Contribution from the Department of Inorganic and Physical Chemistry,
Indian Institute of Science, Bangalore 560 012, India

Diruthenium(III) Compounds, $Ru_2O(O_2CAr)_2(MeCN)_4(PPh_3)_2(ClO_4)_2 \cdot H_2O$ and $Ru_2O(O_2CAr)_4(PPh_3)_2$, with an $\{Ru_2(\mu\text{-}O)(\mu\text{-}O_2CAr)_2{}^{2+}\}$ Core as Model Systems for the Diiron Centers in Hemerythrin

Birinchi K. Das and Akhil R. Chakravarty*

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Diruthenium(III) compounds, $Ru_2O(O_2CAr)_2(MeCN)_4(PPh_3)_2(ClO_4)_2 \cdot H_2O$ (**1**) and $Ru_2O(O_2CAr)_4(PPh_3)_2$ (**2**) (Ar = Ph, C_6H_4-*p*-OMe), were prepared by reacting $Ru_2Cl(O_2CAr)_4$ and PPh_3 in MeCN and characterized by analytical and spectral data. The molecular structures of **1** with Ar = Ph and of **2** with Ar = C_6H_4-*p*-OMe were determined by X-ray crystallography. Crystal data for $Ru_2O(O_2CPh)_2(MeCN)_4(PPh_3)_2(ClO_4)_2 \cdot H_2O$ (**1a**): monoclinic, *C*2/*c*, $a = 27.722$ (3) Å, $b = 10.793$ (2) Å, $c = 23.445$ (2) Å, $\beta = 124.18$ (1)°, $V = 5803$ Å^3, and $Z = 4$. Crystal data for $Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_4(PPh_3)_2$ (**2b**): orthorhombic, *Pnna*, $a = 22.767$ (5) Å, $b = 22.084$ (7) Å, $c = 12.904$ (3) Å, $V = 6488$ Å^3; and $Z = 4$. Both **1** and **2** have an $\{Ru_2O(O_2CAr)_2{}^{2+}\}$ core that is analogous to the diiron core present in the oxidized form of the nonheme respiratory protein hemerythrin. The Ru-Ru distances of 3.237 (1) and 3.199 (1) Å observed in **1** and **2**, respectively, are similar to the M-M distances known in other model systems. The essentially diamagnetic nature of **1** and **2** is due to the presence of two strongly interacting $t_{2g}{}^5$ Ru^{III} centers. The intense colors of **1** (blue) and **2** (purple) are due to the charge-transfer transition involving an $\{Ru_2(\mu\text{-}O)^{4+}\}$ moiety. The presence of labile MeCN and carboxylato ancillary ligands in **1** and **2**, respectively, makes these systems reactive toward amine and heterocyclic bases.

Introduction

Modeling the diiron core, $\{Fe_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2{}^{2+}\}$, present[1] in iron-containing nonheme proteins has received considerable current interest[2-4] in the synthesis of simple transition-metal compounds with an analogous core structure. The studies[5-16] made on several systems suggest the possibility of developing a parallel chemistry of diruthenium compounds, which are, at present, limited[5,6] to a few species containing pyridine or the tridentate triazacyclononane (L) as ancillary ligand(s). Such a development will be particularly useful since the chemistry of the oxo-centered triruthenium compounds with a basic iron acetate structure is well explored.[17-27] The present work stems from our efforts to prepare oxo-bridged diruthenium species using a Ru-Ru multiple-bonded compound, $Ru_2Cl(O_2CAr)_4$, as a precursor complex.

Earlier studies have shown[23] that PPh_3 reacts with $Ru_2Cl(O_2CMe)_4$ to form only $Ru_2O(O_2CMe)_4(PPh_3)_2$, which is proposed to have a μ-oxo and two trans-oriented acetato bridging ligands. On reinvestigation of the reaction using arenecarboxylato species $Ru_2Cl(O_2CAr)_4$ in MeCN, we are, however, successful in isolating two types of diruthenium(III) compounds. It is interesting to note that a similar reaction between $Ru_2Cl(ArCONH)_4$ and PPh_3 is known[28] to form a different type of product. Herein we report the syntheses, properties, and molecular structures of $Ru_2O(O_2CAr)_2(MeCN)_4(PPh_3)_2(ClO_4)_2 \cdot H_2O$ (**1a**, Ar = Ph; **1b**, Ar = C_6H_4-*p*-OMe) and $Ru_2O(O_2CAr)_4(PPh_3)_2$ (**2a**, Ar = Ph; **2b**, Ar

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= C_6H_4-*p*-OMe). The compounds **1a** and **2b** are structurally characterized by X-ray crystallography.

Experimental Section

Materials and Methods. The starting complexes $Ru_2Cl(O_2CPh)_4$ and $Ru_2Cl(O_2CC_6H_4\text{-}p\text{-}OMe)_4$ were prepared by following a literature procedure.[29] All reagents were obtained from commercial sources and used without further purification.

Preparation of $Ru_2O(O_2CPh)_2(MeCN)_4(PPh_3)_2(ClO_4)_2{\cdot}H_2O$ (1a). To a stirred solution of 0.37 g (1.4 mmol) of PPh_3 in 20 mL of MeCN was added 0.5 g (0.7 mmol) of $Ru_2Cl(O_2CPh)_4$. The solution was heated at ca. 50 °C for 30 min under stirring conditions. It was then cooled to room temperature, filtered, and concentrated to a volume of ca. 5 mL. This solution was passed through a column packed with silica gel in C_6H_6. The column was eluted with a C_6H_6–MeCN mixture, gradually increasing the percentage of the latter. Washing was stopped when the eluate was colorless and showed no spot for PPh_3 in TLC. The column at this stage looked blue. The blue compound was then eluted with a 1:3 (v/v) MeOH–MeCN mixture. The blue solution was immediately evaporated to dryness, the solid was redissolved in MeCN, and the mixture was finally treated with $NaClO_4$. The compound was precipitated by adding water, filtered out, and washed, first with water and then with diethyl ether. The dark blue powder was dried in vacuo over P_4O_{10}. Yield: ca. 35%. Anal. Calcd for $C_{58}H_{54}N_4O_{14}P_2Cl_2Ru_2$ (**1a**): C, 50.95; H, 3.98; N, 4.09. Found: C, 51.30; H, 3.63; N, 4.82. Electronic spectroscopy (in MeCN): λ_{max} 579 nm (ϵ 9500 $M^{-1}\ cm^{-1}$). Conductivity (MeCN, 10^{-3} M solution at 25 °C): Λ_M 240 mho $cm^2\ mol^{-1}$. IR (Nujol mull): $\nu(ClO_4^-)$ 1110, $\nu(C{\equiv}N)$ 2290 cm^{-1}.

