

**Metal Chelates of Hydrazo-Dimedone Dyes.
Chelating Tendencies of 5,5-Dimethylcyclohexane-2-(2-Hydroxo-4-Methylphenyl) Hydrazono 1,3 Dione with Samarium(III), Lutetium(III) and Dioxouranium(II)**

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The stability constant of 5,5-dimethylcyclohexane-2-(2-hydroxo-4-methylphenyl) hydrazone-1,3-dione (DC-4-Me-PHD) complexes with Sm(III), Lu(III) and UO₂(II) in 50% (v/v) *isopropanol*-water solvent at 30°C have been investigated by pH-metry and spectrophotometric methods. Probable structures of the metal chelates are inferred from electronic absorption spectra, conductivity measurements and infrared examination of the solid complexes. The use of DC-4-Me-PHD as an analytical reagent for the spectrophotometric determination of samarium, lutetium and uranium ions has also been discussed.

INTRODUCTION

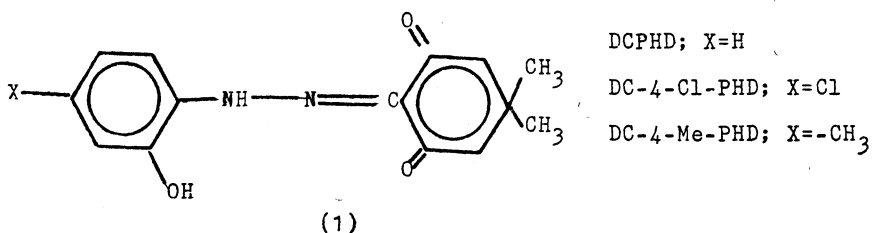
In previous papers¹⁻³ the chelating ability of a series of substituted 5,5-dimethylcyclohexane-2-phenylhydrazo 1,3 dione (DCPHD) have been studied with copper(II) and lanthanide(III) ions. Based in the data obtained for the protonation constants of DCPHD and its complexes with Ni(II), Sm(III) and Yb(III)^{1,2} in various mixed aqueous solvents the values of autoprotolysis constants and the center to center distance of closest approach between the solvated ions were calculated using Faus equation. These values indicated that the protonation of the organic solvent has a significant effect on the variation of the protonation constants, this beside the other solvent characteristics *viz.* dielectric constant of the medium and change of hydrogen bonding in water by organic solvent. The plot of log K vs. 1/D(D-dielectric constant) is not linear. Two intersecting straight lines were obtained for all organic solvent mixtures². The region of composition that corresponding to the first line is 0-60% (v/v) for methanol-water, ethanol-water, and acetone-water and is 0-50% for dioxan-water and *isopropanol*-water. The second straight line is obtained in the region 60-85% (v/v) for the remaining two solvent-water mixtures. The addition of organic solvent to water leads to an increase of the degree of order in the system. Furthermore, the degree of structuredness must increase until it pass through a maximum. Beyond this composition (50%-60% solvent-water) the highly ordered solvent structure begins to collapse. When the proportion of organic solvent becomes sufficiently

large (i.e. above 50%–60%) in organic solvent mixture proton solvation of the organic solvent molecules takes place.

For the reaction between doubly charged donor groups such as DCPHD, DC-4-Cl-PHD and DC-4-Me-PHD and divalent nickel and trivalent samarium or ytterbium, the entropy³ changes were positive. This positive entropy arises from the participation of isopropanol in the aqueous solvation sphere and this results in the increase of degree of structuredness and the highly ordered solvent structure begins to collapse. The enthalpy values for DC-4-Me-PHD, DC-4-Cl-PHD, and DCPHD metal-chelates for a given ion indicate that the first chelating agent (ΔH_1^0) always gives the less negative ΔH^0 values. This was attributed to the steric hindrance caused by the methyl group.

The replacement of phenolic group on DCPHD by carboxylic group⁴ leads to the formation of less stable chelates with lanthanide and transition metal ions.

Continuing our studies in these chelating agents which are antidipetic⁵, the binding characteristics of DC-4-Me-PHD with Sm(III), Lu(III) and UO₂(II) have been studied.



EXPERIMENTAL

Preparation of the Solid Ligand and its Complexes

DC-4-Me-PHD was prepared as described in an earlier publication³. The solid lanthanide(III) and dioxouranium(II) complexes were prepared by adding a dioxan solution of the ligand (0.025 mole) to an aqueous solution of metal nitrate (0.0125 mole). The pH of the solution was then increased (in case of lanthanides) to 5.0 and the mixture was refluxed for 1 hr. Reddish brown crystals were separated gradually. These were filtered, washed several times with aqueous dioxan, dried to constant weight under vacuum. The elemental analysis results are shown in Table 1. For Ln(III) complexes the metal content was obtained by the decomposition of the solid by repeated treatment with concentrated nitric acid, pH adjusted to 5.0 and then titrated against standard EDTA solution using xylenol orange as indicator.

