

### Preliminary communication

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## SYNTHESIS AND X-RAY CHARACTERIZATION OF THE NOVEL ANION $[\text{Co}_6\text{N}(\text{CO})_{13}]^-$ : THE FIRST EXAMPLE OF AN OCTAHEDRAL NITRIDO-CARBONYL CLUSTER COMPOUND IN THE COBALT SUBGROUP

GIANFRANCO CIANI

*Istituto di Chimica Strutturistica Inorganica and Centro del C.N.R., Via G. Venezian 21, 20133 Milano (Italy)*

and SECONDO MARTINENGO

*Centro del C.N.R. di Studio della Sintesi e Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione, Via G. Venezian 21, 20133 Milano (Italy)*

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### Summary

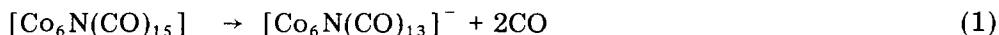
The new anion  $[\text{Co}_6\text{N}(\text{CO})_{13}]^-$ , obtained from the trigonal prismatic  $[\text{Co}_6\text{N}(\text{CO})_{15}]^-$  by thermal decarbonylation in boiling tetrahydrofuran, contains an octahedral metallic cluster, with the nitrogen atom at the centre, which bears nine terminal and four double-bridging carbonyl ligands.

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A few years ago we reported the synthesis and structural characterization of the first examples of carbonyl cluster compounds containing a fully encapsulated nitrogen atom, namely the trigonal prismatic species  $[\text{M}_6\text{N}(\text{CO})_{15}]^-$  ( $\text{M} = \text{Co}$  [1],  $\text{Rh}$  [2]). We subsequently described other species with interstitial N, i.e. the large mixed-metal anion  $[\text{PtRh}_{10}\text{N}(\text{CO})_{21}]^{3-}$  [3] and the family of anions  $[\text{Rh}_6\text{MN}(\text{CO})_{15}]^{2-}$  ( $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$ ), containing a trigonal prismatic cluster capped on a square face [4]. Other nitrides were characterized in this period, but these generally had the N atoms in an exposed or semi-exposed position ( $\mu_4$ -N in butterfly clusters or  $\mu_5$ -N in square pyramidal clusters), and only one other example, of a cluster containing a fully encapsulated N atom has, to our knowledge, been reported, viz. the octahedral  $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$ , but this was structurally not characterized [5].

We are continuing our investigation on these nitrido species and on the reactivity of the trigonal prismatic  $[\text{M}_6\text{N}(\text{CO})_{15}]^-$  anions, and we describe here the synthesis and X-ray crystal structure of  $[\text{Co}_6\text{N}(\text{CO})_{13}]^-$ , the first octahedral cluster in the Co subgroup containing an interstitial N atom.

The  $[\text{Co}_6\text{N}(\text{CO})_{13}]^-$  anion was obtained by decarbonylation of the trigonal prismatic  $[\text{Co}_6\text{N}(\text{CO})_{15}]^-$  in tetrahydrofuran (THF) at reflux under nitrogen according to reaction 1\*.



Reaction 1 is reversible, and under CO the starting anion is readily regenerated. Crystals of the bis(triphenylphosphine)iminium salt suitable for the X-ray study are obtained by the slow diffusion technique from THF/n-hexane.

The IR spectrum in THF solution shows bands at 2053vw, 1999vs, 1980ms, and 1860m  $\text{cm}^{-1}$ , with an average shift to lower frequencies of about 15  $\text{cm}^{-1}$  with respect to the trigonal prismatic  $[\text{Co}_6\text{N}(\text{CO})_{15}]^-$  anion; this shift can be attributed to the fact that delocalization of the negative charge involves a smaller number of CO ligands, so that there is increased back donation, and this is confirmed by the structural data (see later) which show that the octahedral species involves shorter Co—C (terminal 1.69 vs. 1.71 Å, bridging 1.91 vs. 1.94 Å) and longer C—O (terminal 1.18 vs. 1.16 Å, bridging 1.20 vs. 1.19 Å) mean bond distances.

The structure\*\* of the anion is shown in Fig. 1. The main bond lengths are given in Table 1. The metal atom cluster is a rather distorted octahedron centred on the nitrogen atom. The overall idealized anion geometry is  $C_s$ , with the mirror plane passing approximately through Co(1), Co(6), N and the mid point of the Co(2)—Co(3) and Co(4)—Co(5) edges. There are 9 terminal and 4 edge-bridging carbonyls. The three Co atoms of the Co(1,2,3) triangle bear each two terminal CO groups, while those of the Co(4,5,6) triangle each bear one such ligand. The four bridging carbonyls span the sequence of edges Co(2)—Co(4)—Co(6)—Co(5)—Co(3). The electron donation from the CO groups to the metals is uneven: Co(2) and Co(3) receive five electrons whereas the remaining four metal atoms only four electrons each. This feature arises from the difficulty of accommodating 13 carbonyl ligands on an octahedral cluster. Two other related species, i.e. the carbides  $[\text{Rh}_6\text{C}(\text{CO})_{13}]^{2-}$  [6] and  $[\text{Co}_6\text{C}(\text{CO})_{13}]^{2-}$  [7] differ from one another in their ligand dispositions, and both differ in stereochemistry from the present anion. The two carbide compounds show even more distorted cluster geometries. The rhodium species, of  $C_s$  idealized symmetry, bears 7 terminal and 6 edge-bridging carbonyls, while the cobalt species, of  $C_2$  idealized symmetry, has 8 terminal and 5 edge-bridging groups. The dispositions of the CO ligands in the  $\text{Co}_6$  carbide and

\*A stirred solution of  $[(\text{Ph}_3\text{P})_2\text{N}][\text{Co}_6\text{N}(\text{CO})_{15}]$  (0.24 g) in THF (16 ml) under nitrogen is refluxed in an oil bath at 80°C until the IR bands of the starting anion are replaced by those of the product (about 3 h are required). During the heating the colour changes from reddish to dark brown. The product is recovered from the filtered solution by addition of n-hexane (80 ml) in yields of 75–85%. During the long time required for the growth of X-ray suitable specimens by the slow diffusion technique, some decomposition occurs, giving, along with the black crystals of the octahedral species, some red crystal of the trigonal prismatic species and some insoluble powder.

