The Raman Spectrum and Structure of the Ion [{Ru(NH₃)₅}₂N₂]⁴⁺

By J. CHATT,* A. B. NIKOLSKY, R. L. RICHARDS, and J. R. SANDERS

(*A.R.C. Unit of Nitrogen Fixation and the Chemical Laboratory, The University of Sussex, Brighton* BN1 9QJ)

SOME ten reasonably well defined complexes of the Group VIII metals are known containing nitrogen as a ligand. In all but one a strong band in the 1980—2150 cm.$^{-1}$ region of the i.r. spectrum has been assigned to the nitrogen–nitrogen stretching vibration [$\nu(N\equiv N)$], lowered by 350—180 cm.$^{-1}$ by co-ordination of nitrogen to the metal.

However, there is one well characterised complex ion formulated [{Ru(NH₃)₅}₂N₂]⁴⁺, which does not have an i.r. band assignable to $\nu(N\equiv N)$. To account for this absence a symmetrical binuclear structure with a bridging N₂ ligand has been postulated.[1] The Ru–N–N–Ru system might be formulated either as having a bent azo-type structure, [(NH₃)₅Ru–N=N–Ru(NH₃)₅]⁴⁺, formally of ruthenium(III), or having a linear structure, essentially [(NH₃)₅Ru–N≡N–Ru(NH₃)₅]⁴⁺ with a delocalised electronic system, formally of ruthenium(II). Both should show at best a very weak i.r. band but $\nu(N\equiv N)$ of the linear structure would occur at a much higher frequency than that of the azo-structure. Either structure should give a strong Raman band.

We have therefore examined the Raman spectrum of a solid sample of the tetrafluoroborate salt, and of its ¹⁵N₂

analogue prepared as in ref. 1a. By far the strongest Raman band occurs at 2100 ± 2 cm.$^{-1}$ and is shifted to 2030 ± 2 cm.$^{-1}$ in the ¹⁵N₂ analogue. The shift of 70 cm.$^{-1}$ is almost identical with the corresponding shift in the i.r. spectra of the salts having nitrogen as a terminal ligand, *i.e.* [Ru(NH₃)₅(N₂)][BF₄]₂ (2145 ± 5 cm.$^{-1}$) and [Ru(NH₃)₅)(¹⁵N₂)][BF₄]₂ (2080 ± 5 cm.$^{-1}$).[2] This identity of isotopic shift and the relatively high frequency of the Raman band allow us to assign it with certainty to $\nu(N\equiv N)$ of the linear symmetrical structure. We have also confirmed that the binuclear salt is diamagnetic, which such a structure would demand. For comparison with the above Raman spectra we have examined the Raman spectrum of [Ru(NH₃)₅(N₂)] [BF₄]₂ and find the strong $\nu(N\equiv N)$ band at 2133 ± 1 cm.$^{-1}$, lowered relative to free nitrogen, to about the same extent as in the binuclear complex. The exact lowering has little significance in view of the great sensitivity of $\nu(N\equiv N)$ to the anion in the mononuclear complexes.[3] The nitrogen is also inert to reduction by common reducing agents,[4] and it seems therefore that the N–N bond force constant and the reactivity of the nitrogen molecule are much the same whether nitrogen acts as a

terminal or as a bridging ligand. Molecular orbital calculations are now in progress in an attempt to elucidate the detailed electronic structure of the Ru–N–N–Ru system.

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[3] A. D. Allen and C. V. Senoff, *Chem. Comm.*, 1965, 621; also with F. Bottomley, R. O. Harris, and V. P. Reinsalu, *J. Amer. Chem. Soc.*, 1967, **89**, 5595.

[4] J. Chatt, R. L. Richards, J. R. Sanders, and J. E. Fergusson, *Nature*, 1969, **221**, 551.