TABLE 1
ANALYTICAL DATA OF DC-4-Me-PHD AND THEIR METAL COMPLEXES

Species and Formula	Calculated (Found)				$A_M^* \Omega^{-1}$
	%C	%H	%N	%M	
$C_{15}H_{18}N_2O_3$ (DC-4-Me-PHD)	65.45 (65.36)	6.55 (6.51)	10.18 (10.12)		
$[UO_2(C_{15}H_{17}N_2O_3)(H_2O)_3]NO_3$	28.89 (28.96)	3.05 (3.06)	6.74 (6.68)		76.00
$[Sm(C_{15}H_{17}N_2O_3)_2-(H_2O)_2]NO_3$	45.32 (45.47)	4.78 (4.83)	8.81 (8.96)	18.93 (19.01)	73.33
$[Nd(C_{15}H_{17}N_2O_3)_2-(H_2O)_2]NO_3$	45.67 (45.51)	4.82 (4.85)	8.88 (8.92)	18.30 (18.41)	76.45
$[Yb(C_{15}H_{17}N_2O_3)_2-(H_2O)_2]NO_3$	44.06 (44.36)	4.65 (4.51)	8.57 (8.72)	21.18 (21.39)	77.01
$[Lu(C_{15}H_{17}N_2O_3)_2-(H_2O)_2]NO_3$	43.96 (44.18)	4.64 (4.72)	8.55 (8.66)	21.36 (21.48)	75.92

* $\Omega^{-1} \text{ mol}^{-1} \text{ cm}$ in DMF

Reagents and Materials

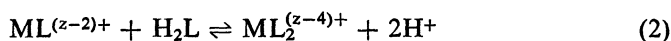
Stock solutions of the metal nitrates were prepared and standardized using EDTA in the presence of suitable indicator⁶. Purification of *iso*-propanol was carried out as described previously³.

Potentiometric titrations and experimental conditions are essentially the same as described in the literature³.

RESULTS AND DISCUSSION

(i) Potentiometric Results

The metal-ligand titration curves show the presence of two inflections at $a = 1$ and $a = 2$ ($a = \text{moles of base added per mole of ligand}$) due to the stepwise formation of 1 : 1 and 1 : 2 complexes, represented by the equilibrium:



The overall equilibrium constants were carried out using standard procedures based on the calculation of the average number of ligand bound per metal ion, \bar{n}_L and the free ligand concentration, $[L]$, then minimising the residuals in the equation (3) using least squares method.

TABLE 2
FORMATION CONSTANTS FOR METAL ION COMPLEXES AT 30°C
 $\mu = 0.10 \text{ M} = \text{KNO}_3, 50\% \text{ (V/V) ISOPROPANOL-WATER}$

Cation	log K ₁	log K ₂	ϵ in 1 mol ⁻¹ cm ⁻¹ (λ nm)	Optimum pH	Limits of Beer's law	Composition (Molar ratio and Job's Methods)
H ⁺	8.78± 0.01	11.78± 0.07				
Sm ³⁺	10.95 (11.05± 0.06)*	10.56	1435 (510)	5.90-6.20	2.0×10 ⁻⁴ - 6.5×10 ⁻⁴ M	1 : 1; 1 : 2
Lu ³⁺	11.35 (11.46± 0.08)*	10.72	1750 (520)	5.80-5.30	2.5×10 ⁻⁵ - 4.0×10 ⁻⁴ M	1 : 1; 1 : 2
UO ₂ ²⁺	16.64 (16.48± 0.09)*	15.45	625 (510)	4.50-5.25	4.0×10 ⁻⁵ - 5.2×10 ⁻⁴ M	1 : 1; 1 : 2

*Spectrophotometric method.

TABLE 3
IMPORTANT INFRARED FREQUENCIES (cm⁻¹) AND THEIR
ASSIGNMENT FOR DC-4-Me-PHD AND ITS COMPLEXES

DC-4-Me-PHD	Nd	Sm	Yb	Lu	UO ₂	Assignment
	3620w	3620w	3620w	3620w		Sym. and antisym.
	3420b	3400b	3400b	3400b	3420w	stretch of H ₂ O
3300b						ν_{OH} (phenolic)
3140b	3140b	3140b	3140b	3140b		ν_{NH}
1660vs						$\nu_{\text{C=O}}$
1620vs	1610b	1600b	1610b	1610b	1600b	$\nu_{\text{C=N}}$
1220s					1220w	δ_{OH}
1190s					1190w	$\nu_{\text{C-OH}}$
					880s	$\nu_{\text{N=O}}$ (U=O)
					570w	$\nu_{\text{U-O}}$
	570w	575w	570w	570w		$\nu_{\text{M-O}}$ (phenolic)
	490w	500w	500w	500w	565s	$\nu_{\text{M-O}}$ (carbonyl)

v = very, s = strong, w = weak, b = broad.

$$\frac{\bar{n}_L}{(1 - \bar{n}_L)[L]} + \beta_{102} \frac{(\bar{n}_L - 2)[L]}{(1 - \bar{n}_L)} - \beta_{101} = 0 \quad (3)$$

The log of the formation constants of metal complexes are presented in Table 2.

