Complexation properties of a heteroditopic cryptand towards Cu^{II} and Ni^{II}, crystal structures of the cryptand and its nickel(II) cascade complex †

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The crystal structure of the heteroditopic cryptand (L) formed by Schiff-base condensation of tris(2-aminoethyl)amine and 2,2′,2″-nitrilotris(ethyleneoxy)tris(benzaldehyde) followed by reduction with NaBH$_4$ has been determined. The molecule has an *endo-endo* conformation with a pseudo-three-fold symmetry axis passing through the two bridgehead nitrogens. This symmetry is maintained in chloroform solution as indicated by its ^{1}H NMR spectrum. The cryptand accepts a metal ion (Cu^{II}, Zn^{II} or Ni^{II}) inside the cavity forming mononuclear cryptates of general formula [ML][ClO$_4$]$_2$. The metal ion occupies the N$_4$ end of the cavity. The light blue CuN$_4$ chromophore thus formed exhibits an axial EPR spectrum with very small $A_\parallel$ value (63×10^{-4} cm^{-1}) and a low-energy ligand-field band. Nickel(II) initially forms a blue [NiL][ClO$_4$]$_2$ complex which on dissolving in moist MeCN solution crystallizes as purple rectangular parallelopipeds with the formulation [NiL(H$_2$O)(MeCN)][ClO$_4$]$_2$·H$_2$O·2MeCN. The crystal structure of this complex has also been determined. The Ni^{II} ion is octahedrally co-ordinated with the equatorial sites occupied by the three secondary amino N atoms of the cryptand and the N atom of the bound MeCN. The axial sites are occupied by the bridgehead N and the O atom of the water molecule which enters the cavity forming a cascade complex.

The synthesis of macropolycyclic compounds with recognition site(s) for transition-metal ions is a subject of considerable current interest [1-10] due to their use in many research areas. It has been observed, that macrobicyclic cryptands incorporating nitrogen donors readily accept transition-metal ion(s) inside their cavities forming cryptates. We have been involved [11-13] in synthesizing heteroditopic cryptands through [1 + 1] Schiff-base condensation of tripodal triamines with tripodal trialdehydes. Only one end of the cavity of such a cryptand is recognized by transition-metal ions leaving the other end vacant. Such cryptates are useful in homogeneous catalysis, [14] or in stabilizing metal–ligand bonds which are otherwise unstable. [13] Besides, they are well suited for studying chelation-enhanced fluorescence, [15] and for making ordered structures like vesicles, [16] *etc.* It is, therefore, important to probe the metal-binding abilities of the heteroditopic cryptands. Here we describe an improved synthesis of a heteroditopic cryptand (L) and its complexing properties towards Cu^{II} and Ni^{II}. The structures of L and of the nickel(II) cryptate, [NiL(H$_2$O)(MeCN)][ClO$_4$]$_2$·H$_2$O·2MeCN, are also described. The latter provides the first example of a water molecule bonded to the metal ion inside the cavity in a cascade fashion. A copper(II) ion bonded to a water molecule inside the cavity of an oxaaza macrobicycle has been reported previously. [17]

Experimental

Reagent-grade chemicals (Aldrich) were used as provided. All the solvents (SD Fine Chemicals, India) were purified prior to use. Spectroscopic and microanalytical data for the complexes were collected as described [18] earlier.

