A new mixed-ligand ruthenium(II) complex with RuN₆ coordination sphere having weak π-accepting ligand

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The preparation and properties of a hetero-chelate ruthenium(II) complex containing tridentate pyridylpyrazole ligand and an asymmetric tridentate nitrogenous ligand giving two different chelate rings are described. Cyclic voltammetric experiments in acetonitrile solutions reveal a quasi-reversible one-electron RuIII→RuI redox couple at 1.14 V vs saturated calomel electrode (SCE). The diffusion coefficient for this quasi-reversible system has been estimated to be 7 x 10⁻⁶ cm² s⁻¹ on the basis of cyclic voltammetric experiments. A moderately good correlation has been obtained for a selected group of ruthenium(II) complexes with weak π-accepting ligands.

Many new tris chelate and mixed-ligand ruthenium(II) complexes with RuN₆ coordination sphere have been prepared in the last 20 years and their spectroscopic and electrochemical properties studied. In most cases, the ligands are confined to the bidentate diimine type, e.g., 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and their derivatives. The use of tridentate ligands to form bis chelates has been rather limited. With the hope of investigating the effect of asymmetry in tridentate ligands on the properties of ruthenium we have chosen the ligand 2-pyridylethyl-(2-pyridylmethyl)methylamine (MeL)₁³. By the combination of a six- and a five-membered chelate ring into a tridentate ligand, two different kinds of coordinating pyridine nitrogen atoms are created in this ligand. We report here the synthesis, spectra and electrochemistry of a heteroleptic ruthenium(II) complex with RuN₆ coordination sphere using two different tridentate ligands.

Experimental

Solvents and reagents were obtained from commercial sources and used without further purification unless otherwise stated. 2,6-Bis(pyrazol-1-ylmethyl)pyridine (H₄bpp)₁⁰, 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (Me₂bpp)₁² and 2-pyridylethyl-(2-pyridylmethyl)methylamine (MeL)₁³ were prepared as described in the literature. (H₄bpp)RuCl₃.3H₂O, [Ru(H₄bpp)₂(ClO₄)₂.H₂O, [Ru-(H₄bpp)(Me₂bpp)][(ClO₄)₂.H₂O and [Ru(Me₂bpp)]2(ClO₄)₂.H₂O were prepared as described previously. Tetra-n-butylammonium perchlorate was synthesized as described earlier. Acetonitrile was purified as reported previously. Water was deionized and then distilled from alkaline KMnO₄. Ethanol was distilled from Mg(OH)₂. Commercial RuCl₃.3H₂O was treated with concentrated HCl and evaporated to dryness on a hot plate. This was repeated three times to obtain pure product as RuCl₃.3H₂O.

[Ru(H₄bpp)(MeL)][(ClO₄)₂.H₂O

A suspension of (H₄bpp)RuCl₃.3H₂O (0.10 g, 0.20 mmol) and MeL (0.048 g, 0.21 mmol) in 10 ml of water was refluxed for 30 min under dinitrogen atmosphere. After the addition of 1.2 ml of sodium hypophosphite solution [prepared by neutralizing 30% H₃PO₂ (1.2 ml) with 2.0 M NaOH (3.4 ml)], it was further refluxed for 2 h and filtered. The desired complex was precipitated as a brownish-green solid by dropwise addition of a saturated aqueous solution of sodium perchlorate. The compound was recrystallised from ethanol/water (1:1) (yield 51%). [Found: C, 40.98; H, 4.11; N, 14.32. Calc. for C₂₇H₃₂Cl₂RuN₈O₉: C, 41.32; H, 4.08; N, 14.8%]. Absorption spectrum (in MeCN, λ, nm (ε, M⁻¹cm⁻¹): 252 (17 780), 283 sh (7 760), 375 (9 560), 580 sh (1 060).

Results and discussion

The synthetic approach employed for the preparation of the ruthenium(II) complex involves the reaction of (H₄bpp)RuCl₃ with tridentate ligand MeL in the presence of sodium hypophosphite as the reducing agent. Preparation of the complex, [Ru(H₄bpp)(MeL)]²⁺ has been reported in the literature following a direct reaction between the ligand and RuCl₃.3H₂O in the presence of NaH₂PO₂ as the reducing agent. The use of (H₄bpp)RuCl₃ has enabled us to
NOTES

1.40
1.30
1.20
1.10
1.00
S~A
S

Fig. 1—(a) Variable-scan (scan rate: (1) 10, (2) 20, (3) 50, (4) 100
and (5) 200 mV s\(^{-1}\)) cyclic voltammograms and (b) differential
pulse voltammogram (scan rate: 5 mV s\(^{-1}\)) of \([\text{Ru(H}_4\text{bpp})\text{MeL}]^{2+}\) in CH\(_3\text{CN}\) (C = 0.85 mM) at a glassy carbon
electrode.