(ii) Spectral Results

The visible spectral properties of the metal complexes are similar to that of proton complexes with significant red shift in λ_{\max} (Figs. 1a, b and

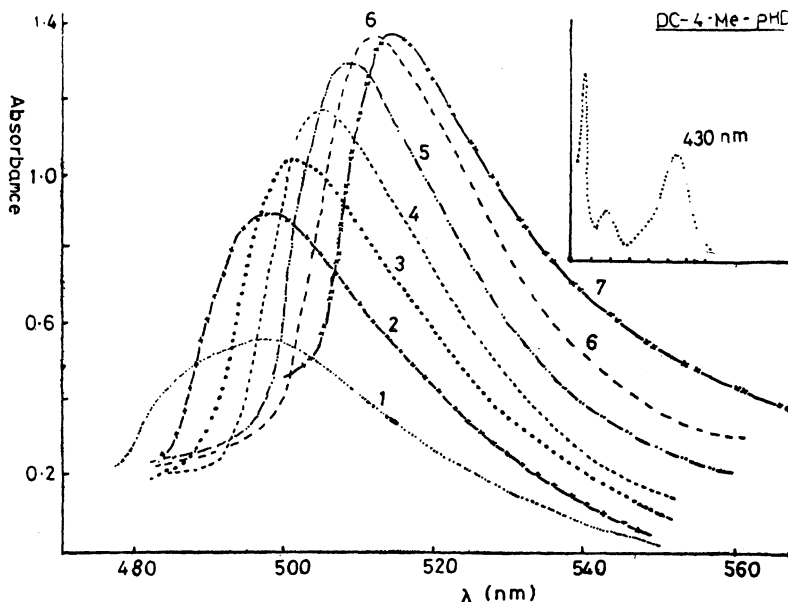


Fig. 1(a) Electronic absorption spectra of Lu(III)-DC-4-Me-PHD chelates in 50% (v/v) *isopropanol*-water at pH = 6.1. The metal concentration is constant at 1×10^{-3} M, the ligand concentration is varied as follows: (1) 2.5×10^{-4} M, (2) 5.0×10^{-4} M, (3) 7.5×10^{-4} M, (4) 1.0×10^{-3} M, (5) 1.5×10^{-3} M, (6) 2.0×10^{-3} M, (7) 3.0×10^{-3} M.

c). The solid ligand and their Sm^{3+} , Lu^{3+} and UO_2^{2+} complexes were characterized by infrared spectroscopy. Important band groups and their assignment are summarized in Table 3.

(iii) Analytical Studies

Samarium, lutetium and uranium can be determined spectrophotometrically with DC-4-Me-PHD. The colour is stable for more than 24 hrs and reaches maximum intensity within 5 min of mixing. The optimum pH is 6.50, 6.00 and 4.80 for samarium, lutetium and uranium respectively. The systems obey Beer's law in the metal concentration

range: 0.3–0.9, 0.1–0.7 and 0.1–1.2 $\mu\text{g/ml}$ respectively. Under optimum conditions, the relative standard deviation of the absorbance was 0.5% for Sm), 7% for Lu and 1.7% for U (all approximately in 3.5 ppm level).

