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Polyhedron 27 (2008) 139-150

N,N'-Bis(aryl)pyridine-2,6-dicarboxamide complexes of ruthenium: Synthesis, structure and redox properties

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Received 16 July 2007; accepted 27 August 2007 Available online 23 October 2007

Abstract

Reaction of five *N*,*N*'-bis(aryl)pyridine-2,6-dicarboxamides (H₂L-R, where H₂ denotes the two acidic protons and R (R = OCH₃, CH₃, H, Cl and NO₂) the *para* substituent in the aryl fragment) with [Ru(trpy)Cl₃](trpy = 2,2',2"-terpyridine) in refluxing ethanol in the presence of a base (NEt₃) affords a group of complexes of the type [Ru^{II}(trpy)(L-R)], each of which contains an amide ligand coordinated to the metal center as a dianionic tridentate N,N,N-donor along with a terpyridine ligand. Structure of the [Ru^{II}(trpy)(L-Cl)] complex has been determined by X-ray crystallography. All the Ru(II) complexes are diamagnetic, and show characteristic ¹H NMR signals and intense MLCT transitions in the visible region. Cyclic voltammetry on the [Ru^{II}(trpy)(L-R)] complexes shows a Ru(II)–Ru(III) oxidation within 0.16–0.33 V versus SCE. An oxidation of the coordinated amide ligand is also observed within 0.94–1.33 V versus SCE and a reduction of coordinated terpyridine ligand within –1.10 to –1.15 V versus SCE. Constant potential coulometric oxidation of the [Ru^{II}(trpy)(L-R)] complexes produces the corresponding [Ru^{III}(trpy)(L-R)]⁺ complexes, which have been isolated as the perchlorate salts. Structure of the [Ru^{III}(trpy)(L-CH₃)]ClO₄ complex has been determined by X-ray crystallography. All the Ru(III) complexes near 1600 nm. © 2007 Elsevier Ltd. All rights reserved.

Keywords: N,N'-Bis(aryl)pyridine-2,6-dicarboxamide ligands; Ruthenium complexes; Redox properties

1. Introduction

The chemistry of ruthenium has been receiving considerable attention [1], primarily because of the fascinating redox, photophysical and photochemical properties exhibited by complexes of this metal. As properties are dependent mostly on the coordination environment around the metal center, complexation of ruthenium by ligands of selected types is of significant importance, and the present work has originated from our continued interest in this area in general [2], and our recent findings on the chemistry of some ruthenium amide complexes in particular [2j]. It may be relevant to mention here that chemistry of the amide ligands is of particular interest with reference to their role in biological processes [3]. For example, the amide linkage plays a key role in the formation and maintenance of protein architectures, which are crucial for their performance in biological systems [4]. Apart from their relevance in biological phenomena, coordination chemistry of the amide ligands is also interesting with regard to their variable binding modes. The amides usually display two modes of binding to metal ions, through the nitrogen (amidate mode) via dissociation of the N–H proton and through the oxygen (amide mode). While binding in the amidate mode is known to stabilize metal ions in their high oxidation states, that in the amide mode is reported to favor relatively lower oxidation states of a metal [5]. Interconversion between the amide and amidate modes

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^{0277-5387/\$ -} see front matter @ 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2007.08.042

of binding has been efficiently utilized to manipulate redox properties of the metal center [6]. In a recent study on a group of tris-complexes of N-(arvl)picolinamides (1) [2i], where the amides are bound to ruthenium through the pyridine-nitrogen (N^p) and the amide-nitrogen (N^a) (as in 2) creating a $N_3^p N_3^a$ coordination sphere, the trivalent state of ruthenium has been found to be highly stable as reflected in the Ru(III)-Ru(II) reduction potential (-0.38 V versus SCE, for the R = H complex). From the magnitude of this reduction potential it became evident that the bivalent state of ruthenium cannot be stabilized in the same $N_3^p N_3^a$ environment. In order to have stable ruthenium(II) complexes of such amides, a logical approach seems to be to reduce the number of hard amide nitrogens and increase that of soft pyridine nitrogens in the coordination sphere. Thus we have planned to create a N₄^pN₂^a coordination sphere around ruthenium, and with this simple strategy a group of N, N'bis(aryl)pyridine-2,6-dicarboxamides (3), derived from 2,2'-dipicolinic acid and five different para-substituted anilines, have been selected as the ligands and $[Ru(trpy)Cl_3](trpy = 2,2',2''-terpyridine)$ as the ruthenium starting material. The selected amides (3) are known to bind to metal ions usually as dianaionic tridentate N^a,N^p, N^a-donors (4) via loss of the two amide protons [7]. However, there are few instances where they also bind to metal ions as monoanaionic N^a,N^p,O-donors as well as neutral O,N^p,O-donors [8]. It may be mentioned here that though chemistry of amide complexes of many transition metals has been extensively studied [9], that of ruthenium appears to have received much less attention [2i,0,7a,10]. As the source of ruthenium the [Ru(trpy)Cl₃] complex has been selected because of its demonstrated ability to accommodate tridentate ligands via displacement of three chlorides and thus providing three pyridine nitrogens in the coordination sphere [11]. Reaction of the selected amides (3) with [Ru(trpy)Cl₃] has indeed been found to afford a family of complexes having the targeted N₄^pN₂^a coordination sphere around ruthenium. An account of the chemistry of all these complexes is presented in this report, with special reference to their formation, characterization and, spectral and electrochemical properties.



2. Experimental

2.1. Materials

Commercial ruthenium trichloride was purchased from Arora Matthey, Kolkata, India. The *para*-substituted anilines, 2,2',2"-terpyridine and 2,6-dipicolinic acid were obtained from Aldrich, India. All other chemicals and solvents were reagent grade commercial materials and were used as received. [Ru(trpy)Cl₃] was synthesized by following a reported procedure [12]. The N,N'-bis(aryl)pyridine-2,6-dicarboxamides (3, H₂L-R) were prepared by condensing 2,6-dipicolinic acid with *para*-substituted anilines [10a]. Purification of dichloromethane and acetonitrile, and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were performed as reported in the literature [13].

2.2. Synthesis

2.2.1. $[Ru^{II}(trpy)(L-R)]$

The $[Ru^{II}(trpy)(L-R)]$ complexes were obtained by following a general procedure. Specific details are given below for a particular complex.

2.2.1.1. $[Ru^{II}(trpy)(L-H)]$. To a solution of the H₂L-H ligand (70 mg, 0.22 mmol) in ethanol (40 mL) was added triethylamine (70 mg, 0.70 mmol) followed by [Ru(tr-py)Cl₃] (100 mg, 0.22 mmol), and the mixture was then refluxed for 24 h to yield a brown solution. The solvent was evaporated and the brown residue, thus obtained, was subjected to purification by thin layer chromatography on a silica plate. With 1:1 acetonitrile-toluene as the eluant, a brown band separated, which was extracted with acetonitrile. Evaporation of this acetonitrile extract gave [Ru^{II}(trpy)(L-H)] as a brown crystalline solid. Yield: 103 mg (70%).

