

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.

References

1. R. K. AGARWAL, A. K. SRIVASTAVA and T. N. SRIVASTAVA, *Proc. Nat. Acad. Sci. (India)* and references therein (In Press).
2. R. K. AGARWAL, P. C. JAIN, MAHESH SRIVASTAVA, A. K. SRIVASTAVA and T. N. SRIVASTAVA, *J. Indian Chem. Soc.*, 1980, **57**, 374.
3. V. V. SAVANT, P. RAMAMURTHY and C. C. PATIL, *J. Less Common Metals*, 1970, **22**, 479.
4. S. K. MADAN and A. M. DONOHUE, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1303.
5. R. K. AGARWAL, A. K. SRIVASTAVA and T. N. SRIVASTAVA, *Indian J. Chem.*, 1979, **18A**, 459.
6. B. J. HATHAWAY and A. E. UNDERHILL, *J. Chem. Soc.*, 1961, 309.
7. S. S. KRISHNAMURTHY and S. SOUNDARARAJAN, *Can. J. Chem.*, 1969, **47**, 995.
8. N. F. CURTIS and Y. M. CURTIS, *Inorg. Chem.*, 1968, **4**, 804.
9. C. C. ADDISON and N. LOGAN, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 95.
10. R. W. HESTER and W. L. GROSSMAN, *Inorg. Chem.*, 1966, **3**, 1308.
11. J. L. BURMEISTER, *Coord. Chem. Rev.*, 1966, **1**, 205; 1968, **3**, 225.
12. V. M. VODOVENKO, A. I. SOKOBLO and D. N. SUGLOBOV, *Russ. J. Inorg. Chem.*, 1968, **13**, 1577.
13. A. R. DAVIES, C. J. MURTHY and R. A. PLANE, *Inorg. Chem.*, 1970, **9**, 423.
14. D. COOK, *J. Amer. Chem. Soc.*, 1958, **80**, 49.

Spectral Investigations of Some Lanthanide Complexes : Bonding

MEGH SINGH, SUDHINDRA N. MISRA, G. K. JOSHI
and

P. P. VAISHNAVA*

Department of Chemistry, University of Jodhpur,
Jodhpur-342 001

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

* Department of Physics, University of Jodhpur, Jodhpur-342 001.

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

TABLE 1—THE ENERGY (IN cm^{-1}) OF THE BANDS AND COMPUTED VALUES OF NEPHELAUXETIC RATIO AND BONDING PARAMETERS OF LANTHANON COMPLEXES OF *o*-PHENANTHROLINE TRIS (TRIFLUOROACETATE) (OPTF)

Pr ³⁺ ion			Nd ³⁺ ion			Sm ³⁺ ion			Ho ³⁺ ion			Er ³⁺ ion		
Levels	Free ^a ion	OPTF	Levels	in LaCl ₃ ^b	OPTF	Levels	in LaCl ₃ ^b	OPTF	Levels	in LaCl ₃ ^b	OPTF	Levels	in LaCl ₃ ^b	OPTF
¹ D ₂	17335	16920	⁴ F _{5/2}	11438	11415	⁴ F _{3/2}	18860	19280	⁶ F ₅	15482	15728	⁴ I _{11/2}	10124	10285
³ P ₀	21390	20708	⁴ F _{3/2}	12466	12345	⁴ G _{7/2}	20010	19801	⁶ F ₄	18554	19047	⁴ I _{9/2}	12346	12531
³ P ₁	22008	21276	⁴ F _{7/2}	14437	13262	⁴ I _{11/2}	20977	20964	⁶ F ₃	20614	19920	⁴ F _{9/2}	15183	15509
³ P ₂	23161	22421	⁴ F _{9/2}	14722	14619	⁴ I _{13/2}	21562	21551	⁶ F ₂	21069	21141	⁴ S _{3/2}	18300	18796
			³ H _{11/2}	15935	16100	⁴ F _{5/2}	22129	22271	⁶ K ₈	21351	21645	³ H _{11/2}	19011	19685
			⁴ G _{5/2}	17135	17211	⁴ G _{9/2}	22850	22522	⁶ G ₈	22101	22935	⁴ F _{7/2}	20494	20964
			⁴ G _{7/2}	19020	19083	(⁶ P, ⁴ P) _{3/2}	23784	24038	(⁶ G, ⁶ G) ₈	23936	24913	⁴ F _{5/2}	22182	22620
			⁴ G _{9/2}	19434	19569	⁴ L _{11/2}	24560	24813	⁶ K ₇	26140	26881	⁴ F _{3/2}	22154	22331
			³ G _{3/2}	21056	21052				(⁶ F, ⁶ F, ⁶ G) ₈	27969	27170	(⁶ G, ⁴ F, ³ H) _{9/2}	24475	25510
			⁴ G _{11/2}	21426	21691							⁴ G _{11/2}	26377	27472
			³ F _{1/2}	23214	22030							⁴ G _{9/2}	27319	27700
			³ D _{3/2}	23780	23310							³ G _{7/2}	27825	28409
	$\beta=0.9697$ $\delta=3.1247$			$\beta=0.9945$ $\delta=0.5580$			$\beta=1.0037$ $\delta=-0.3686$			$\beta=1.0111$ $\delta=-1.0978$			$\beta=1.0240$ $\delta=-2.3438$	

