Letter

Two simple precursor 2,2′-bisoxazoline complexes of ruthenium

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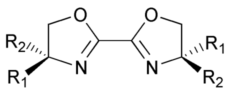
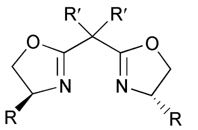
Syntheses, X-ray crystal structures and some electrochemical properties of $Ru^{II}L_2Cl_2$, $Ru^{III}L$(dimethylformamide)Cl_3 and $[Ru^{II}L_2Cl_2]PF_6$, where L is 4,4,4′,4′-tetramethyl-2,2′-bisoxazoline, are described. It is found that the first two complexes serve as very good precursors to synthesise a host of mixed-ligand complexes of Ru(II) and Ru(III) containing L.

In the last decade, various substituted chiral bisoxazolines of the types **1** and **2** have emerged as an efficient class of ligands in metal-catalysed asymmetric syntheses.[1–4] While a number of metal complexes of **2** (Evans's ligand) have been prepared and characterised structurally in various contexts,[1–5] very little attention has been paid to the transition metal chemistry of **1**. This is possibly because in most cases, the bisoxazolines of type **2** have been found to be superior to those of type **1** in producing a greater enantiomeric excess. In an extensive review on the metal complexes of oxazolines[5] that appeared in 1999, Gómez *et al.* write that "unfortunately, to date, no X-ray structures containing chelate" **1** "have been determined." After the appearance of this review, Walther *et al.* have reported the X-ray crystal structures of octahedral Ni(**1a**)(acetylacetonate)$_2$ and square planar Ni(**1a**)(mes)(Br) (mes ≡ mesityl) and Pd(**1a**)(mes)$_2$ in connection with their studies on the catalytic transformations brought about by Pd(II) and Ni(II) complexes.[6] Recently, we have undertaken a project to develop the transition metal chemistry of the bisoxazolines of type **1**. Elsewhere we have reported[7] the photophysics and structure of a copper(I) dimer of a derivative of **1**. Herein we make a preliminary report of our studies on its ruthenium chemistry. The syntheses, structures and some properties of two simple ruthenium complexes of **1a**, from which a host of mixed-ligand complexes of ruthenium(II) and ruthenium(III) can be prepared, are described here.



1a: $R_1 = R_2 = Me$



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Reaction of 1 mol of $RuCl_3 \cdot 3H_2O$ with 2 mol of the ligand **1a** in hot dimethylformamide (DMF) in the presence of 0.5 mol of metallic zinc and an excess of the chloride ion leads to the isolation of Ru(**1a**)$_2$Cl$_2$ in 25% yield; after allowing the filtrate to stand in air for several days, Ru(**1a**)(DMF)Cl$_3$ is obtained in 40% yield. The use of zinc metal in our synthesis is novel. For example, Ru(bpy)$_2$Cl$_2$ or Ru(phen)$_2$Cl$_2$ (bpy ≡ 2,2′-bipyridine; phen ≡ 1,10-phenanthroline) are synthesised in a similar manner without adding metallic zinc to the reaction mixture.[8,9] The role of zinc here is to reduce ruthenium(III) to ruthenium(II); no trace of metallic zinc can be found in the crude product of Ru(**1a**)$_2$Cl$_2$. Incidentally, no bpy or phen analogue of Ru(**1a**)(DMF)Cl$_3$ is known.

The structures of Ru(**1a**)$_2$Cl$_2$ and Ru(**1a**)(DMF)Cl$_3$ as determined by X-ray crystallography are shown in Fig. 1 and 2, respectively. The ligand **1a**, which is a non-aromatic 1,4-diimine, is found to bind ruthenium through the N ends and the DMF molecule in Ru(**1a**)(DMF)Cl$_3$ binds through the O atom. In both the complexes, the metal atom has a slightly distorted octahedral environment; the distortion is mainly caused by the chelate bites [77.6(2)° in Ru(**1a**)$_2$Cl$_2$ and 78.0(4)° in Ru(**1a**)(DMF)Cl$_3$]. The chlorine atoms in Ru(**1a**)$_2$Cl$_2$ are mutually *cis* and those in Ru(**1a**)(DMF)Cl$_3$ span a meridian. The Ru–Cl and the Ru–N bond lengths in Ru(**1a**)(DMF)Cl$_3$ are somewhat shorter than those in Ru(**1a**)$_2$Cl$_2$, indicative of the differences between the radii of Ru(III) and Ru(II). The bidentate ligands are slightly distorted from planarity with deviations of individual atoms from the 5-membered ring planes being less than 0.15 Å; the two rings intersect at angles of 5.2 and 8.1° in Ru(**1a**)$_2$Cl$_2$ and 1.9° in Ru(**1a**)(DMF)Cl$_3$.

