Journal of Organometallic Chemistry, 216 (1981) C15—C18
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

A NEW DIAMAGNETIC TRINUCLEAR COBALT CARBONYL-SULFUR COMPLEX WITH A BRIDGING THIOCARBOXAMIDO GROUP, $SCo_3(CO)_7(CSNMe_2)$

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(Received May 6th, 1981)

Summary

Reaction of dimethylthiocarbamoyl chloride or dimethylthioformamide with dicobalt octacarbonyl affords a new diamagnetic trinuclear cobalt carbonyl-sulfur complex $SCo_3(CO)_7(CSNMe_2)$ containing a bridging bidentate thiocarboxamido ligand linked to the cluster by a cobalt—carbon and a cobalt—sulfur bond. The structure has been determined by X-ray diffraction; comparison with the recently described $SCo_3(CO)_7(\mu\text{-}R^1C{=}NR^2)$ shows a different electronic distribution in the cluster and in the bridge, with important participation of the nitrogen atom.

We have shown that xanthates $[R^1OC(S)SR^2]$ and dithioesters $[R^1C(S)SR^2]$ are readily desulfurized by dicobalt octacarbonyl to give alkyl-, aryl- or alkoxy-alkylidinetricobaltnonacarbonyl clusters [1,2]. More recently we have proposed a general synthesis of the diamagnetic cluster $SCo_3(CO)_7(\mu\text{-}R^1C{=}NR^2)$ (I) containing a bridging bidentate imino ligand [3]. Clusters I are formed by reaction of $Co_2(CO)_8$ on secondary thioamides $[R^1NHC(S)R^2]$ (II), and can be considered as intermediates in the desulfurization process of sulfur-containing organic molecules. It is important to note that compounds II contain one hydrogen atom which can be removed, and a carbon—nitrogen bond much stronger than the carbon—sulfur bond in xanthates or dithioesters. Dimethylthiocarbamoyl chloride (IIIa) and dimethylthioformamide (IIIb) are also of interest because, like compounds II, they offer two sites for complexation, but the hydrogen or chlorine atoms which can be removed are now located on the

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sp^2, carbon atom, and in principle they can be desulfurized to give cobalt clusters in which the apical carbon atom is linked to an amino group or they can behave like thioamides and give sulfur-containing clusters with an aminocarbene ligand. Our results show that cluster formation involves both processes, and affords a new diamagnetic tricobalt complex containing an apical sulfur atom and a bidentate thiocarboxamido group.

Reaction of $Me_2NC(S)X$ (IIIa: X = Cl; IIIb: X = H) with $Co_2(CO)_8$ in THF for 16 h at room temperature under argon gave the same complex IV: $SCo_3(CO)_7(CSNMe_2)$, which was isolated in 38 (X = Cl) or 10% yield (X = H). The air stable black crystals (m.p. 107—108°C) were shown by elemental analysis and mass spectroscopy to contain the sulfur-tricobalt heptacarbonyl moiety associated with the dechlorinated or dehydrogenated ligand, and this was confirmed by other spectroscopic data [4].

An X-ray structure determination was carried out on a single crystal of IV grown from hexane, from which 1918 independent diffracted intensities were observed with $I_o > 2\sigma(I)$ from a set of 3157 independent reflexions measured using a θ—2θ scan technique with graphic monochromatized Mo-K_α radiation on an Enraf-Nonius CAD4 diffractometer. The compound crystallizes with two molecules per unit cell in the space group $P\bar{1}$ and the lattice constants are a 8.553(4); b 9.220(5); c 11.593(6) Å; α 100.08(3); β 93.96(2); γ 107.59(3)°. The structure was solved by direct methods with the MULTAN program; full matrix least squares refinement of atomic positional and thermal (anisotropic Co, S, N, C; isotropic H) parameters converged to the conventional values R = 0.032 and R_ω = 0.038. All the structural calculations were performed on a PDP 11/60 computer with the SDP package [5].

