

1.956 (4) (V) for $L = \text{OH}^-$ to 2.152 (5) (I) and 2.164 (5) Å (II) for $L = \text{OH}_2$. 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

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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)L₂ [$X = \text{H}$ and CH₃, $L = \text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2$ and $\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)$]. 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.

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Crystal density by neutral buoyancy. Precession photography showed only triclinic symmetry. Space group $P\bar{1}$ chosen, confirmed by successful analysis. Crystal used for recording intensity data of approximate dimensions $0.20 \times 0.23 \times 0.28$ mm, $V = 0.012$ mm³, crystal faces $\{001\}$, $\{010\}$ and $\{110\}$. Enraf–Nonius CAD-4F diffractometer, cell parameters from 20 reflections with $20 < 2\theta < 35^\circ$, Mo radiation monochromatized by graphite. ω scans (Furnas, 1966) had an average width at half-height of 0.11° . 5093 observations ($+h$, $\pm k$, $\pm l$) by θ - 2θ scan method, variable speed, dispersion-corrected scans of width 0.7° , 25% extensions at both ends for backgrounds. Maximum time per datum 75 s, maximum 2θ 60° , over a period of 109 h. Index ranges 0 to 11, -18 to 18, and -10 to 10. Standard reflections $1\bar{1}0$, 020, 200 and 004, monitored every 2 h of X-ray exposure time, deviations random, no decay correction necessary. Background, monochromator polarization, crystal polarization and Lorentz corrections applied, Enraf–Nonius (1983) *Structure Determination Package* running on a DEC PDP 11/23+ computer. Gaussian absorption correction, transmission factors from 0.326 to 0.413. R for averaging 306 pairs on F 0.012 before and after correction. 4289 unique reflections with $I > 0$. Solution by Patterson and Fourier techniques. Parameters refined by full-matrix least-squares methods, minimizing $\sum w(|F_o| - |F_c|)^2$, weight $w = 4F_o^2/\sigma^2(F_o^2)$. Scattering factors for neutral atoms from Cromer & Liberman (1970), those for H from Stewart, Davidson & Simpson (1965). Real part of anomalous-dispersion correction applied for all atoms from *International Tables for X-ray Crystallography* (1974). With all 25 non-H atoms refined with anisotropic thermal parameters, refinement converged at agreement factors $R = 0.033$ and $wR = 0.042$. All 31 H atoms located in a difference Fourier synthesis, peak heights from 0.48 (11) to 0.28 (11) e \AA^{-3} , included with idealized sp^2 and sp^3 geometries, isotropic Debye parameters 110% of those of bonded atoms, methyl groups fitted by least-squares procedure, positions optimized as refinement progressed but not refined. 3951 observations with $I > 3\sigma(I)$, $p = 0.05$ (Busing & Levy, 1957) used to refine 164 variables, agreement factors were $R = 0.037$ and $wR = 0.036$, $S = 2.71$. Hexafluorophosphate group had unsatisfactory geometry, all-anisotropic model replaced by anisotropic P atom and three octahedral F_6 groups, F–F 3.16 \AA , multiplicities 0.50, 0.28 and 0.22. Subsequent refinement using the *UWO* program package for the CDC Cyber 835 (Farrar & Payne, 1981). Group positional and orientation parameters (Eisenberg & Ibers, 1965) refined for all three groups, overall isotropic thermal parameters for only two varied. Evidence for secondary extinction, parameter refined to $5.6(2) \times 10^{-6}$ (Zachariasen, 1968). Convergence with updated H-atom positions at $R = 0.030$ and $wR = 0.033$, $S = 2.54$, 3951 unique observations

