

Bi–Co heteronuclear carbonyl compounds. Synthesis of the anion $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$ and X-ray crystal structure of its tetramethylammonium salt

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Abstract

The anion $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$ has been obtained either by reaction of BiCl_3 with the anion $[\text{Co}(\text{CO})_4]^-$, in a 1/4 molar ratio and also by treating the preformed neutral $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ with $[\text{Co}(\text{CO})_4]^-$ in a 1/1 molar ratio. The salt $[\text{NMe}_4][\text{Bi}\{\text{Co}(\text{CO})_4\}_4]$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with a 12.327(3), b 14.181(3), c 19.017(4) Å, β 106.14(2)°, $Z = 4$. The structure was solved by the conventional Patterson and Fourier methods and refined, by use of 2201 significant unique reflections, to a final R value of 0.035. The anion contains a central Bi atom bound with a tetrahedral geometry to four $\text{Co}(\text{CO})_4$ units. The four Bi–Co bonds are very long (mean 2.914 Å) owing to the presence on the Bi atom of an extra electron pair. Each cobalt atom exhibits a distorted trigonal bipyramidal coordination, with the three-fold axis coincident with the Bi–Co direction.

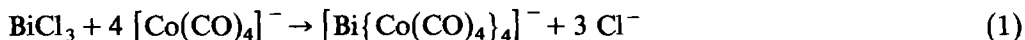
Introduction

We are currently studying heteronuclear carbonyl compounds containing metals of the cobalt subgroup and post-transitional metals such as Sb and Bi, and we recently presented a preliminary account of the reactions of the anion $[\text{Co}(\text{CO})_4]^-$ with BiCl_3 , which gave mainly the anion $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$, the neutral tetrahedral $[\text{BiCo}_3(\text{CO})_9]$, and the paramagnetic cluster $[\text{Bi}_2\text{Co}_4(\text{CO})_{11}]^-$ [1]. The anion $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$ belongs to a class of ‘open’ compounds containing a central non-transition metal bound to $\text{M}(\text{CO})_n$ groups, which includes species as $[\text{Bi}\{\text{Mn}(\text{CO})_5\}_3]$ [2], $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ [3], $[\text{Bi}\{\text{Fe}(\text{CO})_4\}_4]^{3-}$ [4] and $[\text{M}\{\text{Co}(\text{CO})_4\}_4]$

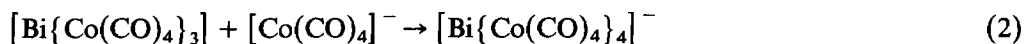
(M = Sn, Pb) [5]. We describe here the details of the synthesis of this new anion and results of a single crystal X-ray diffraction study on its tetramethylammonium salt. The structural parameters are compared with those for related species and of other Bi–Co systems. The steric effects arising from the presence of a lone pair on the bismuth atom are discussed.

Results and discussion

The red-violet $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$ anion (**1**) is formed when BiCl_3 reacts with $\text{Na}[\text{Co}(\text{CO})_4]$ in a 1/4 molar ratio in tetrahydrofuran (THF) at room temperature (eq. 1).



The reaction is performed by adding the BiCl_3 solution dropwise to the stirred $\text{Na}[\text{Co}(\text{CO})_4]$ solution, so that during the reaction the Bi/Co ratio never rises above the stoichiometric value, otherwise some other by-products are formed. However, while an excess of BiCl_3 must be avoided, an excess of $[\text{Co}(\text{CO})_4]^-$ is not detrimental, since it remains unreacted. Reaction 1 is shifted to the right only when the Cl^- ions separate out as an insoluble salt, such as NaCl ; in fact, if in place of $\text{Na}[\text{Co}(\text{CO})_4]$ salts of the $[\text{Co}(\text{CO})_4]^-$ anion with cations whose chlorides have some solubility in THF, such as $[\text{NMe}_4]^+$ or $[\text{PPh}_4]^+$, are used, the reaction is incomplete. The reaction involves the intermediate formation of $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$, which is found as by-product along with some cobalt chloride. Anion **1** can thus also be obtained by reaction of preformed $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ with $\text{Na}[\text{Co}(\text{CO})_4]$ (eq. 2).



Reaction 2 can be considered as the second step in reaction 1, the first being the formation of $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$. Reaction 2 is probably reversible, because it is almost, but not completely, shifted to the right when the reactants are kept in the exact 1/1 molar ratio.

