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SPECTROSCOPIC AND MAGNETIC STUDIES ON ELECTROGENERATED MIXED-VALENCE RUTHENIUM COMPLEXES

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Summary

Electrochemical synthesis has enabled several sequences of triple chloride bridged diruthenium complexes of general type $[L_{3-x}Cl_xRuCl_3RuCl_yL_{3-y}]^{z/z+1/z+2}$ (L = soft neutral ligand) to be generated. The intervalence charge transfer bands in the optical spectra of the mixed-valence $Ru_2^{II,III}$ compounds and variable temperature magnetic measurements for the corresponding $Ru_2^{III,III}$ complexes reveal that the degree of metal—metal interaction in these confacial bioctahedral systems decreases as the molecular asymmetry $(y-x)$ increases.

Triply-chloro-bridged diruthenium complexes of general type $[L_{3-x}Cl_xRuCl_3$-$RuCl_yL_{3-y}]$, where L = soft neutral ligand, are known in three different oxidation levels, ranging from $Ru_2^{II,II}$ to $Ru_2^{III,III}$ [1,2]. Extensive voltammetric studies [1,2] have established that the individual complexes display at least one and generally two stepwise, reversible one-electron transfers without change in their gross molecular structure (see Table 1). A feature of this family of compounds is that the environment of the $RuCl_3Ru$ bridging unit can be modified by either variation of the basicity of the terminal ligands L or by the degree of asymmetry ** in terminal chloride binding.

In order to better explore the structural and electronic changes which might accompany these stepwise electron transfer processes, some of the charged species shown in Table 1 have been electrogenerated on a preparative scale at low temperature, and characterised in situ by a variety of spectroscopic techniques *** and a preliminary report of these studies is given in this communication.

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[*] On leave from the Physical Chemistry Laboratory, University of Patras, Greece.

[**] The degree of asymmetry is defined as $(y-x)$, and for the compounds discussed u takes values of 0, 1 or 2.

[***] With very few exceptions these electrogenerated species readily decompose if the temperature rises above 260 K and therefore no attempts were made to isolate them from solution.

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TABLE 1

ELECTROCHEMICAL BEHAVIOUR OF SOME $[\mathrm{L_{3-x}Cl_xRuCl_3RuCl_yL_{3-y}}]$ COMPLEXES [a,b]

Asymmetry $u = y - x$	36e		35e		34e
0	$\mathit{[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]^+}$	$\overset{+1.20}{\rightleftharpoons}$	$\mathrm{[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]^{2+}}$	$\overset{+1.75}{\rightleftharpoons}$	$\mathrm{[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]^{3+}}$
1	$\mathit{[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]}$	$\overset{+0.47}{\rightleftharpoons}$	$\mathrm{[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]^+}$	$\overset{+1.50}{\rightleftharpoons}$	$\mathrm{[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]^{2+}}$
2	$\mathrm{[(PEt_2Ph)_3RuCl_3RuCl_2(PEt_2Ph)]^-}$	$\overset{-0.28}{\rightleftharpoons}$	$\mathit{[(PEt_2Ph)_3RuCl_3RuCl_2(PEt_2Ph)]}$	$\overset{+1.27}{\rightleftharpoons}$	$\mathrm{[(PEt_2Ph)_3RuCl_3RuCl_2(PEt_2Ph)]^+}$
0	$\mathrm{[(Astol_3)_2ClRuCl_3RuCl(Astol_3)_2]^-}$	$\overset{+0.10}{\rightleftharpoons}$	$\mathit{[(Astol_3)_2ClRuCl_3RuCl(Astol_3)_2]}$	$\overset{+0.83}{\rightleftharpoons}$	$\mathrm{[(Astol_3)_2ClRuCl_3RuCl(Astol_3)_2]^+}$
1	$\mathrm{[(Astol_3)_2ClRuCl_3RuCl_2(Astol_3)]^{2-}}$	$\overset{-0.44}{\rightleftharpoons}$	$\mathrm{[(Astol_3)_2ClRuCl_3RuCl_2(Astol_3)]^-}$	$\overset{+0.58}{\rightleftharpoons}$	$\mathit{[(Astol_3)_2ClRuCl_3RuCl_2(Astol_3)]}$
2	$\mathrm{[(Astol_3)_3RuCl_3RuCl_2(Astol_3)]^-}$	$\overset{-0.22}{\rightleftharpoons}$	$\mathit{[(Astol_3)_3RuCl_3RuCl_2(Astol_3)]}$	$\overset{+1.25}{\rightleftharpoons}$	$\mathrm{[(Astol_3)_3RuCl_3RuCl_2(Astol_3)]^+}$

[a] Starting material for electrosynthesis italicized. [b] $E_{1/2}$ (volts) measured at 20°C in 0.50 *M* n-$\mathrm{Bu_4NBF_4/CH_2Cl_2}$ vs. Ag/AgI reference electrode at which ferrocene is oxidised at +0.60 V.

