New Ruthenium(II) Complexes of α,α′-Diimines. Synthesis, Electrochemical and Optical Spectral Properties of Mononuclear Complexes containing Aryl(2-pyridylmethylene)amine and 2,2′-Bipyridine Ligands†

Subrata Choudhury, Alok K. Deb and Sreebrata Goswami*
Department of Chemistry, North-Eastern Hill University, Shillong 793 003, India

The tris-chelated complexes, $[RuL_n(bipy)_{3-n}][ClO_4]_2 \cdot H_2O$ [L = aryl(2-pyridylmethylene)amine, bipy = 2,2′-bipyridine, n = 0–3], have been prepared based on a direct and general route. For $[RuL_3]^{2+}$, the geometry has been assessed by ^1H NMR spectroscopy. All the complexes show metal-to-ligand charge transfer (m.l.c.t.) transitions in the visible range at *ca.* 475 nm. Preliminary results of emission spectra are also described briefly. The metal oxidation as well as ligand reductions for the complexes have been studied electrochemically in acetonitrile using different working electrodes. It has been shown, for the mixed L–bipy complexes, that the reductions of co-ordinated L occur at comparatively lower negative potentials. The correlation between the electrochemical properties and $\nu_{c.t.}$ (absorption) is discussed.

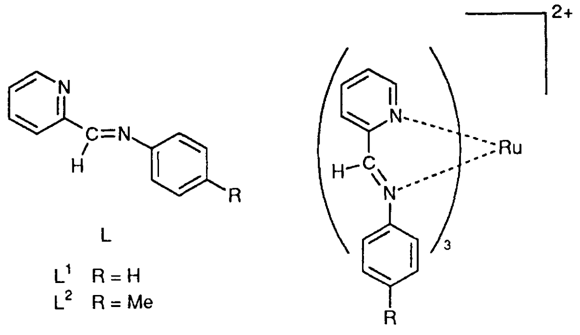
Over the past fifteen years a vast literature[1] has built up around tris(diimino) complexes of ruthenium(II), particularly $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine). This is primarily due to the relevance of this chemistry to photophysical, photochemical and redox phenomena. The properties of this class of complexes are principally determined by the accessibility of a redox-active metal-to-ligand charge transfer (m.l.c.t.) excited state at a low energy which depends on the presence of low-lying π^* levels in the co-ordinated ligand. For example, the m.l.c.t. transition for $[Ru(bipy)_3]^{2+}$ in acetonitrile occurs[2] in the visible region at 454 nm. In view of the vast body of data, a more definite approach toward the design and synthesis of new complexes, by careful selection of diimine ligands, showing m.l.c.t. transitions at lower energies seems appropriate in connection with developing photocatalysts active in the long-wavelength region of the visible spectrum.[3]

In the present report, we describe the synthesis and properties of a new series of tris-chelated complexes of ruthenium(II) derived from neutral aryl(2-pyridylmethylene)amine Schiff-base ligands, L. Our interests in this area arose due to the following reasons. First, like bipy, ligands L have an α,α′-diimine function. Secondly, they form stable complexes[4] with ruthenium(II) and finally, the iron(II) complex, $[FeL^1{}_3]^{2+}$, absorbs[5] at a lower energy than does $[Fe(bipy)_3]^{2+}$.

In recent years, only two reports[6,7] of tris-chelated ruthenium(II) complexes of L or related ligands have appeared in the literature. In 1978, Dose and Wilson[6] first reported the synthesis of $[RuL^2{}_3][PF_6]_2$ from $K_2[RuCl_5(H_2O)]$. It seems, however, that the compound was not purified and that its properties as described did not correspond to the properties of the isomerically pure compound, synthesised by us. A generalised synthetic route using silver(I) complexes of L and bipy is described in the present report, to synthesise a complete series of tris-chelated complexes, $[RuL_n(bipy)_{3-n}]^{2+}$ (n = 0–3).

