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The Structures of [Sn{Co(CO)$_4$}$_4$] and [Pb{Co(CO)$_4$}$_4$]

BY J. SCOTT LEIGH AND KENTON H. WHITMIRE*

Department of Chemistry, Rice University, PO Box 1892, Houston, TX 77251, USA

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Abstract. Tetrakis(tetracarbonylcobaltio)tin, [SnCo$_4$(CO)$_{16}$], $M_r = 802{\cdot}59$, cubic, $F\bar{4}3c$, $a = 17{\cdot}255\,(2)$ Å, $V = 5136{\cdot}7\,(19)$ Å^3, $Z = 8$, $D_x = 2{\cdot}08$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 35{\cdot}60$ cm^{-1}, $F(000) = 3056$, $T = 296$ K, $R = 0{\cdot}017$, $wR = 0{\cdot}022$ for 196 observed unique reflections $[I > 3\sigma(I)]$. The tetrahedral Sn atom sits on a site of 23 symmetry and is surrounded by four trigonal bipyramidal Co(CO)$_4$ groups. Tetrakis(tetracarbonylcobaltio)lead, [PbCo$_4$(CO)$_{16}$], $M_r = 891{\cdot}10$, orthorhombic, $Pccn$, $a = 12{\cdot}184\,(2)$, $b = 12{\cdot}267\,(3)$, $c = 17{\cdot}220\,(2)$ Å, $V = 2574\,(1)$ Å^3, $Z = 4$, $D_x = 2{\cdot}30$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 91{\cdot}64$ cm^{-1}, $F(000) = 1656$, $T = 296$ K, $R = 0{\cdot}077$, $wR = 0{\cdot}100$ for 1139 observed unique reflections $[I > 3\sigma(I)]$. Pb{Co(CO)$_4$}$_4$ is isostructural to Sn{Co(CO)$_4$}$_4$ but possesses only twofold crystallographic symmetry.

Introduction. Cobalt carbonyl compounds of tin and lead have been known for years. The complex [Sn{Co(CO)$_4$}$_4$] has been reported from the reactions of metallic tin, SnCl$_4$ or [SnCl{Co(CO)$_4$}$_3$] with [Co$_2$(CO)$_8$] (Schmid & Etzrodt, 1977; Patmore & Graham, 1968; Bigorgne & Quintin, 1967). [Sn{Co(CO)$_3${P(C$_6$H$_5$)$_3$}}$_4$] has been prepared by treating [Sn{Co(CO)$_4$}$_4$] with P(C$_6$H$_5$)$_3$ (Schmid & Etzrodt, 1977). Species such as [RSn{Co(CO)$_4$}$_3$] (R = C$_6$H$_5$, CH$_3$, CH$_2$=CH, n-C$_4$H$_9$), [XSn{Co(CO)$_4$}$_3$] (X = Cl, Br, I), and [R_nX_{3-n}SnCo(CO)$_4$] (R = C$_6$H$_5$; X = Cl, Br, I; n = 0, 1, 2) have been obtained from reactions of tin halides or alkyl halides with [Co$_2$(CO)$_8$] or [Co(CO)$_4$]$^-$ (Patmore & Graham, 1966, 1968). The complex [Pb{Co(CO)$_4$}$_4$] has been reported from the reaction of metallic Pb with [Co$_2$(CO)$_8$] (Schmid & Etzrodt, 1977). Reactions of metallic Pb with [HCo(CO)$_4$] or Pb(NO$_3$)$_2$ with [NaCo(CO)$_4$] (Vizi-Orosz, Bor & Markó, 1969; Krumholz & Bril, 1960) initially were reported to form [Pb{Co(CO)$_4$}$_2$], but were later shown to give [Pb{Co(CO)$_4$}$_4$] (Schmid & Etzrodt, 1977). [Pb{Co(CO)$_3${P(C$_6$H$_5$)$_3$}}$_4$] and [Pb{Co(CO)$_3${P(C$_6$H$_5$)$_3$}}Co(CO)$_4$] have been prepared by treating [Pb{Co(CO)$_4$}$_4$] with P(C$_6$H$_5$)$_3$ (Schmid & Etzrodt, 1977).