Preparations

Cryptand L. The synthesis of L by tripod–tripod Schiff-base condensation in the presence of Cs^I/Rb^I as the templating metal ion has been reported [11] by us. An improved method on the multigram scale without involving any templating metal ion is
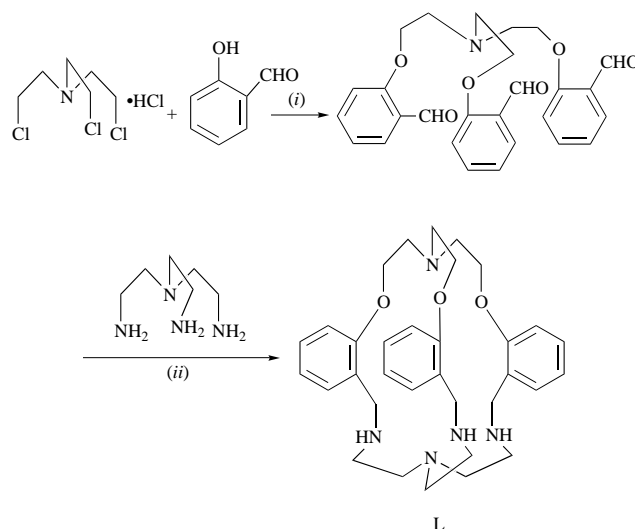
Scheme 1 (*i*) NaOH, EtOH, reflux; (*ii*) 5 °C, MeOH + thf, NaBH$_4$ *in situ*

described here. In a typical experiment, the tripodal trialdehyde (Scheme 1) (3.68 g, 8 mmol) dissolved in a mixture of dry MeOH (500 cm^3) and dry tetrahydrofuran (thf) (50 cm^3) was cooled to 5 °C. To this was added a solution of tris(2-aminoethyl)amine (1.17 g, 8 mmol) in MeOH (300 cm^3) over a period of 12 h with constant stirring while maintaining the temperature at 5 °C. After the addition was complete the light yellow solution was allowed to warm to room temperature and kept for another 4 h. The Schiff base formed was not isolated but immediately treated with an excess of solid NaBH$_4$ (≈1.6 g) and refluxed for 2 h. After complete removal of the solvent the white solid left was shaken with water (40 cm^3) and the desired cryptand (L) was extracted with CHCl$_3$ (4 × 50 cm^3). The organic layer after drying over anhydrous Na$_2$SO$_4$ was completely evaporated to obtain L as a colourless solid in 65% yield, m.p. 144 °C (uncorrected). NMR (CDCl$_3$): ^{1}H (80 MHz), δ 2.5 (m, 12 H), 3.2 (t, 6 H), 3.6 (s, 6 H), 4.1 (t, 6 H) and 7.1 (m, 12 H);

† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

^{13}C (20.1 MHz), δ 47.06, 48.60, 54.37, 55.30, 67.55, 111.29, 120.63, 127.16, 128.70, 131.33 and 156.35. FAB mass spectrum: m/z 560 (L$^+$) (Found: C, 70.25; H, 8.3; N, 12.4. $C_{33}H_{45}N_5O_3$ requires C, 70.8; H, 8.1; N, 12.5%). Colourless X-ray-quality crystals of L were grown by slow evaporation of an acetonitrile solution at room temperature.

[CuL][ClO$_4$]$_2$ 1. A solution of [Cu(H$_2$O)$_6$][ClO$_4$]$_2$ (0.18 g, 0.5 mmol) in MeOH (15 cm^3) was added to a stirred solution of L (0.28 g, 0.5 mmol) dissolved in MeOH (15 cm^3) at room temperature. A blue solid precipitated immediately and was filtered off, washed with MeOH and dried *in vacuo*. Yield 82% (Found: C, 48.15; H, 5.45; N, 8.6. $C_{33}H_{45}Cl_2CuN_5O_{11}$ requires C, 48.2; H, 5.5; N, 8.5%). FAB mass spectrum: m/z 723 (**1** − ClO$_4^-$) and 623 (**1** − 2ClO$_4^-$).

[NiL][ClO$_4$]$_2$ 2. This complex was prepared as above by treating [Ni(H$_2$O)$_6$][ClO$_4$]$_2$ with L in warm (40 °C) MeOH. It was isolated as a blue solid in 68% yield upon partial evaporation of the solvent and dried *in vacuo* (Found: C, 48.65; H, 5.5; N, 8.4. $C_{33}H_{45}Cl_2N_5NiO_{11}$ requires C, 48.5; H, 5.55; N, 8.55%). FAB mass spectrum: m/z 717 (**2** − ClO$_4^-$) and 617 (**2** − 2ClO$_4^-$). When the light blue solid was dissolved in moist MeCN the solution gradually changed to purple overnight. X-Ray-quality crystals (**2a**) were grown upon slow evaporation of this purple solution at 5 °C.

