

Chemistry of ruthenium phenolates. Synthesis, characterization and redox properties of a group of salicylaldiminato complexes of ruthenium

Nimai Chand Pramanik and Samaresh Bhattacharya*

Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Calcutta 700 032, India

(Received 18 June 1996; accepted 16 August 1996)

Abstract—A group of five mixed ligand ruthenium(II) complexes of general formula $[Ru(bpy)(sal-R)_2]$ (bby = 2,2'-bipyridine, sal-R = salicylaldiminate anion) has been synthesized and characterized. The complexes are diamagnetic (low spin d^6 , S = 0) and show intense MLCT transitions in the visible region in solution. In acetonitrile solution they all show a reversible ruthenium(II)–ruthenium(III) oxidation in the range -0.3to 0.04 V versus SCE, followed by another reversible ruthenium(III)–ruthenium(IV) oxidation in the range 1.1 to 1.3 V versus SCE. The potential of these two oxidations is sensitive to the nature of the substituent R in the sal-R ligand. A reversible bpy reduction is also observed near -1.9 V versus SCE. The five $[Ru^{III}(bpy)(sal-R)_2]^+$ complexes have been synthesized by chemical oxidation of their respective ruthenium(II) precursors by iodine, and isolated as perchlorate salts. These oxidized complexes are paramagnetic (low spin d^5 , S = 1/2) and show rhombic ESR spectra at 77 K. They show intense LMCT transitions in the visible region in acetonitrile solution, together with weak ligand-field transitions at lower energies. Chemical reduction of these ruthenium(III) complexes by hydrazine gives back the parent ruthenium(II) complexes. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: ruthenium salicylaldiminates; synthesis; characterization; redox properties.

The present work has originated from our interest in the chemistry of ruthenium in different coordination environments in general [1], and the chemistry of ruthenium phenolates in particular [2]. In the present study we have used salicylaldimine, abbreviated in general as Hsal-R (1; where H stands for the dissociable phenolic proton), as the principal ligand.



* Author to whom correspondence should be addressed.

The two donor atoms of this ligand are of opposite natures. The phenolate oxygen is a hard donor and is known to stabilize the higher oxidation states of ruthenium [3], whereas the imine nitrogen is relatively much softer and is a recognized stabilizer of the lower oxidation states of this metal [4]. It is interesting to note that the chemistry of ruthenium salicylaldiminates has not been much explored [2c-e,5]. However, in all known ruthenium salicylaldiminate complexes, the effect of phenolate oxygen coordination is seen to win over that of imine nitrogen coordination. For example, in the tris-salicylaldiminate complexes, the trivalent state of ruthenium is highly stabilized, which is reflected in the low ruthenium(III)-ruthenium(II) reduction potential [5a]. This also indicates that chelation by salicylaldiminate alone can not stabilize the +2 state of ruthenium, and in order to have a stable salicylaldiminate complex of ruthenium(II) at least one of the three salicylaldiminate ligands of $[Ru(sal-R)_3]$ needs to be replaced by a strong π -acid ligand. In this context we wish to report here the chemistry of some bis-salicylaldiminate complexes of ruthenium. To satisfy the remaining two coordination sites of the $Ru(sal-R)_2$ moiety, 2,2'-bipyridine (bpy), which is a familiar stabilizer of ruthenium(II), has been used as the coligand. The synthesis, characterization and redox properties of a group of $[Ru(bpy)(sal-R)_2]$ complexes are described in this paper.

EXPERIMENTAL

Materials

Commercial ruthenium trichloride, purchased from Arora Matthey, Calcutta, India, was converted to $RuCl_3 \cdot 3H_2O$ by repeated evaporation to dryness with concentrated hydrochloric acid. 2,2'-Bipyridine was purchased from Loba, Bombay, India. [Ru(bpy)Cl₃] was synthesized following a reported procedure [6]. The salicylaldimine ligands were prepared by reacting equimolar amounts of salicylaldehyde and the respective amine in hot ethanol. Purification of acetonitrile and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were performed as reported in the literature [7]. All other chemicals and solvents were reagent grade commercial materials and were used as received.

