EPR Characteristics of Radical Complexes with Coordinated Ammineruthenium(II) Fragments. Evidence for the Metal-to-ligand Charge Transfer (MLCT) Nature of the Low-lying Excited States in Precursor Complexes

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The first EPR study of one-electron reduced ammineruthenium(II) complexes is reported, based on the reversible reduction of the following precursors: $[(\mathrm{mpz})\mathrm{Ru(NH_3)_5}]^{3+}$ (mpz = *N*-methylpyrazinium), $[(\mathrm{bpym})\mathrm{Ru(NH_3)_4}]^{2+}$ (bpym = 2,2′-bipyrimidine), $[(\mathrm{bptz})\mathrm{Ru(NH_3)_4}]^{2+}$ and $\{(\mu\text{-bptz})[\mathrm{Ru(NH_3)_4}]_2\}^{4+}$ [bptz = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine]. The partially resolved EPR spectra of $[(\mathrm{mpz}^{\bullet})\mathrm{Ru(NH_3)_5}]^{2+}$ and $[(\mathrm{bptz})\mathrm{Ru(NH_3)_4}]^{+}$ confirm unambiguously that the unpaired electron resides mainly in the π system of the unsaturated ligand, however, the spin distribution and the $^{99.101}$Ru isotope coupling reveal non-negligible contributions from the metal 4d orbitals to the singly occupied MO. The two other one-electron reduced compounds exhibit less well-resolved EPR spectra but are also $\mathrm{Ru^{II}}$ complexes of radical ligands as judged by their *g* anisotropy in comparison to the $\mathrm{Ru^{III}}$ containing oxidized forms. Distinctly different EPR characteristics of the oxidized and reduced forms support the MLCT formulation of low-lying excited states in the precursor compounds. The effect of the $\mathrm{Ru^{II}}$ ammine complex fragments on the EPR characteristics of the organic radical ligands is compared to that of other low spin $\mathrm{d^6}$ systems.

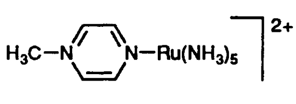
Complexes of $[\mathrm{Ru(NH_3)_4}]^{2+}$ and especially of $[\mathrm{Ru(NH_3)_5}]^{2+}$ with π accepting nitrogen ligands of the pyridine type have been extensively studied in recent years because of their usefulness in electron transfer research.[1,2] Among the favourable properties of these low-spin $\mathrm{d^6}$ species are their facile conversion into the $\mathrm{d^5} = \mathrm{Ru^{III}}$ state with a small reorganization energy, the inert binding to N donor centres in the (+II) and the (+III) state, the solubility in water and the conspicuous colours of the $\mathrm{Ru^{II}}$ compounds because of low-lying metal-to-ligand charge transfer (MLCT) transitions.[1-3] Although a host of physical methods has been applied to the study of the electronic structures of some of these coordination compounds,[1-4] the EPR technique has been used only in connection with the oxidized states, *i.e.* $\mathrm{Ru^{III}}$,[5.6] and not with the one-electron reduced forms which, in agreement with the MLCT formulation,[3] should be described as radical or radical ion complexes of $\mathrm{Ru^{II}}$.

$$(\mathrm{L^0})\mathrm{Ru^{II}(NH_3)}_n \xrightarrow[\text{MLCT}]{h\nu} {}^*[(\mathrm{L}^{\bullet-})\mathrm{Ru^{III}(NH_3)}_n]$$

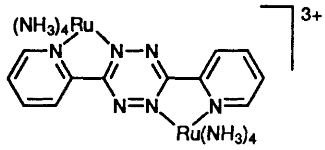
$$(\mathrm{L^0})\mathrm{Ru^{II}(NH_3)}_n \xrightarrow{+e^-} [(\mathrm{L}^{\bullet-})\mathrm{Ru^{II}(NH_3)}_n]^-$$

EPR studies of the reduced forms are also desirable since some radical ion complexes of $[\mathrm{Ru^{II}(bpy)_2}]^{2+}$ and related compounds have been investigated by this method in recent years (bpy = 2,2′-bipyridine).[7-12] The main differences between the bpy and $\mathrm{NH_3}$ ancillary ligands with respect to EPR lie in the π acceptor character of the former[13] and the ability to undergo hydrogen bonding of the latter.[14]

In this work we describe the EPR characteristics of four paramagnetic mono- and di-nuclear complexes with tetra- or penta-ammineruthenium coordination to radical ligands (I–IV).



