

up from PO₄ and SiO₄ tetrahedra and from MoO₆ or VO₆ octahedra offer new possibilities of non-stoichiometry owing to their great flexibility. Moreover the chemistry of Mo^{III} and of mixed-valence compounds Mo^{III}-Mo^{IV} should be carried on further in those oxides.

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Structure of Bis(2,2'-bipyridine)dicyanoiron(III) Perchlorate

BY T.-H. LU, H.-Y. KAO, D. I. WU, K. C. KONG AND C. H. CHENG

National Tsing Hua University, Taiwan 30043

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Abstract. [Fe(CN)₂(C₁₀H₈N₂)₂](ClO₄), *M_r* = 519.71, orthorhombic, *P*2₁2₁2₁, *a* = 10.950 (6), *b* = 11.941 (2), *c* = 16.912 (4) Å, *U* = 2211.1 Å³, *D_x* = 1.561, *D_m* = 1.551 Mg m⁻³, *Z* = 4, λ(Mo *K*α) = 0.71069 Å, μ = 0.843 mm⁻¹, *F*(000) = 1060, *T* = 297 (5) K. Final *R* = 0.044, *wR* = 0.034 for 1853 significant reflections. The iron atom is six coordinate. Each N atom of the two bipyridines and each C atom of the two cyanides shares in the coordination. The two cyanides are in the *cis* configuration. Both five-membered chelate rings are close to an envelope conformation. The two least-squares planes of each bipyridine moiety intersect at an angle of 86.1 (1)°. The two cyanides subtend 85.6 (3)° with the Fe atom as the vertex.

Introduction. Spectral data of Fe(CN)₂(*L-L*)^{0,+1}, where *L-L* = 2,2'-bipyridine or 1,10-phenanthroline, give contradictory results with respect to the geometry of these metal complexes. For example, the IR spectrum of Fe(CN)₂(bipy)₂ shows a single ν_{CN} at 2080 cm⁻¹ favoring a *trans* structure, but its ¹³C NMR data are better interpreted in terms of a *cis* geometry (Agarwala, Ramanathan & Khetrpal, 1985). To present a correct description for the structure of this type of metal complex, a representative of these series was examined by single-crystal X-ray diffraction methods. In this paper, the results of the investigations are reported.

Experimental. A bright red crystal of size 0.95 × 0.25 × 0.25 mm for X-ray structural analysis was obtained from a slow addition of NaClO₄ solution (0.20 g in 5 mL water) to Fe(CN)₂(bipy)₂ ion in hydrochloric acid (1 *M*). The Fe cation was generated by passing Cl gas into a suspension of 0.50 g of Fe(CN)₂(bipy)₂ in 50 mL of 1 *M* hydrochloric acid (Schilt, 1960). *D_m* by flotation (CCl₄ + CHCl₃), CAD-4 diffractometer, setting angles of 25 reflections (18.76 < 2θ < 26.64°) used to determine unit-cell constants and crystal orientation. [(sinθ)/λ]_{max} = 0.594 Å⁻¹ (0 ≤ *h* ≤ 12, 0 ≤ *k* ≤ 14, 0 ≤ *l* ≤ 20), ω-2θ scan, width = 2(0.8 + 0.35 tanθ)°, 2θ scan speed = 20/2 to 20/13° min⁻¹, graphite-monochromated Mo *K*α radiation. Three standard reflections (512, 5̄12, 5̄1̄2) monitored every 2 h, varied within 3σ(*I*). 2388 reflections collected, 1853 observed with *I* > 2.5σ(*I*). Empirical absorption correction based on azimuthal rotation from three reflections: 201̄, 5̄12, 603 (North, Phillips & Mathews, 1968). The minimum, maximum and average normalized correction factors are 0.9235, 0.9998 and 0.9701 respectively. The position of the Fe atom was determined by Patterson synthesis. Other atoms were located by successive difference Fourier synthesis and full-matrix least-squares fit. The positions of the H atoms were located by calculation through the assumption that they were in the radial direction of the pyridines and at a CH bond length of

