

C(3)	0.1566 (4)	0.4040 (4)	-0.0771 (3)	0.059 (2)
C(4)	0.1188 (3)	0.4466 (3)	-0.0154 (3)	0.050 (1)
C(5)	0.0749 (3)	0.4016 (3)	0.0402 (3)	0.040 (1)
H(1)	0.0993 (27)	0.2135 (27)	-0.0236 (23)	0.051 (12)
H(2)	0.1744 (28)	0.2849 (27)	-0.1226 (25)	0.060 (13)
H(3)	0.1803 (33)	0.4315 (33)	-0.1138 (30)	0.079 (15)
H(4)	0.1220 (29)	0.5080 (31)	-0.0132 (28)	0.073 (16)
H(5)	0.0492 (24)	0.4278 (25)	0.0767 (22)	0.037 (12)

Table 2. Selected geometric parameters (Å, °)

Ru(1)—Cl(1)	2.406 (1)	Ru(1)—N(1)	2.073 (3)
N(1)—C(1)	1.341 (5)	N(1)—C(5)	1.355 (5)
C(1)—C(2)	1.371 (6)	C(1)—H(1)	0.970 (40)
C(2)—C(3)	1.365 (7)	C(2)—H(2)	0.974 (42)
C(3)—C(4)	1.375 (7)	C(3)—H(3)	0.843 (49)
C(4)—C(5)	1.365 (6)	C(4)—H(4)	0.964 (46)
C(5)—H(5)	0.845 (36)		
N(1)—Ru(1)—Cl(1)	89.6 (1)	C(1)—N(1)—Ru(1)	122.1 (3)
C(5)—N(1)—Ru(1)	121.7 (3)	C(5)—N(1)—C(1)	116.3 (3)
C(2)—C(1)—N(1)	123.0 (4)	H(1)—C(1)—N(1)	117.0 (25)
H(1)—C(1)—C(2)	120.0 (25)	C(3)—C(2)—C(1)	120.0 (5)
H(2)—C(2)—C(1)	119.5 (26)	H(2)—C(2)—C(3)	120.4 (26)
C(4)—C(3)—C(2)	118.0 (4)	H(3)—C(3)—C(2)	121.5 (37)
H(3)—C(3)—C(4)	120.3 (38)	C(5)—C(4)—C(3)	119.6 (4)
H(4)—C(4)—C(3)	119.5 (29)	H(4)—C(4)—C(5)	120.9 (29)
C(4)—C(5)—N(1)	123.2 (4)	H(5)—C(5)—N(1)	117.0 (27)
H(5)—C(5)—C(4)	119.8 (27)		

Table 3. Crystal data for *trans*-[MCl₂(C₅H₅N)₄] compounds

	[Fe(py) ₄ Cl ₂] ^a	[Co(py) ₄ Cl ₂] ^a	[Ni(py) ₄ Cl ₂] ^{a,b}	[Ru(py) ₄ Cl ₂] ^c
<i>a</i> (Å)	15.945 (2)	15.966 (2)	15.920 (3)	15.664 (2)
<i>c</i> (Å)	17.287 (6)	17.153 (6)	17.046 (12)	16.970 (2)
<i>D_s</i> (Mg m ⁻³)	1.34	1.36	1.37	1.56
<i>μ</i> (mm ⁻¹)	0.96	1.07	1.16	0.97
No. parameters refined	63	63	63	83 ^d
No. observed reflections	533	686	848	757
<i>R</i>	0.0477	0.0483	0.0489	0.0453
<i>wR</i>	0.0652	0.0668	0.0748	0.0320
<i>M</i> —Cl (Å)	2.430 (3)	2.444 (2)	2.437 (2)	2.406 (1)
<i>M</i> —N (Å)	2.229 (6)	2.183 (4)	2.133 (4)	2.073 (3)

Notes: (a) Long & Clarke (1978); (b) crystal corresponds to the formulation Ni_{0.97}Fe_{0.03}(py)₄Cl₂; (c) this work; (d) H atoms refined.

