Inorganica Chimica Acta, 89 (1984) L33–L34

Electronic and Resonance Raman Spectroscopic Evidence for Identification of μ-Trihalobis(triammine–ruthenium)(2+) Ions as Delocalized Ru(II, III) Mixed-valence Complexes

ROBERT S. ARMSTRONG, JAMES K. BEATTIE, PATRICIA DEL FAVERO

Department of Inorganic Chemistry, University of Sydney, N.S.W. 2006, Australia

VIVIENNE M. ELLIS and NOEL S. HUSH*

Department of Theoretical Chemistry, University of Sydney, N.S.W. 2006, Australia

Received April 26, 1984

Ruthenium 'blue' solutions, formed from '$RuCl_3$' and concentrated HCl, were first described over 180 years ago, as noted recently by Bino and Cotton [1], but the structure of the blue species has not been yet definitely established. However, evidence from a number of sources suggests that the compounds are mixed-valence complexes and hence at least binuclear.

Similar intensely coloured species are formed from ruthenium ammine complexes and concentrated halide acids [2–5]. Here, there is reasonable evidence that one species formed [6] has cofacial bioctahedral geometry with three bridging halide ligands [7–8], *i.e.* from HCl solution μ-trichlorobis(triammine–ruthenium)(2+) chloride [**I**] and from HBr μ-tribromobis(triammineruthenium)(2+) bromide [**II**].

There has not yet been any detailed examination of the electronic structures of these compounds. It has been shown by measurement of magnetic moments [4, 5] that they possess one unpaired electron per dimer, as anticipated for a ruthenium (II,III) mixed-valence dimer. A single Ru–Cl stretching frequency was assigned in the infrared spectrum [8]. This was based on the assumption of D_{3h} symmetry, implying the presence of equivalent ruthenium atoms with a delocalized electronic ground state, but this assumption was not founded on other evidence.

We have studied the electronic absorption spectra of **I** and **II** (prepared by the method of ref. 4) in solution and in glycerol glasses down to 4–10 K. Both complexes exhibit a narrow absorption band in the near infrared [ν_{max} = 7.15 and 6.87 kK; $\Delta\nu_{1/2}$ 1.87 and 1.90 kK ϵ_m 1.60 × 10^3 and 1.88 × 10^3 M^{-1} cm^{-1} respectively for **I** and **II** in D_2O at 300 K] and intense broader bands in the visible [ν_{max} = 17.0 and 15.79] kK; $\Delta\nu_{1/2}$ 4.55 and 4.60 kK; ϵ_{max} 3.97 and 3.24 × 10^3 M^{-1} cm^{-1} in H_2O at 300 K; *cf.* also refs. 4 and 5]. These bands are absent in corresponding mononuclear single-valence Ru(II) and Ru(III) complexes. The band maxima are insensitive to solvent dielectric characteristics.

Using a molecular orbital scheme recently described by several authors [9–12] for a cofacial bioctahedral structure, the near infrared and visible bands are attributed to $\delta^* \rightarrow \sigma^*$ (short-axis polarized) and $\sigma \rightarrow \sigma^*$ (long-axis polarized) excitations respectively. (In D_{3h} symmetry these are of the type $e'' \rightarrow a_2''$ and $a_1' \rightarrow a_2''$ respectively). Hence the electronic absorption spectra are consistent with the expected intervalence excitation in delocalized binuclear ions. The temperature dependence of the visible bands was measured in glycerol liquid and glass down to 4–10 K. This was analysed according to a simple model in which the temperature-dependence of the second moment of the band is interpreted in terms of distance-dispersion arising from coupling to a single effective totally symmetric vibration of effective frequency ν_o. In this way, a value of 200 ± 30 cm^{-1} for ν_o for both chloro (**I**) and bromo (**II**) complexes was obtained.

In order to verify the visible spectral assignments, a resonance Raman study was carried out for **I**, **II** and the corresponding triodo complex **III**, which exhibits a similar visible absorption band [ν_m = 14.1 kK; $\Delta\nu_{1/2}$ = 4.96 kK; H_2O, 300 K]. The exciting lines from Kr^+ and Ar^+ lasers used to excite resonance Raman spectra of **I**, **II** and **III** respectively were at 568 nm, 647 nm and 676 nm, these being closest to the relevant band maxima. These were compared with non-resonant Raman spectra. Care has to be exercised owing to the photolability of these complexes, and both solution and solid-state spectra were obtained.