In the ^1H NMR spectrum of **1a** in $CDCl_3$, the methyl protons appear as a singlet at 1.37 ppm and the methylene ones as another singlet at 4.13 ppm. The presence of a twofold axis of symmetry in **1a** is reflected in its ^{13}C NMR spectrum also, in which four types of C atoms are indicated [methyl C, 28.42; $C(CH_3)_2$, 68.80; methylene C, 80.10; imino C, 153.67 ppm with reference to TMS]. However, this symmetry is lost in

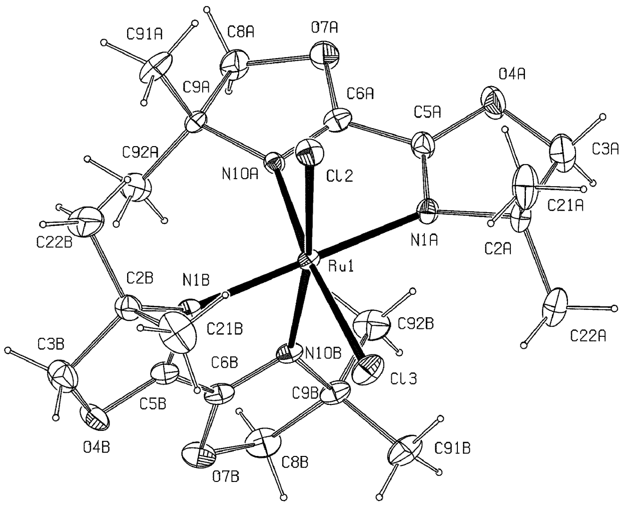

Fig. 1 X-Ray crystal structure of Ru(**1a**)$_2$Cl$_2$ with ellipsoids at 15% probability. Selected bond distances (Å) and angles (°): Ru1–N1A 2.098(5), Ru1–N1B 2.102(5), Ru1–N10A 2.091(5), Ru1–N10B 2.082(4), Ru1–Cl2 2.421(3), Ru1–Cl3 2.416(3), N1A–Ru1–N1B 178.2(2), N10A–Ru1–Cl3 172.2(1), N10B–Ru1–Cl3 88.0(2), N1A–Ru1–Cl3 94.8(2), N1B–Ru1–Cl3 85.8(1).

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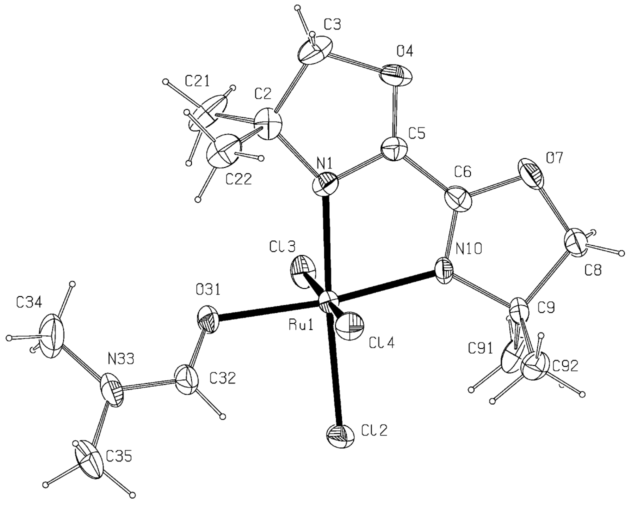


Fig. 2 X-Ray crystal structure of $Ru(\mathbf{1a})(DMF)Cl_3$ with ellipsoids at 15% probability. Selected bond distances (Å) and angles (°): Ru1–N1 2.063(10), Ru1–N10 2.061(9), Ru1–Cl2 2.367(4), Ru1–Cl3 2.330(4), Ru1–Cl4 2.353(4), Ru1–O31 2.109(8), N1–Ru1–Cl2 176.6(3), N10–Ru1–Cl2 98.6(3), Cl2–Ru1–Cl4 91.4(2), Cl2–Ru1–Cl3 91.3(2), Cl3–Ru1–Cl4 176.7(1), N1–Ru1–O31 94.9(4), N10–Ru1–O31 172.9(4), O31–Ru1–Cl2 88.5(3).

