the anion $Re_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}AuPPh_3)^-$ (44 valence electrons) formally requiring two double Re—Re bonds, which results in a delocalization on the three Re—Re edges. The related Re—Re and Re—Au bond lengths have mean values of 2·894 (1) and 2·837 (1) Å respectively (Beringhelli, Ciani, D'Alfonso, de Malde & Freni, 1986). From a comparison of these Re—Re and Au—Re bond lengths with those in (II), it becomes obvious that heteronuclear metal–metal bond lengths show no remarkable change, but Re—Re distances are distinctly shortened. This shows that $\mu\text{-}PPh_2$ groups support a $\pi$-delocalization bonding effect in the Re—Re triangle more than $\mu$-H atoms do. Other structural features are comparable with those in similar phosphido-bridged rhenium clusters (Haupt, Balsaa & Flörke, 1988).

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# Structure of Di-μ-acetato-μ-oxo-bis[bis(2-pyridylmethyl)amine]diiron(III) Diperchlorate 0·9-Acetone Solvate

BY ROBERT J. O'BRIEN, JOHN F. RICHARDSON* AND ROBERT M. BUCHANAN*

*Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, USA*

**Abstract.** $[C_{28}H_{32}Fe_2N_6O_5](ClO_4)_2.0\cdot9(C_3H_6O)$, $M_r = 889\cdot66$, triclinic, $P\bar{1}$, $a = 13\cdot601$ (3), $b = 13\cdot966$ (3), $c = 12\cdot341$ (3) Å, $\alpha = 100\cdot10$ (2), $\beta = 99\cdot56$ (2), $\gamma = 115\cdot19$ (2)°, $V = 2010\cdot6$ Å$^3$, $Z = 2$, $D_x = 1\cdot46$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0\cdot7093$ Å, $\mu = 9\cdot12$ cm$^{-1}$, $F(000) = 915\cdot2$, $T = 296$ K, final $R = 0\cdot057$ for 5092 unique reflections. The structure consists of a binuclear cation with two disordered perchlorate counterions and a partial acetone solvate molecule. The Fe—Fe separation is 3·041 (1) Å with both Fe atoms octahedrally coordinated by a bridging oxo, two bridging acetate groups, and the facial capping ligand bis(2-pyridylmethyl)amine (bpma). The average Fe—O(oxo) bond distance is 1·792 (3) Å and the Fe—O—Fe bond angle is 116·2 (2)°. The pyridine pendants of bpma are located *cis* to the oxo group.

**Introduction.** Synthetic ($\mu$-oxo)bis($\mu$-carboxylato)diiron(III) compounds are of interest due to the presence of this unit at the active site of the non-heme oxo-iron protein hemerythrin (Stenkamp, Sieker & Jensen, 1984). Structures of several diiron complexes containing ($\mu$-oxo)bis($\mu$-carboxylato) core units and

facial capping amine ligands have been reported (Armstrong, Spool, Papaefthymiou, Frankel & Lippard, 1984; Hartman, Rardin, Chaudhuri, Pohl, Wieghardt, Nuber, Weiss, Papaefthymiou, Frankel & Lippard, 1987; Gomez-Romero, Casan-Pastor, Ben-Hussein & Jameson, 1988). These compounds reproduce, in part, the magnetic ($-J > 100$ cm$^{-1}$) and spectroscopic properties reported for methemerythrin (Lippard, 1988; Que & Scarrow, 1988) and are considered to be good structural models of the protein active site. We wish to report herein the structure of $[Fe_2O(bpma)_2(\mu\text{-}O_2CCH_3)_2](ClO_4)_2.0\cdot9$-$(C_3H_6O)$, where bpma is bis(2-pyridylmethyl)amine. The synthesis and physical properties of the analogous benzoate compound have been reported recently (Norman, Yan, Que, Backes, Ling, Sanders-Loehr, Zhang & O'Connor, 1990).

