Polyhedron Vol. 9, No. 10, pp. 1243–1248, 1990
Printed in Great Britain

0277–5387/90 $3.00+.00

RUTHENIUM(II)–BIPYRIMIDINE COMPLEXES: CHARACTERIZATION, SPECTROSCOPY AND PHOTOANATION STUDIES

MIRZA M. TAQUI KHAN,* RAMESH C. BHARDWAJ and CHHAYA BHARDWAJ

Central Salt & Marine Chemicals Research Institute, Bhavnagar—364 002, India

(*Received* 13 *April* 1989; *accepted* 2 *November* 1989)

Abstract—Preparation, characterization and photoanation studies of ruthenium(II) complexes with bipyrimidine are reported. Fluorescence and electrochemical studies have also been conducted. The quantum yield has been calculated for photoanation studies of the complex $[Ru(bipym)_3](PF_6)_2$.

The photochemistry and photophysics of the $Ru(bpy)_3^{2+}$ cation have been intensely investigated[1] during the past decade with a view to develop suitable solar energy conversion catalysts. The study of this species in the excited state has contributed greatly to the understanding of other related photocatalytic molecules[2,3] such as $Ru(bpz)_3^{2+}$ (bpz = bipyrazyl) cation. The $Ru(bipym)_3^{2+}$ (**1**) (bipym = bipyrimidine) cation, which is analogous to $Ru(bpy)_3^{2+}$, is also an excellent photocatalyst[4] and has an added advantage over $Ru(bpy)_3^{2+}$ and $Ru(bpz)_3^{2+}$ as there is no quenching[3] of its emission by molecular oxygen. As in the case of $Ru(bpz)_3^{2+}$ the emission of $Ru(bipym)_3^{2+}$ is quenched by protons at pH < 1, indicating a slightly enhanced basicity of its excited state compared to the ground state. There is, however, no change[4] in the emission of **1** at pH 4.5–8; the formal reduction potential of $Ru(bipym)_3^{2+}$. The presence of the bipyrimidine ligand thus shifts the redox potential to a more positive value compared to the corresponding bipyridine and bipyrazine complexes.

Protonation studies of bipyridine, bipyrazine and their ruthenium(II) complexes have been reported.[3] Recently, protonation of 1,10-phenanthroline in aqueous dioxane was conducted by Ishiguro *et al.*[5] Protonation of 2-pyrimidyl and the 2-pyrazylpalladium(II) complex was reported by Crociani *et al.*[6]

The complexes of bipyrimidine, therefore, have the inherent potential to be better oxidizing photocatalysts than the analogous complexes of bipyridine and bipyrazine. Besides, protonation of bipyrimidine is expected to yield species with even more positive oxidizing potentials than the neutral species, providing a handle to change its redox behaviour in suitable photoreactions.

In this paper we report the synthesis, characterization, fluorescence and electrochemical studies and photoanation (quantum yield) studies of ruthenium(II)–bipyrimidine complexes.

RESULTS AND DISCUSSION

The elemental analysis and conductivity of the complexes are given in Table 1. The conductivity of the acetonitrile complexes shows that complexes **1** and **2** are 1 : 2 electrolytes, complex **5** is a 1 : 1 electrolyte and complexes **3**, **4** and **6** are non-electrolytes.

The IR spectra of the complexes show a weak peak at 480–495 cm^{-1} assigned to the (Ru—N) stretching frequency. The absence of a peak at 310 cm^{-1} in complexes **1** and **2** suggests that the chlorides are in the outer coordination sphere of the metal ion. The peaks at 320 and 310 cm^{-1} in complex **3** can be assigned to the (Ru—Cl) stretching of *cis*-chlorides. The peak at 510 cm^{-1} in **3** can be assigned to the (Ru—P) stretching. The ^{31}P NMR of **3** gives a singlet at 21.49 ppm suggesting a *trans* disposition of the coordinated triphenylphosphine. Complex **4** exhibits a single peak at 315 cm^{-1} corresponding to the (Ru—Cl) stretching of *trans*-

---

* Author to whom correspondence should be addressed.