Results and Discussion

Synthesis, Formulation and Geometry.—The direct reaction of hydrated $RuCl_3$ with L (L^1 or L^2) in solution failed to afford isolable $[RuL_3]^{2+}$ species. Ruthenium trichloride underwent



partial substitution of Cl^- and an isomeric mixture of $[RuCl_2L_2]$ resulted. We then explored the silver(I)-assisted synthetic route[8–10] for the synthesis of the tris chelates. The reactions of chloride salts of ruthenium and the silver complexes $[AgL_2]ClO_4$ ($L = L^1$ or L^2)[10,11] proceeded smoothly in ethanol to yield the tris-chelated complexes, which were isolated from the solutions as their perchlorate salts. The synthetic routes are described by equations (1)–(4).

$$RuCl_3 \cdot 3H_2O + 3[AgL_2]^+ \xrightarrow{EtOH} [RuL_3]^{2+} + 3AgCl + 3L \quad (1)$$

$$cis\text{-}[RuCl_2L_2] + 2[AgL_2]^+ \xrightarrow{EtOH} [RuL_3]^{2+} + 3AgCl + 3L \quad (2)$$

$$cis\text{-}[RuCl_2(bipy)_2] + 2[AgL_2]^+ \xrightarrow{EtOH} [RuL(bipy)_2]^{2+} + 3AgCl + 3L \quad (3)$$

$$cis\text{-}[RuCl_2L_2] + 2[Ag(bipy)_2]^+ \xrightarrow{EtOH} [RuL_2(bipy)]^{2+} + 3AgCl + 3\,bipy \quad (4)$$

The reactions (3) and (4) have been particularly useful for the synthesis of mixed-ligand complexes, which were, otherwise, not obtainable.[6] In all cases, chromatographic purification of

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† *Non-SI unit employed:* eV ≈ 1.60 × 10^{-19} J.

Table 1 Analytical, conductivity and IR spectral data of the complexes $[RuL_n(bipy)_{3-n}][ClO_4]_2{\cdot}H_2O$

Compound	Elemental analyses[a] (%) C	H	N	Λ_m[b]$/\Omega^{-1}$ cm^2 mol^{-1}	IR[c]/cm^{-1} $\nu_{C=N}$	ν_{ClO_4}
$[RuL^1{}_3][ClO_4]_2{\cdot}H_2O$	50.15 (50.00)	3.85 (3.70)	9.80 (9.70)	332	1620	1100, 620
$[RuL^2{}_3][ClO_4]_2{\cdot}H_2O$	52.00 (51.65)	4.10 (4.20)	9.30 (9.25)	320	1615	1100, 620
$[RuL^2{}_2(bipy)][ClO_4]_2{\cdot}H_2O$	50.10 (49.90)	4.00 (3.95)	9.85 (9.70)	325	1620	1100, 620
$[RuL^2(bipy)_2][ClO_4]_2{\cdot}H_2O$	48.05 (47.95)	3.75 (3.65)	10.25 (10.15)	325	1620	1095, 620

[a] Calculated values are in parentheses. [b] In MeCN at 298 K with a solute concentration of *ca.* 10^{-3} mol dm^{-3}. [c] In KBr disc.

the complexes was required and was performed on a silica-gel column using $CHCl_3$–MeCN as eluent (Experimental section). It may be noted here that the reaction of $RuCl_3{\cdot}3H_2O$ and $[AgL_2]^+$ in 1:1 molar ratio yields an isomeric mixture[4] of $[RuCl_2L_2]$ as the major product [equation (5)], as expected.

$$RuCl_3{\cdot}3H_2O + [AgL_2]^+ \xrightarrow{EtOH} [RuCl_2L_2] + AgCl \quad (5)$$

The composition of the new compounds was formulated by elemental analyses. The diamagnetic ($t_2{}^6$) complexes are 1:2 electrolytes[12] in MeCN (Table 1) and show characteristic absorptions for co-ordinated L (ref. 4) and bipy[5] in their IR spectra. Selected group frequencies are presented in Table 1.

The tris chelate $[RuL_3]^{2+}$ containing the unsymmetrical bidentate ligand L, can exist as *fac* or *mer* geometrical isomers[13,14]. The *fac* form is symmetrical (C_3) and in an idealised case the three ligands would be magnetically equivalent whereas the corresponding *mer* isomer, of C_1 symmetry, should show three magnetically inequivalent ligands. We selected the tris complex of the methyl-substituted ligand, L^2, to take advantage of the methyl resonance, to determine the geometry of $[RuL_3]^{2+}$ by ^1H NMR spectroscopy. The ^1H NMR spectrum of $[RuL^2{}_3]^{2+}$ in $CDCl_3$ shows two methyl resonances with intensities 1:2 at δ 2.18 and 2.08 respectively. Meridional tris chelates of unsymmetrical bidentate ligands are well documented[13,15] to display this type of spectrum. We, therefore, conclude that the geometry of $[RuL_3]^{2+}$ ($L = L^1$ or L^2) is meridional.[15] The complex pattern of the spectrum in the range δ 6.00–9.00 further supports the unsymmetrical *mer* geometry of $[RuL_3]^{2+}$. This result is not incompatible with our expectation since the *fac* form would place the three aryl moieties in close proximity and therefore is most likely to be thermodynamically disfavoured relative to the *mer* isomer where the aryl groups would experience the minimum possible non-bonding interactions.

