Asian Journal of Chemistry Vol. 9, No. 4 (1997), 831–836

Infrared and Thermal Studies of Some Six-Coordinated Zirconium(IV) Complexes of Schiff Bases of 4-Aminoantipyrine†

LAKSHMAN SINGH*, AJAY K. MANGLIK‡ and NARESH PAL DHAKA
Department of Chemistry
Lajpat Rai Post-Graduate College, Sahibabad-201 005 (Ghaziabad), India

In the present investigation, we wish to report the synthesis of some six-coordinated zirconium(IV) complexes of Schiff bases derived from 4-aminoantipyrine with the general composition $[Zr(OH)_2L_2]Cl_2$, where L = 4 [(N-benzalidene)amino]antipyrine, 4[(N-*p*-diaminobenzalidene)amino]antipyrine, 4[(N-2-hydroxybenzalidene)amino]antipyrine, 4[(N-*p*-methoxybenzalidene)amino]antipyrine, 4 [(N-4-hydroxy-3-methoxybenzalidene)amino]-antipyrine, 4[(N-2-hydroxy-1-naphthalidene)amino]antipyrine, 4-[(N-cinnamalidene)amino]antipyrine, 4[(N-(3,4,5-trimethoxyben zalidene)amino)]-antipyrine and 4[(N-furfural)amino]antipyrine. All the complexes were characterized by elemental analysis, conductance, molecular weight and infrared. The IR data of the complexes reveal the bidentate nature (O, N) of the ligand. The probable coordination number of zirconium(IV) is found to be six in the present complexes. Thermal data suggest the presence of coordinated water molecule in the complexes.

INTRODUCTION

Comparatively less is known about oxozirconium(IV) complexes of Schiff bases.[1-4] In view of it, we wish to report some six-coordinated oxozirconium(IV) complexes of Schiff bases of 4-aminoantipyrine, *e.g.*, 4[(N-benzalidene)-amino] antipyrine (BAAP), 4[(N-*p*-diaminobenzalidene)amino]antipyrine (DABAAP), 4[(N-2-hydroxybenzalidene)amino]antipyrine (HBAAP), 4[(N-*p*-methoxybenzalidene)amino]antipyrine (MBAAP), 4[(N-4-hydroxy-3-methoxy- benzalidene)-amino]antipyrine (HMBAAP), 4[(N-2-hydroxy-1-naphthalidene)-amino] antipyrine (HNAAP), 4[(N-cinnamalidene)amino]antipyrine (CAAP), 4[(N-3,4,5-trimethoxybenzalidene)amino]antipyrine (TMBAAP) and 4[(N-furfural) amino]antipyrine (FFAAP).

†This work was presented by Naresh Pal Dhaka at National Conference on Spectrophysics (NCONS '97) at Pachaiyappa College, Chennai, India, Feb 10–12, 1997.

‡Department of Chemistry, Meerut College, Meerut-250 001, India.

EXPERIMENTAL

Oxoziconium(IV) chloride was used as received from Reidel. The ligands were synthesized in the laboratory by the following general method. A solution of aromatic aldehyde, *viz.*, benzaldehyde, *p*-dimethylaminobenzaldehyde, salicylaldehyde, *p*-methoxybenzaldehyde, vanillin, 2-hydroxy-1-naphthaldehyde, cinnamaldehyde, 3,4,5-trimethoxybenzaldehyde or furfural in absolute ethanol was mixed with 4-aminoantipyrine (in 1 : 1 molar ratio) in the same solvent and the mixture was refluxed for 2–3 h. On cooling a yellow crystalline product was separated, which was filtered off and recrystallized in the same solvent (yield 80–85%).

All the complexes of ZrO^{2+} with Schiff bases were prepared according to the following method. To the corresponding Schiff base solution (2 mmol), a methonolic solution of oxozirconium(IV) chloride (1 mmol) was added and the mixture was refluxed on a water bath for *ca.* 3 h and then cooled to room temperature. The separated products were suction filtered, washed with methanol followed by ether and dried under vacuum.

The analyses and physical measurements were performed as reported previously.[5]

RESULTS AND DISCUSSION

The physical and analytical data of all the complexes (Table-1) correspond to the formula $ZrOCl_2 \cdot 2L \cdot H_2O$. They are generally soluble in common organic solvents. The observed molar conductance (Table-1) of these complexes suggests that the complexes are ionic in nature and both the chloro ions are present outside the coordination sphere. The molecular weights of the complexes as determined cryoscopically in freezing nitrobenzene are in good agreement with the conductance data. All the complexes are diamagnetic in nature.