The sodium salt of anion **1** can be converted into the $[\text{NMe}_4]^+$ and $[\text{PPN}]^+$ salts by metathesis in aqueous medium. Bulky cations salts can also be prepared directly by reaction 2 by use of the appropriate salts of the $[\text{Co}(\text{CO})_4]^-$ anion; in this case it is better to use a slight excess of $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ in order to ensure the complete reaction of $[\text{Co}(\text{CO})_4]^-$, which otherwise would separate out with the product in the subsequent precipitation with n-hexane, in which the excess of $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ is soluble.

The IR spectrum of the $[\text{NMe}_4]^+$ salt in THF solution (Fig. 1a) shows bands at 2030vs, 1985m(sh) and 1970vs cm^{-1} in the terminal carbonyl stretching region. Two additional weak bands at 2065 and 1885 cm^{-1} are attributable to traces of $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ and $[\text{Co}(\text{CO})_4]^-$, respectively, which reflect the reversible nature of reaction 2. We also observed that if the solution was left under nitrogen for a long time, there was a slow transformation of $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ into $[\text{BiCo}_3(\text{CO})_9]$. This transformation becomes more evident during the long periods required for the crystals' growth, and is probably related to the thermal decomposition (see later).

The ^{13}C NMR spectrum in THF- d_8 solution of the $[\text{NMe}_4]^+$ salt previously enriched by direct exchange with ^{13}CO (Fig. 1b), shows, at -70°C , two peaks of relative intensity 1 and 3 at δ 210.7 and 200.5 ppm ($W_{1/2}$ 64.8 and 113 Hz),

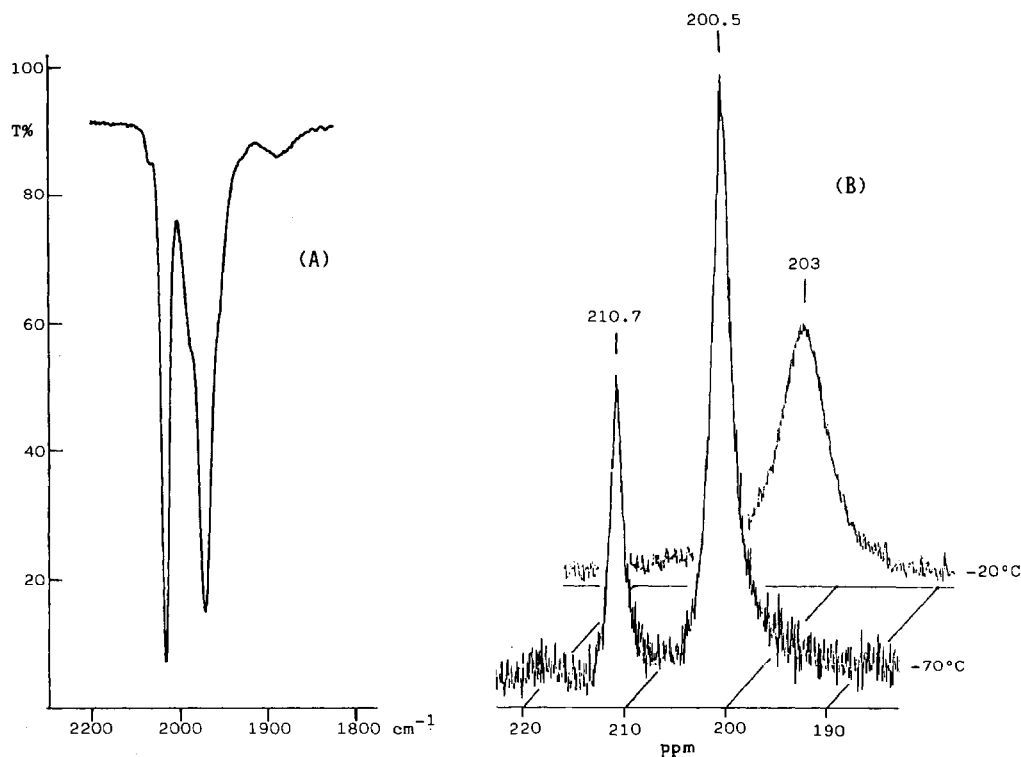


Fig. 1. (a) The IR spectrum of $[\text{NMe}_4][\text{Bi}(\text{Co}(\text{CO})_4)_4]$ in THF solution. (b) The ^{13}C NMR spectrum of $[\text{NMe}_4][\text{Bi}(\text{Co}(\text{CO})_4)_4]$ in $\text{THF-}d_8$ at -70 and -20°C .

