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The Creutz-Taube Complex Revisited†

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Abstract: X-ray single-crystal structures and ^{99}Ru Mössbauer spectra have been obtained for the three binuclear complexes $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{n+}$, $n = 4, 5, 6$ (pyz = pyrazine). Neither the structure nor the Mössbauer spectra of the mixed-valence ion ($n = 5$) can be described as an average of the oxidized ($n = 6$) and reduced ($n = 4$) species. Polarized crystal spectra reveal the presence of more than one electronic transition for the near-infrared absorption band. EPR measurements for the mixed-valence ion confirm that the odd electron is in a d-orbital capable of delocalization into the pyrazine π^*-orbitals. These results, including new infrared and resonance Raman data, imply strong interaction between the metal centers and between the metals and pyrazine.

Since the first report on the pyrazine-bridged decaammineruthenium(II,III) ion, $[(NH_3)_5Ru(pyrazine)Ru(NH_3)_5]^{5+}$, by Creutz and Taube,[2] a wide variety of experimental and theoretical studies has been performed thereon. The various experimental results led to conflicting conclusions concerning the electronic structure of this prototype mixed-valence ion.[3] The critical issue has been and still is the extent of electron delocalization in the mixed-valence ion. Considering the improvement in relevant physical techniques during the past decade and the fact that some of the earlier experiments had been carried out with partially decomposed or impure samples, we decided to embark on a collaborative reinvestigation of the Creutz-Taube complex. This paper reports the salient results from X-ray crystallography and from optical, EPR, ^{99}Ru Mössbauer, infrared, and resonance Raman experiments. In order to obtain as comprehensive a picture as possible we include results on the reduced or oxidized forms and on the mononuclear precursors wherever appropriate.

Experimental Section

The following complexes have been prepared by using slightly modified versions of published procedures[2] (pyz represents pyrazine, tos represents *p*-toluenesulfonate): $[(NH_3)_5Ru(pyz)Ru(NH_3)_5][ZnCl_4]_2$ = $[II,II][ZnCl_4]_2$, $[(NH_3)_5Ru(Pyz)Ru(NH_3)_5]Cl_5{\cdot}5H_2O$ or $(tos)_5{\cdot}4H_2O$ = [II,III] salts, $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]Cl_6{\cdot}2H_2O$ = $[III,III]Cl_6{\cdot}2H_2O$, $[(NH_3)_5Ru(pyz)Rh(NH_3)_5]Cl_5{\cdot}5H_2O$ = $[Ru^{II},Rh^{III}]\ Cl_5{\cdot}5H_2O$, and the mononuclear precursors $[(NH_3)_5Ru(pyz)]Cl_2$ = $[II]Cl_2$ and $[(NH_3)_5Ru(pyz)]Cl_3{\cdot}2H_2O$ = $[III]Cl_3{\cdot}2H_2O$. Stoichiometries were confirmed by elemental analyses. Single crystals of the complexes were grown from aqueous solutions by either slow cooling of a saturated solution or by isothermal evaporation of the solvent.

X-ray crystallography: Nonius CAD4 diffractometer, University of Bern. Mössbauer spectroscopy: Technische Universität München. Optical spectroscopy: Single-crystal specular reflectance and transmission spectroscopy, Australian National University, University of Bern. Infrared and resonance Raman spectroscopy: University College London. EPR: X-band spectra, Varian E9, University of Zürich. Detailed accounts of the experiments will be published separately.

Results and Discussion

The overall molecular conformation determined from single-crystal X-ray diffraction[4] is very similar for the three binuclear complexes [II,II], [II,III], and [III,III] (Figure 1.) Angles between the pyrazine plane and the *cis*-NH_3-Ru bonds are approximately 45°. In $[II,III]Cl_5{\cdot}5H_2O$ the center of the pyrazine bridge coincides with a center of inversion; the two ruthenium sites are therefore symmetrically equivalent. The structure of triclinic $[II,III](tos)_5{\cdot}4H_2O$ was determined at 100 K and shows two crystallographically inequivalent ruthenium sites; the coordination geometries of the two ruthenium atoms are slightly but significantly different from one another (cf. Table I), and Ru1 deviates by 0.42 Å from the least-squares plane containing pyz and Ru2. Some relevant bond lengths are summarized in Table I. Comparison of the data shows that the structure of [II,III] is neither a combination of the mononuclear fragments [II] and [III] nor is it the average of the structures of [II,II] and [III,III]. Rather, the structure of [II,III] closely resembles that of [II,II].

