High Nuclearity Carbonyl Clusters of Rhodium. Part 2.[1] Crystal and Molecular Structure of the Tetramethylammonium Salt of Dodeca-μ-carbonyl-dodecacarbonylhydrido-*polyhedro*-tridecarhodate(4−)–1-Methylpyrrolidin-2-one (1/3)

By **Gianfranco Ciani** * and **Angelo Sironi**, Istituto di Chimica Generale ed Inorganica dell'Università e Centro del C.N.R., Via G. Venezian 21, 20133 Milano, Italy

Secondo Martinengo, Centro di Studio per la Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione del C.N.R., Via G. Venezian 21, 20133 Milano, Italy

The title compound, $[N(CH_3)_4]_4[Rh_{13}H(CO)_{24}]\cdot 3C_5H_9NO$, crystallises in the triclinic space group $P\bar{1}$ with unit-cell dimensions a = 22.596(11), b = 14.263(7), c = 14.512(8) Å, α = 65.56(3), β = 107.58(4), γ = 100.86(5)°, and Z = 2. The structure has been solved by conventional Patterson and Fourier methods from single-crystal *X*-ray counter data and refined by least-squares methods to *R* 0.061 for 3 680 significant reflections. The anion, of idealised C_s symmetry, containing a centred twinned-cuboctahedron of metal atoms, is similar to that of the other members of the family $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ already studied. The mean value of the Rh–Rh bond lengths, ranging from 2.718(3) to 2.894(3) Å, is 2.782 Å. The Rh–C and C–O interactions for the 12 terminal and for the 12 edge-bridging CO groups have mean values of 1.80, 1.18, and 1.97, 1.21 Å, respectively. The hydride atom has been located in a semi-octahedral cavity, *i.e.* on a square face of the cluster, bisected by the ideal mirror plane.

We have already reported the synthesis and structure of two members of the family $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$, namely the dihydride[1] $[Rh_{13}H_2(CO)_{24}]^{3-}$ and the trihydride[2] $[Rh_{13}H_3(CO)_{24}]^{2-}$, both containing a centred twinned-cuboctahedral cluster of metal atoms, a fragment of a hexagonal close-packed lattice of D_{3h} symmetry. Recently, another member of this family has been obtained, the monohydride $[Rh_{13}H(CO)_{24}]^{4-}$. It is prepared, together with other products presently under investigation, by deprotonation of the trihydride with a slight excess of potassium t-butoxide in tetrahydrofuran, and precipitated as the tetramethylammonium salt.[3] The i.r. spectrum in acetonitrile shows carbonyl bands at 1 960s, 1 790m, and 1 780m cm^{-1}; the ^1H n.m.r. spectrum exhibits a complex multiplet centred at τ 35.5, due to the interstitial hydride atom.[3] Crystals suitable for *X*-ray analysis were obtained from 1-methylpyrrolidin-2-one and propan-2-ol by the slow diffusion technique.

In this paper we report the complete results of the *X*-ray investigation on the tetramethylammonium salt of the novel anion, which has shown the presence of solvated molecules of 1-methylpyrrolidin-2-one. The results are discussed in comparison with those of the other members of the family, especially in connection with the location of the hydride ligand.

EXPERIMENTAL

Crystal Data.—$C_{55}H_{76}N_7O_{27}Rh_{13}$, M = 2 604.9, Triclinic, space group $P\bar{1}$ (no. 2), a = 22.596(11), b = 14.263(7), c = 14.512(8) Å, α = 65.56(3), β = 107.58(4), γ = 100.86(5)°, U = 4 048.4 Å^3, D_m = 2.12(2) g cm^{-3} (by flotation), Z = 2, D_c = 2.14 g cm^{-3}, $F(000)$ = 2 512, Mo-K_α radiation (λ = 0.710 7 Å), μ(Mo-K_α) = 25.7 cm^{-1}.

Intensity Measurements.—A small crystal of the compound, sealed in a capillary tube, was mounted on a Philips PW 1100 automatic diffractometer. Diffraction intensities were collected in the range $3 < \theta < 20°$ by the ω-scan method, with scan width 1.8° and scan speed 0.033 3° s^{-1}. The background was measured for 10 s at each side of the scan range. Of the 7 056 reflections measured, 3 680 were significantly above background [$\sigma(I)/I < 0.4$] and were used in the structure solution and refinement. Three standard reflections were measured at regular intervals but showed no crystal decay. The integrated reflections were reduced to F_o by correction for Lorentz and polarisation effects; no correction for absorption was made.

