

Binuclear Complexes of Ruthenium Ammines with 4,4'-Dithiodipyridine Bridging Ligand

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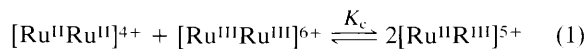
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The binuclear complex of ruthenium pentaammine with 4,4'-dithiodipyridine as the bridging ligand provides the first clear example of the great efficiency of the 'S-S' bridge in conducting electrons.

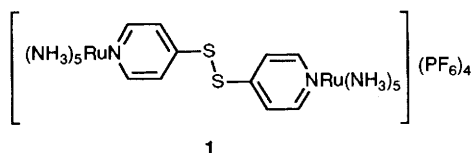
It is well documented in mixed valence chemistry that electronic coupling between metal centres is highly dependent on both the distance between the two metal centres and the nature of the bridging ligand.¹⁻⁴ We report here the first example of strong interaction between two metal centres at moderate internuclear distance where the sulfur-sulfur bridge of the ligand 4,4'-dithiodipyridine (dtdp), plays a decisive role.

The binuclear complex $[\{\text{Ru}(\text{NH}_3)_5\}_2\text{dtdp}](\text{PF}_6)_4$ **1** was synthesized[†] and characterized by spectroscopic[‡] and electrochemical[§] techniques and elemental analysis. The [III, II] mixed valence derivatives and the fully oxidized [III, III] species were generated *in situ*[¶] through electrochemical oxidation of the corresponding [II, II] complexes.

The electrochemical behaviour of these complexes was investigated by cyclic and pulse voltammetry. The observation of two, one-electron, reversible electrochemical processes and the considerable difference between the reduction potentials (E_2) of the [III, III]/[III, II] and [III, II]/[II, II] couples permits the evaluation¹⁻⁴ of the comproportionation constant K_c for the reaction [eqn. (1)] as equal to 8×10^4 . The K_c value indicates



that such complexes exhibit a stronger interaction between the metallic centres than the analogous 4,4'-bipyridine complexes.⁵⁻⁸ For example, K_c for the diruthenium complex of dtdp is nearly four orders of magnitude larger than that of the 4,4'-bipyridine system.^{5,6,8} Of such bipyridine systems, only the Taube-Creutz ion⁷ and the analogue μ -quinoxaline-bis-



[†] The [II, II] species was prepared by adding solid $[\text{Ru}(\text{NH}_3)_5\text{dtdp}](\text{PF}_6)_2$ (142 mg) to acetone (10 ml) containing dissolved $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2$ (101 mg). The complex was precipitated by adding solid NH_4PF_6 (0.5 g), filtered off and washed with 7:3 diethyl ether:acetone mixture, dried and stored under vacuum. (Yields better than 50%.) The $[\text{Ru}(\text{NH}_3)_5\text{dtdp}](\text{PF}_6)$ salt was isolated by reacting $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2$ with dtdp in acetone. (Yields better than 70%.)

[‡] The UV-VIS spectra were recorded in H_2O , $25.0 \pm 0.2^\circ\text{C}$, $\mu = 0.10 \text{ CF}_3\text{CO}_2\text{Na}/\text{CF}_3\text{CO}_2\text{H}$, $\text{C}_{\text{H}^+} = 10^{-3} \text{ mol dm}^{-3}$. The near infrared spectra were recorded in D_2O .

[§] The $(E_1)_1$ and $(E_2)_2$ corresponding to the couples $[\{\text{Ru}(\text{NH}_3)_5\}_2\text{dtdp}]^{5+/4+}$ and $[\{\text{Ru}(\text{NH}_3)_5\}_2\text{dtdp}]^{6+/5+}$ are respectively -0.130 and $+0.160 \text{ V}$ vs. saturated calomel electrode (SCE) at $25.0 \pm 0.2^\circ\text{C}$, $\mu = 0.10 \text{ CF}_3\text{CO}_2\text{Na}/\text{CF}_3\text{CO}_2\text{H}$, $\text{C}_{\text{H}^+} = 10^{-3} \text{ mol dm}^{-3}$.

