Asian Journal of Chemistry Vol. 12, No. 3 (2000), 843–846

Synthesis and Structural Studies on Ternary Complexes of VO(IV) and ZrO(IV) with Isonitrosoacetophenone-2-picoloylhydrazone as Primary and 1-(*o*-Methoxy-Anilinomethyl)-5-Phenoxybenzimidazole as Secondary Ligand

SURESH K. AGARWAL* and SUBHASH CHAND†
Department of Chemistry
L.R. Postgraduate College, Sahibabad-201 005, India

Ternary complexes of VO(IV) and ZrO(IV) with isonitrosoacetophenone-2-picoloylhydrazone (INAPH) as primary and 1-(*o*-methoxyanilinomethyl)-5-phenoxybenzimidazole (MAMPB) as secondary ligand have been synthesised and characterised on the basis of analytical, magnetic and spectral studies. Analytical data suggested 1 : 1 : 1 (M-L-L′) stoichiometric composition for the ternary complexes [where M = VO(IV)/ZrO(IV), L = INAPH and L′ = MAMPB]. Electrolytic conductance data revealed 1 : 1 electrolytic nature of VO(IV) complexes only. However, very low values of conductance in case of ZrO(IV) complexes, indicate their non-electrolytic behaviour. Reflectance spectra of VO(IV) complexes suggested distorted octahedral geometry for them. IR spectra of the ligands and complexes showed tridentate and bidentate behaviour of the hydrazone and Mannich base ligands respectively. ZrO(IV) complexes possess hepta-coordinated structure.

INTRODUCTION

Isonitrosoketones are expected to behave as versatile ligands. They form stable chelates with transition metal ions showing a variety of structural features[1–5]. The isonitroso moiety (>C═NOH), also referred to as hydroxyimino group in the literature, can coordinate either through nitrogen or oxygen atom producing chelate linkage isomers. In the present paper, we report the synthesis and structural features of VO(IV) and ZrO(IV) ternary complexes with isonitrosoacetophenone-2-picoloyl hydrazone as primary and 1-(*o*-methoxy-anilinomethyl)-5-phenoxybenzimidazole as secondary ligand.

EXPERIMENTAL

Isonitrosoacetophenone, 5-phenoxy benzimidazole and 2-picoloyl hydrazide were prepared by following literature procedure[6–8]. Isonitroacetophenone-2-picoloyl hydrazone was obtained by the usual condensation reaction between isonitrosoacetophenone and 2-picoloyl hydrazide. 1-(*o*-Methoxyanilinomethyl)-5-phenoxybenzimidazole was prepared by refluxing a mixture of *o*-methoxy aniline (.01 mole), formaldehyde (40%) and 5-phenoxy benzimidazole (.01 mole) in 20 mL ethanol for 30 min. The ligands were purified by recrystallisation from acetone. All chemicals used were of AnalaR grade. Oxovanadium(IV) chloride and bromide were prepared according to the literature procedure[9]. Oxovanad-

---

†Centre for Biochemical Technology, Mall Road, Delhi-110 007, India.

ium (IV) iodide was prepared by treating an alcoholic solution of VOCl$_2$ with KI[10]. VO(IV) thiocyanate was obtained by treating an aqueous solution of VO(IV) perchlorate with KCNS. Zirconyl salts were obtained as reported earlier[11].

Conductivity measurements were carried out on Toshniwal conductivity bridge. IR spectra were recorded on Perkin-Elmer 621 spectrophotometer.

Synthesis and isolation of the complexes

The ternary complexes of VO(IV) and ZrO(IV) were synthesised by adding an ethanolic solution of the hydrazone (0.01 mole) and Mannich base (0.01 mole) each in a slight excess over 1 : 1 stoichiometric quantity to an ethanolic solution of the respective oxocation salt (0.01 mole) with continuous shaking. The reaction mixture was refluxed for 2 h over a water bath at 80–85°C. On cooling, the separated solid products were filtered, washed with ethanol and finally with dry Et$_2$O and dried over anhydrous CaCl$_2$.

RESULTS AND DISCUSSION

Analytical data reported in Table-1 proposed the formulae [VOLL′]X and [ZrOLL′X] for the complexes (where L = $C_{14}H_{11}N_4O_2$ and L′ = $C_{21}H_{19}N_3O_2$ and X = Cl, Br, I or NCS). The ternary complexes are insoluble in common organic solvents but dissolve considerably in DMF and DMSO. Electrolytic conductance data (Table-1) of the complexes in DMF showed that VO(IV) complexes are 1 : 1 electrolytes while ZrO(IV) complexes are non-electrolytes.