2.2.1.2. $[Ru^{II}(trpy)(L-OCH_3)]$. Anal. Calc. for C₃₆H₂₈-N₆O₄Ru: C, 60.93; H, 3.94; N, 11.84. Found: C, 60.83; H, 3.72; N, 11.95%. ¹H NMR in CDCl₃, δ ppm¹: 3.57 (s, 6H, OCH₃); 5.55 (d, 4H, J = 6.2); 6.57 (d, 4H, J = 6.2); 7.32 (t, 2H, J = 7.8); 7.49–7.61 (4H)*; 7.78 (d, 2H, J = 7.7); 7.81 (d, 2H, J = 7.7); 8.15 (t, 2H, J = 7.4)*; 8.31 (2H)*.

2.2.1.3. $[Ru^{II}(trpy)(L-CH_3)]$. Anal. Calc. for C₃₆H₂₈-N₆O₂Ru: C, 63.81; H, 4.13; N, 12.40. Found: C, 63.77; H, 4.04; N, 12.48%. ¹H NMR in CDCl₃, δ ppm¹: 2.10 (s, 6H, CH₃); 5.35 (d, 4H, J = 6.1); 6.37 (d, 4H, J = 6.2); 7.34 (t, 2H, J = 7.8); 7.51–7.66 (4H)*; 7.77 (d, 2H,

¹ Chemical shifts are given in ppm and multiplicity of the signals along with the associated coupling constants (J in Hz) are given in parentheses. Overlapping signals are marked with an asterisk.

J = 7.7); 7.79 (d, 2H, J = 7.7); 8.11 (t, 2H, J = 7.4); 8.28 (2H)*.

2.2.1.4. $[Ru^{II}(trpy)(L-H)]$. Anal. Calc. for C₃₄H₂₄-N₆O₂Ru: C, 62.86; H, 3.69; N, 12.94. Found: C, 62.45; H, 3.82; N, 13.01%. ¹H NMR in CDCl₃, δ ppm¹: 5.33 (t, 2H, J = 6.1); 5.54 (t, 4H, J = 6.1); 6.45 (d, 4H, J = 6.2); 7.31 (t, 2H, J = 7.8); 7.43–7.62 (4H)*; 7.80 (d, 2H, J = 7.7); 7.82 (d, 2H, J = 7.7); 8.15 (d, 2H, J = 7.7); 8.32 (2H)*.

2.2.1.5. $[Ru^{II}(trpy)(L-Cl)]$. Anal. Calc. for C₃₄H₂₂N₆-O₂Cl₂Ru: C, 56.82; H, 3.06; N, 11.69. Found: C, 56.95; H, 3.10; N 11.85%. ¹H NMR in CDCl₃, δ ppm¹: 5.34 (d, 4H, J = 6.1); 6.48 (d, 4H, J = 6.2); 7.29 (t, 2H, J = 7.8); 7.43–7.62 (4H)*; 7.79 (d, 2H, J = 7.7); 7.86 (d, 2H, J = 7.7); 8.18 (d, 2H, J = 7.4); 8.26 (2H)*.

2.2.1.6. $[Ru^{II}(trpy)(L-NO_2)]$. Anal. Calc. for C₃₄H₂₂-N₈O₆Ru: C, 55.20; H, 2.97; N, 15.15. Found: C, 55.30; H, 2.85; N, 15.25%. ¹H NMR in CDCl₃, δ ppm¹: 5.36 (d, 4H, J = 6.1); 6.47 (d, 4H, J = 6.2); 7.33 (t, 2H, J = 7.8); 7.43–7.62 (4H)*; 7.75 (d, 2H, J = 7.7); 7.83 (d, 2H, J = 7.7); 8.13 (d, 2H, J = 7.4), 8.29 (2H)*.

2.2.2. $[Ru^{III}(trpy)(L-R)]ClO_4$

The $[Ru^{III}(trpy)(L-R)]ClO_4$ complexes were obtained by following a general procedure. Specific details are given below for a particular complex.

2.2.2.1. $[Ru^{III}(trpy)(L-H)]ClO_4$. A solution of $[Ru^{II}-(trpy)(L-H)]$ (22 mg, 0.03 mmol) in 50 mL of 1:9 dichloromethane-acetonitrile (0.1 M TBAP) was coulometrically oxidized at 0.4 V versus SCE. Color of the solution gradually changed from brown to green during the oxidation. After the electrolysis was complete ($Q_{observed} = 3.47$ C, $Q_{calculated} = 3.36$ C), the resulting acetonitrile solution was then layered over toluene. Green crystals of the $[Ru^{III}-(trpy)(L-H)]ClO_4$ complex were obtained upon slow diffusion of toluene into the acetonitrile solution, which were collected manually. The yield was quantitative.

2.2.2.1.1. $[Ru^{III}(trpy)(L-OCH_3)]ClO_4$. Anal. Calc. for $C_{36}H_{28}N_6O_8ClRu: C, 53.43; H, 3.46; N, 10.38.$ Found: C, 53.78; H, 3.34; N, 10.44%.

2.2.2.1.2. $[Ru^{III}(trpy)(L-CH_3)]ClO_4$. Anal. Calc. for C₃₆H₂₈N₆O₆ClRu: C, 55.63; H, 3.60; N, 10.81. Found: C, 55.92; H, 3.32; N, 10.94%.

2.2.2.1.3. $[Ru^{III}(trpy)(L-H)]ClO_4$. Anal. Calc. for $C_{34}H_{24}N_6O_6ClRu: C, 54.50; H, 3.20; N, 11.22$. Found: C, 54.62; H, 3.63; N, 11.10%.

2.2.2.1.4. $[Ru^{III}(trpy)(L-Cl)]ClO_4$. Anal. Calc. for $C_{34}H_{22}N_6O_6Cl_3Ru$: C, 49.90; H, 2.69; N, 10.27. Found: C, 49.75; H, 2.77; N, 10.45%.

2.2.2.1.5. $[Ru^{III}(trpy)(L-NO_2)]ClO_4$. Anal. Calc. for $C_{34}H_{22}N_8O_{10}ClRu$: C, 48.65; H, 2.62; N, 13.35. Found: C, 48.55; H, 2.80; N, 13.45%.

2.3. Physical measurements

Microanalyses (C. H. N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. IR spectra were obtained on a Perkin-Elmer 783 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet. NMR spectra were recorded in CDCl₃ solution with a Bruker AV 300 NMR spectrometer. ESR spectra were recorded with a JEOL JES-FA200 X-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid dinitrogen). All ESR spectra were calibrated with an aid of DPPH (g = 2.0037). Electrochemical measurements were made using a CH Instruments model 600A electrochemical analyzer. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in the cyclic voltammetry experiments. A platinum-wiregauge working electrode was used in the coulometric experiments. All electrochemical experiments were performed under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

2.4. X-ray crystallography

Single crystals of $[Ru^{II}(trpy)(L-Cl)]$ were obtained by slow evaporation of an acetonitrile solution of the complex. Single crystals of $[Ru^{III}(trpy)(L-Me)]ClO_4$ were obtained by slow diffusion of toluene into an acetonitrile solution of the complex. Data were collected on a Bruker SMART APEX CCD diffractometer using graphite monochromated and Mo K α radiation ($\lambda = 0.71073$ Å). X-ray data reduction and, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs [14]. The structures were solved by the direct methods.

