Activation of Chelated Thioethers by Base. Ring-Size-Specific Transformations of Salicylaldimine-Substituted Dithiaalkanes Bonded to Trivalent Cobalt

Partha Chakraborty, Swapan Kumar Chandra, and Animesh Chakravorty*

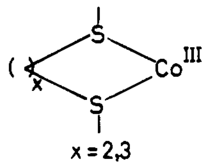
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Calcutta 700 032, India

Received April 13, 1994[⊗]

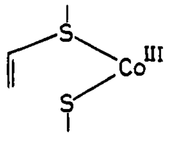
The parent ligands used are bis(salicylaldimines), $C_6H_4(OH)CH{=}N(CH_2)_2S(CH_2)_xS(CH_2)_2N{=}CH(OH)C_6H_4$ (abbreviated H_2sxL, $x = 2, 3$). The complexes $[Co^{III}(sxL)]ClO_4$, **5** ($x = 2$) and **6** ($x = 3$), were prepared in air from H_2sxL and cobalt(II) acetate tetrahydrate and sodium perchlorate. The X-ray structure of **5** has revealed $CoO_2N_2S_2$ coordination—the asymmetric unit consisting of a racemic pair of molecules. In acetonitrile solution, **5** and **6** react with sodium hydroxide affording respectively $Co^{III}_2(sl)_2(sl')_2$, **7**, and $Co^{III}(s3L')$, **8**. The ligands $(sl)^{2-}$ and $(sl')^{-}$ are deprotonated salicylaldimines of $NH_2(CH_2)_2SH$ and $NH_2(CH_2)_2SCHCH_2$, respectively. The ligand $(s3L')^{3-}$ is $(s3L)^{2-}$ with one α-methylene proton dissociated. The X-ray structure of complex **7** has revealed the presence of the rare thiolato-bridged planar motif $Co^{III}_2S_2$. The coordination sphere is of type $O_2N_2Co(\mu\text{-}S)_2CoN_2O_2$; the thioether functions are not coordinated and remain dangling. The primary process is α-methylene deprotonation. In the conversion **5** → **7**, C−S cleavage occurs, followed by thiolato-bridge formation and concomitant thioether displacement. In the transformation **6** → **8**, the metal binding simply shifts from thioether to the adjacent carbanionic site. All complexes have been characterized with the help of ^1H NMR data. Characteristic features: single azomethine signals for **5** and **6** but double signals for **7** and **8**; vinyl multiplets at δ 5.93 and 5.06 for **7** and CoCH triplet at δ 4.89 ($J = 9.7$ Hz) for **8**. Crystal data are as follows: $[Co(s2L)]ClO_4$, crystal system orthorhombic, space group $Pna2_1$, $a = 34.13(2)$ Å, $b = 11.191(7)$ Å, $c = 11.401(6)$ Å, $V = 4355(4)$ Å^3, $Z = 8$, $R = 7.38\%$, $R_w = 7.21\%$; $Co_2(sl)_2(sl')_2{\cdot}2MeCN$, crystal system triclinic, space group $P\bar{1}$, $a = 10.467(5)$ Å, $b = 13.701(7)$ Å, $c = 17.364(10)$ Å, $\alpha = 96.72(4)°$, $\beta = 99.68(4)°$, $\gamma = 107.86(4)°$, $V = 2298(2)$ Å^3, $Z = 2$, $R = 8.23\%$, $R_w = 8.29\%$.

Introduction

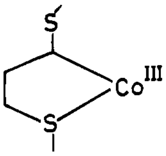
This work stems from our interest in the coordination chemistry of the thioether function,[1−4] especially its activation by chelation.[5−8] It was recently shown that a group of cobalt(III) complexes incorporating the dithiaalkyl chelate motif **1** undergoes base-induced transformations that are ring-size-specific: **1** → **2** when the ring is five-membered ($x = 2$) and **1** → **3** when it is six-membered ($x = 3$). The scope of this fascinating x-selective reactivity pattern is under scrutiny in this laboratory. In this paper, we examine the case of a pair of salicylaldimine chelates incorporating **1**. The synthesis and characterization of the parent and transformed complexes are reported along with X-ray structures of the $x = 2$ parent and the product of its reaction with base. The latter has the thiolato-bridged motif **4** instead of motif **2**.



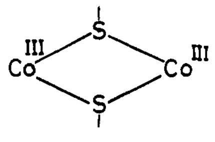
1



2



3



4

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1994.

(1) Chakraborty, P.; Chandra, S. K.; Chakravorty, A. *Inorg. Chem.* **1993**, *32*, 5349.

(2) (a) Choudhury, S. B.; Ray, D.; Chakravorty, A. *Inorg. Chem.* **1991**, *30*, 4354. (b) Ray, D.; Pal, S.; Chakravorty, A. *Inorg. Chem.* **1986**, *25*, 2674. (c) Karmakar, S.; Choudhury, S. B.; Ray, D.; Chakravorty, A. *Polyhedron* **1993**, *12*, 291. (d) Karmakar, S.; Choudhury, S. B.; Ray, D.; Chakravorty, A. *Polyhedron* **1993**, *12*, 2325.

(3) (a) Chattopadhyay, S.; Sinha, C.; Basu, P.; Chakravorty, A. *Organometallics* **1991**, *10*, 1135. (b) Sinha, C.; Bandyopadhyay, D.; Chakravorty, A. *Inorg. Chem.* **1988**, *27*, 1173. (c) Chattopadhyay, S.; Sinha, C.; Choudhury, S. B.; Chakravorty, A. *J. Organomet. Chem.* **1992**, *427*, 111 and references therein.

(4) (a) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365. (b) Blake, A. J.; Schröder, M. *Adv. Inorg. Chem.* **1990**, *35*, 1. (c) Cooper, S. R.; Rawle, S. C. *Struct. Bonding (Berlin)* **1990**, *72*, 1.

(5) (a) Chakraborty, P.; Karmakar, S.; Chandra, S. K.; Chakravorty, A. *Inorg. Chem.* **1994**, *33*, 816. (b) Chakraborty, P.; Chandra, S. K.; Chakravorty, A. *Organometallics* **1993**, *12*, 4726.

(6) (a) Blake, A. J.; Holder, A. J.; Hyde, T. I.; Küppers, H.-J.; Schröder, M.; Stötzel, S.; Wieghardt, K. *J. Chem. Soc., Chem. Commun.* **1989**, 1600. (b) Bennett, M. A.; Goh, L. Y.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1180. (c) Sellman, D.; Barth, I.; Knoch, F.; Moll, M. *Inorg. Chem.* **1990**, *29*, 1822.

