

Reaction of *o*-phenanthroline or dipyridyl with $[\text{Cr}(\text{tu})_2\text{Cl}_2]$ is known⁶ to produce complexes of the type $[\text{Cr}(\text{tu})_2(\text{o-phen/dipy})_2]\text{Cl}_2$. The reaction of 2-(2'-pyridyl) benzimidazole with $[\text{Cr}(\text{tu})_2(\text{o-phen/dipy})_2]\text{Cl}_2$ (prepared *in situ*) gave complexes of the type $[\text{Cr}(\text{PBz})(\text{o-phen/dipy})(\text{tu})_2]\text{Cl}_2$. It is of interest to note that even a large excess of the ligand PBzH could not displace the two thiourea ligands, which are therefore likely to be *trans* disposed. Only at high dilution ($\sim 10^{-4}M$) in methanol a 2 : 1 electrolytic conductance ($\Delta_{\text{cr}} \sim 160 \text{ ohms}^{-1} \text{ cm}^2 \text{ mole}^{-1}$) is observed. Magnetic moments (3.6-3.8 B.M.) are normal. Electronic spectra give 10 Dq values around 17-18 kK (${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition).

Acknowledgement

We are grateful to the University Grants Commission for financial support.

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Studies on Th(IV) and Zr(IV) Complexes of Oxygen Donor Ligands-III. Pyrazolone Derivatives of Oxozirconium(IV)[†]

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Manuscript received 4 April 1979, revised 13 November 1980,
accepted 23 April 1981

CONSIDERABLE attention has recently been focussed on coordination behaviour of pyrazolone ligands such as antipyrine (Apy) and 4 amino antipyrine (AApy)¹. The isolation and characterization of some new complexes of oxozirconium(IV)

with Apy and AApy are reported in this communication.

Experimental

Antipyrine was obtained from Fluka, while 4-amino antipyrine from Koch-Light Laboratories Ltd. (England). Lewis acids were obtained as reported earlier².

The complexes were prepared by the following general method. Methanolic solutions of oxozirconium(IV) salts were mixed with the ligand in the same solvent in the required molar ratio. The thiocyanato complexes separated out immediately; the perchlorato complex was obtained as a brown-yellow crystalline solid after constant stirring of the reaction mixture for about $\frac{1}{2}$ hr; the chloro complexes compound after concentrating the reaction mixture on a water bath while the bromo, iodo and nitrate complexes were obtained after refluxing the reaction mixture for ca 2 hr, removing the excess solvent by distillation and treating the residual mass with ether.

The complexes thus obtained were filtered, washed with appropriate solvent and finally with ether and dried in a vacuum desiccator over P_4O_{10} .

The analyses and physical measurements of the complexes were made as reported earlier².

Results and Discussion

The analytical data of the complexes along with their colour are recorded in Table I. The electrical conductance measurement in nitrobenzene and dimethyl sulphoxide indicate [Table I] that the chloride and bromide complexes are non-electrolytes; nitrate and thiocyanate complexes behave like 1 : 1 while iodide and perchlorate complexes correspond to 1 : 2 electrolytes. The molar conductance measurements of $\text{Zr}(\text{AApy})_2(\text{ClO}_4)_4$ indicate it to be a 1 : 3 electrolyte. The molecular weight determination of the complexes also support the same electrolytic behaviour of the complexes except $[\text{ZrO}(\text{AApy})(\text{NCS})_2]$. The cryoscopic molecular weight determination of this complex indicates the formation of 1.5 species per formula unit. This behaviour can be explained provided the formation of three species per two formula units of the complex is proposed as $[\text{ZrO}(\text{AApy})(\text{NCS})]_2(\text{NCS})_2$.

Detailed ir studies of the pyrazolones have been reported recently^{1,2}. Pertinent ir spectra of the complexes show a considerable shift ($\sim 100 \text{ cm}^{-1}$) of carbonyl absorption to lower frequency, indicating a decrease in the stretching force constant of C=O as a consequence of coordination through its oxygen. Thus C=O stretching frequency which occurs at 1660 cm^{-1} in the free ligand has been observed in the region $1550\text{-}1580 \text{ cm}^{-1}$ in all the complexes. Several absorptions associated with C-H out-of-plane deformation modes appear in the range $920\text{-}720 \text{ cm}^{-1}$ in antipyrine^{1,2}. Such absorptions associated with the pyrazolone ring undergo

[†] Presented at the 48th Annual Session of National Academy of Sciences (India), Gauhati University, Gauhati, on Oct. 22-24, 1978.

