A ruthenium(IV) complex with six sulfur donor atoms

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A stable monomeric ruthenium(IV) octahedral complex is synthesized with 1,2-dicyanoethylene dithiolate(2−) (mnt²⁻) as ligand and its ligand rearranged product obtained in solution is structurally characterized as a novel bis(1,2-dicyano-2-mercaptoethylene)sulfide(2−) (mnts²⁻) coordinated ruthenium(II) compound.

Over thirty years ago there was a great deal of interest in the structural and electronic properties of metal complexes with dithiolate ligands.[1] An interest in the preparation of higher oxidation state ruthenium in a coordination environment composed exclusively of sulfur donor atoms has promoted a re-examination of the use of dithiolate ligands. Tris-dithiolate complexes exhibit a variety of different structural types and reactivities.[2] Trigonal prismatic coordination is commonly observed. Some studies of ruthenium(III) and (IV) 1,1-dithiolate[3] and thiolate[4] complexes have been reported but those with 1,2-dithiolate remain scant.[5] Interestingly, to date there is no report of a tris-dithiolate ruthenium(IV) complex despite the characterization of the corresponding species for iron(IV).[6] Indeed, there is no report of ruthenium(IV) in a coordination environment composed exclusively of sulfur donors.

A facile synthetic route has been developed for $[NEt_4]_3$-$[Ru^{III}(mnt)_3]\cdot2MeCN$ **1**. This tris-dithiolate complex has a geometry which is the closest approximation to an octahedral arrangement of this donor atom set reported to date.[2] $[Ru^{III}(mnt)_3]^{3-}$ is readily oxidized to the deep green compound, $[NEt_4]_2[Ru^{IV}(mnt)_3]$ **2**, by addition of an equivalent amount of an oxidizing agent such as I_2, H_2O_2 or $[NH_4]_2[Ce(NO_3)_6]$.† $[Ru^{III}(mnt)_3]^{2-}$ is the first structurally characterized all sulfur coordinated ruthenium(IV) complex. This species also has an octahedral arrangement of donor atoms. $[Ru^{III}(mnt)_3]^{2-}$ decomposes in the presence of light to the compound $[NEt_4]_2$-$[Ru^{II}(mnts)_2]\cdot0.5H_2O$ **3**, containing a novel tridentate ligand, bis(1,2-dicyano-2-mercaptoethylene)sulfide(2−) (mnts²⁻).

The X-ray structure‡ of $[Ru^{III}(mnt)_3]^{3-}$ (Fig. 1) shows a C_3 axis of symmetry with the Ru located on this axis. The average twist angle[7] is 50.2° and the S–Ru–S *trans* angle is 172.2°, only 4.9° less than the value calculated for the 'octahedral limit' with the constrained ligand bite angle.[8] This is the smallest *trans* angle deviation for transition metal tris-dithiolate complex reported so far.[2] The crystal structure of $[Ru^{IV}(mnt)_3]^{2-}$ (Fig. 2) is more distorted than $[Ru^{III}(mnt)_3]^{3-}$ but again the ruthenium atom is ligated with six sulfur atoms. Two Ru–S distances for one ligand are shorter than the other four. The twist angle is 47.1° and the average S–Ru–S *trans* angle is 169.4°, 7.0° less than the calculated 'octahedral limit.' The *trans* angle deviation is close to that reported for the iron analogue.[6] The increase in the oxidation state of ruthenium between $[Ru^{III}(mnt)_3]^{3-}$ and $[Ru^{IV}(mnt)_3]^{2-}$ is not reflected by any substantial change in the average Ru–S distance. However, the C=C distance in the ligand is shorter in $[Ru^{IV}(mnt)_3]^{2-}$, an unexpected result since formal ligand oxidation involves C–S multiple bonding and would imply the opposite trend for the C=C distance.

Both of these complexes are paramagnetic. Magnetic moments of 1.69 and 2.84 μ_B for $[Ru^{III}(mnt)_3]^{3-}$ and $[Ru^{IV}(mnt)_3]^{2-}$, respectively, correspond to their octahedral low-spin configuration. $[Ru^{IV}(mnt)_3]^{2-}$ $[E°(IV/III) = -0.70$ V, (III/II) = -1.71 V *vs.* Fc^+/Fc in CH_2Cl_2, 0.1 M $NBu^t_4PF_6$,

25 °C] is highly susceptible to reducing agents such as PhSH and gives $[Ru^{III}(mnt)_3]^{3-}$ in good yield. In dilute solution, $[Ru^{IV}(mnt)_3]^{2-}$ is both light and air sensitive. In CH_2Cl_2 or acetone, the green solution of $[Ru^{IV}(mnt)_3]^{2-}$ turns brown on Hg irradiation for 3 h and this product undergoes further decomposition on standing for one day in the presence of air. A major decomposition product is the deep purple ruthenium(II) complex, $[Ru^{II}(mnts)_2]^{2-}$, coordinated with two tridentate sulfur ligands. The unique sulfur ligands have formed from two
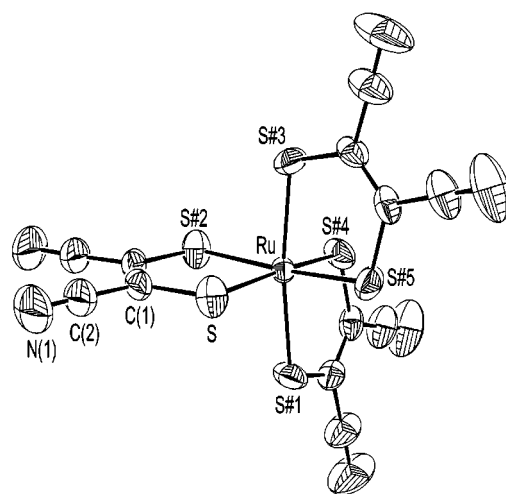