**Experimental.** The ligand bpma was synthesized by a previously reported procedure (Gruenwedel, 1968). The diiron complex was synthesized following the self-assembly method (Gomez-Romero, Casan-Pastor, Ben-Hussein & Jameson, 1988). A dark-green, multi-faceted crystal from acetone:ethanol, 0·28 × 0·32 × 0·32 mm. Enraf–Nonius CAD-4 dif-

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* To whom correspondence should be addressed.

fractometer, Mo $K\alpha$, graphite monochromator. Cell constants and orientation matrix from least-squares refinement of 25 reflections with $12 < \theta < 15°$. Lorentz and polarization corrections applied, absorption corrections from $\psi$ scans, 0·898 to 0·999. Maximum $(\sin\theta)/\lambda = 0·594$ Å$^{-1}$; $h = 0$ to $+16$, $k = -16$ to $+16$, $l = -14$ to $+14$. Three standard reflections measured every 3600 s of X-ray exposure time remained constant, $\omega/2\theta$ scan technique, 7792 measured reflections, 7053 unique, $R_{int}(F_o) = 0·010$; 5092 observed reflections for $I > 3\sigma(I)$. Structure solution from *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent least-squares and difference Fourier maps; H atoms found and included in calculated positions (C—H = 1·0 Å) with $B = 1·3 \times B_{eq}$ of bonded atom but not refined (only N—H atom positional parameters were refined); isotropic extinction parameter refined [4 (2) × 10$^{-8}$]. Model was refined on $F$ by minimizing the function $\sum w(|F_o| - |F_c|)^2$; $w = [\sigma(F)^2 + (0·01F)^2 + 1·0]^{-1}$ (Killean & Lawrence, 1969). $R = 0·057$, $wR = 0·062$, $S = 1·03$, for 5092 observations, 500 variables $(\Delta/\sigma)_{max} = 0·25$ associated with two disordered ClO$_4^-$ ions; all other $(\Delta/\sigma) < 0·02$. $(\Delta\rho)_{max} = 0·76$ (8), $(\Delta\rho)_{min} = -0·70$ (8) e Å$^{-3}$. Scattering factors from Cromer & Waber (1974), anomalous dispersion included in $F_c$ (Ibers & Hamilton, 1964) with values of $f'$ and $f''$ from Cromer (1974). *SDP*/VAX package of programs (Frenz, 1978) using VAX 11/750.

**Discussion.** The atomic positional and isotropic thermal parameters for non-H atoms as well as selected bond distances and angles for [Fe$_2$O(bpma)$_2$($\mu$-O$_2$CCH$_3$)$_2$]$^{2+}$ are given in Tables 1 and 2,* respectively. An *ORTEP* view (Johnson, 1976) of the cation with numbering scheme is shown in Fig. 1. In the [Fe$_2$O(bpma)$_2$($\mu$-O$_2$CCH$_3$)$_2$]$^{2+}$ cation the metal atoms are in distorted octahedral environments with the Fe atoms being bridged by an oxo and two acetate groups. The average Fe—O bond lengths are 1·792 (3) Å (Fe—O$_{oxo}$) and 2·029 (4) Å (Fe—O$_{OAc}$). Comparable short Fe—O$_{oxo}$ bond lengths are reported for methemerythrin (Stenkamp, Sieker & Jensen, 1984) as well as other synthetic oxo-bridged Fe$_2^{III}$ complexes (Lippard, 1988; Que & Scarrow, 1988).

The remaining coordination sites of the complex are occupied by the nitrogen atoms of the bpma ligands which bind in a facial (capping) configura-

Table 1. *Positional parameters and equivalent isotropic thermal parameters for non-H atoms*

For atoms refined anisotropically, $B_{eq}$ is defined as: $(4/3)[a^2\beta_{11} + b^2\beta_{22} + \cdots + ab(\cos\gamma)\beta_{12} + \cdots]$.

| | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$) | Occupancy† |
|---|---|---|---|---|---|
| Fe(1) | 0·29592 (5) | 0·12232 (5) | 0·31730 (6) | 3·47 (2) | |
| Fe(2) | 0·53647 (5) | 0·23292 (6) | 0·29747 (6) | 3·66 (2) | |
| O(1) | 0·3900 (3) | 0·1917 (3) | 0·2388 (3) | 3·65 (8) | |
| O(2) | 0·3450 (3) | 0·0066 (3) | 0·3363 (3) | 4·87 (9) | |
| O(3) | 0·5236 (3) | 0·0927 (3) | 0·3363 (3) | 4·57 (9) | |
| O(4) | 0·3864 (3) | 0·2141 (3) | 0·4797 (3) | 4·9 (1) | |
| O(5) | 0·5564 (3) | 0·3094 (4) | 0·4607 (3) | 5·8 (1) | |
| N(1) | 0·1651 (3) | 0·0336 (3) | 0·3979 (4) | 4·2 (1) | |
| N(2) | 0·1604 (3) | 0·0011 (3) | 0·1753 (4) | 3·9 (1) | |
| N(3) | 0·2071 (3) | 0·2179 (3) | 0·3283 (3) | 3·6 (1) | |
| N(4) | 0·7199 (3) | 0·2967 (4) | 0·3606 (4) | 4·8 (1) | |
| N(5) | 0·6033 (3) | 0·3901 (3) | 0·2635 (4) | 4·7 (1) | |
| N(6) | 0·5822 (3) | 0·1830 (3) | 0·1464 (3) | 3·7 (1) | |
| C(1) | 0·0930 (5) | −0·0785 (5) | 0·3235 (5) | 5·5 (2) | |
| C(2) | 0·0778 (4) | −0·0796 (4) | 0·1994 (5) | 4·6 (1) | |
| C(3) | −0·0132 (5) | −0·1629 (6) | 0·1141 (6) | 6·7 (2) | |
| C(4) | −0·0179 (5) | −0·1611 (6) | 0·0031 (6) | 7·2 (2) | |
| C(5) | 0·0659 (5) | −0·0795 (5) | −0·0229 (6) | 6·1 (2) | |
| C(6) | 0·1553 (4) | 0·0020 (4) | 0·0652 (5) | 4·7 (1) | |
| C(7) | 0·1038 (5) | 0·0932 (5) | 0·4296 (5) | 6·1 (2) | |
| C(8) | 0·1268 (4) | 0·1891 (4) | 0·3824 (4) | 3·9 (1) | |
| C(9) | 0·0687 (4) | 0·2494 (4) | 0·3992 (5) | 4·9 (1) | |
| C(10) | 0·0947 (4) | 0·3393 (4) | 0·3601 (6) | 5·5 (2) | |
| C(11) | 0·1771 (5) | 0·3691 (4) | 0·3029 (6) | 5·6 (2) | |
| C(12) | 0·2322 (4) | 0·3062 (4) | 0·2882 (5) | 4·5 (1) | |
| C(13) | 0·7589 (5) | 0·2364 (5) | 0·2830 (5) | 6·2 (2) | |
| C(14) | 0·6862 (4) | 0·1962 (4) | 0·1616 (5) | 4·4 (1) | |
| C(15) | 0·7257 (4) | 0·1702 (5) | 0·0702 (5) | 6·1 (2) | |
| C(16) | 0·6541 (5) | 0·1284 (5) | −0·0381 (5) | 6·4 (2) | |
| C(17) | 0·5466 (5) | 0·1153 (5) | −0·0541 (5) | 5·6 (2) | |
| C(18) | 0·5125 (4) | 0·1435 (4) | 0·0399 (4) | 4·3 (1) | |
