The First $Ru^{II}Pd^{II}{}_2S_3$ Metallochelate Ring Formed on a $[Ru(bpy)_2]^{2+}$ Core

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The 1:2 reaction of $[RuCl_2(bpy)_2]$ (bpy = 2,2′-bipyridine) with $[Pd(aet)_2]$ (aet = 2-aminoethanethiolate) led to the formation of $[Ru(bpy)_2\{Pd_2(aet)_3\}\{Pd(aet)_2\}]^{3+}$ ($[\mathbf{1}]^{3+}$), which was converted into $[Ru(bpy)_2\{Pd_2(aet)_3\}\{Pd(aet)$(2-aminoethanesulfenato)$\}]^{3+}$ ($[\mathbf{1'}]^{3+}$) and $[Ru(bpy)_2\{Pd_2(aet)_3Cl\}]^{2+}$ ($[\mathbf{2}]^{2+}$) having a six-membered $RuPd_2S_3$ metallochelate ring.

Construction of mixed-metal polynuclear complexes based on square planar $[M(amine)_2(thiolato)_2]$-type ($M = Ni^{II}$ and Pd^{II}) units in combination with transition metal centers has attracted considerable interest, because of their diverse structural and chemical properties.[1–5] It has been recognized that $[M^{II}(amine)_2(thiolato)_2]$-type units act as a bridging or chelating bidentate-*S*,*S* metalloligand toward square-planar,[1] tetrahedral,[1d,2] trigonal-planar,[3] and linear[4] metal centers to produce a variety of S-bridged polynuclear complexes. However, reports on the reactions of $[M(amine)_2(thiolato)_2]$-type complexes with octahedral metal ions/complexes are relatively rare,[5] and thus their ligating behavior toward octahedral metal centers has little been understood. As part of our continuing project on the creation of S-bridged polynuclear complexes showing a novel structural concept, we started to investigate the reactivity of $[M(aet)_2]$ toward a *cis*-$[Ru(bpy)_2]^{2+}$ core, which is expected to bind with thiolato groups retaining its coordination geometry and to exhibit intriguing redox properties.[6] Here, we report that the reaction of *cis*-$[RuCl_2(bpy)_2]$ with $[Pd(aet)_2]$ does not afford an expected S-bridged dinuclear complex, $[Ru(bpy)_2\{Pd(aet)_2\}]^{2+}$, in which *cis*-$[Pd(aet)_2]$ chelates to a Ru^{II} center, but produces the first example of S-bridged multinuclear complexes having a $Ru^{II}Pd^{II}{}_2S_3$ metallochelate ring (Scheme 1).

