is considerably broadened due to the paramagnetic Ru(III) center. The ESR spectrum gives three values for its **g** tensor, 2.55, 2.40, and 1.73, corresponding to g_1, g_2, and g_3 in accord with a compressed rhombic distorted configuration. The structure of complex **13** (structure III) is similar to that of complex **8** with only one of the arsine ends of the ligand DABA coordinating to the metal atom and the other end free. The other DABA acts as a terdentate ligand.

The electronic spectral data for complexes **1**–**13** are presented in Table IV. The molar extinction coefficient values are all higher than the conventional values for d–d transitions due to charge-transfer character of the bands. In the case of Ru(II) complexes with spin-paired $(t_{2g})^6$ ground configurations, two d–d bands are observed in the range 420–490 nm and 330–380 nm. Complexes **6**–**11** and **13** are distorted-octahedral Ru(III) species with spin-paired $(t_{2g})^5$ ground configuration. The bands in the range 500–600 nm in the complexes may be assigned to the d–d transition with LMCT character. The intense bands around 230 nm in both Ru(II) and Ru(III) complexes can be assigned to the π–π^* transitions of the phenyl rings whereas the other higher energy bands may be due to LMCT or the charge transfer involving P or As lone pairs and the phenyl rings.

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Registry No. **1**, 99572-96-0; **2**, 99582-46-4; **3**, 99572-97-1; **4**, 99582-47-5; **5**, 99582-48-6; **6**, 99572-98-2; **7**, 99572-99-3; **8**, 99573-00-9; **9**, 99573-01-0; **10**, 99573-02-1; **11**, 99573-03-2; **12**, 99573-05-4; **13**, 99573-06-5; DPBA, 99573-07-6; DABA, 99573-08-7; $RuCl_2(PPh_3)_3$, 15529-49-4; $RuCl_2(Me_2SO)_4$, 89395-66-4; $RuCl_3(AsPh_3)_2MeOH$, 15692-70-3; $RuBr_3(AsPh_3)_2MeOH$, 15692-69-0; $PhCH_2N(CH_2CH_2Cl)_2$, 55-51-6; $KAsPh_2$, 21498-51-1; $KPPh_2$, 15475-27-1.

Supplementary Material Available: A detailed discussion of ^1H, ^{31}P, and ^{13}C NMR spectra with figures and mass spectra with fragmentation schemes of the ligands DPBA and DABA and the $^{31}P\{^1H\}$ NMR spectrum of complex **3** (9 pages). Ordering information is given on any current masthead page.

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A New Mixed-Ligand Diruthenium(II) Compound. Synthesis and Characterization of $[Ru_2Cl(Me_2PCH_2PMe_2)_2(PhNpy)_2][BPh_4]$

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The title compound was prepared by reacting $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy)$, which was obtained from an in situ reaction of $Ru_2Cl(O_2CCH_3)_4$ and 2-anilinopyridine (PhNHpy), and (dimethylphosphino)methane (dmpm) in the presence of chlorotrimethylsilane in toluene. The compound was isolated as a crystalline mass by cooling a methanolic solution of the complex in the presence of $Na[BPh_4]$. The crystals of composition $[Ru_2Cl(dmpm)_2(PhNpy)_2][BPh_4]\cdot 1.5MeOH$ belong to the monoclinic system, space group $P2_1/n$, with the following unit cell dimensions: $a = 14.064$ (5) Å, $b = 24.047$ (8) Å, $c = 18.642$ (4) Å, $\alpha = \gamma = 90°$, $\beta = 110.52$ (2)°, $V = 5905$ (3) Å^3, $Z = 4$. The cationic species $[Ru_2Cl(dmpm)_2(PhNpy)_2]^+$ consists of a diruthenium(II) core held by two dmpm and two $PhNpy^-$ ligands. The orientation of the $PhNpy^-$ ligands is unidirectional. The ruthenium that is bonded to pyridine nitrogens has an axial Cl^- ligand while the axial site on the other ruthenium is vacant because of two pendant phenyl rings on the amine nitrogen atoms. The Ru–Ru distance is 2.340 (2) Å. The Ru–Cl, average Ru–P, and average Ru–N distances are 2.480 (5) Å, 2.396 [5] Å, and 2.122 [12] Å, respectively. The average torsion angle in N–Ru–Ru–N and P–Ru–Ru–P is 19.84°. The compound is moderately stable in air in the solid state and is soluble in common organic solvents. The complex is paramagnetic and has a magnetic moment of 2.6 μ_B (at 308 K), corresponding to two unpaired spins. The metal–metal bond order is 2.0 according to the $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^4$ ground-state electronic configuration. The electronic spectrum of an acetonitrile solution of the complex exhibits a band at 395 nm ($\epsilon = 2600$ M^{-1} cm^{-1}) and a shoulder at 320 nm. Cyclic voltammetry of the compound in acetonitrile displays two metal-centered one-electron oxidative processes at +0.332 ($\Delta E_p = 64$ mV) and +1.195 V ($\Delta E_p = 74$ mV) at $v = 100$ mV s^{-1}. A ligand-centered reduction is observed at −0.632 V ($\Delta E_p = 95$ mV). A linear correlation is observed between the redox potentials of the Ru(III)Ru(II)/Ru(II)Ru(II) couples and the position of the lowest energy bands in the electronic spectra among diruthenium(II) compounds.