Table 1. Atomic parameters x , y , z and B_{eq} with *e.s.d.*'s in parentheses

	x	y	z	$B_{eq}(\text{\AA}^2)$
Fe	0.98659 (8)	0.23204 (7)	0.13085 (5)	2.94 (4)
Cl	0.02534 (20)	0.31312 (16)	0.63331 (11)	5.03 (9)
O(1)	0.4521 (6)	0.2679 (6)	0.3330 (3)	10.4 (4)
O(2)	0.4625 (6)	0.1246 (5)	0.4259 (3)	8.9 (4)
O(3)	0.0662 (6)	0.3844 (5)	0.6930 (3)	9.1 (4)
O(4)	0.1270 (6)	0.2627 (6)	0.5958 (4)	10.6 (4)
N(1)	0.1333 (4)	0.1340 (4)	0.1390 (3)	3.2 (2)
N(2)	-0.0064 (5)	0.2220 (4)	0.2472 (3)	3.5 (2)
N(3)	-0.1184 (4)	0.0977 (4)	0.1168 (3)	3.3 (3)
N(4)	-0.0160 (5)	0.2300 (4)	0.0152 (2)	3.1 (2)
N(5)	0.2671 (5)	0.1108 (5)	0.8871 (3)	4.9 (3)
N(6)	0.1335 (5)	0.4475 (5)	0.1494 (3)	4.7 (3)
C(N5)	0.3478 (6)	0.1690 (5)	0.8778 (4)	3.4 (3)
C(N6)	0.0820 (6)	0.3667 (6)	0.1427 (4)	3.2 (3)
C(1)	0.1940 (6)	0.0874 (6)	0.0804 (4)	4.1 (4)
C(2)	0.2931 (7)	0.0181 (7)	0.0936 (5)	5.2 (4)
C(3)	0.3323 (7)	-0.0004 (7)	0.1707 (5)	4.9 (4)
C(4)	0.2697 (7)	0.0483 (6)	0.2312 (4)	4.2 (3)
C(5)	0.1695 (6)	0.1145 (5)	0.2155 (4)	3.3 (3)
C(6)	0.0919 (6)	0.1662 (5)	0.2755 (3)	3.4 (3)
C(7)	0.1137 (7)	0.1580 (6)	0.3555 (4)	4.5 (4)
C(8)	0.0348 (8)	0.2088 (7)	0.4074 (4)	5.2 (4)
C(9)	-0.0664 (7)	0.2630 (7)	0.3775 (4)	5.2 (4)
C(10)	-0.0832 (7)	0.2692 (7)	0.2971 (4)	4.7 (4)
C(11)	-0.1698 (7)	0.0387 (6)	0.1734 (4)	4.3 (4)
C(12)	-0.2411 (7)	-0.0534 (6)	0.1556 (4)	4.8 (4)
C(13)	-0.2616 (7)	-0.0809 (7)	0.0763 (5)	5.1 (4)
C(14)	-0.2103 (6)	-0.0180 (6)	0.0186 (4)	4.0 (3)
C(15)	-0.1386 (6)	0.0705 (5)	0.0389 (4)	3.1 (3)
C(16)	-0.0787 (6)	0.1458 (5)	-0.0174 (3)	3.1 (3)
C(17)	-0.0846 (6)	0.1343 (6)	-0.0987 (4)	3.8 (3)
C(18)	0.0275 (7)	0.2088 (6)	0.1459 (3)	4.6 (4)
C(19)	0.0356 (7)	0.2946 (6)	-0.1129 (4)	4.9 (4)
C(20)	0.0417 (6)	0.3050 (6)	-0.0316 (4)	3.9 (3)

B_{eq} is the mean of the principal axes of the thermal ellipsoid.

0.95 Å. Once the positions of the H atoms were calculated, they were fixed in further refinement, and only their thermal parameters were refined. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. Final values of R and wR are 0.044 and 0.034 respectively, based on 1853 independent reflections. 323 parameters with anisotropic temperature factors for non-H atoms. $S = 2.78$, $(\Delta/\sigma)_{\max} = 0.4$, $(\Delta\rho)_{\max} = 0.88$ (9) (around Fe atom), $(\Delta\rho)_{\min} = -0.62$ (9) e Å⁻³. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The atomic parameters are listed in Table 1. Bond lengths and bond angles are listed in Table 2.* Fig. 1 shows a stereoview of the packing for the molecules in the unit cell. The numbering scheme of the molecule excluding perchlorate ion and H atoms is shown in Fig. 2. The least-squares planes of the two pyridines on the upper side (refer to Fig. 2) of the iron center intersect at 4.8 (3)°, and the corresponding planes on the lower side intersect at 13.5 (2)°. The upper bipyridine is coplanar within 0.08 Å, and the lower one within 0.73 Å. The least-squares planes of the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44899 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°)

