

Crystal structure of a compound composed of a cluster cation and a cluster anion

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Abstract

X-Ray crystal structure determination of the crystalline material resulting from Rh-catalysed carbonylation of *N,N*-allylethylamine in the presence of trimethylphosphine revealed the composition $\text{FeRh}_8(\text{PMe})(\text{PMe}_3)_5(\text{CO})_{20}$ for the product, with the iron originating presumably from an impurity in the CO used. The compound is composed of the triangular cluster cation, $[\text{Rh}_3(\mu_3\text{-PMe})(\text{PMe}_3)_4(\text{CO})_5]^+$, and of the octahedral, heterometallic cluster anion, $[\text{FeRh}_5(\text{PMe}_3)(\text{CO})_{15}]^-$, packed at Van der Waals distances in a distorted CsCl arrangement. Both clusters belong to well-documented types; features characteristic for this particular structure can be ascribed to the high basicity and low steric bulk of the phosphine.

Introduction

Carbonylation of *N,N*-allylethylamine yielding *N*-ethyl-2-pyrrolidone has been found [1] to be homogeneously catalysed by $\text{Rh}(\text{acac})(\text{CO})_2$ in the presence of trimethylphosphine at 100 °C under 5 MPa carbon monoxide. Using stoichiometric amounts of $\text{Rh}(\text{acac})(\text{CO})_2$ and amine, an excess of trimethylphosphine, and methanol as the solvent, well-developed crystals containing Rh and P in a 4/3 molar ratio were obtained after slow cooling and then venting the autoclave. Since the structure of this suspected reaction intermediate could not be unambiguously elucidated from spectral data, because of its fluxionality in solution, an X-ray crystal structure determination was undertaken. Surprisingly, the structure is ionic and is composed of a triangular cluster cation and an octahedral, heterometallic cluster anion.

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Experimental

The red prismatic crystals were sufficiently stable to allow data collection in air. Their density was determined by flotation in aqueous ZnBr_2 solution. Crystal data and further details are summarized in Table 1. Application of both direct and heavy atom methods (MULTAN, SHELX-86) led to very similar solutions for the approximate positions of a total of six heavy atoms in the asymmetric unit. With respect to their positions relative to the mirror plane, this corresponds to nine metal atoms in the molecule, composing one triangular and one octahedral cluster separated by some 8 Å. Subsequent Fourier syntheses permitted the location of all non-H atoms except one disordered methyl (vide infra). Further refining produced, however, considerable gaps in the electron density at the octahedral metal sites; this was interpreted as a statistical mixed-metal disorder involving one lighter metal as the elusive ninth atom. At this stage, additional chemical analysis established a content of $2.9 \pm 0.1\%$ Fe in a number of independently prepared samples. Presumably, the iron originates from an iron carbonyl impurity in the technical-grade carbon

Table 1

Crystal data, measurement and refinement details

Formula	$\text{C}_{36}\text{H}_{48}\text{FeO}_{20}\text{P}_6\text{Rh}_8$
Molecular weight	1865.63
Space group	<i>Pnma</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	33.058(8), 16.123(7), 11.186(3)
α , β , γ (°)	90, 90, 90
Cell volume (Å ³)	5962(3)
Z	4
<i>D</i> _m , <i>D</i> _x (g cm ⁻³)	2.06(1), 2.078
Radiation	Mo- <i>K</i> _α , λ 0.71069 Å
Absorption correction	None, μ 2.48 mm ⁻¹
<i>F</i> (000)	3600
Temperature (K)	296
Crystal dimensions (mm ³)	0.20 × 0.20 × 0.25
No. of reflections for latt. par. determination	15(4 < θ < 16°)
Diffractometer	Syntex P2 ₁
Scan mode	ω-2θ
(sin θ/λ) _{max} (Å ⁻¹)	0.6
Standard reflections (variation)	3 after every 30 (< 5%)
<i>h</i>	<0, 39>
<i>k</i>	<0, 19>
<i>l</i>	<0, 10>
No. of reflections measured	4942
No. of reflections used (<i>I</i> > 1.96σ(<i>I</i>))	2572
Resid. electr. density (e Å ⁻³)	1.02, -0.94
(Δ/σ) _{max} for non-H atoms	0.218
Function minimized	$w(F_o - F_c)^2$
Weight	σ ⁻² (<i>F</i> _o), derived from σ(<i>F</i> _o)/ <i>F</i> _o = 1/2σ ₂ (<i>I</i>)/ <i>I</i> and σ ₂ (<i>I</i>) = (σ ₁ ² (<i>I</i>) + 0.06 <i>I</i> ²) ^{1/2}
<i>R</i> , <i>wR</i>	0.065, 0.062