respectively, consistent with the presence of one axial and three equatorial carbonyls in the trigonal bipyramidal environment of the cobalt atoms as revealed by the X-ray study (see below). If the temperature is raised to about -50°C the two peaks broaden, then at ca. -20°C , collapse into a single peak at 203.4 ppm ($W_{1/2}$ 259 Hz), which at room temperature appears at 204.0 ppm with a $W_{1/2}$ of 238 Hz; this behaviour clearly indicates the axial-equatorial scrambling of the carbonyls, and is very similar to that reported for $[\text{BiFe}_4(\text{CO})_{16}]^{3-}$ [4a] for which a similar structure was found [4b]. The rather large value of $W_{1/2}$ at room temperature could be due to the quadrupolar moment of cobalt or to slowness of the scrambling process. Owing to the thermal instability of the compound no measurements could be made at higher temperatures in order to confirm the latter suggestion, but the rather small decrease in $W_{1/2}$ on going from -20 to $+25^\circ\text{C}$ seems to favour the quadrupole moment effect.

Treatment of **1** in THF with an excess of LiCl or LiBr causes immediate decomposition to a mixture of $[\text{Co}(\text{CO})_4]^-$ and Bi^{III} halides, by the reverse of reaction 1; thus $[\text{Bi}(\text{Co}(\text{CO})_4)_3]$, which was found as intermediate in reaction 1, was thought also to be involved in this decomposition. Since we could find no information in the literature on the reactions of $[\text{Bi}(\text{Co}(\text{CO})_4)_3]$ with halide ions, we treated it with LiCl or LiBr in THF and we observed that it is decomposed to a mixture similar to that obtained from compound **1**. This observation provides the explanation of the above mentioned influence of the solubility of the halide salts

formed in reaction 1 on the course of the reaction itself. We also found that the reaction with halides is solvent dependent, since in methanol, for example compound **1** reacts only to a limited extent. In this same solvent, $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ is converted into a mixture of **1**, $[\text{Co}(\text{CO})_4]^-$, and, presumably, bismuth(III) halides; the formation of **1** can be accounted for in terms of the condensation of part of the $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ with the $[\text{Co}(\text{CO})_4]^-$ generated in the decomposition. Solvent dependence is also confirmed by the observation that addition of water to the reaction mixtures obtained from **1** or from $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ with halides in THF, causes immediate regeneration of $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$; this explains also why it was possible to make this compound in aqueous hydrochloric solution [3].

The facile reaction with halide ions to regenerate Bi^{III} derivatives and $[\text{Co}(\text{CO})_4]^-$ suggests that compound **1** can be regarded as a Bi^{III} complex with the ligand $[\text{Co}(\text{CO})_4]^-$ in which the Bi–Co interactions are probably largely electrostatic in nature. This suggestion, together with the presence of an additional electron pair on Bi, could account for the rather long Bi–Co bonds revealed by the X-ray study (see below).

When solutions of **1** are heated there is complete decomposition to a mixture of $[\text{BiCo}_3(\text{CO})_9]$ and $[\text{Co}(\text{CO})_4]^-$. This behaviour can be associated for in terms of the reversibility of reaction 2, the equilibrium being shifted to the left when $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ loses CO to give $[\text{BiCo}_3(\text{CO})_9]$. This decarbonylation, which is slow at room temperature, becomes faster when the temperature is raised [1,6]; and so solutions of **1** in THF are completely decomposed to the above mixture in about half an hour at 50 °C. Under these conditions incipient formation of $[\text{Bi}_2\text{Co}_4(\text{CO})_{11}]^-$ [1] is also observed. Another possibility is that in the thermal decomposition of **1** as soon as loss of CO causes closure of Co–Co bonds, an anion such as $[\text{BiCo}_3(\text{CO})_9\{\text{Co}(\text{CO})_4\}]^-$ that might be initially formed, decomposes into its components $[\text{BiCo}_3(\text{CO})_9]$ and $[\text{Co}(\text{CO})_4]^-$. Both hypotheses are in keeping with our previous observation that no simple adduct is formed between $[\text{BiCo}_3(\text{CO})_9]$ and $[\text{Co}(\text{CO})_4]^-$ [1]. The difference in reactivity between $[\text{BiCo}_3(\text{CO})_9]$ and $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ towards $[\text{Co}(\text{CO})_4]^-$ seems to indicate a different charge density on the Bi atom, which should be lower in $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$, thus allowing the nucleophilic attack; in $[\text{BiCo}_3(\text{CO})_9]$ the Bi atom seems to be sufficiently basic to inhibit nucleophilic attack by $[\text{Co}(\text{CO})_4]^-$ in mild conditions, but not so basic to allow the facile formation of the cyclic trimers observed in the analogous phosphorus and arsenic compounds [7]; it is noteworthy that the iridium derivative $[\text{BiIr}_3(\text{CO})_9]$ [8] also shows no tendency to undergo trimerisation.

