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Ring-Size Specific Transformations of Cobalt(III)–Thioether Chelates Activated by Base. Co–C Formation or C–S Cleavage?

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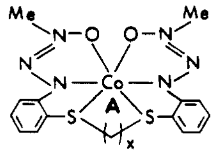
*Summary: The **A** ring which is six-membered in **1** and five-membered in **2** is activated by alkali leading to the transformations **1** → **3** (Co–C bond formation) and **2** → **4** (C–S bond cleavage). This specificity has been rationalized in terms of a simple scheme which is extendable to other systems as well. The X-ray structure of the 1:1 chloroform adduct of complex **3** is reported.*

We wish to disclose a remarkable case of reactivity differentiation between two thioether coordinated cobalt(III) complexes differing in the size of a chelate ring. The implication of the results in the broader context of thioether activation via metal binding is noted. The two complexes[1,2] Co(Me3L)$^+$, **1**, and Co(Me2L)$^+$, **2**, are derived from a pair of homologous hexadentate dithiaalkyl substituted triazene 1-oxides.[3] The chelate ring **A** is six-membered in **1** and five-membered in **2**. The complexes are stable in the solid state and in neutral solutions, but the **A** ring becomes reactive in alkaline media.



Co(MexL)$^+$

1, x = 3; **2**, x = 2

Treatment of an acetonitrile solution (50 mL) of[1] [Co(Me3L)]ClO$_4$·CH$_2$Cl$_2$ (0.40 g) with 1 M methanolic potassium hydroxide (100 mL) under ambient conditions leads to rapid color change from purple to green. After removal of solvent the solid residue was thoroughly washed with water, dried, and then crystallized from chloroform, affording the green organocobalt(III) complex **3** in the form of the chloroform adduct Co(Me3L′)·CHCl$_3$[4] in 65% yield. A similar treatment of [Co(Me2L)]ClO$_4$·CH$_2$Cl$_2$ with alkali led to the isolation of the nonorganometallic complex[2,5] **4** in similar yields. In the conversion **2** → **4** the hexadentate ligand has been cleaved into two parts via the scission of a C–S bond.

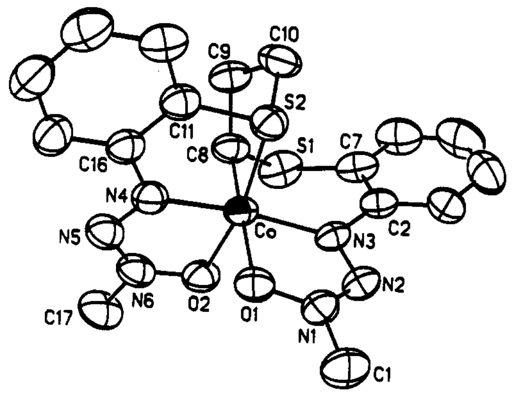
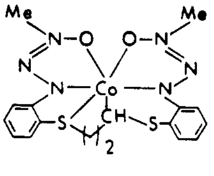


Figure 1. ORTEP plot and labeling scheme for Co(Me3L′) in its chloroform adduct with all atoms represented by their 50% probability ellipsoids.



Co(Me3L′)

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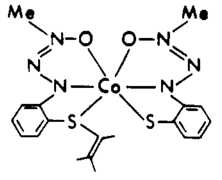

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The X-ray structure[6] of the Co(Me3L′) as its chloroform adduct is shown in Figure 1. The distorted octahedral coordination sphere is of type CoSCN$_2$O$_2$. The Co–C length, 1.969(5) Å, is normal for organocobalt(III) species wherein the coordinated alkyl carbon forms part of a polydentate ligand chain.[7-9] The ^{1}H NMR CoCH resonance in such species usually appear at relatively low

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(1) These purple complexes were prepared and isolated as perchlorates in the form of a 1:1 dichloromethane adduct [Co(Me*x*L)]ClO$_4$·CH$_2$Cl$_2$ by the straightforward solution reaction (MeOH–CH$_2$Cl$_2$) between ligand (H$_2$Me*x*L) and cobalt(II) perchlorate in the presence of hydrogen peroxide. The complexes have been fully characterized including X-ray structure determination in the case of $x = 3$.

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(3) (a) Ray, D.; Pal, S.; Chakravorty, A. *Inorg. Chem.* **1986,** *25,* 2674–2676. (b) Karmakar, S.; Choudhury, S. B.; Ray, D.; Chakravorty, A. *Polyhedron* **1993,** *12,* 291–296.

(4) Data for Co(Me3L′)·CHCl$_3$: UV–vis spectral data in dichloromethane (λ_{max}, nm (ϵ, M^{-1} cm^{-1})) 620 (320); the complex is diamagnetic. Anal. Calcd for C$_{18}$H$_{20}$N$_6$O$_2$S$_2$Cl$_3$Co: C, 37.05; H, 3.44; N, 14.41. Found: C, 37.16; H, 3.39; N, 14.45.

