Binuclear Nitrido-complexes of Ruthenium

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THE reaction between $[Ru(NO)X_5]^{2-}$ (X = Cl or Br) complexes and formaldehyde or stannous halides yields deep red crystalline products which have been variously supposed to contain the $[Ru_2H_4(NO)X_8]^{3-}$ or $[Ru_2(NH_2)(H_2O)X_8]^{3-}$ ions,[1,2] with the aquo- and amido-groups functioning as bridge ligands in the latter case. We have prepared the potassium salts of the chloro- and bromo-complexes by Brizard's methods, and on the basis of chemical analysis, the diamagnetism of the products, and their Raman and i.r. spectra formulate them as $K_3[Ru^{IV}_2NX_8(H_2O)_2]$, with a linear Ru–N–Ru bridge. These are the first reported nitrido-complexes of ruthenium and are also new members of the small group of transition-metal μ-nitrido-complexes {the other known examples are $[Os_2N(NH_3)_8X_2]X_3$ (X = Cl, Br, or I)[3] and the heterometallic species $[(PEt_2Ph)_3Cl_2ReNPtCl_2(PEt_3)]$[4]}.

The i.r. spectrum of $K_3[Ru_2NX_8(H_2O)_2]$ shows very sharp and strong bands at 1078 (chloride) and at 1050 cm.$^{-1}$ (bromide) in addition to water bands, but there are no bands attributable to imide, amide, or ammine modes. In $K_3[Ru_2NCl_8(D_2O)_2]$ the water bands shift as expected in the i.r. spectrum but the 1078 cm.$^{-1}$ band does not shift; it is however replaced by a similarly strong band at 1046 cm.$^{-1}$ in $K_3[Ru_2{}^{15}NCl_8(H_2O)_2]$ (95% isotopic purity). The immobility of this band on deuteriation and its downward shift of 32 cm.$^{-1}$ on ^{15}N-substitution clearly indicates it to be a skeletal metal–nitrogen mode, and we suggest that it is the asymmetric Ru–N–Ru stretch of a linear Ru–N–Ru system of the type illustrated; for this, a shift of 36 cm.$^{-1}$ is calculated for ^{15}N-substitution. In the analogous species $[Os^{IV}_2N(NH_3)_8Br_2]Br_3$ the same band shifts from 1098 to 1063 cm.$^{-1}$ on ^{15}N-substitution.[5] The Raman spectra of the solid chloro-salt (He–Ne 6328 Å excitation) together with the far i.r. spectra suggest that the molecule has a centrosymmetric anion of D_{4d} symmetry (as found in $K_4[Ru_2OCl_{10}]$)[6] since the 1078 cm.$^{-1}$ band is very strong in the i.r. and absent in the Raman, and two metal–chlorine stretches are found in the Raman at 329 and 297 cm.$^{-1}$ and at 318 and 290 cm.$^{-1}$ in the i.r. spectra.

The diamagnetism of the complexes (for the chloro-species $\chi g = -6\cdot 3 \times 10^{-6}$ c.g.s.u.) is consistent with the linear Ru–N–Ru structure; spin-pairing of the $4d_{xz}$ and $4d_{yz}$ ruthenium orbitals takes place *via* the $2p_{\pi}$ nitrogen orbitals, as in $[Ru_2OCl_{10}]$.[4–6]

Substitution reactions of these complexes and preparation of analogous species are being studied.

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