International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

RIJNSDORP, J., DE LANGE, G. J. & WIEGERS, G. A. (1979). *J. Solid State Chem.* **30**, 365–373.

SCHNERING, H. G. VON & BECKMANN, W. (1966). *Z. Anorg. Allg. Chem.* **347**, 231–239.

SHELDRICK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1984). C**40**, 1549–1551

The Structure of Tetramethylammonium Tris[tetracarbonylcobalt(−I)]mercurate(II), $[N(CH_3)_4][Hg\{Co(CO)_4\}_3]$

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Abstract. $M_r = 787{\cdot}7$, monoclinic, $P2_1/a$, $a = 16{\cdot}286\ (3)$, $b = 16{\cdot}460\ (3)$, $c = 19{\cdot}213\ (4)$ Å, $\beta = 96{\cdot}84\ (1)°$, $V = 5113{\cdot}6\ (17)$ Å^3, $Z = 8$, $D_x = 2{\cdot}05$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 79{\cdot}7$ cm^{-1}, $F(000) = 2976$, 293 K, $R = 0{\cdot}048$ for 4470 symmetrically independent reflections. The title compound is prepared by the reaction of $Hg[Co(CO)_4]_2$ with $Co(CO)_4^-$. The two independent $Hg[Co(CO)_4]_3^-$ anions in the unit cell consist of an Hg^{2+} cation coordinated by three $Co(CO)_4^-$ anions. The geometry at mercury is trigonal planar with an average Hg—Co bond distance of 2·686 Å. The cobalt atoms have a distorted trigonal bipyramidal geometry with an average Hg—Co—C(equatorial) angle of 80·9°.

Introduction. The anion $Hg[Co(CO)_4]_3^-$ has been known for several years, but the structure remained unknown. This complex was first postulated to be a radical anion $Hg[Co(CO)_4]_2^-$ (Vizi-Orosz, Papp & Marko, 1969), and later correctly identified as a tetrametallic cluster by several groups (Burlitch, Petersen, Conder & Robinson, 1970; Conder & Robinson, 1972; Cleland, Fieldhouse, Freeland, Mann & O'Brien, 1970).

There have been several reported examples of structures which contain trigonal planar mercury(II) (see Petersen, Ragosta, Whitwell & Burlitch, 1983, for references), including several which contain mercury coordinated to three transition metals (Erner *et al.*, 1983; Duffy, Mackey, Nicholson & Robinson, 1981; and a preliminary report of this work, Petersen *et al.*, 1983). The tetramethylammonium salt of $Hg[Co(CO)_4]_3^-$ was found to give crystals suitable for X-ray single-crystal analysis, and the results are presented here.

Experimental. Title compound prepared from $N(CH_3)_4^+.Co(CO)_4^-$ and $Hg[Co(CO)_4]_2$ (Petersen *et al.*, 1983). Single crystals prepared by cooling a methylene chloride solution. Single crystal mounted in capillary tube under nitrogen, rhombohedral with faces (001) 0·15, (00$\bar{1}$) 0·15, (110) 0·10, ($\bar{1}\bar{1}$0) 0·10, (1$\bar{1}$0) 0·175, ($\bar{1}$10) 0·175 mm (distances from each face to crystal center given). Lattice constants refined from 15 reflections with $15 < 2\theta < 25°$ measured on a Syntex $P2_1$ diffractometer. 6007 reflections in the range $-16 \le h \le 16$, $0 \le k \le 16$, $0 \le l \le 19$ ($2\theta < 42°$) measured with graphite monochromator, Mo $K\alpha$ radiation, ω-scan technique, scan speed 1·0° min^{-1}, scan range 1·0°, background time equal to scan time, three standard reflections every 50 reflections (intensity variation $< \pm 6\%$). Data reduction on a Prime 850 computer: data reduction and Lorentz and polarization corrections – *REDUCE* and *UNIQUE* (Leonowicz, 1978), absorption correction – *ABSORB* (Templeton & Templeton, 1973) using optically measured crystal dimensions listed above (transmission range 0·084 to 0·244). Direct-methods structure solution – *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), plotting – *PLUTO*78 (Motherwell, 1978) and *ORTEP* (Johnson, 1965). All other calculations carried out using *CRYSTALS* (Watkin & Carruthers, 1981). Rejection of reflections with $|F| < 2\sigma(F)$, with $\sigma(F)$ from counting statistics, gave 4470 symmetrically independent observed reflections. Atomic scattering factors and anomalous-dispersion coefficients (real and imaginary) for Hg, Co, O, N and C from *International Tables for X-ray Crystallography* (1974). Structure solved by direct methods. Both mercury atoms and all cobalt atoms of the two independent anions found in E map using set with highest combined figure of merit. All carbonyl carbons and oxygens, except two, found in first difference