I



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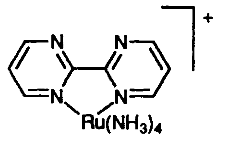

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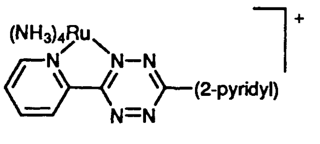


IV

Experimental

The reversibly reducible precursor complexes $[(\mathrm{mpz})\mathrm{Ru(NH_3)_5}](\mathrm{PF_6})_3$,[3.14.15] $[(\mathrm{bpym})\mathrm{Ru(NH_3)_4}]$ $(\mathrm{PF_6})_2$,[16] $[(\mathrm{bptz})\mathrm{Ru(NH_3)_3}]$ $(\mathrm{PF_6})_2$,[13] and $\{(\mu\text{-bptz})[\mathrm{Ru(NH_3)_4}]_2\}$ $(\mathrm{PF_6})_4$[12a.13] were obtained following literature procedures. The pyrazine-bridged complex $\{(\mu\text{-pz})[\mathrm{Ru(NH_3)_5}]_2\}$ $(\mathrm{PF_6})_4$[17] was obtained in a similar way but was found to be reduced irreversibly at −2.1 V *vs.* $\mathrm{FeCp_2}^{0/+}$ in acetonitrile–$\mathrm{Bu_4NPF_6}$ (0.1 mol $\mathrm{dm^{-3}}$).

One-electron reduction to EPR-active radical species was achieved chemically, *i.e.* using cobaltocene in ethanol for the bptz complexes, or electrolytically[9b] in acetonitrile–$\mathrm{Bu_4NPF_6}$ (0.1 mol $\mathrm{dm^{-3}}$) by varying the potential in 0.1 V steps until an EPR signal appeared. Electrolysis was performed at this onset potential until sufficient concentration of radicals had developed. Dried solvents were used and the reductions were carried out under an argon atmosphere.

The EPR spectra were recorded on a Bruker ESP 300 system equipped with a Bruker ERP35M gaussmeter and an HP 5350B microwave counter. Computer simulations were performed using a program which takes account of isotope combinations.[18]

Results and Discussion

The (3+) form of $\{(\mu\text{-pz})[\mathrm{Ru(NH_3)_5}]_2\}^n$ (the Creutz–Taube

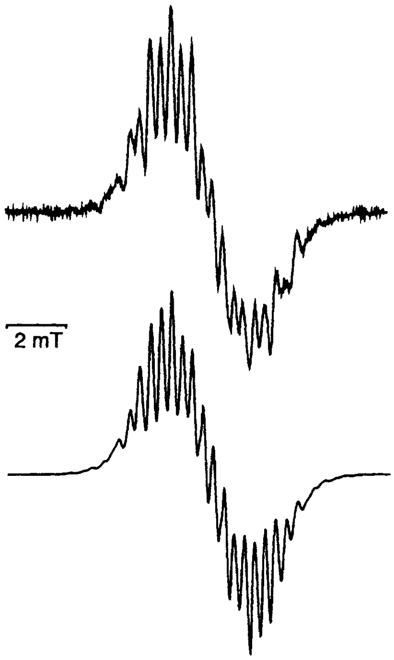


Fig. 1 Top: EPR spectrum of electrochemically generated [(mpz)-Ru$(NH_3)_5]^{2+}$ in acetonitrile–Bu_4NPF_6 (0.1 mol dm^{-3}). Bottom: Computer simulated spectrum with the data from Table 2 and a line width of 0.22 mT.