Table 2

Atomic coordinates ($\times 10^4$) of non-H atoms with estimated standard deviations in parentheses. $U_{\text{eq}} = 1/3 (U_{11} + U_{22} + U_{33})$

Atom	x/a	y/b	z/c	$U_{\text{eq}} (\times 10^3) (\text{\AA}^2)$
Rh(1)	1927.9(4)	1651.7(7)	4954(1)	41.5(4)
Rh(2)	1696.7(5)	2500	6962(1)	37.3(6)
M(1)	3715.4(4)	1635.2(9)	3329(1)	47.7(5)
M(2)	4529.9(4)	1643(1)	3689(1)	61.6(6)
M(3)	4028.0(8)	2500	5194(2)	79(1)
M(4)	4200.4(6)	2500	1761(21)	68(1)
P(1)	1347(2)	2500	5103(5)	39(2)
P(2)	1636(2)	651(3)	3785(4)	59(2)
P(3)	1116(2)	2500	8083(6)	56(2)
P(4)	2174(2)	2500	8434(5)	51(2)
P(5)	4699(3)	2500	312(8)	146(6)
O(1)	2705(4)	708(8)	5133(13)	101(6)
O(2)	3559(4)	28(8)	4682(12)	90(6)
O(3)	2979(4)	1381(10)	1759(14)	124(8)
O(4)	5431(5)	1493(15)	3193(18)	206(13)
O(5)	4536(4)	41(11)	5063(9)	152(9)
O(6)	3896(6)	1220(9)	6984(13)	129(8)
O(7)	3574(6)	2500	-215(17)	160(15)
O(11)	2258(6)	2500	2669(17)	94(9)
O(12)	1758(4)	611(7)	7215(10)	83(6)
O(34)	4269(6)	584(11)	1592(14)	149(9)
O(35)	3113(5)	2500	5085(16)	75(7)
O(45)	4897(7)	2500	5968(19)	122(11)
C(1)	2423(5)	1088(10)	5031(15)	63(3)
C(2)	3616(6)	628(12)	4151(17)	71(6)
C(3)	3264(6)	1518(11)	2334(17)	71(6)
C(4)	5098(8)	1535(14)	3345(21)	105(8)
C(5)	4555(7)	659(14)	4547(20)	89(7)
C(6)	3953(6)	1725(12)	6296(16)	69(5)
C(7)	3750(10)	2500	541(31)	99(11)
C(10A)	1070	2500	3660	390
C(10B)	970	1700	4800	390
C(10C)	870	2500	5980	390
C(11)	2117(7)	2500	3704(20)	47(6)
C(12)	1772(4)	1228(10)	6733(13)	41(4)
C(21)	1259(14)	95(34)	4115(47)	471(22)
C(22)	1371(10)	1037(21)	2611(30)	211(15)
C(23)	1950(11)	-21(26)	2973(34)	290(21)
C(31)	785(6)	1634(12)	7750(18)	95(7)
C(32)	1146(17)	2500	9675(51)	238(25)
C(34)	4243(7)	1197(15)	2120(20)	96(7)
C(35)	3437(8)	2500	4629(22)	56(7)
C(41)	2174(6)	1621(11)	9455(17)	88(6)
C(42)	2683(8)	2500	7880(24)	80(9)
C(45)	4621(9)	2500	5313(28)	88(10)
C(51)	4676(15)	1764(24)	-752(44)	418(37)
C(52)	5209(13)	2500	613(37)	149(15)

monoxide used. Subsequent refinement of the disorder of the metal atoms within the octahedral sites converged at the values of 0.8404, 0.8496, 0.7416 and 0.8382 for the Rh fractional occupancies at M(1), M(2), M(3) and M(4), respectively (the remaining two sites, M(1') and M(2'), are symmetry-related). Interestingly, no such feature occurs for the triangular cluster. The final refinement used the anisotropic model for Rh, P and O, and the isotropic model for C, and H atoms fixed in the calculated positions. Atomic coordinates of the non-H atoms are given in Table 2. Tables of structure factors, anisotropic thermal parameters, bond distances and angles, and H atom coordinates are available from the authors on request.

