J.Serb.Chem.Soc. 67(12)825-832(2002) JSCS-3007 UDC 541.89–034:542.913:543.422.25 Original scientific paper

Synthesis and characterization of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of 2,12-dimethyl-3-13-di-*n*-propyl-1,4,11,14-tetraazacycloeicosa-1,3,11,13-tetraene

RAGHU N. PRASAD* and MALA MATHUR

Department of Chemistry, University of Rajasthan, Jaipur-302 004, India, E-mail: prasadraghunandan@yahoo.com

(Received 15 February, revised 26 August 2002)

Abstract: Metal complexes of a 20-membered tetraazamacrocycle 2,12-dimethyl-3,13-di-*n*-propyl-1,4,11,14-tetraazacycloeicosa-1,3,11,13-tetraene (L) of the type [MLX₂]X (M=Cr(III), Fe(III); X = NO₃) [CoLNO₃]NO₃, [NiL(NO₃)₂], [CuL]Cl₂ and [ZnLCl₂] have been prepared by 2 + 2 cyclocondensation of 2,3-hexanedione with 1,6-diaminohexane in the presence of metal ions as templates. These complexes were characterized by elemental analyses, conductances, IR and electronic spectra and magnetic measurements.

Keywords: Macrocyclic complexes, transition metal complexes, IR spectra, electronic spectra, magnetic moments.

INTRODUCTION

As compared to their open chain analogues, macrocycles are more stable and more selective towards metal ions. Cyclam, a tetraazamacrocycle has long been an extremely useful and versatile macrocyclic ligand in coordination, bio-inorganic and biomimetic chemistry.¹ Many of its derivatives can be used as catalysts in redox reactions.² Various donor pendants have been attached for further functionalization.^{3,4} Mn(II), Co(II), Cu(II) and Ni(II) complexes of the type [MLX₂] of a tetraazamacrocycle derived from benzil and *m*-phenylenediamine have been reported.⁵ Ni(II), Co(II), Cr(II) and Fe(II) complexes of 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetrade-ca-4,7,11,14-tetraene have been synthesized.⁶ Octahedral complexes [NiLX₂] (X = OH₂, ONO-and NCO-; L = 3,4-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0^{1.18}, 0^{7.12}]docosane) were prepared and characterized by X-ray crystallography.⁷ An usual hexacoordinated Ni(II) complexes of 5,12-dioxo-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene. Curtis¹⁰ prepared Ni(II) complexes of 5,12-dioxo-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-di-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-di-

^{*} Author to whom correspondence should be addressed.



ene. Co(II) complexes of 14 to 16-membered ring macrocyles have been prepared by template condensation of 1,2,9,10-tetraphenyl-3,4,7,8-tetraaza-deca-2,4,6,8-tetraene-1,10-dione with diamino-alkanes in the presence of $Co(ClO_4)_2$.¹¹ Ni(II), Cu(II) and Pd(II) complexes of a 16-membered dibenzotetraazamacrocycle have been synthesized using *m*-phenylenediamine and 2-propynal.¹² However, metal complexes of tetraazamacrocycles containing more than 16-membered rings have not been synthesized so far except for a few complexes reported earlier from our laboratories.^{13–17}

In the present paper the synthesis and characterization of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of 2,12-dimethyl-3,13-di-*n*-propyl-1,4,11,14-tetraazacycloeicosa-1,3,11,13-tetraene, L(I) derived from 2,3-hexanedione and 1,6-diaminohexane are described.

EXPERIMENTAL

Materials

 $Cr(NO_3)_3$ 9H₂O (Fluka), Fe(NO₃)₃9H₂O (Fluka), Co(NO₃)₂6H₂O (Fluka), Ni(NO₃)₂6H₂O (Merck), CuCl₂2H₂O (B.D.H.), ZnCl₂ (Fluka), 2,3-hexanedione (Aldrich), 1.6-diaminohexane (Merck) were used as received. *n*-Butanol was distilled before use.