TABLE-1
ANALYTICAL, CONDUCTANCE AND MAGNETIC MOMENT DATA OF VO(IV) AND ZrO(IV) COMPLEXES

Complex	Analysis, % Calcd. (Found)						Λ_m ohm^{-1} cm^2 mole^{-1}	μ_{eff} (B.M.)
	Metal	C	H	N	S	Halogen		
(VOLL′)Cl	7.13	58.79	4.19	13.71	–	4.96	70.9	1.89
	(7.09)	(58.43)	(4.17)	(13.65)		(4.93)		
(VOLL′)Br	6.71	55.34	3.95	12.91	–	10.54	72.3	1.86
	(6.75)	(54.88)	(3.96)	(12.99)		(10.61)		
(VOLL′)I	6.32	53.60	3.72	12.16	–	15.75	69.4	1.90
	(6.27)	(53.31)	(3.70)	(12.04)		(15.84)		
(VOLL′)NCS	6.91	58.62	4.07	15.19	4.34	–	68.4	1.87
	(6.88)	(58.96)	(4.04)	(15.13)	(4.32)			
[(ZrOLL′)Cl]	12.08	55.65	3.97	12.98	–	4.69	2.4	Diamagnetic
	(12.17)	(55.32)	(4.00)	(12.90)		(4.72)		
[(ZrOLL′)Br]	11.41	52.55	3.75	12.26	–	10.01	2.9	Diamagnetic
	(11.35)	(52.25)	(3.73)	(12,18)		(10.07)		
[(ZrOLL′)I]	10.78	49.63	3.54	11.58	–	15.00	3.2	Diamagnetic
	(10.70)	(50.01)	(3.52)	(11.52)		(14.87)		
[(ZrOLL′) NCS]	11.73	55.58	3.85	14,41	4.11	–	2.7	Diamagnetic
	(11.66)	(55.26)	(3.87)	(14.30)	(4.14)			

where L = $C_{14}H_{11}N_4O_2$ and L′ = $C_{21}H_{19}N_3O_2$

Magnetic and reflectance spectral studies of VO(IV) complexes

The observed higher μ_{eff} values (1.86–1.90 B.M.) in comparison to spin only value (1.73 B.M.) suggest the presence of some spin orbit interaction of vanadium ion in VO(IV) complexes.

The spectra of the complexes of VO(IV) showed low energy band at 12,900–13,600 cm^{-1} corresponding to $^2B_2 \longrightarrow {}^2E$ transition. The second band at 15,600–16,500 cm^{-1} was assigned to $^2B_2 \longrightarrow {}^2B_1$ transition (10 Dq)[12]. The high energy band at 24,700–25,300 cm^{-1} was assigned to $^2B_2 \longrightarrow {}^2A_1$ transition plus charge transfer absorption. These spectral results proposed distorted octahedral structure to these complexes. The observed spectral bands and the calculated values of parameters: Dq and Ds (axial parameters), Dt (equatorial parameter), DQ, DS and DT (NSH Hamiltonian parameters) have been tabulated in Table-2. The values of the parameters are in agreement with the distorted octahedral geometry.

TABLE-2
OBSERVED SPECTRAL BANDS, AXIAL, EQUATORIAL AND NSH HAMILTONIAN PARAMETERS OF VO(IV) COMPLEXES

Complex	Observed bands (cm^{-1})	Dq (cm^{-1})	Ds (cm^{-1})	Dt (cm^{-1})	DQ (cm^{-1})	DS (cm^{-1})	DT (cm^{-1})
(VOLL')Cl	12,900 15,900 24,700	1,590	-3,100	720	32,169	21,700	9,759
(VOLL')Br	13,500 15,600 25,000	1,560	-3,271	737	31,069	22,899	9,992
(VOLL')I	13,600 16,500 25,300	1,650	-3,200	800	32,536	22,400	10,844
(VOLL')NCS	13,000 15.900 24,800	1,590	-3,322	731	32,235	21,780	9,890

