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Synthesis, spectroscopic, electrochemical and luminescence studies of ruthenium (II) polypyridyls containing multifunctionalized 1,2,4-triazole as co-ligand

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Abstract. Ruthenium (II) 2,2′-bipyridyl and 1,10-phenanthroline complexes with 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (LH_2) as co-ligand were synthesised and characterized by elemental analysis, IR, UV/Vis, ^1H NMR spectra and FAB-mass data. The electrochemical and luminescent properties of the complexes were also studied.

Keywords. Ruthenium (II) polypyridyls; 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole; N_2-complex.

1. Introduction

Substituted 1,2,4-triazoles have attracted attention owing to their bactericidal[1], fungicidal[2] and pharmacological activities[3,4] in addition to their uses as antiulcer[5] and blood-pressure-lowering agents[6]. Furthermore, it is known[7,8] that $RuCl_3.3H_2O$ reacts with hydrazine to form its N_2 complex which is of great interest in the chemistry of N_2 fixation. Triazoles are also the subject of extensive studies in view of their synthetic properties and other theoretical aspects[9]. Ruthenium (II) polypyridyl complexes have opened a new door for enthusiastic researchers since they act as probes for DNA and hence are potential therapeutic agents[10]. Thus, in view of these facts and in continuation of our earlier studies[11], we selected the commercially available 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole as co-ligand since it possesses properties that can be exploited for use as complexing agent with ruthenium (II) polypyridyls. Our surmise that the hydrazino part of this ligand could be converted into N_2 also enthused us to take up the present investigation.

2. Experimental

2.1 *Materials and physical measurements*

All solvents were distilled prior to use. 4-Amino-3-hydrazino-5-mercapto-1,2,4-triazole, 2,2′-bipyridine, 1,10-phenanthroline, lithium-chloride and $RuCl_3.3H_2O$ were purchased

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from Aldrich and used as supplied, whereas *cis*-Ru(bpy)$_2$Cl$_2$.2H$_2$O (bpy = 2,2′-bipyridine) and Ru(Phen)$_2$Cl$_2$ (Phen = 1,10-phenanthroline) were prepared following the procedure reported[12] by Meyer *et al*. The complexes of ruthenium (II) were prepared under N$_2$ atmosphere and the progress of reaction was monitored by TLC. The complexes were purified by column chromatography using neutral alumina as support.

Microanalyses and FAB-mass data were carried out at the Central Drug Research Institute, Lucknow using Carlo Erba Elemental Analyser 1108 and JEOL SX−102 respectively. Absorption, luminescence and electrochemical studies were carried out at the University of Tokyo, Japan. IR spectra of the triazole and its ruthenium (II) polypyridyl complexes were recorded in the region 4000–400 cm^{-1}, using Perkin–Elmer 783 spectrophotometer whereas ^{1}H NMR spectra (DMSO-d_6) were recorded on JEOL *Fx* 90Q spectrometer.

2.2 *Ligand and complexes*

Commercially available 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (LH$_2$) was used as the ligand for all the complexes. Ruthenium (II) polypyridyl complexes were synthesized following the general procedure reported[11] earlier.

2.2a *[Ru$_2$L(bpy)$_4$] (PF$_6$)$_2$ 2DMSO* (**1**): An ethanolic solution of Ru(bpy)$_2$Cl$_2$.2H$_2$O (0·520 g, 1 mmol) was mixed with a clear solution of the ligand LH$_2$ (0·073 g, 0·5 mmol) in DMSO (5 ml). The resulting solution was refluxed for 25 h, and then filtered after keeping overnight at room temperature. The concentrated filtrate was precipitated by the addition of saturated aqueous solution of NH$_4$PF$_6$, the crystalline solid thus obtained collected by centrifugation, then washed with water and ethanol, and finally with diethyl ether.

2.2b *[Ru(N$_2$)(Phen)$_2$ DMSO] (PF$_6$)$_2$ DMSO* (**2**): An ethanolic solution of Ru(Phen)$_2$Cl$_2$ (0·532 g, 1 mmol) was mixed with a clear solution of the ligand LH$_2$ (0·073 g, 0·5 mmol) in DMSO (5 ml). After refluxing the solution for 25 h, the complex was isolated adopting a procedure similar to that discussed in §2.2a.