Electrochemistry

At a glassy carbon electrode, \([\text{Ru(H}_4\text{bpp})(\text{MeL})]^{2+}\)
synthesise a unique hetero-chelate complex, \([\text{Ru(H}_4\text{bpp})(\text{MeL})]^{2+}\) with two tridentate ligands differing in the donor sites.

The infrared spectrum of the complex displays \(v(\text{OH})\) band at 3400 cm\(^{-1}\) and \(v(\text{ClO}_4^-)\) vibrations at 1100 and 630 cm\(^{-1}\). The molar conductance of the cationic complex in acetonitrile solution (AM = 278 \(\Omega^{-1}\) cm\(^2\) mol\(^{-1}\)) is in the range expected\(^\text{a}\) for 1:2 electrolytes. The complex is a diamagnetic ruthenium(II) species.

The absorption spectral data for the mixed-chelate complex is presented in the Experimental section. The spectrum shows three types of bands. A comparatively less intense shoulder at \(\sim 580\) nm, an absorption of medium intensity at \(375\) nm, and a very strong band due to intraligand transitions at further higher energy.

We assign the low energy shoulder to \((d\pi)^6 \rightarrow (d\pi)^5(d\sigma^*)\) transition\(^\text{a}\). The absorption at \(375\) nm is attributed to the spin-allowed charge transfer transition from the metal \(d\pi\) orbitals to the ligand \(\pi^*\) orbitals (MLCT). The MLCT band intensity is considerably higher than that for the sterically constrained complexes\(^\text{a}\) and \([\text{Ru(H}_4\text{bpp})(\text{Me}_4\text{bpp})]^{2+}\) and the band is at comparatively higher energy. The band at \(\sim 250\) nm and the shoulder at \(\sim 285\) nm are assigned to ligand-localized transitions.

Spectroelectrochemical correlation

Since the frequencies of the charge transfer bands afforded a quasi-reversible \((\Delta E_t = 1.14\) V with peak-to-peak separation, \(\Delta E_p = 100\) mV at a scan rate of 50 mV s\(^{-1}\)) cyclic voltammogram in acetonitrile solution. In Fig. 1 are shown the variable-scan cyclic voltammograms and differential pulse voltamogram of the present complex. Anodic peak currents \((i_{p,a})\) were found to vary linearly with \(v^1/2\) (\(v = \) scan rate). The separations \((\Delta E_p)\) between anodic and cathodic peak potentials were in the range 80-140 mV as scan rates vary between 10 and 200 mV s\(^{-1}\). Using Randles-Sevcik equation\(^\text{a}\) for linear diffusion,

\[
i_{p,a} = 2.72 \times 10^8 n^{3/2} A D^{1/2} v^{-1/2} C
\]

with \(n = 1, A = 0.342\) cm\(^2\), \(C = 0.6 \times 10^{-3}\) mol l\(^{-1}\) and from the slope of the \(i_{p,a}v^1/2\) straight line, we estimated the magnitude of the diffusion coefficient \((D)\) to be \(7.41 \times 10^{-6}\) cm\(^2\) s\(^{-1}\). This value compares well with those of other ruthenium(II) systems\(^\text{a}\).

The electrode area was evaluated from \(i_{p,a}v^1/2\) plot of a standard quasi-reversible system, \(K_4[\text{Fe(CN)}_6]\) in aqueous solution, using diffusion coefficient\(^\text{a}\) of \(\text{Fe(CN)}_6^{4-}\) as \(0.65 \times 10^{-5}\) cm\(^2\) s\(^{-1}\).

The complex also displays two successive irreversible ligand-based reduction waves at \(-1.9\) and \(-2.0\) V when scanned cathodically. Interestingly, the reductive responses are occurring at almost identical potentials when compared with \([\text{Ru}_4\text{bpp}]^{2+}\) complexes implying that the electrons are being added to the \(\text{R}_4\text{bpp}\) ligand and in this regard the MeL ligand is a mere spectator. The potentials are very negative confirming the fact that the LUMO's (lowest unoccupied molecular orbitals) are relatively high in energy compared to \(2,2':6',2''\text{-terpyridine (trpy)}\).
are associated with an intramolecular electron transfer, which can be considered as an intramolecular redox process, one should expect correlation between these frequencies and the formal potentials for a group of electronic-structurally similar compounds. Fig. 2 shows a plot of $E_r$ versus $v$ for a selected group of non-polypyridine ruthenium(II) complexes having weak $\pi$-accepting ligands. Apart from [Ru(H$_4$pp)$_2$]$_2^+$, [Ru(H$_4$pp)(Me$_2$pp)]$^2+$ and [Ru(Me$_2$pp)$_2$]$^2+$, compounds selected in this correlation include, [Ru(pyr)$_2$]$^2+$ (pyr = pyrazine)$^{21}$, [Ru(L)$_2$]$^2+$ ($L = 1-(2$-pyridyl)-3,5-dimethyl pyrazole)$^{22}$ and [Ru(bpp)$_2$]$^2+$ (bpp = 2,6-bis(N-pyrazolyl)pyridine)$^{11}$.

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