(7) (a) Kofod, P.; Larsen, E.; Larsen, S.; Petersen, C. H.; Springborg, J.; Wang, D.-N. *Acta Chem. Scand.* **1992**, *46*, 841. (b) Bjerrum, M. J.; Gajhede, M.; Larsen, E.; Springborg, J. *Inorg. Chem.* **1988**, *27*, 3960. (c) Kofod, P.; Larsen, E.; Petersen, C. H.; Springborg, J. *Acta Chem. Scand.* **1992**, *46*, 1149. (d) Sevdic, D.; Fekete, L. *Polyhedron* **1985**, *4*, 1371.

(8) (a) Coucouvanis, D.; Al-Ahmad, S.; Kim, C. G.; Koo, S.-M. *Inorg. Chem.* **1992**, *31*, 2996. (b) Seela, J. L.; Huffman, J. C.; Christou, G. *Polyhedron* **1989**, *8*, 1797. (c) Seela, J. L.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1987**, 1258. (d) Coucouvanis, D.; Lester, R. K.; Kanatzidis, M. G.; Kessissoglou, B. P. *J. Am. Chem. Soc.* **1985**, *107*, 8279. (e) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. *J. Am. Chem. Soc.* **1986**, *108*, 1358. (f) Kovacs, J. A. *Inorg. Chem.* **1993**, *32*, 1860.

0020-1669/94/1333-4959$04.50/0

Scheme 1

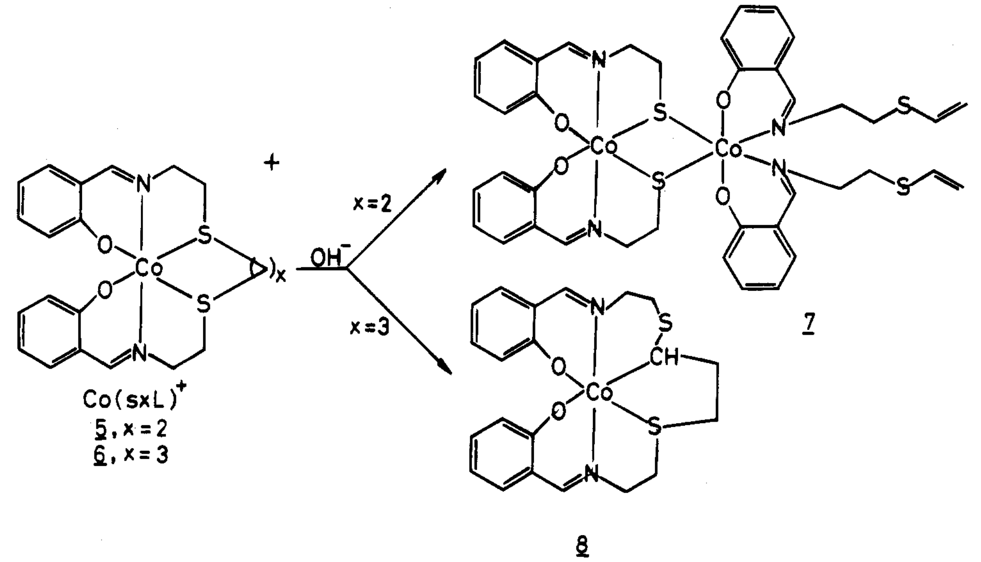


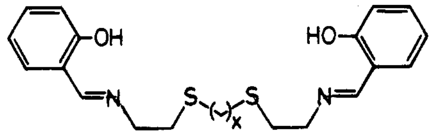
Table 1. Electronic and ^{1}H NMR Spectral Data

compound	UV−vis:[a] λ_{max}, nm (ϵ, M^{-1} cm^{-1})	^{1}H NMR: assignt, δ[b] in ppm
[Co(s2L)]ClO$_4$	680 (670), 460 (970),[c] 380 (4680)	CH=N, 8.37 (s); *o*-H, 6.85 (d); *m*-H, 6.65 (t); *p*-H, 7.23 (t); *m'*-H, 7.43 (d); −SCH$_2$CH$_2$S−, 4.28 (t); −NCH$_2$CH$_2$S−, 3.37−2.97 (m)[d]
[Co(s3L)]ClO$_4$	650 (260), 470 (620), 385 (4900)	CH=N, 8.39 (s); *o*-H, 6.81 (d); *m*-H, 6.59 (t); *p*-H, 7.17 (t); *m'*-H, 7.39 (d); −SCH$_2$CH$_2$CH$_2$S−, 4.48 (m),[e] 2.09 (m);[f] −NCH$_2$CH$_2$S−, 3.08−2.44 (m)[d]
Co$_2$(sl)$_2$(sl')$_2$	620 (270), 360 (5470)	CH=N, 7.87 (s), 7.70 (s); C$_6$H$_4$, 7.29−6.36 (m);[d] −CH=CH$_2$, 5.93 (m),[g] 5.06 (m);[h] other CH$_2$, 4.52−2.57 (m)[d]
Co(s3L')	550 (370), 370 (7600)	CH=N, 7.70 (s), 7.55 (s); C$_6$H$_4$, 7.24−6.37 (m);[d] CoCH, 4.89 (t); other CH$_2$, 4.23−2.0 (m)[d]

[a] Solvent is acetonitrile. [b] Meaning of letters given in parentheses: s, singlet; d, doublet; t, triplet; m, multiplet. Solvent used for [Co(s*x*L)]ClO$_4$ is DMSO-*d*$_6$, and that for Co$_2$(sl)$_2$(sl')$_2$ and Co(s3L') is CDCl$_3$. [c] Shoulder. [d] Group of multiplets. [e] Terminal methylene proton. [f] Middle methylene proton. [g] Vinyl methine proton. [h] Vinyl methylene proton.

Results and Discussion

Parent and Transformed Chelates. The complexes concerning us here are **5**−**8** (Scheme 1). The parent salicylaldimine ligands **9** and **10**,abbreviated as H$_2$s*x*L, are among the earliest



H$_2$sxL
9, x=2
10, x=3

linear hexadentate ligands initially devised for binding cobalt(III).[9] The crystal structure and solution reactivity of these classic complexes have remained unattended so far. We have isolated the Co(s*x*L)$^+$ cations as greenish brown perchlorate salts.

The two homologous (*x* = 2, 3) and otherwise very similar (see below) complexes react with alkali, affording entirely different products. When an acetonitrile solution of Co(s*x*L)$^+$ is stirred with 1 M aqueous sodium hydroxide, the color rapidly changes to brownish red. The complex isolated from the *x* = 2 reaction mixture is Co$_2$(sl)$_2$(sl')$_2$, **7**. For *x* = 3, it is Co(s3L'), **8**. Both **7** and **8** are dark solids obtained in excellent yields. The solvate **7**·2MeCN was used for crystallographic work.