Preparation of complexes

The $[Ru^{II}(bpy)(sal-R)_2]$ and $[Ru^{III}(bpy)(sal-R)_2]$ CIO₄ complexes were synthesized following two general methods. Details are given for two representative cases only.

 $[Ru^{II}(bpy)(sal-H)_2]$. $[Ru(bpy)Cl_3]$ (100 mg, 0.28 mmol) was suspended in ethanol (40 cm³) and Hsal-H (135 mg, 0.69 mmol) was added to it, followed by an ethanolic solution of NaOH (28 mg, 0.70 mmol). The mixture was refluxed for 3 h under nitrogen. The solvent was then evaporated and the solid mass thus obtained was washed thoroughly with water followed by hexane, and dried *in vacuo* over P₄O₁₀. Recrystallization from a 1:1 dichloromethane/hexane solution gave $[Ru(bpy)(sal-H)_2]$ as a dark brown crystalline solid. Yield: 140 mg, 72%.

CAUTION ! Perchlorate salts of metal complexes are potentially explosive. Care should be taken in handling such samples.

 $[Ru^{III}(bpy)(sal-H)_2]ClO_4$. $[Ru(bpy)(sal-H)_2]$ (100 mg, 0.154 mmol) was dissolved in acetonitrile (30 cm³) and to it was added a solution of iodine (40 mg, 0.16 mmol) in acetonitrile. The resulting solution was stirred for 15 min. The initial dark brown colour turned to deep green within 5 min. A saturated aqueous solution of NaClO₄ (10 cm³) was then added and the solution was kept in the refrigerator for 24 h. $[Ru(bpy)(sal-H)_2]ClO_4$ precipitated as a deep green microcrystalline solid which was collected by filtration, washed with cold water and dried *in vacuo* over P₄O₁₀. Yield 80 mg, 69%.

Physical measurements

Microanalyses (C, H, N) were performed using a Perkin-Elmer 240C elemental analyser. IR spectra were obtained on a Perkin-Elmer 783 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a Hitachi U-3400 specsusceptibilities trophotometer. Magnetic were measured using a PAR 155 vibrating sample magnetometer. 'H NMR spectra were obtained on a Hitachi R-60 FT-NMR spectrometer using TMS as the internal standard. X-band ESR spectra were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar for measurement at 77 K (liquid nitrogen) and the spectra were calibrated with DPPH (g = 2.0037). Solution electrical conductivities were measured using a Philips PR9500 bridge with a solute concentration of 10⁻³ M. Electrochemical measurements were made using the PAR model 370-4 electrochemistry system incorporating the following components: 174A polarographic analyser, 175 universal programmer, RE0074 X-Y recorder, 173 potentiostat, 179 digital coulometer, 377 cell system. All electrochemical experiments were performed under dinitrogen. A planar Beckman 39273 platinum inlay working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. A platinum wire gauge working electrode was used in the coulometric experiments. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

RESULTS AND DISCUSSION

Synthesis and characterization

The reaction of $[Ru(bpy)Cl_3]$ with the salicylaldimines proceeds smoothly in refluxing ethanol in the presence of NaOH to afford the [Ru(bpy)(sal- $R)_2]$ complexes in good yields [Eq. (1)]. It may be noted here that during the course of this synthetic reaction, ruthenium undergoes a one-electron reduction.

$$[Ru(bpy)Cl_3] \xrightarrow[EtOH]{HL,NaOH} [Ru(bpy)(sal-R)_2] \quad (1)$$

The solvent may serve as the reductant. Using five different Hsal-R ligands, five such complexes have been synthesized. The compositions of these complexes have been confirmed by their elemental (C, H, N) analytical data (Table 1). Magnetic susceptibility measurements show that all these complexes are diamagnetic, as expected for complexes of ruthenium(II) (low spin d^6 , S = 0).