2.2c *Purification:* Both ruthenium (II) complexes thus obtained were purified using column chromatography on neutral alumina support, using MeCN as eluent. The solid mass from the respective eluates, after evaporation of solvent, was dissolved in acetone then reprecipitated by addition of a saturated aqueous solution of NH$_4$PF$_6$. The crystalline solids obtained for both complexes were washed successively with water, ethanol and diethyl ether, and finally dried under vacuum.

The analytical data along with the physical properties of the complexes are reported in table 1.

3. Results and discussion

Based on elemental (C, H, N) analysis and FAB-mass data, molecular compositions assigned to the ruthenium (II) complexes are shown in table 1. The complexes are thermally stable and soluble in MeCOMe, MeCN, DMF and DMSO.

Table 1. Analytical data and physical properties of ruthenium (II) complexes.

			Elemental analyses found (calc.)			UV-Vis spectral data		Emission data*		
Colour	Yield (%)	FAB–mass found (calc.)	C	H	N	$l_{\max}$ (nm)	(10^{-3} *e*, M^{-1} cm^{-1})	$l_{\max}$ (nm)	$I^{\#}_{\mathrm{Rel}}$ (em)	$f \times 10^3$ (quantum yield)
Reddish-brown	56	1115 (1115)[M-PF_6^-]$^+$	39·31 (38·98)	3·88 (3·39)	13·86 (13·84)	240	(14.1)	614·0	0·060	2·4
		970 (970)[M-2PF_6^-]				287	(33·8)			
		413 (413) [Ru(bpy)$_2$]				428	(4·1)			
Yellowish-brown	58	790 (790)[M-PF_6^-]$^+$	35·92 (35·93)	3·35 (2·99)	8·44 (8·98)	222	(35·2)			
		645 (645)[M-2PF_6^-]				263	(32·1)	596·0	0·265	10·6
		461 (461) [Ru(Phen)$_2$]				424	(3·2)			

°C. Solutions were 10^{-6} M for emission data relative[#] to $[Ru(bpy)_3]^{2+}$. (l_{ex} = 440 nm)

3.1 *IR spectra*

IR spectral peaks observed at 1280 and 1580 cm^{-1} for the free ligand (LH_2) were assigned[13,14] as *n*(C=S) and *n*(C=N), which were shifted to ~ 1250 and 1480 cm^{-1} respectively in the spectra of the complexes. This low energy shift supports their co-ordination with the metal ion. However, the IR spectrum of complex **2** shows an additional intense peak at 1992 cm^{-1} which was not observed in either the earlier complex or in the free ligand. This peak was assigned as *n*(N_2) in view of the earlier reports[9,15,16]. Furthermore, the IR spectrum of the complex isolated after reaction of free LH_2 with $RuCl_3$–$3H_2O$ also shows a strong peak at 1980 cm^{-1} due to *n*(N_2). Thus, in view of this observation, we consider that the ligand during complexation in DMSO is oxidized generating N_2, which then gets coordinated with the metal ion *in situ*. The additional peak observed at 1060 cm^{-1} was assigned to coordinated DMSO[17]; though the distinction between coordinated and uncoordinated DMSO cannot be made out due to the breadth of the peak.

When complex **2** is boiled with conc. HCl using the reported procedure[7], the anticipated peak due to *n*(N_2) disappears which further substantiates the presence of coordinated dinitrogen in **2**. Furthermore, in the lower region of the spectrum of this complex, a weak peak observed at ~ 420 cm^{-1} is not observed in the spectrum of the free ligand. This is considered to arise from *n*(Ru–N_2) vibration[18] whereas the peak due to *n* (PF_6^-) observed at ~ 840 cm^{-1} is consistent with our earlier report[11].