Crystal data for C₅₁H₃₃N₉O₆Cl₃Ru_{1.5}, M = 1125.34, 0.33 × 0.34 × 0.45 mm³, monoclinic, space group C2/c, a = 32.244(7) Å, b = 15.797(4) Å, c = 19.331(4) Å, $\beta =$ 102.458(4)°, V = 9615(4) Å³, Z = 8, $D_{calc} = 1.556$ Mg m⁻³, F(000) = 4536, $\lambda = 0.71073$ Å, T = 293 K, $\mu = 0.702$ mm⁻¹, 49734 reflections collected, 10279 unique ($R_{int} = 0.036$). Final goodness-of-fit = 0.95, $R_1 = 0.0595$, $wR_2 = 0.2266$, R indices based on 8382 reflections with $I > 2\sigma(I)$ (refinement on F_2), 638 parameters.

Crystal data for $C_{36}H_{28}N_6O_6CIRu$, M = 813.20, $0.24 \times 0.28 \times 0.42 \text{ mm}^3$, monoclinic, space group P_{21}/c , a = 14.0441(3) Å, b = 21.9700(5) Å, c = 12.5956(3) Å, $\beta = 115.2980(10)^\circ$, V = 3513.65(14) Å³, Z = 4, $D_{calc} = 1.537 \text{ mg m}^{-3}$, F(000) = 1660, $\lambda = 0.71073$ Å, T = 273 K, $\mu = 0.584 \text{ mm}^{-1}$, 40809 reflections collected, 8523 unique ($R_{int} = 0.032$). Final goodness-of-fit = 1.07, $R_1 = 0.0386$, $wR_2 = 0.1044$, R indices based on 8523 reflections with $I > 2\sigma(I)$ (refinement on F_2), 487 parameters.

3. Results and discussion

3.1. $[Ru^{II}(trpy)(L-R)]$ complexes

3.1.1. Synthesis and crystal structure

As delineated in the introduction, the primary objective of the present study has been to synthesize a group of mixed-ligand complexes of ruthenium containing both 2,2',2''-terpyridine and the N,N'-bis(aryl)pyridine-2,6dicarboxamide (3). For this purpose five N, N'-bis(aryl)pyridine-2.6-dicarboxamides with different substituents $(R = OCH_3, CH_3, H, Cl and NO_2)$ at the *para* position of the two pendant phenyl rings have been used, in order to study their influence, if any, on the redox properties of the resulting ruthenium complexes. These amide ligands (3) are abbreviated in general as H_2L-R , where H_2 stands for the two dissociable protons and R for the substituents. Reactions of the selected amides (3) with $[Ru(trpy)Cl_3]$ proceed smoothly in refluxing ethanol in the presence of triethvlamine to afford the targeted mixed-ligand complexes of type $[Ru^{II}(trpy)(L-R)]$ in decent yields. It may be noted here that during the synthetic reaction ruthenium has undergone a one-electron reduction, and triethylamine might have served as the reducing agent. Preliminary (microanalytical, spectroscopic, magnetic, etc.) characterizations on these complexes (vide infra) are found to be in well accordance with their compositions. In order to find out coordination mode of the N,N'-bis(aryl)pyridine-2,6dicarboxamides in these complexes, structure of a representative member of this family, viz. [Ru^{II}(trpy)(L-Cl)], has been determined by X-ray crystallography. The structure is shown in Fig. 1 and selected bond parameters are listed in Table 1. The structure shows that the N,N'-bis(4'-chlorophenyl)pyridine-2,6-dicarboxamide is coordinated to ruthenium, via dissociation of two acidic protons, as a dianionic tridentate N,N,N-donor (4). A terpyridine is also coordinated to the metal center in the usual fashion. Ruthenium is therefore sitting in a N₆ coordination environment, which is distorted octahedral in nature, as reflected in all the bond parameters around ruthenium. The observed bond distances in the Ru(L-Cl) fragment are all quite normal [2j,n], and so are those in the Ru(trpy) fragment [11a]. In the crystal lattice of the [Ru^{II}(trpy)-(L-Cl)] complex, there are three molecules of water per two complex molecules. In order to find out the link between these water molecules and the complex molecule, packing pattern in the lattice has been scrutinized (Fig. 2), which shows that besides links with the water molecules, the complex molecules also have direct links between themselves. A closer inspection into the network reveals that three types of hydrogen-bonding interactions, viz. C–H–O, O–H–O, C–H–Cl and C–H– π , are active in the lattice. The amide oxygen is linked with one trpy C-H as well as O-H of water. A C-H fragment from the pyridine ring of the amide is hydrogen bonded to water molecule. The central C-H fragment from the pyridine ring of the amide is linked to the π -cloud over a terminal pyridine ring of trpy in a η^2 -fashion. C–H fragments of the terpyridine and the pendent phenyl ring of the amide are found to be hydrogen bonded to the chlorine atom in the amide. One C–H fragment of the terpyridine is also hydrogen bonded to the π -cloud in the pendent phenyl ring of the amide. These hydrogen-bonding interactions appear to be responsible for holding the complex molecules together in the crystal lattice. It may be relevant to note here that such interactions are of significant importance in molecular recognition processes as well as in crystal engineering [15]. As all the [Ru^{II}(trpy)(L-R)] complexes have been synthesized similarly and they show similar properties (vide infra), the other four [Ru^{II}(trpy)(L-R)] (R \neq Cl) complexes are assumed to have similar structure as the [Ru^{II}(trpy)-(L-Cl)] complex.

3.1.2. Spectral properties

¹H NMR spectra of these complexes show many signals, most of which are overlapping, and hence assignment of each signal to a specific proton has not been possible. However, two distinct doublets observed near 5.3 and 6.3 ppm in the complexes with $R \neq H$, each integrating to four protons, are assignable to the hydrogens in the two pendent phenyl rings in the coordinated amide ligand. Signals for the methoxy and methyl groups in the [Ru^{II}(trpy)-(L-OCH₃)] and [Ru^{II}(trpy)(L-CH₃)] complexes are observed respectively at 3.57 and 2.10 ppm. The infrared and ¹H NMR spectral data of the [Ru^{II}(trpy)(L-R)] complexes are therefore consistent with their compositions.

Infrared spectra of each $[Ru^{II}(trpy)(L-R)]$ complex shows many bands of different intensities in the 400- 4000 cm^{-1} region. Assignment of each individual band to a specific vibration has not been attempted. However, comparison with spectrum of the respective uncoordinated ligand shows that the N-H stretch, observed near 3140 cm^{-1} in the uncoordinated ligands, is absent in the complexes. The amide C=O stretch, observed near 1680 cm^{-1} in the uncoordinated ligands, is also found to be shifted to around 1595 cm^{-1} in the complexes. Comparison with the spectrum of $[Ru(trpy)Cl_3]$ shows the presence of some common bands (near 648, 670, 729, 781, 1240 and 1444 cm^{-1}) as well as some new bands (near 808, 1008, 1083, 1379 and 1595 cm⁻¹) in the spectra of the [Ru^{II}(trpy)-(L-R)] complexes indicating presence coordinated terpyridine and amide ligands [8a,2n,j]. The [Ru^{II}(trpy)-(L-R)] complexes are found to be diamagnetic, which is in accordance with the +2 oxidation state of ruthenium (low-spin d^6 , S = 0) in these complexes.

