

Nonacarbonyl- μ_3 -hydrido-tris(μ -diphenylphosphido)-tetrahedro-tetrarhenium, a Two-fold Unsaturated 56-Valence Electron Cluster and a Related Gold Rhenium Compound

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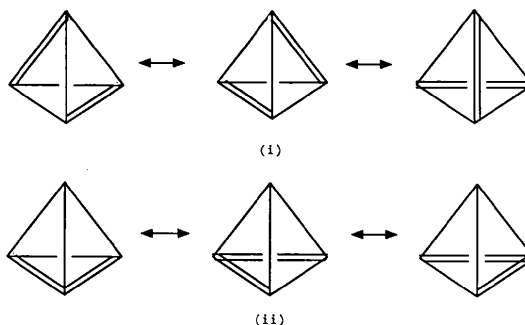
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Abstract. (I) Nonacarbonyl- $1\kappa^3C, 2\kappa^2C, 3\kappa^2C, 4\kappa^2C$ -tris(μ -diphenylphosphido- $2:3\kappa^2P; 2:4\kappa^2P; 3:4\kappa^2P$)- μ_3 -hydrido-tetrahedro-tetrarhenium, $C_{45}H_{31}O_9P_3Re_4$, $M_r = 1553.5$, trigonal, $R\bar{3}$, $a = 17.786$ (4), $c = 28.146$ (7) Å, $V = 7710.9$ Å³, $Z = 6$, $D_x = 2.006$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 9.66$ mm⁻¹, $F(000) = 4308$, $T = 298$ (1) K, $R = 0.0505$ for 1636 unique reflections. The central molecular fragment shows a trigonal pyramidal Re_4 cluster, the equilateral Re_3 base plane of which is $Re-Re$ bridged by diphenylphosphido groups. The mean $Re-Re$ distances are 2.708 (1) (Re_3 ring) and 2.931 (1) Å. (II) Hexacarbonyl- $1\kappa^2C, 2\kappa^2C, 3\kappa^2C$ -tris(μ -diphenylphosphido- $1:2\kappa^2P; 1:3\kappa^2P; 2:3\kappa^2P$)- μ_3 -hydrido-(triphenylphosphine- $4\kappa^1P$)-tetrahedro-goldtrirhenium, $C_{60}H_{46}AuO_6P_4Re_3$, $M_r = 1742.5$, orthorhombic, $Pbcn$, $a = 20.502$ (3), $b = 24.415$ (4), $c = 23.792$ (5) Å, $V = 11909.2$ Å³, $Z = 8$, $D_x = 1.943$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 8.77$ mm⁻¹, $F(000) = 6544$, $T = 298$ (1) K, $R = 0.0732$ for 4388 unique reflections. The $AuPPh_3$ group is bound to all Re atoms of a planar Re_3 ring which is bridged by diphenylphosphido groups. The mean bond distances of the $AuRe_3$ core are $Au-Re = 2.854$ (2) and $Re-Re = 2.753$ (2) Å.

Introduction. The title substance (I) belongs to the family of tetranuclear rhenium carbonyl derivatives which fulfill a valence electron count of 56 (Henly, 1989). The only structurally characterized cluster with two double bonds is $Re_4(CO)_{12}(\mu-H)_4$ (Wilson & Bau, 1976) which has $Re-Re$ bond lengths in the narrow range 2.886 (1)–2.945 (1) Å. They are short compared with a single-bond length of 3.104 (1) Å found in $Re_2(CO)_{10}$ (Churchill, Amon & Wassermann, 1981). To account for these observations the hybrid resonance structure (i) was proposed; the isoelectronic title compound (I) might behave similarly. However, ³¹P NMR measurements obtained from deuteriochloroform solutions of the title substance (196.6; *s*, μ -P) and of the cluster $Re_3(CO)_6(\mu-H)_2(\mu-PPh_2)_3$ (198.2; *s*, μ -P) having a phosphido-

bridged Re_3 ring, formally with two double bonds (Haupt, Flörke & Balsaa, 1988), indicate that the π -delocalization effect in the title substance could be restricted to the phosphido-bridged ring fragment (ii). To clarify the kind of π delocalization, a single-crystal X-ray structural determination of the title substance was undertaken. Additionally, the same was done for $Re_3(CO)_6(\mu-H)(\mu-PPh_2)_3(AuPPh_3)$ (II), which has one $AuPPh_3$ unit with predominant σ -bonding properties instead of a $Re(CO)_3$ group with a σ -, π -bonding pattern.