$Ru(\mathbf{1a})_2Cl_2$, as revealed by its ^{13}C NMR spectrum in $CDCl_3$ where 10 distinct resonances are observed (see Experimental), indicating that none of the ten carbon atoms in a particular ligand fragment in the complex are magnetically equivalent. The ^1H NMR spectrum of $Ru(\mathbf{1a})_2Cl_2$ is very rich and we have not yet been able to decipher it.

The electrochemical behaviour of $Ru(\mathbf{1a})_2Cl_2$ and $Ru(\mathbf{1a})(DMF)Cl_3$ has been examined by cyclic voltammetry at a glassy carbon electrode in acetonitrile under N_2 atmosphere. $Ru(\mathbf{1a})_2Cl_2$ shows (Fig. 3) a quasireversible $Ru^{III/II}$ couple at 0.18 V *vs.* SCE (saturated calomel electrode). This $Ru^{III/II}$ couple appears at −0.34 V *vs.* SCE in $Ru(\mathbf{1a})(DMF)Cl_3$ (Fig. 3). On the positive side of SCE, $Ru(\mathbf{1a})(DMF)Cl_3$ displays a quasireversible $Ru^{IV/III}$ couple at 1.22 V *vs.* SCE. For comparison, we note that the $Ru^{III/II}$ couple in *cis*-Ru-$(bpy)_2Cl_2$ and *cis*-$Ru(phen)_2Cl_2$ appears[10,11] respectively at 0.31 and 0.33 V *vs.* SCE in acetonitrile at a platinum electrode.

Because of the very low potential of the $Ru^{III/II}$ couple, $Ru(\mathbf{1a})_2Cl_2$ is easily oxidised by air. We have found that it is possible to isolate $[Ru(\mathbf{1a})_2Cl_2]PF_6$, the ruthenium(III) counterpart of $Ru(\mathbf{1a})_2Cl_2$, just by refluxing a methanolic solution of $Ru(\mathbf{1a})_2Cl_2$ in air and by subsequent addition of excess NH_4PF_6. It should be noted that an oxidising agent like chlorine is needed in the synthesis of $[Ru(bpy)_2Cl_2]PF_6$ from $Ru(bpy)_2Cl_2$.[12] In X-ray crystallography, $[Ru(\mathbf{1a})_2Cl_2]PF_6$ is found to consist of discrete $[Ru(\mathbf{1a})_2Cl_2]^+$ cations and PF_6^- anions with both the cation (Fig. 4) and anion having crystallographic C_s symmetry. The chlorine atoms in $[Ru(\mathbf{1a})_2Cl_2]^+$ are found to maintain the *cis* configuration. While the Ru–Cl bonds in $[Ru(\mathbf{1a})_2Cl_2]PF_6$ are significantly shorter than those in $Ru(\mathbf{1a})_2Cl_2$, the Ru–N bonds in the complexes $Ru(\mathbf{1a})_2Cl_2$ and $[Ru(\mathbf{1a})_2Cl_2]PF_6$ are comparable. The two 5-membered rings of **1a** in $[Ru(\mathbf{1a})_2Cl_2]PF_6$ intersect at an angle of 5.6°. In cyclic voltammetry at a glassy carbon electrode in acetonitrile under N_2 atmosphere, the $Ru^{III/II}$ couple in $[Ru(\mathbf{1a})_2Cl_2]PF_6$ is found to be lower by 40 mV in potential and much less reversible than that in $Ru(\mathbf{1a})_2Cl_2$ (Fig. 3). In this context, we mention that the $Ru^{III/II}$ couple in $[Ru(bpy)_2Cl_2]^+$ is reported[13] to be lower by 20 mV in potential but somewhat more reversible than that in $Ru(bpy)_2Cl_2$.

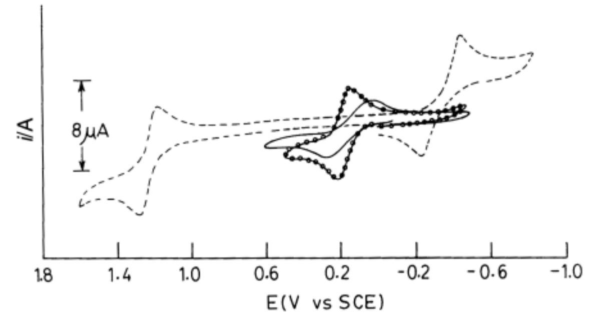


Fig. 3 The cyclic voltammograms of $Ru(\mathbf{1a})_2Cl_2$ (○, c = 1.09 mM), $Ru(\mathbf{1a})(DMF)Cl_3$ (----, c = 1.38 mM) and $[Ru(\mathbf{1a})_2Cl_2]PF_6$ (—, c = 0.42 mM) in acetonitrile (0.1 M in tetraethylammonium perchlorate) at a glassy carbon electrode. Scan rate v = 50 mV s^{-1}. Under the same experimental conditions, the ferrocene–ferrocenium couple appears at 0.35 V *vs.* SCE with a peak-to-peak separation of 80 mV at v = 50 mV s^{-1}.