Table 1. Analytical data for ruthenium–bipyrimidine complexes. Experimental values are given in parentheses

Complex	Colour	Melting point (°C)	%C	%H	%N	Molar conductivity (acetonitrile) (1×10^{-4} M)
$[\mathrm{Ru(bipym)_3}]\mathrm{Cl_2}$ (**1**)	Reddish	180–185	40.6 (41.0)	2.5 (3.0)	23.7 (23.8)	105
$[\mathrm{Ru(bipym)_3}](\mathrm{PF_6})_2$ (**2**)	Orange	—	33.3 (33.6)	2.1 (2.0)	19.2 (18.9)	115
$[\mathrm{Ru(bipym)(PPh_3)_2Cl_2}]$ (**3**)	Brownish red	Decomposes at 110	61.8 (61.3)	4.2 (4.4)	6.5 (6.5)	000
$[\mathrm{Ru(bipym)_2Cl_2}]$ (**4**)	Black	210–215	36.3 (35.7)	3.1 (3.4)	21.4 (20.9)	005
$[\mathrm{Ru(bipym)_2(CH_3CN)(Cl)}]^+[\mathrm{PF_6}]^-$ (**5**)	Dark red	—	33.8 (33.6)	2.3 (2.0)	19.7 (19.6)	098
$[\mathrm{Ru(bipym)_2(NO_2)_2}]\cdot0.5\mathrm{H_2O}$ (**6**)	Red	—	37.7 (37.3)	2.4 (2.6)	27.5 (25.1)	000

chlorides. Complex **5** exhibits (Ru—Cl) at 315 cm^{-1}. The IR spectral data are given in Table 2.

The electronic spectra of complexes **1**–**6** show low-energy bands in the visible region at 24,271 cm^{-1} assigned to ruthenium(II) to bipyrimidine MLCT charge-transfer. The higher energy bands at 30,120 and 40,650 cm^{-1} are π–π^* transitions within the bipyrimidine molecule. The band at 22,123 cm^{-1} in the spectrum of complex **1** is a $d\ \pi$–π^* MLCT transition. Similar bands were reported for analogous ruthenium(II) bipyridyl complexes.[7] The two major peaks in the UV spectra are essentially independent of the nature of the complex and are assigned to π–π^* transitions within the bipyrimidine rings. The weaker absorption near 40,650 cm^{-1} can be assigned to a higher energy MLCT. The major shoulder near 22,123 and 24,271 cm^{-1} can be either a *d*–*d* band or a second MLCT transition. The results are tabulated in Table 2.

Luminescence studies

Luminescence spectra of the complexes were taken in aqueous solution and are uncorrected. The

Table 2. IR spectra of the ruthenium complexes

Complex	ν(Ru—X), (cm^{-1}) X = Cl, PF$_6$, NO$_2$	ν(Ru—P), (cm^{-1})	ν(Ru—N), (cm^{-1})	Other characteristic peaks
$[\mathrm{Ru(bipym)_3}]\mathrm{Cl_2}$ (**1**)	—	—	480(w)	3100(s), 1550(s), 1400(vs), 1030(w), 750(m)
$[\mathrm{Ru(bipym)_3}](\mathrm{PF_6})_2$ (**2**)	—	—	480(w)	3100(s), 1570(m), 1400(vs), 850(s), 750(w)
$[\mathrm{Ru(bipym)(PPh_3)_2Cl_2}]$ (**3**)	320(m) 310(m)	510(s)	490(w)	3100(s), 1610(m), 1470(w), 1390(vs), 1090(m), 740 (m)
$[\mathrm{Ru(bipym)_2Cl_2}]$ (**4**)	315(m)	—	480(w)	3100(s), 1550(m), 1400(vs), 1030(w), 810(m)
$[\mathrm{Ru(bipym)_2(CH_3CN)(Cl)}]^+[\mathrm{PF_6}]^-$ (**5**)	315(m)	—	490(w)	3100(s), 1550(m), 1400(vs), 1090(m), 740(m)
$[\mathrm{Ru(bipym)_2(NO_2)_2}]\cdot0.5\mathrm{H_2O}$ (**6**)	1250(s)	—	495(w)	3100, 1615(m), 1410(vs), 1020(w), 800(m)

Key: s = strong; vs = very strong; w = weak and m = medium.

