Resonance-Raman Studies of the Nitride-bridged Complex $K_3[Ru_2NCl_8(OH_2)_2]$ †

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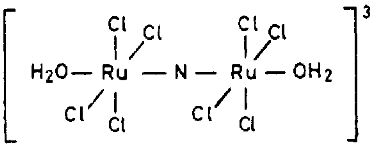
The resonance-Raman spectrum of $K_3[Ru_2NCl_8(OH_2)_2]$, along with Raman-band excitation-profile measurements, indicates that the electronic band at 31 200 cm^{-1} of the complex in the solid state may be assigned to the $e_u^* \leftarrow e_g$, $^1A_{2u} \leftarrow {}^1A_{1g}$ transition of the π-bond system of the linear Ru–N–Ru bridge.

EXTENSIVE resonance-Raman (r.R.) studies on the oxide-bridged ions $[M_2OX_{10}]^{n-}$ ($M = Ru$, Os, Re, or W; $X = Cl$ or Br; $n = 3$ or 4) have led to an understanding of the electronic and vibrational spectra of, and bonding in, these ions.[1-4] An analogous study of an effectively isoelectronic and isostructural nitride-bridged ion, $[Ru_2NCl_8(OH_2)_2]^{3-}$, would be desirable in order to probe the nature of its allowed electronic transitions. The structure of the ion is such that it has a linear O–Ru–N–Ru–O backbone, the chloro-ligands occupying the remaining octahedral sites around each ruthenium atom so that the overall skeletal symmetry is D_{4h} (see below).



In the potassium salt, the RuN, RuO, and RuCl bond distances are 1.720, 2.175, and 2.364—2.367 Å respectively,[5] values which are closely similar to those found for the ammonium salt, *viz.* 1.725, 2.201, and 2.370—2.391 Å respectively.[6]

We report here the r.R. spectrum of the potassium salt, obtained with u.v. excitation, and compare it with the normal off-resonance spectrum obtained with visible excitation. This leads to an assignment for the intense band of the ion at 31 200 cm^{-1} which is consistent with the expected bonding in the ion.

EXPERIMENTAL

The complex $K_3[Ru_2NCl_8(OH_2)_2]$ was prepared by treating $[RuO_4]^{2-}$ with ammonia *via* the intermediate $[Ru_2N(OH)_5] \cdot nH_2O$.[7]

Raman spectra were recorded using a Spex 14018 R6 spectrometer in conjunction with a Coherent Radiation Ltd. CR 12 u.v. laser. The sample was held in the form of a KCl disc. For studies with u.v. excitation (*e.g.* 334.5 nm) power of $\leqslant 20$ mW was necessary and a sample temperature of *ca.* 80 K in order to avoid thermal decomposition.

RESULTS AND DISCUSSION

The r.R. spectrum of $K_3[Ru_2NCl_8(OH_2)_2]$, recorded with 334.5-nm excitation, is displayed in Figure 1 along with the off-resonance spectrum, recorded with 647.1-nm excitation. In the latter spectrum there are bands at 413, 329, 301, 287, 170, and 151 cm^{-1}, in close agreement with those reported by Cleare and Griffith.[7] We also agree with their assignments of the bands at 329, 413, and 301 cm^{-1} to the $\nu_1(a_{1g})$,ν_{sym}(RuNRu), $\nu_2(a_{1g})$,ν_{sym}(RuO), and $\nu_3(a_{1g})$,ν_{sym}(RuCl) fundamentals, respectively. The weak shoulder at 287 cm^{-1} is probably another Ru–Cl stretching mode of b_{1g} or e_g symmetry. The lower-lying bands at 170 and 151 cm^{-1} are assigned to bending modes, one of which is likely to be the $\nu_4(a_{1g})$, δ_{sym}(NRuCl) fundamental.

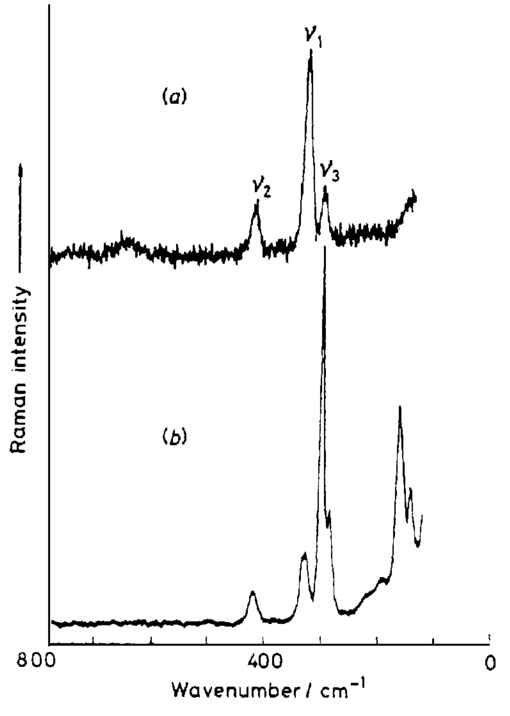


FIGURE 1 Raman spectra of $K_3[Ru_2NCl_8(OH_2)_2]$ as a KCl disc recorded with (*a*) 334.5-nm Ar^{2+} and (*b*) 647.1-nm Kr^+ excitation at *ca.* 80 and 300 K respectively

