Structure of a Dinuclear Ruthenium(II) Complex Containing Bridging Carboxylato Ligands and a Bridging Aqua Ligand: μ-Aqua-bis(μ-trichloroacetato-*O,O'*)-bis{(η⁴-bicyclo[2.2.1]hepta-2,5-diene)(trichloroacetato)ruthenium(II)}

By Michel O. Albers, David C. Liles, Eric Singleton* and Janet E. Stead

National Chemical Research Laboratory, Council for Scientific and Industrial Research, PO Box 395, Pretoria 0001, Republic of South Africa

Abstract. $C_{22}H_{18}Cl_{12}O_9Ru_2$, $M_r = 1053.95$, monoclinic, $P2_1/c$, $a = 12.590$ (3), $b = 10.552$ (2), $c = 27.303$ (6) Å, $\beta = 103.79$ (3)°, $U = 3522.6$ Å³, $Z = 4$, $D_x = 1.987$ Mg m⁻³, Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu = 15.292$ mm⁻¹, $F(000) = 2056$, $T = 293$ K, $R = 0.0675$ for 4647 unique reflections. The complex is dinuclear with the two ruthenium atoms bridged by two trichloroacetato ligands and an aqua ligand. There is no metal–metal bonding: the Ru···Ru distance is 3.675 (1) Å. The coordination of each ruthenium atom is completed by a bicyclo[2.2.1]hepta-2,5-diene ligand and a unidentate trichloroacetato ligand. The noncoordinated oxygen atoms of the unidentate trichloroacetato ligands are hydrogen bonded to the bridging aqua ligand.

Introduction. Carboxylate anions are multifaceted ligand systems which are encountered widely in transition-metal chemistry (Mehrotra & Bohra, 1983). Their distribution ranges from organometallic complexes where the metal atom is typically in a low oxidation state, to classical inorganic systems containing metal ions in high oxidation states. The carboxylato ligand (for instance in the form of asparate or glutamate residues) is also encountered in a range of bioinorganic systems of which the oxo-bridged di-Fe^{III} sites, encountered in the invertebrate oxygen-transport proteins myohemerythrin and hemerythrin, are worthy of particular note.
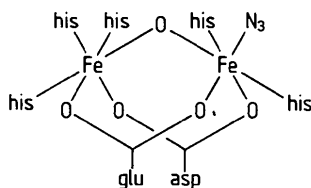
asp = aspartate, glu = glutamate, his = histidine

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* To whom correspondence should be addressed.

Recently Lippard and co-workers (Armstrong, Spool, Papaefthymiou, Frankel & Lippard, 1984) reported the synthesis and characterization of the complexes [{(HBPz₃)Fe}₂(μ-O₂C*R*)₂(μ-O)] (HBPz₃ = tri-1-pyrazolylborate anion; R = H, CH₃, C₆H₅) containing a similar [Fe₂(μ-O₂C*R*)₂(μ-O)] core, and proposed them to be models for the active sites of these metalloproteins. We have reported (Albers, Liles, Singleton & Yates, 1984) the synthesis and characterization of a series of novel dinuclear Ru^{II} carboxylate complexes containing both bridging and monodentate carboxylate ligands and bridging aqua ligands, the core structures of which bear formal resemblance to a doubly protonated, reduced hemerythrin model system. We report here the structure of one of these, the title compound (I).
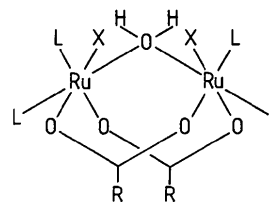
(I) L = (bicyclo[2.2.1]hepta-2,5-diene)/2, X = trichloroacetato; (II) L = (1,5-cyclooctadiene)/2, X = trifluoroacetato; (III) L = PMe₂Ph, X = trifluoroacetato.