Determination and Refinement of the Structure.—The structure was solved by deconvolution of a three-dimensional Patterson map, which showed the metal-atom locations. After a preliminary refinement, successive difference-Fourier maps indicated all the non-hydrogen atom positions. The presence of three independent molecules of 1-methylpyrrolidin-2-one was also observed.

The refinements were carried out by blocked-matrix least squares. Anisotropic thermal factors were assigned to the metal atoms only. The tetramethylammonium cations were refined as rigid groups (tetrahedral geometry, N–C 1.52 Å) with an average isotropic thermal factor. One of the four cations and the solvent molecules show rather high thermal parameters, due to some disorder. The resulting bond parameters in the solvent molecules are, therefore, of very poor quality. The final values of the conventional agreement indices *R* and *R'* were 0.061 and 0.070, respectively. The weights were assigned according to the formula $w = 1/(A + BF_o + CF_o^2)$ where *A*, *B*, and *C*, in the final cycles, had values 137.2, −1.1, and 3.8 × 10^{-3} respectively, and were chosen on the basis of an analysis of $\Sigma w\Delta^2$. Atomic scattering factors were taken from ref. 4 for all atoms, those of Rh being corrected for the real and imaginary parts of the anomalous dispersion.[5]

The final difference-Fourier map showed no peaks exceeding 1.2 e Å^{-3} in the vicinity of the metal atoms. Final atomic positions are reported in Table 1, thermal parameters and observed and computed structure factors in Supplementary Publication No. SUP 22930 (16 pp.).†

All computations were carried out on a UNIVAC 1100/80 at the computing centre of Milan University, using local programs. The ORTEP program ‡ was used for plotting the anion geometry.

---

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

‡ C. K. Johnson, Publication ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1971.

TABLE 1

Positional parameters (× 10⁴) for the compound $[\mathrm{N(CH_3)_4}]_4[\mathrm{Rh_{13}H(CO)_{24}}]\cdot 3\mathrm{C_5H_9NO}$ *