UV/VIS Spectra.—The absorption spectra of $[RuL^2{}_n(bipy)_{3-n}]^{2+}$ (n = 0–3) complexes are shown in Fig. 1 and data are collected in Table 2. All appear to be typical charge-transfer (c.t.) spectra with absorption coefficients for the lowest energy band of *ca.* 10^4 dm^3 mol^{-1} cm^{-1}. The low energy transitions which occur in the range 600–400 nm are assigned[4] to metal-to-ligand charge-transfer (m.l.c.t.) transitions. The spectra of the complexes are very similar to that of $[Ru(bipy)_3]^{2+}$ in intensity and profile. Associated with the intense c.t. band is a shoulder at higher energy. The multiple transitions in these complexes may arise for various reasons,[16–18] one possibility[19] being the presence of different acceptor levels. Remarkably, the lowest energy transition for $[RuL_3]^{2+}$ ($L = L^1$ or L^2) occurs at lower energy than that for $[Ru(bipy)_3]^{2+}$. The complex $[RuL^2(bipy)_2]^{2+}$ displays two components in its absorption spectrum in the range 500–400 nm. The feature at longer wavelength (470 nm) is associated with a $d(Ru) \longrightarrow \pi^*(L)$ transition whereas the band at 430 nm is attributed to the $d(Ru) \longrightarrow \pi^*(bipy)$ transition.

Table 2 UV/VIS spectral data

Compound	Absorption[a] λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	Emission[b] λ_{em}/nm
$[RuL^1{}_3][ClO_4]_2{\cdot}H_2O$	480 (13 760), 445[c] (10 880), 300 (25 600), 270 (55 040)	*d*
$[RuL^2{}_3][ClO_4]_2{\cdot}H_2O$	480 (14 310), 445[c] (11 120), 315 (27 380), 270 (25 120)	535, 580
$[RuL^2{}_2(bipy)][ClO_4]_2{\cdot}H_2O$	482 (11 520), 445 (10 060), 315[c] (17 040), 280 (32 400)	535, 590
$[Ru_2L^2(bipy)_2][ClO_4]_2{\cdot}H_2O$	470 (9 800), 430 (8 660), 320[c] (9 325), 285 (43 540)	540, 590
$[Ru(bipy)_3][ClO_4]_2{\cdot}H_2O$	454 (14 400), 425[c] (11 630) 305[c] (4 400), 280 (69 670)	*d*

[a] In MeCN. [b] Qualitative spectra were recorded in EtOH at 77 K. [c] Shoulder. [d] Not studied.

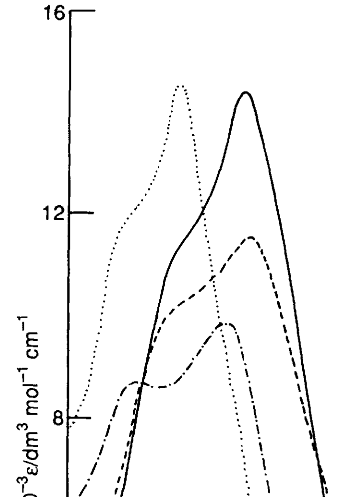

Fig. 1 Visible absorption spectra of $[RuL^2{}_3]^{2+}$ (——), $[RuL^2{}_2(bipy)]^{2+}$ (– – –), $[RuL^2(bipy)_2]^{2+}$ (–·–·–) and $[Ru(bipy)_3]^{2+}$ (· · ·) in MeCN

We also present some preliminary experimental results on the emission spectral properties of the above compounds. Unlike $[Ru(bipy)_3]^{2+}$, acetonitrile solutions of the mixed-ligand complexes and $[RuL_3]^{2+}$ ($L = L^1$ or L^2) do not emit at room temperature. However, excitation of ethanolic solutions of the complexes at 430 nm at 77 K resulted in multiple-band emission spectra. The data have been collected in Table 2.

