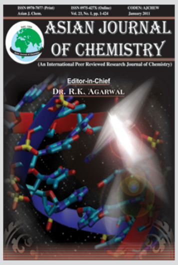
Asian Journal of Chemistry; Vol. 23, No. 12 (2011), 5466-5470

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Synthesis and Characterization of Binuclear Complexes of Oxovanadium(IV), Oxozirconium(IV), Dioxouranium(VI) and Thorium(IV) with N,N'-*bis*[(1E,2E)-2-(Hydroxyimino)-1-phenylethylidine]biphenyl-4,4'-diamine

SAKINA Z. BOOTWALA

Department of Chemistry, Wilson College, Mumbai-400 007, India

*Corresponding author: E-mail: szbootwala@gmail.com

(*Received*: 3 March 2011; *Accepted*: 24 August 2011) AJC-10307

In the present work, the synthesis of oxovanadium(IV), oxozirconium(IV), dioxouranium(VI) and thorium(IV) coordination compounds of tetradentate nitrogen donor ligand N,N'-*bis*[(1E,2E)-2-(hydroxyimino)-1-phenyl-ethylidine]biphenyl-4,4'-diamine is described. Their structures were determined on the basis of elemental analysis, molar conductance, magnetic susceptibility, electronic and thermal analysis, ^1H NMR and IR spectra. Based on analytical and molar conductance data it is revealing that the ligand (L) is coordinated in (N_4) fashion. The complex may be formulated as $[VOL]_2$, $[ZrL(H_2O)]_2$, $[UOL(H_2O)_2]_2$ and $[ThL(NO_3)_2(H_2O)_2]_2$. The result indicates that the VO(IV) complex is square pyramidal; ZrO(IV) is hexacoordinate where as UO_2 (VI) is 8-coordinated and Th(IV) is 10-coordinated complex.

Key Words: Oxovanadium(IV), Oxozirconium(IV), Tetradentate, Coordination number, Oximino, Molar conductance.

INTRODUCTION

Schiff bases are an important class of ligands in coordination chemistry and find extensive application in different fields[1,2]. Metal complexes with Schiff bases have been widely studied subject because of the industrial, antimicrobial and biological applications[3,4]. Schiff bases obtained from 1,8-diaminonaphthalene can be used in optical materials and conducting polymers[5]. Thus new optical and organic conducting materials can be produced by these compounds. Binuclear metal complexes play essential roles in biological systems by mimicking the active sites of some metalloenzymes[6]. They are also important for understanding the mutual influences of two metal centers on the electronic, magnetic and electrochemical properties of such bimetallic cores[7]. Actinides ion generally present a high coordination number and the type of polyhedron obtained influences the nature of the coordinating ligands. Thorium(IV) and uranium(VI) with atomic radii of 1.65 and 1.42 Å, respectively and a high positive charge fulfills the optimum conditions for formation of complexes with high coordination number. A number of workers have investigated the high coordination number of Th(IV) and UO_2(VI) with different Schiff bases[8-11]. In view of interesting ligating behaviour of such system, we consider it worthwhile to prepare VO(IV), ZrO(IV), UO_2(VI) and Th(IV) complexes of tetradentate ligand N,N'-*bis*[(1E,2E)-2-(hydroxyimino)-1-phenyl ethylidine]biphenyl-4,4'-diamine derived from (2E)-2 hydroximino-1-phenyl ethanone and 4,4'-diaminobiphenyl. The complexes have been characterized by various physico-chemical methods.

EXPERIMENTAL

All the chemical used in present work were of AR grade. Benzidine was recrystallized while the solvent were purified and double distilled before use. The ligand N,N'-*bis* [(1E,2E)-2-(hydroxyimino)-1-phenyl ethylidine]biphenyl-4,4'-diamine was synthesized in the laboratory by reported method[12].

A hot dimethyl formamide solution of the ligand (0.01 mol) *i.e.*, 4.46 g and DMF solution (20 mL) of the required metal salt (0.01 mol) $VOSO_4·5H_2O$ (2.53 g), $UO_2(NO_3)_2·6H_2O$ (5.02 g), $ZrO(NO_3)_2$ (2.31 g), $Th(NO_3)_4·6H_2O$ (5.88 g) were mixed together under constant stirring. These reaction mixtures were refluxed at 80-95 ºC for 4 h. On cooling, a coloured complex precipitates out. This was filtered and washed with a H_2O-DMF (1:1) mixture and then dried in vacuum over P_4O_{10}.