Fe-N(1)	1.993 (5)	Fe-N(2)	1.972 (4)
Fe-N(3)	1.988 (5)	Fe-N(4)	1.955 (4)
Fe-C(N5)	1.931 (7)	Fe-C(N6)	1.928 (7)
Cl-O(1)	1.380 (6)	Cl-O(2)	1.424 (6)
Cl-O(3)	1.394 (6)	Cl-O(4)	1.416 (7)
N(1)-C(1)	1.317 (9)	N(1)-C(5)	1.374 (8)
N(2)-C(6)	1.354 (9)	N(2)-C(10)	1.318 (8)
N(3)-C(11)	1.315 (9)	N(3)-C(15)	1.374 (8)
N(4)-C(16)	1.337 (8)	N(4)-C(20)	1.353 (8)
N(5)-C(N5)	1.135 (9)	N(6)-C(N6)	1.123 (9)
C(1)-C(2)	1.383 (11)	C(2)-C(3)	1.391 (12)
C(3)-C(4)	1.361 (11)	C(4)-C(5)	1.378 (10)
C(5)-C(6)	1.461 (9)	C(6)-C(7)	1.377 (9)
C(7)-C(8)	1.372 (11)	C(8)-C(9)	1.379 (11)
C(9)-C(10)	1.375 (9)	C(11)-C(12)	1.383 (11)
C(12)-C(13)	1.398 (11)	C(13)-C(14)	1.353 (11)
C(14)-C(15)	1.360 (9)	C(15)-C(16)	1.466 (9)
C(16)-C(17)	1.383 (8)	C(17)-C(18)	1.350 (10)
C(18)-C(19)	1.356 (11)	C(19)-C(20)	1.382 (9)
N(1)-Fe-N(2)	82.2 (2)	N(1)-Fe-N(3)	90.1 (2)
N(1)-Fe-N(4)	94.2 (2)	N(1)-Fe-C(N5)	178.1 (2)
N(1)-Fe-C(N6)	92.6 (2)	N(2)-Fe-N(3)	95.3 (2)
N(2)-Fe-N(4)	175.6 (2)	N(2)-Fe-C(N5)	98.2 (3)
N(2)-Fe-C(N6)	85.8 (2)	N(3)-Fe-N(4)	82.1 (2)
N(3)-Fe-N(5)	91.7 (2)	N(3)-Fe-C(N6)	177.3 (2)
N(4)-Fe-C(N5)	85.4 (2)	N(4)-Fe-C(N6)	97.0 (2)
C(N5)-Fe-C(N6)	85.6 (3)	O(1)-Cl-O(2)	112.1 (4)
O(1)-Cl-O(4)	108.4 (3)	O(1)-Cl-O(4)	110.1 (5)
O(2)-Cl-O(3)	110.2 (4)	O(2)-Cl-O(4)	106.7 (4)
O(3)-Cl-O(4)	109.4 (4)	Fe-N(1)-C(1)	127.1 (5)
Fe-N(1)-C(5)	113.4 (4)	C(1)-N(1)-C(5)	119.4 (6)
Fe-N(2)-C(6)	114.5 (4)	Fe-N(2)-C(10)	126.0 (5)
C(6)-N(2)-C(10)	119.4 (5)	Fe-N(3)-C(11)	126.3 (5)
Fe-N(3)-C(15)	113.5 (4)	C(11)-N(3)-C(15)	120.2 (6)
Fe-N(4)-C(16)	115.5 (4)	Fe-N(4)-C(20)	124.8 (4)
C(16)-N(4)-C(20)	119.7 (5)	Fe-C(N5)-N(5)	176.4 (6)
Fe-C(N6)-N(6)	177.3 (6)	N(1)-C(1)-C(2)	121.9 (7)
C(1)-C(2)-C(3)	119.2 (7)	C(2)-C(3)-C(4)	118.8 (7)
C(3)-C(4)-C(5)	120.1 (6)	N(1)-C(5)-C(6)	120.6 (6)
N(1)-C(5)-C(6)	114.5 (6)	C(4)-C(5)-C(6)	124.9 (6)
N(2)-C(6)-C(5)	115.1 (5)	N(2)-C(6)-C(7)	121.4 (6)
C(5)-C(6)-C(7)	123.4 (6)	C(6)-C(7)-C(8)	119.1 (7)
C(7)-C(8)-C(9)	118.7 (6)	C(8)-C(9)-C(10)	119.7 (6)
N(2)-C(10)-C(9)	121.7 (7)	N(3)-C(11)-C(12)	120.6 (7)
C(11)-C(12)-C(13)	119.1 (7)	C(12)-C(13)-C(14)	119.6 (7)
C(13)-C(14)-C(15)	119.3 (6)	N(3)-C(15)-C(16)	121.2 (6)
N(3)-C(15)-C(16)	114.0 (5)	C(14)-C(15)-C(16)	124.8 (6)
N(4)-C(16)-C(15)	115.0 (5)	N(4)-C(16)-C(17)	120.7 (6)
C(15)-C(16)-C(17)	124.3 (6)	C(16)-C(17)-C(18)	120.0 (6)
C(17)-C(18)-C(19)	119.4 (6)	C(18)-C(19)-C(20)	120.1 (7)
N(4)-C(20)-C(19)	120.1 (6)		