Electrochemical Properties.—In acetonitrile solution at room temperature, four successive reversible to quasi-reversible one-electron cyclic voltammetric responses are observed for $[RuL_3]^{2+}$ in the range +1.8 to −2.0 V *versus* the saturated calomel electrode (SCE) at a platinum electrode. One of these lies at a positive potential while the other three occur at negative potentials (Table 3). The unco-ordinated ligand L^2 undergoes[4] two successive stepwise reductions at −1.42 and −1.88 V and two oxidative responses are also observable at 1.54 and 1.93 V *vs.* SCE. Since the oxidative response for $[RuL^2{}_3]^{2+}$ occurs at a less positive potential than that of the free ligand L^2, there is little doubt that the response at *ca.* 1.44 V for $[RuL^2{}_3]^{2+}$ (Fig. 2) is a metal-centred process, $[Ru^{III}L^2{}_3]^{3+}$–$[Ru^{II}L^2{}_3]^{2+}$. Similar considerations also apply for the Ru–L^1 system.

We believe[20,21] that the three cathodic couples represent successive reductions of the three co-ordinated ligands (Table 3, Fig. 3). The redox responses of the $[RuL_3]$ system may thus be represented by equation (6).

$$[Ru^{III}L_3]^{3+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Ru^{II}L_3]^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Ru^{II}L_2(L^{\bullet})]^{+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Ru^{II}L(L^{\bullet})_2] \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Ru^{II}(L^{\bullet})_3]^{-} \quad (6)$$

It may be noted here that the first reduction potential of the co-ordinated ligand occurs at a much less negative potential than that for unco-ordinated L. This is quite consistent[13,20,22,23] with the available data for complexes of ruthenium(II) containing heterocyclic ligands.

The ruthenium(III)–ruthenium(II) couple in the complexes, $[RuL_n(bipy)_{3-n}]^{2+}$, occurs in the range 1.3–1.5 V. The electrode reactions in all cases are almost reversible with ΔE_p = 70–80 mV. It is essential to use anhydrous solvent, particularly for complexes containing L, to be able to observe reversible responses. The presence of moisture leads to quasi-reversible to irreversible behaviour where the corresponding reduction wave is either broad or unobserved. This is presumably due to secondary chemical transformations of electrogenerated $[RuL_3]^{3+}$. Very recently, it has been shown[24] that electrogenerated[25] *trans*-$[RuCl_2L_2]^+$ undergoes chemical transformation in the presence of moisture to form *trans*-$[RuCl_2L(L')]$ ($L' = C_6H_5NC(O)C_5H_4N$). The mixed-ligand amido complex has been isolated and characterised by X-ray crystallography.

For the cationic complex, $[RuL_3]^{2+}$ ($L = L^1$ or L^2), six successive reductions in principle could occur[13]. We therefore employed glassy carbon as the working electrode for identification of responses at more negative potentials. Five responses were observed for $[RuL_3]^{2+}$ (Table 4), in the experimentally accessible range (−0.95 to −2.80 V).

For the mixed-ligand complexes, the first reduction may be expected to involve the ligand having the most stable lowest unoccupied molecular orbital (LUMO). We believe this to be L^2 rather than bipy. This proposal is based on the following considerations: (*i*) Each of L^2 and bipy undergoes[4,20] two successive one-electron reductions, (*ii*) the first two reductions for $[RuL^2{}_2(bipy)]^{2+}$ occur at less negative potentials than the first reduction potential for $[Ru(bipy)_3]^{2+}$ and (*iii*) similarly, the first reduction potential for $[RuL^2(bipy)_2]^{2+}$ is much more positive than that for $[Ru(bipy)_3]^{2+}$. Out of the six possible reductions for the mixed complexes five are observed for $[RuL^2{}_2(bipy)]^{2+}$, whereas for $[RuL^2(bipy)_2]^{2+}$ in which the