Experimental. The reaction of [Ru(C₃H₅)₂(C₇H₈)] [C₇H₈ = bicyclo[2.2.1]hepta-2,5-diene (norbornadiene)] with excess trichloroacetic acid in tetrahydrofuran at 298 K yielded the title complex (I). Orange rectangular prism-shaped crystals were obtained by crystallization from dichloromethane–hexane solution. Crystal: $0.30 \times 0.20 \times 0.15$ mm; Philips PW 1100 four-circle diffractometer, graphite-crystal-monochromatized Cu $K\alpha$ radiation; lattice parameters: 25 reflections, $25 \leq \theta \leq 26°$, least-squares refinement; ω–2θ scan mode, scan width 1.00° in ω, scan speed 0.040° s⁻¹ in ω, 12.5 s stationary background at each end of the scan; 5216 unique reflections measured in the quadrant $\pm h$, $+k$, $+l$ with $5 \leq \theta \leq 60°$, three standards

measured every 60 min showed no significant deviations from their mean intensities, empirical absorption corrections (Walker & Stuart, 1983) were applied to the data during refinement of the structure; 4647 reflections $[F_o \geq 4\sigma(F_o)]$, index range $h \pm 12$, k 0–14, l 0–30, used in the analysis; structure solved by normal heavy-atom methods and refined using *SHELX* (Sheldrick, 1978); the H atoms of the aqua ligand were located on a difference map and refined with d(O—H) constrained to 1·04 Å, all other H atoms were added in calculated positions $[d$(C—H) = 0·95 Å (Churchill, 1973)]; anisotropic temperature factors used for all non-H atoms, separate common isotropic temperature factors used for the aqua and norbornadiene H atoms; least-squares refinement, $\sum w(\Delta F)^2$ minimized, $w = \sigma^{-2}(F_o)$, with the matrix blocked so that the parameters for the Ru atoms and the aqua ligand refined in every cycle and those for the norbornadiene ligands, the monodentate carboxylato ligands and the bridging carboxylato ligands refined in separate cycles, converged to give $R = 0\cdot0675$ and $wR = 0\cdot0672$; all reductions in wR significant at the 99·5% level (Hamilton, 1965); complex neutral-atom scattering factors used for all atoms (Cromer & Waber, 1974); in the final cycles 414 parameters varied, comprising 141 positional parameters, 270 anisotropic temperature factor components, 2 common isotropic temperature factors and one overall scale, $\Delta\rho$ +0·58 to −0·48 e Å^{-3}, max. shift/e.s.d. in final least-squares cycle 0·195.

Discussion. The final atomic coordinates are given in Table 1.* Selected bond lengths and angles are given in Table 2. Fig. 1 is a perspective view of the complex showing the atom-numbering scheme; Fig. 2 shows the unit-cell contents.

The structure consists of isolated molecules occupying general positions in the unit cell. The complex is dinuclear with the two ruthenium atoms bridged by two trichloroacetato ligands and an aqua ligand. The coordination of each ruthenium atom is completed by a norbornadiene ligand and a unidentate trichloroacetato ligand. On the basis of the effective atomic number rule there is no formal metal–metal bond and the Ru···Ru distance of 3·675 (1) Å is in accord with this. The non-coordinated oxygen atoms of the unidentate trichloroacetato ligands are strongly hydrogen bonded to the hydrogen atoms of the bridging aqua ligand with O(aqua)···O(carboxylato) distances of 2·49 (1) and 2·48 (1) Å, and O(carboxylato)···H(aqua) distances of 1·48 (16) and 1·50 (16) Å.

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* Lists of structure factors, anisotropic temperature factors and calculated H-atom coordinates and a full list of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42964 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The molecular structure of (I) is similar to that of two other dinuclear Ru^{II} complexes [{RuL_2[O$_2$CCF$_3$]}$_2$-(μ-O$_2$CCF$_3$)$_2$(μ-OH$_2$)] where L_2 = 1,5-cyclooctadiene [(II) Albers, Liles, Singleton & Yates (1984)] or L = PMe$_2$Ph [(III) Albers, Liles, Singleton & Stead (1985)], both synthesized in a similar manner to (I). The Ru···Ru distance in (I) is somewhat shorter than the 3·733 (1) Å in (II), and considerably shorter than the 3·881 (1) Å in (III) where the *trans* influence of the tertiary phosphine ligands causes a lengthening of some of the bridging Ru—ligand bond lengths compared with those in (I) and (II). The Ru—ligand bond lengths in (I) are not significantly different from those in (II) indicating that the substitution of a CF$_3$ group on the carboxylato ligands by a CCl$_3$ group has no significant effect on the coordination sphere of each ruthenium atom.