Fig. 1 Structure of the $[Ru(mnt)_3]^{3-}$ anion with 40% thermal ellipsoids and atomic labeling scheme. Selected bond lengths (Å) and angles (°): Ru–S 2.3468(8), S–C(1) 1.709(4), C(1)–C(1)#2 1.389(7), S–Ru–S#2 87.08(5), S–Ru–S#4 172.18(6).
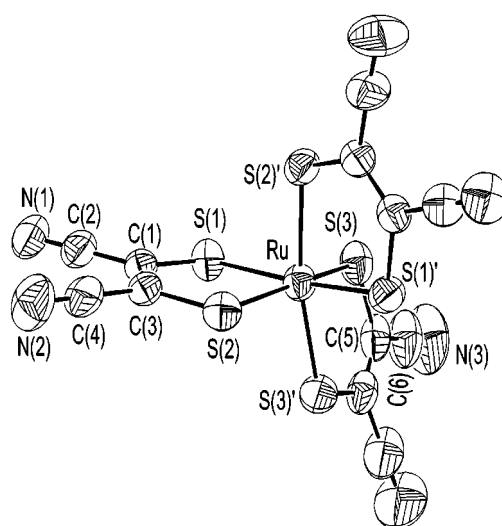

Fig. 2 Structure of the $[Ru(mnt)_3]^{2-}$ anion with 40% thermal ellipsoids and atomic labeling scheme. Selected bond lengths (Å) and angles (°): Ru–S(1) 2.3419(13), Ru–S(2) 2.3512(13), Ru–S(3) 2.3349(14), S(1)–C(1) 1.720(5), S(2)–C(3) 1.722(5), S(3)–C(5) 1.725(5), C(1)–C(3) 1.369(6), C(5)–C(5)#1 1.349(11), S(1)–Ru–S(2) 86.63(5), S(3)–Ru–S(3)#1 86.22(8), S(1)–Ru–S(1)#1 169.99(7).
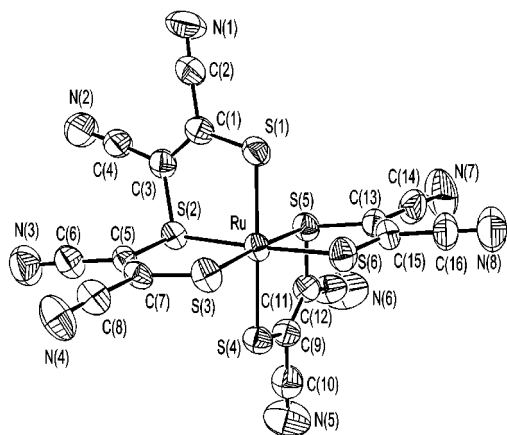
Fig. 3 Structure of the [Ru(mnt)$_2$]$^{2-}$ anion with 40% thermal ellipsoids and atomic labeling scheme. Selected bond lengths (Å) and angles (°): Ru–S(1) 2.341(2), Ru–S(2) 2.311(2), Ru–S(3) 2.329(2), Ru–S(4) 2.352(2), Ru–S(5) 2.318(2), Ru–S(6) 2.341(2), S(1)–C(1) 1.690(8), S(2)–C(3) 1.763(7), S(2)–C(5) 1.747(7), S(3)–C(7) 1.710(8), S(1)–Ru–S(4) 176.43(7), S(1)–Ru–S(2) 88.51(7), S(2)–Ru–S(3) 88.08(7), S(2)–Ru–S(5) 93.23(7).

mnt^{2-} ligands. Attempts to characterize the intermediate brown species structurally were unsuccessful but FAB MS data suggest an oligomeric species. It is conceivable that the complexes link by formation of disulfide bonds[9] and that the mnts^{2-} ligand forms by subsequent elimination of sulfur. The structure of [Ru^{II}(mnts)$_2$]$^{2-}$ [$E°$(III/II) = +0.42 V $vs.$ Fc$^+$/Fc in CH$_2$Cl$_2$, 0.1 M NBu$^t_4$PF$_6$, 25 °C] is shown in Fig. 3. The trivalent sulfur atoms of the two ligands are cis to each other. The average Ru–S distance and S–Ru–S $trans$ angle are 2.332(2) Å and 177°, respectively, with an octahedral arrangement of donors.