The crystal used for X-ray diffraction experiments was found to contain four molecules of water per unit cell. These, however, were not detected during spectroscopic investigations.

Preparation of $[Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_2(MeCN)_4(PPh_3)_2](ClO_4)_2{\cdot}H_2O$ (1b). This compound was prepared by a procedure similar to that given above for **1a**. Yield: ca. 30%. Anal. Calcd for $C_{60}H_{58}N_4O_{16}P_2Cl_2Ru_2$: C, 50.05; H, 4.07; N, 3.92. Found: C, 50.47; H, 4.54; N, 3.34. Electronic spectroscopy (in MeCN): λ_{max} 581 nm (ϵ 10 600 $M^{-1}\ cm^{-1}$). ^1H NMR (CD_3CN, at 22 °C, 270 MHz; δ (ppm, from Me_4Si)): 6.79–7.60 (m), 3.78 (s), 2.19 (s), 1.99 (s) (m, multiplet; s, singlet). Conductivity (MeCN, 10^{-3} M solution at 25 °C): Λ_M 250 mho $cm^2\ mol^{-1}$. IR (Nujol mull): $\nu(ClO_4^-)$ 1090, $\nu(C{\equiv}N)$ 2330 cm^{-1}.

Preparation of $[Ru_2O(O_2CPh)_4(PPh_3)_2]$ (2a). To a solution of 0.74 g (2.82 mmol) of PPh_3 in 50 mL of MeCN was added 1.0 g (1.4 mmol) of $Ru_2Cl(O_2CPh)_4$, and the mixture was heated to reflux for 1 h. The solution was then filtered, and the filtrate was kept at 5 °C for 12 h. The crystalline product precipitated was washed several times with MeCN and finally dried in vacuo over P_4O_{10}. Yield: ca. 45%. Anal. Calcd for $C_{64}H_{50}O_9P_2Ru_2$: C, 62.57; H, 4.08. Found: C, 62.89; H, 4.36. Electronic spectroscopy (in $CHCl_3$): λ_{max} 562 nm.[23]

Preparation of $[Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_4(PPh_3)_2]$ (2b). This compound was prepared by using a method similar to that given above for **2a**. From the crystalline product obtained, single crystals suitable for X-ray investigations were chosen. Yield: 47%. Anal. Calcd for $C_{68}H_{58}O_{13}P_2Ru_2$: C, 60.56; H, 4.34. Found: C, 60.26; H, 4.83. Electronic spectroscopy (in $CHCl_3$): λ_{max} 563 nm (ϵ 6950 $M^{-1}\ cm^{-1}$). ^1H NMR ($CDCl_3$, at 22 °C, 270 MHz; δ (ppm, from Me_4Si)): 6.39–7.84 (m), 3.82 (s), 3.63 (s).

Conversion of 2 to 1. The crystalline products **2** convert readily in MeCN to give a blue solution upon addition of $HClO_4$ diluted with MeCN. These blue solutions give compounds **1a** and **1b** upon precipitation by diethyl ether. The conversion was found to be quantitative.

Measurements. The elemental analyses were obtained from RSIC, Punjab University. IR spectra were taken in Nujol mulls (4000–200 cm^{-1}) with a Perkin-Elmer 597 infrared spectrophotometer. Electronic spectra were recorded with a Hitachi U-3400 spectrophotometer. The ^1H NMR spectra were recorded with a Bruker WH-270 spectrometer. Conductivity measurements were made with a Century CC603 digital conductivity meter.

X-ray Crystallographic Procedures

Collection and Reduction of Data. Trapezoid crystals of $[Ru_2O(O_2CPh)_2(MeCN)_4(PPh_3)_2](ClO_4)_2{\cdot}H_2O$ (**1a**) look dark brown against transmitted light. The crystal used for data collection was obtained from a solution of the compound in a MeCN–H_2O mixture, layered above water containing dissolved $NaClO_4$. The quality of the crystal was checked by rotation and Weissenberg photographic techniques. The crystal, fixed on a glass fiber, was then mounted on an Enraf-Nonius CAD-4 four-circle diffractometer. The unit cell parameters were obtained by a least-squares fit of 25 reflections (16° < 2θ < 31°). Systematic absences observed are as follows: hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$. These may either mean space group Cc or $C2/c$. That it belongs to $C2/c$ (C_{2h}^6, No. 15) was confirmed by the successful solution and refinement of the structure.

Table I. Crystallographic Details for $Ru_2O(O_2CPh)_2(MeCN)_4(PPh_3)_2(ClO_4)_2{\cdot}H_2O$ (**1a**) and $Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_4(PPh_3)_2$ (**2b**)

	1a	**2b**
formula	$C_{58}H_{52}N_4O_5P_2Ru_2$-$(ClO_4)_2{\cdot}H_2O$	$C_{68}H_{58}O_{13}P_2Ru_2$
fw	1366	1347.32
space group	$C2/c$ (No. 15)	$Pnna$ (No. 52)
a, Å	27.722 (3)	22.767 (5)
b, Å	10.793 (2)	22.084 (7)
c, Å	23.445 (2)	12.904 (3)
β, deg	124.18 (1)	
V, $Å^3$	5803	6488
Z	4	4
ρ_{calcd}, g cm^{-3}	1.56	1.38
μ(Mo Kα), cm^{-1}	6.04	4.61
radiation (λ, Å)	Mo Kα (0.7107)	Mo Kα (0.7107)
data collcn instrum	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
scan method	ω	ω–2θ
data colln range (2θ), deg	4–50	4–50
no. of unique data with $F_o > 3\sigma(F_o)$	3570	3294
no. of params refined	359	380
R^a ($R_w{}^b$)	0.079 (0.072)	0.065 (0.055)
g	0.001	0.000 000
largest shift/esd	0.109	0.024
largest peak in the final diff Fourier	0.77	0.72

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = k/[\sigma^2(F_o) + gF_o^2]$.