The $[Ru^{II}(trpy)(L-R)]$ complexes are soluble in acetone, acetonitrile, dichloromethane, chloroform, etc., producing deep brown solutions. Electronic spectra of the complexes have been recorded in dichloromethane solution. All the complexes show several intense absorptions in the visible and ultraviolet regions (Table 2). The absorptions in the ultraviolet region are attributable to transitions within the ligand orbitals and those in the visible region are probably due to charge-transfer transitions. To have a better





Fig. 1. (a) Structure of the [Ru^{II}(trpy)(L-Cl)] complex and (b) view of the Ru(L-Cl) fragment.

insight into the nature of the absorptions in the visible region, qualitative EHMO calculations have been performed [16] on the structurally characterized [Ru^{II}(trpy)-(L-Cl)] complex. Partial MO diagrams are shown in Fig. 3 and composition of selected molecular orbitals is presented in Table S1 (Supplementary material). The highest occupied molecular orbital (HOMO) and the next two filled orbitals (HOMO – 1 and HOMO – 2) have major (~60%) contribution from the ruthenium d_{xy} , d_{yz} and d_{zx} orbitals. These three occupied orbitals may therefore be regarded as the ruthenium t_2 orbitals. The lowest unoccupied molecular orbital (LUMO) has 70% contribution from the coordinated terpyridine and is dispersed over the entire ligand. Among the next few vacant orbitals (LUMO + 1, LUMO + 2, etc.), LUMO + 1 is primarily centered on the amide ligand and concentrated heavily on pyridine nitrogen, while LUMO + 2 is delocalized over both the amide ligand and terpyridine. The lowest energy absorption, displayed by the [Ru^{II}(trpy)(L-R)] complexes near 540 nm, may therefore be assigned to the chargetransfer transition taking place from the highest filled ruthenium t₂ orbital (HOMO) to the vacant orbital delocalized over the terpyridine (LUMO). The other intense absorptions in the visible region may be assigned to

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Table 1 Selected bond distances (Å) and bond angels (°) for $[Ru^{II}(trpy)(L-CI)]$ and $[Ru^{III}(trpy)(L-CH_3)]^+$

	-/-		
[Ru ^{II} (trpy)(L-Cl)]]		
Bond distance (Å)		
Ru1–N1	2.098(3)	Ru1–N4	2.047(4)
Ru1–N2	1.983(4)	Ru1–N5	1.946(4)
Ru1–N3	2.098(3)	Ru1–N6	2.053(4)
C7–O1	1.249(6)		
C13–O2	1.254(6)		
Bond angles (°)			
N1-Ru1-N2	77.22(14)	N4–Ru1–N5	78.64(16)
N2-Ru1-N3	77.81(14)	N5–Ru1–N6	79.43(15)
N1–Ru1–N3	155.01(15)	N4–Ru1–N6	158.01(16)
[Ru ^{III} (trpy)(L-CH	$[H_3)]^+$		
Bond distance (Å)		
Ru1–N1	1.981(2)	Ru1–N4	2.071(2)
Ru1–N2	2.023(2)	Ru1–N5	1.982(2)
Ru1–N3	2.042(2)	Ru1–N6	2.080(3)
C6-O1	1.224(3)		
C14–O2	1.235(3)		
Bond angles (°)			
N1–Ru1–N2	80.24(8)	N4–Ru1–N5	79.51(9)
N1–Ru1–N3	78.81(8)	N5–Ru1–N6	79.19(9)
N2–Ru1–N3	159.05(8)	N4–Ru1–N6	158.67(9)

charge-transfer transitions from the filled ruthenium t_2 orbitals to the higher energy vacant orbitals.

3.1.3. Electrochemical properties

Electrochemical properties of the [Ru^{II}(trpy)(L-R)] complexes have been studied by cyclic voltammetry in 1:9 dichloromethane-acetonitrile solution (0.1 M TBAP).² Each complex shows two oxidative responses at potentials positive of the SCE reference electrode and a reductive response at negative potentials (Table 2). A representative voltammogram is shown in Fig. 4. The first oxidation, observed within 0.16-0.33 V, is reversible in nature, characterized by a peak-to-peak separation (ΔE_p) of ~70 mV, which remains unchanged upon changing the scan rate, and the anodic peak-current (i_{pa}) is almost equal to the cathodic peak-current (i_{pc}) as expected for a reversible electron-transfer process. In view of composition of the HOMO, this oxidation is assigned to Ru(II)-Ru(III) oxidation. It is interesting to note here that in the tris-complexes of N-(aryl)picolinamides (1) [2i], where ruthenium was nested in a $N_3^p N_3^a$ coordination sphere, the Ru(III)-Ru(II) couple appeared on the negative side of SCE (e.g. -0.38 V, for the R = H complex), whereas in these $[Ru^{II}(trpy)(L-R)]$ complexes, in which the coordination environment around the metal center has changed to $N_{4}^{p}N_{2}^{a}$, the same couple appears on the positive side of SCE (e.g. 0.20 V, for the R = H complex). Hence replacement of an amide nitrogen by a pyridine nitrogen in the

coordination sphere of ruthenium has truly stabilized the bivalent state of the metal to a significant extent, which has been manifested in the positive shift of the Ru(II)-Ru(III) potential by about 580 mV.

The second oxidation, observed within 0.94–1.33 V, is quasi-reversible in nature, and is tentatively assigned to Ru(III)-Ru(IV) oxidation. Based on composition of the LUMO, the irreversible reduction observed around -1.1 V is assigned to reduction of the coordinated terpyridine ligand. Potential of Ru(II)-Ru(III) oxidation has been observed to be sensitive to nature of the substituent R in the N, N'-bis(aryl)pyridine-2,6-dicarboxamide. The potential $(E_{1/2})$ increases with increasing electron-withdrawing character of the substituent R. The plot of $E_{1/2}$ versus 2σ $[\sigma = \text{Hammett} \text{ constant} \text{ of } R [17]; \text{ OCH}_3 = -0.27,$ $CH_3 = -0.17$, H = 0.00, Cl = 0.23, $NO_2 = 0.78$] is linear for these complexes (Fig. S1, Supplementary material) with a slope (ρ) of 0.08 (ρ = reaction constant of this oxidation [18]). This linear correlation of the Ru(II)–Ru(III) oxidation potentials with the electronic nature of the substituents having a reasonable slope clearly shows that the substituent on the phenyl ring of the amide, which is six bonds away from the metal center, can still influence the metal-centered redox potential in a predictable manner. Similarly potential $(E_{1/2})$ of the Ru(III)-Ru(IV) oxidation also shows linear correlation with the electron-withdrawing nature (2σ) of substituent R with a slope (ρ) of 0.18 V (Fig. S1, Supplementary materials). The higher slope of the second plot indicates that the second oxidation probably involves an orbital having significant amide character. Potentials of the irreversible reductive responses do not show any systematic variation with the nature of the substituent.