Atom	*x*	*y*	*z*
Rh(1)	1 805(1)	2 659(2)	3 442(1)
Rh(2)	2 909(1)	1 682(2)	4 479(1)
Rh(3)	2 973(1)	3 796(2)	3 273(1)
Rh(4)	2 579(1)	4 471(1)	1 038(1)
Rh(5)	1 422(1)	3 376(2)	1 184(1)
Rh(6)	1 340(1)	1 299(2)	2 444(2)
Rh(7)	2 423(1)	287(2)	3 477(2)
Rh(8)	3 604(1)	1 381(1)	3 342(1)
Rh(9)	3 671(1)	3 480(1)	2 182(1)
Rh(10)	2 898(1)	3 003(2)	530(1)
Rh(11)	1 767(1)	1 942(2)	658(1)
Rh(12)	2 826(1)	924(2)	1 674(1)
Rh(13)	2 521(1)	2 347(1)	2 330(1)
C(1)	1 453(16)	3 544(26)	3 664(25)
O(1)	1 234(13)	4 105(20)	3 857(20)
C(2)	3 290(17)	775(27)	5 750(26)
O(2)	3 533(12)	205(19)	6 565(18)
C(3)	2 869(16)	4 819(26)	3 628(26)
O(3)	2 821(13)	5 494(20)	3 838(20)
C(4)	2 846(13)	5 756(21)	945(21)
O(4)	3 053(12)	6 614(20)	870(19)
C(5)	718(15)	3 705(24)	1 217(23)
O(5)	226(12)	3 925(19)	1 212(19)
C(6)	597(17)	961(27)	1 840(26)
O(6)	51(13)	807(21)	1 366(20)
C(7)	2 661(16)	−778(25)	4 686(25)
O(7)	2 861(13)	−1 521(20)	5 417(20)
C(8)	4 048(15)	432(24)	4 478(23)
O(8)	4 325(10)	−202(17)	5 214(16)
C(9)	4 208(17)	4 285(27)	1 371(26)
O(9)	4 589(13)	4 733(22)	934(21)
C(10)	3 537(16)	2 969(26)	31(25)
O(10)	3 940(14)	3 009(23)	−305(22)
C(11)	1 284(15)	982(24)	205(23)
O(11)	978(14)	337(22)	−75(21)
C(12)	2 839(20)	447(32)	697(31)
O(12)	2 777(15)	96(24)	88(23)
C(13)	3 423(14)	2 891(23)	4 714(22)
O(13)	3 798(10)	2 997(17)	5 413(16)
C(14)	2 214(16)	1 823(25)	4 884(24)
O(14)	2 050(11)	1 517(18)	5 704(17)
C(15)	3 808(14)	4 345(23)	3 005(22)
O(15)	4 222(12)	4 933(19)	3 260(18)
C(16)	1 110(15)	1 606(25)	3 476(24)
O(16)	682(12)	1 285(20)	3 924(20)
C(17)	4 295(13)	2 486(20)	3 215(19)
O(17)	4 839(9)	2 559(15)	3 590(15)
C(18)	1 554(17)	−123(28)	3 290(27)
O(18)	1 232(14)	−948(23)	3 570(22)
C(19)	1 701(14)	4 780(22)	305(21)
O(19)	1 440(11)	5 520(17)	−443(17)
C(20)	3 709(15)	885(24)	2 285(23)
O(20)	4 168(10)	663(16)	2 207(16)
C(21)	2 543(16)	−408(26)	2 646(25)
O(21)	2 457(12)	−1 290(20)	2 700(20)
C(22)	2 829(14)	4 477(23)	−164(22)
O(22)	2 877(11)	5 175(18)	−1 019(17)
C(23)	1 120(14)	2 932(23)	−29(22)
O(23)	684(10)	3 136(17)	−770(16)
C(24)	2 198(16)	2 613(25)	−490(25)
O(24)	2 066(10)	2 755(17)	−1 410(16)
N(T1)	−696(8)	−1 793(12)	3 241(12)
C(T11)	−358(14)	−1 956(21)	2 566(19)
C(T12)	−999(12)	−2 819(15)	3 851(20)
C(T13)	−1 194(11)	−1 039(19)	2 547(19)
C(T14)	−234(13)	−1 358(22)	3 998(19)
N(T2)	4 378(8)	−2 384(12)	3 680(12)
C(T21)	3 941(11)	−2 161(23)	4 169(21)
C(T22)	4 930(10)	−1 586(19)	3 620(22)
C(T23)	4 033(12)	−2 332(22)	2 586(14)
C(T24)	4 606(13)	−3 456(15)	4 346(20)
N(T3)	1 176(11)	−2 907(18)	1 433(18)
C(T31)	901(20)	−1 863(23)	871(30)
C(T32)	1 838(13)	−2 791(33)	1 326(33)
C(T33)	783(19)	−3 658(29)	951(31)
C(T34)	1 183(20)	−3 315(30)	2 584(19)
N(T4)	−4 148(14)	2 655(22)	1 571(22)
C(T41)	−3 968(25)	3 294(38)	2 245(37)
C(T42)	−3 565(19)	2 298(42)	1 539(43)
C(T43)	−4 487(24)	3 311(36)	469(26)
C(T44)	−4 573(22)	1 722(32)	2 032(41)
O(S1)	−1 309(20)	1 686(32)	1 209(32)
N(S1)	−1 795(19)	1 240(31)	2 401(31)
C(S11)	−1 258(28)	1 625(46)	2 156(45)
C(S12)	−830(28)	2 055(44)	2 755(43)
C(S13)	−1 065(27)	1 609(43)	3 676(43)
C(S14)	−1 793(28)	1 318(44)	3 346(43)
C(S15)	−2 372(28)	807(45)	1 819(45)
O(S2)	−527(13)	3 694(22)	5 323(21)
N(S2)	−979(17)	4 447(28)	3 597(27)
C(S21)	−1 041(24)	4 004(38)	4 543(38)
C(S22)	−1 638(19)	3 854(31)	4 668(30)
C(S23)	−1 971(22)	4 255(35)	3 507(34)
C(S24)	−1 537(21)	4 666(35)	2 788(34)
C(S25)	−369(22)	4 624(35)	3 305(35)
O(S3)	−4 567(13)	−2 566(22)	2 050(21)
N(S3)	−3 520(18)	−2 852(29)	2 581(28)
C(S31)	−4 081(19)	−3 187(30)	2 457(30)
C(S32)	−4 274(21)	−4 317(34)	2 870(33)
C(S33)	−3 607(30)	−4 497(47)	3 149(48)
C(S34)	−3 185(21)	−3 745(33)	3 011(32)
C(S35)	−3 266(23)	−1 823(37)	2 213(37)

* Estimated standard deviations are given in parentheses, as for Table 2. S refers to atoms of the solvent molecules, T to those of the tetramethylammonium ions.