| C(19) | 0·7767 (5) | 0·4165 (6) | 0·3828 (6) | 6·6 (2) | |
| C(20) | 0·7138 (5) | 0·4563 (5) | 0·3081 (5) | 5·7 (2) | |
| C(21) | 0·7665 (6) | 0·5578 (6) | 0·2889 (7) | 7·7 (2) | |
| C(22) | 0·7030 (6) | 0·5934 (6) | 0·2228 (7) | 8·8 (2) | |
| C(23) | 0·5886 (6) | 0·5238 (5) | 0·1753 (6) | 7·4 (2) | |
| C(24) | 0·5415 (5) | 0·4222 (5) | 0·1970 (5) | 5·6 (2) | |
| C(25) | 0·4397 (4) | 0·0115 (4) | 0·3424 (4) | 3·8 (1) | |
| C(26) | 0·4513 (5) | −0·0877 (4) | 0·3586 (5) | 5·4 (1) | |
| C(27) | 0·4844 (5) | 0·2864 (4) | 0·5165 (5) | 4·7 (1) | |
| C(28) | 0·5266 (7) | 0·3544 (7) | 0·6394 (6) | 8·9 (3) | |
| O(6) | 0·2686 (6) | 0·4335 (5) | 0·0727 (6) | 11·5 (2) | 0·90 |
| C(29) | 0·2365 (8) | 0·4961 (7) | 0·0495 (8) | 9·2 (3) | 0·90 |
| C(30) | 0·125 (1) | 0·473 (1) | 0·019 (1) | 15·3 (5) | 0·90 |
| C(31) | 0·320 (1) | 0·6081 (9) | 0·058 (1) | 12·7 (5) | 0·90 |
| Cl(1) | 0·1000 (1) | 0·6372 (1) | 0·3321 (2) | 7·03 (5) | |
| Cl(2) | 0·7539 (1) | 0·9229 (1) | 0·2532 (2) | 7·29 (5) | |
| O(11) | 0·0215 (7) | 0·5217 (6) | 0·2842 (7) | 10·9 (2)* | 0·80 |
| O(12) | 0·2054 (7) | 0·6459 (7) | 0·3623 (8) | 11·9 (3)* | 0·80 |
| O(13)A | 0·090 (1) | 0·7013 (9) | 0·423 (1) | 9·7 (3)* | 0·50 |
| O(13)B | 0·049 (1) | 0·637 (1) | 0·436 (1) | 7·9 (4)* | 0·30 |
| O(14)A | 0·1078 (8) | 0·6905 (8) | 0·2393 (9) | 8·0 (3)* | 0·50 |
| O(14)B | 0·0411 (8) | 0·6702 (8) | 0·2593 (9) | 8·2 (3)* | 0·50 |
| O(15) | 0·191 (2) | 0·748 (2) | 0·423 (2) | 7·0 (6)* | 0·20 |
| O(16) | 0·050 (2) | 0·560 (2) | 0·391 (2) | 8·4 (7)* | 0·20 |
| O(17) | 0·180 (3) | 0·605 (2) | 0·291 (3) | 10·6 (9)* | 0·20 |
| O(21) | 0·8181 (5) | 0·8756 (6) | 0·2733 (9) | 16·3 (3) | |
| O(22) | 0·7381 (8) | 0·9755 (7) | 0·1743 (8) | 11·1 (3)* | 0·70 |
| O(23) | 0·6424 (9) | 0·8295 (9) | 0·222 (1) | 13·1 (3)* | 0·70 |
| O(24) | 0·7746 (9) | 1·0025 (9) | 0·370 (1) | 13·3 (3)* | 0·70 |
| O(25) | 0·848 (2) | 1·014 (2) | 0·233 (2) | 9·5 (5)* | 0·30 |
| O(26) | 0·713 (2) | 0·850 (2) | 0·136 (2) | 14·5 (9)* | 0·30 |
| O(27) | 0·687 (2) | 0·922 (2) | 0·321 (2) | 13·1 (8)* | 0·30 |