[CuL(N$_3$)][ClO$_4$] 3. Complex **1** (0.21 g, 0.25 mmol) was dissolved in MeCN (20 cm^3) and stirred with a solution of NaN$_3$ (0.16 g, 0.25 mmol) in water (2 cm^3). The solution immediately changed to dark green which on evaporation afforded a green solid in 75% yield (Found: C, 50.95; H, 5.7; N, 14.45. $C_{33}H_{45}ClCuN_8O_7$ requires C, 51.85; H, 5.95; N, 14.65%). FAB mass spectrum: m/z 723 (**3** − N$_3^-$) and 623 (**3** − N$_3^-$ − ClO$_4^-$).

[NiL(N$_3$)][ClO$_4$] 4. This complex was prepared by treating **2** with NaN$_3$ in 1:1 molar ratio as in the case of **3**. The solution immediately changed to purple and a purple solid precipitated gradually and was filtered off and dried *in vacuo*. Yield 65% (Found: C, 52.3; H, 5.75; N, 14.4. $C_{33}H_{45}ClN_8NiO_7$ requires C, 52.15; H, 5.95; N, 14.75%). FAB mass spectrum: m/z 717 (**4** − N$_3^-$) and 617 (**4** − N$_3^-$ − ClO$_4^-$).

CAUTION: Care should be taken while treating organic compounds with metal perchlorates as potentially explosive mixtures may be formed.

X-Ray crystallography

Crystallographic data for compounds L and **2a** are listed in Table 1. In the case of L a crystal of suitable size was mounted on a glass fibre with epoxy cement. For **2a** a crystal was sealed inside a Lindemann capillary containing a small amount of the mother-liquor. Cell parameters and reflection intensities were measured at 298 K on an Enraf-Nonius CAD4-mach diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods and completed by Fourier-difference syntheses. All non-hydrogen atoms were anisotropically refined by full-matrix least-squares calculations based on F. In each case a few H atoms could be located in the subsequent Fourier-difference maps while others were added at calculated positions. For **2a** the H atoms of the water molecule inside the cavity could be located in the Fourier-difference map. Hydrogen atoms were given a fixed U_{eq} (0.2 for L, 0.1 Å^2 for **2a**). Their positions or thermal parameters were not refined. Computations were made with the XTAL 3.2 program package[19] on a 486-DX personal computer (IBM compatible, PCL, India). Selected bond lengths and angles for both structures are collected in Table 2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/384.

Results and Discussion

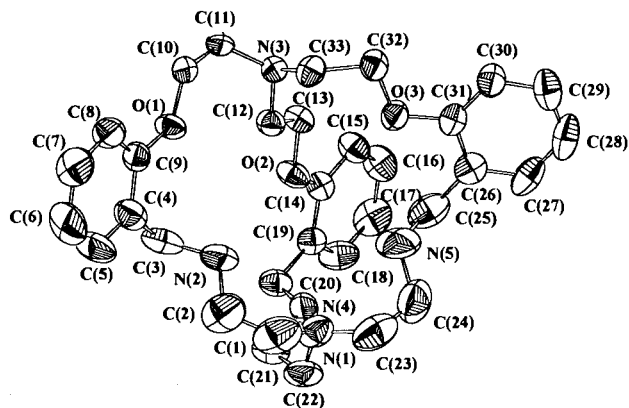The cryptand readily forms mononuclear complexes with Cu^{II},