Analytical methods and physical measurements

Chromium was determined volumetrically as dichromate using potassium dichromate as an intermediate. The iron content in the Fe(III) complex was determined volumetrically as Fe^{2+} ions by their reduction with stannous chloride. Cobalt was determined volumetrically by EDTA using Xylenol orange as the indicator. Nickel and zinc were determined volumetrically by EDTA using Eriochrome Black T as the indicator. Copper was determined volumetrically by sodium thiosulphate solution using starch as the indicator. Nitrogen was determined by the Kjeldahl method. Chlorine was determined gravimetrically as AgCl. IR spectra were recorded on an FT IR Spectrophotometer Magna IR-550 as KBr pellets in the range 4000–400 cm⁻¹. Specific conductances were measured at room temperature in DMSO using a Systronics Direct Reading Conductivity Meter-304. Magnetic measurements were carried out at room temperature using a Gouy Balance at Banasthali Vidyapith, Banasthali.

Synthesis of macrocyclic complexes

To a butanolic solution of $Cr(NO_3)_3 \cdot 9H_2O$ (1.0 mmol in ≈ 20 ml *n*-butanol), a solution of 2,3-hexanedione (2.0 mmol in ≈ 15 ml *n*-butanol) was added under stirring. To this, a solution of 1,6-diaminohexane (2.0 mmol in ≈ 15 ml *n*-butanol) was added dropwise under constant stirring. A solid appeared during the addition of the diamine. The stirring was continued for ≈ 5 h and the solid was filtered, washed with *n*-butanol and dried in vacuum.

Reactions of 2,3-hexanedione with 1,6-diaminohexane in the presence of $Fe(NO_3)_3$ 9H₂O, Co(NO₃)₂6H₂O, Ni(NO₃)₂6H₂O, CuCl₂·2H₂O and ZnCl₂ were carried out using a similar procedure.

RESULTS AND DISCUSSION

The reactions of metal salts with 2,3-hexanedione and 1,6-diaminohexane in 1:2:2 mole ratio result in the formation of metal complexes of a tetraazamacrocycle (L) having 20-membered ring.

$MX_m \cdot xH_2O + 2 CH_3CH_2CH_2COCOCH_3 + 2 H_2N(CH_2)_6NH_2 \rightarrow$

 $[MLX_{m-n}]X_n + (x+4) H_2O$

where L = 2,12-dimethyl-3,13-di-*n*-propyl-1,4,11,14-tetraazacycloeicosa-1,3,11,13-tetraene.

М	Х	т	п	x	Cordination No.
Cr	NO ₃	3	1	9	6
Fe	NO ₃	3	1	9	6
Со	NO ₃	2	1	6	5
Ni	NO ₂	2	0	6	6
Cu	Cl	2	2	2	4
Zn	Cl	2	0	0	6

All the macrocyclic complexes are coloured solids and are stable at room temperature. They are soluble in DMSO but are insoluble in most common organic solvents such as chloroform, carbon tetrachloride, methanol and acetone. All the complexes gave satisfactory elemental analyses. The analyses and characteristics of these complexes are given in Table I.

For tetraazamacrocycles the ideal ring size for metal ions has been investigated and M–N distances for which the strain energy is minimum have been calculated.^{18,19} A larger or smaller metal ion would require a change in M–N distance with an accompanying increase in the strain energy of the ligand causing distortion. The M–N bond lengths for transition metal complexes of 12–16 membered saturated tetraazamacrocycles range from 1.8–2.4 Å and hence many macrocycles of varying ring sizes coordinate readily to transition metal ions to give stable complexes.²⁰ There will be greater flexibility in the larger rings due to which

metal ions smaller than the macrocyclic ring size can also be conveniently accommodated resulting in the formation of stable complexes. Formation constants and molecular mechanics calculations have shown that the chelate ring size is more important in controlling metal ion size-based selectivity than the macrocyclic ring size, and there is a very small effect of macrocyclic ring size on the stability of the complexes due to the flexibility of large ring macrocycles.^{21–24}

During the template synthesis of Fe(II), Co(III) and Ni(II) complexes of MePhTIM, Eggleston and Jackels²⁵ ruled out the possibility of the formation of diazepine(II), a heterocyclic product of 1+1condensation, on the basis or ¹H-NMR studies.