Uranium, zirconium and thorium content were determined as U_3O_8, ZrO_2 and ThO_2, respectively whereas vanadium content was determined as silver vanadate by the standard methods[13]. Molar conductance was measured in DMF (10^{-3} M solution) on an ELICO digital conductivity meter model CM-180. The IR spectra were recorded in KBr disc on a Perkin-Elmer Model 1600 FTIR spectrophotometer. The electronic spectra of the complex in DMF were recorded on UV-Systronic spectrophotometer. The ^{1}H NMR spectra was recorded in DMSO on a VXR-300S Varian Supercon NMR spectrometer using TMS as the internal reference. Magnetic susceptibility measurements was carried out by employing the Gouy method using $Hg[Co(SCN)_4]$ as a calibrant. Thermogravimetric studies of the complex were done on Netzch-429 thermoanalyzer recording at a rate of 10 ºC min^{-1}.

RESULTS AND DISCUSSION

The analytical and physical data of the metal complexes of the ligand are presented in Table-1. The complexes are brightly coloured and thermally stable at least up to 120 ºC. They are insoluble in water and common organic solvents, but are partially soluble in DMF at room temperature. The analytical data of the complexes (Table-1) indicates that the complexes have 1:1 metal: ligand stoichiometry. The value of molar conductance in DMF solution at 10^{-3} M dilution are in the range of 0.18-0.60 ohm^{-1} cm^2 mol^{-1} suggesting a non-electrolyte nature of these complexes[14]. The ligand has four coordination sites but involvement of all the same metal in the formation of a complex[15,16] is sterically not favorable. However, linear dimers are possible and the structure of the complex may be represented as shown in Figs. 3 and 4. The analytical data of the complexes (Table-1) is consistent with their formulation as $[VOL]_2$, $[ZrOL(H_2O)]_2$, $[UO_2L(H_2O)_2]_2$ and $[ThL(NO_3)_2(H_2O)_2]_2$ where L represents the deprotonated Schiff base.