It is found that resonance enhancement occurs for frequencies attributed (on the basis of previous infrared and Raman studies of related complexes) [8, 13–15] to the totally symmetric A_1 ligand bend (ν_3), X–Ru–X, and stretch (ν_2), Ru–X modes. For the chloro (**I**), bromo (**II**) and iodo (**III**) complexes, the frequencies are for ν_3: 145 cm^{-1}, 106 cm^{-1} and 79 cm^{-1} respectively; for ν_2 they are 310 cm^{-1}, 247 cm^{-1} and 187 cm^{-1} respectively. These modes are illustrated in Fig. 1.

For the chloro and bromo complexes, the average of ν_2 and ν_3 is in the range 200 ± 30 cm^{-1} obtained for a single effective A_1 mode from the temperature dependence of the second moment of the absorption bands; there is thus good agreement between the two types of measurement. The depolarization ratios of the resonance-enhanced bands ranged from 0.2 to

---

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

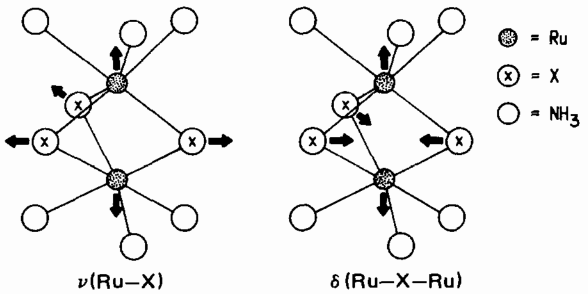

Fig. 1. Totally symmetric ligand bend (ν_3), X–Ru–X and stretch (ν_2), Ru–X, modes enhanced in resonance Raman spectra of $[(NH_3)_6Ru_2X_3]^{2+}$ (X = Cl, Br, I) ions, for exciting lines within the envelope of the principal visible absorption band. This is attributed to a $\sigma \rightarrow \sigma^*$ ($A_1' \rightarrow A_2''$) transition within a D_{3h} delocalized Ru(II,III) mixed-valence complex.

0.4, close to 1/3, consistent with the assignment of $\sigma \rightarrow \sigma^*$, $A_1' \rightarrow A_2''$ to the electronic transition. In addition to fundamentals, combination bands $\nu_2 + \nu_3$ and overtones $2\nu_2$ were observed in the resonance Raman spectra, indicating different ground and excited state geometries. Together with the $\sigma \rightarrow \sigma^*$ assignment of the electronic transitions, it follows that the Ru···Ru internuclear distance is larger in the excited state. The equilibrium excited state geometry must have components along the two ground state coordinates of the ν(Ru–X) and δ(X–Ru–X) modes for the combinations $\nu_2 + \nu_3$ and $2\nu_2 + \nu_3$ to appear. These properties of the excited state of the trihalo-bridged Ru(II,III) complexes confirm that the odd electron is delocalized, in contrast to a localized ground state with non-equivalent ruthenium centres.

The fact that the resonance Raman spectrum is dominated by single quanta excitations of totally symmetric modes and their combinations has interesting implication for the theory of electronic structure of mixed valence complexes [16].

References

1 A. Bino and F. A. Cotton, *J. Am. Chem. Soc., 102,* 608 (1980).
2 F. M. Lever and A. R. Powell, *J. Chem. Soc., (A),* 1477 (1969).
3 J. F. Endicott and H. Taube, *Inorg. Chem., 4,* 437 (1965).
4 F. Bottomley and S. B. Tong, *Can. J. Chem., 49,* 3739 (1971).
5 E. E. Mercer and L. W. Gray, *J. Am. Chem. Soc., 94,* 6426 (1972).
6 F. A. Cotton and D. A. Ucko, *Inorg. Chim. Acta, 6,* 161 (1972).
7 F. Bottomley, *Can. J. Chem., 55,* 2788 (1977).
8 J. R. Durig, Y. Omura and E. E. Mercer, *J. Mol. Structure, 29,* 53 (1975).
9 R. Saillant and R. A. D. Wentworth, *J. Am. Chem. Soc., 91,* 2174 (1969).
10 J. L. Templeton, W. C. Dorman, J. C. Clardy and R. E. McCarley, *Inorg. Chem., 17,* 1263 (1978).
11 R. H. Summerville and R. Hoffman, *J. Am. Chem. Soc., 101,* 382 (1979).
12 W. C. Trogler, *Inorg. Chem., 19,* 697 (1980).
13 K. K. Petrov, V. V. Kravchenko and N. M. Sinitsyn, *Russ. J. Inorg. Chem., 14,* 1420 (1970).
14 R. S. Armstrong, to be published.
15 M. W. Bee, S. F. A. Kettle and D. B. Powell, *Spectrochimica Acta, 30A,* 139 (1974).
16 N. S. Hush, in D. B. Rorabacher and J. F. Endicott, (Eds.), 'Mechanistic Aspects of Inorganic Reactions', ACS Symposium Series 198, Washington D.C. 330, 1982.