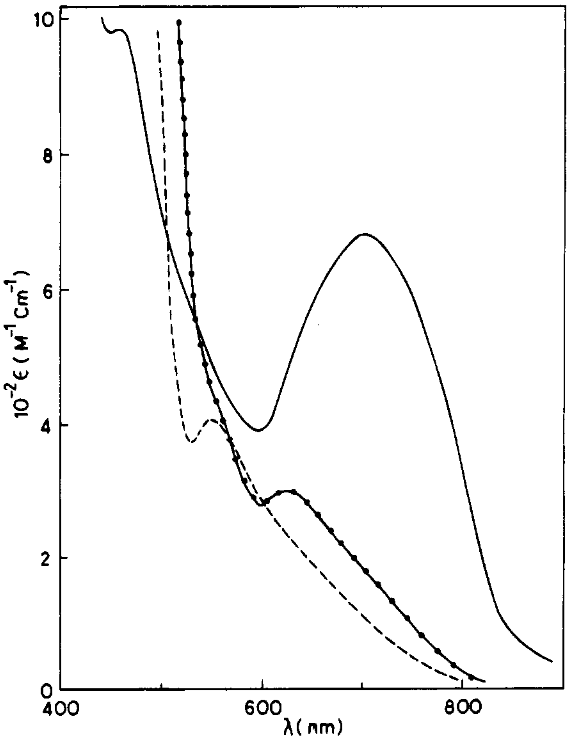


Figure 1. Electronic spectra of [Co(s2L)]ClO$_4$ (—), Co$_2$(sl)$_2$(sl')$_2$ (—•—) and Co(s3L') (---) in acetonitrile solution.

---

(9) (a) Dwyer, F. P. J.; Lions, F. *J. Am. Chem. Soc.* **1950**, *72*, 1545. (b) Dwyer, F. P. J.; Gill, N. S.; Gyarfas, E. C.; Lions, F. *J. Am. Chem. Soc.* **1952**, *74*, 4188. (c) Jones, C. J.; McCleverty, J. A. *Polyhedron* **1989**, *8*, 491 and references therein.

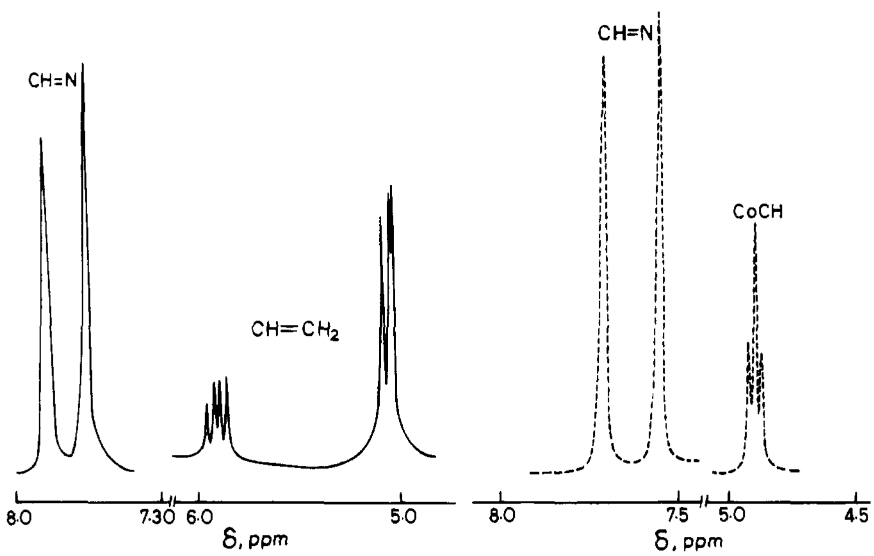


Figure 2. Selected regions of the ^{1}H NMR spectra of $Co_2(sl)_2(sl')_2$ (—) and Co(s3L′) (---) in $CDCl_3$ solution.

Characterization. Selected physical data for the complexes are collected in Table 1. The metal center is uniformly trivalent, and the chelates are diamagnetic. The $[Co(sxL)]ClO_4$ salts behave as 1:1 electrolytes (Λ = 130−140 Ω^{-1} cm^2 M^{-1}) in acetonitrile solution. Tris(salicylaldiminato)cobalt(III) chelates are known[10] to display a $t_2 \rightarrow e$ ($^1A_1 \rightarrow {}^1T_1$) ligand-field transition or split components thereof near 650 nm ($\epsilon \sim 400$ M^{-1} cm^{-1}). Complexes **5**−**7** show a similar band in the 600−700 nm region (Table 1, Figure 1). In **8** the corresponding band lies at significantly higher energy (550 nm) due to the strong ligand-field strength of the coordinated carbanionic site.

The ^{1}H NMR spectra (Table 1) of the complexes at 270 MHz reveal that in solution the $Co(sxL)^+$ species have effective C_2 symmetry, the halves of each molecule being equivalent. The spectra are mostly first order in nature, and the observed resonances are readily assigned to individual proton types on the basis of spin−spin structure and chemical shift trends. In the transformed complexes, $Co_2(sl)_2(sl')_2$ and Co(s3L′), there is no 2-fold symmetry, as is clearly revealed by the appearance of two distinct azomethine singlets in each case (Figure 2) and by the increase in spectral complexity in both the aromatic and aliphatic regions (Table 1).

In $Co_2(sl)_2(sl')_2$, the multiplets in the δ 5−6 region are diagnostic of the vinyl function.[5a,6a,c] Their presence is consistent with C−S cleavage, but beyond this, the NMR results (Table 1, Figure 2) could not provide any clue for the unusual dinuclear binding mode **7**, which was revealed only through X-ray structure determination (see below). In Co(s3L′), a crucial NMR feature is a triplet (J = 9.7 Hz) corresponding to one proton at δ 4.89 (Figure 2). This is assigned to the −SCHCo proton, the spin structure arising due to the adjacent methylene function. Cobalt(III)-coordinated alkyl functions forming part of a polydentate frame usually resonate at low fields.[5−11] In $Co(sxL)^+$, the dithiaalkyl $-SCH_2$ resonances already lie at quite low fields: δ 4.28 (x = 2) and δ 4.48 (x = 3) (Table 1). In Co(s3L′), the −SCHCo resonance is expected to occur at an even lower field and it does. The NMR results are entirely consistent with the formulation **8** for the organocobalt complex Co(s3L′). In the absence of thiolate functions, a complication like dinucleation is not expected to occur here.