None of these complexes, however, has been structurally characterised using X-ray crystallography. Thus, we present here the crystal structures of [Sn{Co(CO)$_4$}$_4$] and [Pb{Co(CO)$_4$}$_4$]. These molecules, which are isostructural, consist of four trigonal bipyramidal [Co(CO)$_4$] groups tetrahedrally surrounding a group 14 atom.

Experimental. [Sn{Co(CO)$_4$}$_4$] was prepared from the dropwise addition over a 10 min period of an aqueous solution of SnCl$_4$.5H$_2$O (1·08 g, 3·08 mmol in 100 ml N$_2$ bubbled H$_2$O) to a stirred aqueous solution of Na[Co(CO)$_4$] (12·3 mmol in 60 ml N$_2$ bubbled H$_2$O). After stirring several hours the resulting burnt-orange precipitate was then isolated by filtration, washed with 100 ml H$_2$O, and dried under vacuum to give [Sn{Co(CO)$_4$}$_4$] in 65% yield (1·61 g, 2·01 mmol). Crystals of the compound were grown from a CH$_2$Cl$_2$ solution cooled at 253 K overnight. A cube of edge approximately 0·5 mm was mounted on the tip of a glass fiber with epoxy cement. The unit-cell parameters were derived from the least-squares best fit of 22 reflections ($26{\cdot}88 \leq 2\theta \leq 41{\cdot}13°$), which indicated an F-centered cubic lattice. Data were collected (2θ–ω scans, 4° ω min^{-1}) using a Rigaku AFC5S automated four-circle diffractometer [Rigaku *CRYSTAN/TEXTL* (3:2:1) *Automatic Data Collection Series* (Molecular Structure Corporation, 1987)] through the range h 0 to 22, k 0 to 22, l 0 to 22, measuring 353 nonequivalent reflections with 196

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* To whom all correspondence should be addressed.

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observed [$I > 3\sigma(I)$], $2\theta_{\max} = 55°$, $[(\sin\theta)/\lambda]_{\max} =$ 0·65 Å^{-1}. Three standards were measured every 150 reflections, showing essentially no decay in intensity. Systematic absences indicated two possible space groups: $F\bar{4}3c$ (No. 219) and $Fm\bar{3}c$ (No. 226). Attempts at solution in the centrosymmetric space group revealed the Sn and Co atoms, but the carbonyl ligands could not be located and refined properly. Attempts at solution in the noncentrosymmetric space group, $F\bar{4}3c$, proceeded normally, proving this to be the correct choice. The structure was solved using the direct-methods program in *SHELXS*86 (Sheldrick, 1986), which located the Sn and Co atoms. Further difference Fourier syntheses using the *TEXSAN* (Version 2.0) structure analysis package (Molecular Structure corporation, 1988*b*) located the C and O atoms. Full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F_o)]^{-1}$ (σ^2 = variance) with all atoms refined anisotropically. The enantiomorph was chosen by first refining both possible configurations without including anomalous-dispersion terms, which gave identical *R* factors for both forms. Inclusion of anomalous-dispersion terms in refinement then caused *R* and *wR* to increase for one enantiomorph, while causing *wR* to decrease for its mirror image. Thus, the enantiomorph chosen as the correct configuration was the form giving the lowest *R* values (0·3% less than the other form). Refinement converged initially with S = 0·81, indicating unusual weights. The *p* factor used for calculating $\sigma(F^2)$ was lowered from 0·05 to 0·03 $\{\sigma(F^2) = [C + 1/4(t_c/t_b)^2 \times (b_1 + b_2) + (pI)^2]^{1/2}$, where C = total number of counts, t_c = time spent counting peak intensity, t_b = time spent counting one side of background, b_1 = high-angle background counts, b_2 = low-angle background counts, p = fudge factor (p factor), $I = C - 1/2(t_c/t_b)(b_1 + b_2)\}$. Refinement then converged with R = 0·017, wR = 0·022, $(\Delta/\sigma)_{\max}$ = 0·00, $(\Delta\rho)_{\max}$ = 0·30 e Å^{-3}, number observations/number variables = 6·76, and S = 1·01. The data were corrected for absorption (ψ scans, transmission range 0·7559–1·0000) and Lp effects.