3.2. $[Ru^{III}(trpy)(L-R)]^+$ complexes

3.2.1. Synthesis and crystal structure

Reversibility of the Ru(II)-Ru(III) oxidation in the $[Ru^{II}(trpy)(L-R)]$ complexes indicates that the one-electron oxidized species, viz. [Ru^{III}(trpy)(L-R)]⁺, might be stable on a time scale much longer than the cyclic voltammetric time scale. To investigate this, each [Ru^{II}(trpy)(L-R)] complex has been coulometrically oxidized at an appropriate potential³ in acetonitrile solution (0.1 M TBAP). The oxidation has been smooth and quantitative, associated with a color change from brown to green, and the oxidized product has been isolated as [Ru^{III}(trpy)(L-R)]ClO₄ in the solid state. Preliminary characterization data on these complexes are found to be consistent with their compositions. To examine the difference in structural features, if any, associated with one-electron oxidation of the metal center, structure of a selected member of this new family, viz. [Ru^{III}(trpy)(L-CH₃)]ClO₄, has also been determined by X-ray crystallography. The structure (Fig. 5) shows that apart from small differences in the Ru–N lengths (Table 1),

² A little dichloromethane was necessary to take the complex into solution. Addition of large excess of acetonitrile was necessary to record the redox responses in proper shape.

³ Coulometric oxidation has been carried out at a potential 200 mV higher than the E_{pa} .



Fig. 2. Packing diagram of the [Ru^{II}(trpy)(L-Cl)] crystal.

Table 2 Electronic spectral and cyclic voltammetric data of [Ru^{II}(trpy)(L-R)]

Compound	Electronic spectral data ^a λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹)	Cyclic voltammetric datab
[Ru ^{II} (trpy)(L-OCH ₃)]	236 (20400), 277 (11000), [°] 314 (9500), 397 (5500), 435 (5000), [°] 541 (3400)	0.16^{d} (70), e 0.94 d (69), e -1.10 f
[Ru ^{II} (trpy)(L-CH ₃)]	236 (19400), 278 (10600), ^c 315 (9400), 396 (4500), 432 (4300), ^c 540 (2700)	0.18^{d} (74), ^e 0.99^{d} (90), ^e -1.15^{f}
[Ru ^{II} (trpy)(L-H)]	235 (19900), 278 (11500), ^c 315 (9900), 395 (5100), 430 (5300), ^c 538 (3500)	0.20^{d} (63), e 1.05 d (96), e -1.11 f
[Ru ^{II} (trpy)(L-Cl)]	233 (19400), 278 (9900), ^c 314 (7400), 394 (3200), 432 (2300), ^c 540 (2200)	0.22^{d} (76), e 1.15^{d} (93), e -1.15^{f}
[Ru ^{II} (trpy)(L-NO ₂)]	230 (19 200), 277 (14 500), ^c 316 (17 800), 326 (17 200), 431 (7100), ^c 541 (3500)	0.33^{d} (66), ^e 1.33^{d} (62), ^e -1.15^{f}

^a In dichloromethane solution.

^b Solvent, 1:9 dichloromethane-acetonitrile; supporting electrolyte, TBAP; scan rate 50 mV s⁻¹.

^d $E_{1/2} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively.

^e $\Delta E_{\rm p} = (E_{\rm pa} - E_{\rm pc}).$ ^f $E_{\rm pc}$ value.

the other features are qualitatively very similar to those of the [Ru^{II}(trpy)(L-R)] complex. The Ru–N distances in the Ru(L-R) fragment are shorter in the Ru(III) complex, probably due to enhanced electrostatic attraction of the dianionic amide ligand with the trivalent metal. The Ru-

N lengths in the Ru(trpy) fragment are, however, slightly longer in the Ru(III) complexes, which is attributable to the lack of back-donation from the oxidized metal center that probably wins over the electrostatic effect. The packing pattern in the lattice (Fig. 6) shows that

^c Shoulder.



Fig. 3. Partial MO diagram of the [Ru^{II}(trpy)(L-Cl)] complex.



Fig. 4. Cyclic voltammogram of the [Ru^{II} (trpy)(L-Cl)] complex in 1:9 dichloromethane–acetonitrile solution (0.1 M TBAP) at a scan rate of 50 mV s⁻¹.

hydrogen-bonding interactions of three types, *viz.* C–H–O, O–H–O and C–H– π , are active. The perchlorate oxygens are hydrogen bonded to water and C–H fragment of the trpy ligand. The amide oxygen is also hydrogen bonded to water and C–H fragment of the trpy ligand. One C–H



Fig. 5. Structure of the [Ru^{III}(trpy)(L-CH₃)]ClO₄ complex.

fragment of the trpy ligand is hydrogen bonded to the π cloud over the tolyl ring of the amide ligand. Due to such hydrogen-bonded arrangements of the complex molecules, several nearly rectangular cavities have been created throughout the lattice. Based on the similarity in their syn-



Fig. 6. Packing diagram of the [Ru^{III}(trpy)(L-CH₃)]ClO₄ crystal.

thesis and properties (*vide infra*), the other four $[Ru^{III}-(trpy)(L-R)]ClO_4$ ($R \neq CH_3$) complexes are assumed to have similar structures as $[Ru^{III}(trpy)(L-CH_3)]ClO_4$.

3.2.2. Spectral properties

Apart from the appearance of two additional intense bands around 1100 and 620 cm⁻¹ due to presence of the perchlorate anion and small shifts in the position of the other bands, infrared spectra of each [Ru^{III}(trpy)-(L-R)]ClO₄ complex is qualitatively similar to that of the respective [Ru^{II}(trpy)(L-R)] complex. Magnetic susceptibility measurements show that the [Ru^{III}(trpy)(L-R)]ClO₄ complexes are one-electron paramagnetic ($\mu_{eff} = 1.83$ – 1.90 μ_B), which corresponds to the +3 oxidation state of ruthenium (low-spin d⁵, S = 1/2) in these complexes. ESR spectra of the [Ru^{III}(trpy)(L-R)]ClO₄ complexes have been recorded in 1:1 dichloromethane–toluene solution at 77 K. Each complex shows an axial ESR spectrum with two distinct signals (g_{\perp} and g_{\parallel} ; in the order of decreasing magni-



Fig. 7. ESR spectrum of the $[Ru^{III}(trpy)(L-Cl)]ClO_4$ complex in 1:1 dichloromethane–toluene solution at 77 K.

tude). A selected spectrum is shown in Fig. 7 and the spectral data for all complexes are given in Table 3. The anisotropy of the spectra reflects the asymmetry of the electronic environment around ruthenium in these [Ru^{III}-(trpy)(L-R)]ClO₄ complexes. When an octahedral geometry suffers from an axial distortion (Δ), the t_2 level splits into a and e components (Fig. 7). Spin-orbit coupling causes minor additional changes in energy of all the three levels. Thus two closely spaced electronic transitions (transition energies ΔE_1 and ΔE_2 ; $\Delta E_1 < \Delta E_2$) are, in principle, probable within these three levels. All these energy parameters have been computed (Table 3) using the observed gvalues, the g-tensor theory of low-spin d⁵ complexes [19], and a reported method [20]. The axial distortion is found to be around 6000 cm^{-1.4} The calculated values of ΔE_1 and ΔE_2 are also close to ~6000 cm⁻¹ (~1670 nm), which indicate that two ligand-field transitions, which are close in energy, should take place in the near-infrared region, and indeed a broad band of weak intensity has been observed in the spectra of all the complexes near the predicted energy (vide infra). Closeness of the two expected transitions appears to have vitiated their resolution. The ESR spectral data thus show that these [Ru^{III}(trpy)-(L-R)]ClO₄ complexes are significantly distorted from the ideal octahedral geometry, as was also indicated by the structure determination.