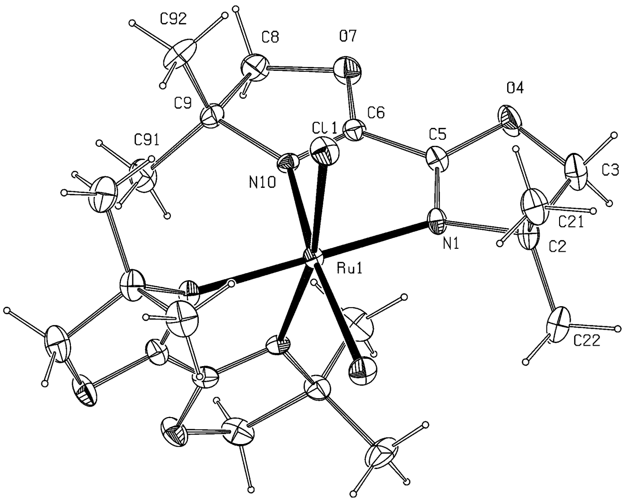


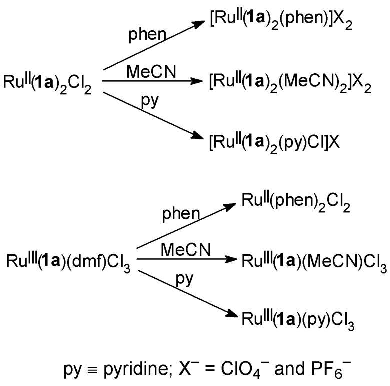
Fig. 4 X-Ray crystal structure of $[Ru(\mathbf{1a})_2Cl_2]PF_6$ with ellipsoids at 15% probability. Selected bond distances (Å) and angles (°): Ru1–N1 2.113(4), Ru1–N10 2.101(3), Ru1–Cl1 2.329(3), N1–Ru1–N10 77.2(2), N1–Ru1–N1 178.7(2), N10–Ru1–Cl1 89.1(1), 168.5(1).

In Scheme 1 we show how[14] a number of mixed-ligand complexes of ruthenium(II) and ruthenium(III) containing 2,2′-bisoxazoline can be synthesised by replacing the chlorine atoms in $Ru(\mathbf{1a})_2Cl_2$ and the DMF molecule in $Ru(\mathbf{1a})(dmf)Cl_3$. Thus, we envisage a ruthenium chemistry of 2,2′-bisoxazoline that will be as rich as that of bipyridine.

Experimental

Methods and materials

The ligand **1a** (4,4,4′,4′-tetramethyl-2,2′-bisoxazoline) was synthesised by following a reported procedure.[15] Micro-



Scheme 1 py≡pyridine; X^- = ClO_4^- and PF_6^-.

analyses were performed on a Perkin–Elmer 2400II elemental analyser. Molar conductance was determined by a Systronics (India) direct reading conductivity meter (model 304). FTIR spectra (KBr disc) were recorded on a Nicolet Magna-IR spectrophotometer (Series II), UV-VIS spectra on a Shimadzu UV-160A spectrophotometer and NMR spectra (in $CDCl_3$) by a Brucker DPX300 spectrometer. Cyclic voltammetry was performed using an EG&G PARC electrochemical analysis system (model 250/5/0) in purified acetonitrile under a dry nitrogen atmosphere in conventional three-electrode configurations. A planar EG&G PARC G0229 glassy carbon milli electrode was used as the working electrode. Magnetic susceptibility was determined at room temperature by a PAR 155 vibrating sample magnetometer. The magnetometer was calibrated with $Hg[Co(SCN)_4]$ and the susceptibility data were corrected for diamagnetism using Pascal's constants. In the calculation of the magnetic moments of the two ruthenium(III) complexes, Ru(**1a**)(DMF)Cl_3 and [Ru(**1a**)$_2$$Cl_2$]$PF_6$, we have ignored the temperature-independent paramagnetism (TIP) of the Ru^{3+} ion.