emission spectra of complex **1** shows a strong intensity peak at 611 nm which seems to be $d\pi^*$ in origin. The substitution of chloride by PF_6 shows a blue shift of the λ_{em} maximum which is observed at 602 nm with slightly lower intensity. The emission intensity of complexes **1** and **2** does not change in the pH range 4.5–8. At lower pH the emission intensity rapidly decreased and no emission was observed below pH 1, indicating a slightly enhanced basicity of the excited state of $Ru(bipym)_3^{2+}$. Complex **3** gave λ_{em}(max) at 546 nm which is due to replacement of two bipyrimidine molecules, responsible for fluorescence. The removal of one bipyrimidine molecule has shown a blue shift in complex **4**, where λ_{em}(max) is at 533 nm. The addition of CH_3CN and Cl to the coordination sphere of the metal ion in complex **5** shows a red shift for the emission wavelength at 644 nm. Addition of NO_2 also exhibits a red shift at 750 nm. The red shift in the emission wavelength is very important because the energy utilized for the excitation wavelength is also less. This fact is helpful for the utilization of these complexes in the visible part of the solar spectrum (with less energy) to realize the harnessing of solar energy. The λ_{em} maximum of complexes **1**–**6** is given in Table 3.

Electrochemical studies

Polarographic $E_{1/2}$ data for ruthenium(II) bipyridimine complexes in aqueous solution with SCE as reference electrode in 0.1 M KNO_3 as supporting electrolyte are compared with those of their bipyridyl analogues. The $E_{1/2}$ value of $Ru(bipym)_3^{2+}$ with bipyrimidine results in a shift of the reduction potentials to more positive values by about 0.5 V. Similar results were reported when bipyridyl was replaced by bipyrazyl ligand.[8] The replacement of bipyrimidine in complex **4** by CH_3CN or NO_2 shows a less positive (more negative) reduction potential because of good σ-donor and poor π-acceptor behaviour of CH_3CN and NO_2 compared to Cl^-, PPh_3 or bipyridine. The shift of the reduction potential to negative values by the replacement of a halogen with good σ-donor groups was reported earlier by Crutchley and Lever.[7] We did not notice the solvolysis of complex **4**.

The diffusion currents for complexes **1**–**6** were calculated using differential pulse polarography and the results are tabulated in Table 4. As expected, higher diffusion currents were observed in complexes **5** and **6** by the replacement of halogen or bipyrimidine in the coordination sphere of the metal ion by the strong σ-donor CH_3CN or NO_2 groups. The more positive potentials of complexes **1**–**4** compared to **5** and **6** are due to the presence of less σ-basic or π-acidic ligands like bipyrimidine, PPh_3 and Cl ligands. The π-acidities decrease in the order $PPh_3 >$ bipyrimidine $> Cl^-$. This is reflected in the increase of i_d for complexes **1**–**4** in the order $\mathbf{3} < \mathbf{1} < \mathbf{2} < \mathbf{4}$.

Photoanation studies

Photoanation studies of $[Ru(bipym)_3](PF_6)_2$ (**2**) in acetonitrile shows the formation of $[Ru(bipym)_2(CH_3CN)(Cl)]PF_6$ (**5**) which corresponds to a quantum yield of 0.14. The results can be compared with the reports of Jones and Cole-Hamilton[9] for the photoanation of the ruthenium(II)–tris-(bipyridyl) dication, $Ru(bipy)_3^{2+}$, by chloride ion in acetonitrile. The only photoproduct reported[9] was $[Ru(bpy)_2(CH_3CN)(Cl)]Cl$ with a maximum quantum yield of 0.01. In solvents of lower polarity such as acetone and CH_2Cl_2 the photoproduct formed was $Ru(bpy)_2Cl_2$ with a slightly higher quantum yield of 0.02.[10,11] These facts are suggestive of an ion-paired mechanism for photoanation. The mech-

Table 3. Electronic and emission spectra of the bipyrimidine complexes of ruthenium(II) in aqueous solution

$[Ru(bipym)_3]Cl_2$ (**1**)	22,123(3.82), 24,271(3.8), 30,120(4.13)	452, 412 332	40,650(4.59)	246	611
$[Ru(bipym)_3](PF_6)_2$ (**2**)	22,075(3.86), 24,271(3.8), 30,180(4.16)	453, 412 331	40,650(4.66)	246	602
$[Ru(bipym)(PPh_3)_2Cl_2]$ (**3**)	24,630(3.68)	406	41,152.2(4.089)	243	546
$[Ru(bipym)_2Cl_2]$ (**4**)	25,315(3.94), 27,178(3.91)	395, 368	41,152(4.43) 51,813(4.50)	243 193	533
$[Ru(bipym)_2(CH_3CN)(Cl)]^+[PF_6]^-$ (**5**)	20,202(3.8), 26,809(4.22)	495, 373	—	—	644
$[Ru(bipym)_2(NO_2)_2]\cdot 0.5H_2O$ (**6**)	28,735(3.97), 20,660(3.94)	484, 348	42,020(4.29) 32,364(4.5)	238 309	750