Infrared spectra

The partial infrared data of all the ligands and their ZrO^{2+} complexes are given in Table 2. The C=O stretching frequency occurs in 1660–1590 cm^{-1} region in the free ligands.[6, 7] The infrared spectra of all the complexes show a considerable shift to lower frequency for the carbonyl (pyrazolone) absorption, $\Delta\nu$(C=O) 45–60 cm^{-1}, indicating a decrease in the stretching force constant of C=O as a consequence of coordination through the oxygen atom of the free bases. This exceptionally high shift to lower frequency of the carbonyl frequency may be attributed to the greater flow of electrons from the carbonyl group to the Zr^{4+} due to greater delocalization of positive charge on the nitrogen atom. Another important band occurs in 1610–1580 cm^{-1} region attributed to the ν(C=N) mode.[6, 7] In spectra of all the complexes this band is shifted to lower wave number and appears in 1580–1550 cm^{-1} region indicating the involvement of the N-atom of the azomethine group in coordination.[6, 7]

TABLE-1

ANALYTICAL, CONDUCTIVITY AND MOLECULAR WEIGHT DATA OF ZrO^{2+} COMPLEXES OF SCHIFF BASES DERIVED FROM 4-AMINOANTIPYRINE

Complex	Yield (%)	% Found (calcd.)			Mol. wt. found (calcd.)	Ω_m (ohm^{-1} cm^2 $mole^{-1}$)
		Zr	N	Cl		
$ZrOCl_2 \cdot 2(BAAP) \cdot H_2O$	70	11.59 (11.69)	10.68 (10.79)	9.04 (9.12)	257 (778)	53.6
$ZrOCl_2 \cdot 2(DABAAP) \cdot H_2O$	65	10.44 (10.53)	11.01 (11.10)	8.13 (8.21)	285 (864)	52.9
$ZrOCl_2 \cdot 2(HBAAP) \cdot H_2O$	72	11.14 (11.23)	10.26 (10.37)	8.69 (8.76)	267 (810)	50.8
$ZrOCl_2 \cdot 2(MBAAP) \cdot H_2O$	62	10.76 (10.85)	9.93 (10.02)	8.38 (8.47)	275 (838)	51.6
$ZrOCl_2 \cdot 2(HMAAP) \cdot H_2O$	65	10.36 (10.45)	9.57 (9.65)	8.08 (8.16)	286 (870)	52.6
$ZrOCl_2 \cdot 2(HNAAP) \cdot H_2O$	70	9.91 (10.00)	9.14 (9.23)	7.72 (7.80)	298 (910)	52.0
$ZrOCl_2 \cdot 2(CAAP) \cdot H_2O$	70	10.85 (10.96)	10.03 (10.12)	8.47 (8.55)	274 (830)	54.0
$ZrOCl_2 \cdot 2(TMBAAP) \cdot H_2O$	68	9.39 (9.49)	8.58 (8.76)	7.34 (7.41)	316 (958)	52.9
$ZrOCl_2 \cdot 2(FFAAP) \cdot H_2O \cdot$	70	11.92 (12.00)	10.96 (11.08)	9.28 (9.36)	247 (758)	51.6

The strong band in the 1600–1590 cm^{-1} range has been assigned to the ring stretching of the 5-membered ring in the present complexes. Five-membered heteroaromatic compounds were found to give two strong bands near 1560 and 1490 cm^{-1} which are considered to be characteristic of a five-membered ring. The bands assigned to the vibrations of the benzene ring compare well with those of mono-substituted derivatives of benzene. Several other absorptions associated with C—H out-of-plane deformation modes appear in the range 920–720 cm^{-1} in the present Schiff bases. Such absorptions associated with the pyrazolone ring undergo a slight shift to higher frequency due to a decrease of electron density on the aromatic ring on complexation.