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^3$) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| | x | y | z | $U_{eq}(\text{\AA}^2)$ |
|-------|------------|------------|------------|------------------------|
| Pt | 2618.2 (3) | 2463.6 (2) | 1282.5 (3) | 43.5 (2) |
| P(1) | 1471 (2) | 1368 (1) | 1198 (2) | 52 (1) |
| P(2) | 3806 (2) | 3546 (1) | 1372 (2) | 51 (1) |
| P(3) | 2253 (2) | 7350 (1) | 4002 (2) | 63 (2) |
| O | 3651 (4) | 1958 (3) | -841 (5) | 51 (3) |
| C(1) | 1764 (8) | 2911 (5) | 3336 (8) | 74 (7) |
| C(2) | 3206 (7) | 2133 (5) | -2092 (7) | 55 (5) |
| C(3) | 1806 (8) | 2789 (5) | -2379 (8) | 68 (6) |
| C(4) | 4102 (8) | 1641 (6) | -3386 (8) | 83 (7) |
| C(5) | 1875 (10) | 621 (6) | 2755 (9) | 91 (8) |
| C(6) | -443 (7) | 1800 (5) | 1187 (9) | 73 (6) |
| C(7) | 1972 (7) | 585 (4) | -426 (7) | 50 (5) |
| C(8) | 1133 (7) | 703 (5) | -1692 (8) | 61 (6) |
| C(9) | 1604 (9) | 138 (6) | -2958 (9) | 75 (7) |
| C(10) | 2895 (10) | -528 (6) | -2978 (10) | 85 (8) |
| C(11) | 3715 (9) | -646 (5) | -1745 (12) | 85 (8) |
| C(12) | 3267 (8) | -105 (5) | -478 (9) | 70 (6) |
| C(13) | 5693 (7) | 3055 (5) | 1015 (9) | 70 (6) |
| C(14) | 3724 (9) | 4247 (6) | 3067 (9) | 84 (7) |
| C(15) | 3142 (6) | 4350 (4) | -50 (7) | 47 (5) |
| C(16) | 1873 (8) | 5046 (5) | 160 (9) | 73 (6) |
| C(17) | 1286 (8) | 5607 (6) | -957 (11) | 89 (8) |
| C(18) | 1969 (9) | 5486 (6) | -2303 (10) | 83 (8) |
| C(19) | 3229 (9) | 4810 (6) | -2526 (8) | 75 (7) |
| C(20) | 3821 (7) | 4249 (5) | -1396 (8) | 60 (6) |
| F(11) | 2516 (9) | 7602 (6) | 5686 (7) | 127 (2) |
| F(12) | 583 (5) | 7821 (6) | 4288 (10) | 127 (2) |
| F(13) | 2118 (10) | 6411 (4) | 4422 (10) | 127 (2) |
| F(14) | 3880 (5) | 6924 (6) | 3727 (10) | 127 (2) |
| F(15) | 2344 (10) | 8334 (4) | 3594 (10) | 127 (2) |
| F(16) | 1946 (10) | 7144 (6) | 2330 (7) | 127 (2) |

with $I > 3\sigma(I)$, 248 variables, $(\Delta/\sigma)_{\max} = 0.01$. Residual electron density 0.84 (11) e \AA^{-3} (-0.214 , 0.250 , 0.423) near F(13), anion disorder. Statistical analysis in terms of wR , F_o , Miller indices, and diffractometer setting angles showed no unusual trends. Final atomic positional parameters are given in Table 1.*

Discussion. The crystal structure consists of discrete anions and cations. The shortest anion–cation non-bonding approach of 2.30 \AA occurs between F(36) and H3C(3) at $(-x, 1-y, -z)$, while the shortest intercation distance is 2.52 \AA between H1C(1) and H2C(4) at $(-x, -y, 1-z)$. A perspective view of the cation showing the atom-numbering scheme is presented in Fig. 1. A stereoview of the cation has been deposited. Selected bond distances and bond angles are given in Table 2, others have been deposited.

The coordination sphere of the Pt atom consists of the two *trans* phosphine ligands, the σ -bonded methyl group and the O-bound acetone in a slightly distorted square plane (details deposited). The Pt–P distances of

* Lists of anisotropic thermal parameters, H-atom parameters, rigid-group parameters, derived group atom parameters, additional bond distances and bond angles, root-mean-square amplitudes of vibration, selected torsion angles, weighted least-squares planes and structure amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42990 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester, CH1 2HU, England.

2.302 (2) and 2.313 (2) Å differ by 4.6σ , but this probably reflects an underestimation of the e.s.d. values, rather than a significant, chemical difference. The dimethyl(phenyl)phosphine groups have a distorted tetrahedral geometry with the Pt—P—Y angles significantly larger than the tetrahedral angle, and average P—C(sp^3) and P—C(sp^2) distances of 1.81 (1) and 1.811 (2) Å respectively. The phenyl rings are planar within experimental error. The phosphine ligands have adopted an orientation in the solid state such that the phenyl rings bracket the acetone ligand side of the coordinate plane. The dihedral angle between the two phosphorus— α -phenyl C-atom vectors is $70.6 (2)^\circ$.

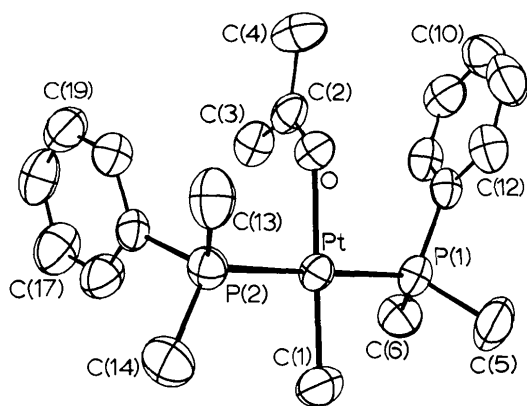


Fig. 1. A perspective view of the cation, showing the atom-numbering scheme.