Results and discussion

The structure is composed of two clusters, triangular $\text{Rh}_3(\mu_3\text{-PMe})(\text{PMe}_3)_4(\mu_2\text{-CO})_3(\text{CO})_2$ and octahedral $\text{FeRh}_5(\text{PMe}_3)(\mu_3\text{-CO})_4(\text{CO})_{11}$, in a 1/1 molar ratio. Both moieties possess odd numbers of valence electrons, 49 for the triangle and 85 for the octahedron (the stable counts according to the Wade rules are 48 and 86, respectively [2]), the compound is diamagnetic and behaves as a semiconductor in the solid state (powder). The only reasonable explanation is that the triangular cluster should be formulated as a monocation and the octahedral cluster as a monoanion, analogous to the well-documented $[\text{FeRh}_5(\text{CO})_{16}]^-$ [3]. Structures composed of cluster cations and cluster anions were unknown until very recently [4]. The unit cell contents (Fig. 1) and molecular packing of the ions, approximated as spheres (Fig. 2), clearly support this type of structure. As expected for a relative ratio of close to 0.9 for r_+/r_- , the molecular packing is of a distorted CsCl type with eight anions surrounding each cation and vice versa. Deviations from the ideal

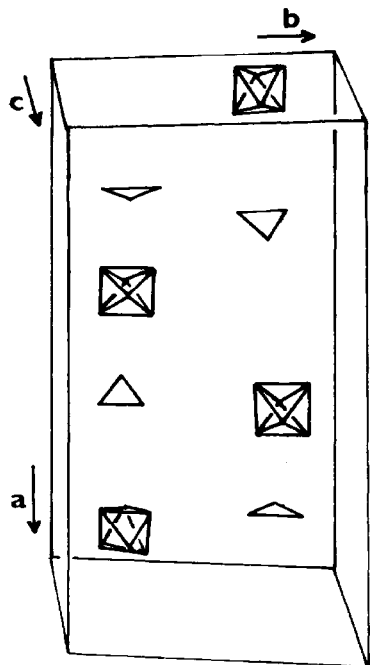


Fig. 1. Packing of metal atoms within the unit cell.

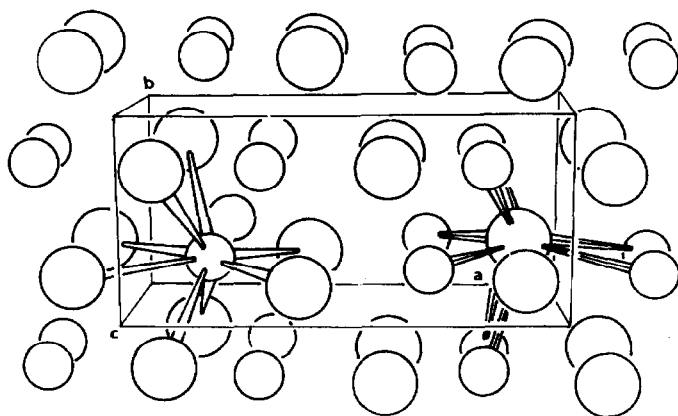


Fig. 2. Molecular packing of clusters, approximated as spheres (the smaller spheres represent the cations).

arrangement are considerable but can be explained easily by the high deformability of the cluster unit forming this "soft salt" [4].

The individual structures of the cation and the anion both belong to well-documented types. Features characteristic for this particular structure arise from the properties of trimethylphosphine, as a ligand with high basicity and low steric bulk. The molecular structure of the cation is depicted in Fig. 3. It belongs to the $Rh_3(\mu_3-L)_3$ type [5], with the methylphosphinidene moiety undoubtedly originating from thermal degradation of trimethylphosphine [6]. The equilateral Rh_3 triangle is capped almost symmetrically, giving a mean Rh–P distance of 2.34(1) Å. The C(10) methyl of the methylphosphinidene group is multiply disordered about the non-crystallographic C_3 -axis that passes through the P(1) atom and the centre of the Rh_3 triangle. As deduced from the Fourier map, the model used in the refinement approximated this disorder as the C(10) atom fixed in four positions with 0.25 relative occupancies. The positions are labelled as A, B, C and B' around the C-axis, the B, B' pair being related through the crystallographic mirror plane. The

