Assignment of the Metal–Dinitrogen Stretching Frequency in Ruthenium and Osmium Pentammine Dinitrogen Salts

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Summary A new assignment is proposed for ν(M–N_2) (M = Ru or Os) in dinitrogen complexes of type $[Ru(NH_3)_5N_2]X_2$ (X = Cl, Br, I, or BF_4) based on deuteriation shifts and solid state Raman intensities, while polarised solution Raman data support a previous assignment of the osmium analogues.

THE highest frequency band in the metal–nitrogen stretching region (550—400 cm^{-1}) of the i.r. spectra of complex salts of type $[Ru(NH_3)_5N_2]X_2$ has been assigned[1] as largely ν(Ru–N_2), while the lower frequency bands have been assigned to ν(Ru–NH_3) stretching motions. We have found that on deuteriation of the bromide and iodide salts the high frequency band (A) shifts appreciably to low frequency, while the lowest frequency band in this region is displaced only a few wavenumbers (see Table 1). On this basis it appears that band (D) should be assigned to ν(Ru–N_2) while bands (A) to (C) are assigned to ν(Ru–NH_3). The small deuteriation shift found for ν(Ru–N_2) clearly results from coupling between metal–ammine and metal–dinitrogen bond stretching modes similar to that reported[2] for the analogous Os^{II} complexes. In this region there is no intermolecular coupling, and intensities in the solid state polycrystalline Raman spectra of ruthenium pentammine dinitrogen complexes[3] appear to support the above assignment since a band corresponding to (A) in the i.r. is not observed in the Raman, whereas that corresponding to (D) appears strongly. Assignment of the metal–ammine stretching modes in this and analogous compounds appears to follow the pattern shown in Table 2. It is surprising that in the dinitrogen complex the E mode appears at higher frequency than the two A_1 modes, but the assignment is supported by the fact that although this mode is formally Raman allowed, it is in fact derived from the Raman inactive T_{1u} in O_h and is not observed in any of these compounds (C_{4v} point group). In all cases the E mode is observed strongly in the i.r. spectrum. All ammine stretching frequencies are sensitive to the anion present in the salt; the frequencies in the order Cl > Br > I are suggestive of the existence of hydrogen bonding.

TABLE 1. *I.r. frequencies (cm^{-1}) for hydro- and deuterio-nitrogenpentammine* Ru^{II} *salts*

Band	(A)	(B)	(C)	(D)
$[Ru(NH_3)_5N_2]Br_2$	499 w	471 vw	434 sh w	424 m
$[Ru(ND_3)_5N_2]Br_2$	466	438	398	420
Shift	33	33	36	4
$[Ru(NH_3)_5N_2]I_2$	492	467	427	415
$[Ru(ND_3)_5N_2]I_2$	457	427	391	410
Shift	35	40	36	5

sh = shoulder, w = weak, vw = very weak, m = medium.

TABLE 2. *I.r. frequencies (cm^{-1}) of* ν(M–NH_3) *in* Ru *ammine complexes*[a] *(Raman only allowed B_1 mode is not observed)*

501 (A_{1g})[b]	460 (T_{1u})		$[Ru^{III}(NH_3)_6]Cl_3$
↓	↙	↘	
485	463	455	$[Ru^{III}(NH_3)_5Cl]Cl_2$
474	455	447	$[Ru^{II}(NH_3)_5CO]Cl_2$
471	445	511	$[Ru^{II}(NH_3)_5N_2]Cl_2$
A_1	A_1	E	Symmetry
(B)	(C)	(A)	Bands

[a] Data taken from ref. 3; Ru^{III} hexammine data have been reported in ref. 5; [b] Raman only.

Borod'ko *et al.*[2] have assigned ν(Os–N_2) in the analogous osmium(II) complexes to 518 cm^{-1} in the chloride salt since this band shifts only 4 cm^{-1} on deuteriation. It has however been suggested[4] that this band might be due to δ(M–N_2) (E) on the same basis. Raman studies on aqueous solutions of $[Os(NH_3)_5N_2]Cl_2$ indicate that the band corresponding to the 518 cm^{-1} in the i.r. is, indeed, polarised proving it to be totally symmetric ν(Os–N_2) and not δ(M–N_2) (E) as suggested. (We have been unable to obtain solution Raman spectra of the corresponding ruthenium salts because of their low water solubility).

The surprisingly low value of ν(Ru–N_2) compared with ν(Os–N_2) (δν = 85 cm^{-1}) presumably reflects a considerable force constant difference in the two bonds, dinitrogen bonding being exceedingly sensitive to the change in metal.

Deuteriation was by recrystallisation from D_2O, all compounds being more than 90% deuteriated.

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