No.		Colour and temp. of decomposition/°C	X 7° 11/07	Analyses / %			
	Complex		Y1eId/%	M Found (Calcd.)	N Found (Calcd.)	Cl Found (Calcd.)	
1.	$[Cr(Me_2Pr_2[20]tetraeneN_4)(NO_3)_2]NO_3$	Light grey, 202	58	8.27 (8.29)	8.84 (8.94)	-	
2.	$[Fe(Me_2Pr_2[20]tetraeneN_4)(NO_3)_2]NO_3$	Brown, 178	55	8.76 (8.85)	8.74 (8.88)	-	
3.	$[Co(Me_2Pr_2[20]tetraeneN_4)(NO_3)_2]NO_3$	Green, 169	45	10.39 (10.31)	9.74 (9.80)	_	
4.	$[Ni(Me_2Pr_2[20]tetraeneN_4)(NO_3)_2]$	Green, 109	50	10.16 (10.27)	9.77 (9.81)	_	
5.	$[Cu(Me_2Pr_2[20]tetraeneN_4)]Cl_2$	Green, 118	33	12.02 (12.14)	10.69 (10.71)	13.40 (13.55)	
6.	$[Zn(Me_2Pr_2[20]tetraeneN_4)Cl_2$	Light yellow, 208	49	12.38 (12.45)	10.59 (10.67)	13.38 (13.51)	

TABLE I. Analyses and physical characteristics of the macrocyclic complexes

TABLE II. IR, conductance and magnetic data of the macrocyclic complexes

No.		IR absorption bands			Molar conductance	
	Complex	v(C=N)	NO3 Coordinated	NO ₃ Ionic	ohm ⁻¹ cm ² mol ⁻¹	μ_{eff} /B M
1.	[Cr(Me ₂ Pr ₂ [20]tetraeneN ₄)(NO ₃) ₂]NO ₃	1580 m	1020 w	1380 s 825 m	149	4.3
2.	[Fe(Me ₂ Pr ₂ [20]tetraeneN ₄)(NO ₃) ₂]NO ₃	1580 m	1025 w	1380 s 820 m	107	6.3
3.	$[Co(Me_2Pr_2[20]tetraeneN_4)(NO_3)]NO_3$	1560 m	1015 w	1380 s 820 w	61	5.4
4.	$[Ni(Me_2Pr_2[20]tetraeneN_4)(NO_3)_2]$	1590 m	1000 w 1040 m	_	65	4.3
5.	$[Cu(Me_2Pr_2[20]tetraeneN_4)]Cl_2$	1630 s	_	_	65	2.5
6.	$[Zn(Me_2Pr_2[20]tetraeneN_4)Cl_2]$	1580 s	_	_	10	diamagnetic

Conductances

Molar conductances of 10⁻³ M solutions of the complexes were determined in DMSO (Table II). The Cr(III) and Fe(III) complexes behave as 3:1 electrolytes indicating that two anions which are coordinated are replaced by solvent molecules. These complexes are hexacoordinated and their probable geometry may be octahedral. Molar conductances ≈ 109 ohm⁻¹ cm²mol⁻¹ in DMSO have been reported for 3 : 1 electrolytes.²⁶ Co(II) complex behaves as 2:1 electrolyte indicating that the coordinated nitrate is replaced by a solvent molecule and the complex is pentacoordinated. Balasurbramanian et al.¹¹ have reported pentacoordinated Co(II) complexes [CoL(OH)]ClO₄·mH₂O, where L is a macrocycle containing 14 to 16-membered ring. The conductance value for the Ni(II) complex corresponds to a 2:1 electrolyte indicating that both the coordinated anions are replaced by solvent molecules. The complex is hexacoordinated and may possess pseudooctahedral geometry. The conductance value for the Cu(II) complex also corresponds to a 2:1 electrolyte suggesting it to be tetracoordinated. Hay and coworkers²⁷ have reported tetracoordination for the Cu(II) complex of the macrocycle 5.6.12.13-tetramethyl-1.4.8.11-tetraazacvclotetradeca-4.11-diene. The conductance of the Zn(II) complex is very low indicating its non-electrolytic nature.²⁶ This suggests that both the chloro groups are coordinated to the zinc atom which is hexacoordinated.