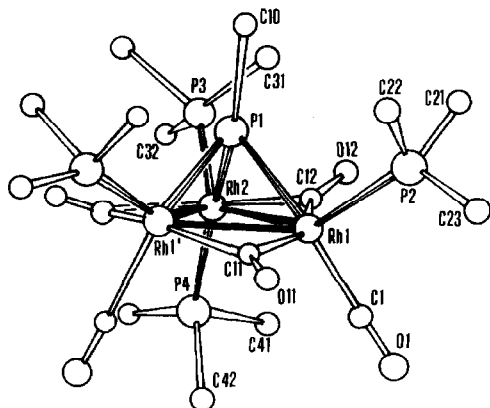


Fig. 3. Perspective view of the cation. For clarity, the disordered C(10) is depicted in one idealized position, with equal Rh–P–C angles.

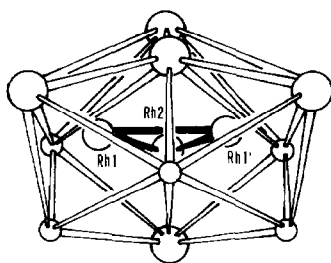


Fig. 4. Ligand environment of the cation.

P(1)–C(10) distance and Rh–P(1)–C(10) angle average 1.84(2) Å and 115(5)°, respectively. Hydrogen atoms of this methyl group were not found. Such an unhindered rotation of the μ_3 -PR group is unique, but could account for the existence of three independent molecules differing in the orientation of the μ_3 -PPh moiety relative to the Ru_3 plane in the related $\text{Ru}_3(\mu_3\text{-PPh})(\mu_2\text{-H})_2(\text{CO})_9$ cluster [7].

The remaining ligands are arranged analogously as in the $\text{Rh}_3(\mu_3\text{-L})\text{L}'_9$ prototype. Significant asymmetry, with Rh–C distances of 2.07(2) and 2.13(2) Å, is characteristic for the bridging carbonyls. As a consequence of the low steric bulk of trimethylphosphine, the degree of substitution of the terminal carbonyls by phosphine is extraordinarily high for such a small cluster. Nevertheless, the overall arrangement of the ligands in the cluster cation (Fig. 4) adopts the energetically most favourable [8] 1/3/(3)/3 distribution, according to Johnson's notation [9].

Figure 5 depicts the structure of the cluster anion. Its geometry closely resembles that of $[\text{FeRh}_5(\text{CO})_{16}]^-$ in the disorder of the metals, the arrangement of the ligands and the bond lengths and angles [4]. The statistical disorder masks any effects that may arise from the cluster being heterometallic. Small distortions of the cluster faces and of the carbonyls adjacent to the axial trimethylphosphine can be ascribed to strong σ -donation by the phosphine rather than to the relative preference of iron for

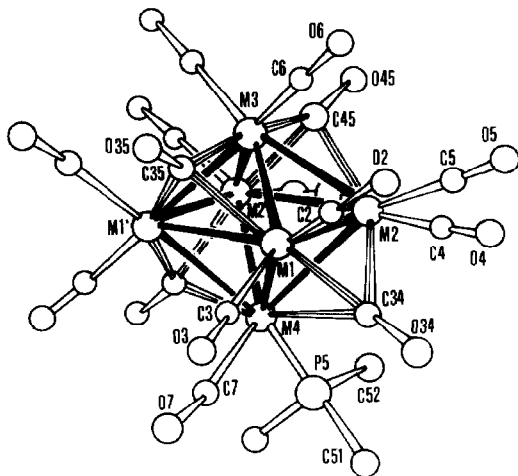


Fig. 5. Perspective view of the anion.

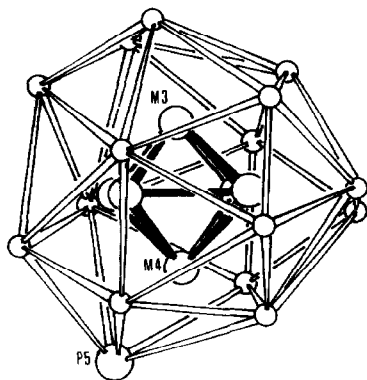


Fig. 6. Ligand environment of the anion.

this position. Again, the overall distribution of the ligands around the octahedron (Fig. 6) does not differ much from the idealized $2/3/(3)/6/2$ picture [9].

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