

Journal of Organometallic Chemistry, 362 (1989) 291–296
 Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
 JOM 09409

Bi–Co heteronuclear carbonyl compounds. Synthesis and crystal structure of the cubane-like species $[\text{Co}(\text{CO})_3(\mu_3\text{-Bi})]_4$

Gianfranco Ciani *, Massimo Moret,

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

Alessandro Fumagalli 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)

(Received July 19th, 1988)

Abstract

The compound $[\text{Co}(\text{CO})_3(\mu_3\text{-Bi})]_4$ has been obtained by prolonged pyrolysis of $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ in refluxing tetrahydrofuran. This species, isomorphous with the analogous $[\text{Co}(\text{CO})_3(\mu_3\text{-Sb})]_4$, crystallizes in the tetragonal space group $I4_1/amd$ (No. 141) with a 14.731(3), c 10.574(3) Å and $Z = 4$. The structure was refined by full-matrix least-squares, on the basis of 447 significant unique reflections, to a final R value of 0.032. The compound has a cubane-like structure, with four tetrahedrally disposed $\text{Co}(\text{CO})_3$ units triply bridged by four Bi atoms. The Bi–Co bonds have a mean value of 2.745 Å. Each cobalt atom exhibits a highly distorted octahedral coordination, with Bi–Co–Bi and C–Co–C angles of mean values 75.48 and 101.1°. The Co...Co contacts are definitely non-bonding (mean 4.291 Å). The non bonding Bi...Bi interactions (mean 3.360 Å) are particularly short. The mean values of the Co–C and C–O bond lengths are 1.78 and 1.19 Å, respectively.

Introduction

In the course of a study on heteronuclear carbonyl compounds containing metals of the cobalt subgroup and post-transitional metals such as Sb and Bi, we have previously reported on the synthesis and characterization of some new compounds, viz. the neutral tetrahedral $[\text{BiCo}_3(\text{CO})_9]$ [1], the paramagnetic cluster $[\text{Bi}_2\text{Co}_4(\text{CO})_{11}]^-$ [1], and the ‘open’ anion $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$ [1,2]. We present here the full details of the synthesis of the cubane-like species $[\text{Co}(\text{CO})_3(\mu_3\text{-Bi})]_4$ and the complete results of an X-ray diffraction study on it. The compound is isomorphous with the analogous $[\text{Co}(\text{CO})_3(\mu_3\text{-Sb})]_4$, which was obtained unexpectedly [3]. The structural parameters are compared with those of related cubane-like $[\text{M}(\text{CO})_3(\mu_3\text{-X})]_4$ species.

Results and discussion

$[\text{Co}(\text{CO})_3(\mu_3\text{-Bi})]_4$ (**1**) has been prepared by prolonged pyrolysis of $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ [4] in refluxing tetrahydrofuran (THF). IR monitoring of the reaction shows that the starting open mixed cluster is first rapidly converted into the tetrahedral $[\text{BiCo}_3(\text{CO})_9]$ [1], which is subsequently slowly transformed into **1**, with considerable decomposition to a black material, mostly metallic cobalt. Pyrolysis is continued until the IR spectrum of the solution shows only the two characteristic bands of **1** in THF (see later).

Traces of **1** have also been found in the residue from attempted sublimation of $[\text{BiCo}_3(\text{CO})_9]$.

Compound **1** is insoluble in acetonitrile, dichloromethane, hexane, and alcohols; it is moderately soluble in THF and in toluene, and gives wine-red solutions. It can be obtained as crystals by slowly cooling the hot-saturated solutions in THF, or by placing a layer of n-hexane over the solution in THF and leaving the solvents to diffuse; crystals suitable for the X-ray analysis were grown by the latter method. The black crystals are stable in air for many days, and the THF solutions can be handled in air for reasonable periods.

The IR spectrum of **1** in nujol mull shows bands at 2020s, 1973m and 1955w cm^{-1} , and is very similar to that reported for the Sb analogue [3], but slightly shifted to lower wavenumbers. The saturated THF solution shows two bands, at 2012 vs and 1971m cm^{-1} .

Description of the structure

The crystal structure consists of $[\text{Co}(\text{CO})_3(\mu_3\text{-Bi})]_4$ molecules with normal Van der Waals' separations, except for some kind of long range interaction between Bi atoms of adjacent molecules (Bi... Bi 4.022 Å). The structure of the compound, with a cubane-like geometry, is shown in Fig. 1 and the interatomic distances and angles are given in Table 1. The complex exhibits a crystallographically imposed $D_{2d}42m$ symmetry, which on the basis of the experimental geometry can be idealized as T_d43m .

