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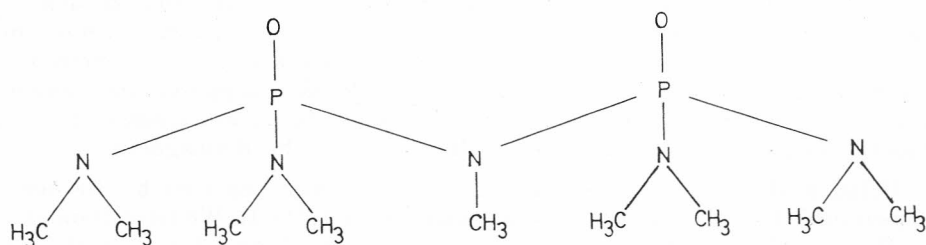
Oxozirconium(IV) Complexes of Nonamethylimidodiphosphoramidate*R. K. Agarwal* and S. C. Rastogi****Department of Chemistry, Lajpat Rai Post-Graduate College, Sahibabad-201 005, India*

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A series of new complexes of the type $ZrOX_2(NIPA)$ ($X = Cl, Br, I, NO_3, NCS, NCSe$ or BPh_4) and $ZrO(ClO_4)_2 \cdot 2(NIPA)$ have been synthesised and characterized through molar conductance, molecular weight, magnetic measurement and in dependence on the nature of anion.

INTRODUCTION

In recent years we have reported a number of oxozirconium(IV) complexes of oxygen donor molecules containing an $X = O$ group (where $X = C, N, S$ or P)¹. Comparatively less is known about the compounds of oxozirconium(IV) with $P = O$ containing ligands. Only triphenyl phosphine oxide², hexamethylphosphoramidate³ and octamethylpyrophosphoramidate⁴ complexes of oxozirconium have been reported. In this series, we wish to report our results on oxozirconium(IV) complexes of nonamethylimidodiphosphoramidate (NIPA) (I). It



I

is a very potential bidentate ligand. Lannert and Joesten^{5,6} and then Bolster⁷ reported the preparation and identification of a large number of transition, non-transition and actinide metal complexes of NIPA.

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EXPERIMENTAL

Material

Zirconyl(IV) nitrate used was obtained from BDH, while perchlorate, thiocyanate and selenocyanate were prepared from nitrate as reported earlier^{8,9} oxo-zirconium(IV) chloride was obtained from Reidal, while the bromide and iodide were prepared from the chloride by displacement method. Oxozirconium(IV) tetraphenylboronate was prepared in solution by mixing acetonic solutions of anhydrous $ZrOCl_2$ and $NaBPh_4$ and filtering out the precipitated $NaCl$ ¹⁰. The ligand NIPA was prepared by reported methods^{5,11}.

Preparation of Complexes

All the complexes were prepared by a general method. A solution of zirconyl(IV) salt in methanol or acetone was treated with an excess of NIPA in the same solvent. The mixture was refluxed for 3 hr. and the excess solvent removed by distillation. The residual mass on treatment with diethyl ether yielded a crystalline solid, which was filtered, washed with diethyl ether and dried in vacuum over P_4O_{10} .

Analytical Procedures

The metal content of the complexes was determined as oxide¹³. The perchlorate was determined by the method of Kurz and the halide contents by Volhard's method, while the thiocyanate was determined by titration of a slightly acidic solution of the complex against standard $AgNO_3$.

The electrical conductances of the complexes were measured with a Toshniwal Conductivity bridge at room temperature and their molecular weights were determined cryoscopically in freezing $PhNO_2$. Magnetic susceptibility measurements on powder form of the complexes were made at room temperature using Gouy's balance at ca. 11000 gauss.