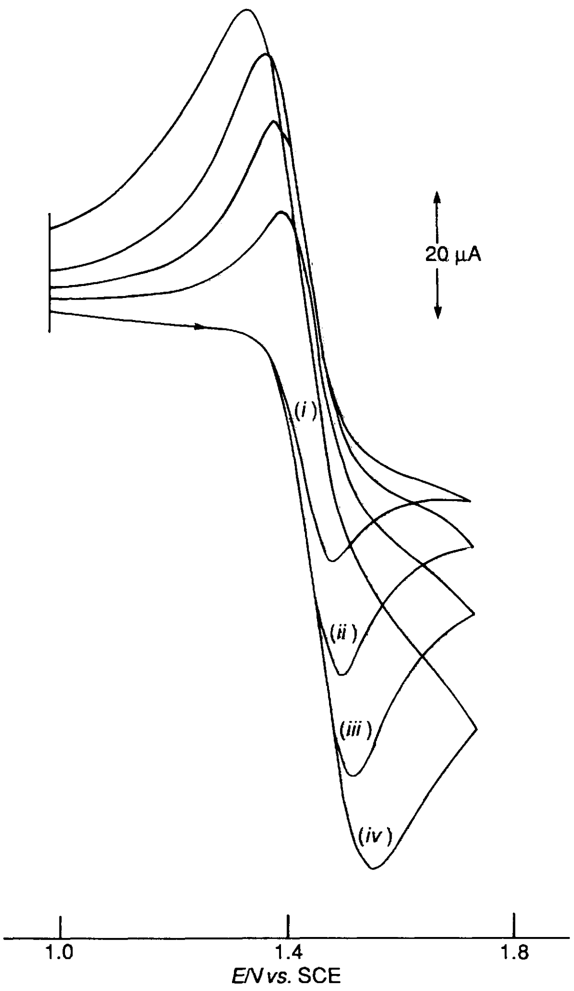

Fig. 2 Cyclic voltammograms of $[RuL^2{}_3]^{2+}$ at different scan rates at potentials positive to SCE; (*i*) 20, (*ii*) 50, (*iii*) 100 and (*iv*) 200 mV s^{-1}

Table 3 Cyclic voltammetric data * at a platinum working electrode for the complexes $[RuL_n(bipy)_{3-n}][ClO_4]_2{\cdot}H_2O$

	Metal-centred oxidation $E^{\circ}{}_{298}$/V (ΔE_p/mV)	Ligand-based reductions $E^{\circ}{}_{298}$/V (ΔE_p/mV)		
Compound	3+/2+	2+/1+	1+/0	0/1−
$[RuL^1{}_3][ClO_4]_2{\cdot}H_2O$	1.43 (75)	0.93 (90)	1.16 (100)	1.49 (110)
$[RuL^2{}_3][ClO_4]_2{\cdot}H_2O$	1.44 (70)	0.90 (90)	1.19 (110)	1.52 (110)
$[RuL^2{}_2(bipy)][ClO_4]_2{\cdot}H_2O$	1.40 (80)	0.95 (90)	1.24 (100)	1.70 (110)
$[RuL^2(bipy)_2][ClO_4]_2{\cdot}H_2O$	1.34 (75)	1.04 (100)	1.52 (110)	1.85 (110)
$[Ru(bipy)_3][ClO_4]_2{\cdot}H_2O$	1.32 (70)	1.30 (90)	1.49 (100)	1.73 (110)

* Cyclic voltammetric experiments were carried out in MeCN at 298 K using 0.1 mol dm^{-3} NBu_4ClO_4 as supporting electrolyte. The reported data correspond to scan rate v = 50 mV s^{-1}.

Table 4 Differential-pulse voltammetric data for $[RuL_n(bipy)_{3-n}][ClO_4]_2{\cdot}H_2O$ at a glassy-carbon electrode at potentials positive to SCE at 298 K

	Ligand reductions, $-E_p{}^a$/V				
Compound	2+/1+	1+/0	0/1−	1−/2−	2−/3−
$[RuL^1{}_3][ClO_4]_2{\cdot}H_2O$	0.98	1.22	1.57	2.04	2.70
$[RuL^2{}_3][ClO_4]_2{\cdot}H_2O$	1.00	1.25	1.59	2.08	2.60
$[RuL^2{}_2(bipy)][ClO_4]_2{\cdot}H_2O$	0.96	1.24	1.70	1.83	2.27
$[RuL^2(bipy)_2][ClO_4]_2{\cdot}H_2O$	1.06	1.58	1.88	2.44	*b*

[a] In MeCN using 0.1 mol dm^{-3} NBu_4ClO_4 as supporting electrolyte. Scan rate = 5 mV s^{-1}, modulation amplitude (ΔE_p) = 10 mV. [b] Not observed.