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Table 1. *Atomic coordinates for* $[N(CH_3)_4][Hg\{Co(CO)_4\}_3]$

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}/U_{iso}(Å^2)
Hg(1)	0·78216 (4)	0·09484 (4)	0·89104 (4)	0·071
Hg(2)	0·73960 (4)	0·14828 (4)	0·37612 (3)	0·064
Co(1)	0·8146 (2)	0·0150 (1)	1·0127 (1)	0·072
Co(2)	0·8367 (2)	0·2489 (1)	0·8768 (1)	0·074
Co(3)	0·6989 (1)	0·0229 (2)	0·7797 (1)	0·076
Co(4)	0·6849 (2)	0·2986 (1)	0·3994 (1)	0·070
Co(5)	0·8701 (2)	0·1143 (1)	0·3079 (1)	0·072
Co(6)	0·6552 (1)	0·0234 (1)	0·4226 (1)	0·068
C(11)	0·7059 (14)	−0·0007 (12)	0·9940 (9)	0·079
O(11)	0·6375 (9)	−0·0104 (12)	0·9859 (8)	0·120
C(12)	0·8347 (12)	−0·0448 (13)	1·0902 (11)	0·087
O(12)	0·8498 (11)	−0·0837 (9)	1·1390 (8)	0·122
C(13)	0·8819 (14)	−0·0359 (14)	0·9604 (10)	0·097
O(13)	0·9215 (12)	−0·0742 (13)	0·9267 (9)	0·146
C(14)	0·8460 (14)	0·1074 (13)	1·0463 (12)	0·099
O(14)	0·8681 (11)	0·1691 (10)	1·0747 (9)	0·136
C(21)	0·9305 (15)	0·1913 (13)	0·8927 (13)	0·094
O(21)	0·9913 (10)	0·1578 (12)	0·9030 (11)	0·139
C(22)	0·8796 (15)	0·3453 (12)	0·8759 (10)	0·089
O(22)	0·9053 (12)	0·4101 (9)	0·8739 (9)	0·130
C(23)	0·7700 (14)	0·2614 (12)	0·9404 (13)	0·098
O(23)	0·7263 (11)	0·2735 (10)	0·9845 (9)	0·128
C(24)	0·7833 (13)	0·2477 (12)	0·7911 (12)	0·081
O(24)	0·7506 (11)	0·2493 (12)	0·7344 (8)	0·131
C(31)	0·7950 (14)	0·0508 (13)	0·7472 (10)	0·092
O(31)	0·8516 (10)	0·0656 (11)	0·7234 (9)	0·118
C(32)	0·6455 (13)	−0·0117 (15)	0·6982 (12)	0·097
O(32)	0·6175 (12)	−0·0331 (13)	0·6440 (8)	0·142
C(33)	0·6291 (16)	0·0969 (15)	0·8024 (13)	0·114
O(33)	0·5815 (11)	0·1457 (13)	0·8129 (12)	0·162
C(34)	0·7027 (13)	−0·0693 (13)	0·8298 (12)	0·089
O(34)	0·7022 (12)	−0·1271 (9)	0·8613 (8)	0·114