[Pb{Co(CO)$_4$}$_4$] was prepared from the addition by syringe of an aqueous solution of Pb($C_2H_3O_2$)$_2$.3H_2O (0·83 g, 2·2 mmol in 20 ml N_2 bubbled H_2O) to a stirred aqueous solution of Na[Co(CO)$_4$] (4·4 mmol in 20 ml N_2 bubbled H_2O). After stirring several hours, the resulting dark precipitate was isolated by filtration, washed with 20 ml H_2O, and dried under vacuum. The solid was then stirred briefly with two 40 ml portions of CH_2Cl_2 to extract [Pb{Co(CO)$_4$}$_4$] (second wash was essentially colorless) from other products that were soluble in acetone with IR ($\tilde{\nu}_{CO}$) bands at 2060 (*m*), 2040 (*s*), 1970 (*vs*), 1894 (*m*) cm^{-1}. The violet CH_2Cl_2 extract containing [Pb{Co(CO)$_4$}$_4$] was filtered, and the solvent removed under vacuum to give [Pb{Co(CO)$_4$}$_4$] in 35% yield (0·34 g, 0·38 mmol). Crystals of the compound were grown from a CH_2Cl_2 solution cooled at 253 K overnight. A black parallelepiped of edge approximately 0·05 mm was mounted on the tip of a glass fiber with epoxy cement. Unit-cell parameters derived from the least-squares best fit of 25 reflections (6·68 ≤ 2θ ≤ 17·72°) suggested an orthorhombic lattice with a = 12·1843 (19), b = 12·2666 (26), c = 8·6102 (11) Å, V = 1286·87 (38) Å^3. Data collected on several different crystals indicated the same cell parameters and showed systematic absences and intensity statistics for the noncentrosymmetric space group $Pmn2_1$ (No. 31, setting No. 6). Attempts at solution in this space group, however, led to seemingly unreasonable results in which the molecule sat on a mirror plane with disordered carbonyls reflecting into each other across the mirror. Least-squares refinement would not proceed below 16%. Attempts at solution and refinement in other potential space groups also proved unsuccessful. After these attempts, axial photographs of a crystal were taken that exhibited faint spots halfway between the lattice spacings along the short axis, indicating a superstructure. The short axis was doubled, and data were recollected (2θ–ω scans, 4°ω min^{-1}) using a Rigaku AFC5S automated four-circle diffractometer [*Rigaku Automatic Data Collection Series CONTROL* (4:0:0) (Molecular Structure Corporation, 1988*a*)] through the range h 0 to 16, k 0 to 22, l 0 to 16, measuring 3347 nonequivalent reflections with 1139 observed [$I > 3\sigma(I)$], $2\theta_{\max} = 55°$, $[(\sin\theta)/\lambda]_{\max}$ = 0·65 Å^{-1}. Three standards were measured every 150 reflections, showing little decay in intensity (0·2%). Systematic absences and Laue symmetry of this new data set unambiguously indicated the space group *Pccn* (No. 56, setting No. 5). After transformation to the standard space-group setting, the structure was solved using the direct-methods program in *SHELXS*86 (Sheldrick, 1986), which located the Pb and Co atoms. Further difference Fourier syntheses using the *TEXSAN* (version 2·0) structure analysis package (Molecular Structure Corporation, 1988*b*) located the C and O atoms. Full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F_o)]^{-1}$ (σ^2 = variance), with the Pb, Co and O atoms refined anisotropically and the C atoms isotropically. The data were corrected for absorption [*DIFABS* (Walker & Stuart, 1983), correction range 0·834–1·050, average correction = 0·978] and Lp effects. Refinement converged with R = 0·077, wR = 0·100, $(\Delta/\sigma)_{\max}$ = 0·05, $(\Delta\rho)_{\max}$ = 7·36 e Å^{-3}, number observations/number variables = 8·9 and S = 2·07. The high values for *R* and *wR* may result, at least in part, from the zone of weak intensity that contributed to the difficulty in determining the correct length of the *c* axis.

Scattering factors: *International Tables for X-ray Crystallography* (Cromer & Waber, 1974).*

Discussion. The crystal structure of $[\mathrm{Sn\{Co(CO)_4\}_4}]$ contains ordered molecules having no unusually short intermolecular contacts. The molecule consists of an Sn atom tetrahedrally surrounded by four $[\mathrm{Co(CO)_4}]$ groups, with the environment about each Co being trigonal bipyramidal. The equatorial carbonyls on the Co atoms lean slightly toward the Sn atom. An *ORTEP* (Johnson, 1976) diagram of the molecule showing 50% thermal probability ellipsoids is given in Fig. 1, and a stereoview of the molecule is shown in Fig. 2. Positional parameters are given in Table 1 and intramolecular distances and angles in Table 2. The Sn atom sits on a site of 23 symmetry, and Co1, C1 and O1 sit at special positions having threefold symmetry.