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NOTES

TABLE 1—ANALYTICAL, CONDUCTIVITY AND MOLECULAR WEIGHT DATA FOR ZrO(IV) COMPLEX OF ANTIPYRINE AND 4-AMINO ANTIPYRINE

Compound	Colour	Metal% Found (Calcd.)	Nitrogen% Found (Calcd.)	Carbon% Found (Calcd.)	Hydrogen% Found (Calcd.)	Anion% Found (Calcd.)	λ_m (ohm ⁻¹ cm ² mole ⁻¹)	Electrolytic nature	Average mol. wt. in PhNO ₂	Formula weight
ZrO(Apy) ₂ Cl ₂	Light yellow	16.89 (16.72)	10.19 (10.10)	47.91 (47.65)	4.31 (4.33)	12.93 (12.81)	1.3 ^a 7.4 ^b	Non- electrolyte	520	554
ZrO(Apy) ₂ Br ₂	Yellow	14.27 (14.15)	8.79 (8.70)	41.16 (41.05)	3.91 (3.73)	24.62 (24.88)	0.8 ^a 7.9 ^b	Non- electrolyte	615	643
ZrO(Apy) ₂ I ₂	Yellow	8.29 (8.17)	10.20 (10.06)	47.61 (47.43)	4.40 (4.31)	22.50 (22.82)	50.9 ^a 78.3 ^b	1 : 2	859	1118
ZrO(Apy) ₂ (NCS) ₂	Light pink	11.71 (11.56)	14.39 (14.28)	53.47 (53.36)	4.49 (4.57)	14.61 (14.73)	23.8 ^a 58.9 ^b	1 : 1	350	787
ZrO(Apy) ₂ (NO ₂) ₂	Light yellow	14.89 (14.99)	13.97 (13.88)	43.61 (43.49)	3.87 (3.97)	—	24.9 ^a 54.3 ^b	1 : 1	282	607
ZrO(AApy) ₂ Cl ₂	Yellow	15.49 (15.58)	14.46 (14.38)	45.29 (45.20)	4.51 (4.45)	12.21 (12.15)	1.1 ^a 8.3 ^b	Non- electrolyte	570	584
ZrO(AApy)Br ₂	Yellow	19.63 (19.36)	9.01 (8.98)	28.16 (28.08)	2.79 (2.76)	34.19 (34.04)	1.7 ^a 9.2 ^b	Non- electrolyte	435	470
ZrO(AApy) ₂ I ₂	Brown	11.73 (11.86)	10.09 (10.95)	34.37 (34.41)	3.49 (3.38)	32.81 (33.11)	49.7 ^a 76.5 ^b	1 : 2	250	767
ZrO(AApy)(NCS) ₂	Light pink	21.59 (21.36)	16.37 (16.43)	36.52 (36.61)	3.12 (3.05)	26.51 (26.29)	23.9 ^a 62.3 ^b	1 : 1	280	426
ZrO(AApy) ₂ (NO ₂) ₂	Light yellow	14.89 (14.28)	17.41 (17.58)	41.27 (41.44)	4.16 (4.08)	—	24.7 ^a 55.9 ^b	1 : 1	302	637
ZrO(AApy) ₂ (ClO ₄) ₂	Brown	10.09 (9.94)	13.68 (13.77)	43.39 (43.27)	4.39 (4.26)	21.21 (21.74)	44.9 ^a 79.7 ^b	1 : 2	290	915

* Insoluble.
a—Nitrobenzene.
b—Dimethylsulphoxide.

TABLE 2—IR SPECTRAL BANDS (cm⁻¹) AND VALUES OF I.P., log K AND -ΔF° OF PYRAZOLONE COMPLEXES OF ZIRCONIUM(IV)