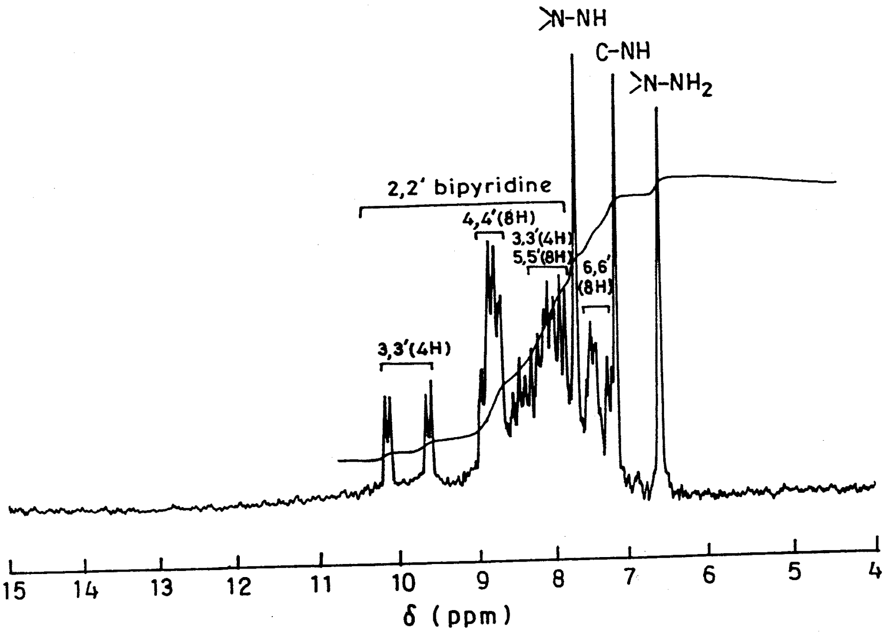
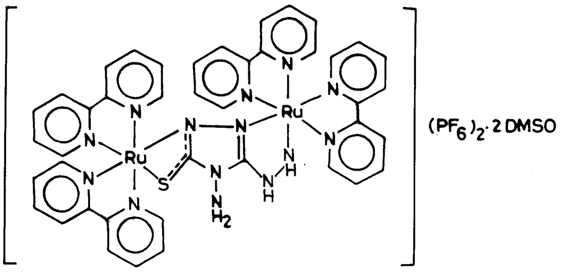
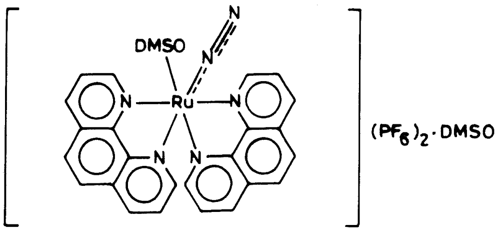


Figure 1. ^1H NMR spectrum of $[Ru_2L(bpy)_4(PF_6)_2$ in the region *d* (ppm) 4·0–15·0 in DMSO-d_6 at room temperature (~ 25°C).



$[Ru_2L(bpy)_4](PF_6)_2\cdot 2DMSO$ (1)



$[Ru(N_2)(phen)_2\ DMSO](PF_6)_2\ DMSO$ (2)

Figure 2. Proposed structures of Ru(II) complexes.

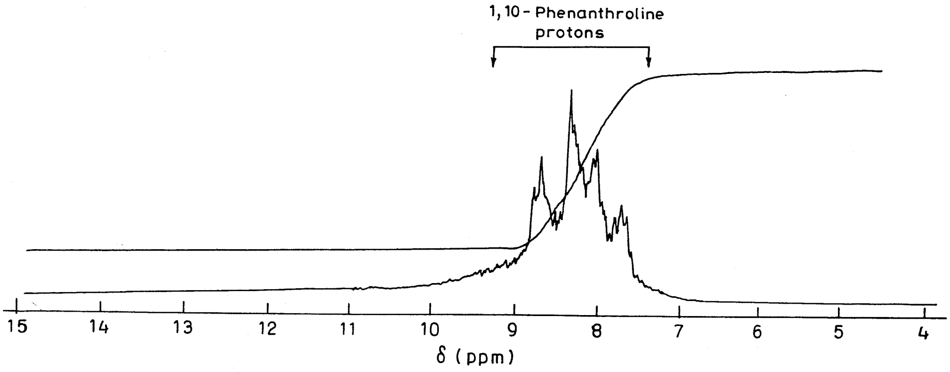


Figure 3. ^{1}H NMR spectrum of complex $[Ru(N_2)(phen)_2DMSO](PF_6)_2$ in the region *d* (ppm) 4·0–15·0 in DMSO-d_6 at room temperature (~25°C).

