Acetonitrile(carbonyl)(2,3,9,10-tetramethyl-1,4,8,11-tetraaza-1,3,8,10-cyclo-tetradecatetraene)iron(II) Hexafluorophosphate

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Abstract. $[Fe(C_2H_3N)(C_{14}H_{24}N_4)(CO)](PF_6)_2$, $C_{17}H_{27}FeN_5O^{2+} \cdot 2PF_6^-$, monoclinic, $P2_1/c$, $Z = 4$, $a = 8.512$ (5), $b = 18.047$ (7), $c = 16.841$ (13) Å, $\beta = 88.92$ (3)°, $V = 2587$ Å^3, $D_x = 1.70$, $D_m = 1.6$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å. The macrocyclic ligand TIM ($C_{14}H_{24}N_4$) presents its four ligating N atoms in a nearly planar array to the Fe atom, the average Fe—N(TIM) distance being 1.954 (1) Å. The Fe—C distance is 1.779 (3) Å and the Fe^{2+} ion is slightly (0.06 Å) displaced toward the carbonyl ligand with respect to the least-squares plane of the four N atoms of TIM. The Fe—N(CH$_3$CN) distance is 1.976 (3) Å, a bond length 0.047 Å longer than in the bis(acetonitrile) complex, $[Fe(CH_3CN)_2(TIM)](PF_6)_2$. Since there appears to be little steric interaction, the change is ascribed to an electronic *trans* influence.

Introduction. Relatively extensive attempts have been made to use structural data to gain insight into the nature of the *trans* influence (Shustorovich, Porai-Koshits & Buslaev, 1975; Appleton, Clark & Manzer, 1973). Crystal structures of the two complexes $[Fe(CH_3CN)_2(TIM)](PF_6)_2$ and $[Fe(CH_3CN)(TIM)(CO)](PF_6)_2$ provide the data to augment these studies of the *trans* influence by comparing the two *trans* pairs CH_3CN—Fe—$NCCH_3$ and CH_3CN—Fe—CO. The synthesis of these two complexes has been reported (Baldwin, Pfeiffer, Reichgott & Rose, 1973; Batschelet, Davidson & Rose, 1979) as has the crystal structure of $[Fe(CH_3CN)_2(TIM)](PF_6)_2$ (Smith, Santarsiero & Lingafelter, 1979).

Here we focus on the crystal structure of $[Fe(CH_3CN)(TIM)(CO)](PF_6)_2$ and on a brief comparison of the two low-spin Fe^{II} complexes. Oscillation, precession, and Weissenberg photographs on a crystal measuring 0.19 × 0.35 × 0.66 mm exhibited monoclinic symmetry. Systematically absent reflections (0*k*0 absent for *k* odd, *h*0*l* absent for *l* odd) indicated the space group $P2_1/c$. Lattice constants were obtained from a least-squares refinement using $\pm 2\theta$ values out to 30° on 29 reflections.

A Picker automatic diffractometer was used to collect the 7497 unique reflections to a maximum

$(\sin \theta)/\lambda$ of 0.703 Å^{-1}. Mo $K\alpha$ radiation was filtered through a thin Nb foil and intensities were measured using the θ–2θ scan technique. Angular settings were calculated by *DIFSET* which corrected at high angles for α_1–α_2 splitting. The peaks were scanned at 2.0° min^{-1} and stationary-crystal stationary-counter background counts of 15 s were taken at the start and finish of each scan. Intensities of two standard reflections, measured periodically, indicated no decomposition.

MULTAN (Germain, Main & Woolfson, 1971) was used to determine the initial atomic positions of the cation. An initial Fourier synthesis based on these coordinates indicated atomic positions of the two unique P atoms and *R* began at 0.283. Addition of F atoms followed by seven cycles of full-matrix least-squares refinement based on *F* with unit weights and isotropic temperature factors reduced *R* to 0.160. At this point, a difference Fourier synthesis indicated that C(4*B*) (Fig. 1) of the trimethylene unit and the PF$_6^-$ anion were disordered. The disorder in the trimethylene unit was modeled by directing one atom, C(4*B*1), toward the acetonitrile ligand and a second atom, C(4*B*2), toward the carbonyl ligand. The partial populations of these C atoms, with their anisotropic temperature factors and atomic positons, were refined throughout the remaining cycles. The disorder of both PF$_6^-$ anions required the refinement of partial populations and anisotropic temperature factors for a total of 17 F atom fragments. H atoms were added to the structure with isotropic temperature factors. All atoms, the non-hydrogen atoms having anisotropic temperature factors, were refined by several cycles of full-matrix least-squares calculations based on *F* with statistical weights: $R = 0.070$, $R_w = 0.055$. All calculations were carried out using the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The fractional atomic positions for the cation and P atoms are listed in Table 1.* Correction of bond