The slight structural differences between $[II,III]Cl_5{\cdot}5H_2O$ and $[II,III](tos)_5{\cdot}4H_2O$ do not show up in the ^{99}Ru Mössbauer spectra. Both compounds yield closely similar spectra consisting of one slightly broadened quadrupole-split doublet. The spectrum of [II,III] is not midway between the spectra of [II,II] and [III,III] (Figure 2). Rather, the observed isomer shift is close to that of [III,III]. Moreover, the spectrum of $[Ru^{II},Rh^{III}]$, where trapped valences may safely be assumed, is significantly shifted toward that of [III,III] away from that of [II,II], and it exhibits considerable quadrupole splitting. The quality of our data has improved sufficiently to exclude the possibility that the spectrum of [II,III] arises from a combination of those of [II] and [III]. The earlier conclusion[5] that the Mössbauer spectra indicates a completely localized structure can thus no longer be maintained.

The most notable optical feature of the Creutz-Taube ion is the intense ($\epsilon = 5500\ M^{-1}\ cm^{-1}$) absorption at 6400 cm^{-1}, the so-called "intervalence band". It is relatively narrow and its position is virtually solvent independent, a result that was taken

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† Dedicated to Professor Henry Taube in admiration.

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(4) Crystal data and parameters of the intensity collection and refinement are given in the following order: compound; space group; *a*, *b*, *c* (Å); α, β, γ (deg); *Z*; d_{obsd}, d_{calcd} (g cm^{-3}); no. of refl. with $I > 2\sigma(I)$; no. of variables; R, R_w: $[II,II][ZnCl_4]_2$: *Pcab*; 11.348 (2), 11.614 (2), 22.144 (3); 4; 1.97, 1.95; 2093; 232; 0.024, 0.024. $[II,III]Cl_5{\cdot}5H_2O$: *Pnnm*; 17.595 (2), 11.308 (2), 7.021 (1); 2; 1.71, 1.72; 972; 133; 0.025, 0.024. $[II,III](tos)_5{\cdot}4H_2O$ at 100 K: $P\bar{1}$; 13.162 (3), 15.116 (5), 15.749 (5); 106.96 (2), 94.40 (2), 103.15 (2); 2; -, 1.59; 5304; 723; 0.033, 0.031. $[III,III]Cl_6{\cdot}2H_2O$: $P2_1/n$; 7.465 (2), 11.401 (2), 14.613 (2); 79.60 (2); 2; 1.86, 1.86; 2465; 207; 0.019, 0.023. Fürholz, U.; Bürgi, H. B.; Ludi, A., to be published.

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Table I. Important Bond Lengths in $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{n+}$, $n = 4, 5, 6$, and in $[Ru(NH_3)_5(pyz)]^{m+}$, $m = 2, 3$

	[II][a]	[II,II]-$[ZnCl_4]_2$[b]	[II,III]$Cl_5\cdot 5H_2O$[b,c]	[II,III]$(tos)_5\cdot 4H_2O$[b,d]		[III,III]$Cl_6\cdot 2H_2O$[b]	[III][a]
site symmetry	1	$\bar{1}$	$2/m$	1(Ru1)	1(Ru2)	$\bar{1}$	m
Ru-N(pyz)	2.006 (6)	2.014 (3)	2.002 (3)	1.971 (4)	1.995 (4)	2.115 (1)	2.076 (8)
Ru-NH_3, trans	2.166 (7)	2.149 (3)	2.135 (3)	2.134 (5)	2.119 (5)	2.090 (1)	2.125 (8)
Ru-NH_3, cis[e]	2.153 (9)	2.131 (5)	2.110 (7)	2.112 (15)	2.114 (7)	2.100 (11)	2.106 (5)

[a] Gress, M. W.; Creutz, C.; Quicksall, C. O. *Inorg. Chem.* 1981, *20*, 1522. [b] This work. [c] For isostructural [II,III]$Br_{5-x}Cl_x$ see also: Beattie, J. K.; Hush, N. S.; Taylor, P. R.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1977, 1121. [d] 100 K. [e] Average.