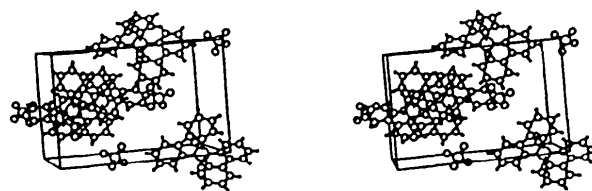


Fig. 1. A stereoview of the packing of the molecules in the unit cell. The origin of the unit cell is at the lower right corner, viewed down the positive b direction, with a upwards and c towards the left in a right-handed coordinate system.

two bipyridines intersect at 86.1 (1)°. The two cyanides stay on the same side of the two bipyridines and are in the *cis* configuration. Each N atom of the two bipyridines and each C atom of the two cyanides contributes to the coordination to Fe, resulting in essentially an octahedral structure. There is no hydrogen bond in this crystal structure because no N-H groups and no water molecules are present. This is confirmed by the large average volume per unit

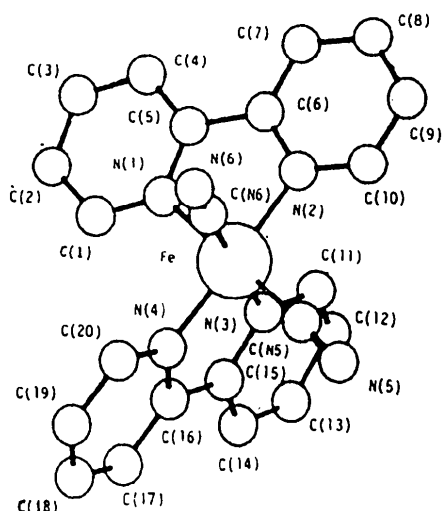


Fig. 2. Numbering scheme of the molecule, excluding perchlorate ion and H atoms.

atom which is equal to $11.06 \text{ \AA}^3/\text{atom}$. The Fe atom and each cyanide are almost in a line and the angle $C(N5)-Fe-C(N6)$ is $85.6(3)^\circ$. The coordination bond

distances of iron and carbon atoms are shorter than those of iron and nitrogen atoms. Other bond lengths and bond angles are normal.

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Structure of 1,2- μ -Acetato-(*O,O'*)-1,1,1,2,2,2,3,3,3,3-decacarbonyl- μ -hydrido-triangulo-triosmium: A Redetermination and Normal Probability Plot Analysis

BY V. D. ALEXIEV, J. EVANS, A. C. STREET AND M. WEBSTER*

Department of Chemistry, The University, Southampton SO9 5NH, England

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Abstract. $[\text{Os}_3(\text{C}_2\text{H}_3\text{O}_2)\text{H}(\text{CO})_{10}]$, $M_r = 910.76$, monoclinic, $P2_1/m$, $a = 7.882(3)$, $b = 12.622(3)$, $c = 9.908(2) \text{ \AA}$, $\beta = 109.73(2)^\circ$, $U = 927.8 \text{ \AA}^3$, $Z = 2$, $D_m = 3.26(2)$, $D_x = 3.259 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 205.4 \text{ cm}^{-1}$, $F(000) = 800$, room temperature, final $R = 0.029$ for 1488 reflections [$F > 3\sigma(F)$]. The structure is fully consistent with that previously reported [Lausarot, Vaglio, Valle, Tiripicchio, Camellini & Gariboldi (1985). *J. Organomet. Chem.* **291**, 221–229]. In addition to the random error present for the positional parameters of the two independent sets of data, systematic errors have been found in the thermal parameters associated with the Os atoms.

Introduction. As part of a study on model compounds of trinuclear osmium clusters grafted on oxide surfaces

(i.e. with bridging oxygen donors), the title compound was studied. The composition of the crystals examined only became clear during the structure solution when it was quickly realized that the structure had already been reported (Lausarot, Vaglio, Valle, Tiripicchio, Camellini & Gariboldi, 1985). These two independent determinations thus provide an opportunity for the application of a normal probability plot analysis to the atomic coordinates and thermal parameters (Abrahams & Keve, 1971).

Experimental. Air-stable yellow crystals from cyclohexane; density by flotation ($\text{CHBr}_3/\text{CH}_2\text{I}_2$). Preliminary data from photographic X-ray examination and accurate cell dimensions from 25 accurately centred reflections using an Enraf-Nonius CAD-4 diffractometer fitted with graphite monochromator and Mo $K\alpha$ radiation. Intensities of 1846 reflections were recorded ($1.5 < \theta < 25^\circ$; $h 0-9$, $k 0-15$, $l -11-11$)

* To whom correspondence should be addressed.