Crystals of the tetramethylammonium salt of **1** were obtained by the slow diffusion technique by placing a layer of n-hexane over a concentrated solution in dichloromethane.

Description of the structure

The crystal structure consists of separate $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$ anions and $[\text{NMe}_4]^+$ cations in the ratio 1/1.

The structure of the anion is shown in Fig. 2 and the bond parameters are given in Tables 1 and 2. The anion may be regarded as a central Bi^{III} surrounded in an almost tetrahedral fashion by four $[\text{Co}(\text{CO})_4]^-$ groups. Each cobalt atom exhibits a distorted trigonal bipyramidal coordination. This overall geometry is present in

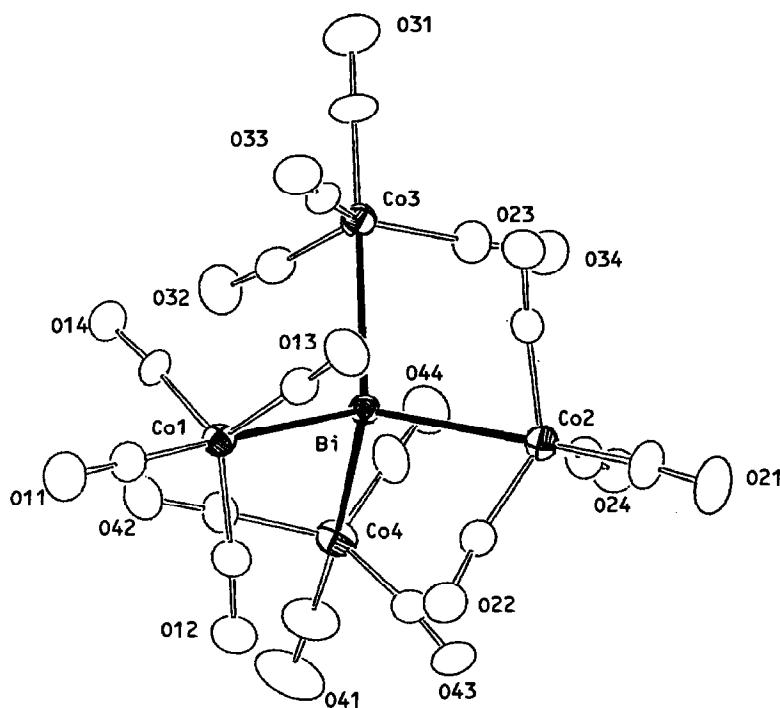


Fig. 2. A view of the anion $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$. The carbonyl ligands are indicated by the numbers of their oxygen atoms.

other species such as $[\text{Bi}\{\text{Fe}(\text{CO})_4\}_4]^{3-}$ [4] and $[\text{M}\{\text{Co}(\text{CO})_4\}_4]$ ($\text{M} = \text{Sn}, \text{Pb}$) [5]. However, the $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$ anion is not isoelectronic with these complexes, since it possesses two extra valence electrons.

Table 1

Bond distances (Å) within the anion $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$

Bi-Co(1)	2.867(2)	Bi-Co(3)	2.969(2)
Bi-Co(2)	2.866(2)	Bi-Co(4)	2.954(2)
Co(1)-C(11)	1.765(14)	Co(3)-C(31)	1.756(17)
Co(1)-C(12)	1.767(15)	Co(3)-C(32)	1.773(18)
Co(1)-C(13)	1.753(16)	Co(3)-C(33)	1.733(18)
Co(1)-C(14)	1.724(15)	Co(3)-C(34)	1.709(17)
Co(2)-C(21)	1.754(18)	Co(4)-C(41)	1.765(18)
Co(2)-C(22)	1.770(15)	Co(4)-C(42)	1.784(16)
Co(2)-C(23)	1.776(16)	Co(4)-C(43)	1.793(24)
Co(2)-C(24)	1.734(16)	Co(4)-C(44)	1.715(20)
C(11)-O(11)	1.159(14)	C(31)-O(31)	1.129(16)
C(12)-O(12)	1.146(14)	C(32)-O(32)	1.135(16)
C(13)-O(13)	1.150(14)	C(33)-O(33)	1.168(17)
C(14)-O(14)	1.155(14)	C(34)-O(34)	1.164(16)
C(21)-O(31)	1.165(17)	C(41)-O(41)	1.156(16)
C(22)-O(22)	1.139(14)	C(42)-O(42)	1.149(15)
C(23)-O(23)	1.156(14)	C(43)-O(43)	1.118(22)
C(24)-O(24)	1.169(15)	C(44)-O(44)	1.184(19)