3.2 ^{1}*H NMR and UV-Vis spectra*

The proton NMR spectrum of the free ligand LH_2 recorded in DMSO-d_6 shows four singlets at *d* 4·0, 5·30, 7·10 and 12·50 ppm which were assigned[13,14] to $-NH_2$, $N-NH_2$ (ring), –NH and –NH–C=S protons respectively. These peaks were exchanged with D_2O but the free ligand peak at *d* 12·50 ppm disappears in the spectrum of complex **1** (figure 1)

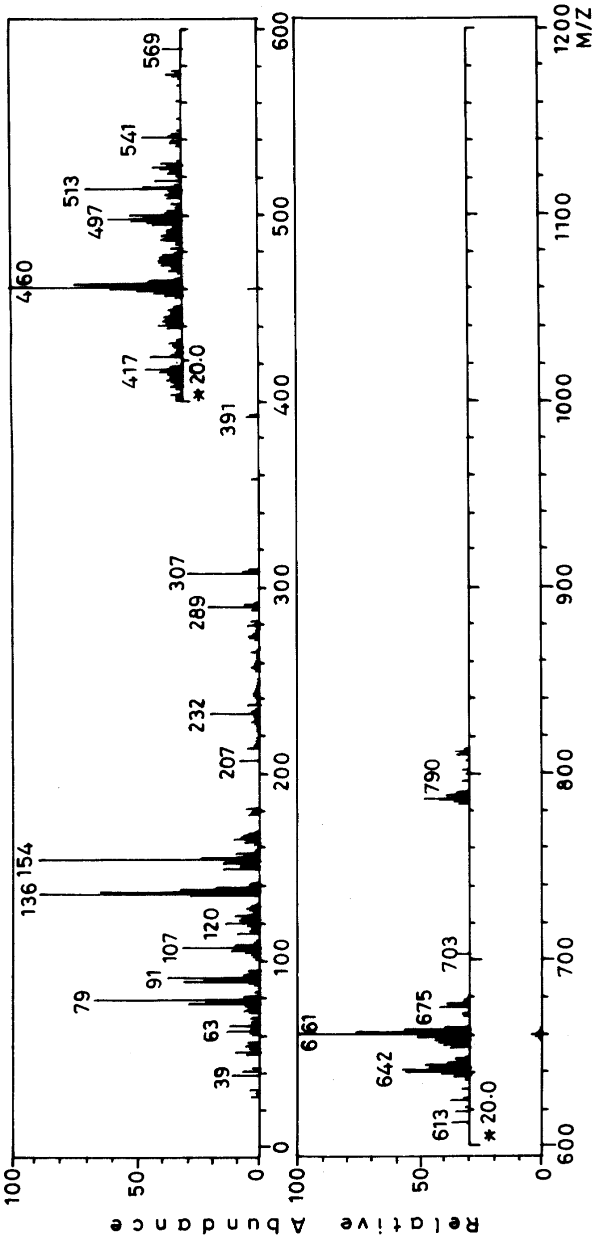


Figure 4. FAB-mass spectrum of complex $[Ru(N_2)(phen)_2DMSO](PF_6)_2.DMSO$.