The ORTEP drawing presented in Fig. 1 illustrates that complex IV is a trinuclear cluster containing an apical sulfur atom linked to the three metal atoms

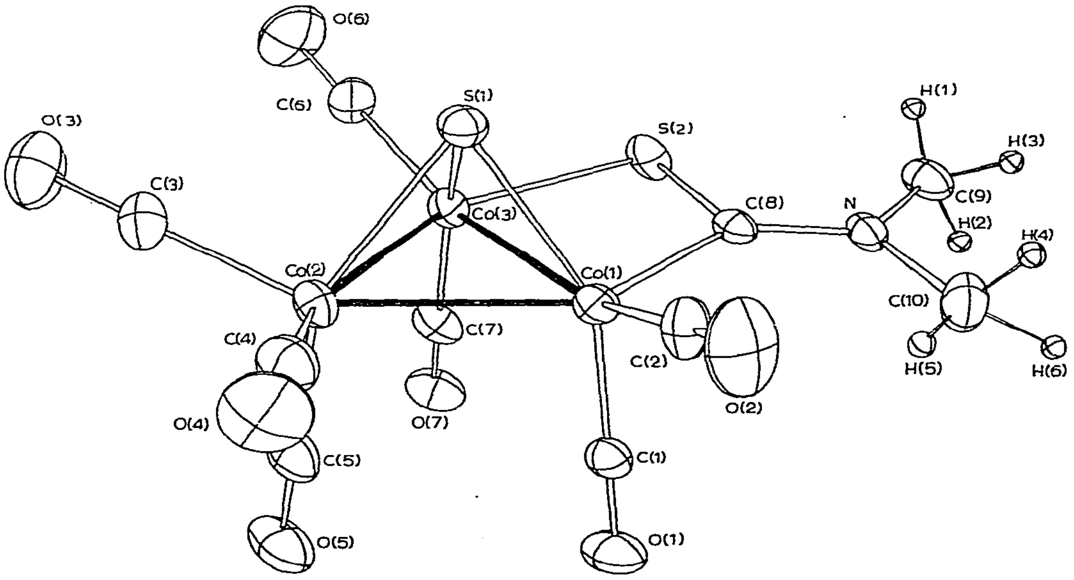


Fig. 1. ORTEP drawing of compound IV.

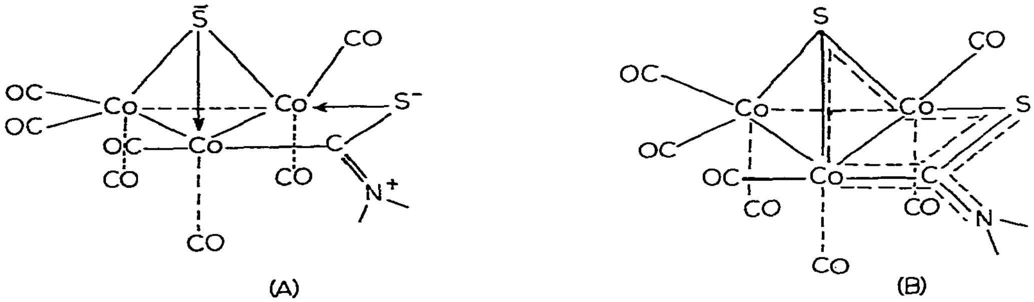
TABLE 1

MOST RELEVANT BOND LENGTHS (Å) AND ANGLES (°) WITH THEIR e.s.d.

Co(1)—Co(2)	2.549(1)	Co(1)—Co(2)—Co(3)	57.49(3)
Co(2)—Co(3)	2.525(1)	Co(1)—Co(3)—Co(2)	61.75(3)
Co(1)—Co(3)	2.440(1)	Co(1)—S(1)—Co(2)	72.40(5)
Co(1)—S(1)	2.148(2)	Co(1)—S(1)—Co(3)	69.28(5)
Co(2)—S(1)	2.168(2)	Co(2)—S(1)—Co(3)	71.69(5)
Co(3)—S(1)	2.145(2)	Co(1)—C(8)—N(1)	131.8(4)
Co(1)—C(8)	1.958(5)	Co(1)—C(8)—S(2)	106.6(3)
Co(3)—S(2)	2.260(2)	Co(1)—Co(3)—S(2)	77.11(5)
C(8)—S(2)	1.695(5)	Co(3)—S(2)—C(8)	93.9(2)
C(8)—N(1)	1.299(7)	C(8)—Co(1)—S(1)	99.6(2)

and one dissymmetric bridging ligand resulting from dechlorination of IIIa or loss of hydrogen from IIIb. Obviously the cluster formation involves two molecules of ligand, one of them being desulfurized; as would be expected, dechlorination is easier than dehydrogenation, and the reaction involving IIIa gives a better yield of cluster.