Table 2

Bond angles (deg.) within the anion $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$

Co(1)–Bi–Co(2)	105.71(6)	Co(2)–Bi–Co(3)	110.13(6)
Co(1)–Bi–Co(3)	110.89(5)	Co(2)–Bi–Co(4)	110.82(6)
Co(1)–Bi–Co(4)	108.38(5)	Co(3)–Bi–Co(4)	110.79(6)
Bi–Co(1)–C(11)	178.6(5)	Bi–Co(2)–C(21)	174.4(6)
Bi–Co(1)–C(12)	84.2(5)	Bi–Co(2)–C(22)	82.5(4)
Bi–Co(1)–C(13)	84.5(5)	Bi–Co(2)–C(23)	82.0(5)
Bi–Co(1)–C(14)	83.3(5)	Bi–Co(2)–C(24)	85.6(6)
Bi–Co(3)–C(31)	176.3(7)	Bi–Co(4)–C(41)	172.7(6)
Bi–Co(3)–C(32)	84.0(5)	Bi–Co(4)–C(42)	80.5(5)
Bi–Co(3)–C(33)	80.8(5)	Bi–Co(4)–C(43)	80.5(6)
Bi–Co(3)–C(34)	83.0(5)	Bi–Co(4)–C(44)	84.9(6)
C(11)–Co(1)–C(12)	94.8(6)	C(21)–Co(2)–C(22)	93.9(8)
C(11)–Co(1)–C(13)	95.1(7)	C(21)–Co(2)–C(23)	96.5(8)
C(11)–Co(1)–C(14)	98.1(7)	C(21)–Co(2)–C(24)	99.9(8)
C(12)–Co(1)–C(13)	121.5(7)	C(22)–Co(2)–C(23)	123.8(7)
C(12)–Co(1)–C(14)	118.1(7)	C(22)–Co(2)–C(24)	117.0(7)
C(13)–Co(1)–C(14)	117.2(6)	C(23)–Co(2)–C(24)	115.1(7)
C(31)–Co(3)–C(32)	98.4(9)	C(41)–Co(4)–C(42)	94.7(9)
C(31)–Co(3)–C(33)	95.5(8)	C(41)–Co(4)–C(43)	98.0(9)
C(31)–Co(3)–C(34)	98.4(8)	C(41)–Co(4)–C(44)	102.2(8)
C(32)–Co(3)–C(33)	117.2(8)	C(42)–Co(4)–C(43)	124.3(8)
C(32)–Co(3)–C(34)	117.0(9)	C(42)–Co(4)–C(44)	114.0(9)
C(33)–Co(3)–C(34)	120.9(8)	C(43)–Co(4)–C(44)	115.7(9)
Co(1)–C(11)–O(11)	178.1(16)	Co(2)–C(21)–O(21)	174.6(19)
Co(1)–C(12)–O(12)	176.1(14)	Co(2)–C(22)–O(22)	172.9(13)
Co(1)–C(13)–O(13)	173.3(13)	Co(2)–C(23)–O(23)	174.5(14)
Co(1)–C(14)–O(14)	175.3(14)	Co(2)–C(24)–O(24)	177.1(17)
Co(3)–C(31)–O(31)	175.6(22)	Co(4)–C(41)–O(41)	173.9(17)
Co(3)–C(32)–O(32)	176.3(15)	Co(4)–C(42)–O(42)	176.5(16)
Co(3)–C(33)–O(33)	174.2(15)	Co(4)–C(43)–O(43)	169.9(20)
Co(3)–C(34)–O(34)	173.5(18)	Co(4)–C(44)–O(44)	174.3(17)

The BiCo_4 moiety shows a C_{2v} rather than a T_d idealized symmetry, exhibiting two longer (mean 2.962 Å) and two shorter (mean 2.866 Å) Bi–Co interactions. Moreover, though the overall mean value of the Co–Bi–Co angles, 109.45°, is coincident with the tetrahedral value (109.47°), the angle involving the two shorter Bi–Co bonds is significantly smaller (105.71(6)°) than the other five (mean 110.20°).

