Preliminary communication

SYNTHESIS AND STRUCTURE OF THE FIRST DIAMAGNETIC TRINUCLEAR COBALT CARBONYL SULFUR COMPLEXES, $SCo_3(CO)_7(\mu\text{-}R^1\text{—}\overset{\frown}{C}=N\text{—}R^2)$

HENRI PATIN*, GERARD MIGNANI, CHRISTIAN MAHE,

Laboratoire de Chimie des Organométalliques, ERA CNRS No. 477, Université de Rennes, 35042 Rennes Cedex (France)

JEAN-YVES LE MAROUILLE, ALAIN BENOIT, DANIEL GRANDJEAN,

Laboratoire de Chimie du Solide et Inorganique Moléculaire, LA CNRS No. 254, Université de Rennes, 35042 Rennes Cedex (France)

and GUY LEVESQUE

Laboratoire de Physicochimie et Photochimie Organique, Université du Maine, 72017 Le Mans (France)

(Received December 15th, 1980)

Summary

Reaction of primary thioamides with dicobalt octacarbonyl affords in good yield the first diamagnetic monomeric trinuclear cobalt carbonyl sulfur complexes $SCo_3(CO)_7(\mu\text{-}R^1\overset{\frown}{C}=NR^2)$, which contain a bridging bidentate imino ligand. The structure of the product with R^1 = Me, R^2 = C_6H_{11} has been determined by X-ray diffraction, and shown to include a very short cobalt—cobalt bond distance and a long cobalt—sulfur bond distance when compared to other cobalt—sulfur clusters.

The reaction of dicobalt octacarbonyl with either elemental sulfur or sulfur-containing molecules (e.g. H_2S, RSH, R_2S, CS_2, $R^1OC(S)SR^2$, $R^1C(S)SR^2$) [1—5] has given rise to a large variety of organometallic complexes which may contain only sulfur, sulfur and the organic residue or only the desulfurized starting material. As part of our research program on the design of new ligands we report a novel reaction between dicobalt octacarbonyl and thio-amides ($R^1C(S)NHR^2$) which leads to the first stable cluster containing three zerovalent cobalt atoms linked to a trihaptosulfur atom. Several lines of evidence suggest that in our complex the bridging ligand and the apical sulfur atom are derived from the same molecule, thus providing a representation of an intermediate step in the well-known process of desulfurization of organic molecules by organometallic reagents [6].

Reaction of the thioamides R^1CSNHR^2 having R^1 = Me, Ph and R^2 = C_6H_{11} with $Co_2(CO)_8$ in THF for 24 h at room temperature under argon gave the complex $SCo_3(CO)_7(\mu-R^1\dot{C}=NR^2)$ (2), which we isolated in 35—50% yield after chromatography. The air stable black crystals (R^1 = Me, m.p. 95—96°C; R^1 = Ph, m.p. 101—102°C) were shown by elemental analysis and mass spectroscopy to contain a tricobalt heptacarbonyl moiety associated with the squeleton of the thioamide minus one hydrogen, and this was confirmed by other spectroscopic information [7]. An X-ray structure determination was carried out on a single crystal of 2a having R^1 = Me, grown from hexane, from which 2847 independent diffracted intensities were observed with $I_0 > 2\sigma(I)$ from a set of 3667 independent reflexions measured using a $\theta-2\theta$ scan technique with graphite monochromatized Mo-K_α radiation on an ENRAF-NONIUS CAD4 diffractometer. The compound crystallizes with four molecules per unit cell in the space group $P2_1/n$ and the lattice constants are a 9.967(4); b 9.733(3); c 21.236(5) Å; β 95.22(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, O, N, C; isotropic H parameters converged to conventional values R = 0.030 and R_ω = 0.033. All the structural calculations were performed on a PDP 11/60 computer with SPD package [8].
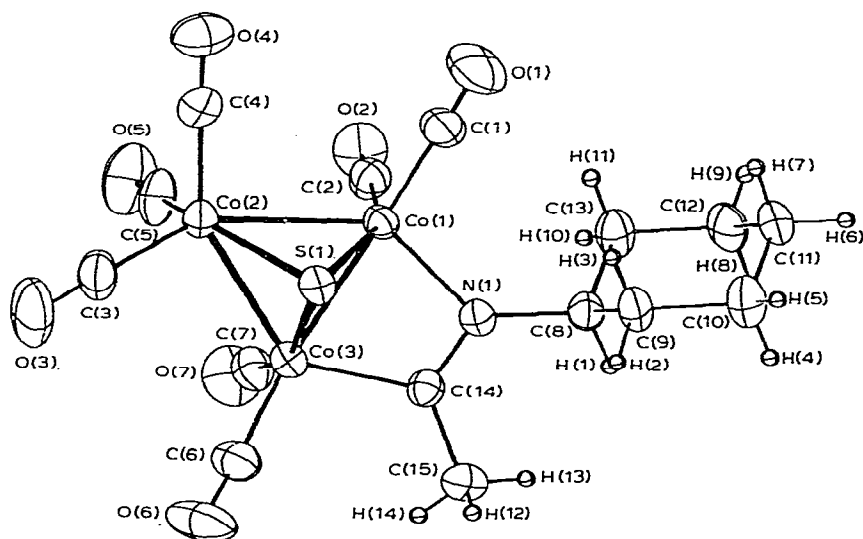