Table 2. Intramolecular bond distances (Å) and angles ($^\circ$)

| | | | | | | | | |
|-------|-------|-----------|------------|-------|------------|-------|-----------|------------|
| Pt | P(1) | 2.302 (2) | P(2) | C(15) | 1.810 (6) | C(11) | C(12) | 1.365 (11) |
| Pt | P(2) | 2.313 (2) | O | C(2) | 1.225 (7) | C(15) | C(16) | 1.380 (9) |
| Pt | O | 2.167 (4) | C(2) | C(3) | 1.470 (9) | C(15) | C(20) | 1.372 (9) |
| Pt | C(1) | 2.037 (7) | C(2) | C(4) | 1.491 (9) | C(16) | C(17) | 1.371 (10) |
| P(1) | C(5) | 1.830 (7) | C(7) | C(8) | 1.396 (9) | C(17) | C(18) | 1.371 (11) |
| P(1) | C(6) | 1.806 (7) | C(7) | C(12) | 1.387 (9) | C(18) | C(19) | 1.361 (11) |
| P(1) | C(7) | 1.811 (7) | C(8) | C(9) | 1.385 (10) | C(19) | C(20) | 1.381 (9) |
| P(2) | C(13) | 1.810 (7) | C(9) | C(10) | 1.367 (11) | | | |
| P(2) | C(14) | 1.806 (7) | C(10) | C(11) | 1.361 (11) | | | |
| P(1) | Pt | P(2) | 179.05 (6) | O | C(2) | C(3) | 122.9 (6) | |
| P(1) | Pt | O | 92.1 (1) | O | C(2) | C(4) | 118.7 (7) | |
| P(1) | Pt | C(1) | 89.1 (2) | C(3) | C(2) | C(4) | 118.3 (6) | |
| P(2) | Pt | O | 87.5 (1) | P(1) | C(7) | C(8) | 121.4 (5) | |
| P(2) | Pt | C(1) | 91.2 (2) | P(1) | C(7) | C(12) | 120.0 (5) | |
| O | Pt | C(1) | 176.6 (2) | C(8) | C(7) | C(12) | 118.4 (7) | |
| Pt | P(1) | C(5) | 113.9 (3) | C(7) | C(8) | C(9) | 119.9 (7) | |
| Pt | P(1) | C(6) | 115.7 (3) | C(8) | C(9) | C(10) | 120.2 (8) | |
| Pt | P(1) | C(7) | 112.1 (2) | C(9) | C(10) | C(11) | 120.0 (8) | |
| C(5) | P(1) | C(6) | 104.2 (4) | C(10) | C(11) | C(12) | 120.9 (8) | |
| C(5) | P(1) | C(7) | 104.3 (4) | C(11) | C(12) | C(7) | 120.6 (7) | |
| C(6) | P(1) | C(7) | 105.6 (3) | P(2) | C(15) | C(16) | 120.2 (5) | |
| Pt | P(2) | C(13) | 113.2 (2) | P(2) | C(15) | C(20) | 121.5 (5) | |
| Pt | P(2) | C(14) | 118.5 (3) | C(16) | C(15) | C(20) | 118.2 (6) | |
| Pt | P(2) | C(15) | 109.7 (2) | C(15) | C(16) | C(17) | 121.0 (7) | |
| C(13) | P(2) | C(14) | 103.3 (4) | C(16) | C(17) | C(18) | 119.9 (7) | |
| C(13) | P(2) | C(15) | 105.8 (3) | C(17) | C(18) | C(19) | 119.9 (7) | |
| C(14) | P(2) | C(15) | 105.3 (3) | C(18) | C(19) | C(20) | 120.0 (7) | |
| Pt | O | C(2) | 129.4 (4) | C(15) | C(20) | C(19) | 121.0 (7) | |

The Pt—C(1) distance of 2.035 (8) Å is significantly shorter than the Pt—C(sp^3) distances ranging from 2.08 (2) to 2.15 (1) Å reported for a series of 'metal-stabilized carbonium ion' complexes prepared from this compound (Stepaniak & Payne, 1973, 1974a,b), though in these compounds the methyl group is *trans* to a ligand with a high *trans* influence. The acetone molecule is bonded to the Pt atom through an sp^2 lone pair on the O atom. The Pt—O distance of 2.168 (5) Å is longer than either the literature value of 2.00 Å for Pt—OR₂ bonds (Shustorovich, Porai-Koshits & Buslaev, 1975) or 1.991 (8) Å for a bis(acac)Pt^{II} complex (Onuma, Horioka, Inoue & Shibata, 1980). It is probably longer than the Pt—O distance of 2.144 (9) Å found in a Pt^{II} complex with an ether ligand *trans* to a phosphine ligand (Clark, McBride, Payne & Wong, 1979), where the extremely large $^1J_{Pt-P}$ coupling constant of 4529.9 Hz for the Pt—P bond *trans* to the ethereal O atom established the ether group as a ligand with a very weak *trans* influence (Appleton & Bennett, 1978; Mather, Pidcock & Rapsey, 1973).