Syntheses

Ru(1a)$_2$Cl$_2$. $RuCl_3 \cdot 3H_2O$ (0.26 g, 1 mmol), 0.39 g (2 mmol) of **1a**, 0.29 g (6.7 mmol) of LiCl and 0.03 g (0.5 mmol) of zinc dust were taken up in 3 ml of DMF. This was heated at ~100 °C until a microcrystalline compound started appearing (almost 1 h was needed). The solution was then cooled to room temperature, 10 ml of acetone was added and the solution kept in the refrigerator overnight. The next day the violet crystalline compound that had appeared was filtered off, washed with 10 ml of water and dried *in vacuo* over fused $CaCl_2$. It was recrystallised from a dichloromethane–hexane mixture. Yield 0.15 g (25%). Anal. calcd for $C_{20}H_{32}Cl_2N_4O_4Ru$: C, 42.53; H, 5.72; N, 9.92; found: C, 42.65; H, 5.66; N, 10.01%. UV/VIS (CH_3CN) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 532 (8000), 464 (4300), 247 (6500), 220 (10,100). ^{13}C NMR (300 MHz, $CDCl_3$, TMS): δ 15.23, 25.07, 27.22, 29.57 (four methyl C), 65.81, 71.44 (two alkyl quaternary C), 82.52, 83.88 (two methylene C), 155.10, 157.59 (two imino C).

Ru(1a)(DMF)Cl$_3$. The dark red filtrate obtained above after filtering Ru(**1a**)$_2$$Cl_2$ was kept in air for a week. The dark yellow crystalline compound that deposited was filtered off, washed with 10 ml of water and dried *in vacuo* over fused $CaCl_2$. Yield 0.20 g (40%). Anal. calcd for $C_{13}H_{23}Cl_3N_3O_3Ru$: C, 32.72; H, 4.86; N, 8.81; found: C, 32.64; H, 4.82; N, 8.91%. FTIR (KBr) ν/cm^{-1}: 1638vs (C=O). μ/μ_B: 2.07 (at 300 K). UV/VIS (CH_3CN) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 235 (10,500), 324 (2250), 379 (5900).

[Ru(1a)$_2$Cl$_2$]PF$_6$. Ru(**1a**)$_2$$Cl_2$ (0.14 g, 0.25 mmol) was dissolved in 20 ml of methanol and refluxed for 48 h. The red reaction mixture was then cooled to room temperature and filtered. To the filtrate, 0.5 g of NH_4PF_6 dissolved in 3 ml of water was added dropwise with constant stirring and the solution left in air for 6 h. The yellow compound that precipitated was filtered off, washed with a few drops of cold water and dried *in vacuo* over fused $CaCl_2$. Yield 0.02 g (15%). Anal. calcd for $C_{20}H_{32}Cl_2N_4O_4RuPF_6$: C, 33.83; H, 4.55; N, 7.89; found: C, 33.72; H, 4.60; N, 7.84%. FTIR (KBr) ν/cm^{-1}: 842vs, 558s (PF_6). μ/μ_B: 2.05 (at 300 K). Λ_M (CH_3CN): 132 Ω^{-1} cm^2 mol^{-1} (1 : 1 electrolyte). UV/VIS (CH_3CN) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 464 (1850), 356 (5500), 241 (9900).

X-Ray crystallography

Single crystals of Ru(**1a**)$_2$$Cl_2$, Ru(**1a**)(DMF)$Cl_3$ and [Ru(**1a**)$_2$$Cl_2$]$PF_6$ were grown by direct diffusion of hexane into a dilute dichloromethane solution of the respective complexes. Data were collected with Mo-Kα radiation using the MAR-research Image Plate System. The crystals were positioned at 70 mm from the Image Plate. One hundred frames were measured at 2° intervals with a counting time of 2 min. Data analyses were carried out with the XDS program.[16] The structures were solved using direct methods with the SHELXS-86 program.[17] In all the structures the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structures were refined on F^2 using SHELXL-93.[18]