\* Atoms were refined isotropically.

† Only occupancies not equal to 1·0 are listed. Occupancies of atoms within disordered groups are fixed at average values determined during refinement.

tion. The secondary amine N atoms are bonded *trans* to the Fe—O$_{oxo}$—Fe bridge with an average Fe—N$_{amine}$ bond length of 2·200 (4) Å, typical of other amine-containing N$_3$-facial ligands. The pyridine pendants, bound *cis* to the oxo group, are bonded more tightly to the Fe centers with an average Fe—N$_{py}$ distance of 2·145 (5) Å.

Table 2. *Bond distances* (Å) *and bond angles* (°) *for selected non-H atoms*

Numbers in parentheses are estimated standard deviations in the least significant digits

| | | | |
|---|---|---|---|
| Fe(1)—Fe(2) | 3·041 (1) | N(5)—C(20) | 1·334 (6) |
| Fe(1)—O(1) | 1·788 (3) | N(5)—C(24) | 1·342 (9) |
| Fe(1)—O(2) | 2·027 (4) | N(6)—C(14) | 1·323 (8) |
| Fe(1)—O(4) | 2·029 (4) | N(6)—C(18) | 1·348 (6) |
| Fe(1)—N(1) | 2·199 (4) | C(1)—C(2) | 1·51 (1) |
| Fe(1)—N(2) | 2·136 (3) | C(2)—C(3) | 1·380 (7) |
| Fe(1)—N(3) | 2·150 (5) | C(3)—C(4) | 1·37 (1) |
| Fe(2)—O(1) | 1·796 (3) | C(4)—C(5) | 1·358 (9) |
| Fe(2)—O(3) | 2·039 (4) | C(5)—C(6) | 1·380 (6) |
| Fe(2)—O(5) | 2·022 (4) | C(7)—C(8) | 1·487 (9) |
| Fe(2)—N(4) | 2·201 (4) | C(8)—C(9) | 1·391 (9) |
| Fe(2)—N(5) | 2·138 (5) | C(9)—C(10) | 1·352 (9) |
| Fe(2)—N(6) | 2·156 (5) | C(10)—C(11) | 1·38 (1) |
| O(2)—C(25) | 1·250 (8) | C(11)—C(12) | 1·38 (2) |
| O(3)—C(25) | 1·246 (5) | C(13)—C(14) | 1·509 (8) |
| O(4)—C(27) | 1·222 (5) | C(14)—C(15) | 1·385 (9) |
| O(5)—C(27) | 1·253 (7) | C(15)—C(16) | 1·373 (9) |
| N(1)—C(1) | 1·465 (6) | C(16)—C(17) | 1·37 (1) |
| N(1)—C(7) | 1·458 (9) | C(17)—C(18) | 1·375 (9) |
| N(2)—C(2) | 1·331 (7) | C(19)—C(20) | 1·49 (1) |
| N(2)—C(6) | 1·351 (8) | C(20)—C(21) | 1·38 (1) |
| N(3)—C(8) | 1·328 (7) | C(21)—C(22) | 1·39 (1) |
| N(3)—C(12) | 1·340 (7) | C(22)—C(23) | 1·386 (9) |
| N(4)—C(13) | 1·474 (9) | C(23)—C(24) | 1·383 (9) |
| N(4)—C(19) | 1·462 (8) | C(25)—C(26) | 1·50 (1) |
| C(27)—C(28) | 1·509 (8) | | |