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* Lists of structure factors, H, and F parameters, and all thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34643 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
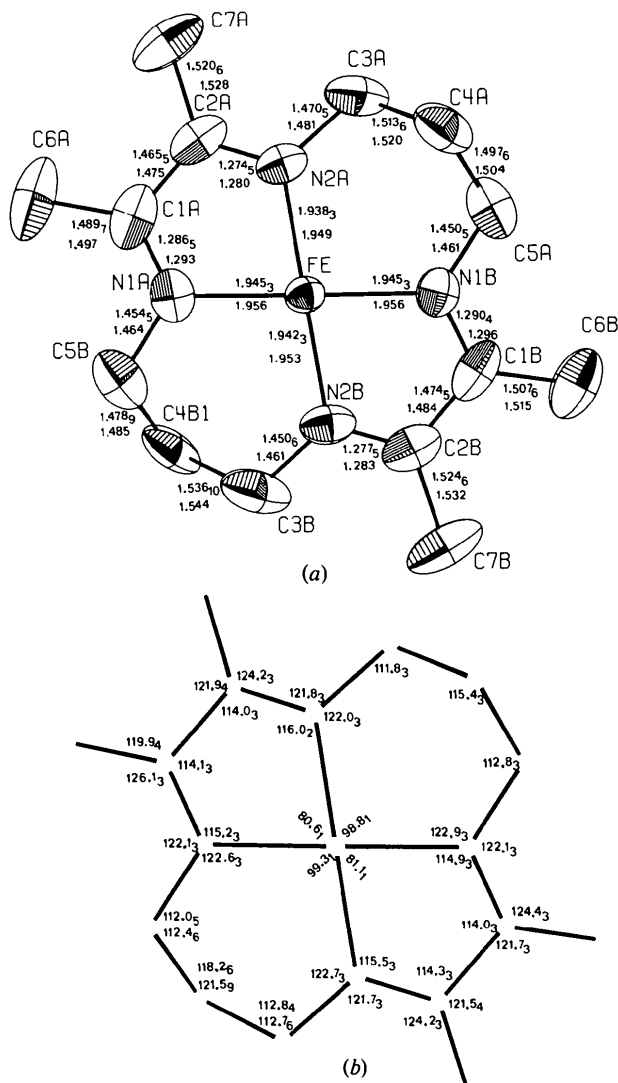
$[Fe(C_2H_3N)(C_{14}H_{24}N_4)(CO)](PF_6)_2$

Fig. 1. (a) Uncorrected (e.s.d.'s shown subscripted) and corrected bond lengths (Å). Not shown: C(3B)–C(4B2) 1·423 (13), 1·431; C(4B2)–C(5B) 1·540 (16), 1·547 Å. (b) Corrected bond angles (°) with e.s.d.'s subscripted. Upper entries around C(4B1) involve C(4B1), lower entries involve C(4B2).

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *of the cation and* P *atoms with e.s.d.'s in parentheses*