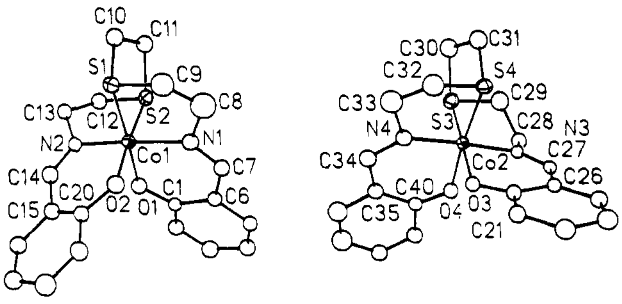


Figure 3. Perspective view and atom-labeling scheme for $Co(s2L)^+$ with 30% probability ellipsoids for cobalt and sulfur atoms.

The $Co(sxL)^+$ cation is spontaneously formed upon reacting H_2sxL with bivalent cobalt salts in air. Evidently, oxygen is the oxidant, and this is consistent with the low cyclic voltammetric $Co(sxL)^+$−Co(sxL) reduction potentials in acetonitrile solution: x = 2, −0.385 V vs SCE; x = 3, −0.380 V vs SCE. The couple is nearly reversible with a peak-to-peak separation of 60−70 mV. The complexes $Co_2(sl)_2(sl')_2$ and Co(s3L′) are not reducible up to −1.0 V. Both thiolate and carbanionic bindings provide extra stability to the trivalent metal center with respect to reduction.[5]

Structures. Single crystals of the complexes were difficult to grow, and for **8** we had no success at all. The X-ray structures of the pair $[Co(s2L)]ClO_4$ and $Co_2(sl)_2(sl')_2{\cdot}2MeCN$ have been determined using the best available crystals, which were still relatively weakly diffracting, resulting in limited data sets and somewhat high bond esd's. Molecular views are shown in Figures 3 and 4, and selected bond parameters are listed in Tables 2 and 3.

Orthorhombic crystals of $[Co(s2L)]ClO_4$ belong to the polar space group $Pna2_1$ with Z = 8, implying that the asymmetric unit consists of two independent molecules. These are metrically very similar (Figure 3 and Table 2), but they differ in their configurations. The two thioether sites in a given molecule have the same chiral configuration, which is enantiomeric to that in the other molecule. The configurations of the cobalt sites in the two molecules are also enantiomeric. The asymmetric unit is thus essentially constituted of a racemic $[Co(s2L)]ClO_4$ pair.

The ligand binds the metal in a hexadentate fashion, each ONS-coordinating half spanning meridionally. Unlike the structure in solution, there is no 2-fold symmetry. The distorted octahedral $CoO_2N_2S_2$ coordination spheres have Co−S lengths

---

[10] (a) Chakravorty, A.; Kalia, K. C.; Kannan, T. S. *Inorg. Chem.* **1966**, *5*, 1623. (b) Chakravorty, A.; Kalia, K. C. *Inorg. Chem.* **1967**, *6*, 690. (c) Chakravorty, A.; Behera, B. *Inorg. Chem.* **1967**, *6*, 1812.

[11] Broderick, W. E.; Kanamori, K.; Willett, R. D.; Legg, J. I. *Inorg. Chem.* **1991**, *30*, 3875.

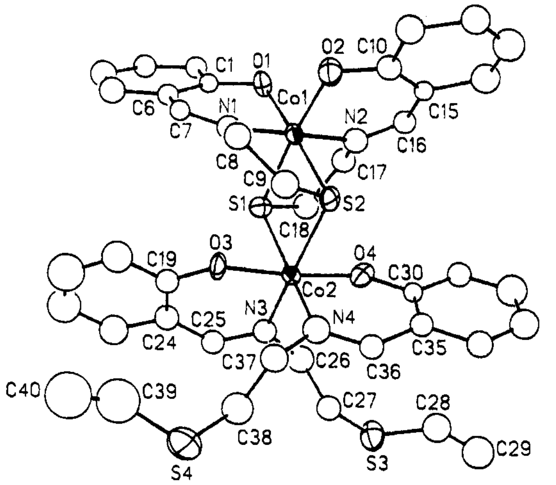


Figure 4. Perspective view and atom-labeling scheme for $Co_2(sl)_2(sl')_2$ with 30% probability ellipsoids for cobalt, sulfur, and oxygen atoms.

Table 2. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $[Co(s2L)]ClO_4$

Distances			
Co(1)−S(1)	2.231(6)	Co(2)−S(3)	2.221(6)
Co(1)−S(2)	2.197(6)	Co(2)−S(4)	2.195(6)
Co(1)−O(1)	1.900(13)	Co(2)−O(3)	1.898(12)
Co(1)−O(2)	1.946(14)	Co(2)−O(4)	1.944(14)
Co(1)−N(1)	1.874(15)	Co(2)−N(3)	1.936(15)
Co(1)−N(2)	1.931(15)	Co(2)−N(4)	1.880(16)

Angles			
O(1)−Co(1)−O(2)	92.4(6)	O(3)−Co(2)−O(4)	90.3(4)
O(1)−Co(1)−N(1)	93.9(6)	O(3)−Co(2)−N(3)	92.7(6)
O(1)−Co(1)−N(2)	84.8(6)	O(3)−Co(2)−N(4)	86.6(6)
O(1)−Co(1)−S(1)	176.6(4)	O(3)−Co(2)−S(3)	178.9(4)
O(1)−Co(1)−S(2)	88.9(5)	O(3)−Co(2)−S(4)	87.5(4)
O(2)−Co(1)−N(1)	82.2(6)	O(4)−Co(2)−N(3)	82.0(6)
O(2)−Co(1)−N(2)	94.1(6)	O(4)−Co(2)−N(4)	94.4(6)
O(2)−Co(1)−S(1)	86.7(4)	O(4)−Co(2)−S(3)	89.1(4)
O(2)−Co(1)−S(2)	176.5(4)	O(4)−Co(2)−S(4)	174.3(4)
N(1)−Co(1)−N(2)	176.0(7)	N(3)−Co(2)−N(4)	176.4(7)
N(1)−Co(1)−S(1)	89.2(5)	N(3)−Co(2)−S(3)	88.0(5)
N(1)−Co(1)−S(2)	94.4(5)	N(3)−Co(2)−S(4)	92.8(5)
N(2)−Co(1)−S(1)	92.0(5)	N(4)−Co(2)−S(3)	92.7(5)
N(2)−Co(1)−S(2)	89.4(5)	N(4)−Co(2)−S(4)	90.7(5)
S(1)−Co(1)−S(2)	92.3(2)	S(3)−Co(2)−S(4)	93.3(2)

in the range 2.195(6)−2.231(6) Å, which can be compared with the range 2.23−2.26 Å observed for certain other thioether complexes of trivalent cobalt.[5,12]