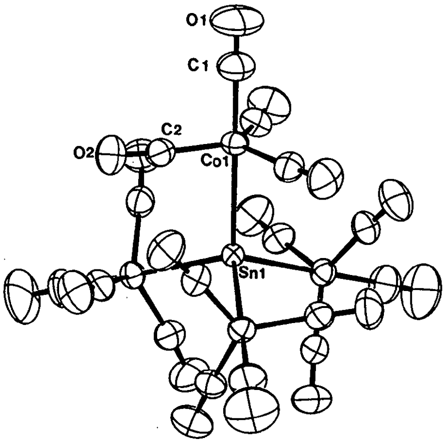

Fig. 1. *ORTEP* (Johnson, 1976) diagram of $[\mathrm{Sn\{Co(CO)_4\}_4}]$ showing 50% thermal probability ellipsoids and atom labeling. Bond distances and angles are given in Table 2.

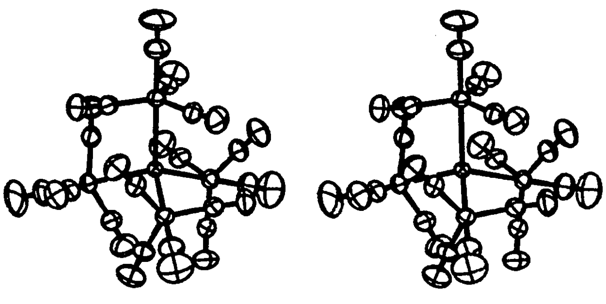

Fig. 2. Stereoview of $[\mathrm{Sn\{Co(CO)_4\}_4}]$.

Table 1. *Positional parameters and* B_{eq} *values for* $[\mathrm{Sn\{Co(CO)_4\}_4}]$

$B_{eq} = (8\pi^2/3)$ trace **U**.

	x	y	z	B_{eq} (Å^2)
Sn1	0	0	0	2·1703 (2)
Co1	−0·08932 (3)	−0·0893	−0·0893	2·9467 (3)
O1	−0·1863 (3)	−0·1863	−0·1863	9·355 (4)
O2	−0·1928 (3)	0·0427 (3)	−0·1090 (3)	6·0 (3)
C1	−0·1499 (4)	−0·1499	−0·1499	5·072 (3)
C2	−0·1507 (3)	−0·0073 (4)	−0·0991 (4)	3·8 (2)

Table 2. *Bond distances* (Å) *and angles* (°) *for* $[\mathrm{Sn\{Co(CO)_4\}_4}]$

Sn1—Co1	2·669 (1)	Co1—C2	1·776 (7)
Co1—C1	1·81 (1)	C1—O1	1·09 (1)
C2—O2	1·141 (7)		
Sn1—Co1—C1	180	Co1—C1—O1	180
Sn1—Co1—C2	86·5 (2)	Co1—C2—O2	175·5 (6)
C1—Co1—C2	93·5 (2)		

The crystal structure of $[\mathrm{Pb\{Co(CO)_4\}_4}]$ also contains ordered molecules having no unusually short intermolecular contacts. The molecule consists of a Pb atom tetrahedrally surrounded by four $[\mathrm{Co(CO)_4}]$ groups, with the environment about each Co being trigonal bipyramidal. As in $[\mathrm{Sn\{Co(CO)_4\}_4}]$, the equatorial carbonyls on the Co atoms lean slightly toward the Pb atom, which sits on a site of twofold symmetry. An *ORTEP* diagram of the molecule showing 50% thermal probability ellipsoids is given in Fig. 3, and a stereoview of the molecule is shown in Fig. 4. Positional parameters are given in Table 3 and intramolecular distances and angles in Table 4.