As the salicylaldiminate ion is an unsymmetrical bidentate ligand, $[Ru(bpy)(sal-R)_2]$ complexes may exist in three different geometrical isomeric forms, **2**, **3** and **4**. Both **2** and **3** have a C_2 axis, which indicates

Compound	Analytical data" (%)			Electronic spectral data ^{<i>h</i>} $\hat{\lambda}_{max}$, nm	Cyclic voltammetric data' E_{298}^0 , V(ΔE_p , mV)		
	С	Н	N	$(\varepsilon, M^{-1} cm^{-1})$	Ru ^{III.IV}	Ru ^{n m}	Ligand reduction
[Ru(bpy)(sal-OMe)_]	64.0	4.4	8.1	705 (2800) ; 567 (4200) ; 440 ^d	1.11 (90)	-0.26 (90)) 1.91 (90)
	(64.3)	(4.5)	(7.9)	(4900); 352 (12,300)			
$[Ru(bpy)(sal-Me)_2]$	67.6	4.9	8.0	700 (2500) ; 570 (3600) ; 440 ^d	1.13 (80)	-0.21 (90)—1.90(80)
	(67.3)	(4.7)	(8.3)	(4900); 352 (12,200)			
[Ru(bpy)(sal-H) ₂]	66.3	4.0	8.4	565 (6800); 440 (11,700);	1.16 (80)	-0.17 (90)-1.88(70)
	(66.6)	(4.3)	(8.6)	340 (12,300)			
[Ru(bpy)(sal-Cl) ₂]	60.5	3.8	7.5	550 (6300); 442 (6900);	1.20(70)	-0.10(70))~ 1.86 (80)
	(60.2)	(3.6)	(7.8)	350 (9600)			
[Ru(bpy)(sal-NO ₂) ₂]	58.3	3.7	11.2	580 (4900) 460 (5300);	1.29 (85)	0.04 (70)- 1.84 (75)
	(58.5)	(3.5)	(11.4)	350 (13,300)			

Table 1. Microanalytical, electronic spectral and cyclic voltammetric data

"Calculated values are in parentheses.

^{*h*} In acetonitrile solution.

^c Conditions : solvent, acetonitrile ; supporting electrolyte, TEAP (0.1 M) ; working electrode, platinum ; reference electode, SCE ; solute concentration, $\sim 10^{-3}$ M ; $E_{298}^0 = 0.5$ ($E_{pa} + E_{pc}$), where E_{pa} and E_{pc} are anodic and cathodic peak potentials. $\Delta E_p = E_{pa} - E_{pc}$; scan rate 50 mV s⁻¹.

^dShoulder.



that the two sal-R ligands and the two pyridine rings of bpy are equivalent. In the case of 4, there is no C_2 axis and hence all the hydrogens present in the complex may give rise to separate ¹H NMR signals (provided no overlap of signals occur). The ¹H NMR spectrum of [Ru(bpy)(sal-OMe)₂], recorded in CDCl₃ solution, shows two methyl signals of equal intensity at δ 3.58 and 3.74. This clearly shows that this complex has structure 4. Similarly, two equally intense methyl signals are observed at δ 1.83 and 2.08 in the ¹H NMR spectrum of [Ru(bpy)(sal-Me)₂], indicating the same stereochemistry, 4, for this complex. Therefore we assume structure 4 for all five [Ru(bpy)(sal-R)₂] complexes.

The [Ru(bpy)(sal-R)₂] complexes are soluble in acetonitrile, dichloromethane, chloroform, etc., producing intense brown solutions. Conductivity measurements show that these complexes are nonelectrolytes in solution, as expected. The electronic spectra have been recorded in acetonitrile solution and spectral data are given in Table 1 and selected spectrum is shown in Fig. 1. All five complexes show several intense absorptions in the visible region, which are due to allowed metal-to-ligand charge-transfer transitions. Multiple charge-transfer transitions in these complexes may result from lower symmetry splitting of the metal level, the presence of different acceptor orbitals and the mixing of singlet and triplet configurations in the excited state through spin-orbit coupling [8]. Such spectral behaviour has been observed before in similar mixed ligand complexes [1d].