The purple crystal of $[Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_4(PPh_3)_2]$ (**2b**) mounted on a glass fiber was examined by both photographic and diffractometer techniques. The unit cell parameters obtained from photographic methods tallied well with those found by using a least-squares fit of 25 reflections (19° < 2θ < 28°) on a CAD-4 diffractometer. Systematic absences observed are as follows: $0kl$, $k + l = 2n + 1$; $h0l$, $h + l = 2n + 1$; $hk0$, $h = 2n + 1$. These unequivocally give the space group $Pnna$ (D_{2h}^6, No. 52).

The unit cell parameters and information related to intensity data collection are summarized in Table I. Intensity data were corrected for Lorentz and polarization effects. No absorption corrections were made on the data.

Structure Solution and Refinement. Both the structures were solved and refined by using the SHELX-76 program[30a] in the DEC-1090 computer system at the Indian Institute of Science. Metal positions for **1a** and **2b** were obtained from Patterson syntheses. All the other atoms were located in successive difference Fourier maps. The hydrogen atoms were not located. For **1a**, except for the bridging μ_2-oxygen atom, the four oxygen atoms in ClO_4^-, and the oxygen atom in H_2O, all the other atoms were refined anisotropically. For **2b**, only the bridging μ_2-oxygen atom was left at the isotropic stage. The ClO_4^- group in **1a** was found to be disordered. For this group and for H_2O, the oxygen atom site occupancies were refined and ultimately fixed. In ClO_4^- the disposition of three of the oxygen atoms were modeled to have been disordered in the ratio 7:3. The carbon atoms of one of the MeCN ligands in **1a** were found to have high thermal parameters. The terminal carbon atom particularly showed a diffused electron density. However, the nitrogen atom of the same MeCN ligand refined well, giving the expected thermal parameter. The least-squares refinement converged to R indices listed in Table I. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = k/[\sigma^2(F_o) + g(F_o)^2]$. The g values observed for structures **1a** and **2b** are also given in Table I.

The atomic coordinates of **1a** and **2b** are presented in Tables II and III, respectively. Tables IV and V list the selected bond distances and angles for **1a** and **2b**, respectively. Complete tables of bond lengths, bond angles, and anisotropic thermal parameters and structure factor data for

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Table II. Fractional Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3) with Their Estimated Standard Deviations for $Ru_2O(MeCN)_4(O_2CPh)_2(PPh_3)_2(ClO_4)_2 \cdot H_2O$

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Ru	4345 (1)	4863 (1)	1808 (1)	35 (1)
P(1)	4200 (1)	3292 (2)	1048 (1)	37 (1)
O(1)	5000	3992 (6)	2500	36 (1)*
N(1)	3792 (3)	4063 (6)	2019 (3)	43 (3)
N(2)	3622 (3)	5910 (7)	1078 (3)	53 (3)
O(11)	4413 (2)	6353 (5)	2433 (3)	46 (3)
O(12)	4775 (2)	5918 (5)	1522 (3)	43 (3)
C(11)	4086 (3)	1731 (7)	1236 (4)	42 (4)
C(12)	3892 (4)	800 (9)	732 (5)	54 (5)
C(13)	3866 (4)	−427 (9)	893 (6)	64 (5)
C(14)	4009 (4)	−731 (9)	1547 (6)	68 (6)
C(15)	4198 (4)	176 (6)	2049 (5)	64 (5)
C(16)	4241 (3)	1426 (8)	1903 (5)	51 (4)
C(21)	4840 (3)	3158 (8)	1013 (4)	42 (4)
C(22)	4999 (4)	4177 (9)	775 (4)	49 (4)
C(23)	5507 (4)	4139 (11)	808 (5)	68 (6)
C(24)	5871 (5)	3078 (13)	1075 (6)	78 (7)
C(25)	5721 (4)	2080 (11)	1304 (5)	70 (6)
C(26)	5199 (4)	2101 (9)	1285 (4)	52 (4)
C(31)	3568 (3)	3553 (8)	156 (4)	48 (4)
C(32)	3629 (4)	3602 (9)	−396 (4)	59 (5)
C(33)	3141 (5)	3918 (11)	−1052 (5)	79 (6)
C(34)	2612 (5)	4112 (11)	−1147 (6)	84 (6)
C(35)	2542 (5)	4005 (11)	−603 (7)	86 (7)
C(36)	3035 (4)	3707 (9)	69 (5)	61 (5)
C(30)	3264 (8)	6327 (17)	734 (9)	152 (14)
C(40)	2658 (13)	7167 (31)	200 (19)	287 (29)
C(10)	3446 (4)	3814 (9)	2102 (5)	53 (4)
C(20)	3000 (5)	3494 (12)	2238 (6)	87 (7)
C(41)	5260 (3)	6471 (7)	1920 (4)	38 (4)
C(42)	5067 (4)	7704 (8)	900 (5)	56 (5)
C(43)	5265 (6)	8501 (10)	597 (6)	80 (7)
C(44)	5847 (6)	8878 (11)	977 (7)	79 (7)
C(45)	5464 (4)	7342 (7)	1593 (4)	43 (4)
C(46)	6225 (5)	8524 (11)	1653 (6)	77 (7)
C(47)	6030 (4)	7737 (9)	1970 (5)	60 (5)
Cl(1)	2278 (2)	6478 (4)	1440 (3)	139 (3)
O(22)	2777 (8)	6063 (18)	1541 (9)	139 (5)*
O(23)	2339 (7)	7816 (15)	1560 (8)	127 (4)*
O(21)	2212 (6)	6016 (15)	2025 (7)	194 (5)*
O(24)	1778 (7)	6189 (14)	868 (8)	124 (4)*
O(25)	1915 (13)	7418 (29)	783 (15)	101 (8)*
O(26)	2459 (16)	5474 (37)	1018 (20)	131 (11)*
O(27)	2728 (23)	6845 (56)	1262 (27)	196 (21)*
O(50)	1481 (7)	8406 (16)	102 (8)	95 (4)*

[a] Starred U_{11} values are for atoms that were refined isotropically. The atoms refined with site occupancy factors (sof) other than 1.0 are the following: O(22), O(23), O(24), (sof 0.7); O(25), O(26), O(27) (sof 0.3); O(50) (sof 0.5). $U_{iso}(eq) = [\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j]/3$.