A least-squares-plane calculation including the O and three acetone C atoms indicates that the group is planar within experimental error. The acetone plane forms an angle of 94.4° with the coordination plane of the Pt atom. The dihedral angle between the acetone plane and the plane of the phenyl ring attached to P(1) is 18.6° ; for that attached to P(2) the value is 19.9° . Angles about C(2) in the acetone ligand ranging from $118.4 (7)$ to $122.9 (7)^\circ$, and the Pt—O—C(2) angle of $129.3 (5)^\circ$, all suggest sp^2 hybridization at both the C and the O atoms. The deviation from the expected angle at O is presumably due to steric effects. The C(2)—O distance of 1.226 (9) Å is statistically equal to values found in studies of both free acetone [1.22 (3) Å by electron diffraction (Allen, Bowen, Sutton & Bastiansen, 1952)], acetone as a solvent molecule [1.25 (3) Å (Stergioudis, Christidis & Rentzeperis, 1979)], and acetone coordinated in an end-bound fashion to Ru^{II} [1.238 (9) Å (Gould, Sime & Stephenson, 1978)] and Ir^{III} [1.216 (8) and 1.242 (8) Å, (Crabtree, Hlatky, Parnell, Segmuller & Uriarte, 1984)]. Although the arrangement of the acetone ligand approximately perpendicular to the Pt coordination plane might allow π back donation from filled *d* orbitals on the metal to a π^* molecular orbital in the ligand, the absence of a significant lengthening of the C—O bond and the very weak *trans* influence of the acetone ligand both indicate that this is not significant.

All these observations are consistent with an extremely weak Pt—O bond and the small *trans* influence attributed to the acetone ligand by Appleton, Clark & Manzer (1973), properties which explain the complex's synthetic utility.

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The Structure of Ferrioxamine D₁–Ethanol–Water (1/2/1)

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Abstract. C₂₇H₄₇FeN₆O₉, $M_r = 737.7$, $P\bar{1}$, $a = 15.035$ (20), $b = 16.240$ (17), $c = 7.852$ (8) Å, $\alpha = 89.30$ (9), $\beta = 100.01$ (11), $\gamma = 101.82$ (10)°, $V = 1847$ (1) Å³, $Z = 2$, $D_x = 1.325$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.43$ mm⁻¹, $F(000) = 784$, $T = 138$ K, $R = 0.064$ for 3532 observed reflections [$I > 2\sigma(I)$]. The crystal structure contains a racemic mixture of *A-cis* and Δ -*cis* coordination isomers. The parameters of the iron coordination geometry, Fe–O(N) = 1.961 (4), Fe–O(C) = 2.049 (4) Å, ligand bite = 1.27, twist angle = 42.9°, agree well with those observed in crystal structures of other trihydroxamate siderophores. Conformational features of ferrioxamine D₁ are compared with those of ferrioxamine E, a cyclic analog of D₁.

Introduction. Siderophores are low-molecular-weight iron-chelating compounds of microbial origin, which act as cellular transport agents for iron in aerobic fungi and bacteria (Emery, 1971; Neilands, 1973, 1981; Raymond, Müller & Matzanke, 1984; Hider, 1984).

Although there is considerable evidence that the siderophore uptake is a receptor-mediated process requiring a structure–function relationship between the siderophores and the membrane ‘carriers’, our understanding of the mechanism of siderophore-mediated iron transport in microorganisms is still very fragmentary. This is partly due to insufficient knowledge concerning the conformation and configuration of the siderophore molecules and largely because of the lack of information about the nature of the transport system in the cell membranes.

The ferrioxamine family, an important class of siderophores, is produced by several species of *Streptomyces* and *Nocardia*. They are characterized as A, B, C, D₁, D₂, E, F and G (Bickel, Bosshardt, Baumann, Reusser, Vischer, Voser, Wettstein & Zähler, 1960). All the ferrioxamines are trihydroxamates and the deferriferrioxamines are either cyclic or linear, consisting of units of α -amino- ω -hydroxyamino alkane and succinate or acetate. Ferrioxamine D₁ is a member of the linear ferrioxamines and is the *N*-acetyl