RESULTS AND DISCUSSION

The crystal structure consists of discrete $[\mathrm{Rh_{13}H(CO)_{24}}]^{4-}$ anions, $[\mathrm{N(CH_3)_4}]^{+}$ cations, and 1-methyl-

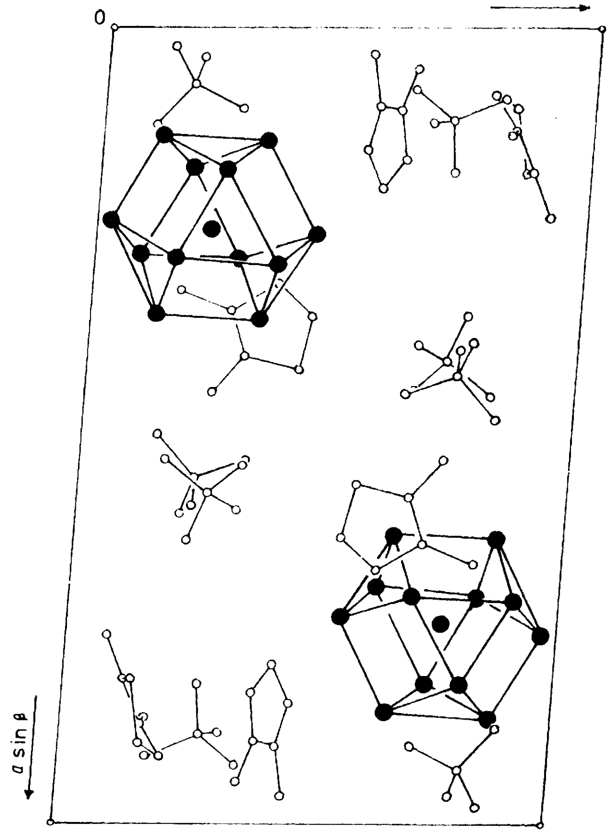

FIGURE 1 View of the packing down the *c* axis. The carbonyl ligands have been omitted for clarity

pyrrolidin-2-one molecules, in the ratio 1 : 4 : 3, as illustrated in Figure 1.