C(41)	0·5941 (15)	0·2533 (13)	0·4222 (10)	0·095
O(41)	0·5322 (10)	0·2293 (10)	0·4382 (8)	0·113
C(42)	0·6652 (12)	0·4006 (12)	0·4115 (9)	0·078
O(42)	0·6498 (10)	0·4681 (9)	0·4211 (7)	0·114
C(43)	0·7730 (15)	0·2875 (13)	0·4581 (12)	0·101
O(43)	0·8294 (11)	0·2818 (10)	0·5017 (10)	0·137
C(44)	0·6880 (11)	0·3048 (11)	0·3108 (11)	0·079
O(44)	0·6872 (10)	0·3100 (9)	0·2495 (7)	0·120
C(51)	0·9079 (11)	0·0824 (14)	0·3927 (13)	0·090
O(51)	0·9383 (10)	0·0584 (11)	0·4458 (8)	0·126
C(52)	0·9548 (14)	0·0854 (14)	0·2612 (12)	0·106
O(52)	1·0045 (11)	0·0672 (12)	0·2304 (10)	0·132
C(53)	0·7901 (14)	0·0603 (14)	0·2594 (11)	0·092
O(53)	0·7415 (11)	0·0196 (13)	0·2283 (9)	0·134
C(54)	0·8760 (11)	0·2187 (14)	0·2990 (10)	0·078
O(54)	0·8846 (10)	0·2891 (10)	0·2886 (9)	0·122
C(61)	0·7345 (12)	−0·0433 (12)	0·4020 (10)	0·085
O(61)	0·7837 (10)	−0·0897 (9)	0·3937 (8)	0·112
C(62)	0·5827 (14)	−0·0443 (11)	0·4523 (11)	0·089
O(62)	0·5340 (10)	−0·0876 (9)	0·4697 (9)	0·118
C(63)	0·6771 (13)	0·0819 (11)	0·5004 (11)	0·079
O(63)	0·6914 (11)	0·1162 (9)	0·5519 (7)	0·113
C(64)	0·5937 (13)	0·0581 (13)	0·3468 (13)	0·098
O(64)	0·5494 (10)	0·0793 (13)	0·2984 (9)	0·137
N(1)	0·4862 (9)	−0·2987 (9)	0·3498 (7)	0·084 (4)
C(1)	0·4452 (13)	−0·3446 (12)	0·2859 (10)	0·102 (6)
C(2)	0·5571 (14)	−0·2481 (14)	0·3288 (11)	0·117 (7)
C(3)	0·4229 (12)	−0·2444 (12)	0·3758 (9)	0·097 (6)
C(4)	0·5193 (16)	−0·3557 (15)	0·4067 (13)	0·138 (8)
N(2)	0·9434 (10)	−0·3230 (10)	0·8931 (9)	0·096 (5)
C(5)	0·9705 (21)	−0·3052 (20)	0·9623 (18)	0·205 (14)
C(6)	0·8501 (19)	−0·3308 (18)	0·8784 (15)	0·170 (11)
C(7)	0·9828 (17)	−0·2774 (17)	0·8384 (14)	0·158 (10)
C(8)	0·9651 (24)	−0·4086 (25)	0·8804 (19)	0·235 (16)

Table 2. *Bond distances* (Å) *and angles* (°) *for* $[N(CH_3)_4][Hg\{Co(CO)_4\}_3]$