RESULTS AND DISCUSSION

The analytical data correspond to the composition $ZrOX_2 \cdot L$ ($X = Cl, Br, I, NO_3, NCS, NCSe$ or BPh_4) and $ZrO(ClO_4) \cdot 2L$ ($L = NIPA$). The complexes are quite sensitive to atmospheric moisture. The molar conductances of the complexes in nitrobenzene indicate that chloro, bromo, iodo, thio & selenocyanato and tetraphenylboronato complexes are non-electrolytes, while the perchlorato complex behaves like uni-bivalent electrolyte. The molecular weight determined cryoscopically in freezing $PhNO_2$ supports the similar electrolytic behaviour of the complexes. The magnetic measurements at room temperature (20 °C) of the complexes show them to be diamagnetic.

Detailed IR studies of the free ligands have been reported by Joesten^{5,6} and boleter⁷. Pertinent IR data are summarized in Table II. We have compared the IR spectra of NIPA and its complexes with those of hexamethylene phosphoramidate³ and octamethylpyrophosphoramidate⁴ and their complexes with zirconyl(IV) ions. The PNP stretch has been assigned to the peak at 885 cm^{-1} , while the PNC stretching has been assigned to 978 cm^{-1} and 745 cm^{-1} . Both the PNP and PNC stretching frequencies for complexes of NIPA are shifted to higher frequencies. The P = O stretch, a broad band in the IR spectrum of the ligand, appears at ca. 1203 cm^{-1} split into a sharp strong at ca. 1200 cm^{-1} and a sharp medium intensity peak at ca. 1180 cm^{-1} in the spectra of all complexes. According to Joesten *et al.*^{5,6} this effect is attributed to the coupling between two PO vibrations via the metal atom to which they are both coordinated. It is further noted that in all NIPA complexes the PO bending

TABLE I
of NIPA
Analytical Conductivity and Molecular Weight of Oxozirconium(IV) Complexes

Compound	Analysis % Found (Calcd.)				Anion	$\Omega \text{ m}_2$ ohm ⁻¹ cm ² mole ⁻¹	Mol. Wt. in PhNO ₂	Formula Weight
	Metal	N	P					
ZrO(NIPA)Cl ₂	18.86 (19.07)	14.39 (14.67)	12.79 (12.99)	14.54 (14.88)		5.02	469	477
ZrO(NIPA)Br ₂	15.92 (16.07)	12.19 (12.36)	11.16 (10.95)	28.06 (28.26)		5.46	559	566
ZrO(NIPA)I ₂	13.59 (13.78)	10.72 (10.60)	9.52 (9.39)	38.06 (38.48)		4.89	638	660
ZrO(NIPA) ₂ (ClO ₄) ₂	9.87 (10.06)	15.69 (15.48)	13.86 (13.71)	21.56 (22.01)		50.96	298	904
ZrO(NIPA)(NO ₃) ₂	16.93 (17.16)	18.82 (18.49)	11.75 (11.69)	—		5.50	521	530
ZrO(NIPA)(NCS) ₂	17.16 (17.43)	18.42 (18.77)	11.95 (11.87)	21.84 (22.22)		4.98	512	522
ZrO(NIPA)(NCSe) ₂	14.52 (14.77)	15.69 (15.90)	10.24 (10.06)	—		4.08	608	616
ZrO(NIPA)(BPh ₄) ₂	18.89 (18.71)	6.34 (6.70)	6.13 (5.93)	—		4.12	1029	1044

vibration is shifted to higher energy; the magnitude and direction of this shift indicates that coordination occurs via the oxygen atoms of the ligand⁷.

It would not be possible to assign a Zr=O (oxocation) stretching frequency, since this occurs in the same region as ν (PNC) (1000—950 cm^{-1}).

Some new medium or weak bands are observed in the range 400—350 cm^{-1} in these complexes where the ligand itself has no absorptions. These new bands are tentatively assigned as ν (M—O). These frequencies are in good agreement with M—O stretching modes observed for several transition metal complexes^{1,12,13}.