Infrared spectra

The infrared spectra of the complexes do not exhibit any absorption band at 3200 or 1700 cm⁻¹ indicating the absence of unreacted NH₂ or CO groups.²⁸ In mononuclear Fe(II), Co(III), Co(II) and Ni(II) complexes of an N₆O₄ macrocycle, Nelson et al.²⁹ reported no absorption band at 1700 or 3200-3400 cm⁻¹ which could be assigned to residual keto or amine groups. All the complexes show a medium intensity absorption band in the region 1560–1630 cm⁻¹ which can be assigned to v(C=N). In [Cu(TIM)]²⁺ complexes, absorption bands at 1600–1620 cm⁻¹ have been assigned to v(C=N) vibrations.³⁰ In the IR spectra of the Cr(III), Fe(III) and Co(III) complexes of macrocycles derived from dihydrazides and aromatic diketones, absorption bands at 1580–1640 cm⁻¹ have been assigned to v(C=N).³¹ Nitrate complexes of Cr(III), Fe(III), Co(II) and Ni(II) show absorption bands at 1000–1040 cm⁻¹ due to coordinated nitrate. In the Co(II) and Ni(II) complexes of a macrocycle derived from 2,3-butanedione and 2,6-diaminopyridine, absorption bands at 1265, 1010 and 860 cm⁻¹ have been assigned to coordinated nitrate.³² All the nitrate complexes show characteristic absorption bands at 810–820 cm⁻¹ and 1380 cm⁻¹ which can be assigned to ionic nitrate. The Cr(III) and Fe(III) complexes of macrocycles derived from dihydrazides and aromatic diketones have been reported to exhibit characteristic bands at ≈1350, 1230 and 825 cm⁻¹ due to ionic nitrate.³¹ The Cr(III) complexes of macrocyclic ligand c-meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane show absorption band at 1384 cm⁻¹ due to the presence of ionic nitrate.³³

PRASAD and MATHUR

Magnetic moments

The μ_{eff} values for macrocyclic complexes are given in Table II. The magnetic moment for the Cr(III) complex is 4.3 BM indicating the presence of three unpaired electrons. For the Cr(III) complex of 6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane Bernhardt et al.³⁴ have reported a magnetic moment of 3.83 BM. The μ_{eff} value for the Fe(III) complex is 6.3 BM indicating a slight ferromagnetic behaviour and suggests the high spin state of Fe(III). For the Fe(III) complexes of the macrocycle 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene, µeff values have been reported in the range 5.65–5.82 BM.³⁵ The μ_{eff} for the Co(II) complex is 5.4 BM suggesting a high spin state of Co(II). Higher value of magnetic moment may be due to a large orbital contribution. Malik and coworkers³⁶ have observed μ_{eff} values in the range 4.81-5.12 BM for Co(II) complexes of a macrocycle derived from 2,3-butanedione and 2,6-diaminopyridine. For Co(II) complexes of the macrocycle derived from 2,4-pentanedione and *m*-phenylenediamine μ_{eff} values have been reported in the range 4.85–5.15 BM.³⁷ It is very interesting to note that the Fe(III) and Co(II) complexes are high spin even in the presence of strong coordinating azomethine groups. This is probably due to the saddle shape of the macrocycle and the sitting atop of the metal centre with respect to the N4 macrocyclic plane. The saddle shape arises from steric strain and the strain is relieved as a result of a distortion of the N₄ planar ring through the twisting of the torsional angles about the C-N bonds on the N₄ ring which is the most readily deformable site. In the saddle shape the nitrogen lone pairs are directed out of the N₄ plane as the metal sits atop and not inside the N₄ cavity.³⁸ Fe(III) complexes of dibenzotetraazamacrocycles possess magnetic moments in the range 5.71-6.19 BM and the macrocycle has been reported to be saddle shaped. ^39 The μ_{eff} value of 4.3 BM for the Ni(II) complex suggests the presence of two unpaired electrons. The higher magnetic moment may be due to an orbital contribution. For Ni(II) complexes of macrocycle derived from 2,3-butanedione and 2,6-diaminopyridine, μ_{eff} values in the range 3.24–3.35 BM have been reported and pseudooctahedral geometry was assigned to the complexes.³⁶ For the Cu(II) complex the μ_{eff} value of 2.5 BM corresponds to one unpaired electron. For Cu(II) complexes of the macrocycle derived from benzil and ethylenediamine, Bhoon and Singh⁴⁰ have reported μ_{eff} values in the range 1.76–1.94 BM. The Zn(II) complex is diamagnetic.