	x	y	z
Fe	5058·1 (5)	8417·1 (2)	7570·8 (3)
C(10)	6029 (4)	7695 (2)	8087 (2)
O	6669 (3)	7260 (1)	8443 (2)
N(3)	4033 (3)	9246 (1)	7015 (2)
C(8)	3518 (4)	9745 (2)	6711 (2)
C(9)	2883 (5)	10392 (2)	6318 (3)
N(1A)	4164 (4)	8786 (1)	8566 (2)
N(2A)	3059 (3)	7903 (1)	7572 (2)
C(1A)	2770 (5)	8554 (2)	8739 (2)
C(2A)	2111 (4)	8058 (2)	8143 (2)
C(3A)	2617 (5)	7405 (2)	6923 (3)
C(4A)	4037 (5)	7039 (2)	6538 (2)
C(5A)	5088 (5)	7542 (2)	6062 (2)
C(6A)	1845 (7)	8730 (3)	9474 (3)
C(7A)	438 (5)	7768 (3)	8212 (5)
N(1B)	5884 (3)	8084 (1)	6547 (1)
N(2B)	6986 (3)	8992 (1)	7530 (2)
C(1B)	7143 (4)	8418 (2)	6304 (2)
C(2B)	7812 (4)	8926 (2)	6893 (2)
C(3B)	7437 (5)	9491 (3)	8162 (3)
C(4B1)*	6018 (9)	9808 (4)	8625 (5)
C(4B2)†	6790 (17)	9282 (7)	8915 (7)
C(5B)	5005 (6)	9289 (3)	9081 (3)
C(6B)	7898 (6)	8312 (3)	5496 (3)
C(7B)	9387 (5)	9308 (3)	6747 (4)
P(1)	2624·8 (13)	6096·4 (6)	9402·1 (7)
P(2)	8736·3 (13)	5967·9 (6)	6346·8 (7)

* Partial population 0·55.
† Partial population 0·45.

distances and angles for librational motion of the TIM macrocycle was carried out by use of the Schomaker & Trueblood (1968) program. The translational tensor **T** and librational tensor **L** were uniquely determined, the translation–libration correlation tensor **S** being identically zero for the centrosymmetric macrocycle. Matrix elements of the tensors were: T_{11} 3·1 (3), T_{12} 0·8 (3), T_{13} −0·6 (3), T_{22} 2·6 (4), T_{23} 0·9 (3), T_{33} 3·7 (3) $\times 10^{-2}$ Å^2; L_{11} 23 (2), L_{12} −3 (1), L_{13} −6 (1), L_{22} 18 (1), L_{23} −5 (1), L_{33} 16 (2) deg^2 relative to an origin at $x = 0·4971$, $y = 0·8356$, $z = 0·7411$. Bond-length corrections were found to be about 0·01 Å. The unusually short C–O bond length, 1·134 (4) Å, was

attributed to the high thermal motion of the O atom. Correction was applied by assuming that C(10) moved in-phase with the O atom (lower-limit model: Johnson, 1970), yielding a corrected bond length of 1·141 Å. Both corrected and uncorrected bond lengths are given in Fig. 1. Corrections to the bond angles were small and only corrected values are shown in Fig. 1.

Discussion. Inter-ligand distances for the two complex cations, $[Fe(CH_3CN)_2(TIM)]^{2+}$ and $[Fe(CH_3CN)(TIM)(CO)]^{2+}$, are given in Table 2, and distances involving the acetonitrile are given in Table 3. In both complexes all bond angles at Fe between axial and macrocycle ligand atoms are in the range $90 \pm 4°$. The principal differences between the two Fe complexes are: (1) the Fe–N(CH$_3$CN) distance is 0·047 Å longer in the carbon-monoxide-containing species than in the bis-(acetonitrile) complex and (2) the Fe^{2+} ion is 0·06 Å displaced toward the carbon monoxide with respect to the least-squares plane described by the four N atoms of TIM in the $[Fe(CH_3CN)(TIM)(CO)]^{2+}$ complex whereas in the bis(acetonitrile) species the Fe^{2+} ion and the four TIM N atoms are constrained to be planar by symmetry. It is to be noted that the Fe–N(TIM) distances, the interatomic distances within the TIM

Table 2. *Structural parameters of the coordination polyhedron for* $[Fe(CH_3CN)(TIM)(X)](PF_6)_2$

Lengths are given in Å. Estimated standard deviations in the least significant figure are in parentheses.