In the far-infrared region, an absorption at *ca.* 660 cm^{-1} has been assigned to C=O in-plane bending in the free ligands. This shows a shift to higher frequency on complexation. The hands in the range 445–370 cm^{-1} have been assigned to ν(Zr—N) and ν(Zr—O) modes.[8,9] In all ZrO^{2+} complexes, the presence of coordinated water was suggested by the very broad absorption centred around

3400 cm^{-1} in the infrared spectra. Bands at *ca.* 930 and 770 cm^{-1} may be attributed to rocking and wagging modes of the coordinated water.[10]

TABLE-2
SELECTED IR BANDS (cm^{-1}) OF ZrO^{2+} COMPLEXES OF BASIS OF 4-AMINOANTIPYRINE

Compound	ν(OH)	ν(C=O) (pyrazolone)	ν(C=N) (azomethine)	ν(Zr—N)/ν(Zr—O)
BAAP	—	1645 vs	1590 s	—
$ZrOCl_2$2(BAAP)·H_2O	3400 s, br	1595 s	1550 s	435 m, 390 m
DABAAP	—	1650 vs 1645 vs	1610 vs 1592 s	—
$ZrOCl_2$·2(DABAAP)·H_2O	3410 s, br	1598 s 1592 m	1580 s	440 m, 392 w
HBAAP	—	1670 vs 1655 sh	1600 s	—
$ZrOCl_2$·2(HBAAP)·H_2O	3400 s, br	1602 s 1590 m	1570 m	435 m, 395 w
MBAAP	—	1640 s 1610 s	1590 s	—
$ZrOCl_2$·2(MBAAP)·H_2O	3405 s, br	1595 s	1565 s	442 m, 385 w
HMBAAP	—	1620 s	1580 s	—
$ZrOCl_2$·2(HMBAAP)·H_2O	3390 s, br	1590 s	1562 s	430 m, 380 w
HNAAP	—	1640 vs 1635 vs	1590 vs	—
$ZrOCl_2$·2(HNAAP)·H_2O	3390 s, br	1595 s	1560 s	435 m, 382 w
CAAP	—	1660 vs	1600 sh 1587 s	—
$ZrOCl_2$·2(CAAP)·H_2O	3410 s, br	1605 s	1580 m	445 m, 375 w
TMBAAP	—	1650 s	1590 s	—
$ZrOCl_2$·2(TMBAAP)·H_2O	3405 s, br	1600 s	1560 s	430 m, 370 w
FFAAP	—	1650 vs	1590 s	—
$ZrOCl_2$·2(FFAAP)·H_2O	3400 s, br	1590 s	1565 s	435 m, 375 w

(Zr=O) cation belongs to class-A oxocations in which the M=O characteristic band falls in the region 1000–900 cm^{-1}. In the case of ZrO^{2+} complexes sometimes ν(Zr=O) band is displaced to a lower spectral region due to polarization of Zr=O band. Paul *et al.*[11] represented the polarization structure in the case of oxozirconium(IV) chloride adducts of amides. In the past, a number of workers have isolated the oxoziroconium(IV) complexes of various Schiff bases[1-3] and tried to locate the ν(Zr=O) stretching. But this assignment is not unambiguous. In the present complexes a weak band in 825–815 cm^{-1} is assigned to the ν(Zr=O) vibration.[12] However, there is no reliable evidence for the existence of the (Zr=O) moiety zirconyl complexes. The structure determination

of $ZrOCl_2 \cdot 8H_2O$ by Clearfield and Vaughan[13] was a great step forward, since it showed that this compound contained $[Zr(OH)_2]^{2+}$ or $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ ions in aqueous solution.

TABLE-3
THERMOANALYTICAL RESULTS OBTAINED FOR THE ZrO^{2+} COMPLEXES OF SCHIFF BASES OF 4-AMINOANTIPYRINE

Complex	Decomp. Temp. (°C)		Decomp. product	TG loss wt. (%)	
	Initial	Final		Found	Calcd.
$ZrOCl_2 \cdot 2(BAAP) \cdot H_2O$	70	125	$ZrOCl_2 \cdot 2(BAAP)$	2.39	2.31
	185	235	$ZrOCl_2(BAAP)$	40.23	39.71
	295	350	$ZrOCl_2$	78.06	77.12
	415	625	ZrO_2	84.92	84.19
$ZrOCl_2 \cdot 2(DABAAP) \cdot H_2O$	80	130	$ZrOCl_2 \cdot 2(DABAAP)$	2.16	2.08
	190	245	$ZrOCl_2 \cdot (DABAAP)$	41.26	40.74
	300	355	$ZrOCl_2$	80.12	79.39
	420	635	ZrO_2	86.16	85.76
$ZrOCl_2 \cdot 2(HNAAP) \cdot H_2O$	80	135	$ZrOCl_2 \cdot 2(HNAAP)$	2.11	1.97
	200	245	$ZrOCl_2 \cdot (HNAAP)$	41.98	41.20
	300	375	$ZrOCl_2$	81.12	80.43
	415	640	ZrO_2	87.09	86.48
$ZrOCl_2 \cdot 2(FFAAP) \cdot H_2O$	75	130	$ZrOCl_2 \cdot 2(FFAAP)$	2.42	2.37
	170	255	$ZrOCl_2 \cdot (FFAAP)$	39.96	39.44
	275	375	$ZrOCl_2$	77.26	76.51
	410	645	ZrO_2	84.26	83.77