Introduction

The present work stems from our current exploration of the chemistry of diruthenium complexes having ruthenium–ruthenium multiple bonds. The systems that have been most thoroughly studied[1-9] are the diruthenium tetracarboxylates, in which the metal atoms are in different formal oxidation states. These compounds are all paramagnetic with three unpaired spins. Recent development in this field has shown that many other types of Ru(II)Ru(III) compounds can be made and that the reactivity pattern and the general nature of these Ru(II)Ru(III) complexes are quite different from those of other dimetallic species. One example is the reactivity of triarylphosphines toward tetrakis(amidato) species $Ru_2Cl(ArCONH)_4$ in which aryl group migration from PAr_3 onto the metal center takes place along with a synergic formation of a P to amidato oxygen bond.[10,11] The resulting complex is an edge-sharing bioctahedral Ru(III)Ru(III) species with an Ru–Ru single bond. The reactions between three-atom-bridging ligands of the type 2-hydroxypyridine and its derivatives, as well as 2-anilinopyridine, which have N,O- and

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N,N-donor sets, and $Ru_2Cl(O_2CCH_3)_4$ produce a new class of compounds in which there is a totally polar arrangement of bridging ligands.[12-14]

Alkali-metal salts of different kinds of three-atom-bridging ligands are known[1] to substitute easily the carboxylate groups in tetracarboxylato compounds of different metals, but the situation is not so simple in the chemistry of ruthenium. In most cases the resulting product is an intractable mixture; for example, the reaction between $Ru_2Cl(O_2CCH_3)_4$ and Na(mhp), studied by Garner, Clegg, et al., is known[15] to yield only 8% of $Ru_2(mhp)_4 \cdot CH_2Cl_2$. Similarly, $Ru_2Cl(O_2CCH_3)_4$ when reacted with Li(ap) does not produce any clean product, but subsequent addition of PMe_2Ph into the reaction mixture gives[17] crystalline $Ru_2(ap)_6(PMe_2Ph)_2$. Reactions between $Ru_2Cl(O_2CCH_3)_4$ and Grignard reagents, studied by Wilkinson and co-workers, are known[18,19] to produce Ru(II)Ru(II) and Ru(III)Ru(III) compounds, viz. $Ru_2(O_2CCH_3)_4(THF)_2$ and Ru_2R_6 (R = CH_2SiMe_3 and CH_2-*t*-Bu).

Our earlier attempts to substitute the bridging acetates in $Ru_2Cl(O_2CCH_3)_4$ by three-atom-bridging diphosphine ligands were unsuccessful. It was also found that polar diruthenium species were unreactive toward diphosphines. In attempts to prepare some mixed-ligand complexes, we were able to isolate $Ru_2Cl(O_2CCH_3)(chp)_3 \cdot CH_2Cl_2$,[20] $Ru_2Cl(O_2CCH_3)_2(mhp)_2 \cdot CH_2Cl_2$,[21] and $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy) \cdot CH_2Cl_2$[20] from the reaction of $Ru_2Cl(O_2CCH_3)_4$ and the respective ligand in boiling methanol. Such complexes provide us an opportunity to attack the acetato bridges and substitute them by diphosphine ligands, while ensuring that the diruthenium core will remain intact because it is held by other bridging ligands.

In this paper we report the synthesis and characterization of the compound $[Ru_2Cl(dmpm)_2(PhNpy)_2][BPh_4] \cdot 1.5MeOH$, which is obtained from the reaction of $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy)$ and dmpm in the presence of chlorotrimethylsilane, followed by crystallization from methanol containing $Na[BPh_4]$. The complex is the first example of a mixed-ligand diruthenium(II) compound, and it also has moderate stability in air. It should be noted that the other known[15,19,22,23] diruthenium(II) complexes are all air-sensitive.

Experimental Section

Preparation of $[Ru_2Cl(dmpm)_2(PhNpy)_2][BPh_4] \cdot 1.5MeOH$ (1). A mixture of 0.1 g of $Ru_2Cl(O_2CCH_3)_4$ and 0.09 g of 2-anilinopyridine in 15 mL methanol was refluxed for 10 h. The color of the solution turned from red-brown to blue. The product in solution was $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy)$ (2).[20] The solution was evaporated to dryness. The resulting blue mass was dissolved in 15 mL of toluene under argon atmosphere. To this solution were added 0.16 g of (dimethylphosphino)methane (dmpm) and 0.5 mL of Me_3SiCl. The solution was then stirred for 36 h at 25 °C. The color of the solution changed from blue to brown. After the solution was evaporated to dryness, the brown solid was dissolved in a minimum volume of tetrahydrofuran (THF) and was passed onto a 20 cm long (1.5 cm diameter) neutral alumina column (E. Merck, W. Germany) in THF under an atmosphere of argon. Initial elution with THF gave very small bright yellow and light green bands, after which a brown band was eluted with methanol. The yellow compound has not been identified; the green one is almost certainly $RuCl(PhNpy)_4$.[12] The brown eluate was concentrated in ca. 10 mL volume and 0.07 g of $Na[BPh_4]$ was added to this solution. Brown crystals were obtained in about 30% yield after cooling the solution at −20 °C. The crystalline material is moderately stable in air but loses the solvent of crystallization on removal from the methanol solution. The compound is soluble in common organic solvents. Anal. Calcd for $[Ru_2Cl(dmpm)_2(PhNpy)_2][BPh_4]$: $Ru_2ClP_4N_4BC_{56}H_{66}$: C, 57.61; H, 5.66. Found: C, 57.83; H, 5.72. Infrared spectrum (KBr disk): 3040 (w), 2980 (w), 1595 (s), 1575 (s), 1545 (m), 1525 (w), 1470 (s), 1420 (s), 1410 (m), 1360 (s), 1290 (m), 1280 (m), 1245 (m), 1225 (m), 1155 (m), 1120 (m), 1065 (w), 1005 (m), 928 (s), 885 (w), 855 (w), 840 (m), 760 (s), 745 (m), 730 (s), 705 (s), 695 (s), 610 (s), 530 (m), 510 (m), 300 (w), 280 (w) cm^{-1} (s, strong; m, medium; w, weak). Electronic spectrum in CH_3CN: λ_{max} = 395 nm (ϵ = 2600 M^{-1} cm^{-1}), 320 nm (sh). Magnetic moment by Evans' method[24] (in CH_3CN): μ_{eff} = 2.6 μ_B (308 K).