Fig. 1. ORTEP drawing of compound 2a.

The ORTEP drawing presented in Fig. 1 illustrates that complex 2a (with R^1 = Me) is a trinuclear cluster containing an apical sulfur atom linked to the three metal atoms, and one dissymetric bridging ligand resulting from desulfurization of the thioamide with concomittent loss of hydrogen. The molecular geometry as far as the tricobalt-sulfur pyramid is concerned closely resembles that reported for $Co_3(CO)_9S$ (3) [9], $FeCo_2(CO)_9S$ (4) [10] and $[SCo_3(CO)_7]_2S_2$ (5) [2], but a more detailed examination shows that the displacement of the two electron pairs of the carbonyl donors by the three elec-

TABLE 1

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

Co(1)—Co(2)	2.554(0)	Co(1)—Co(3)—Co(2)	62.0(1)
Co(2)—Co(3)	2.538(0)	Co(1)—Co(2)—Co(3)	56.6(1)
Co(1)—Co(3)	2.416(0)	Co(1)—S(1)—Co(2)	72.3(1)
Co(1)—S(1)	2.158(1)	Co(1)—S(1)—Co(3)	68.3(1)
Co(2)—S(1)	2.172(1)	Co(2)—S(1)—Co(3)	72.0(1)
Co(3)—S(1)	2.147(1)	Co(1)—N(1)—C(8)	130.1(3)
Co(1)—N(1)	1.985(2)	Co(1)—N(1)—C(14)	104.2(3)
Co(3)—C(14)	1.953(3)	Co(3)—C(14)—N(1)	109.9(2)
C(14)—N(1)	1.265(4)	Co(3)—C(14)—C(15)	124.7(3)
C(8)—N(1)	1.488(4)	S(1)—Co(3)—C(14)	94.2(1)
C(14)—C(15)	1.527(5)	S(1)—Co(3)—N(1)	94.9(1)

tron donor bidentate ligand leads to significant modifications. Two sets of metal—metal bonds are present in complex 2a. Both the Co(1)—Co(2) and Co(2)—Co(3) bond lengths are in the range of metal—metal distances in complexes 4 and 5, but are 0.08 to 0.1 Å shorter than the average value of cobalt—cobalt distance in cluster 3. The most striking feature is the Co(1)—Co(3) distance (2.416 Å), which is the shortest ever observed for this kind of cluster. As a result the base of the pyramid is no longer an equilateral triangle as in compounds 3 and 4, and this entails distortions of the tricobalt-sulfur framework, such as a smaller value for the Co(1)—S(1)—Co(3) angle (68.28° versus a mean value of 72° for the two others and 76° in cluster 3). The metal—sulfur bond lengths are also of significance because while the Co(1)—S(1) distance corresponds exactly to the mean value measured for the Co—S distances in cluster 4 (2.158 Å), the Co(3)—S(1) distance is 0.011 Å shorter and the Co(2)—S(1) distance of 2.172 Å is the longest observed in this kind of complex. The bidentate ligand occupies two equatorial positions and the atoms C(1), C(14), N(1), C(8), Co(1), Co(3) are found coplanar and nearly in the same plane as Co(1), Co(2), Co(3) (dihedral angle of 8°). The planarity around C(14) and N(1) indicates sp^2 hybridization, and furthermore the C(14)—N(1) bond length (1.265(4) Å) is in the range of carbon nitrogen—double bond lengths. For these reasons we prefer canonical formula I to represent the electron distribution in complexes of type 2 rather than formula II (Fig. 2). The latter is only supported by the C(14)—Co(3) distance of 1.953(3) Å,
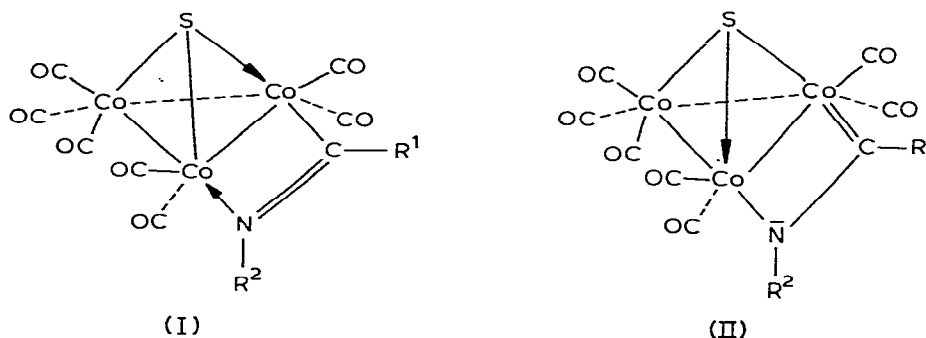