Electronic spectra

The electronic spectrum of the Cr(III) complex exhibits band at ≈ 16528 , ≈ 26315 and ≈ 28985 cm⁻¹ which may be assigned to ${}^{4}B_{1g} \rightarrow {}^{4}E_{g(a)}$, ${}^{4}B_{1g} \rightarrow {}^{4}E_{g(b)}$ and ${}^{4}B_{1g} \rightarrow {}^{4}A_{2g}$ transitions, respectively. The position of these bands is consistent with a distorted octahedral geometry with D_{4h} symmetry. For the macrocyclic complexes of Cr(III) Rana *et al.*³¹ have reported absorption bands at 16700–17150, 25650–26150 and 29010–29400 cm⁻¹ due to ${}^{4}B_{1g} \rightarrow {}^{4}E_{g(a)}$, ${}^{4}B_{1g} \rightarrow {}^{4}E_{g(b)}$ and ${}^{4}B_{1g} \rightarrow {}^{4}A_{2g}$ transitions, respectively. In the spectrum of the Fe(III) complex bands at ≈ 16722 and ≈ 17182 cm⁻¹ may be assigned to the

 $^{6}A_{1g} \rightarrow {}^{4}T_{1g}(E)$ transition. These lower energy bands may be due to a splitting of the ${}^{4}T_{1g}$ term. Another band appears at ≈ 26455 cm⁻¹ which can be assigned to the ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$ transition. The spectrum suggests distorted octahedral geometry with D_{4h} symmetry. For Fe(III) complexes of macrocycles Rana *et al.*³¹ reported bands at \approx 17500 cm⁻¹ due to ⁶A_{1g} \rightarrow ⁴T_{1g}(E) and at \approx 25000 cm⁻¹ due to ⁶A_{1g} \rightarrow ⁴T_{2g} transition. The spectrum of the Co(II) complex exhibits bands at \approx 9756 and \approx 16666 cm⁻¹ due to ⁴A_{1g} \rightarrow ⁴T_{2g} and ⁴T_{1g} \rightarrow ⁴A_{2g} transitions, respectively. The Co(II) complex is pentacoordinated as evidenced by its IR spectrum but the electronic spectrum is quite similar to that of octahedral symmetry. Therefore, it might be possible that nitrate groups are coordinated to some extent giving distorted octahedral geometry and the complex may possess D_{4h} symmetry. For Co(II) macrocyclic complexes Rana et al.37 have reported bands at ≈7930-8920, ≈15380-17540 cm⁻¹ due to ${}^{4}T_{1g} \rightarrow {}^{4}T_{2g}$ and ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}$ transitions, respectively. The spectrum of the Ni(II) complex is characteristic of octahedral geometry and the bands at ≈17094 and \approx 29411 cm⁻¹ can be assigned to ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ transitions, respectively. For Ni(II) complexes of a macrocycle, 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),14,16-triene, Busch et al.41 have assigned absorption bands in the region 18180–18870 and 29400–29850 cm⁻¹ to ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$ and ${}^{3}A_{2g} \rightarrow$ ${}^{3}T_{1g}$ (P) transitions, respectively. The spectrum of the Cu(II) complex shows a band at ≈ 16393 cm⁻¹ due to ligand field transitions. Fujiwara *et al.*⁴² have reported ligand field transitions at ≈16129 cm⁻¹ for Cu(II) complexes of tetraazamacrocyclic Schiff bases. All the complexes exhibit strong absorption bands in the region 29000-36000 cm⁻¹ which may be charge transfer bands. Singh et al.⁶ have reported charge transfer bands at 31500-34000 cm⁻¹ for Cr(II) and Fe(II) complexes of 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene. Rana et al.37 have reported charge transfer bands at ≈ 30700 cm⁻¹ for macrocyclic complexes of Co(II), Ni(II) and Cu(II).