TABLE II
Pertinent Infrared Data (cm^{-1}) of Oxozirconium(IV) Complexes of NIPA

Compound	ν (P=O)	ν (P—N—P)	ν (PNC)	ν (PNC)	ν (M—O)
NIPA	1195s	885s	975m	745w	—
ZrO(NIPA)Cl ₂	1200s 1185s	900m	990m 980m	750w	400m
ZrO(NIPA)Br ₂	1202s 1185s	895m	988m 980sh	749w	395m
ZrO(NIPA)I ₂	1200s 1180m	890m	990m 985sh	750w	390m
ZrO(NIPA) ₂ (ClO ₄) ₂	1198s 1180m	890m	985m	755w	395m
ZrO(NIPA)(NO ₃) ₂	1200s 1180m	885m	990m 980sh	758w	390w, 385sh
ZrO(NIPA)(NCS) ₂	1200s 1185m	900m	985m 980sh	760w	395m
ZrO(NIPA)(NCSe) ₂	1185s 1155sh	885m	980m	752w	380m
ZrO(NIPA)(BPh ₄) ₂	1185s 1160sh	890m	990m 985m	758w	385m

In [ZrO(NIPA)₂](ClO₄)₂, both the ν_3 and ν_4 IR bands of perchlorate appear as a strong absorption at 1082 and 620 cm^{-1} respectively, showing the ionic character of the perchlorate groups. The absence of the ν_3 bands of ionic nitrate (D_{3h}) around 1360 cm^{-1} and the occurrence of two strong bands at 1520 and 1300 cm^{-1} in the spectrum of ZrO(NIPA)(NO₃)₂ suggest the coordination of nitrate in this complex^{14,15}. The bidentate nature of nitrate groups is revealed by the presence of bands at 1030 cm^{-1} (ν_2), 805 cm^{-1} (ν_6), and 720 cm^{-1} (ν_3/ν_5)¹⁶. The combination bands ($\nu_1 + \nu_4$) in 1800—1700 region appear at 1740 and 1700 cm^{-1} in this complex. By applying the Lever separation method¹⁷, the separation of these bands (40 cm^{-1}) clearly indicates bidentate nitrate coordination. Furthermore, the band associated with (Zr—O) (nitrate) is tentatively assigned at ca. 215 cm^{-1} as weak absorption. In thio and selenocyanato complexes the presence of bands in the region 2060 cm^{-1} (ν C \equiv N), 860 cm^{-1} (ν C—X) and 475 cm^{-1} (δ NCX) (X = S or Se) in normally associated with the terminal N-bonding thio and selenocyanato group¹⁸. This is quite possible

since zirconium is a typical hard metal. The N-bonding is further evidenced by a (Zr—N) absorption (tentatively assigned) at 270 cm^{-1} for thiocyanate and 230 cm^{-1} for selenocyanate²⁰. The investigation of $\text{ZrO}(\text{NIPA})(\text{BPh}_4)_2$ shows the four medium or strong bands at 1480, 1450, 1435 and 1390 cm^{-1} , which may indicate the covalent nature of BPh_4 ions, bonded to the metal ion through the π -bond of a phenyl group^{10,21,22}.

In the chloro complex Zr—Cl stretching vibrations occur at 290 cm^{-1} with a shoulder of 275 cm^{-1} . The Zr—Br and Zr—I stretching vibrations could not be observed in the spectral range studied.

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SAŽETAK

Kompleksi oksocirkonija(IV) s nonametimidodifosforamidom

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Sintetiziran je niz kompleksnih spojeva tipa $\text{ZrOX}_2(\text{NIPA})$ (gdje su: NIPA—nonametimidodifosforamid, X = Cl, Br, I, NO_3 , NCS, NCSe i BPh_4) i $\text{ZrO}(\text{ClO}_4)_2 \cdot 2(\text{NIPA})$.

Karakterizacija kompleksnih specija izvršena je određivanjem molarne provodnosti, molarne mase, magnetskih svojstava i IR-spektara.