Table I. Crystal Data for $[Ru_2Cl(dmpm)_2(PhNpy)_2][BPh_4] \cdot 1.5MeOH$

formula	$Ru_2ClP_4O_{1.5}N_4C_{57.5}BH_{72}$
fw	1215.53
space group	$P2_1/n$
syst abs	$0k0$ ($k = 2n + 1$), $h0l$ ($h + l = 2n + 1$)
a, Å	14.064 (5)
b, Å	24.047 (8)
c, Å	18.642 (4)
β, deg	110.52 (2)
V, $Å^3$	5905 (3)
Z	4
d_{calcd}, g/cm^3	1.37
cryst size, mm	0.6 × 0.2 × 0.2
μ(Mo Kα), cm^{-1}	6.97
data collcn instrum	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)
orientation reflections: no.; range (2θ), deg	15; 15 < 2θ < 25
temp, °C	5 ± 2
scan method	ω–2θ
data collcn range (2θ), deg	4–50
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3908, 3096
no. of params refined	603
transmission factors: max, min	1.00, 0.97 (obsd) 0.87, 0.63 (calcd)
R^a	0.0722
$R_w{}^b$	0.0917
quality-of-fit indicator^c	1.755
largest shift/esd, final cycle	0.17
largest peak, e/$Å^3$	1.28

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{observns} - N_{params})]^{1/2}$.

Measurements. The elemental analysis was obtained from Galbraith Laboratories, Inc. The infrared spectrum was recorded with a Perkin-Elmer 785 spectrophotometer. The electronic spectrum was obtained from an acetonitrile solution of 1 by using a Cary 17D spectrophotometer. Magnetic measurements were made in acetonitrile solution by the Evans method on a Varian EM 390 spectrometer. Cyclic voltammetric measurements were carried out under an argon atmosphere with a Bioanalytical System, Inc., Model BAS100 electrochemical analyzer instrument in connection with a Bausch & Lomb, Houston Instruments Model DMP 40 digital plotter. Measurements were made in acetonitrile solution containing 0.1 M (n-$Bu_4N)PF_6$ as supporting electrolyte in a three-electrode cell system, which consists of a platinum disk, Model BAS MF 2032, as a working electrode, a platinum wire as an auxiliary electrode, and a BAS MF 2020 Ag-AgCl cell as a reference electrode (against which ferrocene is oxidized at $E_{1/2}$ = +0.515 V). All potentials were referenced to this electrode at 22 ± 2 °C and were uncorrected for junction potentials.

X-ray Crystallographic Procedures. The crystals of 1 were brown. Microscopic examination of the crystalline mass showed it to be homo-

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geneous with needle-shaped crystals, which are fragile in nature. A typical one was mounted on a glass fiber with epoxy cement. The structure of this single crystal was determined by applying the general procedures that are described elsewhere.[25,26] The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. At the end of data collection, a 30% decay in intensity was observed. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was also made on the basis of azimuthal scans of nine reflections with Eulerian angle χ near 90°.

The compound crystallizes in the monoclinic cell system in space group $P2_1/n$ with one complete **1** molecule per asymmetric unit. The solvent molecule (1.5 MeOH) was found to be disordered. The observed gradual decay in intensity during data collection is possibly due to the loss of the solvent molecule. Attempts to mount the crystal in a capillary with mother liquor failed due to the brittle nature of the crystals.

The positions of the two ruthenium atoms were obtained by the direct methods program MULTAN, and the remainder of the structure was solved by using difference Fourier maps and least-squares refinements. The structure was refined to the values of $R = 0.072$, $R_w = 0.092$. The atoms in the cationic complex and the anion $[BPh_4]^-$ refined well. The high residual values could be due to the loss of crystallinity with time during data collection. The presence of volatile solvent is also evidenced from the elemental analysis of **1**. In the final difference Fourier map there are three peaks near the solvent molecules with e/Å^3 values of 1.28, 1.04, and 0.78.

Results and Discussion

The cationic species $[Ru_2Cl(dmpm)_2(PhNPy)_2]^+$ was prepared by reacting $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy)$ and (dimethylphosphino)methane (dmpm) in toluene in the presence of Me_3SiCl. The crude product was purified by column chromatography on a neutral alumina column using methanol as an eluting agent. Compound **1** was crystallized with $[BPh_4]^-$ as an anion. The compound $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy)$ was prepared in situ by reacting $Ru_2Cl(O_2CCH_3)_4$ with PhNHpy in boiling methanol. The synthesis and structure of this compound was reported[20] earlier from this laboratory. The formation of **1** shows that Me_3SiCl has selectively attacked the acetate ligands of the starting compound. During the reaction process a net one-electron reduction has occurred. Structural studies on **2** show[20] that the arrangement of similar ligands is trans in nature.

$$Ru_2Cl(O_2CCH_3)_4 + PhNHpy \xrightarrow[\text{reflux}]{\text{MeOH}} \underset{\mathbf{2}}{Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy)} \quad (1)$$

$$\mathbf{2} + Me_2PCH_2PMe_2 + Me_3SiCl \xrightarrow{\text{toluene}} [Ru_2Cl(dmpm)_2(PhNpy)_2]^+ \quad (2)$$

The ruthenium that is bonded to two pyridine nitrogens has an axial Cl coordination. The other axial site is occupied by a neutral PhNHpy ligand in which the pyridine nitrogen is coordinated to the ruthenium and the hydrogen of the amine nitrogen is bonded to one oxygen of an acetate bridge to give O···H–N hydrogen bonding. When the acetates are removed by Me_3SiCl (eq 2) and displaced by dmpm ligands, the axial PhNHpy is also removed. The reason could be due to the steric bulk of this axial ligand.

Our attempts to make diphosphine-bridged diruthenium species starting from $Ru_2Cl(O_2CCH_3)_4$ did not yield anything. It was also found that diphosphine ligands do not react with totally polar complexes. Further studies on these systems are in progress.

Compound **1** is fairly air-stable in the solid state. The magnetic moment of **1** in acetonitrile at 308 K is 2.6 μ_B. The presence of two unpaired spins is consistent with the ground electronic configuration of $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^4$ proposed in other diruthenium(II) species.[9,15,19] The electronic spectrum of **1** in acetonitrile solution shows a band at 395 nm (ϵ = 2600 M^{-1} cm^{-1}) (Figure 1) and a shoulder at 320 nm. On exposure to air, the yellow solution gradually turned green. The electronic spectrum of this green solution exhibits a band at 885 nm and a shoulder at 390 nm. Compound **2** in CH_2Cl_2 is known[20] to display a band at 695 nm (ϵ = 6560 M^{-1} cm^{-1}) in its electronic spectrum. Since spectral data on most other diruthenium(II) complexes are not available, it is difficult to assign the bands. However, $Ru_2(O_2CCH_3)_4(THF)_2$ is known[19] to exhibit a band at 438 nm. Spectroelectrochemical studies done on tetraamidato species by Bear and co-workers have shown[27,28] that the electrochemically reduced solutions of $Ru_2(HNOCCF_3)_4$ display bands at 546, 628, and 641 nm in CH_2Cl_2, CH_3CN, and Me_2SO, respectively.