[¶] The applied potentials for the generation of the [II, III] and [III, III] species respectively were $+0.050$ and $+0.400 \text{ V}$ vs. SCE, $\text{CF}_3\text{CO}_2\text{Na}$ 0.10 mol dm^{-3} , pH 7.0.

(pentaammineruthenium)(5+) ion,⁸ with their much shorter pyrazine bridge, have a larger K_c .

The UV-VIS spectra of the binuclear $\text{Ru}^{\text{II}}\text{-Ru}^{\text{II}}$ complex exhibit a maximum at 466 nm ($\epsilon = 1.9 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), in the spectrum assigned to a $4d\pi \rightarrow \pi^*$ metal to ligand charge transfer (MLCT) and occurs at lower energy than the MLCT band observed in the spectrum of the related monomer⁸ $[\text{Ru}(\text{NH}_3)_5\text{dtdp}]^{2+}$ ($\lambda_{\text{max}} = 459 \text{ nm}$, $\epsilon = 1.3 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). As expected,⁸ the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ species does not show the strong MLCT band in the visible region of the spectrum absorbing only in the near ultraviolet ($\lambda_{\text{max}} = 314 \text{ nm}$, $\epsilon = 1.2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The strong and broad band of the III/II species observed in the near ultraviolet region corresponds to more than one process. As judged from spectrum deconvolution, one band can be tentatively assigned at 314 nm ($\epsilon = 1.2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) due to a LMCT transition while the other at 280 nm ($\epsilon \cong 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) is probably due to the ligand itself.

The absorption spectrum of the mixed valence species $\text{Ru}^{\text{II}}\text{-Ru}^{\text{III}}$ also exhibits a MLCT transition in the visible region ($\lambda_{\text{max}} = 468 \text{ nm}$, $\epsilon = 1.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), as has been observed with analogous binuclear complexes.^{1,5-7}

Extending the spectral investigations to the near-infrared region, an intervalence band is observed at 1500 nm ($\epsilon = 4.3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) for the mixed valence $\text{Ru}^{\text{II}}\text{-Ru}^{\text{III}}$ complex. These bands are attributable to the intramolecular electron transfer reaction $[2,3] \rightarrow [3,2]$ in complex $[\{\text{Ru}(\text{NH}_3)_5\}_2\text{dtdp}]^{5+}$ and is very similar to the bands observed for the Taube-Creutz¹¹ ion.

Additional support for the strong electron delocalization on the title complex came from the near infrared spectra of the $[\{\text{Ru}(\text{NH}_3)_5\}_2\text{dtdp}]^{5+}$ ion. Corroborating the large values for K_c and molar absorption coefficient for the intervalence charge transfer transition for the $[\text{Ru}^{\text{II}}\text{-Ru}^{\text{III}}]$ species, the band width (1240 cm^{-1}) is significantly narrower than that expected (3920 cm^{-1}) by Hush's equation¹ for a valence trapped system, indicating a stronger coupling of the metal centres.


The importance of the S-S bridge on the coupling between the two ruthenium centres can also be evaluated by comparing binuclear systems with related bridging ligands containing one or two sulfur atoms. Thus with the ligand bis(4-pyridyl) sulfide, a weak coupling¹³ could be observed for the species $[\{\text{Ru}(\text{NH}_3)_5\}_2(\text{py-S-py})]^{5+}$, $K_c = 158$, $\lambda_{\text{max}} = 858 \text{ nm}$, $\epsilon = 70 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. On the other hand, for a series of ligands containing two separated (unbridged) sulfur atoms^{8,10-12} only weak coupling¹⁰ ($K_c < 200$) could be observed. Although the free ligand is easily cleaved to give 4-mercaptopyridine by reaction with ascorbic acid, the S-S bridge of either the binuclear complexes (II, II) or (III, III) or the mononuclear analogues is not reduced¹³ either by reaction with zinc amalgam or ascorbic acid. Thus, coordination to the $[\text{Ru}(\text{NH}_3)_5]^{2+}$ moiety deactivates the S-S bridge with respect to reductive cleavage.

The data collected on the systems described here demonstrate that dtdp is a bridging ligand which allows strong electronic coupling between metal centres in a manner comparable to pyrazine.^{1,6,7} Such behaviour provides compelling evidence for an intense electron delocalization between the two pyridine rings through the S-S bridge.

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