X = CH₃CN	Uncorrected*	Corrected†	Average‡	X = CO	Uncorrected*	Corrected†	Average‡
N(1)—N(2)	2·505 (3)	2·524		N(1A)—N(2A)	2·507 (4)	2·525 ⎫	
				N(1B)—N(2B)	2·523 (4)	2·542 ⎭	2·534 (3)
N(2)—N(1')	2·952 (2)	2·968		N(2A)—N(1B)	2·951 (4)	2·965 ⎫	
				N(2B)—N(1A)	2·966 (4)	2·980 ⎭	2·973 (3)
N(3)—N(1)	2·733 (2)	2·742 ⎫		N(3)—N(1A)	2·745 (4)	2·755 ⎫	
N(3)—N(1')	2·729 (2)	2·736 ⎪		N(3)—N(1B)	2·729 (4)	2·736 ⎪	
N(3)—N(2)	2·703 (3)	2·712 ⎬ 2·741 (1)		N(3)—N(2A)	2·722 (4)	2·729 ⎬	2·736 (2)
N(3)—N(2')	2·765 (2)	2·774 ⎭		N(3)—N(2B)	2·713 (4)	2·722 ⎭	
				C(10)—N(1A)	2·646 (4)	2·654 ⎫	
				C(10)—N(1B)	2·693 (5)	2·700 ⎪	
				C(10)—N(2A)	2·715 (4)	2·722 ⎬	2·682 (2)
				C(10)—N(2B)	2·645 (4)	2·653 ⎭	

* Atomic positions and therefore contact distances determined by assuming that the electron density could be described by six-parameter thermal ellipsoids.

† Atomic positions were redetermined by rigid-body analysis. See text for discussion.

‡ Average taken over chemically equivalent bond lengths (when present). The estimated standard deviation was calculated by use of the relation $\sigma = [\sum_{i=1}^{N} \sigma_i^2]^{1/2}/N$.

Table 3. *Comparison of bond lengths* (Å) *for acetonitrile*

	Fe—N	C≡N	C—CH₃
[Fe(CH₃CN)₂(TIM)](PF₆)₂[a]	1·929 (1)	1·121 (2)	1·461 (4)
[Fe(CH₃CN)(TIM)(CO)](PF₆)₂[b]	1·976 (3)	1·128 (4)	1·453 (5)
[Fe(CH₃CN)₂(C₁₈H₁₈N₆)](ClO₄)₂[c]	1·938 (4)	1·136 (6)	1·489 (8)
'Free' acetonitrile[d]		1·157 (2)	1·458 (2)

References: (a) Smith et al. (1979); (b) this work; (c) Goedken, Park, Peng & Molin-Norris (1974); (d) Costain (1958).
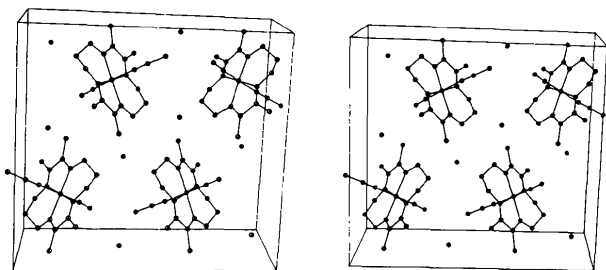

Fig. 2. Packing diagram of cation and P atoms. The a axis is out of the page, b is horizontal, and c is up the page.

ligand and the bonding distances within the CH₃CN molecules are indistinguishable between the two complex cations. However, in both of the complexes the C≡N(CH₃CN) distance is shorter than in free acetonitrile, indicating that for these species the acetonitrile is a significantly better σ donor than it is a π acceptor. Since there is little apparent difference between the two complexes in their steric interactions, the change in the Fe—N(CH₃CN) bond length may be ascribed to an

electronic *trans* influence. The contact distances between the axial N donors N(3) and equatorial (TIM) N donors in the two complexes are indistinguishable (Table 2). The C(10)—N(TIM) contact distance, 2·682 Å, is significantly shorter, a fact consistent with the C atom being positively charged and the N(TIM) atoms being negatively charged (Batschelet et al., 1979). The Fe^{II}—N(TIM) bonds are longer than those reported by Goedken, Peng, Molin-Norris & Park (1976) for the $C_{22}H_{22}N_4$ macrocycle but shorter than those distances observed in the porphyrin complexes (Hoard, 1971).

