Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

The dependence of $\nu(X{\equiv}Y)$ in the infrared spectra of $[Ru(NH_3)_5(X{\equiv}Y)]^{2+}$ upon counter-anion and upon solvent ($X{\equiv}Y = N_2$, CO, MeCN, PhCN or t-BuCN)

J. CHATT*, G.J. LEIGH and N. THANKARAJAN
A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton, BN1 9QJ, Sussex (Great Britain)

(Received October 8th, 1970)

In complexes of dinitrogen $\nu(N_2)$ is some 200–400 cm^{-1} lower than in dinitrogen[1]. On the basis of the bonding model for carbonyl complexes[2], this lowering indicates strong metal to dinitrogen π-bonding. However, in the solid salts of $[M(NH_3)_5(X{\equiv}Y)]^{2+}$ (M = Ru, $X{\equiv}Y$ = CO or N_2; M = Os, $X{\equiv}Y = N_2$)[3,4] $\nu(X{\equiv}Y)$ depends markedly on the counter-anion. This has been attributed in the dinitrogen complexes to direct interaction between the anion and the dinitrogen[4]. Further, in the nitrile derivatives $[Ru(NH_3)_5(N{\equiv}C{-}R)]^{2+}$ (R = aryl or methyl) $\nu(C{\equiv}N)$ is generally found at a lower frequency than in the free nitrile, also indicative of extensive metal to ligand π-bonding, but it is substantially independent of the anion when the IR spectra are measured in potassium bromide discs[5]. Because of the possibility of anion interactions with the dinitrogen ligand, we have investigated in detail the solid state spectral shifts of $\nu(X{\equiv}Y)$ in Nujol mulls. We find however that the prime cause of the spectral shifts is the interaction of the anion with the amine ligands. Our observed $\nu(X{\equiv}Y)$ are listed in Table 1. These sometimes differ from those previously reported[3-5], which are not self-consistent because the spectra of the solids are sensitive to impurities. In all the solid ruthenium salts $\nu(X{\equiv}Y)$ increases with the size of the counter-anion, and in one nitrile complex even rises above the frequency in the free nitrile, the first time this has been observed when a nitrile takes the place of dinitrogen in a complex. In solution, $\nu(X{\equiv}Y)$ is independent of the anion and depends on the solvent. Water gives a value about equal to that of solid iodides and dimethylsulphoxide about or rather lower than that of solid chlorides. However, the positions of all the bands in the infrared spectra depends on the anion, and those assigned to $\nu(N{-}H)$ change regularly from broad rather diffuse bands in the chlorides to narrower sharper bands (generally three) at higher frequencies in the hexafluorophosphates (see also ref. 3). This has been observed in other ammine cation salts where the complex diffuse spectra of chloride and related salts have been attributed to hydrogen bonding between NH and anion, and the sharper spectra of the tetrafluoroborate and related salts to its great weakening or absence[6]. Even when the triple bond is insulated from the anions by a bulky organic group, as in the salts of $[Ru(NH_3)_5(N{\equiv}C{-}R)]^{2}$, we find a distinct dependence of $\nu(X{\equiv}Y)$ on the anions, contrary to a previous report[5]. These observations suggest that the shift of $\nu(X{\equiv}Y)$ in the

TABLE 1

THE DEPENDENCE OF $\nu(X{\equiv}Y)$ UPON COUNTER-ANION AND SOLVENT

$[Ru(NH_3)_5(XY)]Z_2$						$[ReCl(XY)(dp)_2]Z$ [a]	
Z	XY →	N_2	CO	MeCN	PhCN	t-BuCN	N_2
Cl [b]		2105	1923	2237 [c]	2180, 2196 [c]	2212 [c]	2035
Br [b]		2111	1935	2238 [c]	–	2212 [c]	–
I [b]		2125	1948	2239	2190 [c]	2221	–
BF_4 [b]		2145	1972	2253	–	2229	2035
PF_6 [b]		2166	1993	2277	2219 [c]	2235	2044
Solvent [d]							
H_2O [e]		2121	1948	2246	2197	2221	–
$(CH_3)_2SO$ [e]		2092	1923	2230	2178	2209	2048
Free XY [f]		2331	2142	2253	2229	2236	2331

[a] $dp = Ph_2PCH_2CH_2PPh_2$. [b] Spectra in 'Nujol' mulls. [c] Not quite analytically pure.
[d] Generally chlorides and bromides were in water, fluoro-borates and -phosphates in $(CH_3)_2SO$. All salts of $[Ru(NH_3)(NCMe)]^{2+}$ were soluble in the latter and all gave $\nu(CN) = 2230$ cm^{-1}.
[e] Spectra in solution. [f] Spectra of gas or liquid films.

pentammine salts is caused primarily by the electrostatic interaction of the anions with the coordinated ammonia, which could be enhanced by hydrogen bonding.

In confirmation, where electrostatic interaction is weak because of the bulk of the cation, and hydrogen bonding is unlikely, $\nu(N_2)$ is almost independent of anion. Thus no dependence on anion was found in salts of $[ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2]^+$, although the anions are not sterically prevented from interaction with the N_2 ligand, as shown by the formation of adducts with quite bulky addends on the coordinated dinitrogen in the related complex $[ReCl(N_2)(PMe_2Ph)_4]$ [7].

We suggest that in the ammine salts the potential at the surface of the anions polarises the ammine ligands with consequent electron release to the ruthenium atom and thence into the π-antibonding orbitals of the triple bond, so lowering $\nu(X{\equiv}Y)$, this lowering being the greater the smaller the anion. Such an electrostatic effect operating directly upon coordinated $X{\equiv}Y$ would repel electronic charge from the π-antibonding orbitals into the metal and lead to a higher $\nu(X{\equiv}Y)$ with decreasing anion size. Doubtless this latter interaction also occurs but is so minor that it is submerged by the effect on the ammine ligands. Hydrogen-bonding or strongly dipolar solvents should interact with the ammine cation with the same effect as the anions. As a solvent, we find that dimethylsulphoxide has a greater effect on $\nu(X{\equiv}Y)$ than has water, perhaps because hydrogen bonding to the ammine cation is more complete than in aqueous solution where the cation is in competition with strong intermolecular hydrogen bonding. Finally, no anion dependence would be expected in solid state spectra taken in potassium bromide discs because the cations, whatever their provenance, are in an essentially bromide environment, which would explain the contradictory findings reported in ref. 5.

The electrostatic interactions we have discussed are general and not restricted to ammine cations. They are found in analogous anions, thus $\nu(NO)$ in $[RuCl_5(NO)]^{2-}$ rises with decreasing size of the counter-cation[8], where interaction of the nitrosyl group with the increasingly positive potential at the surface of the cation, by attracting electrons to the oxygen, would cause ν(NO) to fall. However, the cation interaction on the chloride ligands, attracting electronic charge ultimately from the metal, should cause ν(NO) to rise, as is observed.

The interaction, being essentially electrostatic, must occur at both the oxygen and the chloride in the complex anion, but that on the much greater surface of the chloride ligands predominates in its effect, as it does on the much greater ammine hydrogen surface of the $[Ru(NH_3)_5(X{\equiv}Y)]^{2+}$ salts. Any type of chemical bonding by the counter ion with the chloride or ammine ligands respectively would enhance the effect of the electrostatic interaction.

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