Table 5 Spectroelectrochemical correlation data for the complexes

Compound	$E°_{298}$/V Metal oxidation	$E°_{298}$/V First ligand reduction	$\Delta E°_{ox/red}$	$\nu_{c.t.}$/cm^{-1} Obs.	Calc.
$[RuL^1{}_3][ClO_4]_2{\cdot}H_2O$	1.43	−0.93	2.36	20 833	20 807
$[RuL^2{}_3][ClO_4]_2{\cdot}H_2O$	1.44	−0.90	2.34	20 833	20 668
$[RuL^2{}_2(bipy)][ClO_4]_2{\cdot}H_2O$	1.40	−0.95	2.35	20 746	20 737
$[RuL^2(bipy)_2][ClO_4]_2{\cdot}H_2O$	1.34	−1.04	2.38	21 276	20 945
cis-$[RuCl_2L^2{}_2]$	0.30	−1.18	1.48	14 814	14 702

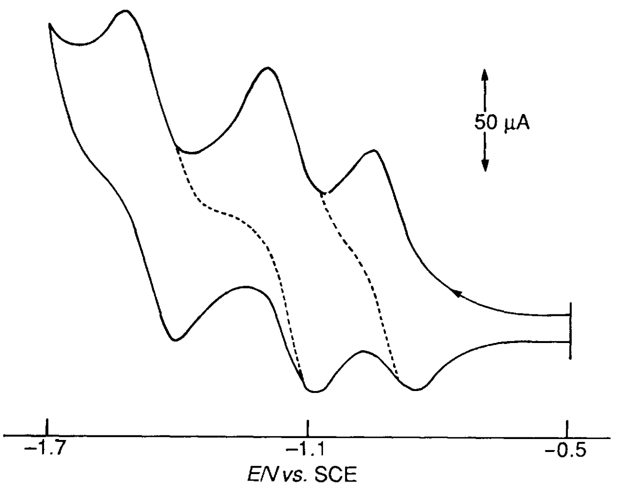

Fig. 3 Cyclic voltammogram of $[RuL^1{}_3]^{2+}$ at potentials negative to SCE at a platinum working electrode

reductions are shifted cathodically (Table 4) only four are observed in the accessible voltage window.

It is interesting that for the complexes $[RuL_n(bipy)_{3-n}]^{2+}$ and $[RuCl_2L_2]$ the m.l.c.t. absorption energies show a linear correlation with $\Delta E°_{ox/red}$ (Table 5), where $\Delta E°_{ox/red}$ refers to the difference in the formal potentials of the Ru^{III}–Ru^{II} couple and the first ligand-reduction couple. The m.l.c.t. transition for these complexes involves excitation to the π* orbital of L while the first ligand reduction in these complexes also involves the same orbital, as discussed above. A least-squares fit of $\nu_{c.t.}$ against ΔE (Fig. 4) leads to equation (7).

$$\nu = 0.86\,\Delta E + 0.55 \qquad (7)$$

It may also be noted that other examples of ruthenium complexes with similar ligands, *e.g.* the 2,2′-bipyridine[26,27] and 2-(arylazo)pyridine system,[13,28] also show similar relationships.

Conclusion

The synthesis of isomerically pure tris-chelate ruthenium(II) complexes of α,α′-diimino Schiff-base ligands has been achieved by a general synthetic procedure using the corresponding silver(I) complexes of L. The spectral as well as the redox properties of the complexes indicate L to have lower energy π* levels compared to bipy. This is in agreement with the conclusion made recently by Dominey *et al.*[21] based on the spectral properties of a group of rhenium complexes of similar ligands. Studies of the reactivities of these complexes, particularly towards oxidants, are underway.