The Bi–Co bond (overall mean 2.914 Å) are very long compared with those in related species e.g. 2.623(2) Å in $[\text{BiCo}_3(\text{CO})_9]$ [1] and 2.744 Å (mean) in $[\text{Bi}_2\text{Co}_4(\text{CO})_{11}]^-$ [1]. In particular, in the related ‘open’ species $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ the mean Bi–Co bond length is 2.766 Å [3]. The values found in these species can be considered as those for normal Bi–Co single bonds, and the marked lengthening in $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$ can be ascribed to the presence of an extra electron pair on the Bi atom.

In Table 3 the mean bond parameters within the BiM_3 and BiM_4 ‘open’ species are shown. The particularly long Bi–Mn bonds in $[\text{Bi}\{\text{Mn}(\text{CO})_5\}_3]$ are clearly due to intramolecular non-bonding repulsions between the bulky $\text{Mn}(\text{CO})_5$ units, with the Mn atoms in octahedral environments. On the other hand, the large difference in the Bi–M bonds for the two strictly related BiM_4 species must arise from the different number of valence electrons.

Table 3

Mean bond parameters within the 'open' BiM_3 and BiM_4 carbonyl species

Compound	Bi-M (Å)	M-Bi-M (deg.)	Ref.
$[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$	2.766	106.8	3
$[\text{Bi}\{\text{Mn}(\text{CO})_5\}_3]$	2.904	108.2	2
$[\text{Bi}\{\text{Fe}(\text{CO})_4\}_4]^{3-}$	2.750	109.47	4b
$[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$	2.914	109.45	this work

From the point of view of the VSEPR model this anion is of the type AB_4E (B = bonding pair; E = non-bonding pair) and its expected stereochemistry is that of an incomplete trigonal bipyramid (saw-horse structure). However bismuth is known sometimes to present sterically ambivalent lone pairs [9,10]. Systems of the AB_4E type are quite uncommon for Bi because of its tendency to give higher coordination numbers. In the tetrahalides BiX_4^- [9] the metal atom attains a distorted octahedral environment through halogen bridging. To our knowledge the only other structurally characterized example of an AB_4E system for bismuth is the $[\text{BiPh}_2(\text{CF}_3\text{COO})_2]^-$ anion, with the expected incomplete trigonal bipyramidal geometry [11]. As stated above, in the $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$ anion the effect of the extra lone pair is a lengthening of the Bi-Co bonds rather than a modification of the tetrahedral geometry.

The coordination around the four cobalt atoms is a distorted trigonal bipyramid with the three-fold axis in the direction of the Bi-Co bond. The mean Co-C bond distances are not significantly different for the axial and equatorial carbonyl groups, 1.76 and 1.75 Å, respectively. The equatorial CO ligands are markedly bent toward the Bi atom, the overall mean values of the Bi-Co-C(eq) and C(ax)-Co-C(eq) angles being 83.0 and 97.1°, respectively. The distortion is more pronounced than in the $[\text{Bi}\{\text{Fe}(\text{CO})_4\}_4]^{3-}$ anion (mean values for the corresponding angles 86.3 and 93.7°, respectively). The C(eq)-Co-C(eq) angles are close to the ideal value of 120°, ranging from 114.0(9) to 124.3(8)°.

Experimental

All operations were carried out under nitrogen. All solvents were distilled and stored under nitrogen. $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ was prepared by a published method [3].

Synthesis of $[\text{NMe}_4][\text{Bi}\{\text{Co}(\text{CO})_4\}_4]$ from BiCl_3 and $\text{Na}[\text{Co}(\text{CO})_4]$

A stirred solution of $\text{Na}[\text{Co}(\text{CO})_4]$ (1.26 g) in THF (25 ml) was treated dropwise with a solution of BiCl_3 (0.5 g) in THF (15 ml). A dark violet-red solution was immediately formed. After about 1 h the solution was added from a syringe to a stirred solution of $[\text{NMe}_4]\text{Cl}$ (2 g) in water (100 ml), and the stirred mixture was evaporated under vacuum at room temperature to give initially an oil, which crystallized when the THF was eliminated. The solid was filtered off, washed ten times with 10 ml of water, then vacuum dried. It was freed from the co-precipitated $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ by washing with n-hexane in 10 ml portions until the washings were colourless. Crystals for the X-ray analysis were obtained by placing a layer of n-hexane over a CH_2Cl_2 solution of the product, and leaving the solvents to diffuse.

