup>A<sub>2g</sub> (*O<sub>h</sub>*) phosphorescence in room-temperature solution. The emission of the *trans* species is exceptionally intense and very long lived (136 μs, Me<sub>2</sub>SO, 20 °C). Both the intensity and lifetime of this *trans* emission display a remarkable 12-fold enhancement in Me<sub>2</sub>SO (20 °C) on N-H deuteration. This latter emission signal is in fact detectable with the naked eye and corresponds to a phosphorescence quantum yield at 20 °C of  $\phi_p = 2.3 \times 10^{-2}$  (comparable to Ru(bipyridine)<sub>2</sub><sup>2+</sup>). The corresponding *cis* species has a much shorter emission lifetime in room-temperature solution and displays only a weak deuterium isotope effect. Photochemically the two isomers also differ dramatically—the *trans* complex is photoinert, while the *cis* species exhibits facile  $\text{NH}_3$  release ( $\phi_{\text{NH}_3} = 0.2$ , aqueous solution, room temperature). These contrasting photobehaviors are compared with those previously reported for Cr( $\text{NH}_3$ )<sub>6</sub><sup>3+</sup>, Cr(en)<sub>3</sub><sup>3+</sup>, and the macrobicyclic sepulchrate ligand system Cr(sep)<sup>3+</sup>. Several different schemes for <sup>2</sup>E<sub>g</sub> excited-state decay are examined as possible rationalizations for these observations.

### Introduction

Considerable debate continues over the question as to which excited state(s) is (are) responsible for the observed photochemistry of octahedral Cr(III) complexes.<sup>2</sup> It has proven especially difficult to design experiments that identify unambiguously the state(s) responsible for the photoreaction component that is quenched on selective <sup>2</sup>E<sub>g</sub> (*O<sub>h</sub>*) excited-state quenching.<sup>2-7</sup> The relative merits of two alternative explanations for this reaction component—namely direct <sup>2</sup>E<sub>g</sub> reaction or “delayed” quartet reaction via <sup>2</sup>E<sub>g</sub> → <sup>4</sup>T<sub>2g</sub> back intersystem crossing (back-ISC)—have been argued for several years.<sup>2</sup> Both pathways have been advanced as rationalizations for the short lifetime and significant temperature dependence generally observed for <sup>2</sup>E<sub>g</sub> → <sup>4</sup>A<sub>2g</sub> phosphorescence in room-temperature solutions. Very recently, Endicott and co-workers<sup>7</sup> have proposed a third model for <sup>2</sup>E<sub>g</sub> relaxation that involves vibrationally promoted surface crossing to a ground-state intermediate species, with subsequent partitioning between reaction and nonradiative relaxation to product and parent

ground-state surfaces, respectively.

As one approach to this problem we have recently examined the photobehavior of *trans*-[Cr(cyclam)(CN)<sub>2</sub>]ClO<sub>4</sub>, where cyclam is the macrocyclic tetradentate amine ligand 1,4,8,11-tetraazacyclotetradecane.<sup>8</sup> The choice of this particular complex for investigation followed from consideration of current theoretical models for predicting Cr(III) photochemical reactivity<sup>2,9,10</sup> and recent experimental data<sup>11,12</sup> for the analogous nonmacrocyclic systems *trans*-Cr( $\text{NH}_3$ )<sub>4</sub>(CN)<sub>2</sub><sup>+</sup> and *trans*-Cr(en)<sub>2</sub>(CN)<sub>2</sub><sup>+</sup>. These latter complexes differ from most Cr(III) amine species in that the axial cyanide ligands have stronger ligand field (LF) strengths than the in-plane amine ligands, and theory predicts (as experimentally observed)<sup>11,12</sup> that photolabilization should be predominantly restricted to the in-plane amine positions. We were hopeful that for the cyclam analogue the presence of the macrocyclic ring would seriously restrict cleavage of an individual Cr-amine bond and render cyclam ligand loss highly improbable.

In keeping with this expectation, *trans*-Cr(cyclam)(CN)<sub>2</sub><sup>+</sup> displayed no discernible photochemical reactivity under LF excitation and exhibited an exceptionally intense, long-lived (340

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