Electronic spectra of the green $[Ru^{III}(trpy)(L-R)]ClO_4$ complexes, recorded in acetonitrile solutions, show absorptions in the near-infrared, visible and ultraviolet regions (Table 4). The absorptions in the ultraviolet region are again believed to be due to transitions within the ligand orbitals. To understand the origin of the absorptions in the visible region, qualitative EHMO calculations have been performed on the structurally characterized $[Ru^{III}-(trpy)(L-CH_3)]ClO_4$ complex. Composition of selected

⁴ The spin–orbit coupling constant (λ) is taken to be 1000 cm⁻¹ for complexed ruthenium(III) [20].

Table 3	
ESR g-values ^a and derived parameters ^b	of the [Ru ^{III} (trpy)(L-R)]ClO ₄ complexes

Compounds	g_\perp	g_{\parallel}	$arDelta, \lambda$	$\Delta E_1, \lambda$	$\Delta E_2, \lambda$
[Ru ^{III} (trpy)(L-OCH ₃)]ClO ₄	2.209	1.921	6.219	5.891	6.805
[Ru ^{III} (trpy)(L-CH ₃)]ClO ₄	2.217	1.916	6.050	5.727	6.638
[Ru ^{III} (trpy)(L-H)]ClO ₄	2.222	1.914	5.988	5.667	6.577
[Ru ^{III} (trpy)(L-Cl)]ClO ₄	2.230	1.909	5.836	5.520	6.428
$[Ru^{III}(trpy)(L\text{-}NO_2)]ClO_4$	2.236	1.903	5.659	5.349	6.254

^a In 1:1 dichloromethane–toluene solution at 77 K. ^b Spin–orbit coupling constant (λ) for complexed Ru(III) is ~1000 cm⁻¹.

Table 4 Electronic spectral data of [Ru^{III}(trpy)(L-R)]ClO₄

Compound	Electronic spectral data ^a λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹)
[Ru ^{III} (trpy)(L-OCH ₃)]ClO ₄	232 (11200), 273 (5900), ^b 287 (5200), ^b 313 (5400), 338 (3500), ^b 424 (1400), 655 (850), 1553 (112)
[Ru ^{III} (trpy)(L-CH ₃)]ClO ₄	231 (10100), 273 (4900), ^b 282 (4700), ^b 314 (4800), 332 (4000), ^b 420 (1300), 652 (1100), 1565 (136)
[Ru ^{III} (trpy)(L-H)]ClO ₄	226 (10000), 276 (6300), ^b 283 (6400), ^b 311 (5500), 338 (3400), ^b 421 (1900), 652 (1500), 1569 (130)
[Ru ^{III} (trpy)(L-Cl)]ClO ₄	231 (10900), 265 (5800), ^b 283 (5600), ^b 314 (5800), 337 (4300), ^b 425 (2000), 651 (1700), 1576 (143)
[Ru ^{III} (trpy)(L-NO ₂)]ClO ₄	226 (11600), 271 (7800), ^b 283 (8700), ^b 319 (11200), 340 (8500), ^b 411 (2300), 646 (1100), 1581 (146)

^a In dichloromethane.

^b Shoulder.

molecular orbitals is given in Table S2 (Supplementary material) and partial MO diagram is shown in Fig. 8. In this complex, the HOMO (singly occupied), HOMO - 1and HOMO - 2 are found to have large contributions (nearly 60%) from ruthenium d_{xy} , d_{yz} and d_{xz} orbitals, while the HOMO - 3 has predominant terpyridine character. The absorption near 650 nm may therefore be assigned to a ligand-to-metal charge-transfer transition from HOMO - 3 to HOMO (singly occupied). The weak absorption in the near-infrared region (near 1600 nm) has already been assigned to ligand-field transitions (vide supra).



Fig. 8. Partial MO diagram of the [Ru^{II}(trpy)(L-CH₃)]ClO₄ complex.

3.2.3. Electrochemical properties

Cyclic voltammetric properties of the $[Ru^{III}(trpy)-(L-R)]^+$ complexes are identical to those of their Ru(II) precursors, only the Ru(II)–Ru(III) couple appears as a reductive response. The green $[Ru^{III}(trpy)(L-R)]^+$ complexes could be quantitatively converted back, upon coulometric reduction at 0.0 V, to the respective brown $[Ru^{II}(trpy)(L-R)]$ complexes, identified by their characteristic electronic spectra. In terms of their Ru(II)–Ru(II) reduction potentials, these green $[Ru^{III}(trpy)(L-R)]^+$ complexes are very mild oxidants.

4. Conclusions

The present study shows that the N,N'-bis(aryl)pyridine-2,6-dicarboxamides (3) can efficiently bind to ruthenium(II) in the dianionic N,N,N-fashion (4) and in combination with 2,2',2"-terpyridine can stabilize the metal in its +2 state. This study further demonstrates that binding by the amides (3) in the N,N,N-fashion (4) can also sufficiently stabilize the +3 oxidation state of ruthenium. The coordination environment provided by the N,N'-bis(aryl)pyridine-2,6-dicarboxamides and 2,2',2"-terpyridine appears to be unique in supporting both the +2 and +3 states of ruthenium.

Acknowledgements

Financial assistance received from the University Grants Commission, New Delhi, [Grant No. F31-124/2005(SR)] is gratefully acknowledged. The authors thank Dr. Samar K. Das, School of Chemistry, University of Hyderabad, India, for his help with recording the ESR spectra. SN thanks the Council of Scientific and Industrial Research, New Delhi, for his fellowship [Grant No. 9/96(401)2003-EMR-I].

Appendix A. Supplementary material

CCDC 651197 and 651198 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.08.042.