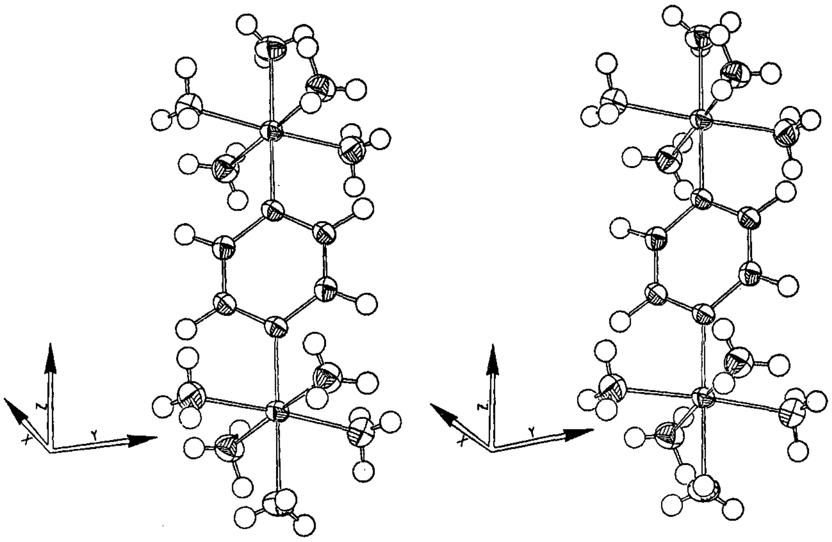

Figure 1. Stereoview of $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$ in the crystal structure of [II,III]$Cl_5\cdot 5H_2O$ and molecular coordinate system (*X, Y, Z*).

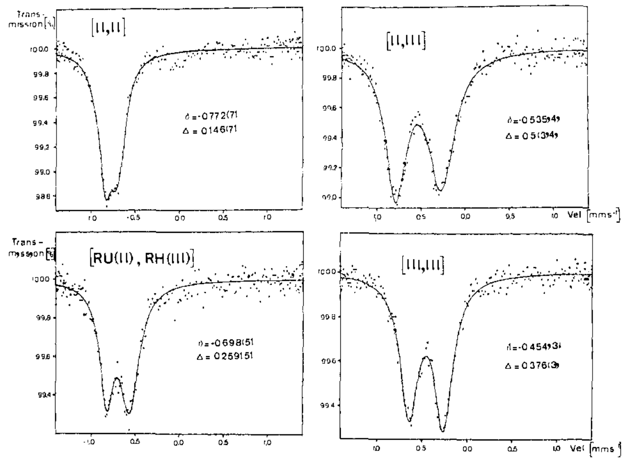

Figure 2. ^{99}Ru Mössbauer spectra of [II,II]$[ZnCl_4]_2$, [II,III]$Cl_5\cdot 5H_2O$, [III,III]$Cl_6\cdot 2H_2O$, and [Ru^{II}, Rh^{III}]$Cl_5\cdot 5H_2O$. Isomer shifts (δ) and quadrupole splittings (Δ) in mm s^{-1}.

as evidence for valence delocalization.[2,3] We have measured the specular reflectance of crystals of [II,III]$Cl_5\cdot 5H_2O$ with light polarized parallel to the molecular *X*-axis or in the molecular *YZ*-plane (Figures 1 and 3). Whereas the former spectrum does not show any dispersion, the latter one exhibits easily resolved dispersion consistent with the expected polarization along the Ru–Ru axis (*Z*). The absorption profile calculated by a Kramers–Kronig transform using inverse Fourier techniques is slightly (200 cm^{-1}) shifted to higher energy but of the same general shape as the solution spectrum (Figure 4A). Transmission spectra of very small (~100 μm) crystals of [II,III]$Cl_5\cdot 5H_2O$ in the same geometry and with light polarized parallel to *X* show resolved bands of very low intensity at 7100, 6400, and 5850 cm^{-1} (Figure 4B). The ratio of intensities for *X*- and (*YZ*)-polarized bands is about 1:100. Preliminary transmission spectra on the triclinic crystals of [II,III]$(tos)_5\cdot 4H_2O$ with only one orientation of the binuclear units exhibit two bands, a very broad *Y*-polarized absorption (8000 cm^{-1}) and a *Z*-polarized band (7000 cm^{-1}). The

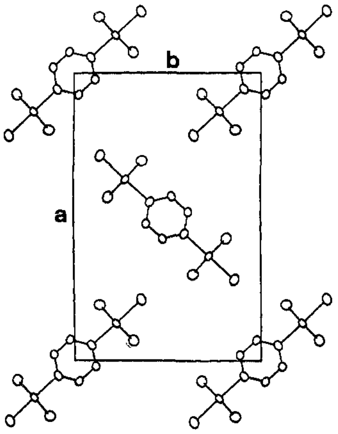

Figure 3. Projection of the unit cell of [II,III]$Cl_5\cdot 5H_2O$ parallel *c* (=X). Cl and H_2O are omitted.