Experimental. Dark-red crystals of $Re_4(CO)_9(\mu_3-H)(\mu-PPh_2)_3$, (I), were prepared by heating $Re_2(CO)_6(\text{eq-NCCH}_3)_2(\mu-PPh_2)_2$ in xylene solution under reflux and orange-red crystals of $Re_3(CO)_6(\mu_3-H)(\mu-PPh_2)_3(AuPPh_3)$, (II), were prepared by heating (I) with an excess of PPh_3AuCl in xylene solution at 493 K in a glass bomb tube (Schnieder, 1990).

Crystal size of (I) 0.25 × 0.26 × 0.31 mm, Nicolet diffractometer, graphite monochromator, $Mo K\alpha$ radiation, $\lambda = 0.71073$ Å, lattice parameters refined from 25 reflections ($10 \leq 2\theta \leq 26^\circ$), ω - 2θ scan, scan speed 2.9° min⁻¹, 2422 intensities collected $3 \leq 2\theta \leq 55^\circ$, $0 \leq h \leq 23$, $-1 \leq k \leq 23$, $0 \leq l \leq 36$, three standards recorded every 400 reflections, only random deviations, Lp correction, empirical absorption correction via ψ -scans, min./max. transmission factors 0.301/0.663, after merging ($R_{\text{int}} = 0.022$) 2388 unique reflections, 1636 with $F > 4\sigma(F)$. Structure solved by

direct methods and subsequent ΔF maps, full-matrix least-squares refinement based on F (70 parameters); Re and P refined anisotropically, phenyl groups treated as rigid bodies (C—C 1.395, C—H 0.96 Å), H atoms fixed in calculated idealized positions with $U_{\text{iso}} = 0.08 \text{ \AA}^2$, max. $(\Delta/\sigma) = 0.001$, max. height in final ΔF syntheses 1.1 e \AA^{-3} near Re position, refinement converged to $R = 0.051$, $wR = 0.044$, $w = 1/[\sigma^2(F) + 0.0001F^2]$. Scattering factors, structure solution and refinement using *SHELXTL-Plus88* (Sheldrick, 1988).

Crystal size of (II) $0.23 \times 0.28 \times 0.30 \text{ mm}$, lattice parameters refined from 38 reflections $10 \leq 2\theta \leq 32^\circ$, ω - 2θ scan, 11 403 intensities $3 \leq 2\theta \leq 50^\circ$, $0 \leq h \leq 24$, $0 \leq k \leq 29$, $0 \leq l \leq 28$, three standards every 400 reflections, only random deviations, min./max. transmission factors 0.07/0.24, 4388 unique reflections with $F > 5\sigma(F)$, full-matrix least-squares refinement on F (229 parameters); Au, Re, P refined anisotropically, μ_3 -H position located from ΔF map but not refined, max. $(\Delta/\sigma) = 0.001$, max. height in final ΔF syntheses 1.9 e \AA^{-3} near Re position, final $R = 0.073$, $wR = 0.062$, $w = 1/[\sigma^2(F) + 0.0001F^2]$; further details of the structural analysis as above.

Discussion. The structures of (I) and (II) are shown in Figs. 1 and 2. Atomic parameters are given in Tables 1 and 2 and selected bond lengths and angles in Table 3.* Both molecules have C_1 point-group symmetry. If the different conformations of the phenyl groups are neglected, the atom arrangement in both fragments $\text{Re}_4(\text{CO})_5(\mu\text{-P})_3(\mu_3\text{-H})$ and $\text{Re}_3(\text{CO})_5(\mu\text{-P})_3(\mu_3\text{-H})\mu_3\text{-Au}$ nearly reaches C_{3v} symmetry. Their common molecular core is $\text{Re}_3(\text{CO})_6(\mu_3\text{-H})(\mu\text{-PPh}_2)_3$. Although the included $\mu_3\text{-H}$ atom for (I) could not be located from the ΔF map, its presence is assured through the $^1\text{H NMR}$ value of $-14.5 [q, 1\text{H}; ^2J(\text{PH}) 9.1 \text{ Hz}]$.