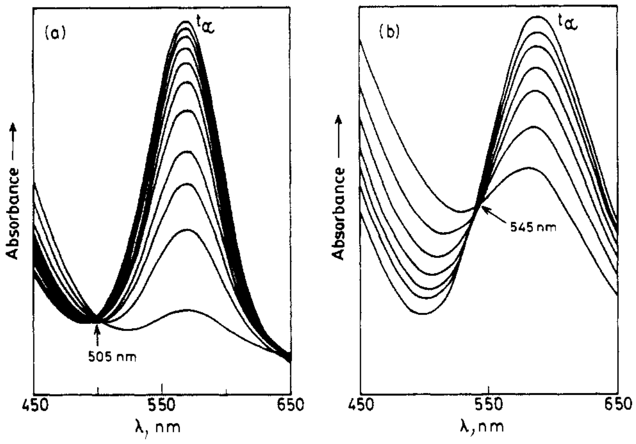

Figure 1. Visible absorption spectra at 25 °C in (a) MeOH and (b) MeCN, showing the progress of the reaction between $Ru_2Cl(O_2CC_6H_4\text{-}p\text{-}OMe)_4$ and PPh_3.

Table III. Fractional Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3) with Their Estimated Standard Deviations for $Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_4(PPh_3)_2$

atom	*x*	*y*	*z*	U_{eq}, Å^2
Ru	3681 (1)	3025 (1)	3354 (1)	26 (1)
P(1)	4423 (1)	3004 (1)	4522 (1)	29 (1)
O(1)	4098 (3)	2500	2500	25 (1)[a]
O(11)	2973 (2)	3165 (2)	2282 (3)	32 (1)
O(12)	3213 (2)	2385 (2)	4133 (3)	33 (2)
O(21)	3334 (2)	3883 (2)	3953 (3)	35 (2)
O(22)	3989 (2)	3838 (2)	2735 (3)	35 (2)
C(11)	2946 (3)	3042 (4)	1324 (4)	30 (2)
C(12)	2580 (3)	3447 (3)	669 (4)	31 (2)
C(13)	2488 (4)	3315 (4)	−383 (5)	42 (3)
C(14)	2170 (4)	3716 (4)	−992 (5)	48 (3)
C(15)	1938 (4)	4256 (4)	−541 (6)	50 (3)
C(16)	2018 (4)	4382 (4)	488 (5)	45 (3)
C(17)	2342 (3)	3972 (4)	1085 (5)	41 (3)
O(13)	1638 (3)	4614 (3)	−1227 (4)	72 (3)
C(18)	1425 (5)	5193 (5)	−341 (8)	92 (5)
C(21)	3658 (3)	4152 (3)	3322 (4)	35 (2)
C(22)	3665 (4)	4824 (3)	3282 (5)	41 (2)
C(23)	4096 (4)	5131 (4)	2689 (5)	50 (3)
C(24)	4095 (5)	5764 (4)	2673 (6)	63 (4)
C(25)	3683 (4)	6081 (3)	3229 (6)	56 (3)
C(26)	3257 (5)	5784 (5)	3808 (7)	73 (4)
C(27)	3258 (4)	5146 (4)	3857 (7)	63 (4)
O(23)	3718 (4)	6692 (3)	3180 (5)	84 (3)
C(28)	3294 (6)	7048 (5)	3738 (10)	105 (6)
C(31)	4207 (3)	3171 (3)	5864 (4)	33 (2)
C(32)	3636 (4)	3255 (4)	6090 (5)	56 (3)
C(33)	3444 (5)	3348 (5)	7129 (6)	68 (4)
C(34)	3879 (5)	3359 (4)	7887 (5)	60 (4)
C(35)	4444 (4)	3290 (4)	7661 (5)	50 (3)
C(36)	4629 (4)	3189 (3)	6643 (5)	45 (3)
C(41)	4821 (3)	2291 (3)	4634 (4)	34 (2)
C(42)	4532 (4)	1758 (3)	4406 (5)	42 (3)
C(43)	4819 (4)	1191 (4)	4547 (5)	56 (3)
C(44)	5385 (5)	1180 (5)	4895 (6)	64 (4)
C(45)	5684 (4)	1727 (5)	5129 (6)	64 (4)
C(46)	5410 (3)	2279 (4)	4973 (6)	50 (3)
C(51)	4996 (3)	3543 (4)	4184 (5)	35 (2)
C(52)	5112 (4)	4060 (4)	4749 (5)	57 (3)
C(53)	5539 (5)	4468 (5)	4415 (7)	73 (4)
C(54)	5851 (5)	4348 (6)	3500 (7)	76 (4)
C(55)	5725 (5)	3828 (6)	2916 (7)	75 (4)
C(56)	5299 (5)	3434 (5)	3257 (6)	59 (3)

[a] U_{11} value for atom that was refined isotropically. U_{eq} values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $U_{iso}(eq) = [\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j]/3$.

1a and **2b** are available as supplementary material. Figures 5 and 6 show the complete molecules of **1a** and **2b**, respectively. The perspective drawings of the molecules were obtained by using the PLUTO[30b] program.

Results and Discussion

Preparations. Compounds **1** and **2** were prepared in moderate yields by reacting $Ru_2Cl(O_2CAr)_4$ with PPh_3 in MeCN. The tetraarene carboxylato compounds were obtained[29] in quantitative yield by reacting $Ru_2Cl(O_2CMe)_4$ and $ArCO_2H$ in a refluxing H_2O–MeOH mixture. The purple compound **2** can be prepared by following a reported procedure.[23] In MeCN, however, the reaction proceeds smoothly to form a green solution from which the blue compound **1**, as a chloride salt, can be isolated by column chromatography. Compound **1** can also be isolated in a quantitative yield by adding $HClO_4$ to a solution of **2** in MeCN. Synthetic pathways are given in eqs 1–3. The source of oxygen

$$Ru_2Cl(O_2CAr)_4 + PPh_3 \xrightarrow{MeCN}$$
$$[\text{green solution}] \xrightarrow[\text{chromatography}]{\text{column}} \text{blue solution} \xrightarrow{NaClO_4} \mathbf{1} \quad (1)$$

$$Ru_2Cl(O_2CAr)_4 + PPh_3 \xrightarrow[\text{reflux}]{MeCN} \underset{\mathbf{2}}{Ru_2O(O_2CAr)_4(PPh_3)_2} \quad (2)$$

$$Ru_2O(O_2CAr)_4(PPh_3)_2 \xrightarrow[HClO_4]{MeCN}$$
$$\underset{\mathbf{1}}{Ru_2O(O_2CAr)_2(MeCN)_4(PPh_3)_2(ClO_4)_2 \cdot H_2O} \quad (3)$$