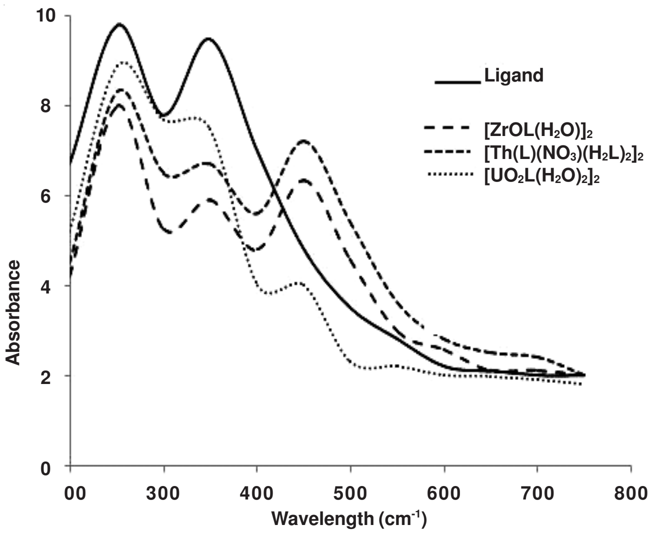


Fig. 1. Electronic spectrum of ligand and its metal complexes in DMF

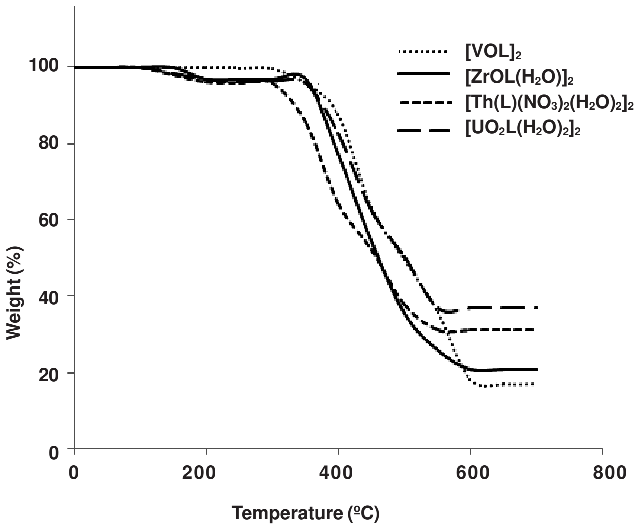


Fig. 2. TG curve of complexes

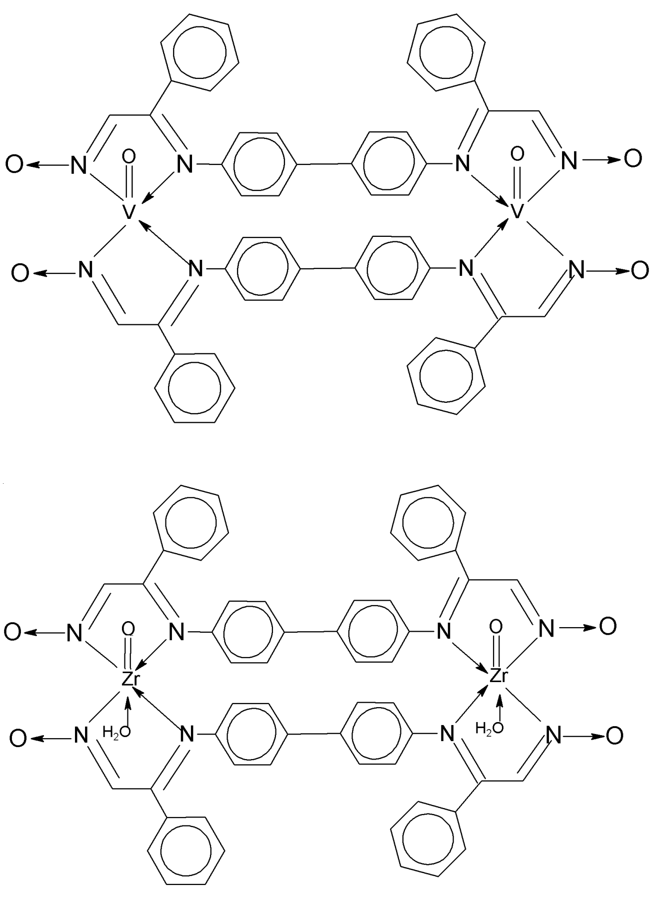


Fig. 3. Suggested geometries of VO(IV) and ZrO(IV) complexes

TABLE-1
YIELD, MOLAR CONDUCTANCE (Λ_M) IN DMF, ELEMENTAL ANALYSIS AND SOME PHYSICAL PROPERTIES OF THE PREPARED COMPLEXES[a]

Complex (m.w.)	Λ_M (S^{-1} cm^2 mol^{-1})	Colour	m.p. (ºC)	Yield (%)	Found/calcd. (%)			
					M	C	H	N
$[VOL]_2$ (1022.85)	0.28	Green	246	62	8.95 (9.66)	65.82 (66.03)	4.04 (4.59)	10.01 (10.62)
$[ZrOL(H_2O)]_2$ (1139.44)	0.18	Brown	202	59	15.76 (16.01)	58.4 (59.03)	3.10 (3.89)	9.26 (9.83)
$[Th(L)(NO_3)_2(H_2O)]_2$ (1673.13)	0.55	Yellow	278	47	26.85 (27.74)	39.73 (40.20)	2.06 (2.89)	9.69 (10.05)
$[UO_2L(H_2O)_2]_2$ (1501.09)	0.60	Black	265	61	30.57 (31.71)	47.80 (48.81)	2.76 (3.22)	7.05 (7.46)

L[a] = N,N'-*bis*[(1E,2E)-2-(hydroxyimino)-1-phenylethylidine]biphenyl-4,4'-diamine.