Thermal studies

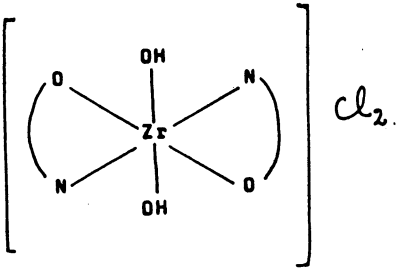
Thermal decomposition data of the ZrO^{2+} complexes are presented in Table-3. The careful analysis of TG curves suggested that the complexes contain one molecule of coordinated water, which is evident by loss in weight of 2.11–2.42% at *ca.*130°C. There is no change up to 200°C, after that there is a break in the curves due to evaporation of one molecule of Schiff base, the remaining Schiff base is removed from the coordination sphere at 375°C. Finally at *ca.* 640°C, ZrO_2 is formed.[14, 15] In brief, the thermal equations of these equations can be presented as follows:

$$ZrOCl_2 \cdot 2L \cdot H_2O \rightarrow ZrOCl_2 \cdot 2L \rightarrow ZrOCl_2 \cdot L \rightarrow ZrOCl_2 \rightarrow ZrO_2$$

(L = BAAP, DABAAR, HNAAP or FFAP)

In conclusion, the data on stoichiometry of ZrO^{2+} complexes and their physico-chemical studies indicate that the probable coordination number for zirconium in these complexes is six. There is no reliable evidence for the existence of the (Zr=O) moiety in zirconyl complexes. The conductance measurement indicates the ionic nature of these complexes which behave as 1 : 2 electrolytes and should have the composition $[Zr(OH)_2L_2]Cl_2$. The infrared data reveal the

bidentate (N, O) nature of these ligands. Thus in $[Zr(OH)_2L_2]Cl_2$, the coordination number of Zr^{4+} is suggested to be six and may have the following structure.



REFERENCES

1. A. Syamal and D. Kumar, *Synth. React. Inorg. Met.-Org. Chem.*, **10**, 63 (1980).
2. Angela Kriza and Marta Narta, *Rev. Roum. Chim.*, **26**, 693 (1981).
3. H.D.S. Yadava, S.K. Sengupta and S.C. Tripathi, *Inorg. Chim. Acta*, **128**, 1 (1987).
4. M. Gaber, M.M. Ayad and M.L. Ayad, *Thermochim. Acta*, **176**, 21 (1991).
5. R.K. Agarwal, P.C. Jain, M. Srivastava, A.K. Srivastava and T.N. Srivastava, *J. Indian Chem. Soc.*, **57**, 374 (1980).
6. G.S. Devi and P. Indrasenan, *Inorg. Chim. Acta*, **133**, 157 (1987).
7. P.S. Radhakrishnan and P. Indrasenan, *Indian J. Chem.*, **28A**, 234 (1989).
8. A.K. Srivastava, R.K. Agarwal and T.N. Srivastava, *J. Indian Chem. Soc.*, **58**, 710 (1981).
9. R.K. Agarwal, M. Srivastava, A.K. Srivastava and T.N. Srivastava, *J. Inorg. Nucl. Chem.*, **43**, 2144 (1981).
10. D.M. Adams, Metal-Ligand and Related Vibrations, Arnold, London (1967).
11. R.C. Paul, S.L. Chadha and S.K. Vashisht, *J. Less Common Metals*,**16**, 288 (1968).
12. J.R. Ferraro, Low Frequency Vibrations of Inorganic and Coordination Compounds, Plenum, New York (1971).
13. A. Clearfield and P.A. Vaughan, *Acta Crystallogr.*, **9**, 555 (1956).
14. A. K. Srivastava, M. Srivastava and R.K. Agarwal, *Ind. Engg. Chem. Products Res. and Dev.*, **21**, 135 (1982).
15. R.K. Agarwal, M. Srivastava, B.S. Tyagi and A.K. Srivastava, *Thermochim. Acta*, **61**, 235 (1983).

(*Received:* 3 March 1997; *Accepted:* 12 June 1997) AJC-1302