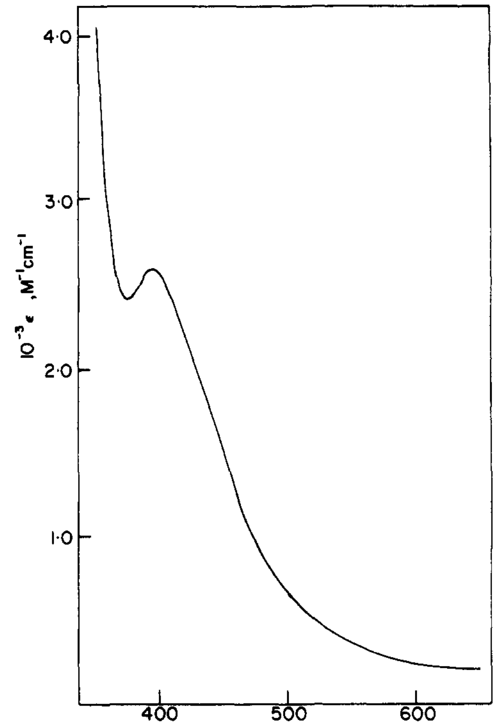

Figure 1. Electronic spectrum of $[Ru_2Cl(dmpm)_2(PhNpy)_2][BPh_4]$ in acetonitrile.

SCF-Xα-SW calculations done on $Ru_2(O_2CH)_4Cl_2^-$, $Ru_2(O_2CH)_4^+$, and $Ru_2(O_2CH)_4$ complexes show[9] that the electronic configurations of Ru(II)Ru(III) and Ru(II)Ru(II) dimers are $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$ and $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^4$, respectively. The prominent visible band in the electronic spectrum of $Ru_2(O_2CR)_4^+$ complexes is assigned to an $O\pi \rightarrow \pi^*$ transition where $O\pi$ is a Ru–O orbital having considerable Ru–Ru π-character.

The assignment of the absorption band in diruthenium(II) complexes cannot be made with certainty. While it might be assigned to a metal → ligand charge transfer transition, there are other possibilities. Experimental results show that an increase in the electronic transition energy on going from amides to acetate to **1** has a parallel increase in the oxidation potential of the Ru(II)Ru(III)/Ru(II)Ru(II) couple. In the electrochemical oxidation the electron is removed from the HOMO level which is either δ^* or π^*. The observed increase in the $E_{1/2}$ values follows the order $[Ru_2Cl(dmpm)_2(PhNpy)_2]^+ > Ru_2(O_2CCH_3)_4(THF)_2 > Ru_2(HNOCCF_3)_4$ and indicates that the HOMO level is of much lower energy in **1**. This makes the compound thermodynamically more stable compared to other diruthenium(II) species. The involvement of the HOMO level in the electronic transition is also consistent with the linear relationship, shown in Figure 2, between the energy of the absorption band and the redox potential of the Ru(II)Ru(II)/Ru(II)Ru(III) couple. However, this re-