Table 1 Crystallographic and refinement data for L and complex **2a** *

	L	2a
Formula	$C_{33}H_{45}N_5O_3$	$(C_{35}H_{50}Cl_2N_6NiO_{12})\cdot$H$_2$O·2CH$_3$CN
M	559.758	976.558
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
a/Å	10.133(2)	13.937(4)
b/Å	11.972(3)	14.547(3)
c/Å	13.433(3)	22.951(7)
$α$/°	106.69(2)	
$β$/°	90.93(2)	
$γ$/°	91.38(2)	
U/Å^3	1560(1)	4653(2)
Z	2	4
D_c/g cm^{-3}	1.192	1.394
$μ$/mm^{-1}	0.08	0.61
Crystal size/mm	0.20 × 0.30 × 0.30	0.20 × 0.20 × 0.15
Transmission (maximum, minimum)	0.9771, 0.9658	0.8745, 0.8360
hkl Ranges	0–15, −14 to ⩽14, −30 to 30	0–16, 0–17, 0–27
Total reflections measured	5808	4589
No. unique reflections	5467	4563
No. reflections used $[I > 2σ(I)]$	2987	2935
No. variables	370	560
R	0.060	0.060
R'	0.054	0.052
Goodness of fit	2.968	2.625
Largest and mean shift/e.s.d.	0.001, 0.0006	0.003, 0.0006
Minimum, maximum peak in Fourier map/e Å^{-3}	−0.42, +0.45	−0.46, +0.53

* Details in common: θ–2θ scans, range 0.80 + 0.35 tan θ; 2θ range 2–50°; $R = \Sigma \|F_o| - |F_c\|/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$, $w = 1/σ(F)$.

Table 2 Selected bond lengths (Å), angles (°) and non-bonded distances (Å)

Complex 2a

Ni–O(1w)	2.042(6)	Ni–N(4)	2.147(5)
Ni–N(1)	2.063(7)	Ni–N(5)	2.180(5)
Ni–N(2)	2.167(6)	Ni–N(61)	2.152(4)

N(1)–Ni–O(1w)	175.6(2)	N(2)–Ni–N(61)	86.69(4)
N(1)–Ni–N(2)	84.87(2)	N(4)–Ni–N(5)	101.86(5)
N(1)–Ni–N(4)	84.04(4)	N(4)–Ni–N(61)	177.55(3)
N(1)–Ni–N(5)	84.85(3)	N(4)–Ni–O(1w)	93.74(2)
N(1)–Ni–N(61)	95.37(2)	N(5)–Ni–O(1w)	98.48(3)
N(2)–Ni–O(1w)	92.26(3)	N(5)–Ni–N(61)	80.44(4)
N(2)–Ni–N(4)	90.89(2)	N(61)–Ni–O(1w)	86.73(4)
N(2)–Ni–N(5)	162.68(5)		

	L	2a
N(1)···N(3)	6.249(5)	6.410(6)
N(2)···N(4)	4.036(6)	3.082(5)
N(2)···N(5)	4.336(5)	4.295(7)
N(4)···N(5)	3.536(5)	3.354(4)
O(1)···O(2)	4.862(7)	4.603(6)
O(1)···O(3)	5.365(5)	5.450(6)
O(2)···O(3)	3.992(3)	3.602(4)
H(1)O(w)···N(3)		3.118(4)
H(1)O(w)···O(1)		3.282(5)
H(2)O(w)···O(1)		2.988(4)
H(2)O(w)···O(3)		2.535(5)
H(2)O(w)···N(3)		2.013(5)

Fig. 1 An ORTEP[22] drawing of L showing the thermal ellipsoids and the atomic numbering scheme. Hydrogen atoms are omitted for clarity
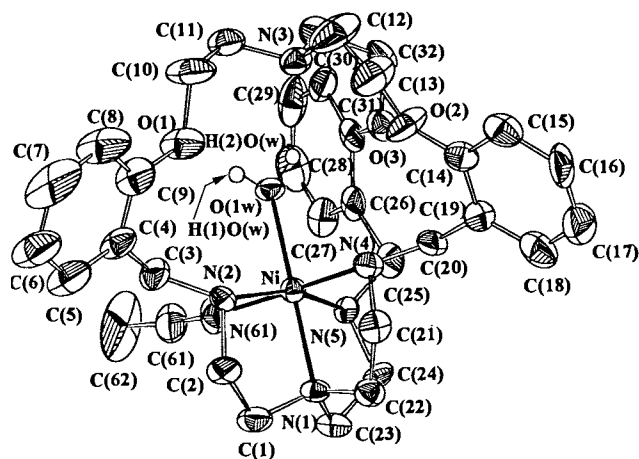