| | | | |
|---|---|---|---|
| O(1)—Fe(1)—O(2) | 99·4 (2) | O(1)—Fe(2)—O(3) | 100·1 (1) |
| O(1)—Fe(1)—O(4) | 100·8 (1) | O(1)—Fe(2)—O(5) | 99·6 (2) |
| O(1)—Fe(1)—N(1) | 173·7 (2) | O(1)—Fe(2)—N(4) | 174·2 (2) |
| O(1)—Fe(1)—N(2) | 98·0 (1) | O(1)—Fe(2)—N(5) | 97·2 (2) |
| O(1)—Fe(1)—N(3) | 99·5 (2) | O(1)—Fe(2)—N(6) | 101·1 (1) |
| O(2)—Fe(1)—O(4) | 90·7 (2) | O(3)—Fe(2)—O(5) | 93·2 (2) |
| O(2)—Fe(1)—N(1) | 84·0 (2) | O(3)—Fe(2)—N(4) | 85·5 (2) |
| O(2)—Fe(1)—N(2) | 88·1 (2) | O(3)—Fe(2)—N(5) | 162·2 (2) |
| O(2)—Fe(1)—N(3) | 161·1 (2) | O(3)—Fe(2)—N(6) | 88·1 (2) |
| O(4)—Fe(1)—N(1) | 84·4 (1) | O(5)—Fe(2)—N(4) | 81·9 (2) |
| O(4)—Fe(1)—N(2) | 161·1 (2) | O(5)—Fe(2)—N(5) | 88·7 (2) |
| O(4)—Fe(1)—N(3) | 85·6 (2) | O(5)—Fe(2)—N(6) | 158·7 (1) |
| N(1)—Fe(1)—N(2) | 76·7 (2) | N(4)—Fe(2)—N(5) | 77·2 (2) |
| N(1)—Fe(1)—N(3) | 77·3 (2) | N(4)—Fe(2)—N(6) | 77·1 (2) |
| N(2)—Fe(1)—N(3) | 89·4 (2) | N(5)—Fe(2)—N(6) | 83·8 (2) |
| Fe(1)—O(1)—Fe(2) | 116·2 (2) | | |
| Fe(1)—O(2)—C(25) | 129·0 (3) | Fe(2)—O(3)—C(25) | 130·1 (5) |
| Fe(1)—O(4)—C(27) | 130·1 (4) | Fe(2)—O(5)—C(27) | 127·5 (3) |
| Fe(1)—N(1)—C(1) | 108·7 (4) | Fe(2)—N(4)—C(13) | 110·1 (3) |
| Fe(1)—N(1)—C(7) | 112·5 (3) | Fe(2)—N(4)—C(19) | 109·5 (4) |
| Fe(1)—N(2)—C(2) | 116·6 (3) | Fe(2)—N(5)—C(20) | 116·7 (5) |
| Fe(1)—N(2)—C(6) | 124·0 (3) | Fe(2)—N(5)—C(24) | 123·6 (3) |
| Fe(1)—N(3)—C(8) | 117·1 (4) | Fe(2)—N(6)—C(14) | 116·6 (3) |
| Fe(1)—N(3)—C(12) | 123·5 (4) | Fe(2)—N(6)—C(18) | 123·7 (4) |
| C(1)—N(1)—C(7) | 114·2 (4) | C(13)—N(4)—C(19) | 116·0 (6) |
| N(1)—C(1)—C(2) | 110·8 (5) | N(4)—C(13)—C(14) | 111·6 (6) |
| C(1)—C(2)—C(3) | 122·2 (5) | C(13)—C(14)—C(15) | 121·2 (5) |
| N(2)—C(2)—C(1) | 116·3 (4) | N(6)—C(14)—C(13) | 117·4 (5) |
| N(2)—C(2)—C(3) | 121·5 (6) | N(6)—C(14)—C(15) | 121·5 (5) |
| C(2)—C(3)—C(4) | 118·6 (7) | C(14)—C(15)—C(16) | 118·8 (6) |
| C(3)—C(4)—C(5) | 120·7 (5) | C(15)—C(16)—C(17) | 119·8 (6) |
| C(4)—C(5)—C(6) | 118·6 (6) | C(16)—C(17)—C(18) | 118·7 (5) |
| C(2)—N(2)—C(6) | 119·5 (4) | C(14)—N(6)—C(18) | 119·8 (5) |
| N(2)—C(6)—C(5) | 121·2 (5) | N(6)—C(18)—C(17) | 121·6 (5) |
| N(1)—C(7)—C(8) | 114·1 (5) | N(4)—C(19)—C(20) | 112·8 (4) |
| C(7)—C(8)—C(9) | 120·5 (5) | C(19)—C(20)—C(21) | 121·5 (5) |
| N(3)—C(8)—C(9) | 121·4 (5) | N(5)—C(20)—C(19) | 116·8 (5) |
| N(3)—C(8)—C(7) | 118·1 (6) | N(5)—C(20)—C(21) | 121·7 (7) |
| C(8)—N(3)—C(12) | 119·4 (5) | C(20)—N(5)—C(24) | 119·6 (6) |
| C(8)—C(9)—C(10) | 119·5 (6) | C(20)—C(21)—C(22) | 119·3 (6) |
| C(9)—C(10)—C(11) | 119·6 (7) | C(21)—C(22)—C(23) | 118·8 (7) |
| C(10)—C(11)—C(12) | 118·6 (7) | C(22)—C(23)—C(24) | 118·7 (8) |
| N(3)—C(12)—C(11) | 121·6 (8) | N(5)—C(24)—C(23) | 121·8 (5) |
| O(2)—C(25)—O(3) | 124·2 (5) | O(4)—C(27)—O(5) | 125·6 (5) |
| O(2)—C(25)—C(26) | 117·0 (4) | O(5)—C(27)—C(28) | 115·2 (5) |
| O(3)—C(25)—C(26) | 118·9 (5) | O(4)—C(27)—C(28) | 119·3 (6) |
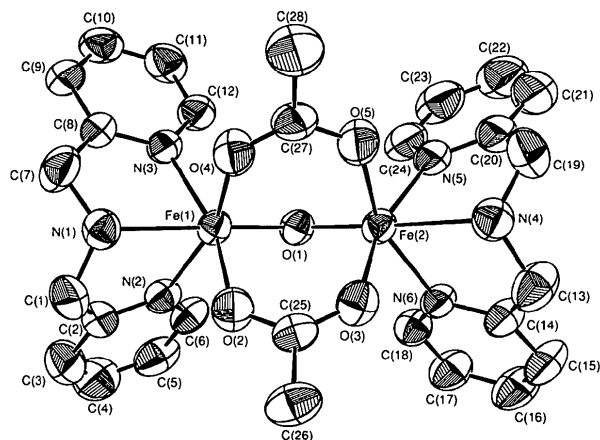


Fig. 1. An *ORTEP* view of the cationic complex showing the 50% probability thermal ellipsoids and the atom-labeling scheme.

greater contribution of $\pi$ bonding involving imidazole donor groups compared to pyridine (Oberhausen, O'Brien, Richardson & Buchanan, 1990). As a result, the Fe—Fe separation [3·041 (1) Å] and Fe—$O_{oxo}$—Fe bridging angle [116·2 (2)°] are smaller for [Fe—O(bpma)$_2$($\mu$-O$_2$CCH$_3$)$_2$]$^{2+}$ than in other $\mu$-oxo bis($\mu$-carboxylato)diiron(III) complexes. The N—Fe—N bond angles in the complex range from 76·7 (2) to 89·4 (2)°, consistent with other oxo-bridged Fe$^{III}$ complexes.