\*\*Crystal data.  $\text{C}_{53}\text{H}_{38}\text{N}_2\text{O}_{14}\text{P}_2\text{Co}_6$ ,  $M = 1342.4$ , orthorhombic, space group  $P2_1nb$  (non-standard of No. 33), with  $a$  15.270(7),  $b$  18.147(6),  $c$  20.183(7) Å,  $D_c$  1.59  $\text{g cm}^{-3}$  for  $Z = 4$ . The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 1382 significant ( $I > 2\sigma(I)$ ) absorption corrected counter data, up to a current  $R$  value of 0.082. The structure was found to contain one molecule of solvated THF per asymmetric unit. (The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.)

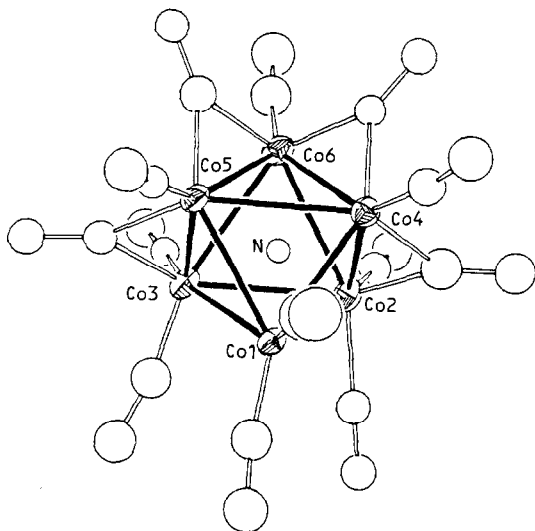


Fig. 1. A view of the anion  $[\text{Co}_6\text{N}(\text{CO})_{13}]^-$ . The ideal mirror plane passes approximately through Co(1), Co(6), N and the middle point of the Co(2)—Co(3) and Co(4)—Co(5) edges.

nitride anions can readily be related: migration of one terminal CO bound to Co(2) or Co(3) of the nitride species to a position bridging to Co(1) gives the ligand arrangement found in the carbide species.

The Co—Co bond lengths spread over the range 2.487(5)—2.788(5) Å. The spread is, however, less pronounced than in  $[\text{Co}_6\text{C}(\text{CO})_{13}]^{2-}$  (2.465—2.926 Å). The four bridged Co—Co edges are shorter than the others, in the range 2.487—2.523(5) Å (mean 2.502 Å). The unbridged edges (range 2.599—2.788(5) Å) have a mean value of 2.669 Å.

TABLE 1

MAIN BOND DISTANCES (Å) IN  $[\text{Co}_6\text{N}(\text{CO})_{13}]^-$

Co(1)—Co(2)	2.599(5)
Co(1)—Co(3)	2.609(5)
Co(1)—Co(4)	2.599(5)
Co(1)—Co(5)	2.655(5)
Co(2)—Co(3)	2.720(5)
Co(2)—Co(4)	2.523(5)
Co(2)—Co(6)	2.689(5)
Co(3)—Co(5)	2.506(5)
Co(3)—Co(6)	2.695(5)
Co(4)—Co(5)	2.788(5)
Co(4)—Co(6)	2.491(5)
Co(5)—Co(6)	2.487(5)
Co(1)—N	1.75(2)
Co(2)—N	1.83(2)
Co(3)—N	1.93(2)
Co(4)—N	1.79(2)
Co(5)—N	1.92(2)
Co(6)—N	1.88(2)
Co—C(term)	1.69 (mean)
C—O(term)	1.18 (mean)
Co—C(bridg)	1.91 (mean)
C—O(bridg)	1.20 (mean)

The Co—N mean bond length is 1.85 Å, shorter than in  $[\text{Co}_6\text{N}(\text{CO})_{15}]^-$  (mean 1.938 Å). The resulting apparent radius of N in the octahedral species is ca. 0.54 Å, close to that of C in the  $[\text{Co}_6\text{C}(\text{CO})_{13}]^{2-}$  anion (0.55 Å), but smaller than that in the larger trigonal prismatic cavity of the parent anion (0.67 Å).

Further work on this class of nitrido-carbonyl compounds in the cobalt triad is in progress.

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## References

- 1 S. Martinengo, G. Ciani, A. Sironi, B.T. Heaton and J. Mason, *J. Am. Chem. Soc.*, **101** (1979) 7095.
- 2 R. Bonfichi, G. Ciani, A. Sironi and S. Martinengo, *J. Chem. Soc. Dalton Trans.*, (1983) 253.
- 3 S. Martinengo, G. Ciani and A. Sironi, *J. Am. Chem. Soc.*, **104** (1982) 328.
- 4 S. Martinengo, G. Ciani and A. Sironi, *J. Chem. Soc. Chem. Commun.*, (1984) 1577.
- 5 M.L. Blohm, D.E. Fjare and W.L. Gladfelter, *Inorg. Chem.*, **22** (1983) 1004.
- 6 V.G. Albano, D. Braga and S. Martinengo, *J. Chem. Soc. Dalton Trans.*, (1981) 717.
- 7 V.G. Albano, D. Braga and S. Martinengo, *J. Chem. Soc. Dalton Trans.*, in press.