Table 1. *Fractional coordinates ($\times 10^4$, $\times 10^5$ for Ru, $\times 10^3$ for H) and equivalent isotropic temperature factors (Å$^2 \times 10^3$, Å$^2 \times 10^4$ for Ru) for (I)*

$$U_{eq} = \tfrac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
Ru(1)	43747 (5)	7961 (6)	14851 (2)	236 (3)
Ru(2)	15181 (5)	18764 (6)	11455 (2)	253 (3)
O(1)	3125 (4)	2013 (6)	1641 (2)	26 (3)
H(1A)	349 (16)	290 (9)	166 (9)	83 (14)†
H(1B)	289 (17)	153 (18)	193 (6)	83 (14)†
C(11)	5624 (7)	1143 (9)	2160 (3)	34 (5)
C(12)	5021 (7)	73 (9)	2237 (3)	31 (5)
C(13)	5623 (8)	−1061 (10)	2075 (4)	41 (5)
C(14)	5391 (7)	−875 (9)	1505 (4)	34 (5)
C(15)	5993 (7)	183 (9)	1434 (4)	36 (5)
C(16)	6600 (7)	628 (9)	1955 (4)	38 (5)
C(17)	6822 (8)	−639 (10)	2239 (5)	49 (6)
C(21)	−266 (7)	1925 (10)	897 (4)	35 (5)
C(22)	159 (8)	2194 (11)	498 (4)	36 (6)
C(23)	308 (9)	3611 (10)	471 (4)	42 (6)
C(24)	1210 (8)	3836 (9)	952 (4)	38 (5)
C(25)	788 (8)	3587 (9)	1358 (4)	38 (5)
C(26)	−408 (8)	3208 (11)	1141 (4)	46 (6)
C(27)	−687 (9)	4058 (11)	673 (4)	48 (6)
O(31)	5111 (5)	2412 (6)	1274 (3)	34 (3)
O(32)	4213 (6)	3954 (6)	1583 (3)	47 (4)
C(31)	4872 (7)	3545 (9)	1341 (4)	33 (5)
C(32)	5416 (8)	4547 (9)	1076 (4)	40 (5)
Cl(31)	5881 (3)	5805 (3)	1488 (2)	71 (2)
Cl(32)	4435 (3)	5063 (4)	551 (1)	82 (3)
Cl(33)	6530 (3)	3924 (3)	861 (2)	61 (2)
O(41)	972 (5)	1204 (7)	1764 (2)	38 (4)
O(42)	2448 (5)	1457 (8)	2394 (3)	44 (4)
C(41)	1525 (7)	1107 (10)	2205 (4)	36 (5)
C(42)	931 (9)	382 (11)	2561 (4)	50 (7)
Cl(41)	1127 (3)	1151 (4)	3141 (1)	78 (2)
Cl(42)	1551 (5)	−1120 (4)	2664 (2)	97 (3)
Cl(43)	−466 (3)	195 (6)	2312 (2)	94 (3)
O(51)	3685 (5)	735 (7)	697 (2)	40 (4)
O(52)	2278 (5)	2134 (6)	546 (2)	35 (3)
C(51)	3007 (8)	1480 (10)	430 (4)	37 (5)
C(52)	3067 (8)	1529 (12)	−119 (4)	45 (6)
Cl(51)	2383 (4)	2879 (5)	−432 (2)	92 (3)
Cl(52)	2461 (4)	141 (6)	−398 (2)	92 (4)
Cl(53)	4399 (3)	1616 (4)	−187 (1)	70 (2)
O(61)	3306 (5)	−718 (6)	1531 (2)	34 (3)
O(62)	1688 (5)	−88 (6)	1030 (2)	36 (3)
C(61)	2364 (7)	−879 (9)	1260 (4)	34 (5)
C(62)	1996 (8)	−2269 (9)	1184 (4)	42 (5)
Cl(61)	2751 (4)	−3267 (3)	1631 (2)	76 (3)
Cl(62)	612 (3)	−2417 (4)	1144 (3)	99 (3)
Cl(63)	2175 (5)	−2727 (4)	600 (2)	104 (3)

† Isotropic temperature factor.