The positions of all the non-H atoms were found by direct methods. Iterative application of least-squares refinement and difference Fourier synthesis led to the development of the entire structure, including the H atoms. All non-H atoms were refined anisotropically, while the H atoms were freely refined using an isotropic model. Crystallographic calculations were performed using the *SHELXTL-Plus* program package (Sheldrick, 1987).

We thank Johnson Matthey PLC for generous loans of ruthenium trichloride and the SERC for financial support (MRJE) and for provision of the X-ray equipment.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: HU1072). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Abel, E. W., Bennett, M. A. & Wilkinson, G. (1959). *J. Chem. Soc.* pp. 3178–3182.
- Al-Zamil, N. S., Evans, E. H. M., Gillard, R. D., James, D. W., Jenkins, T. E., Lancashire, R. J. & Williams, P. A. (1982). *Polyhedron*, **1**, 525–534.
- Aronson, R., Elsegood, M. R. J., Steed, J. W. & Tocher, D. A. (1991). *Polyhedron*, **10**, 1727–1732.
- Bachman, R. E., Whitmire, K. H., Mandal, S. & Bharadwaj, P. K. (1992). *Acta Cryst.* **C48**, 1836–1837.
- Dobinson, G. C., Mason, R. & Russell, D. R. (1967). *J. Chem. Soc. Chem. Commun.* pp. 62–63.
- Elsegood, M. R. J. (1991). PhD thesis, Univ. College London, England.
- Elsegood, M. R. J. & Tocher, D. A. (1988). *J. Organomet. Chem.* **356**, C29–C31.
- Elsegood, M. R. J. & Tocher, D. A. (1989). *Inorg. Chim. Acta*, **161**, 147–149.
- Long, G. J. & Clarke, P. J. (1978). *Inorg. Chem.* **17**, 1394–1401.
- Pullman, P., Hensen, K. & Bats, J. W. (1982). *Z. Naturforsch. Teil B*, **37**, 1312–1315.
- Robertson, D. R. & Stephenson, T. A. (1976). *J. Organomet. Chem.* **116**, C29–C30.
- Robertson, D. R., Stephenson, T. A. & Arthur, T. (1978). *J. Organomet. Chem.* **162**, 121–136.
- Rozière, J., Lehmann, M. S. & Potier, J. (1979). *Acta Cryst.* **B35**, 1099–1102.
- Sheldrick, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet R3m V crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.
- Sinclair, I., Small, R. W. H. & Worrall, I. J. (1981). *Acta Cryst.* **B37**, 1290–1292.

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(μ-H)(μ-OH)Os₃(CO)₁₀

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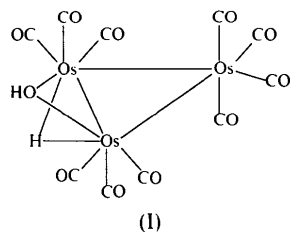
Abstract

The title compound, decacarbonyl-1κ⁴C,2κ³C,3κ³C-μ-hydrido-2:3κ²H-μ-hydroxy-2:3κ²O-trisosmium-(3 Os—Os), consists of an Os triangle, doubly bridged on one side by a hydrido and a hydroxy group. The coordination around the Os atoms was found to be octahedral.

Comment

The trisosmium complex (μ-H)(μ-OH)Os₃(CO)₁₀, (I), was first reported in 1968 as the product of the reduction of Os₃(CO)₁₂ by Na⁺.BH₄⁻ (Johnson, Lewis & Kilty, 1968). Since then two other synthetic

procedures have been reported (Arce, Deeming, Donovan-Mtunzi & Kabir, 1985; Dossi, Fusi, Pizzotti & Psaro, 1990). However, the molecular structure of the complex has not yet been reported. Recently we obtained $(\mu\text{-H})(\mu\text{-OH})\text{Os}_3(\text{CO})_{10}$ in a small yield (approximately 10%) through the reaction of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ with ONMe_3 at 353 K in toluene. We report here the molecular structure of this complex.



