

Notes

Spectral Studies on Bis(β -naphthylidene-*O*-aminophenolate) Chelates of Cerium(III), Samarium(III), Gadolinium(III), Dysprosium(III), Cobalt(II) and Chromium(III)

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C^{III}, Sm^{III}, Gd^{III}, Dy^{III}, Co^{II} and Cr^{III} complexes of tridentate Schiff base derived from the condensation of *o*-aminophenol and β -naphthylglyoxal have been prepared and studied by spectrophotometry and infrared spectroscopy. The stoichiometry of the complexes is established by spectrophotometric methods of analysis and elemental analysis. The binding of the functional groups of the ligand to metal on complexation have been confirmed by infrared spectral study.

Experimental

The ligand β -naphthylidene-*O*-aminophenol was prepared by refluxing equimolar quantities of both glyoxal and amine in ethanolic medium in the presence of a few drops of acetic acid. The contents were refluxed for 2 h and then poured into distilled water and filtered. Finally it was washed with ethanol.

The complexes were prepared by refluxing the metal salt and ligand solutions in dimethylformamide in the ratio of 1:2 for 2 h and after keeping it for 2 or 3 days to concentrate the volume, the crystals of the complexes were recovered and washed. The composition of the complexes was ascertained by elemental analysis. The infrared spectra (200-4 000 cm⁻¹) of the complexes were taken in KBr on a Perkin-Elmer Infra-Cord spectrophotometer.

The colour and melting point of the complexes are given in Table I.

Results and Discussion

For the determination of stoichiometry, Vosburgh and Cooper's method was applied to determine the number of the complexes formed by the interaction of ligand and metal in the system. Equimolar solutions of metal and ligand were prepared and different sets were prepared in the ratios 1:1, 1:2, 1:3 and 1:4. The optical density of the mixture was measured by a Bauch & Lomb Spectronic 20. In the optical density vs wavelength plot, the maxima of curves show the number of the complexes formed in the system. The wavelength at which the maxima occurs is suitable for further study and this method was applied to select the wavelength for each system. Molar-ratio method was applied to determine the composition of the complexes. The curves were plotted between optical density and volume of variant (Fig. 1) and break in the curves shows the stoichiometry of all the complexes.

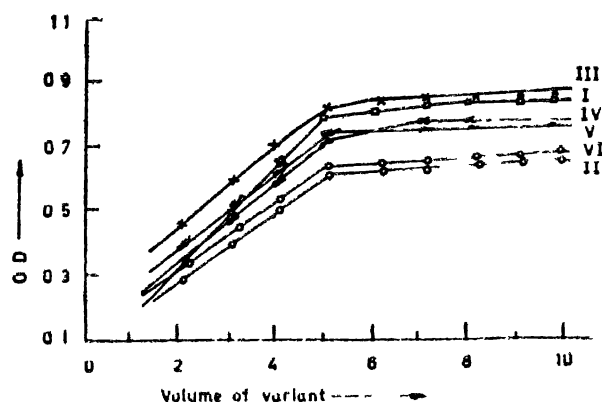


Fig. 1

Stability constant K_s has been evaluated by molar ratio method by the formula $K_s = (1-\alpha)/4\alpha^3 C^3$ where, α is the degree of dissociation and C is the total concentration of the complex in mol dm⁻³.

Free energy ΔF of complex formation has been

TABLE I—COLOUR, M.P., STABILITY CONSTANT AND ANALYTICAL DATA OF COMPLEXES

Compd.	Colour	M p °C	Analysis % : Found/(Calcd)				K_s	ΔF
			C	H	N	Metal		
Ce(C ₁₆ H ₁₁ O ₂ N) ₂ Cl	Lig'it brown	200	59.59 (59.00)	3.58 (3.47)	3.86 (3.80)	19.31 (19.28)	1.285 × 10 ¹¹	-15.476
Dy(C ₁₆ H ₁₁ O ₂ N) ₂ NO ₂	Brown	215	55.98 (55.50)	3.10 (3.00)	5.44 (5.40)	20.98 (20.86)	1.568 × 10 ¹¹	-15.622
Gd(C ₁₆ H ₁₁ O ₂ N) ₂ NO ₂	Dark brown	205	56.32 (56.20)	3.13 (3.07)	5.48 (5.35)	20.47 (20.40)	2.007 × 10 ¹²	-17.169
Sm(C ₁₆ H ₁₁ O ₂ N) ₂ NO ₂	Dark brown	217	56.84 (56.70)	3.16 (3.06)	5.53 (5.38)	19.73 (19.66)	6.621 × 10 ¹⁰	-15.095
Cr(C ₁₆ H ₁₁ O ₂ N) ₂ Cl	Brown	220	68.03 (67.90)	3.78 (3.59)	4.41 (4.48)	8.19 (8.22)	2.717 × 10 ¹¹	-15.958
Co(C ₁₆ H ₁₁ O ₂ N) ₂	Brown	230	71.29 (71.04)	3.96 (3.80)	4.62 (4.85)	9.57 (9.62)	1.783 × 10 ¹¹	-15.702

evaluated by the equation,
 $-\Delta F = -2.303 RT \log K_s$. Stability constant and free energy of the complexes are given in Table 1.

Ir spectral studies: The point of attachment of the ligand with the metal ion has been confirmed by studying the infrared spectrum of the ligand and the isolated chelates.