Cyclic voltammetric studies

The electron transfer properties of the $[Ru(b-py)(sal-R)_2]$ complexes have been studied in acetonitrile solution by cyclic voltammetry. Vol-



Fig. 1. Electronic spectra of [Ru^{II}(bpy)(sal-H)₂] (---) and [Ru^{III}(bpy)(sal-H)₂]ClO₄ (----) in acetonitrile solution.

tammetric data are presented in Table 1 and a representative voltammogram is shown in Fig. 2. All these complexes show three voltammetric responses, two metal-centred oxidations and one ligand (bpy)based reduction. We shall first consider the ligandbased reduction. A one-electron reduction near -1.9V (all potentials are referenced to SCE) is displayed by all these complexes which is assigned to the reduction of the coordinated bpy [Eq. (2)].

$$[Ru^{II}(bpy)(sal-R)_2] + e^- \rightleftharpoons [Ru^{II}(bpy)(sal-R)_2]^- \quad (2)$$

The one-electron nature of this couple has been estab-

lished by comparing its current heights with those of the ruthenium(II)-ruthenium(III) couple displayed by all these complexes near -0.1 V (see below). It is well known [9] that each bpy can successively accept two electrons in its lowest unoccupied molecular orbital. Hence, in these [Ru (bpy)(sal-R)₂] complexes two successive one-electron reductions are expected of which only the first reduction is actually observed. The second reduction, which is expected to occur at much more negative potentials, is not observed owing to solvent cut-off.

The metal-centred oxidations will now be



Fig. 2. Cyclic voltammogram of $[Ru^{II}(bpy)(sal-H)_2]$ in acetonitrile solution (0.1 M TEAP) at a scan rate of 50 mV s⁻¹. The solute concentration was 1×10^{-3} M.

considered. All these complexes show a reversible oneelectron oxidation in the range -0.26 to 0.04 V, which is assigned to the ruthenium(II)-ruthenium(III) oxidation [Eq. (3)].

$$[Ru''(bpy)(sal-R)_2] \rightleftharpoons [Ru'''(bpy)(sal-R)_2]^+ + e^{-\alpha}$$
(3)

Therefore the replacement of only one sal-R ligand of [Ru(sal-R)₃] by bpy has indeed caused a significant increase in the stability of the +2 state of ruthenium. For example, the ruthenium(II)-ruthenium(III) couple is observed at -0.83 V in [Ru(sal-H)₃] [5a], while the same couple appears at -0.17 V in [Ru(bpy)(sal- H_{2} . The positive shift of 660 mV reflects the ability of bpy to stabilize the bivalent state of ruthenium. It is interesting to note here that a gradual decrease in the potential of the ruthenium(II)-ruthenium(III) couple is observed in the series: $[Ru(bpy)_3]^{2+}$, 1.30 V [10]; [Ru(bpy)₂(sal-H)]⁺, 0.63 V [2d]; [Ru(bpy)(sal-H)₂], -0.17 V; [Ru(sal-H)₃], -0.83V [5a]. The plot of these E_{298}^0 values versus the number of bpy ligands in these $[Ru(bpy)_n(sal-H)_{3\dots n}]$ (n = 0, 1, 2, 3) complexes is linear (Fig. 3). A similar linear plot is obtained in any other $[Ru(bpy)_n(sal-R)_{3-n}]$ series. This correlation shows the relative ability of the sal-R and bpy ligands to stabilize the +3 and +2 states of ruthenium.

The potential of the ruthenium(II)-ruthenium(III) couple in the [Ru(bpy)(sal-R)₂] complexes is found to be sensitive to the nature of the substituent R in the salicylaldiminate ligand. The formal potential (E_{298}^0) increases with increasing electron withdrawing character of R. The plot of E_{298}^0 versus 2σ [σ = Hammett constant of R [11]; OMe = -0.27, Me = -0.17, H = 0.0, Cl = 0.23 and NO₂ = 0.78] is



Fig. 3. Variation of ruthenium(II)-ruthenium(III) potential in $[Ru(bpy)_n(sal-H)_{3-n}]$.



Fig. 4. Least-squares plot of E_{298}^0 values of (a) Ru^{II}/Ru^{III} couple versus 2σ and (b) Ru^{III}/Ru^{IV} couple versus 2σ .

linear (Fig. 4) with $\rho = 0.14$ V ($\rho =$ reaction constant of this couple [12]). It is clear from this plot that a single substituent on the sal-R ligand, which is six bonds away from the electroactive metal centre. can influence the metal oxidation potential in a predictable manner.