In $Co_2(sl)_2(sl')_2{\cdot}2MeCN$, the tridentate $(sl)^{2-}$ ligand is the Schiff base condensate of salicylaldehyde and 2-aminoethanethiolate. The $(sl)^{2-}$ pair provides the $CoO_2N_2S_2$ coordination sphere to Co(1), each $(sl)^{2-}$ spanning meridionally. The two thiolate atoms lie in cis positions and bridge Co(1) with Co(2). The $(sl')^{-}$ ligands are bonded only to Co(2) in bidentate ON-coordinating fashion. The vinyl thioether functions dangle from cis positions of the coordination sphere (Figure 4). The coordination sphere of Co(2) is also of the type $CoO_2N_2S_2$. The cobalt−ligand lengths in the present complex are generally comparable to those in $[Co(s2L)]ClO_4$. The Co^{III}−S lengths are not expected to vary much between thioether and thiolate sulfur.[5] The average C=C distance is 1.25(7) Å.

Table 3. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $[Co_2(sl)_2(sl')_2]{\cdot}2MeCN$

Distances			
Co(1)−S(1)	2.228(10)	Co(2)−S(1)	2.294(8)
Co(1)−S(2)	2.225(8)	Co(2)−S(2)	2.261(10)
Co(1)−O(1)	1.930(15)	Co(2)−O(3)	1.893(17)
Co(1)−O(2)	1.926(23)	Co(2)−O(4)	1.918(19)
Co(1)−N(1)	1.932(24)	Co(2)−N(3)	1.946(26)
Co(1)−N(2)	1.917(27)	Co(2)−N(4)	1.909(22)
C(28)−C(29)	1.276(47)	C(39)−C(40)	1.216(76)
Co(1)···Co(2)	3.342(3)	S(1)···S(2)	3.019(7)

Angles			
O(1)−Co(1)−O(2)	92.6(8)	O(3)−Co(2)−O(4)	173.5(8)
O(1)−Co(1)−N(1)	93.7(8)	O(3)−Co(2)−N(3)	94.1(9)
O(1)−Co(1)−N(2)	87.3(8)	O(3)−Co(2)−N(4)	90.2(9)
O(1)−Co(1)−S(1)	92.6(6)	O(3)−Co(2)−S(1)	84.5(5)
O(1)−Co(1)−S(2)	177.6(7)	O(3)−Co(2)−S(2)	91.5(6)
O(2)−Co(1)−N(1)	86.5(10)	O(4)−Co(2)−N(3)	90.3(9)
O(2)−Co(1)−N(2)	93.1(11)	O(4)−Co(2)−N(4)	94.0(9)
O(2)−Co(1)−S(1)	174.6(6)	O(4)−Co(2)−S(1)	90.7(5)
O(2)−Co(1)−S(2)	89.4(6)	O(4)−Co(2)−S(2)	83.6(6)
N(1)−Co(1)−N(2)	179.0(6)	N(3)−Co(2)−N(4)	95.9(11)
N(1)−Co(1)−S(1)	94.4(8)	N(3)−Co(2)−S(1)	90.6(6)
N(1)−Co(1)−S(2)	85.2(6)	N(3)−Co(2)−S(2)	171.1(8)
N(2)−Co(1)−S(1)	85.9(9)	N(4)−Co(2)−S(1)	171.9(9)
N(2)−Co(1)−S(2)	93.9(7)	N(4)−Co(2)−S(2)	91.0(9)
S(1)−Co(1)−S(2)	85.4(3)	S(1)−Co(2)−S(2)	83.0(3)
Co(1)−S(1)−Co(2)	95.3(9)		
Co(1)−S(2)−Co(2)	96.3(3)		

Table 4. Crystallographic Data

	$[Co(s2L)]ClO_4$	$[Co_2(sl)_2(sl')_2]{\cdot}2MeCN$
chem formula	$C_{20}H_{22}N_2O_6S_2ClCo$	$C_{44}H_{48}N_6O_4S_4Co_2$
fw	544.9	971.0
space group	$Pna2_1$	$P\bar{1}$
a, Å	34.13(2)	10.467(5)
b, Å	11.191(7)	13.701(7)
c, Å	11.401(6)	17.364(10)
α, deg		96.72(4)
β, deg		99.68(4)
γ, deg		107.86(4)
V, Å^3	4355(4)	2298(2)
Z	8	2
T, °C	23	23
λ, Å	0.710 73	0.710 73
ϱ_{calcd}, g cm^{-3}	1.662	1.403
μ, cm^{-1}	11.44	9.51
transm coeff	0.6132−0.7145	0.6944−0.9229
R,[a] %	7.37	8.23
R_w,[b] %	7.15	8.29
GOF[c]	1.28	0.53

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; $g = 0.001$ for $[Co(s2L)]ClO_4$ and 0.0003 for $Co_2(sl)_2(sl')_2{\cdot}2MeCN$. [c] The goodness of fit is defined as $[w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o and n_v denote the numbers of data and variables, respectively.

The Co_2S_2 bridge in $Co_2(sl)_2(sl')_2{\cdot}2MeCN$ has an anti configuration and is excellently planar with a mean deviation of 0.02 Å. The average Co(1)−S length is 0.05 Å shorter than the corresponding Co(2)−S length. The Co···Co and S···S contacts are 3.342(3) and 3.019(7) Å, respectively. Structurally characterized complexes incorporating thiolato-bridged cobalt(III) pairs are very rare,[13,14] and only one other example[15] of the $Co^{III}_2S_2$ motif is known to us.

Comparison with Other Systems. Our findings for the triazene 1-oxide system **11** taken collectively with certain

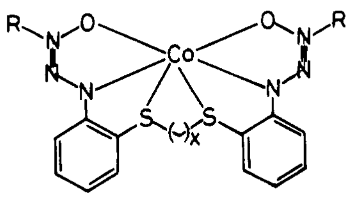
---

(12) Küppers, H.-J.; Neves, A.; Pomp, C.; Ventur, D.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 2400.

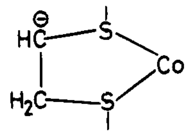
(13) $Co^{II}_2S_2$ species are more common: (a) Hagen, K.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 418. (b) Tremel, W.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 634. (c) Power, P. P.; Shoner, S. C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 330.

(14) Triply thiolate-bridged binuclear/trinuclear cobalt(III): (a) Mikuriya, M.; Kida, S.; Ueno, S.; Murase, I. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1857. (b) Heeg, M. J.; Blinn, E. L.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 1118.

