Resonance Raman Spectra of the Trinuclear Dinitrogen-bridged Complex $[\{Cl(PMe_2Ph)_4Re(N_2)\}_2MoCl_4]$

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Summary The resonance Raman spectrum of $[\{Cl(PMe_2Ph)_4Re(N_2)\}_2MoCl_4]$ indicates that the intense 23 300 cm^{-1} electronic band of the complex should be assigned to an $e_g \leftarrow e_u$ $^1A_{2u} \leftarrow {}^1A_{1g}$ transition of the axial π-system of the linear chain and it is proposed that the principal geometric changes within the complex on undergoing this transition are a lengthening of the Re–N and a shortening of the N–N bonds

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Recent publications[1–3] have discussed the changes in geometry accompanying promotion to the excited state in mononuclear dinitrogen complexes and their relevance to the reactivity of the co ordinated dinitrogen Polynuclear dinitrogen complexes have received less attention and we here report the results of resonance Raman studies of the complex $[\{Cl(PMe_2Ph)_4Re(N_2)\}_2MoCl_4]$ prepared by the reaction of $[Re(N_2)(PMe_2Ph)_4Cl]$ with $[MoCl_4(PPh_3)_2]$ in dichloromethane[4] This complex contains a linear Cl–Re–N–N–Mo–N–N–Re–Cl backbone (Figure 1) with Re–N N–N and Mo–N bond lengths of 1 75 1 28 and 1 99 Å respectively[4] Such bond lengths suggest approximate double bonding in the Re–N and N–N bonds and partial double bonding in the Mo–N bond The symmetry of the molecule is D_{4h} if the phosphine ligands are taken to be cylindrically symmetrical We report here that it is possible to excite within the contour of the 23 300 cm^{-1} band associated with the Re–N–N–Mo π bond system of the linear chain and to resonance enhance seven bands of the complex attributable to a_{1g} modes but in particular the two attributable to the N–N and M–N stretching modes The structural implications of this observation are outlined

The key results are shown in Figure 2 The Raman spectrum of the complex at ν_0 *ca* 19 000 cm^{-1} (effectively off resonance) changes systematically with increase in ν_0, the seven enhanced bands (those at 1818 1117 689 635 564 318 and 290 cm^{-1}) all being totally symmetric as shown by measurements in dichloromethane and other solvents of their depolarisation ratios (ρ) Of these bands, the two which are most resonance-enhanced and which follow most closely the contour of the very intense 23 300 cm^{-1} electronic band of the complex are those at 1818 and 689 cm^{-1} These bands are readily assigned to the ν_s (N–N) fundamental the in phase stretching mode of the collinear N–N bonds and to the ν_s (M–N) fundamental

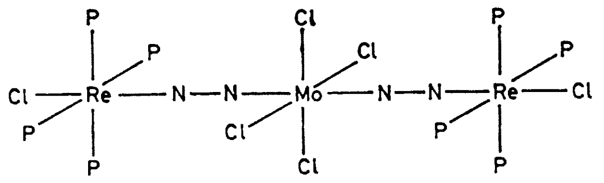

FIGURE 1. Skeletal structure of $[\{Cl(PMe_2Ph)_4ReN_2\}_2MoCl_4]$.

which is best described (on the basis of approximate force constant calculations) as an in-phase movement of the two N_2 entities between the Re and Mo atoms; *cf.*[5] the ν_s (Ru–O) fundamental at 827 cm^{-1} of the ruthenium red cation $[Ru_3O_2(NH_3)_{14}]^{6+}$.

The resonant electronic transition at 23 300 cm^{-1}, which must, on energy grounds, almost certainly be associated with the π-bond system of the linear chain, is axially (z) polarised since the ρ-values of the a_{1g} Raman bands approximate to $\frac{1}{3}$ on resonance.[6] This result therefore indicates that the resonant electronic transition is of the type $^1A_{2u} \leftarrow {^1A_{1g}}$ in D_{4h} nomenclature.

The 22 valence d- and p-electrons ($16\pi + 6\delta$) associated with the formal $Re^I(d^6)N_2(p^4)Mo^{IV}(d^2)N_2(p^4)Re^I(d^6)$ linear chain give rise, on the basis of simple molecular-orbital considerations, to the ground-state electronic configuration $(1e_g^b)^4(e_u^b)^4(2e_g^b)^4(e_u)^4(1b_{2g})^2(b_{1u})^2(2b_{2g})^2(e_g)^0(^1A_{1g})$. The lowest allowed z-polarised transition is thus $e_g \leftarrow e_u$, $^1A_{2u} \leftarrow {^1A_{1g}}$. Since the highest filled e_u orbital contains two Re–N π-bonds and a node between each pair of N atoms, but the e_g excited-state orbital (the LUMO) is non-bonding between both Re and N as well as between N and N, the transition in question would be expected to lead to a lengthening of the Re–N bonds and a shortening of the N–N bonds. A similar orbital scheme has been proposed for the complexes $[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ (M = Mo, W).[2] The LUMO and HOMO have similar bonding characteristics to the binuclear system above and excitation again weakens the M-N bonding. However in the mononuclear complexes the lowest observed charge-transfer band occurs at higher energy (26 000 cm^{-1}).

According to Raman theory, the mode(s) enhanced at resonance with an electric-dipole allowed transition is (are) the totally symmetric one(s) most effective in changing the molecule from the ground-state geometry to the excited-state geometry,[7] *viz.* clearly ν_s(N–N) and ν_s(M–N). These modes are precisely the ones giving rise to the most enhanced Raman bands, thus providing experimental evidence for the nature of the geometric change, deduced above, for the molecule on $^1A_{2u} \leftarrow {^1A_{1g}}$ electronic excitation.

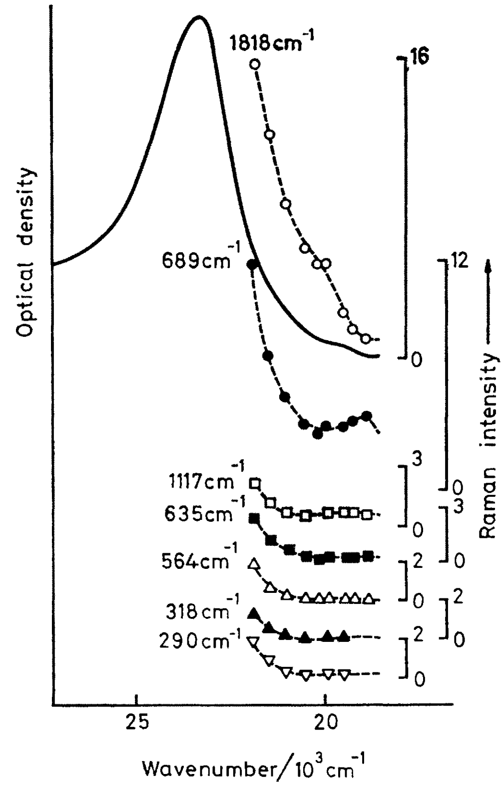

FIGURE 2. Excitation profiles for the key a_{1g} fundamentals of the complex in the vicinity of the 23 300 cm^{-1} electronic band.

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