Yields 65–75%. Analysis. Found: C, 24.5; H, 1.35; N, 1.55; Co, 24.2. $C_{20}H_{12}BiCo_4NO_{16}$ calcd.: C, 24.8; H, 1.25; N, 1.45; Co, 24.38%.

Synthesis of [PPN][Bi{Co(CO)₄}]₄ from [Bi{Co(CO)₄}]₃ and [PPN][Co(CO)₄]

A stirred solution of [PPN][Co(CO)₄] (0.225 g) in THF (15 ml) was treated with an excess of [Bi{Co(CO)₄}]₃ (0.3 g). The solution turned immediately deep red-violet. The product was obtained as crystals by placing a layer of n-hexane (80 ml) over the THF solution and leaving the solvents to diffuse. The crystals were filtered off, washed with n-hexane, and vacuum dried. Yield 0.42 g, 92% based on the tetracarbonylcobaltate. The brown mother liquor contained mostly [BiCo₃(CO)₉].

Reaction of [Bi{Co(CO)₄}]₄⁻ and [Bi{Co(CO)₄}]₃ with halide ions

A stirred solution of [NMe₄][Bi{Co(CO)₄}]₄ (0.01 g) in THF (1 ml) was treated with LiCl or LiBr (0.02 g). The solution rapidly turned light yellow, and the IR spectrum showed only the characteristic band of the tetracarbonylcobaltate anion at 1885 cm⁻¹. Treatment of the solution with water (4 ml) caused immediate separation of a red oil, which solidified when the THF was evaporated off under vacuum. The red product was identified as [Bi{Co(CO)₄}]₃ by extraction of the aqueous mixture with n-hexane (1 ml) and IR examination of the extract. A similar reaction performed in methanol resulted only in a little decomposition, even after addition of larger amounts of halides.

In THF [Bi{Co(CO)₄}]₃ behaved exactly like [NMe₄][Bi{Co(CO)₄}]₄, but in methanol it was converted into a mixture of [Bi{Co(CO)₄}]₄⁻ and [Co(CO)₄]⁻, probably by condensation with the [Co(CO)₄]⁻ derived by partial decomposition.

Thermal decomposition of [NMe₄][Bi{Co(CO)₄}]₄

A solution of [NMe₄][Bi{Co(CO)₄}]₄ (0.06 g) in THF (6 ml) was stirred on an oil bath at 50°C. IR monitoring of the solution showed that after about half an hour the starting material had completely disappeared to give a mixture of [BiCo₃(CO)₉], [Co(CO)₄]⁻ and traces of [Bi₂Co₄(CO)₁₁]⁻. The presence of [BiCo₃(CO)₉] was confirmed by evaporation of the THF in vacuum, extraction with n-hexane, and IR examination of the extract.

X-ray analysis

Crystal data. $C_{20}H_{12}BiCo_4NO_{16}$, $M = 967.0$, monoclinic, space group $P2_1/c$ (No. 14), with a 12.327(3), b 14.181(3), c 19.017(4) Å, β 106.14(2)°, U 3193.3 Å³, $F(000) = 1832$, D_c 2.01 g cm⁻³ for $Z = 4$; Mo- K_α radiation (λ 0.71073 Å), $\mu(\text{Mo-}K_\alpha)$ 75.74 cm⁻¹.

Intensity measurements. A crystal sample of dimensions 0.18 × 0.19 × 0.22 mm was sealed into a capillary tube and mounted on Enraf–Nonius CAD4 automated diffractometer. The intensity data were collected by use of 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 by the ω -scan method in the range $3 < \theta < 25^\circ$. A variable scan-speed (from 2 to 20°/min) and a variable scan-range of $(0.8 + 0.35 \tan \theta)^\circ$ were used, with a 25% extension at each end of the scan-range for background determination. The total number of collected reflec-