Treatment of *cis*-$[RuCl_2(bpy)_2]\cdot 2H_2O$[7] (0.58 mmol) with $[Pd(aet)_2]$[8] (1.24 mmol) in acetone/water (6:1) under reflux gave a dark red solution, from which a dark red crystalline product ($[\mathbf{1}](ClO_4)_3$) was isolated by the addition of an aqueous solution of $NaClO_4$ (69% yield).[9] After several attempts, a small number of red crystals ($[\mathbf{1'}](ClO_4)_3$) suitable for X-ray analysis were obtained on diffusing diethyl ether into an acetonitrile solution of $[\mathbf{1}](ClO_4)_3$.[10] As shown in Figure 1, the complex cation $[\mathbf{1'}]^{3+}$ contains a *cis*-$[Ru(bpy)_2]^{2+}$ core (av. Ru–N = 2.067(3) Å) that is bound by a S-bridged $[Pd_2(aet)_3]^+$ dinuclear moiety through two thiolato S atoms (S1 and S3) to form a six-membered $RuPd_2S_3$ metallochelate ring with a chair-like conformation (av. Ru–S = 2.376(2) Å, Pd–S = 2.293(1) Å). To the $[Pd_2(aet)_3]^+$ moiety a pendant $[Pd(N)_2(S)_2]$ unit is attached through a S atom (S4) (Pd2–S4 = 2.370(4) Å), which completes a unique S-bridged $Ru^{II}Pd^{II}{}_3$ tetranuclear structure. Of note is the presence of an O atom on the nonbridging S atom (S5) in the $[Pd(N)_2(S)_2]$ unit (av. S–O = 1.48(1) Å). Thus, the complex cation $[\mathbf{1'}]^{3+}$ is formulated as $[Ru(bpy)_2\{Pd_2(aet)_3\}\{Pd(aet)(aese)\}]^{3+}$ (aese = 2-aminoethanesulfenate). One may assume that the parental $[\mathbf{1}]^{3+}$ is identical with $[\mathbf{1'}]^{3+}$. However, the FAB mass spectrum of $[\mathbf{1}](ClO_4)_3$ gave a main signal at $m/z = 1313$, the calculated molecular mass and the isotopic distribution of which match well with those for $\{[Ru(bpy)_2\{Pd_2(aet)_3\}\{Pd(aet)_2\}](ClO_4)_2\}^+$, rather than those for $\{[Ru(bpy)_2\{Pd_2(aet)_3\}\{Pd(aet)(aese)\}](ClO_4)_2\}^+$ ($m/z = 1329$). On the basis of this result, together with the elemental and plasma emission analytical results, it is assigned that $[\mathbf{1}]^{3+}$ has a S-bridged $Ru^{II}Pd^{II}{}_3$ tetranuclear structure in $[Ru(bpy)_2\{Pd_2(aet)_3\}\{Pd(aet)_2\}]^{3+}$, which is converted into $[\mathbf{1'}]^{3+}$ by air oxidation of the nonbridging thiolato group of the pendant $[Pd(aet)_2]$ unit (Scheme 1). This assignment is supported by the ^{13}C NMR spectrum of $[\mathbf{1}](ClO_4)_3$ in CD_3CN, which showed 10 methylene carbon signals due to aet ligands, besides 20 aromatic carbon signals due to bpy ligands.[9]

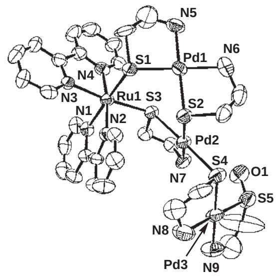
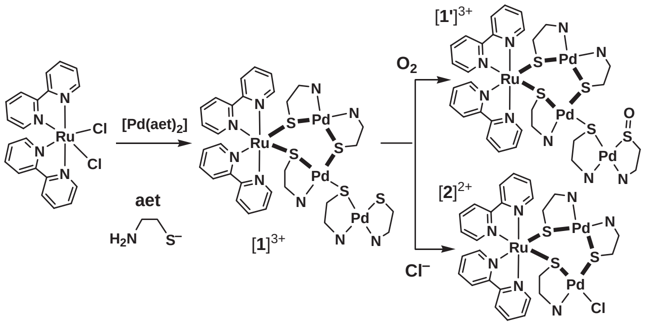


Figure 1. A perspective view of one of the two independent complex cations $[\mathbf{1'}]^{3+}$ with the atomic labeling scheme.



Scheme 1.

When an aqueous solution of $[\mathbf{1}](ClO_4)_3$ was chromatographed on an SP-Sephadex C-25 column, a dark red band was eluted with a 1.5 M aqueous solution of NaCl, although a considerable part of the compound was adsorbed on the top of column. From the dark red eluate, dark red crystals ($[\mathbf{2}](ClO_4)_2$) were isolated by the addition of an aqueous solution of $NaClO_4$ (24% yield).[11] The elemental analysis of $[\mathbf{2}](ClO_4)_2$ is consistent with the formula of $[Ru(bpy)_2][Pd_2(aet)_3]Cl(ClO_4)_2$, and its structure was established by X-ray analysis.[12] As shown in Figure 2, the complex cation $[\mathbf{2}]^{2+}$ contains a *cis*-$[Ru(bpy)_2]^{2+}$

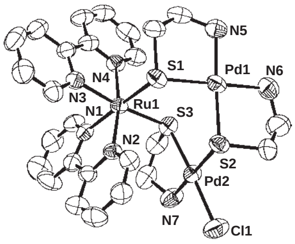


Figure 2. A perspective view of the complex cation $[\mathbf{2}]^{2+}$ with the atomic labeling scheme.