All the $[Ru(bpy)(sal-R)_2]$ complexes show a second, reversible one-electron oxidation in the range 1.1–1.3 V which is assigned to the ruthenium(III) ruthenium(IV) oxidation [Eq. (4)].

$$[\mathbf{R}\mathbf{u}^{\mathrm{III}}(\mathrm{bpy})(\mathrm{sal-R})_2]^* \rightleftharpoons [\mathbf{R}\mathbf{u}^{\mathrm{IV}}(\mathrm{bpy})(\mathrm{sal-R})_2]^{2+} + e$$
(4)

The potential of this oxidation is *ca* 500 mV more positive than that in the respective [Ru(sal-R)₃] complexes [5a], which is owing to the strong π -acidity of the bpy ligand, as discussed above. The potential of this oxidation also correlates linearly with the Hammett constant (σ) of R (Fig. 4). The slope in this case is $\rho = 0.09$ V, which indicates that this ruthenium(III)-ruthenium(IV) oxidation potential is relatively less sensitive to the nature of R than the ruthenium(II)-ruthenium(III) oxidation potential.

[Ru^{III}(bpy)(sal-R)₂]⁺ complexes

The reversibility of the ruthenium(II)-ruthenium-(III) couple in the $[Ru(bpy)(sal-R)_2]$ complexes, and its relatively low potential, point to the possibility of the oxidized complex, $[Ru^{III}(bpy)(sal-R)_2]^+$, being stable on a much longer time-scale. To investigate this, the $[Ru(bpy)(sal-R)_2]$ complexes have been oxidized in acetonitrile solution (0.1 M TEAP) by constant-potential coulometry near 0.3 V. The oxidations have been smooth and quantitative [*n* (number of electron-transfer)=0.97] affording deep green solutions of $[Ru^{III}(bpy)(sal-R)_2]^+$ which show similar cyc-

lic voltammograms to their respective precursors, except that the ruthenium(II)-ruthenium(III) couple now appears as a reductive response. Upon coulometric reduction of the green solutions near -0.5 V, deep brown solutions of $[Ru(bpy)(sal-R)_2]$ are obtained. The [Ru^{III}(bpy)(sal-R)₂]⁺ complexes have also been synthesized by chemical oxidation of $[Ru^{(l)}(bpy)(sal-R)_2]$ in acetonitrile solution by iodine and the complex cations have been isolated as perchlorate salts in the solid state. Microanalytical data (Table 2) agree well with the compositions of these complexes. Conductivity measurements in acetonitrile solution show that these complexes behave as 1:1 electrolytes (Table 2), as expected. Electronic spectra recorded in acetonitrile solution show intense absorptions in the visible region together with a weak absorption at lower energies (Table 2, Fig. 1). The intense absorptions in the visible region are probably owing to ligand-to-metal charge-transfer transitions. The low intensity absorptions in the near-IR region are discussed below. Addition of hydrazine hydrate to the deep green solution of [Ru(bpy)(sal-R)₂]ClO₄ in acetonitrile brings about an instantaneous reduction affording a deep brown solution of [Ru(bpy)(sal-R)₂].

The [Ru(bpy)(sal-R)₂]ClO₄ complexes are one-electron paramagnetic (Table 2), which corresponds to the +3 oxidation state of ruthenium (low spin d^5 , $S = \frac{1}{2}$) in these complexes. ESR spectra of these complexes have been recorded in 1:1 dichloromethane/toluene solution at 77 K. All five complexes show rhombic ESR spectra with three dis-

tinct g-values (Fig. 5, Table 3). The rhombic nature of the spectra indicates the asymmetry of the electronic environment around ruthenium in these complexes. This asymmetry is understandable in terms of the stereochemistry of these complexes (4, vide supra) which has no C_2 axis. The observed spectra may be considered as pseudo-axial, consisting of a rather isolated signal near 1.90 (g_1 in the axial case) and two relatively close signals near 2.25 and 2.10 (rhombic



Fig. 5. ESR spectrum in 1:1 dichloromethane/toluene solution at 77 K and t₂ splittings of [Ru^{III}(bpy)(sal-H)₂]ClO₄.