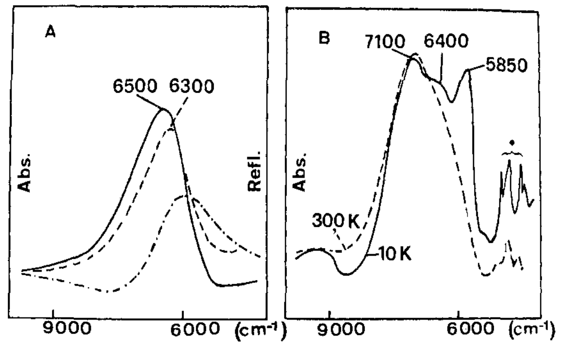

Figure 4. (A) Specular reflectance (–·–·) and absorption profile obtained from Kramers–Kronig transform (—) of a [II,III]$Cl_5\cdot 5H_2O$ crystal (light polarized in the *YZ*-plane). The absorption spectrum of [II,III] in a poly(vinyl alcohol) foil (- - -) is shown for comparison. (B) Transmission spectra of a crystal of [II,III]$Cl_5\cdot 5H_2O$ with light polarized parallel to *X* at 10 and 300 K. Bands marked with an asterisk represent combinations of NH_3 vibrations.

two bands show similar intensity. These crystal spectra demonstrate the presence of more than one transition beneath the asymmetric envelope of the "intervalence band", a fact which the solution spectra could not show.

The magnetic susceptibility of $[\mathrm{II,III}]\mathrm{Cl_5 \cdot 5H_2O}$ between 1.6 and 100 K shows Curie behavior corresponding to a magnetic moment of 2.0 μ_B. For $[\mathrm{III,III}](\mathrm{tos})_6$ antiferromagnetic coupling was deduced from preliminary magnetic measurements.[6] This is confirmed by our data for $[\mathrm{III,III}]\mathrm{Cl_6 \cdot 2H_2O}$ (1.6 to 100 K). The ordering temperature is 6.5 K, with the triplet lying approximately 6 $\mathrm{cm^{-1}}$ above the singlet. EPR measurements (3 K) were performed on $[\mathrm{II,III}]\mathrm{Cl_5 \cdot 5H_2O}$ single crystals with the magnetic field either in the YZ plane or in the plane containing the c-axis (X) and the normal to a 110 face (Figure 3). In the YZ plane two resonance lines appear, one each from the two structurally equivalent binuclear ions with different orientation. The principal axes of the g-tensors are collinear to the molecular axes X, Y, Z: $g_X = 1.346$ (3), $g_Y = 2.799$ (3), $g_Z = 2.487$ (3).

The angle between the Z-axes of the two magnetically inequivalent complexes is 86 (1)°, in agreement with the diffraction results. The Hamiltonian is of the form

$$\mathcal{H} = \frac{D}{3}\left\{L_Z^2 - \frac{1}{3}L(L+1)\right\} + \lambda L \cdot S + \frac{E}{6}(L_X^2 - L_Y^2) + (kL + gS)\beta\vec{H}$$

The EPR spectrum was simulated by diagonalizing the perturbation matrix using the one-center basis set $|XZ\rangle$, $|YZ\rangle$, and $|X^2 - Y^2\rangle$[7] with the parameters $D/\lambda = -0.60$ (2), $E/\lambda = -2.69$ (2), $k = 0.981$ and $g_X = 1.347$, $g_Y = 2.800$, $g_Z = 2.485$. A value of 1000 $\mathrm{cm^{-1}}$ for $\lambda(\mathrm{Ru^{3+}})$[6] yields the following energies: $E_1 = -1793(10)$ $\mathrm{cm^{-1}}$, $E_2 = 378$ (10) $\mathrm{cm^{-1}}$, $E_3 = 1415$ (10) $\mathrm{cm^{-1}}$. These energies show that both an axial and a rhombic component of the ligand field must be considered to reproduce the g-tensor anisotropy, the rhombic distortion (XY) of the ligand field being larger than the tetragonal distortion (Z).[8] The unpaired electron is predominantly in the $|XZ\rangle$-orbital, in agreement with earlier results.[9] This orbital is parallel to the π^*-orbitals of the pyrazine bridge. Interaction between the two sets of orbitals and delocalization of the unpaired electron are therefore possible.