The Bi-Co bond lengths (weighted mean 2.745 Å) are comparable with those in related species, e.g. 2.623(2) Å in $[\text{BiCo}_3(\text{CO})_9]$ [1] and, particularly, 2.744 Å (mean) in $[\text{Bi}_2\text{Co}_4(\text{CO})_{11}]^-$ [1] and 2.766 Å (mean) in $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ [4].

The Co...Co interactions are definitely non-bonding, their weighted mean value being 4.291 Å.

The coordination around each cobalt atom is highly distorted octahedral, with *cis*-X-Co-X angles ranging from the quite acute Bi-Co-Bi (weighted mean 75.48°) to the quite obtuse C-Co-C ones (weighted mean 101.1°).

A comparison of the structure of the present species with that of the isomorphous Sb complex shows only some minor differences in dimensions due to the greater atomic radius of Bi than of Sb. In the Co_4Bi_4 moiety the two non-bonded interpenetrating tetrahedra have slightly increased dimensions (ca. 5%) compared with those in Co_4Sb_4 . As a consequence the Bi-Co-Bi and the Co-Bi-Co angles are respectively ca. 1° less acute and 1° less obtuse than the Sb-Co-Sb and Co-Sb-Co angles.

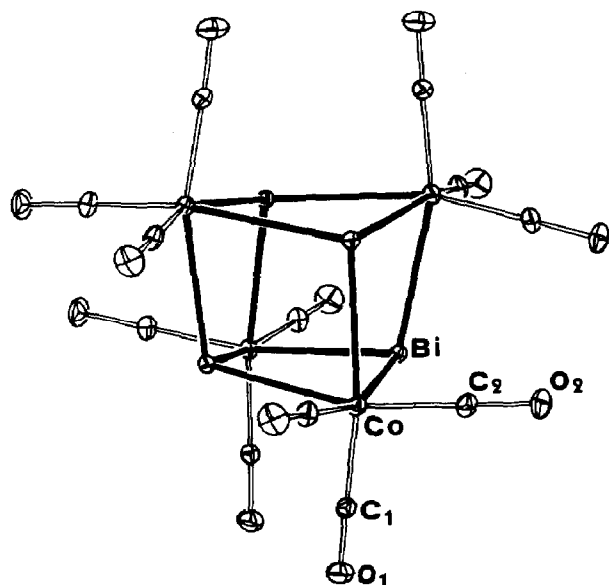


Fig. 1. A view of $[\text{Co}(\text{CO})_3(\mu_3\text{-Bi})]_4$.

Table 1

Interatomic distances (Å), bond angles (deg.) and weighted mean values within $[\text{Co}(\text{CO})_3(\mu_3\text{-Bi})]_4$

<i>Bonding distances</i>					
Bi-Co	2.742(2)	Co-C(1)	1.81(2)	C(1)-O(1)	1.15(2)
	2.751(2)	Co-C(2)	1.77(1)	C(2)-O(2)	1.21(2)
w.mean	2.745		1.78		1.19
<i>Non-bonding distances</i>					
Co...Co	4.291(4)	Bi...Bi	3.364(1)		
	4.292(4)		3.351(1)		
w.mean	4.291		3.360		
Bi...C(1)	3.30(1)	C(1)...C(2)	2.77(2)		
Bi...C(2)	3.26(1)	C(2)...C(2)	2.72(3)		
	3.28(1)				
w.mean	3.28		2.75		
<i>Bond angles</i>					
Co-Bi-Co	102.73(5)	Bi-Co-Bi	75.35(6)		
	103.02(6)		75.54(6)		
w.mean	102.83		75.48		
Bi-Co-C(1)	90.6(4)	C(1)-Co-C(2)	101.4(6)		
Bi-Co-C(2)	90.6(4)	C(2)-Co-C(2)	100.4(8)		
	89.7(4)				
w.mean	90.3		101.1		
Bi-Co-C(1)	162.4(5)	Co-C(1)-O(1)	179(2)		
Bi-Co-C(2)	161.7(4)	Co-C(2)-O(2)	179(1)		
w.mean	161.9		179		

Table 2

Selected mean distances (Å) and angles (deg.) for some $[\text{M}(\text{CO})_3(\mu_3\text{-X})]_4$ systems calculated from the independent parameters only.