The molecular structure of (I) is also similar to that observed for a series of dinuclear nickel complexes, e.g. [{Ni(Me$_2$NC$_2$H$_4$NMe$_2$)}$_2$(μ-O$_2$CCF$_3$)$_2$(μ-OH$_2$)] (Ahlgren & Turpeinen, 1982), which exhibit similar features such as strong intramolecular hydrogen bond-ing between the non-coordinated oxygen atom of the unidentate carboxylato ligands and the bridging aqua ligands.

Perhaps more significant though is the formal relationship between (I) [and indeed also (II) and (III)] and the hemerythrin model complexes [{(HBPz$_3$)Fe}$_2$-(μ-O$_2$CR)$_2$(μ-O)] [(IV), HBPz$_3$ = tri-1-pyrazolylborate anion; R = H, CH$_3$, C$_6$H$_5$] containing the di-Fe^{III} core [Fe$_2$(μ-O$_2$CR)$_2$(μ-O)] (Armstrong, Spool, Papaefthymiou, Frankel & Lippard, 1984), and the protonated analogue [{(HBPz$_3$)Fe}$_2$(μ-O$_2$CCH$_3$)$_2$(μ-OH)]$^+$, (V), containing the [Fe$_2$(μ-O$_2$CCH$_3$)$_2$(μ-OH)] core (Armstrong & Lippard, 1984). The metal—oxygen bond lengths for the bridging carboxylato ligands exhibit relatively small differences between the Fe^{III} and Ru^{II} complexes with mean values of 2·052 (2) [(IV), R = H], 2·043 (2) [(IV), R = CH$_3$], 1·999 (4) (V), 2·112 (7) (I) and 2·108 (9) Å (II). The metal—oxygen bond lengths for the bridging ligand L (= O^{2-}, OH$^-$ or OH$_2$) show the expected marked increases with the increasing protonation of L. For all the complexes L is symmetrically bridging with mean metal—oxygen bond lengths ranging from 1·781 (2) [(IV), R = H] and 1·784 (2) Å [(IV), R = CH$_3$] for L = O^{2-} through