TABLE 2

Bond distances (Å) and angles (°) for the anion $[Rh_{13}H(CO)_{24}]^{4-}$

(*a*) Distances

Rh(1)–Rh(2)	2.781(3)	Rh(1)–C(1)	1.79(5)	C(1)–O(1)	1.18(6)
Rh(1)–Rh(3)	2.847(3)	Rh(2)–C(2)	1.82(3)	C(2)–O(2)	1.16(4)
Rh(1)–Rh(5)	2.894(3)	Rh(3)–C(3)	1.81(5)	C(3)–O(3)	1.16(6)
Rh(1)–Rh(6)	2.757(4)	Rh(4)–C(4)	1.78(3)	C(4)–O(4)	1.20(4)
Rh(2)–Rh(3)	2.792(3)	Rh(5)–C(5)	1.76(4)	C(5)–O(5)	1.21(5)
Rh(2)–Rh(7)	2.808(4)	Rh(6)–C(6)	1.73(4)	C(6)–O(6)	1.25(4)
Rh(2)–Rh(8)	2.789(4)	Rh(7)–C(7)	1.79(3)	C(7)–O(7)	1.19(4)
Rh(3)–Rh(4)	2.870(3)	Rh(8)–C(8)	1.80(3)	C(8)–O(8)	1.17(3)
Rh(3)–Rh(9)	2.748(5)	Rh(9)–C(9)	1.84(4)	C(9)–O(9)	1.16(5)
Rh(4)–Rh(5)	2.800(3)	Rh(10)–C(10)	1.82(4)	C(10)–O(10)	1.14(6)
Rh(4)–Rh(9)	2.781(3)	Rh(11)–C(11)	1.80(3)	C(11)–O(11)	1.18(5)
Rh(4)–Rh(10)	2.760(5)	Rh(12)–C(12)	1.82(6)	C(12)–O(12)	1.15(7)
Rh(5)–Rh(6)	2.769(3)	Rh(2)–C(13)	1.98(3)		
Rh(5)–Rh(11)	2.760(5)	Rh(3)–C(13)	2.01(3)	C(13)–O(13)	1.15(4)
Rh(6)–Rh(7)	2.765(4)	Rh(1)–C(14)	1.96(3)		
Rh(6)–Rh(11)	2.773(4)	Rh(2)–C(14)	1.91(4)	C(14)–O(14)	1.23(5)
Rh(7)–Rh(8)	2.843(3)	Rh(3)–C(15)	1.99(3)		
Rh(7)–Rh(12)	2.767(4)	Rh(9)–C(15)	1.97(4)	C(15)–O(15)	1.21(4)
Rh(8)–Rh(9)	2.764(3)	Rh(1)–C(16)	1.96(3)		
Rh(8)–Rh(12)	2.770(4)	Rh(6)–C(16)	1.95(4)	C(16)–O(16)	1.24(5)
Rh(9)–Rh(10)	2.763(4)	Rh(8)–C(17)	1.99(3)		
Rh(10)–Rh(11)	2.730(4)	Rh(9)–C(17)	1.99(3)	C(17)–O(17)	1.19(3)
Rh(10)–Rh(12)	2.735(3)	Rh(6)–C(18)	1.95(3)		
Rh(11)–Rh(12)	2.723(4)	Rh(7)–C(18)	1.91(4)	C(18)–O(18)	1.24(4)
Rh(13)–Rh(1)	2.802(4)	Rh(4)–C(19)	1.98(3)		
Rh(13)–Rh(2)	2.758(3)	Rh(5)–C(19)	1.98(3)	C(19)–O(19)	1.24(3)
Rh(13)–Rh(3)	2.808(4)	Rh(8)–C(20)	2.02(4)		
Rh(13)–Rh(4)	2.829(3)	Rh(12)–C(20)	1.92(3)	C(20)–O(20)	1.19(5)
Rh(13)–Rh(5)	2.817(3)	Rh(7)–C(21)	1.95(5)		
Rh(13)–Rh(6)	2.817(3)	Rh(12)–C(21)	1.97(3)	C(21)–O(21)	1.21(5)
Rh(13)–Rh(7)	2.718(3)	Rh(4)–C(22)	1.99(4)		
Rh(13)–Rh(8)	2.734(3)	Rh(10)–C(22)	1.93(3)	C(22)–O(22)	1.25(3)
Rh(13)–Rh(9)	2.806(3)	Rh(5)–C(23)	2.00(4)		
Rh(13)–Rh(10)	2.730(4)	Rh(11)–C(23)	1.96(3)	C(23)–O(23)	1.19(3)
Rh(13)–Rh(11)	2.723(4)	Rh(10)–C(24)	1.99(3)		
Rh(13)–Rh(12)	2.833(5)	Rh(11)–C(24)	1.99(4)	C(24)–O(24)	1.21(4)

(*b*) Angles

Rh(1)–C(1)–O(1)	177(3)	Rh(4)–C(19)–O(19)	135(2)
Rh(2)–C(2)–O(2)	179(4)	Rh(5)–C(19)–O(19)	135(2)
Rh(3)–C(3)–O(3)	177(3)	Rh(8)–C(20)–O(20)	129(2)
Rh(4)–C(4)–O(4)	177(3)	Rh(12)–C(20)–O(20)	142(3)
Rh(5)–C(5)–O(5)	178(3)	Rh(7)–C(21)–O(21)	134(3)
Rh(6)–C(6)–O(6)	175(3)	Rh(12)–C(21)–O(21)	136(3)
Rh(7)–C(7)–O(7)	171(4)	Rh(4)–C(22)–O(22)	132(3)
Rh(8)–C(8)–O(8)	178(3)	Rh(10)–C(22)–O(22)	138(3)
Rh(9)–C(9)–O(9)	174(3)	Rh(5)–C(23)–O(23)	133(3)
Rh(10)–C(10)–O(10)	176(3)	Rh(11)–C(23)–O(23)	138(3)
Rh(11)–C(11)–O(11)	179(3)	Rh(10)–C(24)–O(24)	138(3)
Rh(12)–C(12)–O(12)	172(4)	Rh(11)–C(24)–O(24)	136(3)
Rh(2)–C(13)–O(13)	134(2)	Rh(2)–C(13)–Rh(3)	89(1)
Rh(3)–C(13)–O(13)	137(2)	Rh(1)–C(14)–Rh(2)	92(2)
Rh(1)–C(14)–O(14)	132(3)	Rh(3)–C(15)–Rh(9)	88(1)
Rh(2)–C(14)–O(14)	136(2)	Rh(1)–C(16)–Rh(6)	90(2)
Rh(3)–C(15)–O(15)	136(3)	Rh(8)–C(17)–Rh(9)	88(1)
Rh(9)–C(15)–O(15)	136(3)	Rh(6)–C(18)–Rh(7)	91(1)
Rh(1)–C(16)–O(16)	136(3)	Rh(4)–C(19)–Rh(5)	90(1)
Rh(6)–C(16)–O(16)	134(3)	Rh(8)–C(20)–Rh(12)	89(2)
Rh(8)–C(17)–O(17)	138(2)	Rh(7)–C(21)–Rh(12)	90(2)
Rh(9)–C(17)–O(17)	135(2)	Rh(4)–C(22)–Rh(10)	90(1)
Rh(6)–C(18)–O(18)	133(3)	Rh(5)–C(23)–Rh(11)	88(1)
Rh(7)–C(18)–O(18)	136(3)	Rh(10)–C(24)–Rh(11)	87(1)