Table IV. Selected Bond Distances (Å) and Angles (deg) for $Ru_2O(O_2CPh)_2(MeCN)_4(PPh_3)_2(ClO_4)_2 \cdot H_2O$ (**1a**)

Ru–Ru′	3.237 (1)	Ru–P(1)	2.325 (2)
Ru–O(1)	1.872 (4)	Ru–N(1)	2.048 (9)
Ru–N(2)	2.090 (6)	Ru–O(11)	2.113 (6)
Ru–O(12)	2.015 (7)	P(1)–C(11)	1.814 (9)
P(1)–C(21)	1.826 (11)	P(1)–C(31)	1.846 (7)
N(1)–C(10)	1.115 (15)	N(2)–C(30)	0.969 (17)
C(10)–C(20)	1.479 (20)	C(30)–C(40)	1.688 (33)
O(11)–C(41)′	1.261 (9)	O(12)–C(41)	1.275 (8)
C(41)–C(45)	1.511 (15)		

P(1)–Ru–O(1)	87.9 (2)	P(1)–Ru–N(1)	92.7 (2)
P(1)–Ru–N(2)	95.4 (2)	P(1)–Ru–O(11)	175.4 (1)
P(1)–Ru–O(12)	92.1 (2)	O(1)–Ru–N(1)	94.1 (2)
O(1)–Ru–N(2)	176.7 (3)	O(1)–Ru–O(11)	96.7 (2)
O(1)–Ru–O(12)	96.1 (2)	N(1)–Ru–N(2)	85.5 (3)
N(1)–Ru–O(11)	86.5 (3)	N(1)–Ru–O(12)	168.9 (2)
N(2)–Ru–O(11)	80.0 (2)	N(2)–Ru–O(12)	84.1 (3)
O(11)–Ru–O(12)	87.9 (3)	Ru–O(1)–Ru′	119.7 (4)
Ru–N(1)–C(10)	168.3 (7)	Ru–N(2)–C(30)	174.5 (14)
N(1)–C(10)–C(20)	178.0 (9)	N(2)–C(30)–C(40)	173.8 (23)
Ru–P(1)–C(11)	118.0 (4)	Ru–P(1)–C(21)	109.8 (3)
Ru–P(1)–C(31)	113.7 (3)	Ru–O(11)–C(41)′	129.4 (6)
Ru–O(12)–C(41)	126.7 (6)	O(11)′–C(41)–O(12)	125.8 (8)

Table V. Selected Bond Distances (Å) and Angles (deg) for $Ru_2O(O_2CC_6H_4$-*p*-$OMe)_4(PPh_3)_2$ (**2b**)

Ru–Ru′	3.199 (1)	Ru–P(1)	2.264 (2)
Ru–O(1)	1.859 (3)	Ru–O(11)	2.148 (4)
Ru–O(12)	2.035 (4)	Ru–O(21)	2.193 (5)
Ru–O(22)	2.087 (4)	P(1)–C(31)	1.838 (6)
P(1)–C(41)	1.821 (8)	P(1)–C(51)	1.818 (8)
O(11)–C(11)	1.267 (7)	O(12)′–C(11)	1.267 (6)
O(21)–C(21)	1.249 (8)	O(22)–C(21)	1.274 (8)
C(11)–C(12)	1.486 (9)	C(21)–C(22)	1.485 (10)

P(1)–Ru–O(1)	90.1 (1)	P(1)–Ru–O(11)	172.8 (1)
P(1)–Ru–O(12)	92.8 (1)	P(1)–Ru–O(21)	93.0 (1)
P(1)–Ru–O(22)	91.2 (1)	O(11)–Ru–O(12)	91.4 (2)
O(11)–Ru–O(21)	80.4 (2)	O(11)–Ru–O(1)	95.2 (2)
O(12)–Ru–O(21)	103.8 (2)	O(12)–Ru–O(22)	164.3 (2)
O(12)–Ru–O(1)	97.3 (1)	O(21)–Ru–O(22)	60.8 (2)
O(21)–Ru–O(1)	158.6 (1)	O(22)–Ru–O(1)	97.9 (1)
Ru–O(1)–Ru′	118.7 (3)	Ru–P(1)–C(31)	115.0 (2)
Ru–P(1)–C(41)	116.2 (2)	Ru–P(1)–C(51)	111.3 (2)
Ru–O(11)–C(11)	129.3 (4)	Ru–O(12)–C(11)	122.5 (4)
Ru–O(21)–C(21)	92.4 (4)	O(11)–C(11)–O(12)′	126.1 (6)
O(21)–C(21)–O(22)	118.5 (6)		

in the formation of the oxo bridge could be H_2O present as an impurity in MeCN. The facile conversion of **2** to **1** (eq 3) indicates the lability of the two carboxylato ligands in **2**. A similar conversion of **1** to **2** is noticed when **1** is reacted with NaO_2CR in MeOH. Otherwise, **1**, which is unstable in solvents like C_6H_6, Me_2CO, CH_2Cl_2, $CHCl_3$, etc., converts to **2** to the extent of 30% when monitored by visible spectroscopy. When the reaction (eq 1) is followed over a period of time in MeOH and MeCN, the positions of the isosbestic points are found to be different, as shown in Figure 1. While it remains invariant in MeCN, a gradual shift is observed toward lower wavelength side in MeOH, indicating the formation of other species besides **1** and/or **2**. When the reactions are followed under pseudo-first-order conditions with $[Ru_2Cl(O_2CAr)_4] \ll [PPh_3]$, the observations are in agreement with our earlier report[31] showing that the final products obtained from alcoholic solvents, RCH_2OH, containing two β-hydrogen atoms are the pale yellow monomeric ruthenium carbonyl and hydrido compounds (vide infra).