The structure is shown in Fig. 1. The three Os atoms define an approximate isosceles triangle [Os1—Os2 = 2.8295 (5), Os1—Os3 = 2.8196 (5), Os2—Os3 = 2.8061 (5) Å]. The ten carbonyl groups are in terminal positions with four bonded to Os1 and three bonded to each of Os2 and Os3. The O atom of the μ -hydroxy ligand was located; this ligand bridges Os2 and Os3 symmetrically. The H atoms were not located but ^1H NMR, IR and mass spectroscopy show that the crystals we obtained are of the title complex, reported previously by Ditzel, Gomez-Sal, Johnson, Lewis & Raithby (1987). The $(\mu\text{-O})\text{Os}_3(\text{CO})_{10}$ unit in the title compound is similar to those in $(\mu\text{-H})(\mu\text{-OMe})\text{Os}_3(\text{CO})_{10}$ (Churchill & Wasserman, 1980) and $(\mu\text{-H})(\mu\text{-OSiEt}_3)\text{Os}_3(\text{CO})_{10}$ (D'Ornelas, Choplin, Basset, Hsu & Shore, 1985).

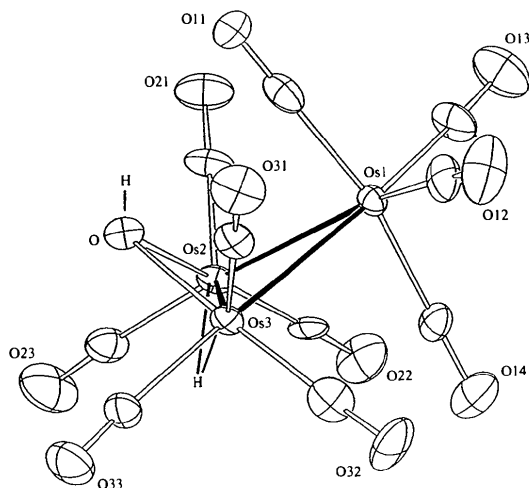


Fig. 1. ORTEP (Johnson, 1965) drawing of $(\mu\text{-H})(\mu\text{-OH})\text{Os}_3(\text{CO})_{10}$, showing displacement ellipsoids at the 50% probability level for non-H atoms and the atomic labeling scheme (H represents possible H-atom positions as estimated by the authors).

The ruthenium cluster $(\mu\text{-H})(\mu\text{-OSiEt}_3)\text{Ru}_3(\text{CO})_{10}$ (Puga, Fehlner, Gates, Braga & Grepioni, 1990) contains a $(\mu\text{-O})\text{Ru}_3(\text{CO})_{10}$ unit similar to those observed in these osmium complexes.

While the hydrido ligand was not observed in the title compound, it is expected to bridge Os2 and Os3 on the opposite side of the Os₃ plane to the O atom of the OH group. This type of multiple bridging has also been observed in the related clusters $(\mu\text{-H})(\mu\text{-OMe})\text{Os}_3(\text{CO})_{10}$ (Churchill & Wasserman, 1980), $(\mu\text{-H})(\mu\text{-OSiEt}_3)\text{Os}_3(\text{CO})_{10}^\dagger$ (D'Ornelas, Choplin, Basset, Hsu & Shore, 1985) and $(\mu\text{-H})(\mu\text{-OSiEt}_3)\text{Ru}_3(\text{CO})_{10}$ (Puga, Fehlner, Gates, Braga & Grepioni, 1990), thus giving each Os atom pseudo-octahedral coordination geometry.