The infrared spectra (298 and 20 K) agree with earlier data.[2] The occurrence of one $\delta_s(\mathrm{NH_3})$ band at 1295 $\mathrm{cm^{-1}}$ for [II,III] in between the analogous bands at 1280 $\mathrm{cm^{-1}}$ for [II,II] and at 1330 $\mathrm{cm^{-1}}$ for [III,III], together with the observation of two bands at 1275 and 1310 $\mathrm{cm^{-1}}$ for [Ru(II), Rh(III)], may be taken as evidence for a symmetrical structure (D_{2h}) of [II,III] on the vibrational time scale. The near coincidence of infrared bands (possibly pyrazine ring modes) at ca. 700, 1230, and 1585 $\mathrm{cm^{-1}}$ with Raman bands at 699, 1232, and 1594 $\mathrm{cm^{-1}}$ (pyrazine $\mathrm{a_g}$ modes) suggests, however, the absence of a center of symmetry (C_{2v}). Attempts to refine assignments by deuterium substitution were unsuccessful. Arguments[10] based on resonance enhancement of a Raman band at 1080 $\mathrm{cm^{-1}}$ are irrelevant because our reinvestigation clearly shows that this band definitely arises from a photodecomposition product appearing even after a comparatively short period of irradiation at 20 K. This follows from the observation that upon irradiation the intensity of the intervalence band decreases rapidly whereas that of the visible band changes little. Modes showing resonance enhancement with the visible absorption band ($\lambda_0 = 568.2$ nm) of [II,III] are probably $\mathrm{a_g}$ fundamentals of the pyrazine ring (1584, 1015, and 609 $\mathrm{cm^{-1}}$ for free pyrazine). Although this result suggests D_{2h} symmetry for the ion, additional very weak bands at 1007 and 1453 $\mathrm{cm^{-1}}$ also develop at resonance. Owing to their weakness, we could not establish whether these bands arise from $\mathrm{a_g}$ or $\mathrm{b_{1u}}$ modes of free pyrazine or from transient decomposition products. Hence the Raman results, like the infrared results, do not unambiguously establish the ground-state symmetry of the Creutz–Taube ion.

In summary, the combined single-crystal X-ray and $^{99}\mathrm{Ru}$ Mössbauer studies show that the Creutz–Taube ion cannot be described as the combination of its mononuclear precursors or as the average of the [II,II] and [III,III] ions. In combination with the rhombic distortion shown by the EPR data, they do imply strong interaction not only between the metal centers but also between the metals and the pyrazine bridge. The latter interaction has been largely ignored by current models for discussing mixed-valence properties.[3] The sum of structural and spectroscopic evidence reported here does not allow one to decide the question whether the odd electron in the Creutz–Taube ion is trapped on one Ru or delocalized equally over both. Resolution of this issue has to await a fuller understanding of the electronic structure of this ion.

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Registry No. $[\mathrm{II,II}][\mathrm{ZnCl_4}]_2$, 87922-19-8; $[\mathrm{II,III}]\mathrm{Cl_5 \cdot 5H_2O}$, 87922-20-1; $[\mathrm{II,III}](\mathrm{tos})_5\mathrm{\cdot 4H_2O}$, 87922-21-2; $[\mathrm{III,III}]\mathrm{Cl_6 \cdot 2H_2O}$, 87922-22-3; $[\mathrm{Ru^{II},Rh^{III}}]\mathrm{Cl_5}$, 87922-23-4.

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(7) Griffith, J. S. "The Theory of Transition Metal Ions"; Cambridge University Press: Cambridge, 1961; p 363.

(8) If the EPR convention $E \leq 2/3|D|$ is followed the coordinate axes should be rearranged as $X \rightarrow y'$, $Y \rightarrow z'$, $Z \rightarrow x'$. The appropriate parameters are $D'/\lambda = +2.31$ (2); $E'/\lambda = 0.74$ (2); $E'/D' = 0.32$.

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(10) Strekas, T. C.; Spiro, T. G. *Inorg. Chem.* **1976**, *15*, 974.