The strong bond appearing at 1700 cm^{-1} (C=O) in the ligand is shifted to lower frequency at $1630-1690 \text{ cm}^{-1}$ on complexation in all the systems, suggesting the formation of C—O—M bonding. The strong bond at 1630 cm^{-1} in the ligand was assigned to azomethine group. On complexation, this gets lowered to $1590-1610 \text{ cm}^{-1}$ indicating the formation of M—N bond. Hence, it is concluded that coordination occurs through CH=N and C=O group. A peak observed at 3400 cm^{-1} (OH) in the ligand vanishes on complexation; therefore, it is concluded that the third point of attachment of metal to ligand occurs through the oxygen atom of OH group of the ligand.

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Isolation of Halogeno and Complex-halogeno Anions as Salts of Oxinate Chelates of Bis(cyclopentadienyl)-titanium(IV) and -zirconium(IV)

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DOYLE and Tobias¹ pointed out that coordination of four oxygen atoms by strong covalent bonds to $\text{Cp}_2\text{M}^{2+}(\text{IV})$ moiety ($\text{M}=\text{Ti}, \text{V}$) would lead to weakening of the metal-ring bonds. In order to investigate, whether or not the coordination of two nitrogen and two oxygen atoms around the titanium(IV)/zirconium(IV) ion would produce a similar weakening of the metal-ring bonds, we studied the interaction of $\text{Cp}_2\text{TiCl}_2/\text{Cp}_2\text{ZrCl}_2$ with 8-quinolinol in aqueous medium. We failed to isolate derivatives in which two 8-quinolate groups coordinated to the Cp_2M^{2+} ($\text{M}=\text{Ti}^{IV}, \text{Zr}^{IV}$). However, ionic complexes of the type, $[\text{Cp}_2\text{M}(\text{8-quinolinol})]^+\text{Cl}^-$ in which only one bidentate 8-quinolate group is coordinated to the titani-

um(IV)/zirconium(IV) ion are readily obtained. A number of halogeno and complex-halogeno salts of these complexes of the type $[\text{Cp}_2\text{M}(\text{8-quinolinol})]^+\text{X}^-$ ($\text{M}=\text{Ti}$ or Zr ; $\text{X}^-=\text{Br}^-, \text{I}^-, \text{CuCl}_2^-, \text{ZnCl}_2(\text{H}_2\text{O})^-, \text{CdCl}_2^-, \text{HgCl}_2^-$) have been isolated in aqueous medium and characterised.

Experimental

All reagents used were of analytical grade. Nitrogen and halogens were determined by standard gravimetric methods². Conductance measurements were made in nitrobenzene at $30 \pm 0.05^\circ$ with a Systronic 304 digital direct reading conductivity meter. Infrared spectra (KBr) were recorded in the region $4000-200 \text{ cm}^{-1}$ with a Perkin-Elmer 621 grating spectrophotometer. ¹H nmr spectra were recorded in deuterated acetone at a sweep width of 900 Hz with a Perkin-Elmer R-32 spectrophotometer. Chemical shifts are expressed relative to an internal reference of TMS (1% by volume).

Preparation of complexes: An aqueous solution of $[\text{Cp}_2\text{Ti}(\text{8-quinolinol})]^+\text{Cl}^-/[\text{Cp}_2\text{Zr}(\text{8-quinolinol})]^+\text{Cl}^-$ was obtained by stirring an aqueous solution of $\text{Cp}_2\text{TiCl}_2/\text{Cp}_2\text{ZrCl}_2$ with an excess of solid 8-quinolinol for about 1 h. The solution was filtered and the filtrate added separately to a hot solution of KBr, KI, CuCl_2 , ZnCl_2 , CdCl_2 and HgCl_2 . The solution was digested over water-bath for 4 h. Ionic complexes of the type, $[\text{Cp}_2\text{Ti}(\text{8-quinolinol})]^+\text{X}^-$ and $[\text{Cp}_2\text{Zr}(\text{8-quinolinol})]^+\text{X}^-$ ($\text{X}^-=\text{Br}^-, \text{I}^-, \text{CuCl}_2^-, \text{ZnCl}_2^-, \text{CdCl}_2^-$ and HgCl_2^- , respectively) were precipitated. These were filtered and washed with petroleum ether.

Results and discussion

Table 1 lists the analytical data and physical characteristics of the complexes. The complexes are thermally stable and decompose at higher temperatures without melting. They are soluble in acetone and THF, and partially soluble in chloroform and dichloromethane. With ZnCl_2 , an aquotrichlorozincate(II) anion, $[\text{Cp}_2\text{M}(\text{8-quinolinol})]^+\text{ZnCl}_2(\text{H}_2\text{O})^-$ is precipitated. The presence of coordinated water is identified by its intense infrared absorption at $\sim 3450 \text{ cm}^{-1}$. Conductivity measurements show that all the complexes except CdCl_2^+ salts are 1:1 electrolytes in nitrobenzene. However, in case of CdCl_2^+ salts, the results are consistent with those of 1:2 electrolytes, indicating that the dinegative anions are precipitated.

Infrared spectra: No halide bridging is observed in halide and complexhalo anion salts. The frequencies at $350-370 \text{ cm}^{-1}$ region for complex-halogeno salts are characteristic of complex chloro anions^{1,2}. A strong band at 1500 cm^{-1} in the free 8-hydroxyquinoline may be assigned to C=N bond. In complexes, this band is shifted to lower wavenumber at $\sim 1330 \text{ cm}^{-1}$ indicating the coordination of nitrogen atom of 8-hydroxyquinoline ligand to the metal⁴. Further, in the spectra of complexes,