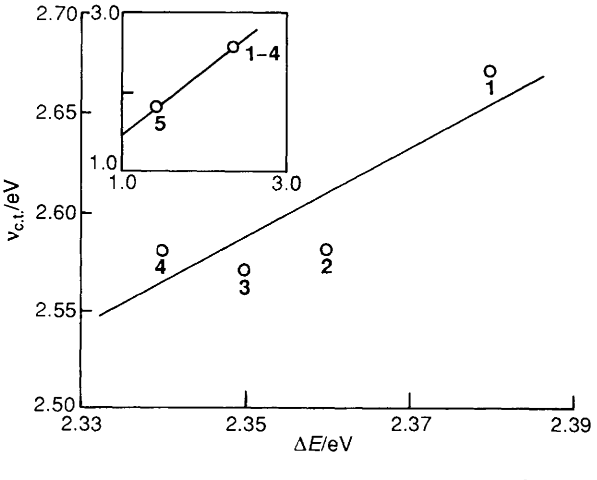

Fig. 4 Linear correlation between $\nu_{c.t.}$ and $\Delta E_{ox/red}$ for $[RuL^2(bipy)_2][ClO_4]_2{\cdot}H_2O$ **1**, $[RuL^1{}_3][ClO_4]_2{\cdot}H_2O$ **2**, $[RuL^2{}_2(bipy)][ClO_4]_2{\cdot}H_2O$ **3**, $[RuL^2{}_3][ClO_4]_2{\cdot}H_2O$ **4** and *cis*-$[RuCl_2L^2{}_2]$ **5**

Experimental

Materials.—The salt, $RuCl_3{\cdot}nH_2O$ was obtained from Arora Matthey, Calcutta and was digested thrice with concentrated HCl before use. The silver complexes, $[AgL_2]ClO_4$ (L = L^1 or L^2) and $[Ag(bipy)_2]ClO_4$ were synthesised as before.[10,11] The complexes *cis*-$[RuCl_2L_2]$,[4] *cis*-$[RuCl_2(bipy)_2]$[8] and $[Ru(bipy)_3][ClO_4]_2{\cdot}H_2O$[29] were prepared by published procedures. The purification of dry solvents for electrochemical and spectral work was performed as described earlier.[30] All other chemicals and solvents used for the preparative work were of reagent grade and were used as received.

Physical Measurements.—Infrared spectra were obtained on KBr discs (4000–600 cm^{-1}) with a Perkin-Elmer IR-297 spectrophotometer. Solution electronic spectra were recorded on a Hitachi 330 spectrophotometer and solution emission spectra were recorded with a Perkin-Elmer MPF-44A fluorescence spectrophotometer. Solution electrical conductivity measurements were performed on an Elico CM 82T conductivity bridge with a solute concentration of *ca.* 10^{-3} mol dm^{-3}. Proton NMR spectra in $CDCl_3$ were obtained on a Bruker 400-WM Fourier-transform spectrometer using $SiMe_4$ as the internal standard. The magnetic susceptibilities of the samples were measured on a PAR 155 vibration sample magnetometer fitted with a Walker scientific L75 FBAL magnet. Electrochemical measurements were carried out using a PAR model 370-4 electrochemical system consisting of 174A polarographic analyser, 175 universal programmer, RE 0074 XY recorder. All experiments were done under a dinitrogen atmosphere in a three-electrode configuration by using either a planar platinum disc electrode or a glassy-carbon electrode. All results were collected at 298 ± 1 K and are referenced to a saturated calomel electrode. The reported potentials are uncorrected for the junction contribution.

Preparations.—**CAUTION**: Perchlorate salts of metal complexes are generally explosive. Care should be taken in handling such samples.

(*i*) *Tris*[*aryl*(2-*pyridylmethylene*)*amine*]*ruthenium*(II) *perchlorate monohydrate*, $[RuL_3][ClO_4]_2{\cdot}H_2O$ ($L = L^1$ *or* L^2) *from* $RuCl_3{\cdot}3H_2O$. The compounds were synthesised using a general procedure given below.

To a sample of $RuCl_3{\cdot}3H_2O$ (1 mmol) dissolved in ethanol (20 cm^3) was added a solution of $[AgL_2]ClO_4$ (3 mmol) in ethanol (20 cm^3) and the mixture was heated to reflux for 2 h. The solution was then cooled and filtered through a G-4 sintered glass funnel to remove insoluble AgCl. The filtrate was evaporated to dryness over a water-bath and the dried mass was extracted with boiling water (4 × 25 cm^3). To this cooled water extract an aqueous solution of $NaClO_4$ (*ca.* 1 g in 25 cm^3 water) was added. The reddish brown precipitate thus obtained was filtered and dried *in vacuo* over P_4O_{10}. This was then subjected to column chromatography on a silica gel (60–120 mesh) column eluting with different mixtures of $CHCl_3$–MeCN. A reddish brown band was eluted with $CHCl_3$–MeCN (3:2). This was collected and evaporated. Finally it was recrystallised from $CHCl_3$–hexane (1:1).

The yields of the complexes were 40 (L^1) and 45% (L^2).

(*ii*) $[RuL_3][ClO_4]_2{\cdot}H_2O$ ($L = L^1$ *or* L^2) *from cis*-$[RuCl_2L_2]$. The syntheses were performed by using a general procedure given below.