The feature of interest in $(\mu\text{-H})(\mu\text{-OH})\text{Os}_3(\text{CO})_{10}$ is the μ -hydroxy ligand, which symmetrically spans the Os2—Os3 edge. The metal—oxygen bond distances and angle associated with the bridging OH unit [Os2—O 2.146 (7), Os3—O 2.136 (7) Å, Os2—O—Os3 81.9 (2)°] are comparable to those found in $(\mu\text{-H})(\mu\text{-OMe})\text{Os}_3(\text{CO})_{10}$ (Os—O 2.112–2.093 Å, Os—O—Os 83.9°; Churchill & Wasserman, 1980) and those found for the —OSiEt₃ unit in $(\mu\text{-H})(\mu\text{-OSiEt}_3)\text{Os}_3(\text{CO})_{10}$ (Os—O 2.110–2.126 Å, Os—O—Os 81.9°; D'Ornelas, Choplin, Basset, Hsu & Shore, 1985) or in $(\mu\text{-H})(\mu\text{-OSiEt}_3)\text{Ru}_3(\text{CO})_{10}$ (Ru—O 2.106–2.107 Å, Ru—O—Ru angle not reported; Puga, Fehlner, Gates, Braga & Grepioni, 1990). The slightly longer bond lengths observed in the hydroxy-bridged osmium cluster compared to those in the analogous methoxy-bridged complex (Churchill & Wasserman, 1980) are as expected, and can be explained by the fact that the hydroxyl group is not as strong an electron donor as the methoxy group, resulting in weaker σ bonds to the Os atoms. The OH bridging ligand in the title compound is also similar to that in the hydroxide cluster $(\mu\text{-OH})(\mu\text{-dppm})\text{Os}_3(\text{CO})_8\text{H}$, where dppm bridges the same Os atoms as the OH bridging ligands [Os—O 2.157–2.167 Å, Os—O—Os = 79.8° (angle calculated based on the O—Os—Os angles given in the literature); Hodge, Johnson, Lewis & Raithby, 1987] as well as that in $(\mu\text{-OH})\text{HOs}_3(\text{CO})_9\text{PMe}_2\text{Ph}$ (Os—O 2.135–2.118 Å, Os—O—Os 82.4°; Deeming, Manning, Rothwell, Hursthouse & Walker, 1984).

[†] At the time of publication the hydrido ligand had not been successfully located, but was discovered in a subsequent X-ray structure determination.

Experimental

Crystal data

$[\text{Os}_3\text{H}(\text{OH})(\text{CO})_{10}]$
 $M_r = 868.7$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Monoclinic

 $P2_1/n$ $a = 7.347 (1) \text{ \AA}$ $b = 24.849 (6) \text{ \AA}$ $c = 9.001 (1) \text{ \AA}$ $\beta = 107.14 (1)^\circ$ $V = 1570.5 \text{ \AA}^3$ $Z = 4$ $D_x = 3.674 \text{ Mg m}^{-3}$

Cell parameters from 25 reflections

 $\theta = 12-15^\circ$ $\mu = 24.3 \text{ mm}^{-1}$ $T = 213 \text{ K}$

Cube

 $0.25 \times 0.23 \times 0.21 \text{ mm}$

Orange

Crystal source: CH₂Cl₂ at 298 K

Table 2. Selected bond distances (Å) and angles (°)