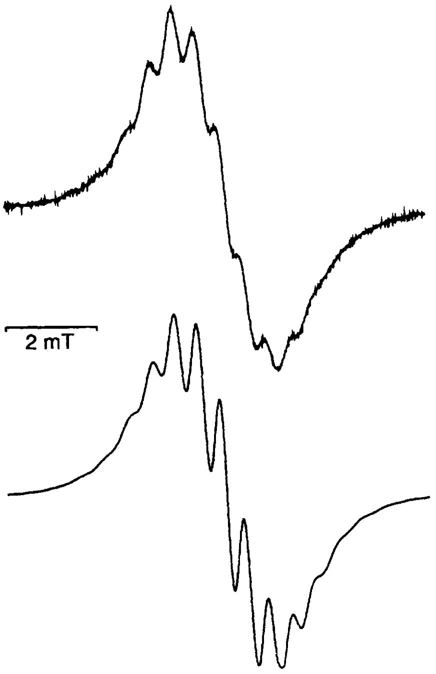


Fig. 2 Top: EPR spectrum of $[(bptz)Ru(NH_3)_4]^+$, obtained by reduction of the dication with cobaltocene in ethanol. Bottom: Computer simulated spectrum with the data from Table 1 and a line width of 0.45 mT.

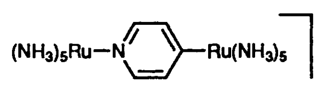
system)[17] V could not be obtained due to totally irreversible redox behaviour at about −2.1 V *vs.* $FeCp_2^{0/+}$ in acetonitrile (0.1 mol dm^{-3}). The other four complexes I–IV were obtained by chemical or electrochemical reduction of known diamagnetic precursors. Figs. 1 and 2 show representative solution EPR spectra, Tables 1 and 2 summarize the relevant data.

$[(mpz)Ru(NH_3)_5]^{2+}$.—This ion was derived from the (3+) precursor which had been found to contain a very short Ru–N bond due to strong π back donation.[15] The reduced form shows a comparatively well resolved EPR spectrum (Fig. 1) centred at $g = 2.0021$ which already indicates that a low-spin ruthenium(II) (d^6) centre is binding to an *N*-methylpyrazinium radical ligand, supporting the MLCT assignment of the low-lying transition. In fact, there are a number of related complexes (Table 2)[19,20] of low-valent d^6 metals with that 'spin label' ligand.

Table 1 EPR data[a] of ammineruthenium(II) radical complexes

Radical complex	$\langle g \rangle$	$a(^{99.101}Ru)$	$a(^{14}N)$
$[(mpz)Ru(NH_3)_5]^{2+\bullet b}$	2.0021	0.580	0.683 (N^4)[c]
$[(bpym)Ru(NH_3)_4]^{+\bullet b}$	1.9893 1.965 ($g_{\parallel}$) 2.003 ($g_{\perp}$)	n.o.	n.o.
$[(bptz)Ru(NH_3)_4]^{+\bullet d}$	1.9997	0.67	0.505[e]
$\{(\mu\text{-bptz})[Ru(NH_3)_4]_2\}^{3+\bullet d}$	2.000 1.989 ($g_{\perp}$) 2.022 ($g_{\parallel}$)	n.o.	n.o.

[a] Coupling constants *a* in mT (1 T = 10^4 Gauss). [b] In acetonitrile–Bu_4PF_6 (0.1 mol dm^{-3}). [c] For additional hyperfine splitting see Table 2. [d] In ethanol. [e] Average value for four different tetrazine N coupling constants.



V

The analysis of the spectrum by computer simulation shows a splitting pattern which is surprisingly similar to that found for the $W(CO)_5$ complex (Table 2). Additional features at the wings can be reproduced by including a $^{99.101}Ru$ isotope coupling constant (^{99}Ru: 12.7%, $I = 5/2$, $A_{iso} = -37.62$ mT; ^{101}Ru: 17.1%, $I = 5/2$; $A_{iso} = -42.13$ mT).[9,21] The line width did not allow us to determine the small ring proton coupling constant H(3,5), possible reasons being an inhomogeneous broadening due to unresolved hyperfine coupling from the numerous ^{14}N and ^1H nuclei of the ammine ligands. The size of the metal isotope coupling is unusually large for a radical complex,[22] the ratio $a(X)/A_{iso}(X)$ is more than twice as high as for *e.g.* molybdenum(0) or tungsten(0) complexes.[18,20,23,24] This result indicates efficient spin transfer from the ligand radical to the metal and thus confirms the concept of a particular strong interaction between Ru^{II} and nitrogen coordination centres of unsaturated acceptor ligands.[1,15]

By following an electrochemical approach recently described for determining the amount of metal/ligand orbital mixing in ground and excited states of ammineruthenium(II) complexes[25] a value of $p = 0.64$ is obtained for the mixing parameter when values of $E_{1/2}(Ru^{3+/2+})$ *vs.* $E_{1/2}(L^{0/-})$ are correlated in various solvents.[26] From this parameter, a 29% electronic delocalization on the Ru atom can be estimated for the MLCT excited state, in broad agreement with the results from EPR data of the reduced complex.