To indicate the multiple-bond character in both diphenylphosphido-bridged Re_3 rings, the average Re—Re bond length of 2.708 (1) Å in (I) and of 2.752 (2) Å in (II) is compared with that of 2.730 (1) Å in $\text{Re}_3(\text{CO})_6(\mu_3\text{-H})_2(\mu\text{-PPh}_2)_3$ which has such a bond character in a twofold unsaturated Re_3 ring (Haupt, Flörke & Balsaa, 1988). This shows that the π delocalization in the $\text{Re}_3(\mu\text{-P})_3$ base plane of the aforementioned common molecular core is somewhat strengthened by the addition of one apical $\text{Re}(2)(\text{CO})_3$ group with a σ -, π -bonding pattern as in (I) and somewhat reduced by that of one apical

AuPPh_3 group with a predominant σ -bonding pattern as in (II) (Owen, 1988). In the case of the reinforcement of the π -bonding system it is extended through the apical $\text{Re}(2)$ atom, and has an average $\text{Re}(2)$ —Re bond length of 2.931 (1) Å equivalent to the range of such π metal—metal bond lengths in $\text{Re}_4(\text{CO})_{12}(\mu\text{-H})_4 [2.886(1)–2.945(1) \text{ \AA}]$. It is evident from these findings in (I) that the related π -bonding pattern in resonance structure (i) is modified through a strengthened π -delocalization effect originating from three bridging diphenylphosphido groups and is like a superposition of the resonance structures (i) and (ii). In the other case, the π -delocalization effect is weakened, since one $\mu_3\text{-H}$ atom of smaller atomic size is replaced by a larger $\mu_3\text{-Au}$ atom in (II). The mean Re—Au bond length of 2.854 (2) Å in (II) is in accordance with that of 2.796 (2) Å in the valence electron saturated cluster $\text{Re}_2(\text{CO})_8(\mu\text{-PPh}_2)(\text{AuPPh}_3)$ (Haupt, Heinekamp & Flörke, 1990).

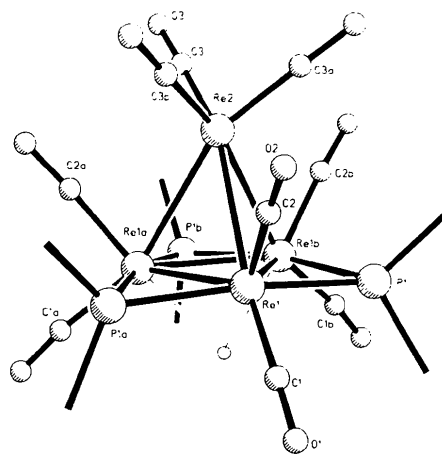


Fig. 1. General view of the molecule of (I). (Phenyl groups omitted for clarity.)

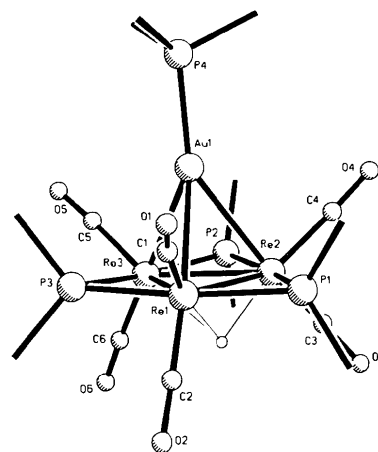


Fig. 2. General view of the molecule of (II). (Phenyl groups omitted for clarity.)

* Lists of structure factors, anisotropic temperature factors, H-atom coordinates and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54238 (54 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (I)