The fractional acetone solvate molecule is well behaved and has been modeled using an occupancy factor of 0·9 for each non-H atom (0·9 is the average of the refined individual occupancies of the four atoms of the group). The perchlorate counterions were found to be severely disordered. The perchlorate ion containing Cl(1) displayed both positional and rotational disordering with three separate perchlorate orientations being required to model the oxygen atom positions. The groups were assigned occupancy factors of 0·5, 0·3 and 0·2 as determined from the average occupancies of the atoms in each group. The second perchlorate counter ion displayed threefold rotational disordering about the Cl(2)—O(21) axis. The three remaining oxygen atoms formed two groups, assigned occupancy factors of 0·70, and 0·30 (again from average occupancies of the atoms in each group).

When the donor groups, *cis* to the oxo group, are benzimidazole moieties, there is a greater difference between the Fe—N$_{amine}$ and Fe—N$_{heterocycle}$ bond lengths (Gomez-Romero, Casan-Pastor, Ben-Hussein & Jameson, 1988). This is due presumably to the

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# Structure of (1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane)silver(II) Diperchlorate

BY HENRY N. PO AND ELIZABETH BRINKMAN

*Department of Chemistry, California State University, Long Beach, California 90840, USA*

AND ROBERT J. DOEDENS

*Department of Chemistry, University of California, Irvine, California 92717, USA*

**Abstract.** $[Ag(C_{14}H_{32}N_4)](ClO_4)_2$, $M_r = 563\cdot21$, monoclinic, $P2_1/n$, $a = 9\cdot2653$ (7), $b = 9\cdot3626$ (8), $c = 12\cdot8516$ (8) Å, $\beta = 90\cdot740$ (5)°, $V = 1114\cdot74$ (13) Å$^3$, $Z = 2$, $D_x = 1\cdot678$ Mg m$^{-3}$, $\lambda(Mo\ K\alpha) = 0\cdot71073$ Å, $\mu = 1\cdot181$ mm$^{-1}$, $F(000) = 578$, $T = 296$ K, $R = 0\cdot034$ for 2789 independent reflections with $I > 3\sigma(I)$. The structure is comprised of monomeric, centrosymmetric molecules, in which the silver atom is bound to the four nitrogen atoms of the macrocycle and also participates in weak axial interactions with two perchlorate oxygen atoms. The mean Ag—N bond length is $2\cdot195$ (3) Å and the Ag—O distance is $2\cdot889$ (4) Å.

**Introduction.** Two structure types are known for tetraaza macrocyclic complexes of silver(II). In [Ag(tet *a*)](NO₃)₂* (Mertes, 1978) and one isomer of [Ag(cyclam)](ClO₄)₂ (Ito, Ito & Toriumi, 1981), the silver is situated at a center of inversion and is bound

to nitrogen atoms of the macrocycle in a square-planar configuration. Additional long interactions to an oxygen atom of each anion are present. In a second isomer of [Ag(cyclam)](ClO₄)₂, however, the silver is located on a mirror plane that bisects the two six-membered chelate rings and is displaced by 0·24 Å below the plane of the four nitrogen atoms (Ito, Ito & Toriumi, 1981). In this isomer, no axial interaction with the perchlorate is observed. Based on the EPR spectrum of [Ag(tmc)](ClO₄)₂($g_{\parallel} < g_{\perp}$), a possible structure with a folded ligand and a single coordinated perchlorate was suggested (Barefield & Mocella, 1973). In this paper, we report the crystal structure of [Ag(tmc)](ClO₄)₂.

**Experimental.** [Ag(tmc)](ClO₄)₂ was prepared according to the literature procedure (Barefield & Mocella, 1973; Trismitro & Po, 1988) by adding 5 mmol of the macrocycle to 10 mmol of silver perchlorate in 30 ml water and stirring for 1 h. The solution was then filtered and the filtrate was cooled at 278 K overnight. The needle-shaped dark orange-brown crystals were collected by vacuum filtration and washed with

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* Ligand abbreviations: tet *a* = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; cyclam = 1,4,8,11-tetraazacyclotetradecane; tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.