The distribution of spin within the metal-perturbed *N*-methylpyrazinium radical ligand follows an established correlation,[19] *i.e.* increasing electron donation from the metal leads to a higher H(2,6) splitting and to lowered *N*-methyl and H(3,5) hyperfine coupling.

The *g* factor of $[(mpz)Ru(NH_3)_5]^{2+}$ is rather high for an Ru^{II} containing radical,[7-12] indicating the absence of very low-lying excited states with considerable metal contributions.[9,22,24] Nevertheless, the ruthenium complex exhibits the lowest *g* factor of all mpz complexes listed in Table 2.

$[(bpym)Ru(NH_3)_4]^+$.—Electrochemical reduction of the dicationic precursor at −1.72 V *vs.* $FeCp_2^{0/+}$ in acetonitrile–

Table 2 EPR data[a] of *N*-methylpyrazinium radical compounds $[Me–NC_4H_4N–X]^n$

		X = H	$Ru(NH_3)_5$	$W(CO)_5/Fe(CN)_5$			$M(CO)_3(PR_3)$[b]	
							M = Mo	M = W
		n = 1+[c]	2+[d]	0[e]	0[f]	3−[g]	0[h]	0[h]
a:								
	1H(Me)	0.851	0.723	0.714	0.732	0.718	0.646	0.617
	$^{14}N(–Me)$	0.891	0.870	0.784	0.828	0.821	0.738	0.709
	H(2,6)	0.310	0.387	0.386	0.458	0.477	0.409	0.394
	H(3,5)	0.292	>0.180	0.154	0.121	0.102	0.087	0.077
	$^{14}N(–X)$	0.705	0.683	0.870	0.700	0.718	0.846	0.862
	X	0.756	0.580 (^{99}Ru)				0.312 (^{95}Mo)	
			0.650 (^{101}Ru)				0.319 (^{97}Mo)	
	R(X)[i]		0.0154				0.0068	
g		2.0034	2.0021	2.0051	2.0034	2.0032	2.0041	2.0087

[a] Coupling constants *a* in mT. [b] R = isopropyl. [c] In DMF–Bu_4NClO_4 (0.1 mol dm^{-3}) (from ref. 28). [d] In acetonitrile–Bu_4NPF_6 (0.1 mol dm^{-3}). [e] In acetonitrile–Bu_4NClO_4 (0.1 mol dm^{-3}) (ref. 20). [f] In methanol (ref. 19). [g] In aqueous $CH_3OH–CH_2Cl_2$ (ref. 19). [h] In THF (ref. 20). [i] $R(X) = a(X)/A_{iso}(X)$ (A_{iso} values from ref. 21).

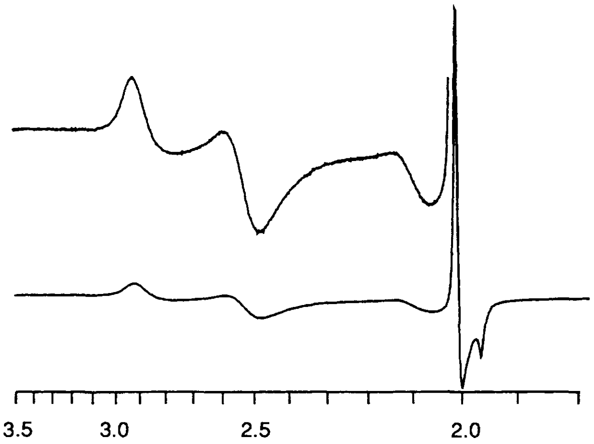


Fig. 3 EPR spectra at 3.5 K of the electrolysis products from $[(bpym)Ru(NH_3)_4]^{2+}$ in acetonitrile–Bu_4NPF_6 (0.1 mol dm^{-3}): Axial signal near $g = 2$ of the reduced radical complex form, rhombic signal at $g_1 = 2.920$, $g_2 = 2.527$ and $g_3 = 2.050$ of the oxidized Ru^{III} state.