core (av. Ru–N = 2.070(4) Å) that is chelated by a $[Pd_2(aet)_3]^+$ moiety to form a S-bridged $Ru^{II}Pd^{II}_2$ trinuclear structure (av. Ru–S = 2.380(2) Å, Pd–S = 2.281(1) Å). This trinuclear structure is essentially the same as that found in $[\mathbf{1'}]^{3+}$. However, in $[\mathbf{2}]^{2+}$ a Cl^- ion is attached to a Pd atom (Pd2) of the $[Pd_2(aet)_3]^+$ moiety (Pd–Cl = 2.355(4) Å), instead of the pendant [Pd(aet)(aese)] unit in $[\mathbf{1'}]^{3+}$. This indicates that the pendant Pd^{II} unit in $[\mathbf{1}]^{3+}$ is replaced by a Cl^- ion in the course of the column chromatographic procedure eluting with an aqueous NaCl solution (Scheme 1). Compatible with the crystal structure of $[\mathbf{2}]^{2+}$, the ^{13}C NMR spectrum of $[\mathbf{2}](ClO_4)_2$ in CD_3CN showed 6 carbon signals due to aet ligands, besides 20 signals due to bpy ligands.[11] In addition, a main signal at $m/z = 990$ corresponding to $\{[Ru(bpy)_2\{Pd_2(aet)_3Cl\}](ClO_4)\}^+$ is observed in the FAB mass spectrum of $[\mathbf{2}](ClO_4)_2$.

The electronic absorption spectra of $[\mathbf{1}]^{3+}$ and $[\mathbf{2}]^{2+}$ in CH_3CN are very similar to each other, giving a MLCT ($Ru \rightarrow \pi^*_{bpy}$) band at 462 and 459 nm, respectively.[9,11] On the other hand, in the cyclic voltammetry in CH_3CN each of $[\mathbf{1}]^{3+}$ and $[\mathbf{2}]^{2+}$ displays a reversible redox couple at appreciably different potential (+0.99 V for $[\mathbf{1}]^{3+}$ and +0.90 V for $[\mathbf{2}]^{2+}$ vs Ag/AgCl), which is assigned to the one-electron process due to the $Ru^{III/II}$ center.[13] Thus, it is seen that the $Ru^{III/II}$ redox potential is tuned by the substituent group attached to the $Pd^{II}{}_2S_3$ chelating metalloligands. From the redox potentials, the ligand electrochemical parameter (Lever parameter), $E_L(L)$, which is used to predict the metal-centered redox potentials, was estimated to be 0.07 and 0.03 V for the $Pd^{II}{}_2S_3$ metalloligands in $[\mathbf{1}]^{3+}$ and $[\mathbf{2}]^{2+}$, respectively.[14] These $E_L(L)$ values are just between those for thiolate-type (−0.33–−0.56 V) and thioether-type (0.31–0.38 V) ligands,[14] reflecting the electron-donating ability of sulfur donor atoms.

In summary, it was found in this study that the reaction of $[RuCl_2(bpy)_2]$ with $[Pd(aet)_2]$ causes the partial dissociation of aet ligand from $[Pd(aet)_2]$ to give a novel S-bridged $Ru^{II}Pd^{II}_3$ tetranuclear structure in $[\mathbf{1}]^{3+}$. The pendant $[Pd(aet)_2]$ unit in $[\mathbf{1}]^{3+}$ was found to be air-oxidized to produce a sulfenato derivative ($[\mathbf{1'}]^{3+}$) and also replaced by a Cl^- ion to afford a S-bridged $Ru^{II}Pd^{II}_2$ trinuclear structure in $[\mathbf{2}]^{2+}$.[15] Interestingly, these complexes possess a $Ru^{II}Pd^{II}{}_2S_3$ metallochelate ring on the $[Ru(bpy)_2]^{2+}$ core, which has never been found in the previous literatures. The construction of different S-bridged metallochelate rings on the $[Ru(bpy)_2]^{2+}$ core, along with the replacement of the Cl^- ion in $[\mathbf{2}]^{2+}$ by other ligands, are currently underway.