Fig. 2 An ORTEP[22] drawing of complex **2a**. Details as in Fig. 1

Table 3 Ligand-field bands, magnetic and EPR spectral data for the cryptates

Cryptate	λ(d–d) [a]/nm	μ_eff/μ_B [b]	g∥	g⊥	$10^4 A_∥$/cm^{-1}
1	990 (sh)	1.89	2.07 (g_{av}) [c]		
	810 (335)		2.12 [d]	2.07	63
	680 (260)		2.18 [e]	2.06	95
	415 (430)				
2	940 (20)	2.98			
	565 (15)				
	360 (55)				
2a	960 (25)				
	870 (20)				
	560 (30)				
3	805 (175)	2.04	2.09 (g_{av}) [c]		
	670 (250)		2.03 [d]	2.13	65
			2.01 [e]	2.26	64
4	950 (15)	3.07			
	570 (15)				

[a] Electronic spectra of **1**–**4** at 298 K in MeOH or in MeCN; molar absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are in parentheses. [b] At 298 K. [c] Solid sample at 298 K. [d] In MeCN at 298 K. [e] In MeCN glass at 77 K.

(H_2O) [25] bond distances are within normal ranges. The non-bonding distances between the secondary amino N atoms are only slightly shorter than those in L (Table 2). Hence, there is a high degree of preorganization of the cryptand prior to metal binding.

For complex **1** in MeOH the ligand-field band positions and their intensities (Table 3) are similar to those obtained for a copper(II) cryptate where the co-ordination geometry is[26] distorted trigonal pyramidal. The corresponding bands of **3** are consistent with a trigonal-bipyramidal geometry.[27,28]

The nickel cryptate **2** in MeOH shows three weak ligand-field bands. The geometry around the Ni^{II} is probably distorted trigonal pyramidal (when H_2O and the MeCN are not bonded as in **2a**). While pseudo-tetrahedral NiN$_4$ complexes are rare,[29] no nickel(II) complex with a distorted trigonal-pyramidal geometry is known. The bands shift gradually when exposed to moist air and correspond[30] to that obtained for a typical octahedral nickel(II) complex (Table 3). In case of **4** the electronic spectral data compare well[31] with those for high-spin trigonal-bipyramidal nickel(II) complexes.

The effective magnetic moments (μ_eff/μ_B) for the copper(II) cryptates after diamagnetic corrections range between 1.89 and 2.04 at 301 K consistent with[32] discrete, mononuclear formulations for these complexes. For the nickel(II) cryptates **2** and **4**, μ_eff is 2.98 and 3.07 μ_B respectively consistent with four-[33] and five-[31]-co-ordination. Both **1** and **3** display broad EPR signals (Table 3) in the solid state at 298 K which become sharper at 77 K without revealing any fine structure. Complex **1** in MeCN (*ca.* 1 × 10^{-3} mol dm^{-3}) at 298 K exhibits an axial spectrum. In acetonitrile glass (77 K) the signal is still axial although with significant changes in the g∥ and A∥ values. This type of behaviour has been observed previously[26] and is attributable to a change in the ligand superstructure or solvent co-ordination at low temperature. In case of **3** the EPR parameters in MeCN at 298 and 77 K are consistent[27] with a distorted trigonal-bipyramidal geometry.