Table 2. *Selected bond lengths (Å) and angles (°) for (I)*

|			
Ru(1)–O(1)	2·150 (6)	Ru(1)–C(11)	2·150 (8)
Ru(1)–C(12)	2·159 (8)	Ru(1)–C(14)	2·172 (9)
Ru(1)–C(15)	2·174 (9)	Ru(1)–O(31)	2·087 (6)
Ru(1)–O(51)	2·121 (6)	Ru(1)–O(61)	2·112 (6)
Ru(2)–O(1)	2·154 (5)	Ru(2)–C(21)	2·186 (8)
Ru(2)–C(22)	2·174 (9)	Ru(2)–C(24)	2·147 (9)
Ru(2)–C(25)	2·166 (10)	Ru(2)–O(41)	2·093 (7)
Ru(2)–O(52)	2·101 (7)	Ru(2)–O(62)	2·115 (6)
O(1)–H(1A)	1·04 (8)	O(1)–H(1B)	1·04 (8)
C(11)–C(12)	1·403 (14)	C(11)–C(16)	1·565 (14)
C(12)–C(13)	1·536 (14)	C(13)–C(14)	1·53 (2)
C(13)–C(17)	1·535 (14)	C(14)–C(15)	1·389 (14)
C(15)–C(16)	1·519 (13)	C(16)–C(17)	1·54 (2)
C(21)–C(22)	1·35 (2)	C(21)–C(26)	1·54 (2)
C(22)–C(23)	1·51 (2)	C(23)–C(24)	1·536 (13)
C(23)–C(27)	1·56 (2)	C(24)–C(25)	1·36 (2)
C(25)–C(26)	1·533 (13)	C(26)–C(27)	1·53 (2)
O(31)–C(31)	1·257 (11)	O(32)–C(31)	1·253 (13)
O(41)–C(41)	1·244 (11)	O(42)–C(41)	1·212 (11)
O(51)–C(51)	1·257 (11)	O(52)–C(51)	1·248 (12)
O(61)–C(61)	1·251 (10)	O(62)–C(61)	1·250 (10)
O(1)–Ru(1)–C(11)	98·6 (3)	O(1)–Ru(1)–C(12)	98·7 (3)
C(11)–Ru(1)–C(12)	38·0 (4)	O(1)–Ru(1)–C(14)	159·2 (3)
C(11)–Ru(1)–C(14)	79·1 (4)	C(12)–Ru(1)–C(14)	66·6 (4)
O(1)–Ru(1)–C(15)	158·7 (3)	C(11)–Ru(1)–C(15)	66·5 (4)
C(12)–Ru(1)–C(15)	79·0 (4)	C(14)–Ru(1)–C(15)	37·3 (4)
O(1)–Ru(1)–O(31)	87·7 (2)	C(11)–Ru(1)–O(31)	79·4 (3)
C(12)–Ru(1)–O(31)	117·4 (3)	C(14)–Ru(1)–O(31)	111·9 (3)
C(15)–Ru(1)–O(31)	74·9 (3)	O(1)–Ru(1)–O(51)	94·4 (2)
C(11)–Ru(1)–O(51)	156·1 (3)	C(12)–Ru(1)–O(51)	157·6 (3)
C(14)–Ru(1)–O(51)	95·6 (3)	C(15)–Ru(1)–O(51)	95·1 (3)
O(31)–Ru(1)–O(51)	81·2 (3)	O(1)–Ru(1)–O(61)	86·2 (2)
C(11)–Ru(1)–O(61)	115·1 (3)	C(12)–Ru(1)–O(61)	77·1 (3)
C(14)–Ru(1)–O(61)	76·4 (3)	C(15)–Ru(1)–O(61)	113·5 (3)
O(31)–Ru(1)–O(61)	165·0 (2)	O(51)–Ru(1)–O(61)	85·7 (3)
O(1)–Ru(2)–C(21)	159·3 (3)	O(1)–Ru(2)–C(22)	160·0 (3)
C(21)–Ru(2)–C(22)	36·2 (4)	O(1)–Ru(2)–C(24)	100·2 (3)
C(21)–Ru(2)–C(24)	77·8 (4)	C(22)–Ru(2)–C(24)	65·8 (4)
O(1)–Ru(2)–C(25)	99·9 (3)	C(21)–Ru(2)–C(25)	66·0 (4)