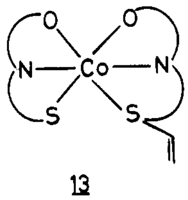
(15) Lewis, D. F.; Lippard, S. J.; Zubieta, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 1563.



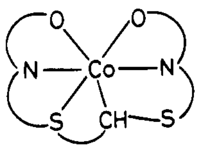
11



12



13



14

literature results led us to propose a general rationale for the base-induced transformation of motif **1**.[5] The primary process is α-methylene deprotonation, affording intermediate **12**, which transforms to **2** when $x = 2$ and to **3** when $x = 3$. In case of **11**, the coordination types of the products are **13** (for $x = 2$) and **14** (for $x = 3$), both structurally characterized.[5] Coordination type **14** is similar to that of Co(s3L′), **8**. Thus the transformation behaviors of Co(s3L)$^+$ and **11** ($x = 3$) are entirely parallel.

On the other hand, Co(s2L)$^+$ and **11** ($x = 2$) appear to behave differently, the products being $Co_2(sl)_2(sl')_2$ and **13**, respectively. The origin of this difference is believed to lie primarily in the nature of the thiolate function. Since Co(s2L)$^+$ is mononuclear (X-ray work), C−S cleavage should indeed afford a species of coordination type **13**. But here the thiolate function is aliphatic, while in the triazene 1-oxide system it is aromatic. The aliphatic thiolate function bonded to cobalt(III) is known to be a potent bridge-maker.[16] We propose that coordination type **13** originating from Co(s2L)$^+$ undergoes intermolecular reorganization to accommodate thiolate bridging with concomitant displacement of coordinated thioether, finally affording $Co_2(sl)_2(sl')_2$. This proposal preserves the basic $x = 2$ transformation sequence **1** → **12** → **2** for Co(s2L)$^+$, the formation of the dinuclear complex being only a subsequent complication. In the general scheme[5] of activation of the chelate motif **1**, the $x = 2$ salicylaldimine is an interesting variant but in the final product only.

Concluding Remarks

The main findings will now be stated. The scope of homolog-selective base-activated transformation of the dithiaalkyl chelate motif **1** has been expanded to include the classic salicylaldimine complexes Co(s*x*L)$^+$, and in this process an interesting variation has been revealed.

The Co(s3L)$^+$ complex, like the other $x = 3$ systems scrutinized so far, has afforded a stable organocobalt product Co(s3L′), **8**, incorporating motif **3**. On the other hand, Co(s2L)$^+$, unlike other $x = 2$ species, did not yield a product having motif **2**. Instead, dinuclear $Co_2(sl)_2(sl')_2$, **7**, is isolated. It is proposed that a mononuclear intermediate of type **13** is formed only to undergo dinucleation promoted by the strong bridging ability of the aliphatic thiolate function. The basic transformation scheme applies to Co(s2L)$^+$ as well as to other systems, dinucleation being a secondary process.

The X-ray structure of dinuclear **7**·2MeCN has revealed the presence of the very rare $Co^{III}_2S_2$ motif **4**, which is excellently

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients[a] (Å^2 $\times 10^3$) for [Co(s2L)]ClO$_4$

	x	*y*	*z*	*U*(eq)
Co(1)	1249(1)	1044(2)	0	31(1)
Co(2)	3715(1)	1240(2)	536	29(1)
Cl(1)	−303(2)	−2325(6)	1339(7)	57(2)
Cl(2)	2269(2)	7356(8)	1363(7)	71(3)
S(1)	1119(1)	−909(4)	38(6)	38(2)
S(2)	1444(2)	966(5)	−1834(5)	36(2)
S(3)	4181(2)	770(5)	−707(5)	39(2)
S(4)	3339(2)	−281(5)	−7(6)	45(2)
O(1)	1385(3)	2689(11)	28(14)	46(4)
O(2)	1044(4)	1100(12)	1591(12)	44(4)
O(3)	3339(4)	1613(12)	1762(12)	40(4)
O(4)	4029(3)	2559(11)	998(11)	32(3)
O(5)	13(7)	−2327(28)	2070(23)	179(17)
O(6)	−641(5)	−2125(19)	1921(17)	100(9)
O(7)	−335(6)	−3332(17)	585(19)	106(9)
O(8)	−268(5)	−1296(19)	514(25)	125(10)
O(9)	2439(9)	8340(29)	1949(32)	195(19)
O(10)	2555(7)	6928(26)	664(24)	168(14)
O(11)	2151(6)	6497(17)	2288(22)	120(11)
O(12)	1924(6)	7793(25)	862(24)	159(14)
N(1)	723(4)	1336(13)	−378(13)	33(4)
N(2)	1782(4)	787(14)	498(15)	39(4)
N(3)	3488(5)	2274(14)	−569(15)	37(4)
N(4)	3928(4)	222(13)	1750(13)	28(4)
C(1)	1123(5)	3578(16)	125(19)	37(5)
C(2)	1288(6)	4743(17)	266(19)	48(6)
C(3)	1043(7)	5689(21)	415(22)	63(7)
C(4)	626(6)	5543(18)	408(20)	49(6)
C(5)	475(6)	4461(18)	266(18)	45(6)
C(6)	731(6)	3448(17)	97(20)	41(5)
C(7)	551(6)	2318(19)	−215(20)	49(6)
C(8)	483(6)	309(19)	−811(19)	42(6)
C(9)	589(6)	−832(19)	−188(20)	48(6)
C(10)	1324(6)	−537(19)	−2304(20)	48(6)
C(11)	1297(6)	−1515(19)	−1332(19)	47(6)
C(12)	1936(7)	1000(24)	−1572(24)	70(8)
C(13)	2064(8)	594(26)	−458(27)	89(9)
C(14)	1916(6)	748(19)	1543(19)	41(6)
C(15)	1669(6)	850(17)	2568(18)	35(5)
C(16)	1855(6)	771(19)	3696(19)	39(6)
C(17)	1652(6)	759(19)	4711(19)	50(6)
C(18)	1228(7)	817(20)	4669(20)	56(7)
C(19)	1049(6)	898(20)	3567(20)	46(6)
C(20)	1248(5)	959(16)	2553(16)	30(5)
C(21)	3030(6)	2213(17)	1633(17)	32(5)
C(22)	2787(6)	2363(19)	2641(19)	43(6)
C(23)	2463(6)	3064(20)	2625(21)	47(6)
C(24)	2360(8)	3604(25)	1603(26)	78(9)
C(25)	2564(7)	3499(21)	645(25)	67(7)
C(26)	2930(6)	2812(17)	605(20)	39(5)
C(27)	3142(6)	2828(19)	−477(20)	44(6)
C(28)	3685(7)	2393(21)	−1718(24)	67(7)
C(29)	4091(7)	2026(21)	−1694(23)	61(7)
C(30)	3995(6)	−553(21)	−1432(21)	54(7)
C(31)	3560(7)	−707(22)	−1394(22)	58(7)
C(32)	3530(7)	−1452(22)	970(22)	66(7)
C(33)	3671(6)	−840(19)	2055(20)	44(6)
C(34)	4246(5)	395(16)	2288(17)	27(5)
C(35)	4506(5)	1436(16)	2151(17)	28(5)
C(36)	4864(5)	1488(18)	2701(18)	39(5)
C(37)	5101(7)	2403(19)	2634(21)	51(6)
C(38)	4981(6)	3385(20)	2037(20)	48(6)
C(39)	4638(5)	3475(17)	1406(18)	38(5)
C(40)	4385(5)	2475(17)	1496(18)	33(5)