All the complexes discussed here have been generated at 223 K in 0.50 *M* n-Bu_4NBF_4/CH_2Cl_2 solutions at a platinum gauze working electrode. The solutions were then transferred, with rigorous exclusion of air, to pre-cooled NMR or ESR tubes and, at the end of the spectroscopic measurement, the integrity of the solutions was confirmed by voltammetric monitoring. In contrast the optical measurements were recorded in situ using a chilled Optically Transparent Thin Layer Electrode cell.

Results and discussion

Hitherto, the only representatives of diruthenium(III) complexes of this general type were asymmetric ($u = 1$) $[(AsR_3)_2ClRuCl_3RuCl_2(AsR_3)]$ (R = Ph, *p*-tolyl) which have "normal" room temperature magnetic moments [1b,2]. However, the electrogeneration of complementary systems with $u = 0$ and 2, together with variable temperature magnetic measurements (by the Evans' method [3]) provide further insight. Thus, the $Ru_2^{III,III}$ complexes all show a depression of μ_{eff} with decreasing temperature and the degree of antiferromagnetic interaction is markedly sensitive to the mismatch (*u* value) between the adjacent metal centres (Table 2).

Interestingly, none of the electrogenerated $Ru_2^{III,III}$ or $Ru_2^{II,III}$ cations gave any ESR signals even at 133 K, whereas the 35 electron anion $[Ru_2Cl_6(Astol_3)_3]^-$ does show strong ESR peaks at this temperature. Meyer et al. [4] have attributed the absence of ESR signals in their $Ru_2^{III,III}$ binuclear cations $[(N—N)_2(NO_2)RuORu(NO_2)(N—N)_2]^{2+}$ (N—N = bipy, phen) to the presence of strong spin-orbit coupling interactions. In our complexes, at least, it seems reasonable that the increased solvent interactions on going from anionic or neutral to cationic species will also be an important factor in shortening the electron spin-lattice relaxation time.

The electrogenerated $Ru_2^{II,III}$ products all have magnetic moments corre-

TABLE 2

THE MAGNETIC PROPERTIES OF SOME $Ru_2^{III,III}$ AND $Ru_2^{II,III}$ COMPLEXES [a]

$u = y—x$	Complex	Solution μ_{eff} [b]	(at $T(K)$)	$—2\,J$ cm^{-1} [c]
2	$[(PEt_2Ph)_3RuCl_3RuCl_2(PEt_2Ph)]^+$	1.78	(233)	185
2	$[(Astol_3)_3RuCl_3RuCl_2(Astol_3)]^+$	2.01	(233)	150
1	$[(Astol_3)_2ClRuCl_3RuCl_2(Astol_3)]$	1.45	(229)	276
0	$[(Astol_3)_2ClRuCl_3RuCl(Astol_3)_2]^+$	0.91	(233)	420
1	$[(Astol_3)_2ClRuCl_3RuCl_2(Astol_3)]^-$	1.73	(227)	—
1	$[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]^+$	2.02	(231)	—
1	$[(PPh_3)_2CORuCl_3RuCl(PPh_3)_2]^+$	1.64	(235)	—
1	$[(PPh_3)_2CSRuCl_3RuCl(PPh_3)_2]^+$	1.60	(235)	—
1	$[(Ptol_3)_2CORuCl_3RuCl(Ptol_3)_2]^+$	2.10	(231)	—
0	$[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]^{2+}$	1.78	(228)	—

[a] Measured in 0.50 *M* n-Bu_4NBF_4/CH_2Cl_2 by Evans' method [3]. [b] For $Ru_2^{III,III}$ compounds, μ_{eff} quoted per Ru; for $Ru_2^{II,III}$ compounds μ_{eff} quoted per molecule. [c] Exchange coupling constant from numerical fitting to the Bleaney—Bowers equation. $\chi_A = (Ng^2\beta^2/3kT)[1 + \frac{1}{3}\exp(—2J/kT)]^{-1}$ [8] where χ_A is the molar susceptibility calculated per metal ion.

TABLE 3

INTERVALENCE CHARGE TRANSFER BANDS FOR SOME $Ru_2^{II,III}$ COMPLEXES [a]

$u = y - x$	Complex	$\bar{\nu}_{max}$ (cm^{-1})	ϵ_{max} (M^{-1} cm^{-1})	10^3 α^2 [b]
0	$[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]^{2+}$	4 350	3750	delocalised
1	$[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]^+$	9 700	700	9.5
2	$[(PEt_2Ph)_3RuCl_3RuCl_2(PEt_2Ph)]$	13 500	550	5.1
0	$[(Astol_3)_2ClRuCl_3RuCl(Astol_3)_2]$	5 900	1700	delocalised
1	$[(Astol_3)_2ClRuCl_3RuCl_2(Astol_3)]^-$	7 800	830	8.9
2	$[(Astol_3)_3RuCl_3RuCl_2(Astol_3)]$	12 200	400	3.2
1	$[(PPh_3)_2CORuCl_3RuCl(PPh_3)_2]^{+}$ [c]	14 800	~100	~0.7
1	$[(PPh_3)_2CSRuCl_3RuCl(PPh_3)_2]^{+}$ [c]	14 800	~100	~0.7
1	$[(Ptol_3)_2CORuCl_3RuCl(Ptol_3)_2]^{+}$ [c]	14 800	~100	~0.7
1	$[(PPh_3)_2CSRuCl_3RuCl(CS)(PPh_3)]^+$	10 850	200	1.6