Metal distances			
Os1—Os2	2.8295 (5)	Os2—Os3	2.8061 (5)
Os1—Os3	2.8196 (5)		
Bridge distances			
Os2—O	2.146 (7)	Os3—O	2.136 (7)
Metal-carbon distances			
Os1—C11	1.93 (1)	Os2—C22	1.89 (1)
Os1—C12	1.92 (1)	Os2—C23	1.92 (1)
Os1—C13	1.949 (9)	Os3—C31	1.88 (1)
Os1—C14	1.95 (1)	Os3—C32	1.89 (1)
Os2—C21	1.906 (9)	Os3—C33	1.95 (1)
Carbonyl distances			
C11—O11	1.12 (1)	C22—O22	1.13 (1)
C12—O12	1.15 (1)	C23—O23	1.13 (1)
C13—O13	1.10 (1)	C31—O31	1.16 (1)
C14—O14	1.15 (1)	C32—O32	1.12 (1)
C21—O21	1.13 (1)	C33—O33	1.12 (1)
Metal angles			
Os2—Os1—Os3	59.57 (1)	Os1—Os3—Os2	60.39 (1)
Os1—Os2—Os3	60.04 (1)		
Bridge angles			
Os1—Os2—O	84.0 (2)	O—Os2—C22	171.6 (3)
Os1—Os3—O	84.5 (2)	O—Os2—C23	93.2 (4)
Os3—Os2—O	48.9 (2)	O—Os3—C31	97.1 (4)
Os2—Os3—O	49.2 (2)	O—Os3—C32	169.7 (4)
Os2—O—Os3	81.9 (2)	O—Os3—C33	93.3 (4)
O—Os2—C21	98.0 (4)		
Metal-carbonyl angles			
Os1—C11—O11	176 (1)	Os2—C22—O22	179 (1)
Os1—C12—O12	176 (1)	Os2—C23—O23	175 (1)
Os1—C13—O13	175 (1)	Os3—C31—O31	178.2 (8)
Os1—C14—O14	178.8 (9)	Os3—C32—O32	177 (1)
Os2—C21—O21	177 (1)	Os3—C33—O33	173.1 (9)
Metal-metal-carbon angles			
Os2—Os1—C11	84.3 (3)	Os1—Os2—C23	172.7 (3)
Os2—Os1—C12	154.2 (3)	Os3—Os2—C21	134.5 (3)
Os2—Os1—C13	107.5 (3)	Os3—Os2—C22	122.7 (3)
Os2—Os1—C14	82.9 (3)	Os3—Os2—C23	113.1 (3)
Os3—Os1—C11	86.6 (3)	Os1—Os3—C31	88.6 (3)
Os3—Os1—C12	94.6 (3)	Os1—Os3—C32	88.4 (3)
Os3—Os1—C13	167.1 (3)	Os1—Os3—C33	173.8 (3)
Os3—Os1—C14	84.9 (3)	Os2—Os3—C31	132.9 (3)
Os1—Os2—C21	90.7 (3)	Os2—Os3—C32	120.6 (3)
Os1—Os2—C22	90.5 (3)	Os2—Os3—C33	113.9 (3)

Data collection

Enraf-Nonius CAD-4 diffractometer

 ω - 2θ scans

Absorption correction:

 ψ -scans $T_{\min} = 0.633$, $T_{\max} = 0.998$

5606 measured reflections

2714 independent reflections

2165 observed reflections

 $[I \geq 3\sigma(I)]$ $R_{\text{int}} = 0.034$ $\theta_{\text{max}} = 25^\circ$ $h = 0 \rightarrow 8$ $k = -29 \rightarrow 29$ $l = -10 \rightarrow 10$