| | x | y | z | $U_{\text{iso}}/U_{\text{eq}}$ |
|-------|-----------|-----------|-----------|--------------------------------|
| Re(1) | 2332 (1) | 6311 (1) | -48 (1) | 36 (1)* |
| Re(2) | 3333 | 6667 | -928 (1) | 56 (1)* |
| P(1) | 2709 (3) | 7792 (3) | 11 (2) | 46 (3)* |
| C(1) | 1343 (15) | 5949 (15) | 380 (7) | 69 (6) |
| O(1) | 821 (12) | 5772 (12) | 666 (6) | 100 (6) |
| C(2) | 1549 (13) | 6037 (13) | -555 (7) | 57 (5) |
| O(2) | 1023 (10) | 5848 (10) | -847 (5) | 81 (5) |
| C(3) | 4238 (16) | 6853 (16) | -1315 (8) | 77 (7) |
| O(3) | 4821 (13) | 6958 (12) | -1557 (6) | 111 (6) |
| C(11) | 2441 (10) | 8358 (9) | -432 (4) | 56 (5) |
| C(12) | 3076 | 9200 | -555 | 76 (7) |
| C(13) | 2905 | 9652 | -903 | 105 (9) |
| C(14) | 2099 | 9262 | -1129 | 112 (10) |
| C(15) | 1464 | 8420 | -1006 | 125 (11) |
| C(16) | 1635 | 7968 | -658 | 78 (7) |
| C(21) | 2461 (9) | 8138 (9) | 572 (4) | 50 (5) |
| C(22) | 2081 | 8659 | 580 | 89 (8) |
| C(23) | 1900 | 8915 | 1014 | 125 (11) |
| C(24) | 2100 | 8650 | 1439 | 95 (8) |
| C(25) | 2480 | 8128 | 1430 | 90 (8) |
| C(26) | 2661 | 7872 | 996 | 75 (7) |

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (II)

| | x | y | z | $U_{\text{iso}}/U_{\text{eq}}$ |
|-------|-----------|-----------|-----------|--------------------------------|
| Au(1) | 7533 (1) | 5567 (1) | 5141 (1) | 50 (1)* |
| Re(1) | 7817 (1) | 6160 (1) | 4130 (1) | 46 (1)* |
| Re(2) | 7258 (1) | 5141 (1) | 4035 (1) | 45 (1)* |
| Re(3) | 8529 (1) | 5241 (1) | 4400 (1) | 48 (1)* |
| P(1) | 6732 (4) | 5979 (4) | 3828 (4) | 45 (6)* |
| P(2) | 7929 (5) | 4407 (4) | 4336 (4) | 52 (6)* |
| P(3) | 8895 (4) | 6158 (4) | 4523 (4) | 51 (6)* |
| P(4) | 7212 (5) | 5587 (4) | 6092 (4) | 53 (6)* |
| C(1) | 7555 (19) | 6762 (14) | 4509 (15) | 63 (11) |
| O(1) | 7293 (12) | 7178 (10) | 4699 (10) | 70 (8) |
| C(2) | 8077 (20) | 6499 (17) | 3522 (20) | 80 (14) |
| O(2) | 8267 (14) | 6754 (12) | 3095 (13) | 96 (10) |
| C(3) | 7054 (18) | 4768 (16) | 3428 (18) | 70 (12) |
| O(3) | 6885 (12) | 4557 (10) | 2961 (11) | 71 (8) |
| C(4) | 6514 (18) | 4827 (15) | 4350 (16) | 64 (10) |
| O(4) | 6045 (14) | 4604 (11) | 4578 (12) | 88 (9) |
| C(5) | 9004 (20) | 4995 (17) | 5049 (20) | 83 (14) |
| O(5) | 9317 (14) | 4873 (12) | 5434 (13) | 98 (10) |
| C(6) | 9177 (20) | 5018 (17) | 3921 (18) | 78 (13) |
| O(6) | 9581 (12) | 4868 (11) | 3590 (12) | 82 (9) |
| C(11) | 6052 (9) | 6249 (9) | 4247 (10) | 47 (9) |
| C(12) | 5987 | 6078 | 4804 | 68 (12) |
| C(13) | 5485 | 6286 | 5137 | 83 (13) |
| C(14) | 5048 | 6666 | 4914 | 65 (11) |
| C(15) | 5113 | 6837 | 4357 | 65 (11) |
| C(16) | 5615 | 6629 | 4024 | 70 (12) |
| C(21) | 6507 (10) | 6148 (9) | 3118 (7) | 44 (8) |
| C(22) | 6665 | 6653 | 2881 | 52 (10) |
| C(23) | 6429 | 6793 | 2350 | 97 (15) |
| C(24) | 6035 | 6427 | 2056 | 75 (13) |
| C(25) | 5876 | 5921 | 2292 | 78 (13) |
| C(26) | 6112 | 5782 | 2823 | 57 (11) |
| C(31) | 8273 (10) | 3860 (9) | 3821 (10) | 59 (11) |
| C(32) | 8439 | 4036 | 3282 | 63 (11) |
| C(33) | 8730 | 3672 | 2905 | 86 (14) |
| C(34) | 8854 | 3133 | 3068 | 77 (12) |
| C(35) | 8688 | 2958 | 3607 | 60 (11) |
| C(36) | 8398 | 3322 | 3984 | 70 (12) |
| C(41) | 7673 (14) | 4019 (11) | 4957 (10) | 76 (13) |
| C(42) | 7955 | 4093 | 5485 (10) | 96 (16) |
| C(43) | 7717 | 3804 | 5947 (10) | 83 (12) |
| C(44) | 7195 | 3442 | 5882 (10) | 111 (16) |