Compound	ν (NH) asym sym	ν (C=O)	ν (M-O)/ ν (M-N)	$\Delta \nu$ (C=O) cm ⁻¹	I.P. e.v.	log K	-ΔF° k cal
Antipyrine	—	1660vs	—	—	—	—	—
ZrO(Apy) ₂ Cl ₂	—	1560s 1545s	410m	107	4.9815	1.9648	2.6509
ZrO(Apy) ₂ Br ₂	—	1575vs	400m	85	5.6849	2.9061	3.9219
ZrO(Apy) ₂ I ₂	—	1570vs	405w	90	5.5136	2.6920	3.6330
ZrO(Apy) ₂ (NCS) ₂	—	1580vs	385m	80	5.8561	3.1201	4.2107
ZrO(Apy) ₂ (NO ₂) ₂	—	1560s 1550s	410m	110	4.8287	1.8358	2.4776
4-Amino antipyrine	3430s 3320s	1670s 1640vs	—	—	—	—	—
ZrO(AApy) ₂ Cl ₂	3230s 3190m	1560s 1540s	400m 370m	105	4.8287	1.8359	2.4777
ZrO(AApy)Br ₂	3220s 3120m	1560s 1556s	397m 365m	97	5.1027	2.1784	2.9399
ZrO(AApy) ₂ I ₂	3220m 3000w	1560s	395w 382m	95	5.1712	2.2640	3.0554
ZrO(AApy)(NCS) ₂	3310m 3180m	1560s 1560vs	398m 360w	100	5.0000	2.0500	2.7665
ZrO(AApy) ₂ (NO ₂) ₂	3318m 3090s	1560vs 1540s	400m 372m	105	4.8287	1.8359	2.4777
ZrO(AApy) ₂ (ClO ₄) ₂	3290m 3195m	1580s	390m	75	5.8561	3.1201	4.2108

Values calculated at 20°.

slight positive shift due to decrease of electron density on the aromatic ring on complexation. In the far infrared region, an absorption at ~630 cm⁻¹ has been assigned to C=O in-plane bending in the free ligand. This undergoes a slight shift on complexation. Some new medium or weak bands are observed in the 415-350 cm⁻¹ region in these complexes, and have been tentatively assigned as M-O frequencies^{3,4}.

In 4-amino antipyrine, the frequencies in the N-H stretching as well C=O stretching decrease in all the compounds (Table 2). Thus, zirconyl ions form chelates with 4-amino antipyrine using N-atom of the -NH₂ group and O-atom of the carbonyl group. This is also confirmed by the appearance of M-N and M-O bands in far ir region. Other ir frequencies are almost similar to antipyrine molecule. A weak band in 970-950 cm⁻¹ region in all

the complexes is attributed as Zr=O double bond stretching frequency^{4,5}.

In ZrO(AApy)(ClO₄)₂, the ν_3 and ν_4 bands for the perchlorate ion appear at 1082 and 620 cm⁻¹ respectively, indicating that the ClO₄ ions are not bonded to the metal ions⁴⁻⁷. In nitrate complexes, the appearance of bands at 1360 and 830 cm⁻¹ due to ionic nitrate⁸ and 1530 and 1280 cm⁻¹ due to covalent nitrate group⁹, indicate the presence of both ionic and covalent nitrate groups. The bidentate nature of the covalent nitrate group in these complexes is established by the presence of bands at ~1030 cm⁻¹ (ν_8), ~817 cm⁻¹ (ν_8) and 725 cm⁻¹ (ν_8/ν_8)¹⁰. In [ZrO(Apy)₂(NCS)](NCS) the new bands are assigned as ν_{CN} (~2050 cm⁻¹), ν_{CS} (~830 cm⁻¹) and δ_{NCS} (~465 cm⁻¹) modes; a band at ~2040 cm⁻¹ seems to be due to CN stretch of ionic SCN⁻ in the complex. We, therefore, concluded that the metal ion is coordinated with terminal N-bonded isothiocyanate¹¹. Corresponding bands in [ZrO(AApy)(NCS)](NCS) have been observed at 2052 and 2040 (ν_1), 830(ν_3) and 465 cm⁻¹ (ν_2). The band at 2040 cm⁻¹ seems to be due to CN stretch of ionic SCN⁻ in the complex. From

these frequencies N-bonding of the thiocyanate groups in the oxozirconium(IV) complex may be inferred. The solution studies, however, require this complex to be binuclear containing both bridged and ionic thiocyanates. The lower value of ν_{CN} at 2052 than expected for a bridging thiocyanate may be due to the strong interaction of nitrogen on one side and weak interaction of the sulphur on the other sides of the bridging thiocyanate with zirconium atoms^{12,13}.