The overall anion, of idealised C_s symmetry, is shown in Figure 2, while the metal-atom cluster, of idealised D_{3h} symmetry, is illustrated in Figure 3. Bond distances and angles within the anion are listed in Table 2. Both the cluster geometry, a centred twinned-cuboctahedron, and the carbonyl stereochemistry are similar to those of the previously determined $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ (n = 2 [2] or 3 [1]). However, small differences are present due to the change of the anionic charge and, especially, of the number of interstitial hydride atoms, which will be described in some detail.

The Rh–Rh bond distances range from 2.718(3) to 2.894(3) Å, their overall mean (2.782 Å) being slightly lower than in the dihydride anion and in accord with a trend $Rh_{13}H_3 > Rh_{13}H_2 > Rh_{13}H$ (see Table 3) However, the distribution of the Rh–Rh bonds must be

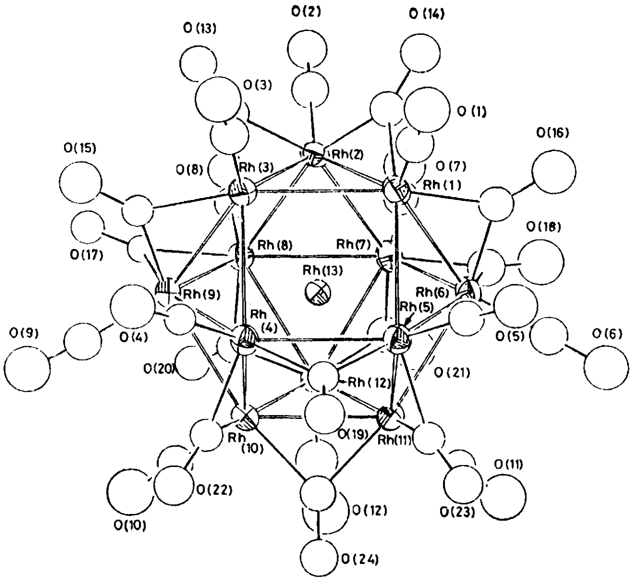

FIGURE 2 ORTEP drawing of the anion $[Rh_{13}H(CO)_{24}]^{4-}$

discussed in connection with the probable location of the interstitial hydride atom and its lengthening effects (see later).

TABLE 3

Comparison of mean Rh–Rh bond lengths (Å) in the three anions $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$