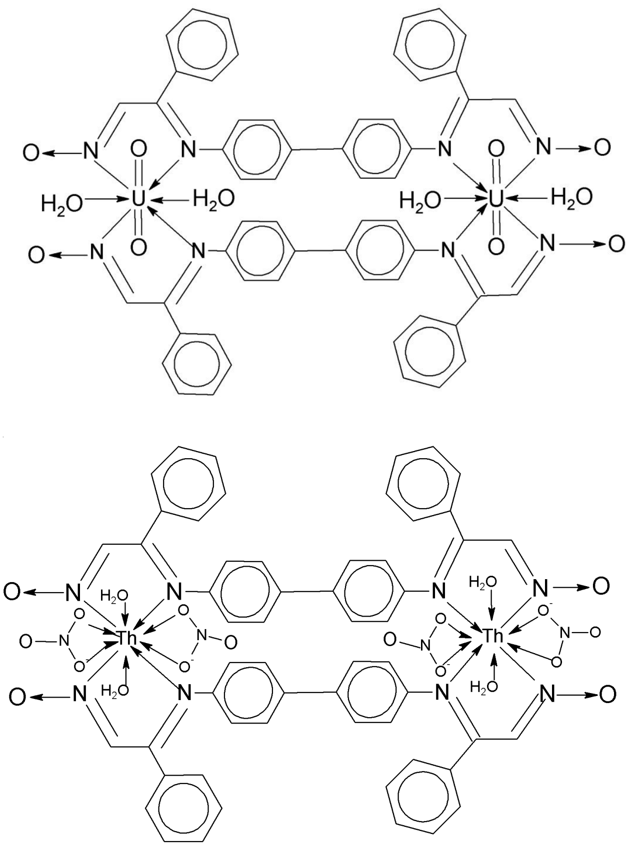


Fig. 4. Suggested geometries of UO_2(VI) and Th(IV) complexes

The ^{1}H NMR spectrum of the ligands and complex are recorded in DMSO medium. Comparison of the ^{1}H NMR spectra of the ligand[7] and its metal complexes revealed that the ligand behaves as a tetra dentate binegative NNNN donor. The disappearance of the signals at 11.9 ppm was ascribed to the fact that the ligand underwent deprotonation of the oximino group during complexation. A multiplet appearing in the region 6.6-7.2 ppm may be assigned to proton of biphenyl ring, where as phenyl proton show a multiplet at 7.4-8.0 ppm. The C-H proton of 1-ethylidine is at 8.4 ppm. This signal appears downfield shift by 0.2-0.4 ppm in the complexes indicating the coordination of hydroxyimino nitrogen. However, the position of other band does not change appreciably because of the coordination of the metal ions with the ligand.

Several structurally significant vibrational bond have been evaluated based on infrared spectra of related compounds like imino complex of some carbonyl oximes[17,18], isonitrosoacetophenone[19] and benzidine[20]. There are two types of (C=N) group (azomethine and oximino) are present in these complexes. The band around 1620-1590 cm^{-1} are assigned to the azomethine group, whereas those around 1580-1500 cm^{-1} are attributed to oximino ν(C=N) vibrations. In all metal complexes the ν(C=N) vibration undergo a shift to lower energy indicating coordination of the azomethane nitrogen and oximino nitrogen atom of the ligand. The view is further supported by the appearance of the band corresponding to the metal-nitrogen (M-N) stretching vibration at 523-515 cm^{-1} in all the complexes[21]. A broad band at 3210 cm^{-1} due to ν(NOH) in ligand was absent in all complexes indicating deprotonation of the oximino group during complexation. A new medium to strong intensity band observed in the region 1280-1200 cm^{-1} in the spectra of all the complexes is ascribed to ν(N→O) appearing due to the

TABLE-2
^{1}H NMR SPECTRAL DATA IN ppm (No. of SIGNALS IN PARENTHESIS)

Compound	NOH	Phenyl proton of biphenyl ring	Phenyl proton of phenyl ethanone	C-H Proton of 1-ethylidene
L	11.9(s)	6.8 (m)	7.9 (m)	8.4 (s)
$[VOL]_2$	–	6.5 (m)	7.8 (m)	8.2 (s)
$[ZrOL(H_2O)]_2$	–	6.7 (m)	7.7 (m)	8.1 (m)
$[Th(L)(NO_3)_2(H_2O)]_2$	–	7.0 (m)	7.8 (m)	8.2 (m)
$[UO_2L(H_2O)_2]_2$	–	6.8 (m)	7.7 (m)	8.0 (m)