Notes and references

† *Syntheses*: compound **1**: a solution of Na$_2$(mnt) (0.600 g, 3.23 mmol) in water is added to a stirred aqueous solution of RuCl$_3$·3H$_2$O (0.207 g, 1.0 mmol) and the mixture is warmed to 50 °C. Addition of NEt$_4$Br (0.735 g, 3.5 mmol) to the resultant red–brown solution gives **1** which is washed with cold water and propan-2-ol and recrystallized from MeCN–Pr^{i}OH to give dark brown crystalline compound, **1**, yield 0.5 g, (50%). Anal: calc. (found) for C$_{40}$H$_{66}$N$_{11}$S$_6$Ru: C, 48.31 (47.50); H, 6.68 (6.81); N, 15.49 (15.24); S, 19.34 (18.88)%. IR (KBr pellet, cm^{-1}): 2183vs [ν(CN)] UV–VIS [CH$_2$Cl$_2$, λ/nm (ε/M^{-1} cm^{-1})]: 327(19050), 405(14930), 500(sh).

Compound **2**: a solution of **1** (0.167 g, 0.1 mmol) in 10 mL acetone is oxidized with I$_2$ (0.0127 g, 0.05 mmol) in 5 mL CH$_2$Cl$_2$ under argon. The solvent is evaporated completely by the argon flow and the green product extracted with 5 mL CH$_2$Cl$_2$, filtered, and the microcrystals precipitated on addition of 10 mL of light petroleum (bp 35–60 °C), yield 0.15 g, 90%. The AsPh$_4^+$ salt of [Ru(mnt)$_3$]$^{2-}$ is prepared by metathesis of **2** with AsPh$_4$Cl. Anal: calc. (found) for C$_{60}$H$_{40}$N$_6$S$_6$As$_2$Ru: C, 55.93 (55.82); H, 3.12 (3.30); N, 6.52 (6.26); S, 14.93 (15.06)%. IR (KBr pellet, cm^{-1}): 2198vs [ν(CN)],UV–VIS [CH$_2$Cl$_2$, λ/nm (ε/M^{-1} cm^{-1})]: 376(11261), 649(3429), 681(3413).

Compound **3**; a solution of **2** (0.391 g, 0.5 mmol) in acetone (30 mL) is irradiated by a Hg-vapor lamp in a photochemical reactor for 3 h and then

left in air for 1 day. The resulting solution is evaporated and the solid chromatographed on silica gel with CH$_2$Cl$_2$ as eluent. The purple product is recrystallized from Pr^{i}OH–light petroleum to give purple-red crystals, yield (25%). Anal: calc. (found) for C$_{32}$H$_{41}$N$_{10}$S$_6$O$_{0.5}$Ru: C, 44.42 (44.65); H, 4.77 (4.39); N, 16.18 (16.47); S, 22.23 (21.95)%. IR (KBr pellet, cm^{-1}): 2190vs, 2217w [ν(CN)] UV–VIS [CH$_2$Cl$_2$, λ/nm (ε/M^{-1} cm^{-1})]: 297(17550), 362(14676), 400(sh), 524(9642).

‡ All data were collected on an Enraf-Nonius CAD4 diffractometer at 293(2) K and the structures were solved by direct methods and refined by full-matrix least squares on F^2. Absorption correction based on ψ-scan was applied.

Crystal data: for [NEt$_4$]$_3$[Ru(mnt)$_3$]·2MeCN: M = 994.47, hexagonal, space group $P\bar{6}2c$, $a = b = 13.494(2)$, $c = 16.834(2)$ Å, $\gamma = 120°$, U = 2654.6 (6) Å^3, $Z = 2$, $D_c = 1.244$ g cm^{-3}. Of a total of 1797 reflections collected, 916 were unique. $R_1 = 0.0219$ and $wR_2 = 0.0568$; largest peak, hole in the final difference map = 0.168, −0.235 e Å^{-3}.

For [AsPh$_4$]$_2$[Ru(mnt)$_3$]: M = 1288.25, orthorhombic, space group $Pbcn$, $a = 20.399(2)$, $b = 15.674(2)$, $c = 18.020(2)$ Å, $U = 5761.8(10)$ Å^3, Z = 4, $D_c = 1.485$ g cm^{-3}. Of a total of 5068 reflections collected, 2984 were unique. $R_1 = 0.0471$ and $wR_2 = 0.0999$; largest peak, hole in the final difference map = 0.283, −0.411 e Å^{-3}.

For [NEt$_4$]$_2$[Ru^{II}(mnts)$_2$]·0.5H$_2$O: M = 867.20, monoclinic, space group $P2_1/c$, $a = 13.182(2)$, $b = 27.145(5)$, $c = 12.767(3)$ Å, $\beta = 111.319(10)°$, $U = 4255.6(14)$ Å^3, $Z = 4$, $D_c = 1.353$ g cm^{-3}. Of a total of 7790 reflections collected, 7448 were unique. $R_1 = 0.0705$ and $wR_2 = 0.1907$; largest peak, hole in the final difference map = 0.854, −0.679 e Å^{-3}. CCDC 182/1449. See http://www.rsc.org/suppdata/cc/1999/2349/ for crystallographic files in .cif format.

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