4 standard reflections

frequency: 180 min

intensity variation: -2.2%

Refinement

Refinement on F $R = 0.026$ $wR = 0.031$ $S = 0.947$

2165 reflections

218 parameters

H atoms not located

 $w = [\sigma^2(I) + 0.03(I)^2]^{-1/2}$ $(\Delta/\sigma)_{\text{max}} = 0.02$ $\Delta\rho_{\text{max}} = 1.726 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -2.461 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Os1	0.18135 (4)	0.34516 (1)	0.10752 (4)	1.454 (7)
Os2	0.37618 (4)	0.38640 (2)	-0.09610 (4)	1.467 (7)
Os3	0.50486 (4)	0.41106 (1)	0.22203 (4)	1.424 (7)
O	0.3730 (8)	0.4605 (3)	0.0257 (7)	1.9 (1)
O11	-0.0526 (9)	0.4481 (3)	0.024 (1)	3.6 (2)
O12	0.122 (1)	0.3314 (4)	0.4289 (8)	4.4 (2)
O13	-0.160 (1)	0.2798 (4)	-0.082 (1)	4.5 (2)
O14	0.470 (1)	0.2517 (3)	0.1446 (9)	3.4 (2)
O21	0.0001 (9)	0.4024 (3)	-0.3472 (8)	3.3 (2)
O22	0.404 (1)	0.2747 (3)	-0.2219 (9)	3.4 (2)
O23	0.632 (1)	0.4283 (9)	-0.2823 (9)	4.4 (2)
O31	0.309 (1)	0.4620 (3)	0.4417 (8)	3.4 (2)
O32	0.669 (1)	0.3259 (3)	0.4611 (9)	3.9 (2)
O33	0.8719 (9)	0.4773 (3)	0.3306 (9)	3.4 (2)
C11	0.036 (1)	0.4110 (4)	0.060 (1)	2.3 (2)
C12	0.138 (1)	0.3362 (4)	0.307 (1)	2.7 (2)
C13	-0.032 (1)	0.3024 (4)	-0.016 (1)	2.5 (2)
C14	0.365 (1)	0.2868 (4)	0.132 (1)	2.0 (2)
C21	0.141 (1)	0.3955 (4)	-0.256 (1)	2.2 (2)
C22	0.393 (1)	0.3165 (4)	-0.174 (1)	1.8 (2)
C23	0.536 (1)	0.4153 (4)	-0.211 (1)	2.4 (2)
C31	0.386 (1)	0.4423 (4)	0.360 (1)	1.9 (2)
C32	0.611 (1)	0.3570 (5)	0.370 (1)	2.7 (2)
C33	0.736 (1)	0.4542 (4)	0.282 (1)	2.2 (2)

The data were corrected for Lorentz-polarization factors. The structure was solved by a combination of direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and difference Fourier techniques. The full-matrix least-squares refinement, which minimized $w(|F_o| - |F_c|)^2$, was carried out using anisotropic displacement parameters for all non-H atoms. Other programs used included *SDP* (B. A. Frenz & Associates, Inc., 1982). All calculations were performed on a DEC VAXstation 3100 computer.

We thank the National Science Foundation for support of this work through grant CHE91-04035.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: GR1012). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Arce, A. J., Deeming, A. J., Donovan-Mtunzi, S. & Kabir, S. E. (1985). *J. Chem. Soc. Dalton Trans.* pp. 2479–2482.
- B. A. Frenz & Associates, Inc. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.
- Churchill, M. R. & Wasserman, H. J. (1980). *Inorg. Chem.* **19**, 2391–2395.
- Demming, A. J., Manning, P. J., Rothwell, I. P., Hursthouse, M. B. & Walker, N. P. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 2039–2045.
- Ditzel, E. J., Gomez-Sal, M., Johnson, B. F. G., Lewis, J. & Raithby, P. R. (1987). *J. Chem. Soc. Dalton Trans.* pp. 1623–1630.
- D'Ornelas, L., Choplin, A., Basset, J. M., Hsu, L. & Shore, S. G. (1985). *Nouv. J. Chim.* **9**, 155–157.
- Dossi, C., Fusi, A., Pizzotti, M. & Psaro, R. (1990). *Organometallics*, **9**, 1994–1995.
- Hodge, S. R., Johnson, B. F. G., Lewis, J. & Raithby, P. R. (1987). *J. Chem. Soc. Dalton Trans.* pp. 931–937.
- Johnson, B. F. G., Lewis, J. & Kilty, P. A. (1968). *J. Chem. Soc. A*, pp. 2859–2864.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1972). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- Puga, J., Fehlnert, T. P., Gates, B. C., Braga, D. & Grepioni, F. (1990). *Inorg. Chem.* **29**, 2376–2381.