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Table II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $[Ru_2Cl(dmpm)_2(PhNpy)_2][BPh_4]\cdot 1.5MeOH$[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Ru(1)	0.1520 (1)	0.38424 (7)	0.66597 (9)	2.51 (4)	C(26)	0.265 (1)	0.4229 (8)	0.831 (1)	3.3 (5)
Ru(2)	0.3085 (1)	0.34013 (7)	0.72452 (9)	2.25 (3)	C(27)	0.442 (2)	0.4026 (7)	0.862 (1)	2.8 (5)
Cl(1)	−0.0143 (4)	0.4305 (2)	0.6040 (3)	4.2 (2)	C(28)	0.483 (1)	0.4594 (9)	0.881 (1)	3.4 (5)
P(1)	0.2187 (5)	0.4706 (2)	0.6401 (4)	4.0 (2)	C(29)	0.590 (2)	0.4630 (9)	0.916 (1)	3.7 (6)
P(2)	0.0478 (4)	0.3081 (2)	0.6765 (3)	3.4 (1)	C(30)	0.654 (2)	0.4156 (9)	0.932 (1)	4.4 (6)
P(3)	0.3967 (4)	0.3996 (2)	0.6649 (3)	3.5 (2)	C(31)	0.613 (1)	0.3630 (9)	0.914 (1)	3.8 (6)
P(4)	0.2430 (4)	0.2746 (2)	0.7915 (3)	3.2 (1)	C(32)	0.505 (1)	0.3569 (8)	0.879 (1)	3.0 (5)
N(1)	0.149 (1)	0.3466 (6)	0.5600 (8)	3.0 (4)	B(1)	−0.579 (2)	0.370 (1)	0.306 (1)	3.2 (6)
N(2)	0.169 (1)	0.4202 (6)	0.7746 (8)	2.6 (3)*	C(33)	−0.485 (1)	0.3843 (8)	0.384 (1)	3.4 (5)
N(3)	0.339 (1)	0.3961 (5)	0.8168 (7)	2.0 (4)	C(34)	−0.394 (2)	0.356 (1)	0.402 (1)	5.7 (7)
N(4)	0.273 (1)	0.2872 (6)	0.6304 (8)	2.8 (4)	C(35)	−0.310 (2)	0.366 (1)	0.470 (1)	5.8 (7)
C(1)	0.361 (2)	0.471 (1)	0.672 (1)	4.6 (6)	C(36)	−0.313 (2)	0.403 (1)	0.523 (1)	5.2 (7)
C(2)	0.187 (2)	0.5315 (9)	0.690 (1)	5.8 (8)	C(37)	−0.400 (2)	0.438 (1)	0.504 (1)	5.3 (7)
C(3)	0.175 (2)	0.491 (1)	0.539 (1)	6.4 (7)	C(38)	−0.485 (1)	0.4273 (8)	0.434 (1)	3.4 (5)
C(4)	0.378 (2)	0.391 (1)	0.563 (1)	5.5 (7)	C(39)	−0.545 (2)	0.3713 (8)	0.228 (1)	3.7 (6)
C(5)	0.539 (2)	0.4022 (8)	0.709 (1)	3.9 (5)*	C(40)	−0.612 (2)	0.3583 (9)	0.155 (1)	4.5 (6)
C(6)	0.122 (2)	0.2467 (8)	0.726 (1)	3.8 (6)	C(41)	−0.591 (2)	0.362 (1)	0.089 (1)	6.9 (8)
C(7)	−0.030 (2)	0.279 (1)	0.578 (2)	7.0 (8)	C(42)	−0.498 (2)	0.3824 (9)	0.093 (1)	5.9 (7)
C(8)	−0.042 (2)	0.324 (1)	0.727 (1)	6.6 (7)	C(43)	−0.419 (2)	0.3985 (9)	0.164 (1)	5.0 (6)
C(9)	0.219 (1)	0.2976 (8)	0.876 (1)	3.4 (5)*	C(44)	−0.449 (2)	0.3941 (8)	0.233 (1)	3.6 (5)*
C(10)	0.318 (2)	0.2093 (8)	0.826 (1)	4.5 (6)	C(45)	−0.672 (2)	0.4175 (8)	0.297 (1)	4.2 (6)
C(11)	0.081 (2)	0.368 (1)	0.489 (1)	4.2 (6)	C(46)	−0.675 (2)	0.4661 (9)	0.249 (1)	4.9 (7)
C(12)	0.077 (2)	0.343 (1)	0.420 (1)	4.9 (6)	C(47)	−0.747 (2)	0.5094 (9)	0.241 (2)	6.4 (8)
C(13)	0.142 (2)	0.298 (1)	0.422 (1)	5.6 (7)	C(48)	−0.819 (2)	0.507 (1)	0.279 (2)	7.3 (9)
C(14)	0.213 (2)	0.2758 (9)	0.492 (1)	5.1 (7)	C(49)	−0.811 (2)	0.458 (1)	0.325 (1)	6.8 (8)
C(15)	0.210 (2)	0.3028 (8)	0.563 (1)	3.5 (6)	C(50)	−0.739 (1)	0.4133 (9)	0.334 (1)	4.7 (6)
C(16)	0.326 (2)	0.2351 (8)	0.641 (1)	3.1 (5)	C(51)	−0.627 (2)	0.3081 (9)	0.315 (1)	4.4 (6)
C(17)	0.433 (1)	0.2345 (9)	0.689 (1)	3.5 (5)	C(52)	−0.720 (2)	0.2907 (9)	0.263 (2)	7.5 (9)
C(18)	0.484 (2)	0.1829 (9)	0.707 (1)	4.3 (6)	C(53)	−0.761 (2)	0.237 (1)	0.266 (2)	7.5 (9)
C(19)	0.433 (2)	0.131 (1)	0.680 (1)	5.4 (7)	C(54)	−0.712 (2)	0.203 (1)	0.326 (1)	6.8 (7)
C(20)	0.331 (2)	0.1336 (9)	0.632 (1)	4.5 (6)	C(55)	−0.619 (2)	0.219 (1)	0.379 (2)	9 (1)
C(21)	0.275 (2)	0.1847 (8)	0.613 (1)	3.8 (6)	C(56)	−0.574 (2)	0.2709 (9)	0.378 (1)	6.8 (8)
C(22)	0.087 (1)	0.4416 (8)	0.788 (1)	3.9 (6)	O1(M1)	0.455 (2)	0.0749 (9)	0.496 (1)	14.2 (9)*
C(23)	0.099 (2)	0.4691 (9)	0.860 (1)	4.8 (6)	C1(M1)	0.559	0.075	0.562	16 (2)*
C(24)	0.197 (2)	0.474 (1)	0.915 (1)	4.9 (7)	O1(M2)	0.648 (3)	0.226 (2)	0.551 (2)	14 (2)*
C(25)	0.279 (2)	0.4502 (8)	0.904 (1)	3.6 (5)	C1(M2)	0.580	0.280	0.562	10 (2)*

[a] Starred values are for isotropically refined atoms. The isotropic equivalent thermal parameters of the anisotropically refined atoms are defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

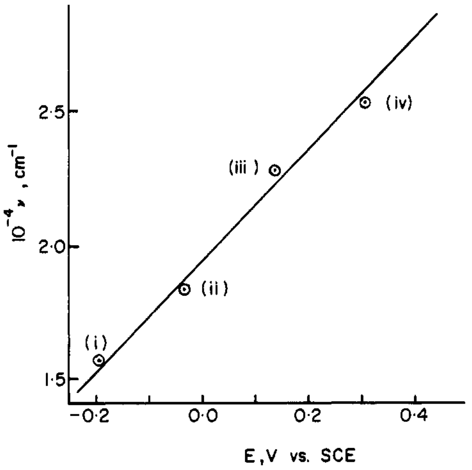

Figure 2. Plot showing the linear relationship between the energies of the absorption bands in the electronic spectra of the Ru(II)Ru(II) compounds and the formal redox potentials of the Ru(II)Ru(III)/Ru(II)-Ru(II) couples: (i) $Ru_2(HNOCCF_3)_4$ in Me_2SO (ref 27); (ii) $Ru_2(HNOCCF_3)_4$ in CH_2Cl_2 (ref 27); (iii) $Ru_2(O_2CCH_3)_4(THF)_2$ (ref 19); (iv) $[Ru_2Cl(dmpm)_2(PhNpy)_2][BPh_4]$ (this work).