Relation between $\Delta\nu$ (C=O) and I. P., log K and $-\Delta F^\circ$: With the help of ir spectra of different compounds we have made an attempt to correlate the magnitude of the shift in the carbonyl stretching i.e., $\Delta\nu$ (C=O) in various complexes with ionization potential (I. P.), stability constant (log K) and change in free energy ($-\Delta F^\circ$)^{11,14}. The calculated values of I. P., log K and $-\Delta F^\circ$ and $\Delta\nu$ (C=O) values are shown in Table 2. On plotting a graph between $\Delta\nu$ (C=O) and I. P., log K and $-\Delta F^\circ$; a straight line is obtained (Figs. 1 and 2) in all the cases which can be extrapolated to find these values,

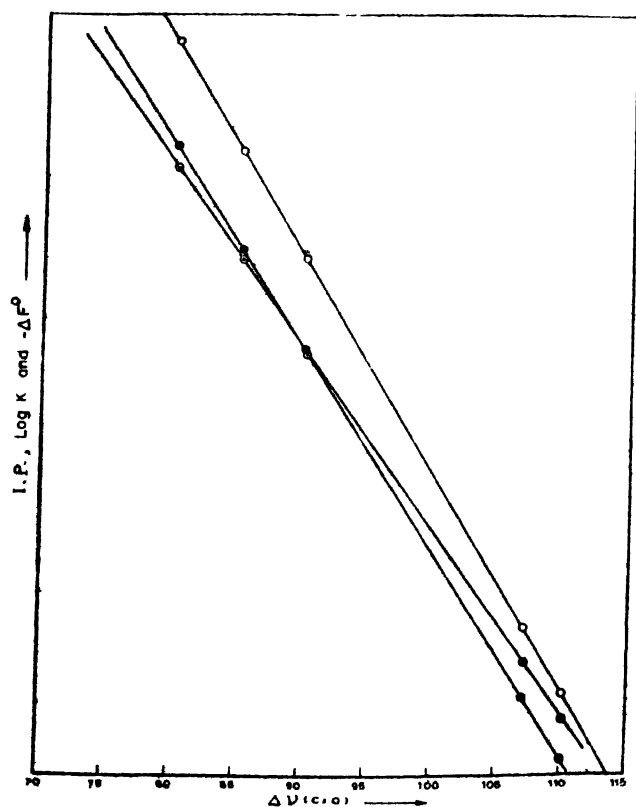


Fig. 1. Plot of $\Delta\nu$ (C=O) and I.P., LogK, $-\Delta F^\circ$ of oxozirconium(IV) complexes of antipyrine

- Ionization Potential
1 cm=0.0500 (starts from 4.7000 e.v.)
- Log K
1 cm=0.0600 (starts from 1.800)
- ⊙—⊙ $-\Delta F^\circ$
1 cm=0.1000 (starts from 2.300 K cal)

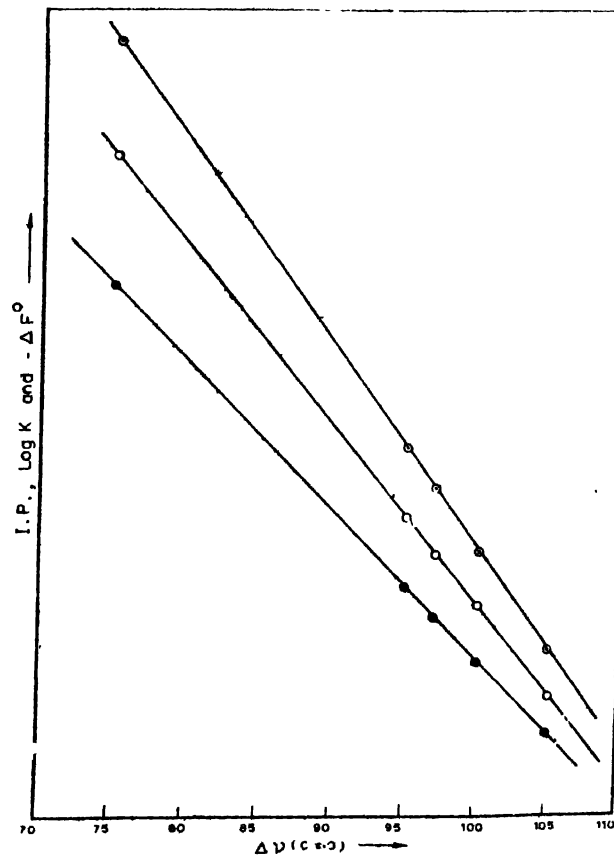


Fig. 2. Plot of $\Delta\nu$ (C=O) and I.P., LogK, $-\Delta F^\circ$ of oxozirconium(IV) complexes of 4-amino antipyrine