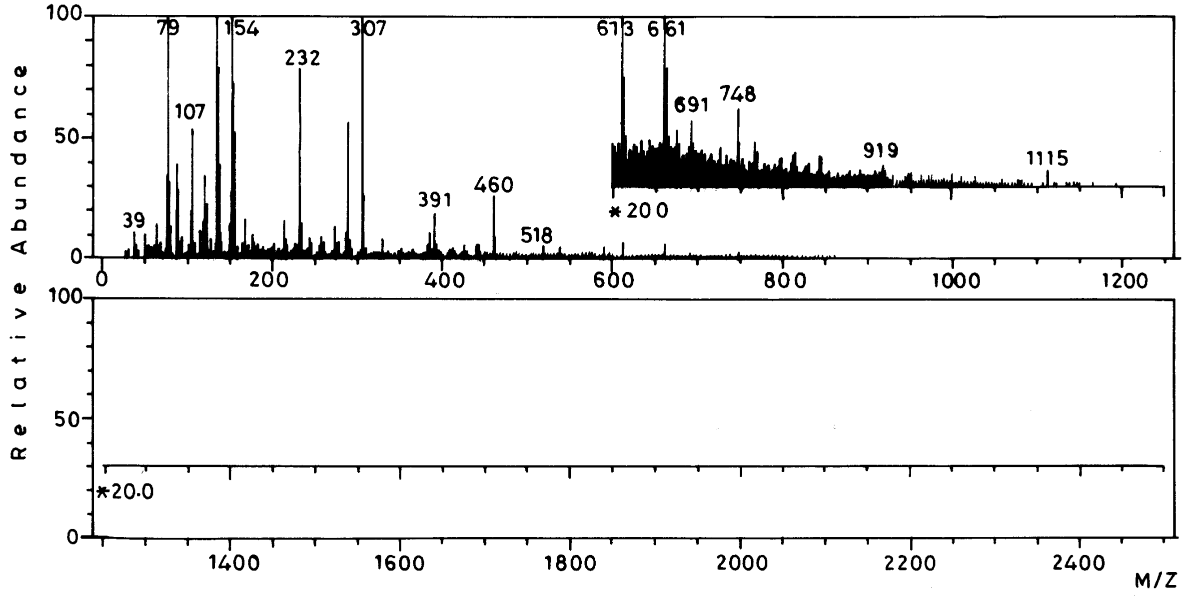


Figure 5. FAM-mass spectrum of complex $[Ru_2L(bpy)_4(PF_6)_2.2$ DMSO.

indicating that this proton is deprotonated during complexation with the metal ion. Peaks due to N–NH_2, NH–NH_2 and –NH protons observed at lower field, viz. *d* 6·60, 7·80 and 7·20 (ppm) respectively, could be understood in view of their coordination with the metal ion. The larger downfield shift of NH_2 protons and its integration area fitted with one proton suggests the structure of the ligand as shown in figure 2 and this further substantiated by the elemental composition showing $2PF_6^-$ per two ruthenium (II) ions.

The presence of the 2,2′ bipyridyl group in complex **1** was considered in view of the peaks observed in its spectrum at *d* 8·00, 8·80, 9·60 and 10·2 (ppm) due to 6,6′, 5,5′, 4,4′ and 3,3′ protons respectively in consonance with reported[19] values. It is further noticed that the ^1H NMR spectrum of the complex **2** (figure 3) does not show any peak due to ligand (LH_2) whereas multiplets due to phenanthroline protons are observed. This observation is further substantiated by its mass spectrum (figure 4) as compared to that obtained for complex **1** (figure 5). The additional peak observed at *d* 2·65 ppm was assigned to coordinated DMSO.

The UV/Vis spectral data of the complexes recorded in MeCN (10^{-5} M) as shown in table 1 indicates that the broad peak observed between 460–424 nm can be assigned to MLCT (M → polypyridyl) transition in view of an earlier report[11], whereas transition arising from LH_2 and polypyridyls cannot be distinguished owing to the overlapping regions.

Thus, in view of elemental (C, H, N) analysis, NMR (figures 1 and 3), FAB mass (figures 4 and 5) and other spectroscopic data, the proposed structures for the ruthenium (II) complexes are depicted in figure 2.

3.3 *Electrochemical and luminescence studies*

Cyclic voltammetric study for the ruthenium (II) complexes was carried out in MeCN (5×10^{-3} M) solution containing 0·1 M $[Bu_4N]^+$ ClO_4^- as supporting electrolyte using Ag/Ag^+ as reference and glassy carbon as working electrode. Complex **1** showed two quasi-reversible oxidations, centred at + 1·14 V and + 0·50 V (figure 6), most likely due to oxidation of two ruthenium (II) centres lying in two different environments as the free ligand did not show any oxidation in this region. Furthermore, complex **2**, showed only one irreversible metal-based oxidation Ru^{III}/Ru^{II} at + 1·18 V (figure 7). Reduction peaks observed at –1·77 and –1·46 V in the complex **1** as well as at – 1·75 and – 1·45 V in the complex **2** were assigned to reductions of bipyridyl and phenanthroline respectively in view of earlier reports[11,20,21].

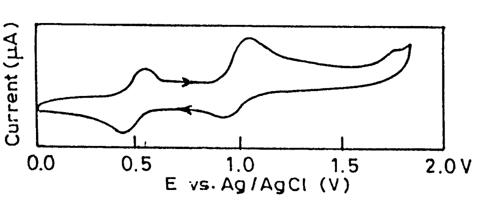


Figure 6. Cyclic voltammogram of $[Ru_2L(bpy)_4](PF_6)_2$.2 DMSO in MeCN solution ($5{\cdot}0 \times 10^{-3}$ M) using 0·1 M TBAP as supporting electrolyte, Ag/Ag^+ as reference electrode and glassy carbon as working electrode at scan rate = 400 m Vs^{-1}.