References

- [1] (a) M. Turki, C. Daniel, Coord. Chem. Rev. 216–217 (2001) 31;
 (b) V. Balzani, A. Juris, Coord. Chem. Rev. 211 (2001) 97;
 - (c) B.-Z. Shan, Q. Zhao, N. Goswami, D.M. Eichhom, D.P. Rillema, Coord. Chem. Rev. 211 (2001) 117;
 - (d) N.A.P. Kane-Maguire, J.F. Wheeler, Coord. Chem. Rev. 211 (2001) 145;
 - (e) L.-N. Ji, X.-H. Zou, J.-G. Liu, Coord. Chem. Rev. 216–217 (2001) 513;

- (f) G. Simonneaux, P. Le Maux, Coord. Chem. Rev. 228 (2002) 43;
- (g) H. Yersin, C. Kratzer, Coord. Chem. Rev. 229 (2002) 75;
- (h) J.F. Endicott, H.B. Schlegel, M.J. Uddin, D.S. Seniveratne, Coord. Chem. Rev. 229 (2002) 95;
- (i) S.I. Gorelsky, A.B.P. Lever, M. Ebadi, Coord. Chem. Rev. 230 (2002) 97;
- (j) F. Hartl, M.P. Aarnts, H.A. Nieuwenhuis, J. van Slageren, Coord. Chem. Rev. 230 (2002) 106;
- (k) C.-M. Che, J.-S. Huang, Coord. Chem. Rev. 231 (2002) 151;
- (l) M.J. Clarke, Coord. Chem. Rev. 232 (2002) 69;
- (m) E. Tfouni, M. Krieger, B.R. McGarvey, D.W. Franco, Coord. Chem. Rev. 236 (2003) 57;
- (n) B. Serli, E. Zangrando, T. Gianferrara, L. Yellowless, E. Alessio, Coord. Chem. Rev. 245 (2003) 73;
- (o) I. Ando, Coord. Chem. Rev. 248 (2004) 185;
- (p) M.J. Clarke, Coord. Chem. Rev. 236 (2003) 209;
- (q) M.A.S. Aquino, Coord. Chem. Rev. 248 (2004) 1025;
- (r) R.F. Winter, S. Záli, Coord. Chem. Rev. 248 (2004) 1565;
- (s) S. Rigaut, D. Touchard, P.H. Dixneuf, Coord. Chem. Rev. 248 (2004) 1585;
- (t) M.K. Nazeeruddin, S.M. Zakeeruddin, J.-J. Lagref, P. Liska, P. Comte, C. Barolo, G. Viscardi, K. Schenk, M. Graetzel, Coord. Chem. Rev. 248 (2004) 1317;
- (u) L. Spiccia, G.B. Deacon, C.M. Kepert, Coord. Chem. Rev. 248 (2004) 1329;
- (v) Y. Saito, T. Azechi, T. Kitamura, Y. Hasegawa, Y. Wada, S. Yanagida, Coord. Chem. Rev. 248 (2004) 1469;
- (w) Md.K. Nazeeruddin, C. Klein, P. Liska, M. Grätzel, Coord. Chem. Rev. 249 (2005) 1460.
- [2] (a) F. Basuli, S.M. Peng, S. Bhattacharya, Inorg. Chem. 36 (1997) 5645;
 - (b) F. Basuli, M. Ruf, C.G. Pierpont, S. Bhattacharya, Inorg. Chem. 37 (1998) 6113;
 - (c) A.K. Das, A. Rueda, L.R. Falvello, S.M. Peng, S. Bhattacharya, Inorg. Chem. 38 (1999) 4365;
 - (d) A.K. Das, S.M. Peng, S. Bhattacharya, J. Chem. Soc., Dalton Trans. (2000) 181;
 - (e) F. Basuli, S.M. Peng, S. Bhattacharya, Inorg. Chem. 39 (2000) 1120;
 - (f) F. Basuli, S.M. Peng, S. Bhattacharya, Inorg. Chem. 40 (2001) 1126;
 - (g) I. Pal, F. Basuli, T.C.W. Mak, S. Bhattacharya, Angew. Chem., Int. Ed. 40 (2001) 2923;
 - (h) K. Majumder, R.J. Butcher, S. Bhattacharya, Inorg. Chem. 41 (2002) 4605;
 - (i) R. Acharyya, S.M. Peng, G.H. Lee, S. Bhattacharya, Inorg. Chem. 42 (2003) 7378;
 - (j) A. Das, S.M. Peng, G.H. Lee, S. Bhattacharya, New. J. Chem. 28 (2004) 712;
 - (k) S. Nag, P. Gupta, R.J. Butcher, S. Bhattacharya, Inorg. Chem. 43 (2004) 4814;
 - (l) P.K. Sinha, L.R. Falvello, S. Bhattacharya, Indian J. Chem. 43A (2004) 1846;
 - (m) P. Gupta, S. Dutta, F. Basuli, S.M. Peng, G.-H. Lee, S. Bhattacharya, Inorg. Chem. 45 (2006) 460;
 - (n) S. Halder, R. Acharyya, S.M. Peng, G.H. Lee, M.G.B. Drew, S. Bhattacharya, Inorg. Chem. 45 (2006) 9654;
 - (o) S. Nag, R.J. Butcher, S. Bhattacharya, Eur. J. Inorg. Chem. (2007) 1251.
- [3] (a) P. Ford, D.E.P. Rudd, R.G. Gaunder, H. Taube, J. Am. Chem. Soc. 90 (1968) 1187;
 - (b) A.W. Zanella, P.C. Ford, Inorg. Chem. 14 (1975) 42;
 - (c) T. Matsubara, P.C. Ford, Inorg. Chem. 15 (1976) 1107;
 - (d) Y. Ilan, H. Taube, Inorg. Chem. 22 (1983) 1655;
 - (e) Y. Ilan, M. Kapon, Inorg. Chem. 25 (1986) 2350;
 - (f) H.Y. Huang, W.J. Chen, C.C. Yang, A. Yeh, Inorg. Chem. 30 (1991) 1862;

(g) M.H. Chou, C. Creutz, N. Sutin, Inorg. Chem. 31 (1992) 2318;

(h) M.H. Chou, B.S. Brunschwig, C. Creutz, N. Sutin, A. Yeh, R.C. Chang, C.-T. Lin, Inorg. Chem. 31 (1992) 5347;

(i) M.H. Chou, D.J. Szalda, C. Creutz, N. Sutin, Inorg. Chem. 33 (1994) 1674;

(j) S.M. Redmore, C.D.F. Rickard, S.J. Webb, L.J. Wright, Inorg. Chem. 36 (1997) 4743.

- [4] B. Albert, D. Bray, J. Lewis, M. Raff, K. Roberts, J.D. Watson, Molecular Biology of the Cell, third ed., Garland Publishing, New York, 1994, Chapter 3.
- [5] (a) H. Sigel, C.F. Naumann, B. Prijs, D.B. McCormick, M.C. Falk, Inorg. Chem. 16 (1977) 790;
 - (b) H. Sigel, Inorg. Chem. 14 (1975) 1535;

(c) M.F. El-Shazly, A. El-Dissowky, T. Salem, M. Osman, Inorg. Chim. Acta 40 (1980) 1;

- (d) D.W. Margerum, Pure Appl. Chem. 23 (1983) 23;
- (e) A.S. Borovik, T.M. Dewey, K.N. Raymond, Inorg. Chem. 32 (1993) 413;
- (f) T.J. Collins, Acc. Chem. Res. 27 (1994) 279;
- (g) M.J. Bartos, S.W. Gordon-Wylie, B.G. Fox, L.J. Wright, S.T.