C(22)–Ru(2)–C(25)	77·7 (4)	C(24)–Ru(2)–C(25)	36·9 (4)
O(1)–Ru(2)–O(41)	87·5 (2)	C(21)–Ru(2)–O(41)	75·4 (3)
C(22)–Ru(2)–O(41)	111·2 (3)	C(24)–Ru(2)–O(41)	116·7 (4)
C(25)–Ru(2)–O(41)	79·9 (4)	O(1)–Ru(2)–O(52)	86·9 (2)
C(21)–Ru(2)–O(52)	112·3 (3)	C(22)–Ru(2)–O(52)	76·3 (3)
C(24)–Ru(2)–O(52)	76·9 (4)	C(25)–Ru(2)–O(52)	113·7 (3)
O(41)–Ru(2)–O(52)	166·0 (3)	O(1)–Ru(2)–O(62)	92·6 (2)
C(21)–Ru(2)–O(62)	96·3 (3)	C(22)–Ru(2)–O(62)	96·8 (3)
C(24)–Ru(2)–O(62)	157·9 (3)	C(25)–Ru(2)–O(62)	157·0 (3)
O(41)–Ru(2)–O(62)	81·5 (3)	O(52)–Ru(2)–O(62)	86·0 (3)
Ru(1)–O(1)–Ru(2)	117·3 (3)	Ru(1)–O(1)–H(1A)	102 (11)
Ru(2)–O(1)–H(1A)	116 (10)	Ru(1)–O(1)–H(1B)	102 (11)
Ru(2)–O(1)–H(1B)	93 (10)	H(1A)–O(1)–H(1B)	127 (16)
C(12)–C(11)–C(16)	105·8 (8)	C(11)–C(12)–C(13)	105·2 (8)
C(12)–C(13)–C(14)	101·9 (7)	C(12)–C(13)–C(17)	102·0 (8)
C(14)–C(13)–C(17)	101·3 (9)	C(13)–C(14)–C(15)	105·5 (8)
C(14)–C(15)–C(16)	106·7 (9)	C(11)–C(16)–C(15)	100·4 (7)
C(11)–C(16)–C(17)	100·6 (8)	C(15)–C(16)–C(17)	101·2 (8)
C(13)–C(17)–C(16)	93·3 (7)	C(22)–C(21)–C(26)	105·9 (9)
C(21)–C(22)–C(23)	108·9 (10)	C(22)–C(23)–C(24)	100·8 (8)
C(22)–C(23)–C(27)	99·4 (9)	C(24)–C(23)–C(27)	98·3 (8)
C(23)–C(24)–C(25)	108·2 (9)	C(24)–C(25)–C(26)	105·9 (8)
C(21)–C(26)–C(25)	101·1 (8)	C(21)–C(26)–C(27)	100·4 (9)
C(25)–C(26)–C(27)	100·2 (9)	C(23)–C(27)–C(26)	94·2 (8)
Ru(1)–O(31)–C(31)	126·8 (7)	H(1A)–O(32)–C(31)	109 (8)
O(31)–C(31)–O(32)	128·1 (9)	O(31)–C(31)–C(32)	115·9 (9)
O(32)–C(31)–C(32)	116·0 (8)	Ru(2)–O(41)–C(41)	126·4 (6)
O(41)–C(41)–O(42)	130·2 (10)	O(41)–C(41)–C(42)	113·8 (8)
O(42)–C(41)–C(42)	115·9 (9)	Ru(1)–O(51)–C(51)	128·8 (7)
Ru(2)–O(52)–C(51)	128·7 (6)	O(51)–C(51)–O(52)	129·5 (9)
O(51)–C(51)–C(52)	114·0 (9)	O(52)–C(51)–C(52)	116·4 (8)
Ru(1)–O(61)–C(61)	126·5 (6)	Ru(2)–O(62)–C(61)	131·4 (6)
O(61)–C(61)–O(62)	130·0 (9)	O(61)–C(61)–C(62)	115·0 (8)
O(62)–C(61)–C(62)	115·0 (7)		
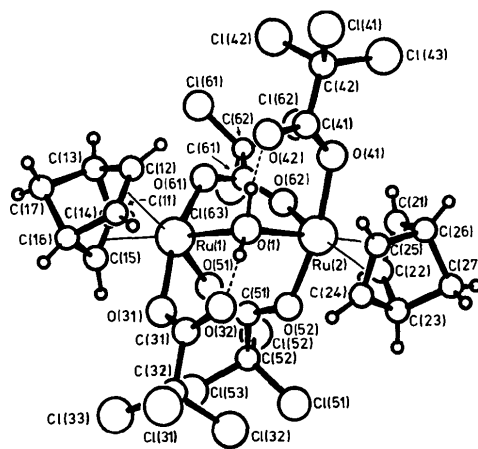
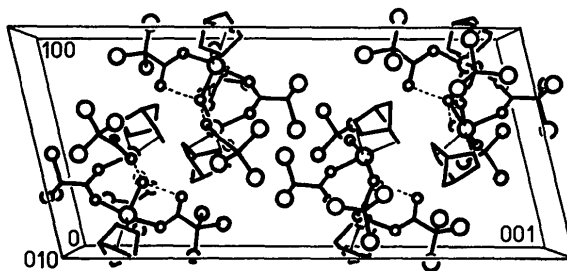Fig. 1. A perspective view of (I) showing the atom-numbering scheme.