L = N,N'-*bis*[(1E,2E)-2-(Hydroxyimino)-1-phenyl ethylidine] Biphenyl-4,4'-diamine

TABLE-3
SIGNIFICANT IR SPECTRAL BAND OF LIGAND AND COMPLEXES

	ν(O-H) (coordinated water)			ν(C=N) azomethine	ν(C=N) oximino	ν(N→O)	ν(M-N)	ν(M=O)	ν(M-O)
	ν(OH)	$\rho_r(H_2O)$	$\rho_w(H_2O)$						
L	–	–	–	1620	1600	990	–	–	–
$[VOL]_2$	–	–	–	1580	1540	1195	522	980 (s)	–
$[ZrOL(H_2O)]_2$	3340 (b)	957 (w)	630 (w)	1600	1550	1220	520	885 (s)	450
$[Th(L)(NO_3)_2(H_2O)_2]_2$	3370 (b)	955 (w)	635 (w)	1575	1555	1210	512	–	485
$[UO_2L(H_2O)_2]_2$	3420 (b)	962 (w)	633 (w)	1595	1560	1248	517	940(s) 836	462

L = N,N'-*bis*[(1E,2E)-2-(Hydroxyimino)-1-phenyl ethylidine]biphenyl-4,4'-diamine.

TABLE-4
THERMAL ANALYSIS OF COMPLEXES

Complex	Wt. for Tg (mg)	Temp. (ºC)	Percentage of water loss found (cacld.)	Decomposition temperature (ºC)	Percentage wt. of residue found (cacld.)	Composition of the residue
$[VOL]_2$	120	–	–	360-600	16.86 (17.77)	V_2O_5
$[ZrOL(H_2O)]_2$	145	150-195	3.08 (3.16)	390-540	20.78 (21.62)	ZrO_2
$[Th(L)(NO_3)_2(H_2O)_2]_2$	136	135-175	4.05 (4.30)	350-530	30.94 (31.56)	ThO_2
$[UO_2L(H_2O)_2]_2$	115	130-160	4.26 (4.79)	385-528	36.86 (37.40)	U_3O_8

UO_2(VI) < Th(IV) < ZrO_2(IV) < VO(IV). L = N,N'-*bis*[(1E,2E)-2-(Hydroxyimino)-1-phenyl ethylidine]biphenyl-4,4'-diamine.

formation of (N→O) linkage in the complex[22]. This is indicative of bonding through oximino nitrogen atom leading to a 5-membered chelate ring formation. Bonding through oximino oxygen donor leading to formation of a six membered chelate ring is ruled out as ν(N-O) due to O-coordinated oximino group[23] expected to occur around 1000 cm^{-1} is not observed in the present complexes. All the metal complexes except VO(IV) also show a broad band around 3450-3350 cm^{-1} and a medium or weak band at 962-956 and 635-630 cm^{-1} owing to $\nu(H_2O)$, $(\rho_r(H_2O))$ and $(\rho_w(H_2O))$, respectively. Their centre of gravity near 3400 cm^{-1} implies coordination of water molecule to the metal ion[24,25]. This view is further supported by the appearance of a band corresponding to ν(M-O) around 485-450 cm^{-1} in the complex[21]. The vanadyl complex shows one strong band in 980 cm^{-1} which can be attributed to the ν(V=O) vibration[26], where as zirconyl complex exhibit one strong band in the region 885 cm^{-1}, indicating the presence of (Zr=O) moiety in the complex[27]. The uranyl complex exhibit a strong band at 940 cm^{-1} and the medium intensity band at 836 cm^{-1} assignable to ν_{as}(O=U=O) and ν_s(O=U=O) mode, respectively[28]. A comparison of five infrared bands in thorium(IV) nitrato complex which occurs at 1530 (ν_4), 1285 (ν_1), 1028 (ν_2), 808 (ν_6), 736 (ν_3) and 709 (ν_5) with the known band of $Th(NO_3)_4 \cdot 5H_2O$[29] in which bidentate character of the nitrato group has been established by X-ray diffraction[30] and neutron diffraction studies[31]. The presence of nitrato ion on the coordination sphere in Th(IV) complexes has also been supported by non-electrolytic nature of complex in DMF.