Weintraub, K.E. Kauffmann, E. Münck, K.L. Koskta, E.S. Uffelman, C.E.F. Rickard, K.R. Noon, T.J. Collins, Coord. Chem. Rev. 174 (1998) 361:

- (h) A. White, X. Ding, J.C. vanderSpek, J.R. Murphy, D. Ringe, Nature 394 (1998) 502;
- (i) E. Pohl, R.K. Holmes, W.G.J. Hol, J. Mol. Biol. 292 (1997) 653;
- (j) B.M. Trost, C.B. Lee, J. Am. Chem. Soc. 123 (2001) 3671;

(k) M.D. Feese, B.P. Ingason, J. Goranson-Siekierke, R.K. Holmes, W.G.J. Hol, J. Biol. Chem. 276 (2001) 5959;

(1) T.J. Collins, Acc. Chem. Res. 35 (2002) 782;

- (m) B.M. Trost, K. Dogra, I. Hachiya, T. Emura, D.L. Hughes, S. Krska, R.A. Reamer, M. Palucki, N. Yasuda, P.J. Reider, Angew. Chem., Int. Ed. 41 (2002) 1929;
- (n) B.M. Trost, M. Crawley, J. Am. Chem. Soc. 124 (2002) 9328.
- [6] T. Kojima, K. Hayashi, Y. Matsuda, Inorg. Chem. 43 (2004) 6793.
- [7] (a) A.K. Singh, V. Balamurugan, R. Mukherjee, Inorg. Chem. 42 (2003) 6497;
- (b) D.B. Dellamico, F. Calderazzo, F. Dicolo, G. Gugliemetti, L. Labella, F. Marchetti, Inorg. Chim. Acta 359 (2006) 127.
- [8] Kalagouda B. Gudasi, Transition Met. Chem. 30 (2005) 569.
- [9] (a) H. Sigel, R.B. Martin, Chem. Rev. 82 (1982) 385;
 (b) H.E. Bryndza, W. Tam, Chem. Rev. 88 (1988) 1163;
 (c) K. Severin, R. Bergs, W. Beck, Angew. Chem., Int. Ed. 37 (1998) 1634;
 (d) J.R. Fulton, A.W. Holland, D.J. Fox, R.G. Bergman, Acc. Chem.

(d) J.K. Futton, A.W. Honand, D.J. Fox, K.G. Bergman, Acc. Chem. Res. 35 (2002) 44.

- [10] (a) S. Dutta, S. Pal, P.K. Bhattacharya, Polyhedron 18 (1999) 2157;
 (b) S. Dutta, P.K. Bhattacharya, E. Horn, E.R.T. Tiekink, Polyhedron 20 (2001) 1815;
 - (c) S. Dutta, P.K. Bhattacharya, E.R.T. Tiekink, Polyhedron 20 (2001) 2027.

- [11] (a) N.C. Pramanik, K. Pramanik, P. Ghosh, S. Bhattacharya, Polyhedron 17 (1998) 1525;
 (b) P.K. Sinha, L.R. Falvello, S. Bhattacharya, Ind. J. Chem. 43 (2004) 1846;
 (c) E. Lebon, I.M. Dixon, L. Vendier, A. Igau, P. Sutra, Inorg. Chim. Acta 360 (2007) 1235;
 (d) M. Fabre, J. Jaud, M. Hliwa, J.P. Launay, J. Bonvoisin, Inorg. Chem. 45 (2006) 9332;
 (e) H.S. Chow, E.C. Constable, C.E. Housecroft, M. Neuburger, S.
- Schaffner, Polyhedron 25 (2006) 1831. [12] B.P. Sullivan, J.M. Calvert, T.J. Meyer, Inorg. Chem. 19 (1980) 1404.
- [12] D.T. Sauyer, J.L. Roberts Jr., Experimental Electrochemistry for Chemists, vol. 167, Wiley, New York, 1974, p. 167;

(b) M. Walter, L. Ramaley, Anal. Chem. 45 (1973) 165.

- [14] G.M. Sheldrick, SHELXS-97 and SHELXL-97, Fortran Programs for Crystal Structure Solution and Refinement, University of Gottingen, Gottingen, Germany, 1997.
- [15] (a) S.K. Burley, G.A. Petsko, Science 229 (1985) 23;
 - (b) H.C. Weiss, D. Blaser, R. Boese, B.M. Doughan, M.M. Haley, Chem. Commun. (1997) 1703;

(c) N.N.L. Madhavi, A.K. Katz, H.L. Carrell, A. Nangia, G.R. Desiraju, Chem. Commun. (1997) 1953;

- (d) S.K. Burley, G.A. Petsko, Adv. Protein Chem. 39 (1988) 125;
- (e) M. Nishio, M. Hirota, Y. Umezawa, The CH– π Interactions (Evidence, Nature and Consequences), Wiley-VCH, New York, 1998; (f) Y. Umezawa, S. Tsuboyama, K. Honda, J. Uzawa, M. Nishio, Bull. Chem. Soc., Jpn. 71 (1998) 1207;

(g) G.R. Desiraju, T. Steiner, The Weak Hydrogen Bond (IUCr Monograph on Crystallography 9), Oxford Science Pub., 1999;

- (h) M.J. Hannon, C.L. Painting, N.W. Alcock, Chem. Commun. (1999) 2023;
- (i) B.J. Mcnelis, L.C. Nathan, C.J. Clark, J. Chem. Soc., Dalton Trans. (1999) 1831;
- (j) K. Biradha, C. Seward, M.J. Zaworotko, Angew. Chem., Int. Ed. 38 (1999) 492;
- (k) M.J. Calhorda, Chem. Commun. (2000) 801;
- (1) C. Janiak, S. Temizdemir, S. Dechert, Inorg. Chem. Commun. 3 (2000) 271;

(m) C. Janiak, S. Temizdemir, S. Dechert, W. Deck, F. Girgsdies, J. Heinze, M.J. Kolm, T.G. Scarmann, O.M. Zipffel, Eur. J. Inorg. Chem. (2000) 1229.

- [16] (a) C. Mealli, D.M. Proserpio, CACAO Version 4.0, Italy, 1994;
 (b) C. Mealli, D.M. Proserpio, J. Chem. Educ. 67 (1990) 399.
- [17] L.P. Hammett, Physical Organic Chemistry, second ed., McGraw Hill, New York, 1970.
- [18] R.N. Mukherjee, O.A. Rajan, A. Chakravorty, Inorg. Chem. 21 (1982) 785.
- [19] (a) J.S. Griffith, The Theory of Transition Metal Ions, Cambridge University Press, Cambridge, 1961, 364;
 (b) B. Bleany, M.C.M. O'Brien, Proc. Phys. Soc. London, Sect. B 69 (1956) 1216.
- [20] S. Bhattacharya, A. Chakravorty, Proc. Indian Acad. Sci. (Chem. Sci.) 95 (1985) 159.