The overall reaction leading to the formation of **1** and **2** is of redox type in which the Ru_2^{5+} unit of $Ru_2Cl(O_2CAr)_4$ gets oxidized to Ru_2^{6+} along with the rearrangement of bonds in the coordination sphere.[28-34] A similar oxidation is known[28] to occur in the reaction between $Ru_2Cl(ArCONH)_4$ and PPh_3, resulting in the formation of $Ru_2(Ph)_2(ArCONH)_2[Ph_2POC(Ar)N]_2$, a diruthenium(III) compound with an Ru–Ru bond order of 1.0.

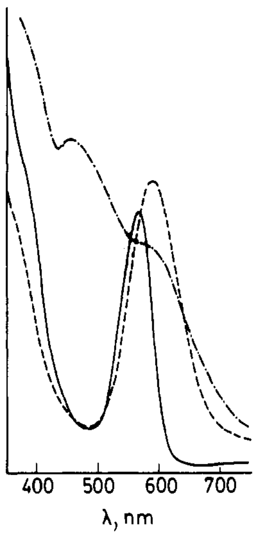

Figure 2. Visible absorption spectra of $Ru_2Cl(O_2CC_6H_4$-*p*-$OMe)_4$ (- - -), $Ru_2O(O_2CC_6H_4$-*p*-$OMe)_4(PPh_3)_2$ (—), and $Ru_2O(O_2CC_6H_4$-p-*OMe*$)_2(MeCN)_4(PPh_3)_2(ClO_4)_2 \cdot H_2O$ (- - -) in DMF, $CHCl_3$, and MeCN, respectively.

The synthetic routes followed[5,6] by other groups in preparing analogous diruthenium(III) complexes are different from ours. In the formation of **2**, two μ-O_2CAr groups of $Ru_2Cl(O_2CAr)_4$ are opening up to form chelate rings that can be substituted readily by MeCN on addition of $HClO_4$ in an acetonitrile medium. The reported diruthenium model complexes, on the other hand, are prepared by reacting $RuCl_3$ with py-HO_2CR[6] or by treating $LRuCl_3$[5] with NaO_2CR. In these reactions the monomeric units are getting dimerized in the presence of bridging carboxylato ligands and the oxo bridge without any change in the oxidation state of ruthenium during the process of oxo-bridge formation.

Properties. The electronic spectra of **1** and **2** are shown in Figure 2. In MeCN, **1** exhibits a strong absorption band near 580 nm. The $CHCl_3$ solutions of **2** display an equally intense band near 560 nm. The molar extinction coefficients for both **1** and **2** are high. The origin of the absorption is believed to be charge transfer in nature, involving the ruthenium(III) $d\pi$ and μ-oxo $p\pi$ orbitals and is similar[20] to those observed in other oxo-bridged triruthenium(III) carboxylato compounds. Similar intense low-energy absorptions are known[5,6] to occur in $Ru_2O(O_2CMe)_2(L)_2(PF_6)_2$[5] and $Ru_2O(O_2CMe)_2(py)_6(PF_6)_2$ at 542 and 581 nm, respectively. The visible band position is found to be dependent on the π-acceptor ability of the ancillary ligands. However, the available data are insufficient for drawing any definite conclusion. Conductivity measurements on **1** and **2** show that **1** is a 1:2 electrolyte in MeCN, while **2** is a nonconductor of electricity. IR spectra of **1** show the characteristic stretches for the ClO_4^- group and the MeCN ligands.

^1H NMR spectra of **1** and **2** indicate the essentially diamagnetic nature of the compounds.[35] Compound **1b** exhibits a sharp methyl signal for the methoxy group of the bridging carboxylato ligands. The MeCN ligands on each ruthenium atom are in chemically different environments, as is evidenced by the appearance of two sharp methyl signals of equal intensity in the spectrum as shown in Figure 3. Keeping the solution of **1b** in CD_3CN overnight causes the methyl resonances of the MeCN ligands to disappear

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(35) Both 1 and 2 do not show any EPR signal in the solid state, in frozen solution at −196 °C, and in benzene/MeCN solution at 25 °C.

Table VI. Comparison of the Structural Parameters for the Diruthenium(III) Complexes with an $\{Ru_2O(O_2CR)_2{}^{2+}\}$ Core

complex	Ru···Ru, Å	Ru–O$_{oxo}$, Å	Ru–O–Ru, deg	ref
$[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(py)_6](PF_6)_2$	3.251	1.857	122.2	6
$[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2L_2](PF_6)_2\cdot 0.5H_2O$[a]	3.258	1.884	119.7	5
$[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CPh)_2(MeCN)_4(PPh_3)_2](ClO_4)_2\cdot H_2O$	3.237	1.872	119.7	this work
$[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CC_6H_4\text{-}p\text{-}OMe)_2(O_2CC_6H_4\text{-}p\text{-}OMe)_2(PPh_3)_2]$	3.199	1.859	118.7	this work

[a] L = 1,4,7-trimethyl-1,4,7-triazacyclononane.

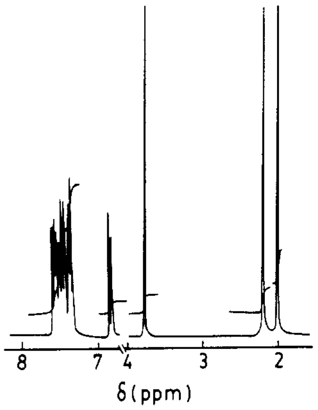

Figure 3. 270-MHz ^1H NMR spectrum of $Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_2(MeCN)_4(PPh_3)_2(ClO_4)_2\cdot H_2O$ (**1b**) in CD_3CN. Solvent peaks are removed for clarity.