The Sn—Co bond distance in $[\mathrm{Sn\{Co(CO)_4\}_4}]$ is 2·669 (1) Å, and the Pb—Co bond distances in $[\mathrm{Pb\{Co(CO)_4\}_4}]$ are 2·738 (5) and 2·761 (5) Å. The Sn—Co distance is shorter than the Pb—Co distances as might be expected due to the smaller covalent radius of Sn compared to Pb. For comparison with other characterized Sn or Pb/first-row transition-metal complexes, this Sn—Co distance is longer than the Sn—Fe (av.) distances in $[\mathrm{Sn\{Fe_2(CO)_8\}_2}]$ [2·54 (1) Å] (Lindley & Woodward, 1967) and $[\mathrm{Fe_3(CO)_9\{\mu_3\text{-}SnFe(CO)_2Cp\}_2}]$ [Sn—Fe(core) = 2·537 (4) Å; Sn—Fe(terminal) = 2·471 (5) Å] (McNeese, Wreford, Tipton & Bau, 1977) and the Sn—Mn (av.) bond lengths in $[\mathrm{Mn_2(CO)_8\{\mu\text{-}Sn(Cl)Mn(CO)_5\}_2}]$ [2·623 (1) Å] (Haupt, Preut & Wolfes, 1978) and $[\mathrm{Mn_2(CO)_8\{\mu\text{-}Sn(Br)Mn(CO)_5\}_2}]$ [2·630 (1) Å] (Preut & Haupt, 1976). It is shorter than the Sn—Mn (av.) distance in $[\mathrm{SnBr\{Mn(CO)_5\}_3}]$ [2·740 (2) Å] (Haupt, Preut & Wolfes, 1978). The Pb—Co distances are longer than the Pb—Fe distances in $[\mathrm{Pb\{Fe_2(CO)_8\}_2}]$ [2·606 (3) and 2·635 (3) Å] (Whitmire, Lagrone, Churchill, Fettinger & Robinson, 1987) and the Pb—Fe(terminal) distances in

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52416 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$[Et_4N]_2[Pb\{Fe(CO)_4\}_2\{Fe_2(CO)_8\}]$ [2·651 (5) and 2·659 (5) Å] (Lagrone, Whitmire, Churchill & Fettinger, 1986), but they are shorter than the Pb—Fe bond lengths of the $PbFe_2$ fragment in the latter compound [2·823 (4) and 2·832 (4) Å]. The differences in bond lengths in $[Pb\{Fe(CO)_4\}_2\{Fe_2(CO)_8\}]^{2-}$ are probably due to steric interactions of the metal carbonyl groups.

Another mixed cluster complex that is isostructural and isoelectronic with $[Sn\{Co(CO)_4\}_4]$ and $[Pb\{Co(CO)_4\}_4]$ is $[Bi\{Fe(CO)_4\}_4]^{3-}$ (Churchill, Fettinger, Whitmire & Lagrone, 1986). The Bi—Fe (av.) distance in this molecule, which is longer than the Sn—Co distance in $[Sn\{Co(CO)_4\}_4]$ but statistically similar to the Pb—Co bond lengths in $[Pb\{Co(CO)_4\}_4]$, is 2·750 (2) Å {where the standard deviation σ has been calculated from the scatter formula $\sigma = [\sum(d_i - d_{av})^2/(N-1)]^{1/2}$}. Other tetrahedral cobalt/main-group-element clusters are $[Sb\{Co(CO)_3PPh_3\}_4]^+$ [Sb—Co (av.) = 2·596 Å] (Cobbledick & Einstein, 1979) and $[Bi\{Co(CO)_4\}_4]^-$ [Bi—Co (av.) = 2·906 Å] (Leigh & Whitmire, 1988). $[Bi\{Co(CO)_4\}_4]^-$ is isostructural but not isoelectronic, having two additional electrons in the metal framework.

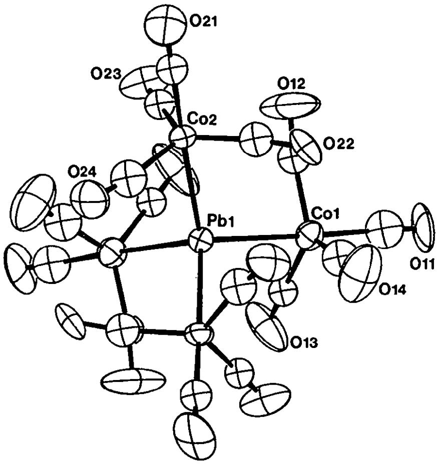

Fig. 3. *ORTEP* (Johnson, 1976) diagram of $[Pb\{Co(CO)_4\}_4]$ showing 50% thermal probability ellipsoids and atom labeling. Carbonyl C atoms are labeled according to their respective O atoms. Bond distances and angles are given in Table 4.