$[\text{M}(\text{CO})_3(\mu_3\text{-X})]_4$	$d_{\text{M-X}}$	$d_{\text{M-M}}$	$d_{\text{X-X}}$	X-M-X	M-X-M	Ref.
$[\text{Cr}(\text{CO})_3(\mu_3\text{-OH})]_4^{4-}$	2.121	3.345	2.556	74.6	103.4	<i>a</i>
$[\text{Cr}(\text{CO})_3(\mu_3\text{-OCH}_3)]_4$	2.115	3.306	2.585	75.3	102.9	<i>b</i>
$[\text{Mn}(\text{CO})_3(\mu_3\text{-F/OH})]_4$	2.052	3.199	2.529	76.1	102.4	<i>c</i>
$[\text{Re}(\text{CO})_3(\mu_3\text{-OH})]_4$	2.207	3.480	2.653	73.9	104.0	<i>e</i>
$[\text{Re}(\text{CO})_3(\mu_3\text{-SCH}_3)]_4$	2.503	2.898	3.097	76.8	101.7	<i>f</i>
$[\text{Re}(\text{CO})_3(\mu_3\text{-F})]_4$	2.200	3.475	2.644	74.2	103.8	<i>d</i>
$[\text{Fe}(\text{CO})_3(\mu_3\text{-AsCH}_3)]_4$	2.412	3.762	2.965	75.9	102.5	<i>g</i>
$[\text{Os}(\text{CO})_3(\mu_3\text{-O})]_4$	2.06	3.221	—	77	101	<i>h</i>
$[\text{Co}(\text{CO})_3(\mu_3\text{-Sb})]_4$	2.614	4.115	3.156	74.3	103.8	<i>i</i>
$[\text{Co}(\text{CO})_3(\mu_3\text{-Bi})]_4$	2.746	4.291	3.358	75.4	102.9	<i>j</i>

^a T.J. McNeese, T.E. Mueller, D.A. Wierda, D.J. Darensbourg, T.J. Delord, *Inorg. Chem.*, 24 (1985) 3465. ^b T.J. McNeese, M.B. Cohen, B.M. Foxman, *Organometallics*, 3 (1984) 552. ^c E. Horn, M.R. Snow, P.C. Zeleny, *Aust. J. Chem.*, 33 (1980) 1659. ^d B. Nuber, F. Oberdorfer, M.L. Ziegler, *Acta Cryst.*, B, 37 (1981) 2062. ^e W. Harrison, W.C. Marsh, J. Trotter, *J. Chem. Soc. Dalton Trans.*, (1972) 1009. ^f E. Horn, M.R. Snow, *Aust. J. Chem.*, 34 (1981) 737. ^g E. Röttinger, H. Vahrenkamp, *J. Organomet. Chem.*, 213 (1981) 1. ^h D. Bright, *Chem. Commun.*, (1970) 1169. ⁱ A.S. Foust, L.F. Dahl, *J. Am. Chem. Soc.*, 92 (1970) 7337. ^j This work.

Although many cubane-like compounds are known, the number of cubane species of formula $[\text{M}(\text{CO})_3(\mu_3\text{-X})]_4$ (M = transition metal, X = suitable μ_3 -ligand) is limited. Table 2 shows the mean intramolecular parameters for all the structurally characterized species of this type that we have been able to find in the literature. The mean values reported have been computed as unweighted averages of the experimental independent parameters.

The effect of the relative variation of the M-M and X-X distances, quantitatively described by the distance ratio $d_{\text{X-X}}/d_{\text{M-M}}$, gives rise to a nearly linear relationship between the X-M-X and M-X-M angles, even though the data set contains different transition metals and different μ_3 -bridging groups and in spite of the variety of the site symmetries shown by the listed compounds*.

Another interesting feature that can be outlined is the presence, as a result of strain in the cage, of relatively short non-bonding X-X contacts, smaller than the sum of the Van der Waals' radii. In particular in $[\text{Co}(\text{CO})_3(\mu_3\text{-Bi})]_4$ the intramolecular non-bonding Bi...Bi contacts (weighted mean 3.360 Å) are very short compared with the Bi-Bi bond length in the bulk metal (3.07 Å for the nearest neighbours) [5].

* The linear regression of the M-X-M vs. the X-M-X angles (the data of the $[\text{Os}(\text{CO})_3(\mu_3\text{-O})]_4$ species were omitted in the computations because of the small number of significant digits) yields a satisfactory correlation coefficient of -0.99 (slope = -0.779, intercept = 161.6). The best-fit straight line may be, with care, extrapolated toward the 'perfect cube region' (X-M-X = M-X-M = 90°), with a very small shift of the angles from their ideal values (the line passes through the point: 90.8°, 90.8°). Thus, the geometrical changes that occur in the path from a 'perfectly cubic' structure to a cubane-shaped structure may be described to a good approximation by the linear relationship presented here.

Experimental

All the operations were carried out under nitrogen. The $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ was prepared as previously described [4].