[a] Measured in 0.50 M $n\text{-}Bu_4NBF_4/CH_2Cl_2$ at 223 K unless otherwise stated. [b] Degree of delocalisation $\alpha^2 = (4.24 \times 10^{-4})\epsilon_{max}\Delta\bar{\nu}_{1/2}/\bar{\nu}_{max} \times R^2$, where ϵ_{max} = maximum extinction coefficient; $\bar{\nu}_{max}$ = position of band centre $\Delta\bar{\nu}_{1/2}$ = full width of band at half height; R = internuclear distance between ruthenium ion centres (a value of 3.3 Å is assumed here) [5]. [c] Measured in 0.50 M $LiClO_4$/THF at 223 K.

sponding to one unpaired electron per molecule and, in marked contrast to the $Ru_2^{III,III}$ systems, the μ_{eff} values are invariant over the accessible temperature range (Table 2). This behaviour parallels that of the limited number of previously synthesised neutral, mixed valence complexes [1]. Similarly, $[(Astol_3)_2ClRuCl_3RuCl_2(Astol_3)]^-$ displays a two g-value ESR spectrum very like that of the isoelectronic $[(Astol_3)_3RuCl_3RuCl_2(Astol_3)]$ [1b] in accord with their common axial symmetry.

As indicated above, the magnetic behaviour of these 35 electron complexes is not responsive to the degree of metal—metal interaction. However, the intervalence charge transfer transitions ($Ru^{II}Ru^{III} \rightarrow Ru^{III}Ru^{II}$) which may arise in such trapped-valence systems [5] should offer an independent and sensitive means of exploring the tendency to partial charge delocalisation in the $(RuCl_3Ru)^{2+}$ core. We now confirm that all the 35-electron systems do indeed have characteristic near-infrared or visible absorption bands, absent in their $Ru_2^{II,II}$ and $Ru_2^{III,III}$ congeners, and directly attributable to intervalence excitation (Table 3).

Several significant observations are immediately possible from an examination of Table 3. First, both the triad of PEt_2Ph complexes and the triad of $As(tol)_3$ complexes having u = 0, 1, 2 show a significant trend to higher transition energies and lower intensities as the molecular asymmetry increases. This shift in $\bar{\nu}_{max}$, which reflects the increasing difference in orbital energies for the two ruthenium centres, is roughly comparable to the influence of asymmetric ligation on the observed separation of electrode potentials for the two $Ru^{II/III}$ couples (ca. 0.5 eV or 4000 cm^{-1} per excess Cl^-, see Table 1 *).

Furthermore, for these two triads, analysis of the implied degree of delocali-

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* A full analysis of the thermodynamic relationship between the optical transition energies and the measured and inferred E^0 values will be published elsewhere [6].

sation, α^2, following Hush [5], clearly indicates that this interaction is markedly increased by closer matching of the adjacent metal sites, to the extent that the symmetric ($u = 0$) complexes are "highly delocalised" and outside the scope of Hush's weakly interacting model. Table 3 also reveals the considerable influence exerted by π-acid CO and CS ligands, both in reducing the tendency to delocalisation and, when asymmetrically located, in shifting the transition to higher energies.

Thus, the general observation of assignable intervalence bands for all the mixed-valence triple chloride bridged complexes so far examined confirms our preliminary conclusion based on electrode potential data [1,2], that the asymmetrically substituted complexes, at least, can be realistically viewed as trapped-valence systems.

Further confirmation of the presence of isolated valencies is provided by $^{31}P\text{-}\{^1H\}$ NMR spectra of the set of electrogenerated cations $[(PR_3)_2YRuCl_3RuCl(PR_3)_2]^+$ (Y = CO, CS; R = Ph; Y = CO, R = *p*-tolyl). In each case a broad contact-shifted resonance is observed (Ru^{III} site) together with a sharp AB pattern (Ru^{II} site) virtually unshifted from the ^{31}P NMR resonance which is characteristic of the $RuY(PR_3)_2$ site in the $Ru_2^{II,II}$ precursor [7].

The symmetric complexes however have some features deserving further examination. In particular the near infrared spectra reveal an additional band unique to the $u = 0$ system, whose position appears to parallel the degree of interaction between the metal centres.

Furthermore $[(Astol_3)_2ClRuCl_3RuCl(Astol_3)_2]$ which has previously been noted to have uniquely sluggish charge transfer properties [1a] also shows slight but significant anomalies in the position of its intervalence band and the separation of its successive redox couples. These features are consistent with an additional degree of stabilisation in the symmetrically substituted complex. These and related complexes are receiving further study with particular attention paid to the effects of varying the polarisability of the bridging and terminal ligands.

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