a Reference 11.
b Reference 4.

into charge transfer from metal to ligand. This tendency of charge transfer increases with the increase in atomic number of lanthanons and is attributed to continuous decrease of covalency from Pr³⁺ OPTF to Er³⁺ OPTF in the present study.

References

1. C. K. JØRGENSEN, 'Absorption Spectra and Chemical Bonding in Complexes', Pergamon Press, Oxford, 1962.
2. B. G. WYBOURNE, 'Spectroscopic Properties of Rare Earths', John Wiley and Sons, New York, 1965.
3. G. H. DIEKE, 'Spectra and Energy Levels of Rare Earth Ions in Crystals', John Wiley and Sons, New York, 1968.
4. W. T. CARNALL, P. R. FIELDS and K. RAJNAK, *J. Chem. Phys.*, 1968, 49, 4413, 4424.
5. S. P. TANDON and P. C. MEHTA, *J. Chem. Phys.*, 1970, 52, 4313.
6. S. P. TANDON, P. P. VAISHNAVA and R. C. MATHUR, *Sol. State. Comm.*, 1974, 15, 787.
7. S. P. TANDON and P. P. VAISHNAVA, *Can. J. Spectry.*, 1977, 22, 17.
8. C. K. JØRGENSEN, *Prog. Inorg. Chem.*, 1962, 4, 73.
9. E. U. CONDON and G. H. SHORTLEY, 'The Theory of Atomic Spectra', Cambridge University Press, Cambridge, 1957.
10. S. P. SINHA, *Spectrochim. Acta*, 1966, 22, 57.
11. MEGH SINGH, Ph.D. Thesis, University of Jodhpur, Jodhpur, 1977.
12. J. SUGAR, *Phys. Rev.*, 1965, 14, 731.

Piperidyl and Morpholyl Dithiocarbamate Cadmium(II) with Nitrogen Donors

BIPIN B. MAHAPATRA, S. K. PUJARI and A. CHIRANJEEVI

Department of Chemistry, G. M. College, P.O./Dt. Sambalpur (Orissa)

Manuscript received 11 November 1980, revised 2 February 1981, accepted 19 May 1981

SINCE dithiocarbamate can act as monovalent, mono or bidentate ligands, the complex forming ability of these sulphur donor ligands has invoked

considerable attention. Dithiocarbamate complexes of transitional and non-transitional metal ions have been prepared by various workers¹⁻⁴. The present communication reports the preparation and characterisation of cadmium(II) complexes with these two title ligands and nitrogen donor heterocyclic bases, viz., pyridine, α -picoline, β -picoline, isoquinoline and piperidine.

Experimental

All the chemicals used were of AnalaR grade. Sodium salts of the respective dithiocarbamic acids were prepared by standard procedure. Aqueous solutions of cadmium chloride and sodium salts of respective dithiocarbamic acids were reacted in 1 : 2 ratio. White precipitate separated out immediately. It was filtered and dried *in vacuo* for 15 minutes.

The ethanolic suspension of the above metal chelate was reacted with different nitrogen donor ligands in stoichiometric ratio and refluxed for 2 hrs, when a clear solution was obtained. On cooling the solution, crystalline precipitate separated out. It was filtered, washed with ethanol followed by ether and dried *in vacuo*.

Metal in the complexes was estimated by EDTA method. Conductance was measured in M/1000 acetone solution. Ir spectra were recorded in KBr phase on a Beckmann IR-12 spectrophotometer. Analytical, conductance and ir spectra data are recorded in Table 1.

Results and Discussion

All the complexes reported in this investigation are of the composition [Cd(L/L')₂B], where L = piperidyl dithiocarbamate, L' = morpholyl dithiocarbamate and B is a heterocyclic base like pyridine, α -picoline, β -picoline and piperidine. These compounds are white to brownish-white in colour, have