$[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ (0.27 g) was placed under nitrogen into a 150 ml Schlenk tube equipped with a magnetic stirring bar, and dissolved in tetrahydrofuran (30 ml). The tube was fitted with a cold finger, and placed in an oil bath thermostatted at 75°C , and the stirred solution was refluxed. The reaction was monitored by taking an IR spectrum every hour, and refluxing was continued until the IR spectrum of the solution showed only the two characteristic bands of the product at 2012vs and 1971m cm^{-1} . The reaction was complete in 5–8 h. During the reaction considerable decomposition occurred, with separation of a black powder, mostly metallic cobalt. At the end, the wine-red solution was filtered into another 100 ml Schlenk tube and the solution was concentrated in vacuum to about 15 ml. From this solution the product was obtained (a) as a finely crystalline black powder by slow addition, with stirring, of n-hexane (50–60 ml), or (b) as crystals suitable for the X-ray analysis by cautiously placing a layer of n-hexane (60 ml) above the solution, and leaving the solvents to diffuse. Yields (based on Bi): 50–60 mg, 38–46%. Analysis: found: C, 10.35. $\text{C}_{12}\text{Bi}_4\text{Co}_4\text{O}_{12}$ calcd.: C, 10.23%.

X-ray Analysis

Crystal data. $\text{C}_{12}\text{Bi}_4\text{Co}_4\text{O}_{12}$, $M = 1407.8$, tetragonal, space group $I4_1/amd$ (No. 141), with $a = b = 14.731(3)$, $c = 10.574(3)$ Å, $U 2294.6$ Å³, $F(000) = 2432$, $D_c 4.075$ g cm⁻³ for $Z = 4$; Mo- K_α radiation ($\lambda 0.71073$ Å), μ (Mo- K_α) 333.4 cm⁻¹.

Intensity measurements. A suitable crystal of dimensions $0.10 \times 0.14 \times 0.25$ mm was mounted on a glass fibre in the air. The intensity data were collected on an Enraf–Nonius CAD4 automated diffractometer, using graphite monochromatized Mo- K_α radiation. The setting angles of 25 random intense reflections ($16 < 2\theta < 25^\circ$) were used to determine accurate cell constants and orientation matrix by least-squares. The data collection was performed for the reflections of the (+h, +k, +l) octant, by the ω -scan method, within the limits $3 < \theta < 26^\circ$. A variable scan-speed (from 2 to $20^\circ/\text{min}$) and a variable scan-range of $(0.85 + 0.35 \tan \theta)^\circ$ were used, with a 25% extension at each end of the scan-range for background determination. The total number of collected reflections was 1221. Three standard intense reflections, measured at regular intervals, showed no significant decay during the collection. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to the data set, based on ψ -scans ($\psi 0\text{--}360^\circ$ every 10°) of suitable reflections with χ values close to 90° ; the maximum, minimum and average relative transmission factors were 1.00, 0.49 and 0.84, respectively. A set of 447 independent significant reflections, with $I > 3\sigma(I)$, was used in the structure refinements.

Structure solutions and refinements. All computations were performed on a PDP 11/34 computer, using the Enraf–Nonius Structure Determination Package (SDP).

The structure was solved using as starting positions for the metal atoms those previously determined for the isomorphous Sb species [3]. A subsequent difference-Fourier map showed the positions of the carbonyl atoms. The refinements were carried out by full-matrix least-squares. Anisotropic thermal factors were assigned to all atoms. The final difference-Fourier map showed some residual peaks not

Table 3

Atom coordinates for $[\text{Co}(\text{CO})_3(\mu_3\text{-Bi})_4]$

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Bi	0.000	0.36375(4)	-0.01207(5)
Co	0.1457(2)	0.250	0.0184(2)
C(1)	0.129(1)	0.250	0.188(2)
O(1)	0.121(1)	0.250	0.296(1)
C(2)	0.2213(8)	0.3423(9)	-0.001(1)
O(2)	0.2738(8)	0.4043(7)	-0.015(1)

exceeding ca. $1.5 \text{ e } \text{\AA}^{-3}$. Weights were assigned according to the formula $w = 4F_o^2/\sigma(F_o^2)^2$, where $\sigma(F_o^2) = [\sigma(I)^2 + (pI)]^{1/2}/L_p$ (I and L_p being the integrated intensity and the Lorentz-polarization correction, respectively); p was optimized to 0.06. The final values of the conventional agreement indices R and R_w were 0.032 and 0.041, respectively; the error in an observation of unit weight was 1.168.

The final positional parameters are given in Table 3. A table of thermal parameters and list of observed and calculated structure factors can be obtained from the authors.

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