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

planar. The vinyl thioether functions are not coordinated and remain dangling. The lattice of [Co(s2L)]ClO$_4$ has the interesting feature of possessing an asymmetric unit constituted of a racemic pair of molecules.

---

[16] (a) Konno, T.; Nakayuki, T.; Okamoto, Ken-ichi; Hidaka, J. *Inorg. Chem.* **1992**, *31*, 1160. (b) Konno, T.; Okamoto, K.; Hidaka, J. *Inorg. Chem.* **1992**, *31*, 160.

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients[a] (Å^2 $\times$ 10^3) for $[Co_2(sl)_2(sl')_2]\cdot 2MeCN$

	x	*y*	*z*	*U*(eq)
Co(1)	−1326(4)	4532(3)	2505(2)	37(2)
Co(2)	1887(4)	4613(3)	2467(2)	36(2)
S(1)	−276(8)	3863(6)	1675(5)	48(3)
S(2)	771(8)	5316(6)	3261(5)	48(3)
S(3)	5606(9)	6132(6)	813(5)	82(4)
S(4)	5537(10)	3224(8)	4109(7)	110(5)
O(1)	−3121(18)	3802(12)	1834(10)	52(8)
O(2)	−2065(21)	5203(15)	3270(11)	69(10)
O(3)	1455(16)	3375(12)	2897(10)	52(7)
O(4)	2118(18)	5867(14)	2035(10)	53(8)
N(1)	−1442(22)	3468(17)	3155(13)	51(6)
N(2)	−1185(25)	5605(19)	1875(14)	62(8)
N(3)	2674(23)	4066(18)	1649(13)	55(7)
N(4)	3565(25)	5190(19)	3247(14)	67(7)
N(5)	7934(36)	816(27)	4345(20)	149(12)
N(6)	−58(29)	7833(22)	336(17)	112(9)
C(1)	−3597(22)	2751(17)	1634(13)	36(6)
C(2)	−4577(25)	2337(19)	890(14)	51(7)
C(3)	−5065(26)	1287(20)	694(15)	57(7)
C(4)	−4782(29)	634(24)	1165(17)	75(9)
C(5)	−3825(29)	1027(22)	1874(16)	69(8)
C(6)	−3221(24)	2125(18)	2129(13)	44(6)
C(7)	−2278(22)	2534(18)	2885(13)	37(6)
C(8)	−704(26)	3776(20)	3948(15)	59(8)
C(9)	622(28)	4624(21)	4036(16)	64(8)
C(10)	−1714(26)	6252(21)	3446(15)	56(7)
C(11)	−1951(28)	6609(22)	4192(16)	71(8)
C(12)	−1691(28)	7715(22)	4378(17)	72(8)
C(13)	−1298(32)	8326(27)	3865(19)	91(10)
C(14)	−1115(30)	7976(24)	3147(18)	81(9)
C(15)	−1318(22)	6872(17)	2929(13)	36(6)
C(16)	−1170(25)	6524(19)	2147(14)	52(7)
C(17)	−1251(28)	5324(21)	1032(14)	63(8)
C(18)	−436(30)	4618(22)	884(16)	72(8)
C(19)	1326(26)	2420(19)	2538(15)	52(7)
C(20)	649(32)	1593(25)	2859(20)	88(10)
C(21)	518(40)	606(34)	2491(24)	129(14)
C(22)	942(37)	400(32)	1836(22)	112(12)
C(23)	1652(32)	1232(25)	1488(20)	86(10)
C(24)	1835(27)	2286(22)	1823(16)	59(8)
C(25)	2538(26)	3081(19)	1466(15)	55(7)
C(26)	3361(30)	4694(22)	1083(17)	77(9)
C(27)	4834(27)	5314(20)	1452(16)	62(8)
C(28)	5966(33)	7383(24)	1336(19)	87(10)
C(29)	6793(37)	8204(28)	1186(20)	111(12)
C(30)	2991(23)	6838(16)	2427(13)	35(6)
C(31)	2726(27)	7674(20)	2088(15)	58(7)
C(32)	3543(35)	8654(27)	2414(19)	93(10)
C(33)	4591(33)	8862(26)	3008(18)	81(9)
C(34)	4874(28)	8065(21)	3331(16)	62(8)
C(35)	4012(25)	7025(19)	3066(14)	49(7)
C(36)	4333(26)	6183(18)	3435(14)	52(7)
C(37)	4153(28)	4567(21)	3798(16)	64(8)
C(38)	4883(33)	3933(24)	3389(18)	85(10)
C(39)	4220(51)	2045(38)	3883(31)	156(17)
C(40)	3973(56)	1347(40)	4265(27)	169(18)
C(41)	7841(35)	1264(27)	4900(21)	102(11)
C(42)	7860(41)	1834(31)	5596(22)	126(14)
C(43)	721(41)	8222(31)	13(22)	120(13)
C(44)	1661(38)	8760(29)	−397(22)	120(13)

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

Experimental Section

Materials. The purification of acetonitrile and dichloromethane and the preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were done as before.[17a] All other chemicals and solvents were of analytical grade and were used as received.

Physical Measurements. Spectra were recorded on the following equipment: UV−vis spectra, Hitachi 330 spectrophotometer; IR spectra, Perkin-Elmer 783 IR spectrophotometer; NMR spectra, Varian XL 270-MHz FTNMR spectrometer. Magnetic susceptibilities of solids were measured with a Model 155PAR vibrating-sample magnetometer fitted with a Walker Scientific L75FBAL magnet. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (CHN). Electrochemical measurements were performed on a PAR Model 370-4 electrochemistry system as reported earlier.[17b] All potentials reported in this work are uncorrected for junction contribution. Solution ($\sim 10^{-3}$ M) electrical conductivities were measured with the help of a Philips PR 9500 bridge. All electrochemical experiments were performed under a dinitrogen atmosphere.