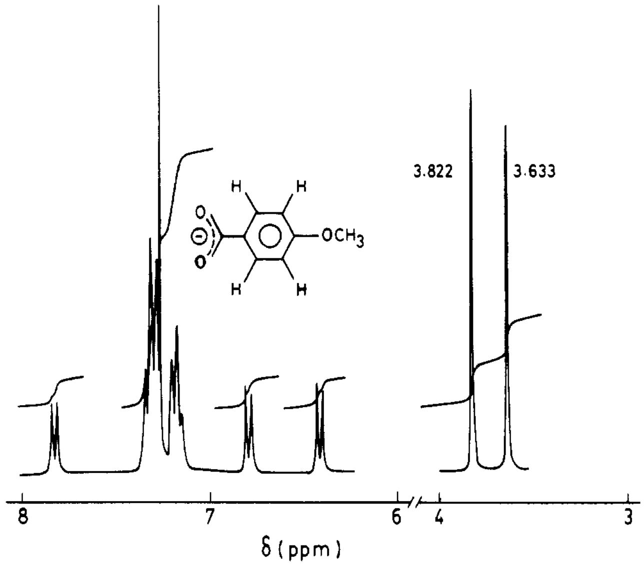

Figure 4. 270-MHz ^1H NMR spectrum of $Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_4(PPh_3)_2$ (**2b**) in $CDCl_3$. The intense peak at δ 7.26 is due to solvent.

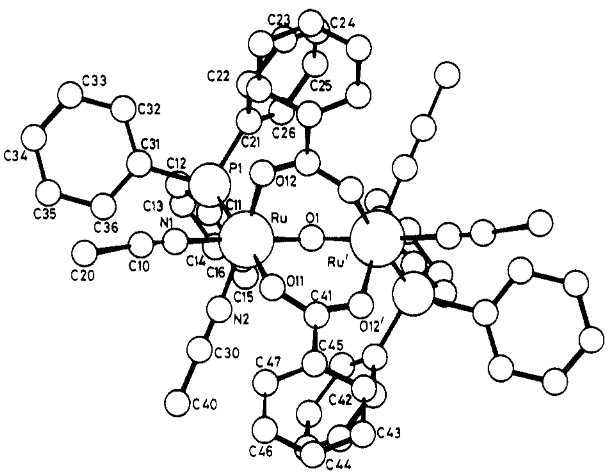

Figure 5. Perspective view of $[Ru_2O(O_2CPh)_2(MeCN)_4(PPh_3)_2]^{2+}$ cation along with the atom-labeling scheme.

completely, leaving the remaining spectral features essentially unaffected. The presence of two types of carboxylato ligands in **2b** is observed in the NMR spectrum of **2b**, shown in Figure 4, displaying two singlets of equal intensity. Other reported compounds with an $\{Ru_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2{}^{2+}\}$ core are known[5,6] to be diamagnetic. However, analogous diiron(III) compounds are paramagnetic and the two metal centers are antiferromagnetically coupled.[36]

The presence of labile MeCN and O_2CR facial ligands in **1** and **2** makes these systems reactive toward a variety of amines and heterocyclic bases. While pyridine reacts with **1** in MeCN to form a green complex, $Ru_2O(O_2CAr)_2(py)_4(PPh_3)_2(ClO_4)_2$, the compound **2** reacts with ethylenediamine (en) in benzene to form a blue unstable species, which readily converts to a yellow product that can be isolated as a ClO_4^- salt. Similarly NaO_2CR or NaO_2CAr react with **1** in MeOH to give mixed carboxylato complexes similar to **2**. Further investigations on the details of these observations are on. In the alcoholic solvents, species similar to **1** and **2** are believed to be the reactive intermediates in the reaction given in eq 4. Both **1** and **2** are found to be suitable

$$Ru_2Cl(O_2CAr)_4 + PPh_3\ (\text{excess}) \xrightarrow[\text{reflux}]{\text{EtOH}} Ru(CO)Cl(O_2CAr)(PPh_3)_2 + RuHCl(O_2CAr)(PPh_3)_2 + RuH(O_2CAr)(PPh_3)_3 \quad (4)$$

for designed synthesis of model compounds for hemerythrin and other structurally similar proteins and for substrate binding studies in the absence of facially blocking ligands like tridentate amines and heterocyclic bases present in other reported[2-16] model systems with an $\{M_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2{}^{n+}\}$ core.

Molecular Structures. The X-ray structures of **1a** and **2b** are shown in Figures 5 and 6, respectively. Both the molecules consist of a diruthenium(III) unit held by an oxo bridge and two bridging carboxylato ligands in a cis disposition, forming an $\{Ru_2(\mu\text{-}O)(\mu\text{-}O_2CAr)_2{}^{2+}\}$ core that is analogous to the diiron core in the met form of hemerythrin.[1-3] Although the ruthenium centers are in a near-octahedral geometry, the conformations of the molecules are essentially staggered. This is in contrast to the eclipsed conformation observed[37] in the $\{Ru_2(\mu\text{-}O_2CR)_4{}^+\}$ unit. In **1a**, the ancillary ligands in each metal center are one PPh_3 and two MeCN. The MeCN ligands are essentially linear. In **2b**, the ancillary ligands include one PPh_3 and a chelating carboxylato ligand. The ^1H NMR data on **1a** and **2b** are thus consistent with the solid-state structures obtained from X-ray crystallography. In both **1a** and **2b**, the PPh_3 ligands are cis to the μ-oxo group, possibly, because of steric reasons, which also account for the trans arrangement of two PPh_3 ligands with respect to each other. The steric bulk of the PPh_3 ligands causes the P–Ru–N and P–Ru–O(carboxylato) angles in **1a** and **2b**, respectively, to be obtuse and the other angles to be acute.

The atomic coordinates along with the isotropic thermal parameters of **1a** and **2b** are given in Tables II and III, respectively. Selected bond distances and angles for **1a** and **2b** are presented in the respective Tables IV and V. The Ru–Ru distances, observed

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(36) In the diiron(III,III) compounds, the spin exchange takes place between two high-spin ferric centers, with coupling constants ranging from −115 to −135 cm^{-1}. In the analogous diruthenium(III) compounds, the spin exchange is believed to occur between two low-spin $t_{2g}{}^5$ Ru(III) centers.