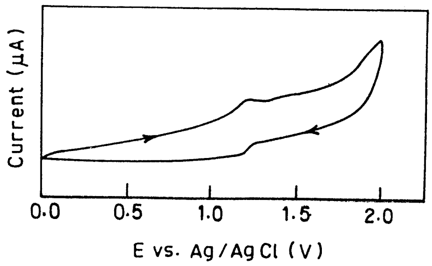


Figure 7. Cyclic voltammogram of $[Ru_2(N_2)(phen)_4](PF_6)_2$.2 DMSO in MeCN solution ($5{\cdot}0 \times 10^{-3}$ M) using 0·1 M TBAP as supporting electrolyte, Ag/Ag^+ as reference electrode and glassy carbon as working electrode at scan rate = 400 m Vs^{-1}.

Luminescence data shown in table 1 indicate that dinuclear ruthenium (II) 2,2′-bipyridyl and mononuclear ruthenium (II) 1,10-phenanthroline complexes emit at 614 and 596 nm respectively when they are excited at 440 nm. The observed intense luminscence from the mononuclear ruthenium (II) complex as compared to that from the dinuclear ruthenium (II) complex is consistent with the earlier report[22].

4. Conclusion

Oxidation of hydrazino ligand (LH_2) in presence of $Ru(Phen)_2$ unit can be understood in terms of planarity and rigidity of 1,10-phenanthroline ring as compared to that of the 2,2′-bipyridine ring[23]. However, this surmise calls for further and more in-depth investigation.

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References

1. Patti S A, Bodiger B M, Kudasi S M and Kulkarni V H 1984 *J. Indian Chem. Soc.* **61** 713
2. Ram V J, Dube V, Pieters L A C and Vlietinck A J 1989 *J. Heterocycl. Chem.* **26** 625
3. Kane J M, Dudley M W, Sorenson S M and Miller F P 1988 *J. Med. Chem.* **31** 1253
4. Sung K and Lee A 1992 *J. Heterocycl. Chem.* **29** 1101
5. Sinha A K, Rastogi S N, Patnaik G K and Srimal R C 1993 *Indian J. Chem.* **B32** 738
6. Leclerc G, Amlaiky N and Rout B 1989 *Eur. J. Med. Chem.* **17** 69
7. Cotton F A and Wilkinson G 1988 *Advanced inorganic chemistry* (New York: John Wiley) p. 887
8. Douglas B, Daniel D M and Alexander J 1994 *Concepts and models of inorganic chemistry* (New York: John Wiley) p. 749
9. Deeth R J and Langford S A 1995 *J. Chem. Soc., Dalton Trans.* 1
10. Hartshorn R M and Barton J K 1992 *J. Am. Chem. Soc.* **114** 5919
11. Mishra L, Yadaw A K, Choi C S and Araki K 1999 *Indian J. Chem.* **A38** 339
12. Sullivan B P, Salmon D J and Meyer T J 1978 *Inorg. Chem.* **17** 3334
13. Iqbal R, Rama N H, Ahmad N, Zamani K, Ebrahim S and Iqbal N 1998 *Indian J. Chem.* **B37** 506
14. Gupta R, Paul S, Gupta A K, Kachroo P L and Bani S 1998 *Indian J. Chem.* **B37** 498
15. Chatt J, Jonathan R D and Raymond L R 1978 *Chem. Rev.* **78** 589

16. Nakamoto K 1978 *Infrared and Raman spectra of inorganic and coordination compounds* (New York: John Wiley) p. 301
17. Nakamoto K 1978 *Infrared and Raman spectra of inorganic and coordination compounds* (New York: John Wiley) p. 345
18. Allen A D, Bottomley F, Harrish R O, Reinsalu V P and Senaff C V 1967 *J. Am. Chem. Soc.* **89** 5595
19. Mishra L, Choi C S and Araki K 1997 *Chem. Lett.* 447
20. Beer P D, Dent S W, Fletcher N C and Wear T J 1996 *Polyhedron* **15** 2983
21. Lawrence G A 1985 *Polyhedron* **4** 817
22. Boyd S, Strouse G F, Jones W E and Meyer T J 1990 *J. Am. Chem. Soc.* **112** 7395
23. Sammes P G and Yahioglu G 1994 *Chem. Soc. Rev.* **23** 327