Electronic spectra: The present system of ligand display only two band corresponding to λ_{max}, 250-270 nm and 310-320 nm assignable to π-π* and n-π* transition, respectively indicating extensive conjugation. The electronic spectra of UO_2(IV) complexes display mainly one weak band at 420 nm and a highly intense band at 285 nm, which may be due to $^1\Sigma^+_g \rightarrow {}^3\pi_\mu$ transition and change transfer transition, respectively[32]. The first one of the transition is typical of the O=U=O symmetric stretching frequency of the first excited state. It may be noted that the band occurring at 350 nm due to uranyl moiety because of apical → $f^o(u)$ transition[27] is being merged with the ligand band due to n-π* transition as evident from broadness and intensity. The electronic spectra of Th(IV) and ZrO(IV) complex exhibit only highly intensive additional band in the region 400-410 nm, which may be due to charge transfer besides the ligand bands. However, the electronic spectra could not provide structural details of these complexes. The electronic spectra of VO(IV) complex show two bands at 860 and 350 nm corresponding to the $^2B_2 \rightarrow {}^2E_1$ and $^2B_2 \rightarrow {}^2A_1$, transition, respectively indicating square pyramidal geometry of vanadyl complex.

Magnetic susceptibility: All the complexes except VO(IV) are diamagnetic consistent with their d^o and f^o electronic configuration. The magnetic moment values for oxovanadium(IV) complex is 1.63 BM these values are less than required for one unpaired electron indicating spin-spin coupling in the solid state between unpaired electron belonging to two vanadium atoms in the structural unit.

Thermal studies: The decomposition temperature (Table-4) indicates that for various metal complexes the thermal stability increases in the order of UO_2(VI) < Th(IV) < ZrO_2(IV) < VO(IV). The observed order of thermal stability indicates the trend in metal-ligand bond strength in the solid state. The weight loss between 130-195 ºC in the complex of ZrO(IV), Th(IV) and UO_2(VI) corresponds to the loss of coordinated water molecule. The observed and calculated weight loss for the metal complexes is presented in Table-4. The loss of coordinated water molecules at a temperature in the range of 110-150 ºC has also been reported in many benzidine complexes[33]. Thus, the result of the thermal studies indicate the presence of coordinated water molecules in the metal complexes further corroborates the assumption made on the basis of infrared spectral studies. The anhydrous complexes show rapid degradation presumably due to decomposition of organic constituent of the complex molecule as indicated by the steep fall in the percentage weight loss. The decomposition continues up to 620 ºC and reaches to stable products in each complex as indicated by the consistency in weight in the plateau of the thermogram. This corresponds to the composition of their stable oxides. The decomposition temperature varies for different complexes as shown in Table-4.

Conclusion

The present study revealed square pyramid, octahedral, 8-coordinated and10-coordinated geometry for the VO(IV), ZrO(IV), UO_2(VI) and Th(IV) complexes, respectively. The ligand acts in tetradentate manner coordinating through four nitrogen of which two are of the azomethine and other two are of oximino group in an NNNN fashion, which lead to a five membered chelate ring formation. The satisfactory analytical data and all physio-chemical studies presented above suggest that these complexes may be formulated as $[VOL]_2$, $[ZrO(L)H_2O)]_2$, $[UO_2L(H_2O)_2]_2$ and $[Th(L)(NO_3)_2(H_2O)_2]_2$ where L = N,N'-*bis*[(1E,2E)-2-(hydroxyimino)-1-phenylethylidine]biphenyl-4,4'-diamine.

ACKNOWLEDGEMENTS

The author gratefully acknowledged the financial support provided by UGC (No. 47-811/09) WRO. The author also thanks to Mr. Jaywant Harlikar from Invent Farma for providing spectral and analytical support.