Hg(1)–Co(1)	2·678 (2)	Hg(2)–Co(4)	2·686 (2)
–Co(2)	2·712 (3)	–Co(5)	2·687 (2)
–Co(3)	2·669 (2)	–Co(6)	2·686 (2)
		Hg–Co(av)	2·686
Co(1)–C(11)	1·784 (23)	Co(4)–C(41)	1·759 (23)
–C(12)	1·783 (22)	–C(42)	1·730 (20)
–C(13)	1·782 (22)	–C(43)	1·726 (24)
–C(14)	1·708 (23)	–C(44)	1·710 (21)
Co(2)–C(21)	1·793 (26)	Co(5)–C(51)	1·751 (25)
–C(22)	1·736 (23)	–C(52)	1·796 (23)
–C(23)	1·741 (23)	–C(53)	1·751 (25)
–C(24)	1·768 (25)	–C(54)	1·732 (22)
Co(3)–C(31)	1·812 (23)	Co(6)–C(61)	1·777 (21)
–C(32)	1·794 (24)	–C(62)	1·767 (22)
–C(33)	1·756 (28)	–C(63)	1·777 (22)
–C(34)	1·795 (25)	–C(64)	1·761 (26)
		Co–C(av)	1·762
C(11)–O(11)	1·117 (20)	C(41)–O(41)	1·158 (21)
C(12)–O(12)	1·137 (20)	C(42)–O(42)	1·160 (19)
C(13)–O(13)	1·153 (21)	C(43)–O(43)	1·171 (22)
C(14)–O(14)	1·188 (21)	C(44)–O(44)	1·181 (20)
C(21)–O(21)	1·130 (24)	C(51)–O(51)	1·151 (22)
C(22)–O(22)	1·148 (21)	C(52)–O(52)	1·101 (21)
C(23)–O(23)	1·185 (22)	C(53)–O(53)	1·150 (23)
C(24)–O(24)	1·154 (22)	C(54)–O(54)	1·187 (20)
C(31)–O(31)	1·104 (21)	C(61)–O(61)	1·131 (19)
C(32)–O(32)	1·141 (23)	C(62)–O(62)	1·145 (20)
C(33)–O(33)	1·151 (26)	C(63)–O(63)	1·140 (20)
C(34)–O(34)	1·129 (22)	C(64)–O(64)	1·161 (23)
		C–O (av)	1·149
N(1)–C(1)	1·527 (22)	N(2)–C(5)	1·380 (32)
–C(2)	1·516 (24)	–C(6)	1·517 (31)
–C(3)	1·494 (22)	–C(7)	1·499 (28)
–C(4)	1·492 (25)	–C(8)	1·480 (38)
		N–C (av)	1·488
Co(1)–Hg(1)–Co(2)	120·9 (1)	Co(4)–Hg(2)–Co(5)	124·8 (1)
Co(1)–Hg(1)–Co(3)	120·7 (1)	Co(4)–Hg(2)–Co(6)	117·2 (1)
Co(2)–Hg(1)–Co(3)	118·4 (1)	Co(5)–Hg(2)–Co(6)	118·0 (1)
		Co–Hg–Co (av)	120·0
Hg(1)–Co(1)–C(11)	78·9 (6)	Hg(2)–Co(4)–C(41)	87·4 (7)
–C(12)	175·8 (6)	–C(42)	170·8 (7)
–C(13)	79·1 (6)	–C(43)	75·2 (7)
–C(14)	85·0 (8)	–C(44)	80·8 (6)
Hg(1)–Co(2)–C(21)	76·8 (6)	Hg(2)–Co(5)–C(51)	79·6 (6)
–C(22)	173·6 (7)	–C(52)	176·5 (8)
–C(23)	78·5 (7)	–C(53)	77·5 (6)
–C(24)	87·3 (6)	–C(54)	84·1 (6)
Hg(1)–Co(3)–C(31)	77·6 (6)	Hg(2)–Co(6)–C(61)	89·1 (6)
–C(32)	171·5 (7)	–C(62)	168·2 (6)
–C(33)	77·0 (8)	–C(63)	78·7 (6)
–C(34)	88·0 (6)	–C(64)	74·9 (7)
		Hg–Co–C(eq) (av)	80·9
		Hg–Co–C(ax) (av)	172·7
Co(1)–C(11)–O(11)	176·3 (18)	Co(4)–C(41)–O(41)	174·8 (21)
–C(12)–O(12)	177·8 (20)	–C(42)–O(42)	177·6 (20)
–C(13)–O(13)	174·6 (24)	–C(43)–O(43)	175·1 (22)
–C(14)–O(14)	175·0 (21)	–C(44)–O(44)	177·5 (18)
Co(2)–C(21)–O(21)	177·2 (21)	Co(5)–C(51)–O(51)	174·1 (19)
–C(22)–O(22)	177·5 (22)	–C(52)–O(52)	177·2 (24)
–C(23)–O(23)	176·8 (21)	–C(53)–O(53)	174·6 (22)
–C(24)–O(24)	177·4 (20)	–C(54)–O(54)	174·2 (18)
Co(3)–C(31)–O(31)	175·4 (20)	Co(6)–C(61)–O(61)	174·0 (18)
–C(32)–O(32)	174·4 (21)	–C(62)–O(62)	177·8 (21)
–C(33)–O(33)	175·6 (26)	–C(63)–O(63)	176·8 (17)
–C(34)–O(34)	177·6 (22)	–C(64)–O(64)	176·2 (20)
		Co–C–O (av)	176·0
C(1)–N(1)–C(2)	109·4 (14)	C(5)–N(2)–C(6)	113·3 (22)
C(1)–N(1)–C(3)	108·2 (14)	C(5)–N(2)–C(7)	116·9 (22)
C(1)–N(1)–C(4)	111·2 (15)	C(5)–N(2)–C(8)	107·7 (23)
C(2)–N(1)–C(3)	109·8 (15)	C(6)–N(2)–C(7)	114·6 (19)
C(2)–N(1)–C(4)	108·7 (16)	C(6)–N(2)–C(8)	98·3 (22)
C(3)–N(1)–C(4)	109·6 (15)	C(7)–N(2)–C(8)	103·4 (21)
		C–N–C (av)	109·3