Bonds		$n = 4$	$n = 3$	$n = 2$
Overall mean (36 values)		2.782	2.794	2.81
Surface (24 values)		2.783	2.794	2.81
Centre-to-surface (12 values)		2.781	2.793	2.81
Cavity [1] Rh(1,3,4,5,13)	Surface	2.853	2.853	2.85
	Centre-to-surface	2.814	2.791	2.79
	Mean	2.833	2.822	2.82
Cavity [2] Rh(1,2,6,7,13)	Surface	2.778	2.770	2.79
	Centre-to-surface	2.774	2.775	2.80
	Mean	2.776	2.773	2.79
Cavity [3] Rh(2,3,8,9,13)	Surface	2.773	2.774	2.79
	Centre-to-surface	2.777	2.794	2.79
	Mean	2.775	2.784	2.79
Cavity [4] Rh(4,5,10,11,13)	Surface	2.763	2.773	2.78
	Centre-to-surface	2.775	2.787	2.81
	Mean	2.769	2.780	2.79
Cavity [5] Rh(6,7,11,12,13)	Surface	2.757	2.775	2.82
	Centre-to-surface	2.773	2.790	2.84
	Mean	2.765	2.783	2.83
Cavity [6] Rh(8,9,10,12,13)	Surface	2.758	2.801	2.83
	Centre-to-surface	2.776	2.821	2.83
	Mean	2.767	2.811	2.83
Surface edges of the occupied cavities		2.853	2.827	2.83
Surface edges of the unoccupied cavities		2.766	2.773	2.78
Rh–Rh CO-bridged edges		2.766	2.776	2.79
Rh–Rh CO-unbridged edges		2.800	2.813	2.83

As in the other two anions, there are 12 terminal and 12 symmetric edge-bridging CO groups, giving three Rh–C contacts per metal atom. The mean values of the Rh–C and C–O bond lengths for the terminal and bridging groups are 1.80, 1.18 and 1.97, 1.21 Å, respectively. These mean values, compared with the corresponding ones in the trianion (1.81, 1.17 and 2.00, 1.20 Å),[1] show the expected moderate decrease of the Rh–C bond lengths and moderate increase of the C–O distances due to the augmentation of the anionic charge (the corresponding data for the dianion[2] were of insufficient quality for comparison). A discussion on the possible edge-bridging carbonyl geometries in these Rh_{13} anions has already been outlined.[1]

As to the location of the hydride atom, we have followed the same criteria used for the other two anions, *i.e.* we have looked for holes in the ligand disposition and for metal–metal bond lengthenings. As previously pointed out, considering the polyhedron described by the carbon atoms (see Figure 4 of ref. 1), the largest holes are located within the three square faces of the cluster, Rh(1,3,4,5), Rh(6,7,11,12), and Rh(8,9,10,12), which can contain hydride ligands in semi-interstitial positions. The first hole is bisected by the ideal mirror plane, while the other two are related by the symmetry plane. In contrast to the dihydride species we have found here more similar values of the corresponding C • • • C contacts for the two mirror-related holes.

A comparison of the Rh–Rh bond lengths in the three Rh_{13} anions is given in Table 3. This clearly shows that the hydride atom of $[Rh_{13}H(CO)_{24}]^{4-}$ must be located in cavity [1], the largest of the six semi-octahedral cavities (mean edge of cavity [1], 2.833 *vs.* 2.770 Å for the others). The analysis also confirms the previous assignments for the di- and tri-hydride: in the former the occupied cavities are [1] and [6], and in the latter they are [1], [5], and [6].