Acknowledgements: The authors wish to thank the Head of the Chemistry Department, University of Rajasthan, Jaipur for providing laboratory facilities.

ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА КОМПЛЕКСА Сr(III), Fe(III), Co(II), Ni(II), Cu(II) и Zn(II) СА 2,12-ДИМЕТИЛ-3,13-ДИ-*n*-ПРОПИЛ-1,4,11,14-ТЕТРААЗАЦИКЛОЕИКОСА--1,3,11,13-ТЕТРАЕНОМ

RAGHU N. PRASAD и MALA MATHUR

Department of Chemistry, University of Rajasthan, Jaipur-302 004, India, e-mail: prasadraghunandan@yahoo.com

Припремљени су метални комплекси са 20-то чланим тетраазамаакроциклом 2,12-диметил-3,13-ди-*n*-пропил-1,4,11,14-тетраазациклоеикоса-1,3,11,13-тетраеном (L) типа [MLX₂]X (M = Cr(III), Fe(III); X = NO₃) [CoLNO₃]NO₃, [NiL(NO₃)₂], [CuL]Cl₂ и [ZnLCl₂] 2 + 2 кондензацијом 2,3-хександиона са 1,6-диаминохексаном у присуству јона метала као темплата. Ови комплекси су карактерисани елементалном анализом, проводљивошћу, IR и електронским спектрима, као и магнетним мерењима.

(Примељено 15. фебруара, ревидирано 26. августа 2002)