Fourier map. Remaining non-hydrogen atoms found in second difference map. Refinement by blocked diagonal least squares [each $Co(CO)_4$ group and each cation refined in a separate block]. All atoms in anion refined with anisotropic and atoms in cation with isotropic thermal parameters. Refinement based on F; secondary-extinction parameter refined ($\xi = 4{\cdot}36 \times 10^{-3}$). Final $R = 0{\cdot}048$, $R_w = 0{\cdot}051$, $w = 1/\sigma(F)$, $S = 3{\cdot}3$. Max.

Δ/σ in final cycle 0·17. Largest peaks in final difference map located about 1·3 Å from mercury atoms.*

Discussion. The $Hg[Co(CO)_4]_3^-$ anions have trigonal planar coordination at mercury [one mercury atom is 0·016 (2) Å from the plane of the cobalt atoms and the other is 0·024 (2) Å from the plane]. One of the two independent anions is shown in Fig. 1 and the crystal packing in Fig. 2. The final atomic coordinates are given in Table 1 with equivalent isotropic thermal parameters assigned to each atom that was refined anisotropically. The bond distances and angles are given in Table 2. Each mercury atom is bonded to three cobalt atoms with an average Hg—Co distance of 2·686 Å; this is 0·187 Å longer than that found for $Hg[Co(CO)_4]_2$ (Sheldrick & Simpson, 1968). This bond lengthening is due to increased electron density on mercury in the anion and higher coordination number as discussed earlier (Petersen *et al.*, 1983). Both independent molecules in the unit cell are nearly identical except for the larger range of Hg—Co distances in molecule 1, possibly due to crystal packing forces. Axial and equatorial carbonyls have nearly identical structural parameters. The distorted trigonal bipyramidal $Co(CO)_4$ units in the $Hg[Co(CO)_4]_3^-$ anion are very similar to those in $Hg[Co(CO)_4]_2$. The average distances and angles for the anion are {with the distance for $Hg[Co(CO)_4]_2$ in parentheses}: Co—C 1·762 (1·75), C—O 1·149 (1·17) Å, Hg—Co—C(eq) 80·9 (83), Hg—Co—C(ax) 172·7 (176)°. In spite of the acute Hg—Co—C(eq) angles, the carbonyls apparently have no semibridging character, as shown by the near-linear Co—C—O angles (range 174·0–177·8°).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39480 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