(5) Completely characterized via elemental analysis, UV–vis, and ^{1}H NMR spectroscopy as well as single crystal X-ray crystallography. Selected analytical data for **4**: ^{1}H NMR vinyl multiplets in CDCl$_3$ δ 6.07 (methine proton), 5.66 and 5.60 (methylene protons). Anal. Calcd for C$_{16}$H$_{17}$N$_6$O$_2$S$_2$Co: C, 42.86; H, 3.79; N, 18.75. Found: C, 42.90; H, 3.81; N, 18.71.

(6) X-ray quality crystals of Co(Me3L′)·CHCl$_3$ were obtained by slow evaporation of a chloroform solution of the complex. X-ray parameters for Co(Me3L′)·CHCl$_3$: C$_{18}$H$_{20}$N$_6$O$_2$S$_2$Cl$_3$Co, space group, $P2_1/n$ (No. 14), $a = 12.818(7)$ Å, $b = 14.597(8)$ Å, $c = 13.194(6)$ Å, $\beta = 97.67(4)°$; $V = 2447(2)$ Å^3; $Z = 4$; ρ calcd = 1.585 g/cm^3; λ(Mo Kα) = 0.710 73 Å. Data were collected ($3° \leqslant 2\theta \leqslant 52°$) on a Nicolet R3m/V diffractometer (296 K), corrections for Lorentz–polarization and absorption effects were made, and 2438 reflections satisfying $I > 3\sigma(I)$ were used for structure solution by direct methods using the SHELXTL-PLUS program package. Refinement was done by the full-matrix least-squares method. All nonhydrogen atoms were made anisotropic. Hydrogen atoms were added at calculated positions with fixed $U = 0.08$ Å^2 in the last cycle of refinement. The final $R = 4.03\%$, $R_w = 4.07\%$ and the largest residual was +0.39/−0.29 e/Å^3.

(7) Kofod, P.; Larsen, E.; Larsen, S.; Petersen, C. H.; Springborg, J.; Wang, D.-N. *Acta Chem. Scand.* **1992,** *46,* 841–853.

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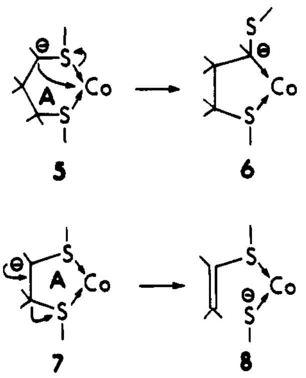
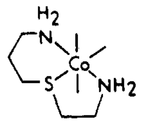
Scheme I



fields.[2,10] The resonance in Co(Me3L′) lies at δ 4.50, the splitting pattern being consistent with coupling to two inequivalent methylene protons ($CDCl_3$ solution). The two NMe resonances occur as singlets at δ 4.03 and 3.86 and the dimethylene bridge affords a multiplet centered at δ 2.04.

The logical first step in base-promoted activation of coordinated thioether functions is α-methylene deprotonation.[11,12] The observed formation of 3 and 4 can be rationalized as in Scheme I. In the case of 1 where the A ring is six-membered a simple rearrangement to a five-membered metallacycle as in 3 occurs. Here the metal center merely shifts its binding from a sulfur to an adjacent α-carbanionic site: a Co–C bond is formed with concomitant cleavage of a Co–S bond (5 → 6, Scheme I). In this process an adjacent chelate ring (incorporating the affected thioether function) becomes six-membered. In 2 the A ring is five-membered and a rearrangement as above would afford an unstable four-membered metallacycle. This route is therefore not followed and instead the anionic charge finds proximity to cobalt(III) via migration to a coordinated sulfur site resulting in heterolytic C–S cleavage and increase in the order of a C–C bond from one to two (7 → 8, Scheme I).

Certain reported instances of base-promoted activation of coordinated thioethers fit smoothly into the above scheme. The transformation 9 → 10 has been documented in 1,6-diamino-3-thiahexane complexes of cobalt(III).[7,8,12] On the other hand, complexes of 1,4,7-trithiacyclononane undergo C–S bond cleavage, 11 → 12.[11,13] The two reactions have so far remained as isolated and apparently unrelated events of thioether activation. Indeed, the process 11 → 12 has been considered to be a specialty of macrocyclic ligation.[7,11,13] Clearly, this is not so: vide 2 → 4. We further note that there is complete correspondence between 1 → 3 and 9 → 10 as well as between 2 → 4 and 11 → 12 in terms of the transformations observed vis-a-vis the size of the activated chelate ring. *When the ring is six-membered, rearrangement to a five-membered metallacycle with one Co–C bond occurs, and when it is five-membered, the ligand is cleaved into two parts at a C–S bond, generating a vinyl group and a coordinated thiolate function.* Ongoing studies indicate that the prospect of generalization of this rule for a wide variety of thioether chelates is bright.



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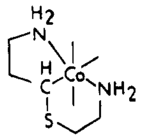

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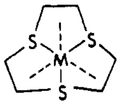

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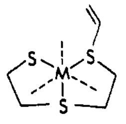

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Supplementary Material Available: For Co(Me3L′)·$CHCl_3$ tables of atomic coordinates with isotropic thermal parameters (Table S1), complete bond distances (Table S2) and angles (Table S3), anisotropic thermal parameters (Table S4), and hydrogen atom positional parameters (Table S5) (5 pages). Ordering information is given on any current masthead page.

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