To a suspension of *cis*-$[RuCl_2L_2]$ (1 mmol) in ethanol (20 cm^3) was added a solution of $[AgL_2]ClO_4$ (2 mmol) in ethanol (20 cm^3) and the mixture was heated to reflux for 2 h. The rest of the procedure was the same as that described in (*i*). The yields of the complexes were 50 (L^1) and 52% (L^2).

The analytical and spectral data of the complexes, thus obtained, corresponded exactly to those of samples prepared by method (*i*).

(*iii*) (2,2′-*Bipyridine*)*bis*[2-*pyridylmethylene*(p-*tolyl*)*amine*]*ruthenium*(II) *perchlorate monohydrate*, $[RuL^2{}_2(bipy)][ClO_4]_2{\cdot}H_2O$. To a suspension of *cis*-$[RuCl_2L^2{}_2]$ (1 mmol) in ethanol (20 cm^3) was added a solution of $[Ag(bipy)_2][ClO_4]$ (2 mmol) in ethanol (20 cm^3) and the resulting mixture was heated to reflux for 2 h. It was then cooled and filtered through a G-4 sintered glass funnel to remove insoluble AgCl. Isolation and purification of the compound from the filtrate was done similarly as described in (*i*). Yield, 50%.

(*iv*) *Bis*(2,2′-*bipyridine*) [2-*pyridylmethylene*(p-*tolyl*)*amine*]*ruthenium*(II) *perchlorate monohydrate* $[RuL^2(bipy)_2][ClO_4]_2{\cdot}H_2O$. To a suspension of *cis*-$[Ru(bipy)_2Cl_2]$ (1 mmol) in ethanol (20 cm^3) was added a solution of $[AgL^2{}_2]ClO_4$ (2 mmol) in ethanol (20 cm^3) and the resulting mixture was heated to reflux for 2 h. The rest of the procedure was the same as that described in (*iii*). Yield, 50%.

(*v*) *Reaction of* $RuCl_3{\cdot}3H_2O$ *with* $[AgL_2]ClO_4$ ($L = L^1$ *or* L^2) *in* 1:1 *ratio*. The reactions were performed by following a general procedure as described below.

The salt $RuCl_3{\cdot}3H_2O$ (1 mmol) was dissolved in ethanol (20 cm^3) and heated to reflux for 15 min over a water-bath. To this red-brown solution was added an ethanolic solution (10 cm^3) of $[AgL_2]ClO_4$ (1 mmol). Immediately, a dark violet solution resulted, which was further heated for 1 h over a water-bath. After cooling, the resulting solution was filtered through a G-4 sintered glass funnel. Insoluble white AgCl along with dark crystals of $[RuCl_2L_2]$ were separated from the dark filtrate. The residue was then extracted with chloroform. On slow evaporation of chloroform, dark crystals of isomeric mixtures of $[RuCl_2L_2]$ resulted. Isomeric purification of $[RuCl_2L_2]$ was performed on a silica gel column (60–120 mesh). The first moving green band of *trans*-$[RuCl_2L_2]$ was eluted with MeCN–$CHCl_3$ (1:10) and the second bluish green band of *cis*-$[RuCl_2L_2]$ was eluted with MeCN–$CHCl_3$ (1:5).

A further crop of isomeric $[RuCl_2L_2]$ was also obtained from the filtrate. The filtrate was evaporated to dryness and washed thoroughly with water. The dried residue was then extracted with chloroform and the solution was subjected to column chromatography as described above to obtain pure *trans* and *cis* isomers of $[RuCl_2L_2]$. Finally, the products were recrystallised from $CHCl_3$–hexane (1:1).

The yields of the different isomers were 40, 15, 45 and 20% for *trans*-$[RuCl_2L^1{}_2]$, *cis*-$[RuCl_2L^1{}_2]$, *trans*-$[RuCl_2L^2{}_2]$ and *cis*-$[RuCl_2L^2{}_2]$ respectively.

Acknowledgements

Financial support received from the Council of Scientific and Industrial Research, New Delhi, is gratefully acknowledged. We acknowledge the technical assistance of the Central Drug Research Institute, Lucknow, and thank Ms. Rina Dey, Indian Association for the Cultivation of Science, Calcutta, for emission spectral data.

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Received 15*th September* 1993; *Paper* 3/05568J