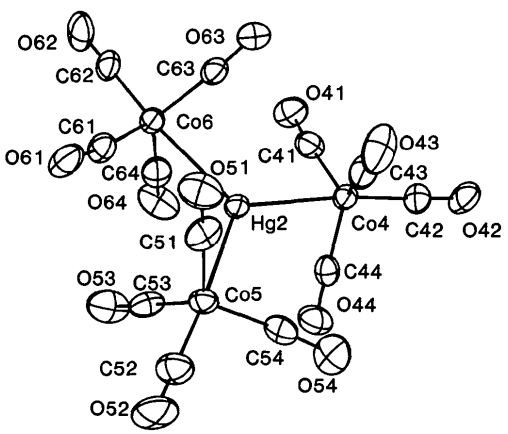

Fig. 1. *ORTEP* drawing of one of the $Hg\{Co(CO)_4\}_3^-$ anions.

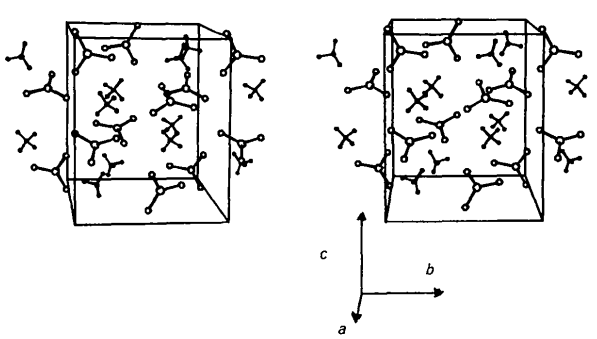

Fig. 2. *PLUTO* unit-cell packing diagram for $[N(CH_3)_4]$-$[Hg\{Co(CO)_4\}_3]$. Carbonyl groups have been omitted for clarity.

References

BURLITCH, J. M., PETERSEN, R. B., CONDER, H. L. & ROBINSON, W. R. (1970). *J. Am. Chem. Soc.* **92**, 1783–1784.

CLELAND, A. J., FIELDHOUSE, S. A., FREELAND, B. H., MANN, C. D. M. & O'BRIEN, R. J. (1970). *Inorg. Chim. Acta*, **4**, 479–480.

CONDER, H. L. & ROBINSON, W. R. (1972). *Inorg. Chem.* **11**, 1527–1532.

DUFFY, D. N., MACKEY, K. M., NICHOLSON, B. K. & ROBINSON, W. T. (1981). *J. Chem. Soc. Dalton Trans.* pp. 381–384.

ERNER, S., KING, K., HARDCASTLE, K. I., ROSENBERG, E., LANFREDI, A. M. M., TIRIPICCHIO, A. & CAMELLINI, M. T. (1983). *Inorg. Chem.* **22**, 1339–1344.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

LEONOWICZ, M. E. (1978). *REDUCE* and *UNIQUE*. Cornell Univ., Ithaca, New York.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MOTHERWELL, W. D. S. (1978). *PLUTO78*. Cambridge Crystallographic Data Centre, England.

PETERSEN, R. B., RAGOSTA, J. M., WHITWELL, G. E. II & BURLITCH, J. M. (1983). *Inorg. Chem.* **22**, 3407–3415.

SHELDRICK, G. M. & SIMPSON, R. N. F. (1968). *J. Chem. Soc. A*, pp. 1005–1009.

TEMPLETON, L. K. & TEMPLETON, D. H. (1973). *ABSORB*. Univ. of California, Berkeley.

VIZI-OROSZ, A., PAPP, L. & MARKO, L. (1969). *Inorg. Chem. Acta*, **3**, 103–104.

WATKIN, D. J. & CARRUTHERS, J. R. (1981). *CRYSTALS*. Chemical Crystallographic Laboratory, Univ. of Oxford, England.