Table 4. Electrochemical data of ruthenium–bipyrimidine complexes

Complex	Oxidation $E_{1/2}$ (V)	Reduction $E_{1/2}$ (V)			Differential pulse i_d (μA)
$[Ru(bipym)_3]Cl_2$ (1)	1.69	−0.80	−0.95	−1.2	7.0 7.5
$[Ru(bipym)_3](PF_6)_2$ (2)	1.67	−0.92	−1.06	−1.09	5.5 5.75
$[Ru(bipym)(PPh_3)_2Cl_2]$ (3)	—	−0.76	—	—	3.6
$[Ru(bipym)_2Cl_2]$ (4)	—	−0.75	−1.16	—	4.9 7.25
$[Ru(bipym)_2(CH_3CN)(Cl)]^+[PF_6]^-$ (5)	—	−1.37	—	—	27.5
$[Ru(bipym)_2(NO_2)_2]\cdot 0.5H_2O$ (6)	—	−1.18	−1.45	—	7.9 12.75

anism of photoanation of $Ru(bipym)_3^{2+}$ by analogy to that of $Ru(bpy)_3^{2+}$ is believed to be dissociative, resulting in a five-coordinate intermediate with an end-bonded bipyrimidine ligand. Monodentate bipyridyl intermediates have been isolated and their electronic spectra recorded.[12,13] However, these intermediates are unstable and it is probably that in the case of $Ru(bipym)_3^{2+}$, the formation of a monodentate bipyrimidine complex is not detected spectrophotometrically because of its rapid conversion of $Ru(bipym)_3^{2+}$ to $[Ru(bipym)_2(CH_3CN)(Cl)]^+$. As soon as the five-coordinate intermediate is formed, anation results from the Cl^- associated in the ion pair. The difference in the quantum yields of $Ru(bipym)_3^{2+}$ ($\phi = 0.14$) and $Ru(bpy)_3^{2+}$ ($\phi = 0.01$) may be due to the conversion of the latter species to $[Ru(bpy)_2(solvent)(Cl)]^+$ in solution as observed by Van Houten and Watts.[12]

Our interest in the bipyrimidine(II) species is in the design of the highly photo-oxidizable photocatalyst and it is pertinent that the redox couples associated with $Ru(bpy)_3^{2+}$ do shift to positive values in sulphuric acid by a significant amount.[14] The excited state protonation studies using fluorescence spectroscopy are also of interest to us and are under investigation. The electrochemical properties of these complexes and the replacement of Cl^- by ligands such as NCS, Br_2, I_2, oxalate etc. also falls under our future interest of work.

EXPERIMENTAL

Preparation of complexes

(1) *Tris(bipyrimidine)ruthenium*(II) *dichloride.* The complex was prepared by refluxing $Ru(Me_2SO)_4Cl_2$ (0.4 g) and bipyrimidine (0.8 g) in water (50 cm^3) for 20 h. The reaction mixture was filtered and evaporated to dryness. The residue was washed with acetone and chloroform and again with acetone. The crude product (0.6 g) was dissolved in water (10 cm^3) and filtered. To the boiling filtrate was added slowly a 1:2 mixture of ethanol and propanol (20 cm^3). On cooling the solution, reddish crystalline $[Ru(bipym)_3]Cl_2$ precipitated out (0.55 g); yield: 80%.

(2) *Tris(bipyrimidine)ruthenium*(II) *hexafluorophosphate.* A solution of $[Ru(bipym)_3]Cl_2$ (0.4 g in water to cm^3) was heated to boiling. To this was added an aqueous solution of 0.2 M (50 cm^3) NH_4PF_6 and an orange precipitate was immediately formed. The solution was allowed to cool to room temperature and then filtered. The crude product was washed with water and recrystallized with acetone–ethanol solution to give the orange-coloured crystalline $[Ru(bipym)_3](PF_6)_2$; yield: 76%.