	Analytical data" (%)			Molar conductivity data ^b		Electronic spectral data	
Compound	C	н	N	$(\Omega^{-1} \operatorname{cm}^2 \mathrm{M}^{-1})$	$\mu_{ m eff}$ (BM)	λ_{\max} , nm (ε , M ⁻¹ cm ⁻¹)	
[Ru(bpy)(sal-OMe) ₂]ClO ₄	56.7	4.2	7.1	155	1.90	1550 ^d (80) ; 700 ^d (2600) 575 (4400) ; 350 (21,000)	
	(56.4)	(4.0)	(6.9)				
$[Ru(bpy)(sal-Me)_2]ClO_4$	58.5	4.3	7.4	151	1.88	1550(68); 670 ^d (1800); 570 (2600); 355 (25,300)	
	(58.3)	(4.1)	(7.2)				
[Ru(bpy)(sal-H) ₂]ClO ₄	57.5	3.5	7.2	144	1.82	1520(80) ; 675 (3500) ; 566 (4300) ; 355 (12,800)	
	(57.7)	(3.7)	(7.5)				
[Ru(bpy)(sal-Cl) ₂]ClO ₄	53.1	3.5	6.4	148	1.85	1500 (60) ; 650 ^d (3200) ; 570 (4500); 360 (17,900)	
	(52.8)	(3.2)	(6.8)				
$[Ru(bpy)(sal-NO_2)_2]ClO_4$	51.8	3.3	9.8	138	1.81	1450 (85) ; 600 (4800) ; 360 (15,700)	
	(51.5)	(3.1)	(10.0)			× · · /	

Table 2. Microanalytical, molar conductivity, magnetic susceptibility and electronic spectral data

"Calculated values are in parentheses.

^{*b*} In acetonitrile solution.

^c In acetonitrile solution

^d Shoulder

Compound	g_1	<i>g</i> ₂	g_3	Δ/λ	ν/λ	$\Delta E_{ m L} \dot{\lambda}$	ΔE_2 i
[Ru(bpy)(sal-OMe) ₂]ClO ₄	2.264	2.092	1.903	6.24	4.07	4.31	8.45
[Ru(bpy)(sal-Me) ₂]ClO ₄	2.259	2.091	1.902	6.17	3.95	4.30	8.33
[Ru(bpy)(sal-H) ₂]ClO ₄	2.257	2.092	1.900	6.07	3.80	4.27	8.15
[Ru(bpy)(sal-Cl) ₂]ClO ₄	2.226	2.099	1.900	5.77	2.89	4.42	7.43
$[Ru(bpy)(sal-NO_2)_2]ClO_4$	2.232	2.119	1.901	5.73	2.46	4.57	7.17

Table 3. ESR g-values^{*a*} and derived energy parameters^{*b*}

^a In 1:1 dichloromethane/toluene solution at 77 K.

^b Spin-orbit coupling constant (λ) for complexed ruthenium(III) is *ca* 1000 cm⁻¹.

component of g_{\perp}). Accordingly, the axial distortion (Δ) that splits the t₂ level into a and e components is expected to be larger than the rhombic distortion (V), which splits e (Fig. 5). Spin-orbit coupling causes further changes in the energy gaps. Thus, two electronic transitions (transition energies ΔE_1 and ΔE_2 ; $\Delta E_1 < \Delta E_2$) are possible within these three levels. All these energy parameters have been computed (Table 3) using the observed g-values, the g-tensor theory of low spin d^5 complexes [13] and a reported method [14]. The axial distortion is indeed larger than the rhombic one. The ΔE_2 transition has been observed in the spectra of all $[Ru(bpy)(sal-R)_2]^+$ complexes near the predicted energies (Table 2). However, the ΔE_1 transition could not be detected because the solvent (acetonitrile) itself is not transparent in this region.

Acknowledgements -Financial assistance received from the Department of Science and Technology, (SR/OY/C-08/93), New Delhi, is gratefully acknowledged. The authors thank Professor Animesh Chakravorty of the Indian Association for the Cultivation of Science, Calcutta, and Professor Rabindranath Mukherjee of the Indian Institute of Technology, Kanpur, for their help. Thanks are also due to the referee for his suggestions at the revision stage.

