Benzonitrile Complexes of Ruthenium(II) and Ruthenium(III): Analogues of the Molecular Nitrogen Complex Ion $Ru(NH_3)_5N_2^{2+}$

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WE report the synthesis of some penta-ammineruthenium(II) and penta-ammineruthenium(III) substituted benzonitrile complexes. Since organonitriles have ligand properties analogous to molecular nitrogen (the co-ordinating atom is nitrogen, attached to the rest of the uncharged ligand by a triple bond, Ru–N≡), organonitrile co-ordination compounds are potential models of N_2 complexes in which the metal–N–N linkage is linear.[1] In particular, the Ru^{II} compounds reported, are analogous to the N_2 complex $Ru(NH_3)_5N_2^{2+}$ which has been synthesized by several routes.[2] The i.r. spectra of these compounds show the bonding between Ru^{II} or Ru^{III} and ligands of this type. Co-ordination to Ru^{II} leads to a decrease in the C≡N stretching frequency ν_{CN} in all cases while co-ordination to Ru^{III} leads, with one exception, to increased ν_{CN}. To our knowledge, these are the first reported examples of decreased ν_{CN} resulting from co-ordination of monodentate organonitriles to a metal cation.†

The complex ions, $Ru(NH_3)_5(NC–R)^{2+}$, were synthesized by the procedure reported for the preparation of penta-ammineruthenium(II) complexes of aromatic heterocycles.[4] Reduction of aqueous $[Ru(NH_3)_5Cl](CF_3CO_2)_2$ over Zn(Hg) in the presence of an excess of nitrile gave the desired complex ion which could be isolated as the bromide or tetrafluoroborate salt in *ca.* 50% yield. The identities of some complexes were confirmed by elemental analysis.

Oxidation of the Ru^{II} complexes with Ce^{IV} or Ag^{I} gave the corresponding Ru^{III} complexes which were isolated as the Br^- or BF_4^- salts. These proved only marginally stable, decomposing slowly in aqueous solution and during recrystallization. For this reason, analysis results were poor although consistent with the Ru^{III} oxidation state. The oxidation was shown to be reversible by reducing the Ru^{III} compounds with Zn(Hg) to give the original Ru^{II} salts which were identified by their characteristic electronic and i.r. spectra.

The i.r. data reported in the Table demonstrate that each nitrile co-ordination to penta-ammineruthenium(II) decreases ν_{CN}, with $\delta\nu_{CN}$ ranging from -31 to -57 cm.$^{-1}$. Such behaviour parallels the large decrease in ν_{NN} from free N_2 (2330 cm.$^{-1}$) to $Ru(NH_3)_5N_2^{2+}$ (2105—2167 cm.$^{-1}$, anion dependent, KBr disc),[2b] and is in sharp contrast to the typical increase in ν_{CN} for organonitriles on co-ordination

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† A recent communication notes a decrease in ν_{CN} resulting from Ru^{II} co-ordination with acrylonitrile; however, evidence is presented suggesting the olefinic bond as the co-ordination site (reference 3).

to Lewis acids.[4] The Table also shows that, with one exception, co-ordination to penta-ammineruthenium(III) increases ν_{CN}. Unlike ν_{NN} for $Ru(NH_3)_5N_2^{2+}$, ν_{CN} (KBr disc) values for the Ru^{II} and Ru^{III} benzonitrile complexes are relatively insensitive to the identity of the anion. This fact and the observation that ν_{CN} for the 4-toluonitrile complexes changed little from the spectra obtained in a KBr disc to those obtained in aqueous solution confirms that the values of $\delta\nu_{CN}$ are inherent in the complexes and not due to solid-state effects.

The decrease in ν_{CN} on co-ordination to penta-ammineruthenium(II) undoubtedly results from a decreased C–N bond order due to metal-electron backbonding into nitrile π^* orbitals. Consistent with this explanation is the observation that the larger $\delta\nu_{CN}$ values occur with electron-withdrawing phenyl substituents. However, the magnitude of the shift is unlikely to be a quantitative measure of backbonding interaction as there is no information about delocalization into the phenyl ring.

Infrared spectral data, ν_{CN} (cm.$^{-1}$)[a]

R–	RCN	$[Ru(NH_3)_5(RCN)]Br$	$[Ru(NH_3)_5(RCN)]Br_3$
Ph	2231s[b]	2194s	2268m
(BF_4^- salts)		2194s	2272m
p-$MeC_6H_4^-$	2230s[c]	2198s	2263m
		2199m[d]	2263w[d]
p-$ClC_6H_4^-$	2228s	2192s	2264m
	2232s[c]		
p-$HO_2C{\cdot}C_6H_4^-$	2231s	2179s	2208m, 2275w
Ph	2246s[b]	2189s	

[a] Spectra taken on a Beckman IR-7 spectrophotometer in KBr disc except where noted; [b] neat; [c] in $CHCl_3$; in aqueous solution, Irtran liquid cell.

Co-ordination normally increases ν_{CN} for organonitriles,[5] and this effect has been ascribed both to kinematic coupling of the carbon–nitrogen and nitrogen–metal stretching vibrations[6] and to a larger C≡N force constant.[7] Apparently these effects predominate for most benzonitriles co-ordinated to Ru^{III}. The one exception is the Ru^{III} 4-carboxybenzonitrile complex which has two absorption bands in the nitrile region, the weaker one at a higher frequency than the free ligand and the stronger band at a frequency 23 cm.$^{-1}$ less than the free ligand. Since 4-carboxybenzonitrile is bidentate, it is possible that the stronger band is the result of Ru^{III} co-ordination at the carboxylate and the weaker band the result of co-ordination at the nitrile. Similar decreases in ν_{CN} have been seen for 4-cyanopyridine co-ordinated at the pyridine nitrogen to metal ion centres which increase ν_{CN} when co-ordinated to aryl nitriles.[8] However, the electronic spectra of the Ru^{II} and Ru^{III} 4-carboxybenzonitrile complexes are markedly similar to the spectra of the 4-chlorobenzonitrile analogues, which implies similarity in structure.

The difference in the sign of $\delta\nu_{CN}$ for Ru^{II} as opposed to Ru^{III} benzonitrile complexes suggests that while penta-ammineruthenium(II) is capable of substantial π-backbonding towards ligands of this type, penta-ammineruthenium(III) is a much "harder" acid and hence acts primarily as a σ-acceptor for the lone electron pair on the nitrile nitrogen. A similar conclusion has been drawn concerning the bonding between these moieties and aromatic heterocycles.[3] Since oxidation of $Ru(NH_3)_5N_2^{2+}$ leads to quantitative release of N_2,[2c] it is apparent that the substantial π-backbonding is essential to the Ru^{II}–N_2 bond stability.

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