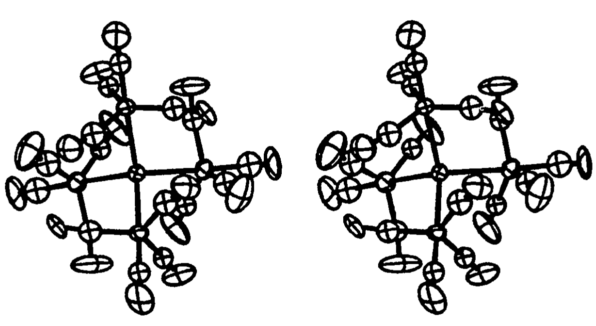

Fig. 4. Stereoview of $[Pb\{Co(CO)_4\}_4]$.

Table 3. *Positional parameters and B_{eq} values for* $[Pb\{Co(CO)_4\}_4]$

$B_{eq} = (8\pi^2/3)$ trace U.

	x	y	z	B_{eq} (Å^2)
Pb1	$\frac{1}{4}$	$\frac{3}{4}$	0·4157 (1)	2·82 (6)
Co1	0·0660 (4)	0·7695 (4)	0·3231 (3)	3·6 (2)
Co2	0·2314 (4)	0·5691 (3)	0·5079 (3)	3·4 (2)
O11	−0·125 (2)	0·785 (3)	0·227 (2)	7 (2)
O12	0·059 (3)	0·530 (2)	0·316 (2)	10 (2)
O13	0·193 (3)	0·908 (3)	0·226 (2)	8 (2)
O14	−0·037 (3)	0·871 (3)	0·455 (2)	10 (3)
O21	0·207 (3)	0·375 (3)	0·606 (2)	10 (2)
O22	0·005 (2)	0·635 (2)	0·531 (2)	6 (2)
O23	0·306 (3)	0·442 (2)	0·373 (2)	7 (2)
O24	0·403 (3)	0·662 (2)	0·612 (2)	7 (2)
C11	−0·060 (4)	0·777 (4)	0·260 (3)	6 (1)
C12	0·069 (3)	0·624 (3)	0·318 (2)	4·1 (8)
C13	0·145 (3)	0·855 (3)	0·262 (2)	3·5 (7)
C14	0·002 (4)	0·831 (4)	0·407 (3)	6 (1)
C21	0·216 (3)	0·452 (3)	0·569 (2)	4·1 (8)
C22	0·095 (3)	0·602 (3)	0·518 (2)	4·8 (9)
C23	0·277 (3)	0·494 (3)	0·428 (2)	3·7 (8)
C24	0·332 (4)	0·633 (4)	0·572 (3)	6 (1)

Table 4. *Bond distances* (Å) *and angles* (°) *for* $[Pb\{Co(CO)_4\}_4]$

Pb1—Co1	2·761 (5)	Pb1—Co2	2·738 (5)
Co1—C11	1·88 (5)	Co1—C12	1·78 (4)
Co1—C13	1·77 (4)	Co1—C14	1·80 (5)
Co2—C21	1·79 (4)	Co2—C22	1·71 (4)
Co2—C23	1·76 (3)	Co2—C24	1·83 (5)
C11—O11	0·98 (5)	C12—O12	1·17 (4)
C13—O13	1·08 (4)	C14—O14	1·08 (5)
C21—O21	1·14 (4)	C22—O22	1·20 (4)
C23—O23	1·18 (4)	C24—O24	1·16 (5)
Co1—Pb1—Co2	109·8 (1)	Pb1—Co1—C11	178 (1)
Pb1—Co1—C12	86 (1)	Pb1—Co1—C13	87 (1)
Pb1—Co1—C14	86 (1)	Pb1—Co2—C21	179 (1)
Pb1—Co2—C22	87 (1)	Pb1—Co2—C23	87 (1)
Pb1—Co2—C24	87 (1)	C11—Co1—C12	92 (2)
C11—Co1—C13	94 (2)	C11—Co1—C14	95 (2)
C12—Co1—C13	123 (2)	C12—Co1—C14	118 (2)
C13—Co1—C14	118 (2)	C21—Co2—C22	92 (2)
C21—Co2—C23	94 (2)	C21—Co2—C24	93 (2)
C22—Co2—C23	121 (2)	C22—Co2—C24	119 (2)
C23—Co2—C24	119 (2)	Co1—C11—O11	177 (5)
Co1—C12—O12	173 (4)	Co1—C13—O13	178 (4)
Co1—C14—O14	178 (5)	Co2—C21—O21	178 (4)
Co2—C22—O22	172 (4)	Co2—C23—O23	179 (3)
Co2—C24—O24	171 (4)		