REFERENCES

1. S.D. Dubey, K. Singh and J.P. Tandon, *Synth. React. Inorg. Met-Org. Chem.*, **23**, 1251 (1993).
2. S.A. Mohand, A. Levina and J. Muzard, *J. Chem. Res. (S)*, **25**, 2051 (1995).
3. M.S. EL-Medani, A.M.A. Omyana and R.N. Ramadan, *J. Mol. Struct.*, **738**, 171 (2005).
4. S. Vats and L.M. Sharma, *Synth. React. Inorg. Met-Org. Chem.*, **27**, 1565 (1997).
5. F. Yakubhanuglo and M. Sekerci, *J. Mol. Struct.*, **751**, 200 (2005).
6. Y. Agnus, R. Louis, J.P. Gisselbrecht and R. Weiss, *J. Am. Chem. Soc.*, **103**, 93 (1984).
7. K.D. Karlin, R.W. Cruse and Y.A. Gultneh, *J. Chem. Soc. Chem. Commun.*, **8**, 599 (1987).
8. R.K. Agarwal, K. Arora, P. Ganga and I. Chakraborti, *Polish J. Chem.*, **67**, 1913 (1993).
9. Z.A. Filmwala, S.M. Nandavadekar and R.M. Patil, *Asian J. Chem.*, **20**, 3301 (2008).
10. H. Han, W.J. Ruan, X.J. Zhao, G.H. Hu and Z.A. Zhu, *Synth. React. Inorg. Met-Org. Chem.*, **33**, 1011 (2003).

11. D.C. Darh, A. Mahapatra, P. Naik, S.K. Naik, R.N. Mohapatra and S. Ghosh, *J. Indian Chem. Soc*., **28**, 595 (2008).
12. N.V. Thakkar and S.Z. Bootwala, *Synth. React. Inorg. Met-Org. Chem.*, **26**, 1053 (1996).
13. A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, Longman ELBS, edn. 4, pp. 483, 487, 488, 490 (1978).
14. W.J. Geary, *Coord. Chem. Rev*., **7**, 81 (1971).
15. M. Sayeed and K. Iftikhar, *Indian J. Chem. Soc*., **22A**, 259 (1983).
16. M. Sayeed and K. Iftikhar, *Indian J. Chem. Soc*., **26**, 170 (1987).
17. R.G. Deshmukh and N.V. Thakkar, *Indian J. Chem*., **24**, 1066 (1985).
18. N.J. Patel and B.C. Haldar, *J. Inorg. Nucl. Chem*., **29**, 1037 (1967).
19. C. Natarajan and A.N. Hussain, *Indian J. Chem*., **22**, 527 (1983).
20. R. Constantines and R. Micusemeniue, *Synth. React. Inorg. Met-Org. Chem*., **7**, 399 (1977).
21. K. Nakamato, Infrared Spectra of Inorganic and Coordiantion Compound, John Wiley, New York, pp. 155, 167 (1970).
22. N.S. Dixit and C.C. Patel, *J. Indian Chem. Soc*., **54**, 176 (1977).
23. N.V. Thakkar and R.G. Deshmukh, *Indian J. Chem*., **33A**, 224 (1994).
24. F.A. Ej-saed, M.I. Ayad and R.M. Issa, *Polish J. Chem*., **75**, 773 (2001).
25. N. Raman, V. Mathuraj, S. Ravichandra and A. Kulandaisamy, *J. Chem. Sci*., **45**, 167 (2003).
26. R.C. Maurya and P. Sharma, *Indian J. Chem*., **38A**, 509 (1999).
27. M.C. Saha, R. Roy, M.K. Ghuh and P.S. Roy, *Indian J. Chem*., **26A**, 48 (1987).
28. K.B. Gudani and T.R. Goudar, *J. Indian Chem. Soc*., **79**, 529 (2002).
29. J.R. Ferraro and A. Walker, *J. Chem. Phys*., **45**, 552 (1966).
30. T. Ueki, A. Zalkin and D. Templeton, *Acta Crstallogr*., **20**, 836 (1966).
31. J.C. Taylor, M.H. Mueller and R.L. Hitterman, *Acta Crystallogr*., **20**, 842 (1966).
32. R. Chandra, *Synth. React. Inorg. Met.-Org. Chem*., **20**, 645 (1990).
33. M. Sayeed and K. Iftikar, *Indian J. Chem*., **25A**, 589 (1986).