(3) *Dichlorobis(triphenylphosphine)bipyrimidineruthenium*(II). A solution of $RuCl_2(PPh_3)_2$ (0.6 g) and bipyrimidine (0.36 g) in acetone (50 cm^3) was refluxed for 6 h to give a reddish-brown precipitate which was filtered and dissolved in chloroform (100 cm^3). The solution was concentrated to 20 cm^3 and $[Ru(bipym)(PPh_3)_2Cl_2]$ crystallized out on cooling. The complex was recrystallized from chloroform; yield: 42%.

(4) *Dichlorobis(bipyrimidine)ruthenium*(II). The complex was prepared by refluxing $RuCl_3\cdot xH_2O$ (0.25 g) and bipyrimidine (0.3 g) in DMF (20 cm^3) for 2 h. The purple solution obtained was filtered and evaporated to dryness in a roto-evaporator. The dry mass was dissolved in 50 cm^3 of acetonitrile and concentrated to 10 cm^3, when black crystalline $[Ru(bipym)_2Cl_2]$ was obtained. The complex was recrystallized from water; yield: 62%.

(5) *Chlorobis(bipyrimidine)acetonitrileruthenium*(II) *hexafluorophosphate.* To a solution of [Ru(bipym)$_3$](PF$_6$)$_2$ (0.3 g) in CH_3CN (100 cm^3) was added slowly over 30 min, tetrabutyl ammonium chloride (TBA)Cl (0.07 g). The solution was irradiated at 350 nm when the orange-coloured solution started to turn deep red. After 3 h the excess of acetonitrile was removed over a roto-evaporator and the crude product was digested in boiling propanol. The residue was dissolved in acetone (20 cm^3), and on cooling dark red crystalline [Ru(bipym)$_2$(CH_3CN)(Cl)]PF$_6$ separated out. The complex was recrystallized from water; yield: 37%.

(6) *Bis(dinitrito)bis(bipyrimidine)ruthenium*(II). A solution of Ru(bipym)$_2$Cl$_2$ (0.2 g) and $NaNO_2$ (0.4 g) in a 1 : 1 ethanol–water mixture (30 cm^3) was refluxed for 8 h and the orange solution turned deep red. The deep red solution was concentrated and the complex precipitated by an excess of acetone, when red crystals of [Ru(bipym)$_2$(NO_2)$_2$]·0.5 H_2O were obtained. The complex was recrystallized from a water–alcohol mixture; yield: 78%.

Acetonitrile was distilled over anhydrous $AlCl_3$ and P_2O_5. Tetrabutylammonium chloride was used without purification. Bipyrimidine and tetrabutylammonium chloride was used as purchased from Lancaster Chemicals and Aldrich without further purification. $RuCl_2(Me_2SO_4)$ was prepared as reported earlier.[15] Photoanation studies were conducted using a 450 W Xenon lamp from Applied photo physics in a quartz cell of 1 cm path length. All the solutions were made in double-distilled water or acetonitrile. Fresh stock solutions were prepared for spectroscopic studies.

Electrochemical studies were conducted on a PAR Model 174 electrochemical analyser using DME. The solutions contained 9×10^{-4} M ruthenium complex in 0.1 M KNO_3 as the supporting electrolyte. All measurements were performed at 26°C in degassed (N_2) aqueous solution and all potentials are reported against a SCE.

Electronic spectra of all the complexes were recorded with a Beckman DU-7 UV–vis spectrometer. IR spectra were recorded on a Nicolet 200 SX FT–IR spectrophotometer. Fluorescence emission spectra were recorded on a Hitachi Model 650 Fluorometer with microprocessor. Irradiation of a vacuum degassed solution of [Ru(bipym)$_3$](PF$_6$)$_2$ (8.0×10^{-5} M) and (TBA)Cl (2×10^{-4} M) was carried out in a 1 cm quartz cell under N_2. The light source was a 450 W xenon lamp with an interference filter of 436 nm for photoanation of **2**. The light intensity was calculated using ferrioxalate actinometry.[16] The photolysis was interrupted periodically and the absorption spectra recorded. Quantum yields were calculated on the basis of the disappearance of the peak corresponding to Ru(bipym)$_3^{2+}$ at 30,120 cm^{-1}.