where L = $C_{14}H_{11}N_4O_2$ and L′ = $C_{21}H_{19}N_3O_2$

IR Spectra

Comparison of IR spectra of the synthesised ternary complexes and the ligands (INAPH and MAMPB) do not reveal a band in the complexes, attributable to OH stretching frequency of NOH group present in the hydrazone which clearly indicates the replacement of the proton of NOH group by metal ion. The bond formation of the metal with oximino nitrogen of the hydrazone (INAPH) is indicated by the shift of ν(N—O) (*ca.* 1,015 cm^{-1}) band to higher frequency band[13] (1,035–1,045 cm^{-1}) in the complexes. A positive shift of 20–25 cm^{-1} in ν(C═N) vibrations (*ca.* 1,610 cm^{-1} in INAPH) in the complexes suggests the participation of azomethine nitrogen in complexation. A sharp band is seen at 1,665 cm^{-1} in the spectrum of hydrazone ligand which is indicative of the presence of amide-I band ν(C═O). Further, two additional bands observed at 1,510(w) and 1,325(sh) cm^{-1} in INAPH may be assigned as amide-II and amide-III bands[14] respectively. In the ternary complexes, these bands appear around at 1,650 1,525 and 1,310 cm^{-1} suggesting the coordination carbonyl oxygen.

The band present at 1,590 cm^{-1} (δNH) in the spectrum of MAMPB shifted to lower range 1565–1560 cm^{-1} band in the ternary complexes showing the involvement of nitrogen of NH group of MAMPB which is further confirmed by the negative shift (20–25 cm^{-1}) of ν(CH_2—N) vibrations observed at 2,800 cm^{-1}. ν(C═N) of benzimidazole ring (present in MAMPB) existing at 1,575 cm^{-1} shifted to lower frequency band (1,540–1,535 cm^{-1}) in the complexes suggesting the involvement of nitrogen of C═N.

Two non-ligand medium intensity bands appearing at 515–510 cm^{-1} and 415–405 cm^{-1} in the spectra of all the complexes may tentatively be assigned as ν(M—O) and ν(M—N) vibrations respectively. M—X (where X = Cl, Br, I) stretching vibration appears at 220–175 cm^{-1} in oxozirconium complexes only. In the spectrum of isothiocyanato complex of ZrO(IV), bands existing at 2,056, 844 and 477 cm^{-1} assigned to ν(C═N), ν(C—S) and δ(NCS) respectively are expected to be due to the terminal N-bonded isothiocyanato group[15, 16]. The characteristic ν(M═O) band occurs[17, 18] at 980 ± 30 cm^{-1} in all the complexes.

REFERENCES

1. N.V. Thakkar and B.C. Haldar, *J. Inorg. Nucl. Chem.*, **42,** 843 (1980).
2. C. Natarajan and A.M. Hussain, *Indian J. Chem.*, **20A,** 307 (1981).
3. B.C. Haldar, *J. Indian Chem. Soc.*, **51,** 224 (1974).
4. N.S. Dixit and C.C. Patel, *J. Indian Chem. Soc.*, **54,** 176 (1977).
5. R.R. Iyengar and C.C. Patel, *J. Coord. Chem.*, **8,** 135 (1978).
6. F.J. Welcher, Organic Analytical Reagents, Van Nostrand, N.Y., Vol. 3, p. 279 (1955).
7. Rajendra S. Verma, Vijay A. Singh, H.N. Verma and M.M. Abid Ali Khan, *J. Indian Chem. Soc.*, **62,** 475 (1985).
8. L. Gatterman and H. Wieland, Laboratory Methods of Organic Chemistry, Macmillan, N.Y., p. 144 (1943).
9. D.N. Sathyanarayana and C.C. Patel, *Indian J. Chem.*, 3, 486 (1965).
10. S.K. Madan and H.H. Denk, *J. Inorg. Nucl. Chem.*, **27,** 1049 (1965).
11. R.K. Agarwal, P.C. Jain, Mahesh Srivastava, A.K. Srivastava and T.N. Srivastava, *J. Indian Chem. Soc.*, **57,** 374 (1980).
12. W.J. Eilbeck, R.Y. Tyree and D.L. Venezky, *Inorg. Chem.*, **1,** 844 (1962).
13. A. Palm and H. Werbin, *Can. J. Chem.*, **1,** 1004 (1954).
14. K. Nakamoto, Infrared and Raman Spectra of Inorganic Coordination Compounds, Wiley-Interscience, N.Y., 308 (1978).
15. J.L. Burmeister, Coord. *Chem. Rev.*, **1,** 205 (1966); **3,** 225 (1968).
16. H. Mohanta and K.C. Dash, *J. Indian Chem. Soc.*, **54,** 166 (1977).
17. S.K. Madan and A.M. Donohue, *J. Inorg. Nucl. Chem.*, **28,** 1330 (1966).
18. C.G. Barraclough, J. Lewis and R.S. Nyholm, *J. Chem. Soc.*, 3552 (1959).

(*Received*: 1 March 2000; *Accepted*: 29 April 2000) AJC-2009