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9 Anal. Calcd for $[\mathbf{1}](ClO_4)_3$: C, 25.52; H, 3.29; N, 8.93%. Found: C, 25.44; H, 3.59; N, 8.92%. UV–vis spectrum in CH_3CN [λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1})]: 462 (11200), 346 (10400), 292 (42000), 237 (47800). ^{13}C NMR in CD_3CN (δ from $SiMe_4$); 30.12, 30.61, 34.21, 36.44, 36.65, 49.68, 49.88, 50.00, 50.76, 52.78, 124.41, 125.07, 125.33, 125.39, 127.76, 127.80, 128.56, 137.68, 137.88, 138.27, 138.31, 150.98, 151.62, 153.97, 154.04, 157.32, 157.75, 158.36, 158.60.

10 Crystal Data for $[\mathbf{1'}](ClO_4)_3 \cdot CH_3CN \cdot 1/2H_2O$: fw 2955.47, triclinic, $P\bar{1}$, $a = 17.984(7)$ Å, $b = 25.060(8)$ Å, $c = 11.776(3)$ Å, $\alpha = 98.01(2)°$, $\beta = 104.86(3)°$, $\gamma = 91.12(4)°$, $V = 5071(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.935$ g cm^{-3}, $R1$ ($wR2$) = 0.053 (0.177) for 7966 reflections with $I > 2.0\sigma(I)$. Two crystallographycally independent, yet nearly identical complex cations are present in the crystal.

11 Anal. Calcd for $[\mathbf{2}](ClO_4)_2 \cdot H_2O$: C, 28.21; H, 3.28; N, 8.86%. Found: C, 28.02; H, 3.39; N, 8.76%. UV–vis spectrum in CH_3CN [λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1})]: 459 (10600), 344 (8900), 292 (40000). ^{13}C NMR in CD_3CN (δ from TMS); 30.13, 34.17, 35.48, 48.69, 49.30, 49.69, 123.80, 123.88, 124.30, 124.73, 127.18, 127.21, 127.45, 127.90, 137.18, 137.27, 137.74, 150.65, 151.06, 153.41, 154.15, 156.72, 157.35, 157.65, 158.02.

12 Crystal Data for $[\mathbf{2}](ClO_4)_2 \cdot 2H_2O$: fw 1125.04, triclinic, $P\bar{1}$, $a = 13.710(4)$ Å, $b = 14.199(1)$ Å, $c = 11.059(2)$ Å, $\alpha = 93.93(1)°$, $\beta = 108.99(2)°$, $\gamma = 84.12(2)°$, $V = 2023.6(7)$ Å^3, $Z = 2$, $D_{calcd} = 1.846$ g cm^{-3}, $R1$ ($wR2$) = 0.058 (0.196) for 4368 reflections with $I > 2.0\sigma(I)$.

13 No other redox couple was observed in the positive potential region up to +1.2 V for each of $[\mathbf{1}]^{3+}$ and $[\mathbf{2}]^{2+}$.

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15 The reaction of $[\mathbf{1}]^{3+}$ with hydrogen peroxide in CH_3CN gave its sulfinato derivative, $[Ru(bpy)_2\{Pd_2(aet)_3\}\{Pd(aet)(aesi)\}]^{3+}$ (aesi = $NH_2CH_2CH_2SO_2^-$), which was characterized by the elemental analysis, FAB mass, UV–vis, IR, and ^1H NMR spectra. Anal. Calcd for $[Ru(bpy)_2\{Pd_2(aet)_3\}\{Pd(aet)(aesi)\}](ClO_4)_3 \cdot H_2O$: C, 24.60; H, 3.31; N, 8.62%. Found: C, 24.50; H, 3.40; N, 8.48%. FAB-mass: $m/z = 1345$ for $\{[Ru(bpy)_2\{Pd_2(aet)_3\}\{Pd(aet)(aesi)\}](ClO_4)_2\}^+$. UV–vis spectrum in CH_3CN [λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1})]: 460 (10200), 349 (11200), 292 (46700), 240 (44400). The figures of its UV–vis, IR, and ^1H NMR spectra are shown in supporting information, together with the spectra of $[\mathbf{1}]^{3+}$ and $[\mathbf{2}]^{2+}$.

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