Conclusion

The cryptand L recognizes Cu^{II} and Ni^{II} at the N$_4$ end of the cavity forming four-co-ordinate mononuclear cryptates with the other end vacant. The nickel(II) cryptate accepts a water molecule inside the cavity which binds, the H atoms of which are bonded to two of the ether O and bridgehead N atoms. The strong tendency of Ni^{II} to six-co-ordination is manifested in the crystal structure of the nickel(II) cryptate where the metal ion

1, and Ni^{II}, **2**, as their perchlorate salts. When **1** and **2** are allowed to react with NaN$_3$ in 1:1 molar ratio, five-co-ordinate cascade complexes [CuL(N$_3$)][ClO$_4$] **3** and [NiL(N$_3$)][ClO$_4$] **4** are formed respectively with the azide group directly bonded to the metal ion. For **3** and **4**, ν_asym shows[20] blue shifts of about 25 cm^{-1} with respect to the free azide group and compares well with the literature data.[21] Complexes **1**–**4** exhibit a strong and broad peak at 1100 cm^{-1} attributable to ionic perchlorates. The molar conductivity values in MeCN (*ca.* 1 × 10^{-3} mol dm^{-3}) are consistent with the formulations. The complexes are stable in air and soluble in common organic solvents.

In the solid state L has an *endo-endo* conformation with a distance of 6.249(5) Å between the bridgehead nitrogens through which a pseudo-three-fold symmetry axis passes (Fig. 1). The bond distances and angles in the molecule are normal within statistical errors. Both ^{1}H and ^{13}C NMR data also indicate a three-fold symmetry in the molecule in chloroform solution.

The structure of complex **2a** consists of the cation [NiL-(H$_2$O)(MeCN)]$^{2+}$ (Fig. 2) and two perchlorate anions. In addition, two molecules of MeCN and one of H$_2$O are present in the crystal lattice. The Ni^{II} recognizes the N$_4$-end of the cavity. The water molecule occupies the empty space inside the cavity making hydrogen bonds with the bridgehead N and ether O atoms of the cryptand while its O atom binds the metal ion (Table 2) forming a cascade complex. Similar cascade complexes are known for sodium[23] and copper(II).[17] The two bridgehead N atoms in **2a** are in an *endo-endo* conformation with a separation of 6.410(6) Å which compares well with that found in L. The Ni^{II} achieves six-co-ordination by binding a MeCN molecule from outside the cavity. The Ni–N[24] and Ni–O

binds to a MeCN group from outside the cavity to complete its co-ordination.