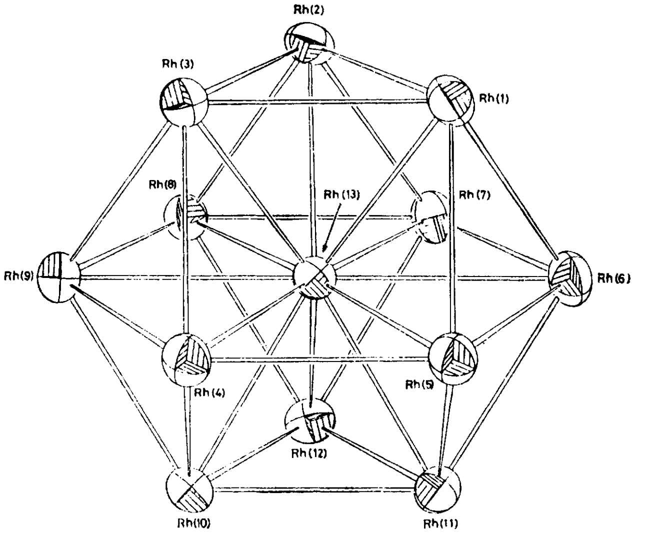

FIGURE 3 View of the metal-atom cluster

Some features common to the three anions are as follows. (*i*) The Rh–Rh surface bonds bridged by CO groups are, on average, shorter than the unbridged ones, a fact which is often observed in carbonyl cluster species. It does not, however, obscure the analysis of the hydride-containing cavities based on bond lengthenings as can be seen, for instance, by comparing the mean surface metal–metal bonds in cavities [4], [5], and [6] of the dihydride. (*ii*) The Rh(7)–Rh(8) bond length is rather long, although it is never involved in hydride-containing cavities. An explanation of this lengthening may be related to the particular disposition of the CO groups bound to these metals, and to their non-bonding repulsions. (*iii*) The Rh(12)–Rh(13) bond is slightly longer than any other centre-to-surface bond. This was previously ascribed, in the trihydride, to the fact that this bond is shared by two hydride-containing cavities, [5] and [6].[1] However, the finding of the same feature also in the present structure might suggest that, in part, the lengthening is due to a structural *trans* influence of the hydride ligand lying in cavity [1] [H–Rh(13)–Rh(12) *ca.* 160°].

The reasonable location of the hydride atom in the barycentre of the square face Rh(1,3,4,5) leads to an average Rh(1,3,4,5)–H bond distance of 2.02 Å and to a Rh(13)–H bond length of 1.96 Å. These values are comparable to the Ru–H bond lengths found [2.03—2.06(1) Å], by *X*-ray and neutron-diffraction analyses, in $[Ru_6H(CO)_{18}]^-$, with the H atom at the centre of an octahedral cluster.[6] Moreover, the contacts of the hydride atom with the surrounding carbonyl ligands are normal, the shortest H • • • C interaction, with the bridging group CO(19), being 2.62 Å. An outward displacement of H, leading to the extreme situation of a μ_4-H face-bridging ligand, seems improbable, since it gives Rh–H bonds which are too long and a short H • • • C(19) contact. On the other hand, a slight inward displacement cannot be excluded, although it gives a larger difference between the two types of Rh–H distances. In fact, an inner location would be in better accord both with the complete fluxionality inside the cluster of these hydrides, observed in the n.m.r. spectra in solution at room temperature,[3,7] and also with the finding in the anions $[Ni_{12}H_{4-n}(CO)_{21}]^{n-}$ ($n = 2$ or 3), containing H atoms in octahedral holes, of shorter Ni–H bonds with the central metal atoms.[8]

The family of anions $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$, of which two other members have also been isolated, namely $[Rh_{13}H_4(CO)_{24}]^-$ and $[Rh_{13}(CO)_{24}]^{5-}$,[3] shows the, at present, unique feature of semi-interstitial hydride ligands, in semi-octahedral (*i.e.* square-pyramidal) holes,* while all the other known interstitial hydrides are found in octahedral holes.[6,8,9] These ' nearly-on-surface ' hydride locations, due to the cluster geometry, agree well with the ready hydrogen exchanges and interconversions, at least for the central members of the series, observed by their reaction with acids and bases.[3]

We thank the Italian C.N.R. for financial support.

[0/1178 *Received, 25th July,* 1980]

REFERENCES

[1] Part 1, V. G. Albano, G. Ciani, S. Martinengo, and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1979, 978.

[2] V. G. Albano, A. Ceriotti, P. Chini, G. Ciani, S. Martinengo, and W. M. Anker, *J. Chem. Soc., Chem. Commun.*, 1975, 859.

[3] S. Martinengo, B. T. Heaton, and P. Chini, unpublished work.

[4] D. T. Cromer and J. B. Mann, *Acta Crystallogr.*, 1968, **A24**, 321.

[5] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3.

[6] P. F. Jackson, B. F. G. Johnson, J. Lewis, P. R. Raithby, M. McPartlin, V. J. H. Nelson, K. D. Rouse, J. Allibon, and S. A. Mason, *J. Chem. Soc., Chem. Commun.*, 1980, 295.

[7] S. Martinengo, B. T. Heaton, R. J. Goodfellow, and P. Chini, *J. Chem. Soc., Chem. Commun.*, 1977, 39.

[8] R. W. Broach, L. F. Dahl, G. Longoni, P. Chini, A. J. Schultz, and J. M. Williams, *Adv. Chem. Ser.*, 1978, **167**, 93.

[9] D. W. Hart, R. G. Teller, C.-Y. Wei, R. Bau, G. Longoni, S. Campanella, P. Chini, and T. F. Koetzle, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 80.

---

* *Note added at proof.* A similar situation is believed to be present in $[Rh_{14}H(CO)_{25}]^{3-}$ (G. Ciani, A. Sironi, and S. Martinengo, *J. Organomet. Chem.*, 1980, **192**, C42).