In the r.R. spectrum of the complex the only clearly defined bands are those corresponding to ν_1, ν_2, and ν_3, the most intense now being ν_1 and not ν_3. The low signal-to-noise ratio is a consequence of having to use

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† Tripotassium μ-nitrido-bis[aquatetrachlororuthenate(IV)].

low laser powers in order to avoid sample decomposition. Excitation profiles of the three a_{1g} bands are displayed in Figure 2 along with electronic spectra of the complex; the $\nu_1(a_{1g}),\nu_{sym}$(RuNRu) band is the most enhanced at resonance. The main features of the profiles are that they all display maxima at *ca.* 29 000 cm^{-1}, which is within the contour of the strong band (ε *ca.* 10^4 dm^3 mol^{-1} cm^{-1}) centred at 31 200 cm^{-1} in the solid-phase electronic spectrum of the complex. This behaviour is similar to that found for $[M_2OX_{10}]^{n-}$ ions [3,4] for exciting into the $e_u^* \leftarrow e_g$ transition of the M–O–M π-bond system. Since the $[Ru_2NCl_8(OH_2)_2]^{3-}$ ion is effectively isoelectronic and isostructural with the $[Ru_2OCl_{10}]^{4-}$ ion and is similarly diamagnetic [7] [ground-state electronic configuration $(e_u^b)^4(e_g)^4(b_{2g})^2(b_{1u})^2(e_u^*)^0$],[3] we assign the band at 31 200 cm^{-1} of the former to the $e_u^* \leftarrow e_g, {}^1A_{2u} \leftarrow {}^1A_{1g}$ transition of the Ru–N–Ru π-bond system. Weaker features in the profiles are also apparent at lower wavenumber, probably due to interference effects resulting from weak visible absorption bands (the relative intensities of which are shown more clearly in the solution electronic spectrum, Figure 2).

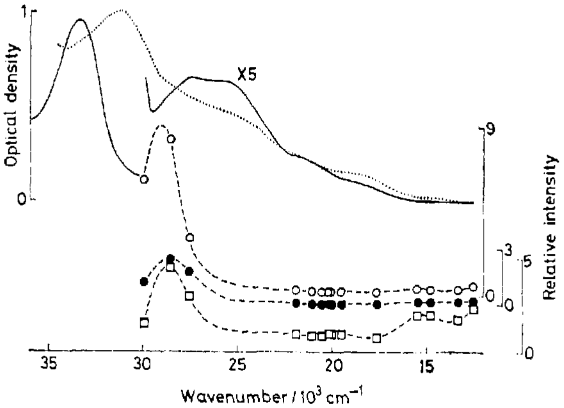

FIGURE 2 Excitation profiles of the ν_1 (○), ν_2 (●), and ν_3 (□) bands of $K_3[Ru_2NCl_8(OH_2)_2]$, together with electronic spectra of the complex in 6 mol dm^{-3} aqueous HCl solution at *ca.* 300 K (the HCl being necessary in order to suppress replacement of chloride by hydroxide ions) (——) and as a KCl disc at *ca.* 80 K (· · ·)

The r.R. results for the $[Ru_2NCl_8(OH_2)_2]^{3-}$ ion differ from those for the analogous oxide-bridged species in that no long overtone progressions in the $\nu_1(a_{1g}),\nu_{sym}$(RuNRu) mode were observed. This implies that the change in RuN bond length for this ion on excitation to the ${}^1A_{2u}$ state, although more than that of any other bond in the ion, is much less than the change in RuO bond length of the $[Ru_2OCl_{10}]^{4-}$ ion on excitation to this state.[8] In this respect the r.R. behaviour of the $[Ru_2NCl_8(OH_2)_2]^{3-}$ ion more closely resembles that of ruthenium red, $[Ru_3O_2(NH_3)_{14}]^{6+}$, and related ions,[9] than that of the $[Ru_2OCl_{10}]^{4-}$ ion.

The results reported here are consistent with the following facts. The Ru–N bond length of the $[Ru_2NCl_8(OH_2)_2]^{3-}$ ion (1.72 Å) [6] is considerably less than the Ru–O bond length of the $[Ru_2OCl_{10}]^{4-}$ ion (1.80 Å),[10] with the implications that the π-orbital overlap is stronger and the e_u^* orbital of the π-bond system is more destabilised for the former ion. This would account for the increase in the wavenumber of the $e_u^* \leftarrow e_g$ transition from *ca.* 20 000 cm^{-1} for the $[Ru_2OCl_{10}]^{4-}$ ion to 31 200 cm^{-1} for the $[Ru_2NCl_8(OH_2)_2]^{3-}$ ion.

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