PRASAD and MATHUR

REFERENCES

- 1. M. Shionoya, E. Kiumura, Y. Iitaka, J. Am. Chem. Soc. 112 (1990) 9237
- 2. E. K. Barefield, G. M. Freeman, G. Donald, V. Derveer, Inorg. Chem. 25 (1986) 552
- 3. T. A. Kaden, Comments Inorg. Chem. 10 (1990) 25
- 4. E. Kimura, Crown Ethers and Analogous Compounds, M. Hiraoka Ed.; Elsevier, Amsterdam, 1992, p. 381
- 5. P. R. Shukla, R. Rastogi, N. Ahmad, N. Gopal, J. Indian Chem. Soc. 65 (1988) 663
- 6. A. K. Singh, S. Chandra, S. Baniwal, J. Indian Chem. Soc. 75 (1998) 84
- 7. K. Y. Choi, Y. J. Kim, H. Ryu, I. H. Suh, Inorg. Chem. Commun. 2 (1999) 176
- 8. K. Y. Choi, K. M. Chun, I. H. Suh, Inorg. Chem. Commun. 2 (1999) 210
- 9. M. Shakir, S. P. Varkey, T. A. Khan, Indian J. Chem. 34(A) (1995) 72
- 10. N. F. Curtis, Inorg. Chim. Acta 317 (2001) 27
- 11. S. Balasubramanian, D. A. Gani, M. Kandaswamy, Synth. React. Inorg. Met.-Org. Chem. 18 (1988) 285
- 12. S. Chandra, R. Singh, Indian J. Chem. 34(A) (1995) 1003
- 13. R. N. Prasad, A. K. Gupta, P. K. Rai, Ann. Chim. (Rome) 81 (1991) 85
- 14. P. K. Rai, A. K. Gupta, R. N. Prasad, Z. Naturforsch. 47b (1992) 1701
- 15. R. N. Prasad, A. K. Gupta, P. K. Rai, Egyptian J. Chem. 36 (1993) 341
- 16. P. K. Rai, R. N. Prasad, Synth. React. Inorg. Met.-Org. Chem. 24 (1994) 749
- 17. P. K. Rai, A. K. Gupta, R. N. Prasad, Bull. Korean Chem. Soc. 14 (1993) 179
- 18. V. L. Goedken, J. Case, G. G. Cristoph, Inorg. Chem. 12 (1974) 2894
- 19. J. L. Hoard, M. J. Hamor, T. A. Hamor, W. S. Gaughey, J. Am. Chem. Soc. 87 (1965) 2312
- 20. L. Y. Martin, L. J. Dehayes, L. J. Zompa, D. H. Busch, J. Am. Chem. Soc. 96 (1974) 4046
- 21. R. D. Hancock, M. P. Ngwenya, A. Evers, P. W. Wade, J. C. A. Boeyens, S. M. Dobson, *Inorg. Chem.* 29 (1990) 264
- 22. V. J. Thom, R. D. Hancock, J. Chem. Soc. Dalton Trans. (1985) 1877
- 23. R. D. Hancock, M. P. Ngwenya, J. Chem. Soc. Dalton Trans. (1987) 2911
- 24. V. J. Thom, C. C. Fox, J. C. A. Boeyens, R. D. Hancock, J. Am. Chem. Soc. 106 (1984) 5947
- 25. D. S. Eggleston, S. C. Jackels, Inorg. Chem. 19 (1980) 1593
- 26. W. J. Geary, Coord. Chem. Rev. 7 (1971) 81
- 27. R. W. Hay, D. P. Piplani, B. Jeragh, J. Chem. Soc. Dalton Trans. (1977) 1951
- 28. R. Saraswat, S. Singh, V. B. Rana, J. Indian Chem. Soc. 73 (1996) 478
- 29. S. M. Nelson, M. Mc Cann, C. Stevenson, M.G.B. Drew, J. Chem. Soc. Dalton Trans. (1979) 1477
- 30. M. J. Maroney, N. J. Rose, Inorg. Chem. 23 (1984) 2252
- 31. R. Saraswat, V. B. Rana, J. Indian Chem. Soc. 74 (1998) 493
- 32. M. G. B. Drew, A. H. bin Othman, P. D. A. Mc Ilroy, S. M. Nelson, J. Chem. Soc. Dalton Trans. (1975) 2507
- 33. N. A. P. K. Maguire, K. C. Wallace, D. P. Cobranchi, J. M. Derrick, D. G. Speece, *Inorg. Chem.* 25 (1986) 2101
- 34. P. V. Bernhardt, P. Comba, N. F. Curtis, T. W. Hambley, G. A. Lawrance, M. Maeder, A. Siriwardena, *Inorg. Chem.* 29 (1990) 3208
- 35. S. M. Nelson, D. H. Busch, Inorg. Chem. 8 (1969) 1859
- 36. W. U. Malik, R. Bembi, R. Singh, Polyhedron 2 (1983) 369
- 37. V. B. Rana, P. Singh, D. P. Singh, M. P. Teotia, Polyhedron 1 (1982) 377
- 38. M. C. Weiss, V. L. Goedken, J. Chem. Soc. Chem. Commun. (1976) 531
- 39. W. U. Malik, R. Bembi, R. Singh, S. P. Taneja, D. Raj, Inorg. Chim. Acta 68 (1983) 223
- 40. Y. K. Bhoon, R. P. Singh, J. Inorg. Nucl. Chem. 43 (1981) 1685
- 41. M. C. Rakowski, M. Rycheck, D. H. Busch, Inorg. Chem. 14 (1975) 1194
- 42. M. Fujiwara, Y. Nakajima, T. Matsushita, T. Shono, Polyhedron 4 (1985) 1589.