Table 2 (cont.)

| | x | y | z | $U_{\text{iso}}/U_{\text{eq}}$ |
|-------|-----------|-----------|-----------|--------------------------------|
| C(45) | 6913 | 3369 | 5354 (10) | 121 (19) |
| C(46) | 7151 | 3658 | 4891 (10) | 95 (15) |
| C(51) | 9573 (12) | 6463 (12) | 4135 (12) | 62 (11) |
| C(52) | 9729 | 6237 | 3613 | 83 (14) |
| C(53) | 10273 | 6424 | 3318 | 98 (14) |
| C(54) | 10661 | 6838 | 3545 | 94 (19) |
| C(55) | 10506 | 7064 | 4066 | 83 (14) |
| C(56) | 9962 | 6877 | 4361 | 75 (12) |
| C(61) | 9062 (13) | 6391 (10) | 5253 (8) | 67 (12) |
| C(62) | 8637 | 6735 | 5545 | 60 (11) |
| C(63) | 8794 | 6910 | 6086 | 82 (13) |
| C(64) | 9376 | 6740 | 6336 | 73 (12) |
| C(65) | 9801 | 6397 | 6044 | 92 (15) |
| C(66) | 9644 | 6222 | 5503 | 88 (14) |
| C(71) | 7716 (11) | 5174 (9) | 6558 (9) | 54 (10) |
| C(72) | 7451 | 4785 | 6921 | 53 (9) |
| C(73) | 7858 | 4485 | 7277 | 87 (14) |
| C(74) | 8530 | 4576 | 7269 | 70 (12) |
| C(75) | 8795 | 4965 | 6906 | 98 (15) |
| C(76) | 8388 | 5265 | 6551 | 69 (12) |
| C(81) | 7220 (11) | 6278 (7) | 6393 (10) | 61 (10) |
| C(82) | 7025 | 6697 | 6032 | 63 (11) |
| C(83) | 6995 | 7236 | 6227 | 84 (14) |
| C(84) | 7159 | 7354 | 6783 | 70 (12) |
| C(85) | 7354 | 6935 | 7144 | 75 (12) |
| C(86) | 7384 | 6397 | 6949 | 80 (13) |
| C(91) | 6386 (9) | 5318 (10) | 6196 (11) | 56 (10) |
| C(92) | 6215 | 4878 | 5852 | 69 (11) |
| C(93) | 5579 | 4676 | 5859 | 78 (13) |
| C(94) | 5113 | 4914 | 6209 | 85 (14) |
| C(95) | 5283 | 5355 | 6553 | 86 (14) |
| C(96) | 5920 | 5556 | 6546 | 81 (13) |

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond lengths (\AA) and angles ($^\circ$)

| (I) | | | |
|---------------------|-----------|--------------------|-----------|
| Re(1)—Re(1) | 2.708 (1) | Re(1)—Re(2) | 2.931 (1) |
| Re(1)—P(1) | 2.377 (5) | Re(1)—P(1a) | 2.381 (5) |
| Re(1a)—Re(1)—Re(1b) | 60.0 (1) | Re(1a)—Re(1)—Re(2) | 62.5 (1) |
| Re(1a)—Re(1)—P(1) | 115.2 (1) | Re(1b)—Re(1)—P(1) | 55.4 (1) |
| Re(1a)—Re(1)—P(1a) | 55.2 (1) | Re(2)—Re(1)—P(1) | 90.8 (1) |
| P(1)—Re(1)—P(1a) | 167.6 (2) | Re(1)—Re(2)—Re(1a) | 55.0 (1) |
| Re(1)—P(1)—Re(1a) | 69.4 (2) | | |
| (II) | | | |
| Au(1)—Re(1) | 2.865 (2) | Au(1)—Re(2) | 2.884 (2) |
| Au(1)—Re(3) | 2.814 (2) | Re(1)—Re(2) | 2.748 (2) |
| Re(1)—Re(3) | 2.752 (2) | Re(2)—Re(3) | 2.757 (2) |
| Re(1)—Au(1)—Re(2) | 57.1 (1) | Re(1)—Au(1)—Re(3) | 58.0 (1) |
| Re(2)—Au(1)—Re(3) | 57.8 (1) | Au(1)—Re(1)—Re(2) | 61.8 (1) |
| Au(1)—Re(1)—Re(3) | 60.1 (1) | Re(2)—Re(1)—Re(3) | 60.2 (1) |
| Au(1)—Re(2)—Re(1) | 61.1 (1) | Au(1)—Re(2)—Re(3) | 59.8 (1) |
| Re(1)—Re(2)—Re(3) | 60.0 (1) | Au(1)—Re(3)—Re(1) | 61.9 (1) |
| Au(1)—Re(3)—Re(2) | 62.3 (1) | Re(1)—Re(3)—Re(2) | 59.8 (1) |