REFERENCES

- (a) Chakravarty, J. and Bhattacharya, S., Polyhedron 1994, 13, 2671; (b) Ghatak, N. and Bhattacharya, S., Polyhedron 1994, 13, 2999; (c) Ghatak, N., Chakravarty, J. and Bhattacharya, S., Trans. Met. Chem. 1995, 20, 138; (d) Ghatak, N., Chakravarty, J. and Bhattacharya, S., Polyhedron 1995, 14, 3591; (e) Chakravarty, J. and Bhattacharya, S., Polyhedron 1995, 107, 361; (f) Ghatak, N. and Bhattacharya, S., Trans. Met. Chem. 1996, 21, 158.
- (a) Bhattacharya, S., *Polyhedron* 1993, **12**, 235;
 (b) Bhattacharya, S., *Polyhedron* 1994, **13**, 451;
 (c) Chakravarty, J. and Bhattacharya, S., *Polyhedron* 1996, **15**, 257;
 (d) Chakravarty, J. and Bhattacharya, S., *Polyhedron* 1996, **15** 1047;

Sinha, P. K., Chakravarty, J. and Bhattacharya, S., *Polyhedron* 1996, **15**, 2931.

- (a) Lahiri, G. K., Bhattacharya, S., Mukherjee, M., Mukherjee, A. and Chakravorty, A., *Inorg. Chem.* 1987, **26**, 3359; (b) Bhattacharya, S., Boone, S. R., Fox, G. K. and Pierpont, C. G., J. *Am. Chem. Soc.* 1990, **112**, 1088; (c) Bardwell D. A., Black, D., Jeffery, J. C., Schatz, E. and Ward, M. D., J. Chem. Soc., Dalton Trans. 1993, 2321.
- (a) Reinhold, J., Beuedix, R., Birner, P. and Henning, H., *Inorg. Chim. Acta* 1979, 33, 209; (b) Goswami, S., Chakravarty, A. R. and Chakravorty A., *Inorg. Chem.* 1981, 20, 2246.
- (a) Lahiri, G. K., Bhattacharya, S., Ghosh, B. K. and Chakravorty, A., *Inorg. Chem.* 1987, 26, 4324; (b) El-Hendawy, A. M., El-Ghany, A., El-Kourashy and Shanab, M. M., *Polyhedron* 1992, 11, 523; (c) El-Hendawy, A. M., Alkubaisi, A. H., El-Ghany, A., El-Kourashy and Shanab, M. M., *Polyhedron* 1993, 12, 2343.
- 6. Anderson, S. and Seddon, K. R., J. Chem. Res. (S) 1979, 74.
- (a) Sawyer D. T. and Roberts J. L. Jr, Experimental Electrochemistry for Chemists. John Wiley, New York, 1974, pp. 167–215; (b) Walter M. and Ramaley, L., Anal. Chem. 1973, 45, 165.
- (a) Pankuch, B. J., Lacy, D. E. and Grosby, G. A., J. Phys. Chem. 1980, 84, 2061; (b) Ceulemans, A. and Vanquickenborne, L. G., J. Am. Chem. Soc. 1981, 103, 2238; (c) Decurtius, S., Felix, F., Ferguson, J., Gudel, H. U. and Ludi, A., J. Am. Chem. Soc. 1980, 102, 4102; (d) Kober, E. M. and Meyer, T. J., Inorg. Chem. 1982, 21, 3967.
- 9. (a) Vleck, A. A., Coord. Chem. Rev. 1982, 43, 39;
 (b) Kahl, J. L., Hanck, K. W. and DeArmond, K., J. Phys. Chem. 1978, 82, 540.
- Tokel-Takvorian, N. E., Hemingway, R. E. and Bard, A. J., J. Am. Chem. Soc. 1973, 95, 6582.
- 11. Hammett, L. P., *Physical Organic Chemistry*, 2nd edn. McGraw Hill, New York, 1970.
- Mukherjee, R. N., Rajan, O. A. and Chakravorty, A., *Inorg. Chem.* 1982, 21, 785.
- (a) Bleany B. and O'Brien, M. C. M., Proc. Phys. Soc., London, Sect. B 1956, 69, 1216; (b) Griffith, J. S., The Theory of Transition Metal Ions. Cambridge University Press, London, 1961, p. 364.
- Bhattacharya S. and Chakravorty, A., Proc. Ind. Acad. Sci. (Chem. Sci.) 1985, 95, 159.