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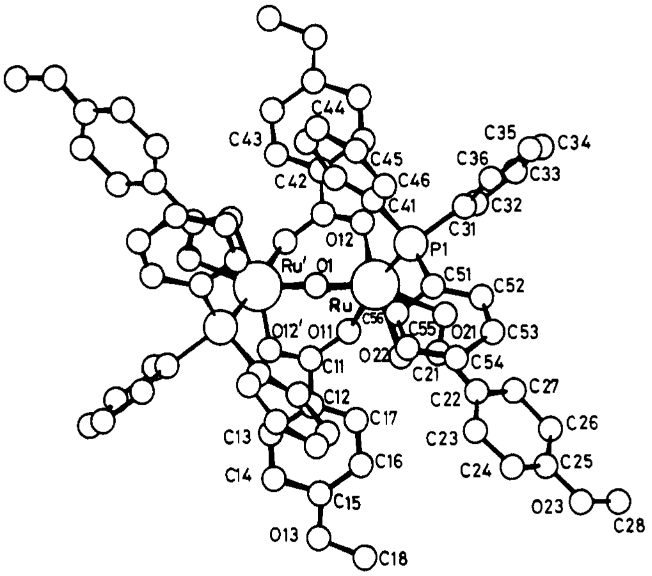

Figure 6. Perspective view of $Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_4(PPh_3)_2$ (**2b**) along with the atom-labeling scheme.

in **1a** and **2b**, are similar to the M-M distances known[5] in complexes with an $\{M_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2{}^{2+}\}$ core. The Ru-O-Ru angles in **1a** and **2b** are near 120°. The important structural parameters in these compounds are (i) the Ru-Ru distance and (ii) the Ru-O-Ru angle. Table VI lists the available data on diruthenium compounds.[5,6] The Ru-Ru interaction is expected to be dependent on the two above-cited parameters. The smaller Ru-O-Ru angle is expected to shorten the Ru-Ru distance. The data presented in Table VI show that the compound **2b** has the shortest Ru-Ru distance and the smallest Ru-O-Ru angle. The distance is still much longer than the Ru-Ru single bond distances known in the following edge-sharing bioctahedral diruthenium(III) compounds with a $\sigma^2\pi^4\pi^{*4}$ configuration: $Ru_2Cl_6(dmpm)_2$, 2.933 (1) Å;[33] $Ru_2(ap)_6(PMe_2Ph)_2$, 2.573 (2) Å;[32] $Ru_2(Ph)_2(PhCONH)_2[Ph_2POC(Ph)N]_2$, 2.566 (1) Å[28] (Hap = 2-aminopyridine). The formation of a direct Ru-Ru bond in **1** and **2** seems to be unlikely. The diamagnetic nature of **1** and **2** is, possibly, due to the coupling of the two $t_{2g}{}^5$ Ru(III) centers through the oxo bridge, as is proposed[20] for related oxo-bridged triruthenium systems. The diosmium(IV) compounds $Os_2O(O_2CR)_2(PPh_3)_2Cl_4$, are also known[15] to be diamagnetic with an Os-Os separation of 3.440 Å. Structural data on these systems containing the $\{Ru_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2{}^{2+}\}$ core strongly suggest[38] that the intense colors of these compounds are due to charge-transfer transitions involving the $\{Ru_2(\mu\text{-}O)^{4+}\}$ unit held by two carboxylato bridges.

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Supplementary Material Available: For $Ru_2O(O_2CPh)_2(MeCN)_4(PPh_3)_2(ClO_4)_2 \cdot H_2O$ (**1a**) and $Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_4(PPh_3)_2$ (**2b**), tables of thermal parameters and bond lengths and angles (10 pages); tables of observed and calculated structure factors (39 pages). Ordering information is given on any current masthead page.

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(38) A recent report by Neubold et al. (ref 5) has shown that protonation of the μ-oxo bridge has a profound effect on the magnetic and electronic properties of the diruthenium(III) compounds. After submission of this manuscript, an article on similar types of diruthenium(III) compounds containing tris(1-pyrazolyl)methane facial ligands is reported: Llobet, A.; Curry, M. E.; Evans, H. T.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 3131.

Contribution from the Department of Chemistry,
University of Illinois at Chicago, Chicago, Illinois 60680

Molecular Architecture of a Novel Vertex-Sharing Biicosahedral Cluster $[(p\text{-}Tol_3P)_{10}Au_{13}Ag_{12}Br_8](PF_6)$ Containing a Staggered-Staggered-Staggered Configuration for the 25-Atom Metal Framework

Boon K. Teo,* Hong Zhang, and Xiaobo Shi

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The crystal and molecular structure of a 25-atom metal cluster, $[(p\text{-}Tol_3P)_{10}Au_{13}Ag_{12}Br_8]^+(PF_6)^-$ (**1**), has been determined by single-crystal X-ray crystallography. The complex $[(p\text{-}Tol_3P)_{10}Au_{13}Ag_{12}Br_8](PF_6) \cdot 10EtOH$ crystallizes in a unit cell of triclinic $P\bar{1}$ symmetry with lattice parameters $a = 16.971$ (2) Å, $b = 17.431$ (2) Å, $c = 21.825$ (2) Å, $\alpha = 78.20$ (6)°, $\beta = 72.33$ (6)°, $\gamma = 72.13$ (4)°, and $Z = 1$. The structure was refined to $R_1 = 9.8\%$, $R_2 = 11.6\%$ for 9150 independent reflections with $I > 3\sigma(I)$. The metal framework of **1** can be described as two 13-atom centered icosahedra sharing a common vertex. As such, it belongs to a novel series of high-nuclearity Au-Ag clusters whose structures are based on vertex-sharing (centered) icosahedra. The structural systematics of this new class of supraclusters led to the concept of "cluster of clusters", which is useful in the design, preparation, and characterization of large metal clusters of increasingly high nuclearity via vertex-, edge-, and face-sharing and/or close packing of smaller cluster units as building blocks.

(I) Introduction

A cluster is an aggregate of atoms or molecules. Current interest in clusters stems from the fact that the collective behavior of a cluster often differs significantly from that of its constituents.

Chemists have been able to prepare and/or observe a wide variety of clusters in gas, liquid, solution, or solid phases. Some clusters are naked (for example, $Bi_8{}^{2+}$ [1a] and $Ge_9{}^{2-}$ [1b]), while others are ligated with ligands such as phosphines (e.g., $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$ [2]) and carbonyls (e.g., $[Pt_{19}(CO)_{22}]^{4-}$ [3]). They can either be discrete clusters in solution or extended clusters in solid states. Finally, atoms (or molecules) within a cluster can be held together by ionic, covalent, metallic, or hydrogen bonding,

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