The cluster in (II), therefore, represents a metal-atom tetrahedron with π delocalization restricted on the plane of the $\text{Re}_3(\mu\text{-PPh}_2)_3$ ring. This means that one way to the resonance hybrid structure (ii) is the substitution of a transition-metal atom by a metal atom with a predominant σ -bonding pattern like AuPPh₃. The first known compound of this type was

the anion $\text{Re}_3(\text{CO})_9(\mu\text{-H})_3(\mu_3\text{-AuPPh}_3)^-$ (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 π -delocalization bonding effect in the Re—Re triangle more than $\mu\text{-H}$ 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

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Abstract. $[\text{C}_{28}\text{H}_{32}\text{Fe}_2\text{N}_6\text{O}_5](\text{ClO}_4)_2 \cdot 0.9(\text{C}_3\text{H}_6\text{O})$, $M_r = 889.66$, triclinic, $P\bar{1}$, $a = 13.601$ (3), $b = 13.966$ (3), $c = 12.341$ (3) Å, $\alpha = 100.10$ (2), $\beta = 99.56$ (2), $\gamma = 115.19$ (2)°, $V = 2010.6$ Å³, $Z = 2$, $D_x = 1.46$ g cm⁻³, $\text{Mo } K\alpha$, $\lambda = 0.7093$ Å, $\mu = 9.12$ cm⁻¹, $F(000) = 915.2$, $T = 296$ K, final $R = 0.057$ 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 (μ -oxo)bis(μ -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 (μ -oxo)bis(μ -carboxylato) core units and

- ### References
- BERINGHELLI, T., CIANI, G., D'ALFONSO, G., DE MALDE, V. & FRENI, M. (1986). *J. Chem. Soc. Chem. Commun.* pp. 735–737.
 CHURCHILL, M. R., AMON, K. N. & WASSERMANN, H. J. (1981). *Inorg. Chem.* **20**, 1609–1611.
 HAUPT, H.-J., BALSAA, P. & FLÖRKE, U. (1988). *Inorg. Chem.* **27**, 280–286.
 HAUPT, H.-J., FLÖRKE, U. & BALSAA, P. (1988). *Acta Cryst.* **C44**, 61–63.
 HAUPT, H.-J., HEINEKAMP, C. & FLÖRKE, U. (1990). *Inorg. Chem.* **29**, 2955–2963.
 HENLY, J. T. (1989). *Coord. Chem. Rev.* **93**, 269–295.
 OWEN, S. M. (1988). *Polyhedron*, **7**, 253–283.
 SCHNIEDER, H. (1990). Dissertation, pp. 126, 131. Univ. of Paderborn, Germany.
 SHELDRIK, G. M. (1988). *SHELXTL-Plus88. Structure Determination Software Programs*. Nicolet Instrument Corporation, Madison, Wisconsin, USA.
 WILSON, R. D. & BAU, R. (1976). *J. Am. Chem. Soc.* **98**, 4687–4689.

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 $[\text{Fe}_2\text{O}(\text{bpma})_2(\mu\text{-O}_2\text{CCH}_3)_2](\text{ClO}_4)_2 \cdot 0.9(\text{C}_3\text{H}_6\text{O})$, 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, $0.28 \times 0.32 \times 0.32$ mm. Enraf-Nonius CAD-4 dif-

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