Preparation of Compounds. The diamines 1,10-diaza-4,7-dithiadecane and 1,11-diaza-4,8-dithiaundecane were synthesized as before,[2a] and from these the ligands **9** and **10** were prepared according to literature methods.[9a,b] Our synthesis of the cobalt(III) complexes $[Co(s\mathit{x}L)]ClO_4$ has certain differences from the previous reports, and the details are given below.

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

[1,8-Bis(salicylideneamino)-3,6-dithiaoctane]cobalt(III) Perchlorate, $[Co(s2L)]ClO_4$, 5. To a dichloromethane solution (15 mL) of H_2s2L (0.20 g, 0.41 mmol) was added a methanolic solution (10 mL) of 0.102 g (0.41 mmol) of $Co(CH_3COO)_2\cdot 4H_2O$, and the resulting mixture was stirred in air at room temperature for 0.5 h. Then 0.056 g (0.40 mmol) of solid $NaClO_4\cdot H_2O$ was added, and the reaction mixture was stirred for further a period of 0.5 h. The dark solid was filtered off, washed with water and methanol, and finally dried in vacuo. Yield: 0.196 g (88%). Anal. Calcd for $C_{20}H_{22}N_2O_6S_2ClCo$: C, 44.04; H, 4.03; N, 5.14. Found: C, 43.98; H, 4.08; N, 5.17.

The complex $[Co(s3L)]ClO_4$, **6**, was prepared similarly (yield: 89%). Anal. Calcd for $C_{21}H_{24}N_2O_6S_2ClCo$: C, 45.08; H, 4.29; N, 5.01. Found: C, 45.12; H, 4.25; N, 4.96.

Conversion of $[Co(s2L)]ClO_4$, 5, to $Co_2(sl)_2(sl')_2$, 7. To an acetonitrile solution (15 mL) of 0.18 g (0.32 mmol) of **5** was added 50 mL of 1 M aqueous sodium hydroxide cooled to 283 K. The reaction mixture was then stirred at room temperature for 0.5 h. The color of the solution changed from greenish brown to brownish red. The acetonitrile layer was isolated and evaporated, affording a red mass, which was washed with water, extracted with dichloromethane, and chromatographed on silica gel with benzene−acetonitrile (1:3 v/v) as eluent. A red band was collected that upon removal of solvent furnished a brownish red solid, which was dried in vacuo. Yield: 0.211 g (74%). Anal. Calcd for $C_{40}H_{42}N_4O_4S_4Co_2$: C, 54.06; H, 4.73; N, 6.31. Found: C, 53.99; H, 4.78; N, 6.37.

Conversion of $[Co(s3L)]ClO_4$, 6, to Co(s3L′), 8. Complex **6** (0.15 g, 0.27 mmol) was dissolved in 15 mL of acetonitrile, and to this solution was added 50 mL of 1 M cold aqueous sodium hydroxide. The mixture was treated in the same manner as above. Chromatography on silica gel was performed with benzene−acetonitrile (1:4 v/v) as eluent. Yield: 0.092 g (75%). Anal. Calcd for $C_{21}H_{23}N_2O_2S_2Co$: C, 55.03; H, 5.02; N, 6.11. Found: C, 54.98; H, 4.99; N, 6.16.

X-ray Structure Determination. Crystals were grown (298 K) by slow diffusion of hexane into dichloromethane ($[Co(s2L)]ClO_4$, **5**, 0.14 × 0.22 × 0.46 mm^3) or acetonitrile into water ($Co_2(sl)_2(sl')_2\cdot 2MeCN$, **7**·2MeCN, 0.12 × 0.14 × 0.41 mm^3). The latter crystal was epoxy-coated to prevent solvent loss.

Cell parameters were determined by least-squares fits of 30 machine-centered reflections ($2\theta = 15-30°$). The space group for **7**·2MeCN was triclinic, and the structure was successfully solved in $P\bar{1}$. Systematic absences for **5** were compatible with space groups $Pna2_1$ and *Pnam*, but the latter did not afford any chemically significant structure while the former readily did. Data were collected by ω-scan technique in the ranges $2.0 \leqslant 2\theta \leqslant 42.0°$ for **7**·2MeCN and $3.0 \leqslant 2\theta \leqslant 46.0°$ for **5** on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo Kα radiation. Two check reflections measured after every 98 reflections showed no significant intensity reduction during exposure to X-rays (53 h for **7**·2MeCN and 37 h for **5**). Data were corrected for Lorentz−polarization and absorption effects. Of the 5323 (**7**·2MeCN) and 3593 (**5**) reflections collected,

---

(17) (a) Datta, D.; Mascharak, P. K.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 1673. (b) Chandra, S. K.; Basu, P.; Ray, D.; Pal, S.; Chakravorty, A. *Inorg. Chem.* **1990**, *29*, 2423.

4974 and 3276 were unique, of which 1686 ($I > 2\sigma(I)$) and 2014 ($I > 1.5\sigma(I)$) were respectively taken as observed for structure solutions.

Both structures were solved by direct methods. Due to the paucity of observed data, only the following atoms were made anisotropic: in **7**·2MeCN, Co, S, and O; in **5**, Co, S, and ClO_4. Hydrogen atoms were added at calculated positions with fixed $U = 0.08$ Å^2 in the last cycle of refinement. All refinements were performed by full-matrix least-squares procedures. The highest residuals were 0.51 e/Å^3 for **7**·2MeCN and 0.61 e/Å^3 for **5**. All calculations were done on a MicroVax II computer with the programs of SHELXTL-PLUS.[18] Significant crystal data are listed in Table 4. Atomic coordinates and isotropic thermal parameters are collected in Tables 5 and 6.

Acknowledgment. Crystallography was performed at the National Single Crystal Diffractometer Facility, Department of Inorganic Chemistry, Indian Association for the Cultivation of Science. We are thankful to the Department of Science and Technology and the Council of Scientific and Industrial Research for financial support. Affiliation with the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India, is acknowledged.

Supplementary Material Available: For [Co(s*x*L)]ClO_4 and $Co_2(sl)_2(sl')_2$·2MeCN complete bond distances (Tables S1 and S5) and angles (Tables S2 and S6), anisotropic thermal parameters (Tables S3 and S7), and hydrogen atom positional parameters (Tables S4 and S8) (14 pages). Ordering information is given on any current masthead page.

---

[18] Sheldrick, G. M. SHELXTL-PLUS 88. *Structure Determination Software Programs*; Nicolet Instrument Corp.: Madison, WI, 1988.