- Ionization Potential
1 cm=0.0666 (starts from 4.600 e.v.)
- Log K
1 cm=0.1000 (starts from 1.6000)
- ⊙—⊙ $-\Delta F^\circ$
1 cm=0.1000 (starts from 2.000 K cal)

if $\Delta\nu$ ($C=O$) is known. A linear relationship is observed between $\Delta\nu$ ($C=O$) and these values.

Thus the work presented on pyrazolone complexes shows that the coordination number of Zr(IV) in all these complexes is expected to be five or seven depending on the nature of the anion.

Acknowledgement

One of us (R. K. A.) is thankful to U.G.C., New Delhi, for award of a teacher fellowship.

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Spectral Investigations of Some Lanthanide Complexes : Bonding

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Manuscript received 3 May 1980, revised 28 July 1980,
accepted 17 August 1980

THE absorption spectra of lanthanide ions have been a subject of several investigations¹⁻⁷. The comparative study of the bonding in *o*-phenanthroline-tris(trifluoroacetate) complexes of lanthanide ions has not been reported so far. Consequently it was thought worthwhile to carry out the present investigation.

Taking the free ion as standard, the ligands other than fluoride cause a slight red shift of the bands⁸. It has been generally agreed that the nature of red shift may be conveniently used as a measure of metal-ligand covalent bonding. The red shift or nephelauxetic effect⁹ according to Jørgensen occurs

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due to change in the interelectronic repulsion (Slater-Condon or Racah) parameters. The effect may be visualized to be due to an expansion of the wave functions which results from interactions between the metal cations and neighbouring anions.

The nephelauxetic ratio β is defined as⁹

$$\beta = \frac{F_k^c}{F_k^f} \quad \dots (1)$$

where the F_k^c and F_k^f are the Slater-Condon parameters for the complex and the free-ion respectively and are given by

$$F_k = \frac{1}{D_k} \int_0^\infty \int_0^\infty \frac{r_1^k}{r_2^{k+1}} \cdot R^2(r_1)R^2(r_2)dr_1 dr_2 \quad \dots (2)$$

In eq. (2) D_k are the denominators given by Condon and Shortley⁹, R is the 4f radial wave function, r_1 and r_2 denote the radii of the nearer and distant electron from the nucleus respectively.

The nephelauxetic ratio is also defined as¹⁰

$$\beta = \frac{\bar{\nu}_c}{\bar{\nu}_f} \quad \dots (3)$$

where $\bar{\nu}_c$ and $\bar{\nu}_f$ are energies (in cm^{-1}) of the transitions in complex and free ion respectively.

The values of β is calculated using eq. (3) and taking into account as many transitions as possible. The mean β value, $\bar{\beta}$, can be used to compute a new parameter of bonding¹⁰ δ (in percent) which is given as

$$\delta = \left(\frac{1 - \bar{\beta}}{\bar{\beta}} \right) \times 100 \quad \dots (4)$$

Depending upon the ligands the value of δ may either be positive, indicating covalent bonding, or negative, indicating ionic bonding. Although the absolute values of δ are of less importance, they can be used in assessing the relative covalent character of the complexes.

The present communication reports the values of nephelauxetic ratio and bonding parameter for *o*-phenanthroline-tris(trifluoroacetate) (OPTF) or Pr^{3+} , Nd^{3+} , Sm^{3+} , Ho^{3+} and Er^{3+} ions. The lanthanide complexes under study were prepared¹¹ and analysed in our laboratory. Absorption measurements of the complexes in ethanol, were carried out on Carl-Zeiss VSU-2 Spectrophotometer. The energies of the bands and computed values of nephelauxetic ratio and δ have been collected in Table 1.

It is clear from Table 1 that the covalency decreases from Pr^{3+} OPTF to Er^{3+} OPTF. This observation can be explained with the fact that due to lanthanide contraction ionic radii of lanthanons decrease with the increase in atomic number resulting in the increase in electron density of the central metal ion. Ligand *o*-phenanthroline used in the present study has high electronegativity and vacant π -molecular orbitals. On complexation such molecular orbitals overlap with filled orbitals of cation resulting