Acknowledgements

References

1 C. Bazzicalupi, A. Bencini, V. Fusi, L. Mazzanti, P. Paoletti and B. Valtancoli, *Inorg. Chem.*, 1995, **34**, 3003.
2 J.-L. Pierre, P. Chautemps, S. M. Refaif, C. G. Beguin, A. El-Marzouki, G. Serratric, P. Rey and J. Laugier, *J. Chem. Soc., Chem. Commun.*, 1994, 1117.
3 M. G. B. Drew, O. W. Howarth, G. G. Morgan and J. Nelson, *J. Chem. Soc., Dalton Trans.*, 1994, 3149.
4 Y. S. Yan, L. Q. Hui and S. M. Chang, *Inorg. Chem.*, 1994, **34**, 1251.
5 J.-L. Pierre, P. Chautemps, S. M. Refaif, C. G. Beguin, A. El-Marzouki, G. Serratrice, E. Saint-Aman and P. Rey, *J. Am. Chem. Soc.*, 1995, **117**, 1965.
6 M. G. B. Drew, C. J. Harding, V. McKee, G. G. Morgan and J. Nelson, *J. Chem. Soc., Chem. Commun.*, 1995, 1035.
7 R. Menif, J. Reibenspies and A. E. Martell, *Inorg. Chem.*, 1991, **30**, 3446; R. J. Motekaitis, A. E. Martell, I. Murase, J.-M. Lehn and M. W. Hosseini, *Inorg. Chem.*, 1988, **27**, 3630; R. J. Motekaitis, A. E. Martell, J.-M. Lehn and E. Watanabe, *Inorg. Chem.*, 1982, **21**, 4253.
8 H. An, J. S. Bradshaw and R. M. Izzat, *Chem. Rev.*, 1992, 543 and refs. therein.
9 K. G. Ragunathan and P. K. Bharadwaj, *J. Chem. Soc., Dalton Trans.*, 1992, 1653.
10 J.-M. Lehn, in *Perspectives in Coordination Chemistry*, eds. A. F. Williams, C. Floriani and A. F. Merbach, VCH, New York, 1992, p. 447 and refs. therein.
11 K. G. Ragunathan and P. K. Bharadwaj, *Tetrahedron Lett.*, 1992, 7581.
12 P. Ghosh, R. Shukla, D. K. Chand and P. K. Bharadwaj, *Tetrahedron*, 1995, **51**, 3265.
13 K. G. Ragunathan and P. K. Bharadwaj, *Proc. Indian Acad. Sci.* (*Chem. Sci.*), 1995, **107**, 519.
14 D. K. Chand and P. K. Bharadwaj, unpublished work.
15 P. Ghosh, P. K. Bharadwaj, S. Mandal and S. Ghosh, *J. Am. Chem. Soc.*, 1996, **118**, 1553.
16 P. Ghosh, T. K. Khan and P. K. Bharadwaj, *Chem. Commun.*, 1996, 189.
17 C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, C. Giorgi, P. Paoletti and B. Valtancoli, *J. Chem. Soc., Dalton Trans.*, 1994, 3581.
18 S. Mandal and P. K. Bharadwaj, *Polyhedron*, 1992, **11**, 1037.
19 S. R. Hall, J. M. Stewart and H. B. Flack, *The XTAL 3.2 Reference Manual*, Universities of Western Australia and Maryland, 1993.
20 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1987, p. 290.
21 R. Cortes, J. I. R. de Larramendi, L. Lezama, T. Rojo, K. Urtiaga and M. I. Arriorlua, *J. Chem. Soc., Dalton Trans.*, 1992, 2723; M. I. Arriorlua, R. Cortes, L. Lezama, T. Rojo, X. Solens and M. Font-Bardia, *Inorg. Chim. Acta*, 1990, **174**, 263.
22 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1971.
23 V. McKee, M. R. J. Dorrity, J. F. Malone, D. Marrs and J. Nelson, *J. Chem. Soc., Chem. Commun.*. 1992, 383.
24 G. J. Colpas, M. Kumar, R. O. Day and M. J. Maroney, *Inorg. Chem.*, 1990, **29**, 4779.
25 J. Burgess, *Ions in Solution: Basic Principles of Chemical Interactions*, Ellis Horwood, Chichester, 1988, p. 40.
26 D. K. Chand and P. K. Bharadwaj, *Inorg. Chem.*, 1996, **35**, 3380.
27 A. W. Addison, H. M. J. Hendricks, J. Reedjik and L. K. Thompson, *Inorg. Chem.*, 1981, **20**, 103.
28 M. Duggan, N. Ray, B. Hathaway, G. Tomlinson, P. Brint and K. Peein, *J. Chem. Soc., Dalton Trans.*, 1980, 1342.
29 S. Knapp, T. P. Keenan, X. Zhang, R. Fikar, J. A. Potenza and H. J. Schugar, *J. Am. Chem. Soc.*, 1990, **112**, 3452 and refs. therein.
30 K. Ragunathan and P. K. Bharadwaj, *J. Chem. Soc., Dalton Trans.*, 1992, 2417 and refs. therein.
31 J. W. Dawson, T. J. McLennan, W. Robinson, A. Merle, M. Dartiguenave, Y. Dartiguenave and H. B. Gray, *J. Am. Chem. Soc.*, 1974, **96**, 4428; B. B. Chastain, E. A. Rick, R. L. Pruett and H. B. Gray, *J. Am. Chem. Soc.*, 1968, **90**, 3994 and refs. therein.
32 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn, Wiley, New York, 1988, p. 768
33 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn, Wiley, New York, 1988, p. 747