Table 4

Final potential parameters within compound 1

Atom	x	y	z	Atom	x	y	z
Bi	0.24514(4)	0.12509(4)	0.22363(2)	C(32)	0.239(1)	-0.094(1)	0.2800(8)
Co(1)	0.3621(1)	0.1166(1)	0.11288(8)	O(32)	0.181(1)	-0.1469(8)	0.2430(6)
Co(2)	0.2833(1)	0.3115(1)	0.28366(9)	C(33)	0.459(1)	0.010(1)	0.3172(7)
Co(3)	0.3355(2)	-0.0171(1)	0.33974(9)	O(33)	0.5466(7)	0.0223(8)	0.3064(5)
Co(4)	0.0023(2)	0.0930(2)	0.1535(1)	C(34)	0.282(1)	0.058(1)	0.3916(7)
C(11)	0.433(1)	0.114(1)	0.0442(6)	O(34)	0.241(1)	0.1020(8)	0.4292(5)
O(11)	0.4785(8)	0.1106(8)	-0.0016(5)	C(41)	-0.139(1)	0.075(2)	0.1009(9)
C(12)	0.238(1)	0.168(1)	0.0566(7)	O(41)	-0.2278(9)	0.066(1)	0.0611(6)
O(12)	0.1584(8)	0.1994(9)	0.0167(5)	C(42)	0.061(1)	0.011(1)	0.1029(6)
C(13)	0.465(1)	0.184(1)	0.1745(6)	O(42)	0.0927(9)	-0.0437(8)	0.0688(5)
O(13)	0.5375(7)	0.2294(8)	0.2096(4)	C(43)	0.007(1)	0.219(1)	0.1439(7)
C(14)	0.362(1)	-0.0030(9)	0.1290(6)	O(43)	-0.0059(9)	0.2957(8)	0.1322(6)
O(14)	0.3661(8)	-0.0838(7)	0.1366(5)	C(44)	-0.001(1)	0.053(1)	0.2381(8)
C(21)	0.316(1)	0.427(1)	0.3155(8)	O(44)	-0.0122(9)	0.023(1)	0.2938(5)
O(21)	0.3374(8)	0.5057(8)	0.3309(5)	N	-0.1683(9)	0.3415(8)	-0.0757(6)
C(22)	0.260(1)	0.3428(9)	0.1905(7)	Ct(1) ^a	-0.219(1)	0.347(1)	-0.1599(9)
O(22)	0.247(1)	0.3723(7)	0.1331(5)	Ct(2)	-0.221(2)	0.411(2)	-0.038(1)
C(23)	0.410(1)	0.259(1)	0.3377(6)	Ct(3)	-0.042(2)	0.360(2)	-0.057(1)
O(23)	0.4952(8)	0.2314(7)	0.3743(5)	Ct(4)	-0.196(3)	0.245(2)	-0.045(2)
C(24)	0.165(1)	0.292(1)	0.3138(6)	Ct(2')	-0.245(5)	0.325(5)	-0.034(3)
O(24)	0.0835(8)	0.2825(9)	0.3333(5)	Ct(3')	-0.118(4)	0.245(3)	-0.069(2)
C(31)	0.398(1)	-0.099(1)	0.4082(7)	Ct(4')	-0.117(5)	0.430(5)	-0.054(3)
O(31)	0.444(1)	-0.149(1)	0.4528(6)				

^a Ct = cationic carbon atoms.

tions was 5646. Three standard intense reflections, measured at regular intervals, showed a total decay during the collection of ca. 5%. The intensities were corrected for Lorentz, polarization, and decay effects. An empirical absorption correction was applied to the data set, based on ψ -scans (ψ 0–360°, every 10°) of suitable reflections with χ values close to 90°; the maximum, minimum and average relative transmission factors were 1.00, 0.84 and 0.93, respectively. A set of 2201 independent significant reflections, with $I > 3\sigma(I)$, was used in the structure solution and refinement.

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

The structure solution was determined from a three-dimensional Patterson map, which gave the positions of the metal atoms. Successive difference-Fourier maps showed the locations of all the remaining non-hydrogen atoms.

The tetramethylammonium cation is disordered. The disorder was interpreted in terms of two models having the two atoms N and Ct(1) in common; the three other C atoms are doubled by a rotation about the N–Ct(1) axis, with populations, estimated by preliminary refinements, of 0.65 for atoms Ct(2), Ct(3) and Ct(4) and 0.35 for atoms Ct(2'), Ct(3') and Ct(4').

The refinements were carried out by full-matrix least-squares. Anisotropic thermal factors were assigned to all atoms except those in the cation. The cationic hydrogen atoms were ignored. The final difference-Fourier maps were rather flat showing residual peaks not exceeding ca. 1 e Å⁻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 taken as 0.04. The final values of R and R_w were 0.035 and 0.037, respectively.

The final positional parameters are given in Table 4. A list of observed and calculated structure factors and a table of thermal parameters can be obtained from the authors.

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