As far as the tricobalt-sulfur pyramid is concerned the molecular geometry closely resembles that of complex I [3]. The Co(1)—Co(2) and Co(2)—Co(3) distances are very close to the values found for I, and again the Co(1)—Co(3) bond length corresponding to the two metal atoms linked to the bridging ligand is significantly shorter (0.1 Å) than the others, and only slightly longer than in complex I (2.441(0) Å vs. 2.416(0). The thiocarboxamido group occupies two equatorial positions and the atoms S(2), C(8), N are coplanar, and nearly in the same plane as the three cobalt atoms (dihedral angle of 5°). The planarity around C(8) and the values of the angles (Table 1) are in agreement with sp^2 hybridization of this carbon atom; but although the Co(1)—C(8) bond length (1.958(5) Å) is in the range for transition metal-stabilized carbenes, we must regard the C(8)—N(1) bond as having a high degree of double bond character in view of the low value found for this bond length (1.299(7) Å). On the other hand the C(8)—S(2) bond is more accurately described as a single bond, because the bond length (1.695(5) Å) is closer that of a carbon—sulfur single bond (1.741(2) Å) [6] than to that of a carbon—sulfur double bond in xanthates 1.618(2) Å [7] or trithiocarbonates 1.634(3) Å [6]. These characteristics of the thiocarboxamido ligand can be compared with those of the same grouping linked to two iron atoms [8], although in the latter case the longer metal—metal



(A) (B)

Fig. 2. Alternative valence bond formulations of complex IV.

bond (2.630(2) Å) results in significant increases in the metal—sulfur, metal—carbon, carbon—sulfur and carbon—nitrogen bond lengths.

To account for the diamagnetic nature of cluster IV and to permit all the metal atoms to attain the closed-shell electronic configuration, we must conclude that the apical sulfur shares four of its valence electrons with the metals and that the thiocarboxamido group is a three electron ligand. Thus the canonical formula A of Fig. 2 might represent the electron distribution in the complex. But the formal donation of an electron pair from sulfur to Co(1) implies for complex I a metal—sulfur bond significantly shorter than the other two, and this is not the case for complex IV where the S(1)—Co(3) and S(1)—Co(1) bonds are equal in length and shorter than the S(1)—Co(2) bond. Consequently we think that formula B, with electron delocalization over six centers, gives a better representation of the electronic state of the molecule.

Although the thioamides and thiocarbamoyl chloride behave differently they both provide a direct and convenient access to chiral clusters, because in both cases the bridging ligand is dissymmetrical. We are now making efforts to obtain clusters I and IV in their optically active form, because they are suitable species for investigating the process of optical induction during cluster catalysed reactions, and they may also provide information about the ability of clusters, as a structural entity to catalyse reactions.

We thank the D.G.R.S.T. for grants to C.M. and A.B.

References

1 G. Mignani, H. Patin and R. Dabard, J. Organometal. Chem., 169 (1979) C19.

2 H. Patin, G. Mignani and M.T. Van Hulle, Tetrahedron Lett., (1979) 2441.

3 H. Patin, G. Mignani, C. Mahé, J.Y. Le Marouille, A. Benoit, D. Grandjean and G. Levesque, J. Organometal. Chem., 208 (1981) C39.

4 IR (Nujol) only terminal carbonyls (2020—2140 cm^{-1}), in ^{1}H NMR ($CDCl_3$) the two methyl give separate singlets at 3.4 and 3.63 ppm and two peaks in ^{13}C NMR at 46.7 and 47.3 ppm.

5 B.A. Frenz in M. Schenk and R. Olthof-Hazekamp (Eds.), Enraf-Nonius CAD4-SDP, a real-time system for concurrent X-ray data collection and crystal structure determination. Computing in crystallography, Delft, 1978.

6 H. Patin, G. Mignani, C. Mahé, J.Y. Le Marouille, A. Benoit and D. Grandjean, J. Organometal. Chem., 193 (1980) 93.

7 J.Y. Le Marouille, A. Benoit, D. Grandjean, H. Patin, G. Mignani and C. Mahé, Acta Crystallogr. B, in press.

8 W.K. Dean and D.G. Van der Veer, J. Organometal. Chem., 146 (1978) 143.