Fig. 2. Alternative valence bond formulations of complexes of type 2.

which is in the range for transition metal stabilized carbenes [11]. Formula I is also in agreement with a shorter Co(3)—S(1) distance corresponding to the formal donation of an electron pair from sulfur to cobalt to enable this atom to attain the closed-shell electronic configuration.

So one of the main features of the imino ligand is that it brings three electrons to the cluster, which makes the sulfur share four electrons and consequently prevents the cluster of type 2 from being paramagnetic, in contrast to cluster compound 3, where one electron remains unpaired. It has been suggested by Dahl [10] that the electron in excess of the closed shell electronic configuration of each metal atom in complex 3 occupies a strongly antibonding metal symmetry orbital, and this is responsible for the lengthening and weakening of the metal—metal bond. This concept has recently been discussed by Vahrenkamp [12] and we now provide additional arguments in support of these conclusions. But it is also necessary to emphasize the influence of the bridging ligand on the metal—metal distance, as shown by the Co—Co bond length in 5 (mean value of 2.47 Å when the interatomic distance in the bridging ligand is 2.04 Å) compared to our value of 2.416 Å for a shortest bridge (1.265 Å). This importance of metal-bridging ligand interactions in determining the molecular geometry has been recognized for binuclear species [13] but less frequently for trinuclear compounds.

References

1 L. Markó, G. Bor, E. Klumpp, B. Markó and G. Almasy, Chem. Ber., 96 (1963) 955.
2 D.L. Stevenson, V.R. Magnuson and L.F. Dahl, J. Amer. Chem. Soc., 89 (1967) 3727 and ref. cited therein.
3 G. Mignani, H. Patin and R. Dabard, J. Organometal. Chem., 169 (1979) C19.
4 H. Patin, G. Mignani and M.T. Van Hulle, Tetrahedron Letters, (1979) 2441.
5 L. Stanghellini, G. Gervasio, R. Rossetti and G. Bor, J. Organometal. Chem., 187 (1980) C37.
6 H. Alper and H.N. Paik, J. Org. Chem., 42 (1977) 3522.
7 IR (Nujol) no NH and only terminal carbonyls (2100—1950 cm^{-1}); ^{1}H NMR (CDCl$_3$) upfield shift for the methyl protons (0.1 ppm) and for the tertiary proton of the cyclohexyl (1.2 ppm) by comparison with the starting material; in ^{13}C NMR (CDCl$_3$) the sp^2 carbon is found at 191.4 ppm vs. 199.1 ppm in the thioamide.
8 B.A. Frenz, 1978, in M. Schenk and R. Olthof-Hazekamp (Ed.), Enraf-Nonius CAD4-SDP, a real-time system for concurrent X-ray data collection and crystal structure determination. Computing in Crystallography.
9 C.H. Wei and L.F. Dahl, Inorg. Chem., 6 (1967) 1229.
10 D.L. Stevenson, C.H. Wei and L.F. Dahl, J. Amer. Chem. Soc., 93 (1971) 6027.
11 H. Patin, G. Mignani, C. Mahé, J.Y. Le Marouille, T.G. Southern, A. Benoit and D. Grandjean, J. Organometal. Chem., 197 (1980) 315 and ref. cited therein
12 H. Beurich, T. Madach, F. Richter and H. Vahrenkamp, Angew. Chem. Int. Ed., 18 (1979) 690.
13 J.K. Burdett, J. Chem. Soc. Dalton, (1977) 423.