Bu_4NClO_4 (0.1 mol dm^{-3}) leads to a radical complex with an unresolved single EPR line (peak-to-peak distance 1.2 mT) at $g = 1.9893$. This *g* factor is smaller than the value of $g = 1.9942$ for the related radical cation $[(bpym)Ru(bpy)_2]^{+\cdot}$.[9b] The causes of this difference are seen in the smaller ligand field splitting exerted by the non-π-accepting ammine co-ligands and in the relatively poor π acceptor capacity of 2,2′-bipyrimidine.[27] The high-lying π* orbital of bpym thus favours orbital mixing with unoccupied 4d orbitals of ruthenium, resulting in a higher metal contribution to the radical ground and excited states. Due to the high spin–orbit coupling constant of about 1000 cm^{-1} for ruthenium in lower oxidation states[9] this 'Ru^I' contribution causes an appreciable deviation of *g* from the free ligand value of 2.0030.[24b] Consequently, the tetraammineruthenium(II) complex of 2,2′-bipyrimidine radical anion exhibits a comparatively[9] large *g* anisotropy of the axial EPR signal in frozen acetonitrile solution, confirming the presence of non-negligible metal contributions to the singly occupied MO. On the other hand, electrochemical oxidation at a relatively low potential[16] to the trication clearly yields a low-spin ruthenium(III) species[5,6] with *g* components at 2.920, 2.527 and 2.050; Fig. 3 illustrates the EPR signals of both (+) and (3+) ions and thus provides clear spectral evidence for the MLCT (d→π*) character of the low-lying optical transitions.[16]

$[(bptz)Ru(NH_3)_4]^{+\cdot}$.—In contrast with the bpym complex with its rather high lying π* orbital the mononuclear bptz complex contains a much better π accepting heterocyclic ligand; bptz is reduced more easily than bpym by about 1 V.[27b] Accordingly, the EPR spectrum of the chemically generated species is partially resolved (Fig. 2) and is centred at a *g* factor closer to the value (2.0040) of the ligand radical anion.[24b] Analysis of the EPR spectrum along established lines[9] shows a nonet splitting for the coupling of one unpaired electron with four rather similar ^{14}N centres. In fact, the π* orbital of bptz is localized at the four tetrazine nitrogen centres and is slightly perturbed by metal coordination.[9a,24b] The nitrogen coupling constant of 0.505 mT (average) is smaller than the 0.55 mT found for $\{(\mu\text{-bptz})[Ru(bpy)_2]_2\}^{3+}$,[9] on the other hand, the $^{99,101}Ru$ isotope coupling as detected at the wings of the spectrum (Fig. 2) is larger (0.67 mT *vs.* 0.55 mT). This observation is in agreement with the results obtained for the mpz complex, supporting again the strong interaction between radical and coordinated metal centre.

$\{(\mu\text{-bptz})[Ru(NH_3)_4]_2\}^{3+}$.—The low-temperature EPR spectrum of this dinuclear radical complex has been presented previously.[12a] While the *g* factor and its anisotropy are not unusual in comparison with the mononuclear compound or the dinuclear $Ru(bpy)_2$ analogue,[9] the failure to observe a signal at temperatures above 70 K is quite unusual for a radical complex.[22] Similar effects were noted for the related complexes $\{(\mu\text{-adc})[Ru(bpy)_2]_2\}^{3+}$, adc = azodicarbonylate ligands,[10a,b] which, however, clearly have a strong contribution from the Ru^{II}/Ru^{III} mixed-valent form with a dianionic adc^{2-} ligand (large *g* anisotropy).[10a,b] The one-electron oxidized species $\{(\mu\text{-bptz})[Ru(NH_3)_4]_2\}^{5+}$ shows typical[6] features of a Ru^{II}/Ru^{III} mixed valent complex.[12a]

Summarizing, the persistent one-electron reduced forms of the ammineruthenium(II) complexes described here must be characterized as radical complexes rather than Ru^I species. EPR spectroscopic results confirm the strong π interactions between Ru^{II} and the unsaturated N ligands. Orbital mixing and as yet unexplained rapid relaxation for the dinuclear example can cause line broadening, however, informative EPR resolution is not impossible to obtain when good π acceptor ligands are used. Fig. 3 contains an illustrative juxtaposition of EPR signals from one-electron reduced and oxidized species, supporting the MLCT interpretation of low-lying excited states of the precursor compounds.

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