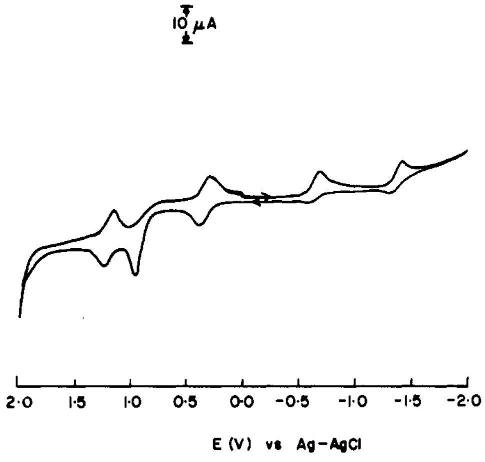

Figure 3. Cyclic voltammogram of $[Ru_2Cl(dmpm)_2(PhNpy)_2][BPh_4]$ in acetonitrile at a scan rate of 100 mV s^{-1} in the presence of 0.1 M $(TBA)PF_6$ as a supporting electrolyte.

lationship creates a problem insofar as the M → L charge-transfer assignment is concerned, since it would seem to imply a constant energy for the receptor orbital. While that is not impossible, it seems unlikely, and perhaps this empirical relationship implies that another assignment should be sought. In the absence of further information, however, speculation would be unjustified.

Cyclic voltammetry of compound **1** in acetonitrile in the presence of 0.1 M $(TBA)PF_6$ as the supporting electrolyte and an Ag–AgCl reference electrode shows two nearly reversible and one irreversible oxidations at +0.332 (ΔE_p = 64 mV), +1.195 (ΔE_p = 74 mV), and +0.950 V, respectively, at v = 100 mV s^{-1}. Besides these, two quasi-reversible reductions occur at −0.632 (ΔE_p = 95 mV) and −1.362 V (ΔE_p = 75 mV). The voltammograms are shown in Figure 3. The processes at +0.950 and −1.362 V are due to oxidation and reduction of $[BPh_4]^-$, respectively, since addition of $Na[BPh_4]$ into the solution increases the current height of these two responses.

We have confirmed that the process occurring at +0.332 V is due to oxidation of the compound by constant-potential oxidation at a potential 200 mV higher than the anodic peak potential. If we compare our results with the redox behaviors of other known

Table III. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $[Ru_2Cl(dmpm)_2(PhNpy)_2][BPh_4]\cdot1.5MeOH$[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Ru(1)	Ru(2)	2.339 (2)	P(1)	C(3)	1.83 (2)	N(2)	C(22)	1.36 (2)
Ru(1)	Cl(1)	2.480 (5)	P(2)	C(6)	1.86 (2)	N(2)	C(26)	1.39 (2)
Ru(1)	P(1)	2.396 (5)	P(2)	C(7)	1.91 (2)	N(3)	C(26)	1.33 (2)
Ru(1)	P(2)	2.397 (5)	P(2)	C(8)	1.86 (2)	N(3)	C(27)	1.41 (2)
Ru(1)	N(1)	2.159 (13)	P(3)	C(1)	1.81 (2)	N(4)	C(15)	1.32 (2)
Ru(1)	N(2)	2.138 (13)	P(3)	C(4)	1.83 (2)	N(4)	C(16)	1.43 (2)
Ru(2)	P(3)	2.405 (5)	P(3)	C(5)	1.88 (2)	B(1)	C(33)	1.62 (3)
Ru(2)	P(4)	2.387 (5)	P(4)	C(6)	1.84 (2)	B(1)	C(39)	1.67 (3)
Ru(2)	N(3)	2.107 (11)	P(4)	C(9)	1.81 (2)	B(1)	C(45)	1.69 (3)
Ru(2)	N(4)	2.082 (12)	P(4)	C(10)	1.88 (2)	B(1)	C(51)	1.68 (3)
P(1)	C(1)	1.88 (2)	N(1)	C(11)	1.43 (2)			
P(1)	C(2)	1.87 (2)	N(1)	C(15)	1.35 (2)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Ru(2)	Ru(1)	Cl(1)	179.6 (1)	N(3)	Ru(2)	N(4)	177.4 (5)	C(9)	P(4)	C(10)	102.1 (8)
Ru(2)	Ru(1)	P(1)	96.7 (1)	Ru(1)	P(1)	C(1)	112.9 (6)	Ru(1)	N(1)	C(11)	119 (1)
Ru(2)	Ru(1)	P(2)	96.7 (1)	Ru(1)	P(1)	C(2)	113.4 (7)	Ru(1)	N(1)	C(15)	119 (1)
Ru(2)	Ru(1)	N(1)	87.2 (4)	Ru(1)	P(1)	C(3)	115.4 (7)	C(11)	N(1)	C(15)	122 (2)
Ru(2)	Ru(1)	N(2)	88.2 (4)	C(1)	P(1)	C(2)	104.8 (9)	Ru(1)	N(2)	C(22)	120 (1)
Cl(1)	Ru(1)	P(1)	83.7 (2)	C(1)	P(1)	C(3)	105.1 (9)	Ru(1)	N(2)	C(26)	119 (1)
Cl(1)	Ru(1)	P(2)	82.9 (2)	C(2)	P(1)	C(3)	104 (1)	C(22)	N(2)	C(26)	120 (2)
Cl(1)	Ru(1)	N(1)	92.8 (4)	Ru(1)	P(2)	C(6)	113.4 (6)	Ru(2)	N(3)	C(26)	121 (1)
Cl(1)	Ru(1)	N(2)	91.8 (4)	Ru(1)	P(2)	C(7)	111.4 (7)	Ru(2)	N(3)	C(27)	115 (1)
P(1)	Ru(1)	P(2)	166.6 (2)	Ru(1)	P(2)	C(8)	114.9 (7)	C(26)	N(3)	C(27)	123 (1)
P(1)	Ru(1)	N(1)	93.6 (4)	C(6)	P(2)	C(7)	102.5 (9)	Ru(2)	N(4)	C(15)	121 (1)
P(1)	Ru(1)	N(2)	85.4 (4)	C(6)	P(2)	C(8)	105.8 (9)	Ru(2)	N(4)	C(16)	118 (1)
P(2)	Ru(1)	N(1)	86.4 (4)	C(7)	P(2)	C(8)	108 (1)	C(15)	N(4)	C(16)	121 (1)
P(2)	Ru(1)	N(2)	95.7 (4)	Ru(2)	P(3)	C(1)	109.2 (6)	P(1)	C(1)	P(3)	105 (1)
N(1)	Ru(1)	N(2)	175.2 (5)	Ru(2)	P(3)	C(4)	120.2 (6)	P(2)	C(6)	P(4)	105.5 (8)
Ru(1)	Ru(2)	P(3)	93.9 (1)	Ru(2)	P(3)	C(5)	117.4 (5)	N(1)	C(15)	N(4)	118 (2)
Ru(1)	Ru(2)	P(4)	94.1 (1)	C(1)	P(3)	C(4)	103.8 (9)	N(2)	C(26)	N(3)	117 (2)
Ru(1)	Ru(2)	N(3)	88.8 (4)	C(1)	P(3)	C(5)	102.5 (8)	C(33)	B(1)	C(39)	113 (2)
Ru(1)	Ru(2)	N(4)	88.7 (4)	C(4)	P(3)	C(5)	101.7 (8)	C(33)	B(1)	C(45)	108 (2)
P(3)	Ru(2)	P(4)	172.0 (2)	Ru(2)	P(4)	C(6)	109.5 (6)	C(33)	B(1)	C(51)	109 (2)
P(3)	Ru(2)	N(3)	90.4 (4)	Ru(2)	P(4)	C(9)	118.6 (6)	C(39)	B(1)	C(45)	111 (1)
P(3)	Ru(2)	N(4)	89.0 (4)	Ru(2)	P(4)	C(10)	117.4 (6)	C(39)	B(1)	C(51)	110 (1)
P(4)	Ru(2)	N(3)	90.0 (4)	C(6)	P(4)	C(9)	105.8 (8)	C(45)	B(1)	C(51)	106 (1)
P(4)	Ru(2)	N(4)	90.9 (4)	C(6)	P(4)	C(10)	101.6 (8)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