Acta Cryst. (1995). **C51**, 45–48

Low-Temperature Structures of
 $[\text{py}_2\text{H}]^+[\text{Co}(\text{CO})_4]^-$ (py = Pyridine) and
 $[(\text{tmen})\text{H}]^+[\text{Co}(\text{CO})_4]^-$ (tmen =
 N,N,N',N' -Tetramethylethylenediamine)

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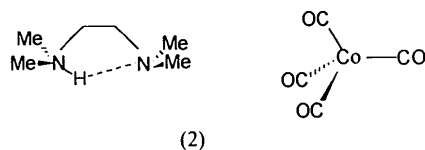
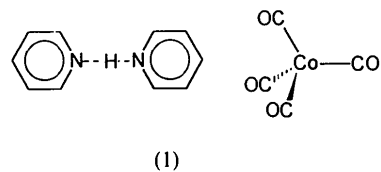
Abstract

The crystal structures of salts arising from the reaction of $\text{HCo}(\text{CO})_4$ with pyridine and tetramethylethylenediamine, respectively, have been determined. The former, bis(pyridine) hydrogen tetracarbonylcobaltate(1⁻), consists of a $[(\text{C}_5\text{H}_5\text{N})_2\text{H}]^+$ cation, with a symmetrical (within experimental error) $\text{N}\cdots\text{H}\cdots\text{N}$ hydrogen bond, and a $\text{Co}(\text{CO})_4^-$ anion which is distorted towards C_{2v} symmetry. The latter, dimethyl[2-(dimethylamino)-

ethyl]ammonium tetracarbonylcobaltate(1⁻), involves protonated tetramethylethylenediamine, $[(\text{C}_6\text{H}_{16}\text{N}_2)\text{H}]^+$, which forms an intramolecular $\text{N}\cdots\text{H}\cdots\text{N}$ hydrogen bond, and a $\text{Co}(\text{CO})_4^-$ anion of C_s symmetry. No unusual interactions between anions and cations are observed. In each structure the cation exhibits the shortest $\text{N}\cdots\text{N}$ separation observed to date for this hydrogen-bonded cation: 2.634 (4) Å for $[(\text{C}_5\text{H}_5\text{N})_2\text{H}]^+$ and 2.711 (5) Å for the $(\text{tmen})\text{H}^+$ cation.

Comment

We have recently synthesized and structurally characterized a number of salts formed from the reaction of $\text{HCo}(\text{CO})_4$ with amines or diamines (Brammer, McCann, Bullock, McMullan & Sherwood, 1992; Brammer, Zhao & Ladipo, 1994; Brammer & Zhao, 1994). In some cases the resulting salts exhibit unusual $\text{N}\cdots\text{H}\cdots\text{Co}$ hydrogen bonds; in others, particularly when an excess of the (di)amine is used, the resulting salt consists of $\text{N}\cdots\text{H}\cdots\text{N}$ hydrogen-bonded cations and non-interacting $\text{Co}(\text{CO})_4^-$ anions. The salts reported here, $[(\text{C}_6\text{H}_5\text{N})_2\text{H}]^+[\text{Co}(\text{CO})_4]^-$ (1) and $[(\text{tmen})\text{H}]^+[\text{Co}(\text{CO})_4]^-$ (2), were prepared in the manner previously reported for the preparation of $(\text{Et}_3\text{NH})^+[\text{Co}(\text{CO})_4]^-$ (Brammer, McCann, Bullock, McMullan & Sherwood, 1992; Calderazzo, Fachinetti, Marchetti & Zanazzi, 1981) and $[(\text{DABCO})\text{H}]^+[\text{Co}(\text{CO})_4]^-$ (Brammer, Zhao & Ladipo, 1994) using $\text{HCo}(\text{CO})_4$ to (di)amine ratios of 1:10 and 1:2.3 for (1) and (2), respectively. Thus, both salts exhibit $\text{N}\cdots\text{H}\cdots\text{N}$ rather than $\text{N}\cdots\text{H}\cdots\text{Co}$ hydrogen-bonding interactions.



The structures of (1) and (2) are shown in Figs. 1 and 2, respectively. Both ions in (2) have exact C_s symmetry; methylene C(12) and C(13) of the anions are disordered about the mirror plane at $y = \frac{3}{4}$. The $\text{N}\cdots\text{N}$ separation in compound (1) is smaller than that previously reported for other salts which include the same or similar $\text{N}\cdots\text{H}\cdots\text{N}$ bonded cations (e.g. see Table 5). The $\text{N}\cdots\text{N}$ separation in (2) is also