The crystal packing in [Fe(CH₃CN)(TIM)(CO)]-(PF₆)₂ is such that there is intermolecular contact between the axial ligands (NCCH₃···OC) as well as between cation and anion (Fig. 2). No contact distances are found to be shorter than 0·1 Å below their predicted values.

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Structure of Dioxouranium(VI) Formate Hydroxide Monohydrate at 120 K

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Abstract. $UO_2(HCOO)(OH).H_2O$, orthorhombic, *Pbca*, $a = 6\cdot3226$ (3), $b = 10\cdot5320$ (6), $c = 15\cdot949$ (4) Å (120 K) and $a = 6\cdot362$ (2), $b = 10\cdot576$ (3), $c = 15\cdot999$ (5) Å (293 K), $Z = 8$, $D_m = 4\cdot38$, $D_c = 4\cdot35$ Mg m^{-3} (293 K). The final $R_w = 0\cdot07$ for 487 reflections. The sevenfold coordination consists of a pentagonal arrangement of O atoms in the equatorial plane perpendicular to the axis of the uranyl group. U–O lengths range from $1\cdot77$ (2) to $2\cdot45$ (2) Å.

Introduction. An X-ray powder study of precipitates from ammonium diuranate (ADU) solutions led to the identification of a compound which was originally prepared by different means (Bideau, Bressat, Mentzen & Navarro, 1970). The latter investigators reported $D_m = 3\cdot45$ Mg m^{-3} and $b = 13\cdot52$ Å, which are not in agreement with our values.

Single crystals for the present investigation were obtained by dissolving $1\cdot0$ g ADU in 2 ml 25% aqueous HCOOH and diluting with 50 ml CH₃OH and 50 ml HOC₂H₄OH. The methanol and excess formic acid were slowly removed by a water pump. Suitable orthorhombic greenish-yellow crystals were obtained after 38 days by partial precipitation. They were washed several times with water, methanol and ether, in that order, before drying.

A powder diffractogram taken on an IRDAB XDC700 Guinier camera ($114\cdot6$ mm diameter) with quartz-monochromated Cu $K\alpha_1$ radiation yielded d values in agreement with those reported by Bideau *et al.* (1970). The room-temperature cell constants were refined from the first 15 powder lines.

A crystal $0\cdot1 \times 0\cdot07 \times 0\cdot04$ mm was mounted on a Stoe reciprocal-lattice explorer with the long axis of the crystal parallel to the rotation axis. From a rotation photograph the lattice constant which corresponded to the crystal rotation axis turned out to be $a = 6\cdot35$ (6) Å. A De Jong–Bouman zero-layer exposure supplied the other lattice constants and from higher-layer photographs, as well as Buerger precession exposures, the space group was determined unambiguously. The crystal faces were found to be the major crystallographic faces {100}.

A method based on Boyle's law was used for density measurements. 893 reflections with $\sin \theta/\lambda \le 0\cdot71$ Å^{-1} were measured on a Philips PW 1100 automatic diffractometer with graphite-monochromated Mo $K\alpha_1$ radiation. The thermal background was reduced by cooling the sample to 120 (2) K with an Enraf–Nonius universal low-temperature device. The low-temperature cell constants were refined from 15 non-axial reflections with diffractometer 2θ values.

A set of 487 contributing reflections ($I > 3\sigma$) formed the basis for the data reduction which included

Table 1. *Atomic parameters* ($\times 10^4$) *at* 120 K

	x	y	z	U (Å^2)
U	1479 (2)	589 (1)	1011 (1)	*
O(1)	417 (42)	5756 (22)	6533 (14)	463 (73)
O(2)	2621 (32)	3141 (19)	5427 (13)	362 (60)
O(3)	1703 (28)	5664 (16)	4758 (10)	168 (54)
O(4)	835 (32)	7750 (18)	8424 (11)	213 (60)
O(5)	1976 (34)	8731 (20)	7307 (12)	218 (63)
O(6)	10 (34)	4687 (18)	1011 (13)	291 (59)
C	3019 (44)	2823 (25)	7796 (17)	184 (76)

* Anisotropic parameters: $U_{11} = 76$ (13), $U_{22} = 200$ (13), $U_{33} = 143$ (12), $U_{12} = -6$ (6), $U_{13} = 3$ (5), $U_{23} = -6$ (6).