diruthenium species (see Figure 2), it can be inferred that the two one-electron-oxidative processes at +0.332 and +1.195 V are metal-centered.

$$[Ru^{III}Ru^{III}]^{3+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Ru^{II}Ru^{III}]^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \underset{\mathbf{1}}{[Ru^{II}Ru^{II}]^+}$$

$$E_{1/2} = 1.195 \text{ V } (\Delta E_p = 74 \text{ mV})$$

$$E_{1/2} = +0.332 \text{ V } (\Delta E_p = 64 \text{ mV})$$

The one-electron reduction observed at −0.632 V is believed to be ligand-centered.

In $Ru_2Cl(PhNpy)_4$, the Ru(II)Ru(III)/Ru(II)Ru(II) and Ru(III)Ru(III)/Ru(II)Ru(III) couples have formal potential values of −0.75 (ΔE_p = 67 mV) and +0.50 V (ΔE_p = 60 mV), respectively.[29] Removal of two $PhNpy^-$ ligands by two dmpm ligands caused a dramatic positive shift of the redox potentials. Previous electrochemical studies[29] on diruthenium(II,III) complexes have implied that oxopyridine ligands may in general tend to stabilize diruthenium(II) complexes relative to the diruthenium(II,III) complexes. Thus, it might be worthwhile to attempt the preparation of a complex analogous to that reported here with oxopyridine or substituted oxopyridine ligands in place of the PhNpy ligands.

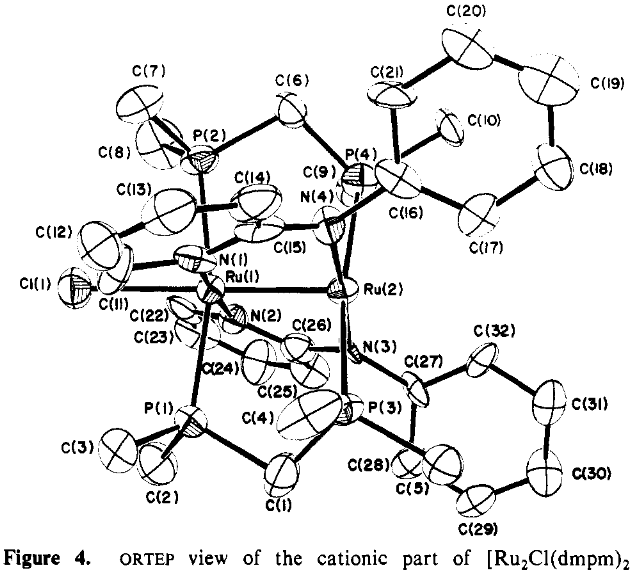

Figure 4. ORTEP view of the cationic part of $[Ru_2Cl(dmpm)_2(PhNpy)_2][BPh_4]\cdot1.5MeOH$. Atoms are represented by thermal ellipsoids at the 50% level and the atom-labeling scheme in this molecule is defined.

In diruthenium tetracarboxylates, the reduction process is known[6] to occur in the range 0.0 to −0.34 V vs. SCE depending on the solvent. In $Ru_2(O_2CCH_3)_4(THF)_2$, the oxidation takes place at +0.17 V vs. SCE.[19] Comparing the electrochemical results of all diruthenium species, we can conclude that the presence of the dmpm bridge in **1** is responsible for stabilizing the Ru(II)-Ru(II) state.

The structure of **1** was determined by a single-crystal X-ray diffraction study. The positional parameters along with the isotropic thermal parameters are given in Table II. Selected bond distances and angles are presented in Table III. Figure 4 shows the ORTEP view of the complex cation.

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(29) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A.; Tocher, J. H. *Polyhedron*, in press.

The diruthenium(II) unit is bridged by two anionic PhNpy and two neutral dmpm ligands. The arrangement of ligands is trans in nature. The geometry of Ru(1) is pseudooctahedral with one axial Cl coordination, while Ru(2) is in a square-pyramidal environment. In **2**, the axial ligand of Ru(2) was a neutral PhNHpy ligand. In **1**, the presence of two dmpm ligands makes the axial coordination on Ru(2) difficult because of the presence of methyl groups on the P atoms and the presence of two pendant phenyl groups on the amine nitrogen atoms.