Crystal data. Ru(**1a**)$_2$$Cl_2$: $C_{20}H_{32}Cl_2N_4O_4Ru$, $M_w = 564.47$, monoclinic, space group $P2_1/a$, $a = 15.42(2)$, $b = 9.832(14)$, $c = 16.076(19)$ Å, $\beta = 96.67(1)°$, $U = 2421(6)$ Å^3, $Z = 4$, $D_c = 1.549$ g cm^{-3}, $\mu = 0.901$ mm^{-1}, 6185 reflections collected, 3926 unique, R(int) = 0.031, final residuals: $R1 = 0.0457$ and $wR2 = 0.1207$ for observed data, $R1 = 0.0857$ and $wR2 = 0.1429$ for all data. Ru(**1a**)(DMF)Cl_3 : $C_{13}H_{23}Cl_3N_3O_3Ru$, $M_w = 476.76$, orthorhombic, space group $P2_12_12_1$, $a = 8.607(14)$, $b = 14.48(2)$, $c = 15.73(2)$ Å, $U = 1960(5)$ Å^3, $Z = 4$, $D_c = 1.615$ g cm^{-3}, $\mu = 1.223$ mm^{-1}, 2046 unique reflections collected, final residuals : $R1 = 0.0581$ and $wR2 = 0.1598$ for observed data, $R1 = 0.0994$ and $wR2 = 0.1835$ for all data. [Ru(**1a**)$_2$$Cl_2$]$PF_6$: $C_{20}H_{32}Cl_2N_4O_4RuPF_6$, $M_w = 709.44$, orthorhombic, space group $P22_12_1$, $a = 8.545(12)$, $b = 12.001(16)$, $c = 14.002(20)$ Å, $U = 1436(4)$ Å^3, $Z = 4$, $D_c = 1.641$ g cm^{-3}, $\mu = 0.860$ mm^{-1}, 5008 reflections collected, 2750 unique, R(int) = 0.027, final residuals: $R1 = 0.0354$ and $wR2 = 0.0780$ for observed data, $R1 = 0.0479$ and $wR2 = 0.0832$ for all data.

CCDC reference numbers 174511–174513. See http://www.rsc.org/suppdata/nj/b1/b109294b/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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References

1 F. Fache, E. Schultz, M. L. Tommasino and M. Lemaire, *Chem. Rev.*, 2000, **100**, 2159.
2 J. S. Johnson and D. A. Evans, *Acc. Chem. Res.*, 2000, **33**, 325.
3 D. A. Evans, K. A. Scheidt, N. Johnston and M. C. Willis, *J. Am. Chem. Soc.*, 2001, **123**, 4480.
4 R. Annuziata, M. Beneglia, M. Cinquini, F. Cozzi and M. Pitillo, *J. Org. Chem.*, 2001, **66**, 3160.
5 M. Gómez, G. Muller and M. Rocamora, *Coord. Chem. Rev.*, 1999, **193–195**, 769.
6 D. Walther, T. Döhler, K. Heubach, O. Klobes, B. Schweder and H. Görls, *Z. Anorg. Allg. Chem.*, 1999, **625**, 923.
7 G. K. Patra, I. Goldberg, S. K. Chowdhury, B. C. Maiti, A. Sarkar, P. R. Bangal, S. Chakravorti, N. Chattopadhyay, D. A. Tocher, M. G. B. Drew, G. Mostafa, S. Chowdhury and D. Datta, *New J. Chem.*, 2001, **25**, 1371.
8 B. P. Sullivan, D. J. Salmon and T. J. Meyer, *Inorg. Chem.*, 1978, **17**, 3334.
9 P. Bonneson, J. L. Walsh, W. T. Pennington, A. W. Cordes and B. Durham, *Inorg. Chem.*, 1983, **22**, 1761.
10 B. P. Sullivan, D. J. Salmon, T. J. Meyer and J. Peedin, *Inorg. Chem.*, 1979, **18**, 3369.
11 T. Matsumura-Inoue, I. Ikemoto and Y. Umezawa, *J. Electroanal. Chem.*, 1986, **209**, 135.

12 J. N. Braddock and T. J. Meyer, *Inorg. Chem.*, 1973, **12**, 723.
13 T. R. Weaver, T. J. Meyer, S. A. Adeyemi, G. M. Brown, R. P. Eckberg, W. E. Hatfield, E. C. Johnson, R. W. Murray and D. Untereker, *J. Am. Chem. Soc.*, 1975, **97**, 3039.
14 P. K. Pal, M. G. B. Drew and D. Datta, manuscript in preparation.
15 I. Butala and G. Karlovic, *Liebigs Ann. Chem.*, 1976, 1455.
16 W. Kabsch, *J. Appl. Crystallogr.*, 1988, **21**, 916.
17 G. M. Sheldrick, *Acta Cystallogr., Sect. A*, 1990, **46**, 467.
18 G. M. Sheldrick, SHELXL-93, A Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1993.