Fig. 2. A perspective view of the unit cell of (I) viewed down the *y* axis.

1·956 (4) (V) for $L = OH^-$ to 2·152 (5) (I) and 2·164 (5) Å (II) for $L = OH_2$. The variations in the other ligands notwithstanding, the complexes (I)–(V) provide an unusual series of dimetal centres supporting the oxo, hydroxo and aqua bridging ligands.

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An Acetone Complex of Platinum

BY A. G. THAYER AND N. C. PAYNE*

Chemistry Department, University of Western Ontario, London, Ontario, Canada N6A 5B7

Abstract. *trans*-(Acetone)bis[dimethyl(phenyl)phosphine]methylplatinum(II) hexafluorophosphate, [Pt(CH₃)(C₃H₆O)(C₈H₁₁P)₂]PF₆, $M_r = 689·47$, triclinic, $P\bar{1}$, $a = 9·914$ (2), $b = 15·342$ (3), $c = 9·039$ (1) Å, $\alpha = 93·37$ (1), $\beta = 90·47$ (1), $\gamma = 71·91$ (1)°, $V = 1304·4$ (5) Å³, $Z = 2$, $D_m = 1·772$ (3), $D_x = 1·757$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0·71073$ Å, $\mu = 5·67$ mm⁻¹, $F(000) = 672$, $T = 295$ K. 3951 unique reflections with $I > 3\sigma(I)$ were used to refine 248 variables on F giving agreement factors of $R = 0·030$ and $wR = 0·033$. The cation has a slightly distorted square-planar geometry at the platinum atom. The acetone ligand is coordinated to the metal atom as a Lewis base through donation of an sp^2 electron pair on the oxygen atom. The carbon–oxygen double-bond length of 1·225 (7) Å in the acetone ligand shows no significant lengthening.

Introduction. Cationic Pt^{II} complexes containing monodentate tertiary phosphines and an acetone ligand are convenient intermediates in the preparation of numerous square-planar Pt^{II} complexes (Chisholm & Clark, 1972). The acetone ligand is readily lost, creating a free site on the metal atom and allowing for coordination of the desired ligand. Appleton, Clark & Manzer (1973) assigned the acetone ligand an extremely weak *trans* influence as determined both from Pt–H IR stretching constants, and from $^1J_{\text{Pt–H}}$ and

$^2J_{\text{Pt–C–H}}$ coupling constants, in complexes of the type *trans*-PtX(acetone)L_2 [$X = $ H and CH₃, $L = $ P(CH₃)(C₆H₅)₂ and P(CH₃)₂C₆H₅)]. The chemistry of Pt with weak donor ligands has been reviewed recently (Davies & Hartley, 1981). Ketone ligands are characterized by both a π-electron system and non-bonded electron pairs on the oxygen atom through which the ketone can bond to a metal. Crystal structures of Ru^{II} acetone complexes (Gould, Sime & Stephenson, 1978; Bennett, Matheson, Robertson, Steffen & Turney, 1978) and an Ir^{III} bisacetone complex (Crabtree, Hlatky, Parnell, Segmuller & Uriarte, 1984) all describe the ligand as end-bound to the metal through donation of a non-bonding electron pair on the O atom. Countryman & Penfold (1972) reported the structure of a side-bound hexafluoroacetone ligand in a Pt^{II} complex, while Tsou, Huffman & Kochi (1979) have described the preparation and molecular structure of a Ni⁰ complex of benzophenone. The weak *trans* influence of the acetone ligand in the Pt^{II} complexes strongly suggests that bonding occurs through a lone pair on the O atom, but to determine the exact mode of coordination, an analysis of the complex *trans*-[PtCH₃(acetone)-{P(CH₃)₂C₆H₅}₂]PF₆ was carried out, and the results are reported herein.

Experimental. A sample of the complex was prepared by the method of Chisholm & Clark (1972), and recrystallized from acetone by addition of diethyl ether and pentane as clear, transparent parallelepipeds.