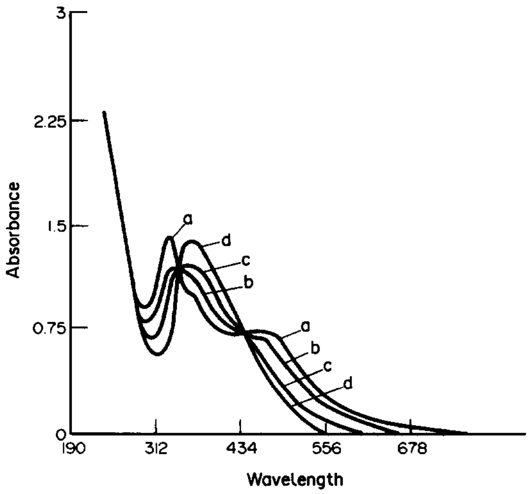

Fig. 1. Absorption spectrum of photoanation studies, Ru(bipym)$_3^{2+}$ (10^{-5} M) and (TBA)Cl (10^{-4} M) in acetonitrile: (a) without illumination; (b) 5 min; (c) 30 min; (d) 45 min for illuminated.

For the photoanation studies a solution of the complex [Ru(bipym)$_3$](PF$_6$)$_2$ (**2**) in acetonitrile is relatively stable when irradiated at λ = 436 nm even in the presence of Cl$^-$. However, on irradiation at 350 nm in the presence of Cl$^-$, photoanation takes place as shown in Fig. 1. Figure 1 shows the spectrum of a typical photoanation experiment. The presence of two isobestic points at 356 and 456 nm suggests the formation of two intermediates but only one photoproduct could be isolated. Photolysed solutions of **2** in the presence of Cl$^-$ were extracted with hexane. The UV–vis spectrum before and after hexane extraction showed no change in the position of MLCT bands and a drop in intensity and a narrowing of the ligand π–π^* bands. The hexane extract was evaporated and the melting point and UV–vis spectrum of the residue confirmed the product to be bipyrimidine. The elemental analysis of the photoproduct agrees with the formation [Ru(bipym)$_2$(CH_3CN)(Cl)]PF$_6$.

The photolysis at 359 nm seems to give rise to an ion-paired five-coordinate intermediate [Ru(bipym)$_2$bipy)]$^+$Cl$^-$ (**1**), where one of the bipyrimidines is monodentate. This intermediate then collapses to the product [Ru(bipym)$_2$(CH_3CN)(Cl)]PF$_6$ (**5**). Irradiation at 350 nm seems to be essential to obtain **1** since irradiation at 450 nm cannot give the photoanation product.

REFERENCES

1. K. Kalyanasundaram, *Coord. Chem. Rev.* 1979, **46**, 159.

2. R. J. Crutchley and A. B. P. Lever, *J. Am. Chem. Soc.* 1980, **102**, 7128.
3. R. J. Crutchley, N. Kress and A. B. P. Lever, *J. Am. Chem. Soc.* 1983, **105**, 1170.
4. M. Hunziker and A. Lundi, *J. Am. Chem. Soc.* 1977, **99**, 7370.
5. Shin-ichi Ishiguro, Hides Wada and Hitoshi Ohtaki, *Bull. Chem. Soc. Jpn* 1985, **58**, 982.
6. B. Crociani, F. Bibianca, A. Giovenco and S. Scri Vanti, *J. Organomet. Chem.* 1985, **291**, 259.
7. R. J. Crutchley and A. B. P. Lever, *Inorg. Chem.* 1983, **22**, 2647.
8. R. J. Crutchley and A. B. P. Lever, *Inorg. Chem.* 1982, **21**, 2276.
9. R. F. Jones and D. J. Cole-Hamilton, *Inorg. Chim. Acta* 1981, **53**, L3.
10. M. Gleria, F. Minto, G. Beggiato and P. Bortous, *J. Chem. Soc., Chem. Commun.* 1978, 285.
11. P. E. Hoggard and G. B. Porter, *J. Am. Chem. Soc.* 1978, **100**, 1457.
12. J. Van Houten and R. J. Watts, *Inorg. Chem.* 1978, **17**, 3381.
13. B. Durham, J. L. Walsh, C. L. Carter and J. J. Meyer, *Inorg. Chem.* 1980, **19**, 860.
14. P. G. Bradley, N. Kress, B. A. Horbuyer, R. F. Dallinger and W. H. Woodruff, *J. Am. Chem. Soc.* 1981, **103**, 7441.
15. I. P. Ivan and G. Wilkinson, *J. Chem. Soc., Dalton Trans.* 1973, 204.
16. C. G. Hatchard and C. A. Parker, *Proc. R. Soc. A.* 1956, **235**, 518.