The Ru(1)–Ru(2) distance in **1** is 2.340 (2) Å. The Ru–Ru distances in Ru(II)Ru(III) complexes[1-5,12-14,20,21] lie in the range 2.25–2.31 Å. In $Ru_2Cl(PhNpy)_4$,[12] **2**,[20] and $Ru_2Cl(O_2CCH_3)_4$,[3,5] the Ru–Ru bond lengths are 2.275 (3), 2.308 (1), and 2.287 (2) Å, respectively. The lengthening of the metal–metal bond in **1** could be due to the addition of one electron to the antibonding level. The other reasons could be due to a greater bite of the dmpm ligands over other ligands and due to the presence of a strong axial Ru–Cl bond. The shortest Ru–Ru distance of 2.238 (1) Å was observed[16] in $Ru_2(mhp)_4 \cdot CH_2Cl_2$ in which the metal centers do not have any axial ligand. A 2:2 arrangement of mhp ligands across the diruthenium core prohibits any kind of axial ligation. In $Ru_2(O_2CCH_3)_4(THF)_2$, the Ru–Ru distance is slightly longer, 2.260 (2) Å, and the metals have axial THF ligands. When the diruthenium core is not held by any bridging ligand, the Ru–Ru distance is long; e.g. in Ru_2L_2 (L = tetraazaannulene), the distance is 2.379 (1) Å.[22] Similarly, in $(Ru(OEP))_2$, the bond length is 2.408 (1) Å.[23]

The Ru(1)–Cl(1) distance in **1** is 2.480 (5) Å. The Ru(2)–Ru(1)–Cl(1) angle is essentially linear. As in **2**, the orientation of the PhNpy ligands in **1** is unidirectional. Such an arrangement allows the formation of a strong axial coordination on one ruthenium. In all polar molecules,[12-14] the Ru–Cl distances are short, having a value of ca. 2.43 Å, compared to those where both metal centers have axial coordinations.

The Ru–P bond lengths in **1** are in the range 2.387 (5)–2.405 (5) Å. The P–C bond lengths are normal. The P(1)–Ru(1)–P(2) and P(3)–Ru(2)–P(4) angles are 166.6 (2) and 172.0 (2)°, respectively. While the Ru–Ru–P angles are all obtuse (average 95.3°), the Cl–Ru(1)–P angles are all acute (average 83.3°). Among the Ru–N bond lengths, the Ru–N(amine) distances are shorter than the Ru–N(pyridine) bonds. This is expected if we assume the negative charge of the $PhNpy^-$ ligand to be concentrated primarily on the amine nitrogen atoms. The average value of the Ru–N distances is 2.122 [12] Å. The N–Ru–N angles are essentially linear. The Ru–Ru–N angles are all acute, but the Cl–Ru–N angles are obtuse. This could be due to the steric strain present in the molecule. Both PhNpy and dmpm ligands undergo considerable twist. The average P–Ru–Ru–P and N–Ru–Ru–N torsion angles are 22.4 and 17.3°, respectively. The torsion angles N–Ru–Ru–N observed[12,20] in **2** and $Ru_2Cl(PhNpy)_4$ are 3.2 and 22.7°, respectively.

Acknowledgment. We are grateful to the National Science Foundation for support.

Registry No. **1**, 99582-45-3; **1** (2+ ion), 99572-92-6; **1** (3+ ion), 99572-93-7; **2**, 99572-91-5; $Ru_2Cl(O_2CCH_3)_4$, 38833-34-0.

Supplementary Material Available: Listings of bond distances, bond angles, anisotropic thermal parameters, and observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Preparation and Structural Characterization of a Novel Hexanuclear Complex of Platinum(II) with 2-Aminoethanethiolate

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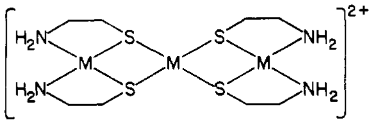
(Ethylenediamine)dibromoplatinum(II) reacts with 2-aminoethanethiol (AETH) at pH 10.5 in water to form light yellow crystals of $[Pt_6(AET)_8]Br_4 \cdot 6H_2O$. In the hexanuclear $[Pt_6(SCH_2CH_2NH_2)_8]^{4+}$ cation, which is crystallographically required to be centrosymmetric, two of the platinum atoms have a *cis*-$[Pt(AET)_2]$ square-planar (PtN_2S_2) structure, while square-planar ($PtNS_3$) geometry is achieved for the other four platinum atoms by coordination to a chelating AET ligand and two bridging sulfur atoms. The six platinum atoms do not form a regular polyhedron but rather are joined by doubly bridging thiolate sulfur atoms into three fused rings, a central Pt_4S_4 eight-membered ring and two outer Pt_3S_3 six-membered rings. All eight 2-aminoethanethiolate ligands are both chelating and bridging. The average Pt–S and Pt–N bond lengths are 2.30 (2) and 2.085 (10) Å, respectively. The compound crystallizes in the triclinic space group $P\bar{1}$, with a = 12.231 (2) Å, b = 12.400 (2) Å, c = 9.212 (1) Å, α = 107.13 (1)°, β = 108.88 (1)°, γ = 105.67 (1)°, V = 1156 Å^3, and Z = 1. The final $R(F)$ value was 0.036 for 2448 observed reflections.

Introduction

The metal complexes of 2-aminoethanethiol (AETH) were first studied by Jensen, who observed the formation of two Ni(II) complexes in solution.[1] In subsequent work, Jicha and Busch isolated two distinct types of compounds, one of which had the expected $[M(AET)_2]$ stoichiometry, M = Ni, Pd, while the other had the rather unusual formula $[M_3(AET)_4]Cl_2$.[2] The structure



was proposed[2] for the trinickel(II) complex and was subsequently confirmed by single-crystal X-ray diffraction work.[3] A closely related trinickel(II) complex, $[Ni_3L_2]Cl_2 \cdot 4H_2O$, LH_2 = *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)ethylenediamine,[4] was prepared and structurally characterized in 1975.[5]

Although mono- and trinuclear complexes of 2-aminoethanethiol with Ni(II) and Pd(II) have been thoroughly investigated,[1-3,6-8] reports of the chemistry of Pt(II) with this ligand are scarce, and for binary compounds we have found reference only

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