$[Sn\{Co(CO)_4\}_4]$ and $[Pb\{Co(CO)_4\}_4]$ are soluble in most common organic solvents. IR ($\tilde{\nu}_{CO}$ of crystals in CH_2Cl_2) for $[Sn\{Co(CO)_4\}_4]$: 2080 (*s*), 2020 (*s*), 1994 (*sh*) cm^{-1}. Previously reported IR ($\tilde{\nu}_{CO}$) frequencies for this compound: 2080 (*vs*), 2033 (*w*), 2020 (*vs*), 1996 (*w*) cm^{-1} [in hexane; Schmid & Etzrodt (1977)]; 2079 (*vs*), 2032 (*m*), 2018 (*vs*), 1999 (*sh*), 1994 (*w*) cm^{-1} [in cyclohexane; Patmore & Graham (1968)]. IR ($\tilde{\nu}_{CO}$ of crystals in CH_2Cl_2) for $[Pb\{Co(CO)_4\}_4]$: 2078 (*s*), 2034 (*m*), 2018 (*s*), 1994 (*sh*) cm^{-1}. Previously reported IR ($\tilde{\nu}_{CO}$) frequencies for this compound: 2073 (*vs*), 2031 (*m*), 2016 (*vs*), 1994 (*w*) cm^{-1} [in hexane; Schmid & Etzrodt (1977)].

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Structure of Na_3OCl

BY KARIN HIPPLER, STEPHAN SITTA, PETRA VOGT AND HORST SABROWSKY

Anorganische Chemie I, *Ruhr-Universität Bochum, Universitätsstraße* 150, *D*-4630 *Bochum* 1,
Federal Republic of Germany

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Abstract. $M_r = 120\cdot422$, cubic, $Pm3m$, $a = 4\cdot496\,(2)$ Å, $V = 90\cdot88$ Å^3, $Z = 1$, $D_x = 2\cdot200$ g cm^{-3}, λ(Mo $K\alpha$) = $0\cdot71069$ Å, $\mu = 11\cdot58$ cm^{-1}, $F(000) = 58$, $T = 293$ K, $R = 0\cdot0269$ for 74 unique observed reflections. The compound crystallizes in the perovskite structure type. The Na atom is coordinated by two O atoms (axial) and four Cl atoms (equatorial) in a distorted octahedral environment. Oxygen is surrounded octahedrally by six Na atoms and chlorine is coordinated by 12 Na atoms.

Introduction. Recently we described the preparation of Na_3OCl and Na_3OBr (Sabrowsky, Paszkowski, Reddig & Vogt, 1988) as part of our investigations on the existence of ternary alkali metal chalcogenide halides. In agreement with the rule of Goldschmidt (1926) the compounds should crystallize in the antiperovskite structure type. Meanwhile we succeeded in preparing single crystals of Na_3OCl. We present here the results of the single-crystal structure determination.

Experimental. Polycrystalline samples of Na_3OCl can be obtained by sintering a stoichiometric mixture of Na_2O and NaCl in closed silver crucibles between 573 and 873 K in an argon atmosphere (3 bar). Well shaped colourless single crystals of Na_3OCl were grown from equimolar mixtures of Na_2O and NaCl at 873 K. The crystals are sensitive to air and moisture. D_m was not measured. A crystal with the dimensions $0\cdot1 \times 0\cdot1 \times 0\cdot1$ mm was used for the data collection. The unit-cell parameters were determined by least-squares treatment of the adjusted angular settings of 25 reflections ($2\theta = 14 - 26°$) measured on

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