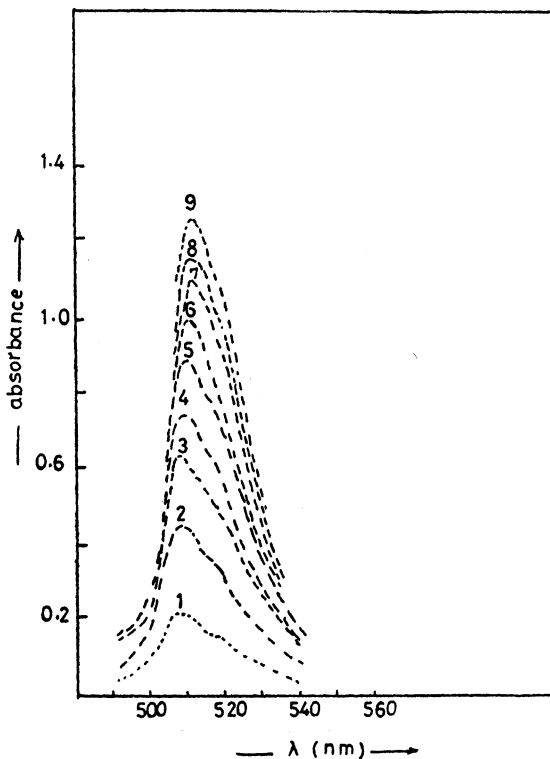


Fig. 1(b) Electronic absorption spectra of Sm(III)-DC-4-Me-PHD chelates in 50% (v/v) *isopropanol-water* at pH = 6.7. The ligand concentration is constant at 1.5×10^{-3} M, the metal concentration is varied as follows: (1) 2×10^{-4} M, (2) 3.0×10^{-4} M, (3) 4×10^{-4} M, (4) 5.0×10^{-4} M, (5) 6×10^{-4} M, (6) 8×10^{-4} M, (7) 9.0×10^{-4} M, (8) 1.0×10^{-3} M.

(iv) Composition and Stability of the Complexes

The molar ratio and Job's plots depicts the formation of 1:1 and 1:2, M:L complex types (Figs. 2a and b). The $\log K_1$ values for different complexes were calculated using the following equation⁷:

$$\log K_1 = \log \frac{A}{\epsilon} \log [L^{2-}] - \log [M] \quad (4)$$

A is the absorbance of the metal in the presence of the ligand, [M] is the total metal concentration, $[L^{2-}]$ is the free ligand concentration and ϵ the molar extinction of the complex. The free ligand concentration has been

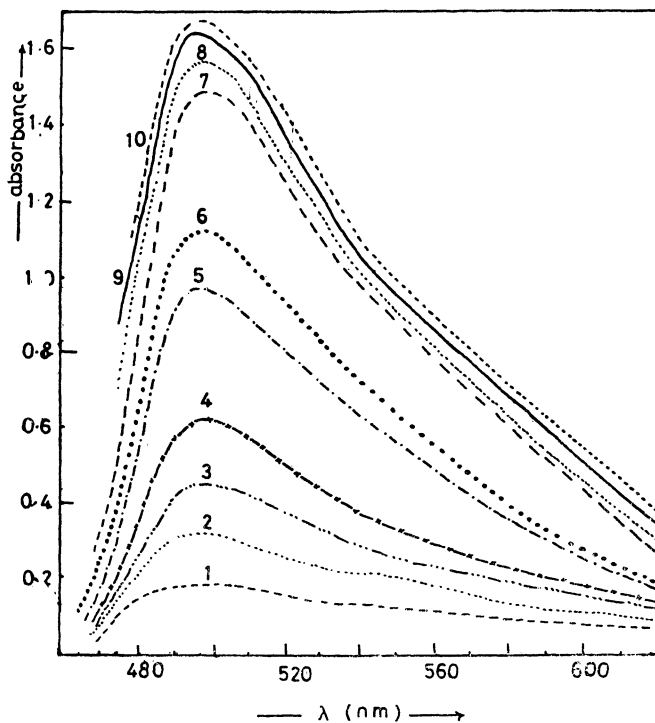


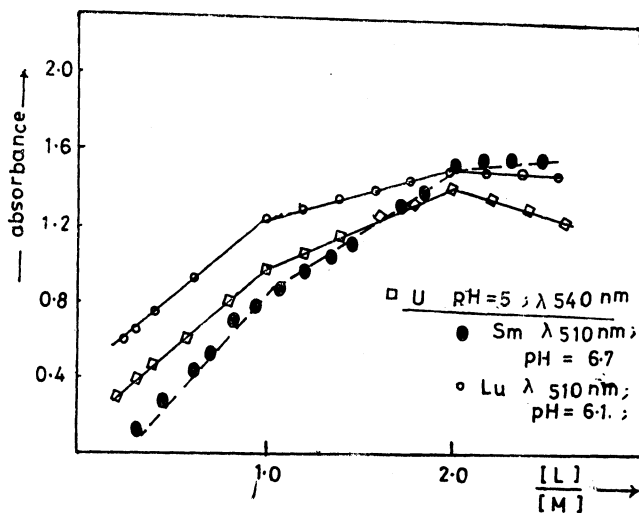
Fig. 1(c) Electronic absorption spectra of $\text{UO}_2(\text{II})$ -DC-4-Me-PHD chelates in 50% (v/v) *isopropanol-water* at pH = 5.0. The metal concentration is constant at 4×10^{-4} M, the ligand concentration is varied as follows: (1) 4.0×10^{-5} M, (2) 8.0×10^{-5} M, (3) 1.6×10^{-4} M, (4) 2.4×10^{-4} M, (5) 3.2×10^{-4} M, (6) 4.0×10^{-4} M, (7) 5.6×10^{-4} M, (8) 6.4×10^{-4} M, (9) 7.2×10^{-4} M, (10) 8.8×10^{-4} M.

calculated at any particular pH using the following equation;

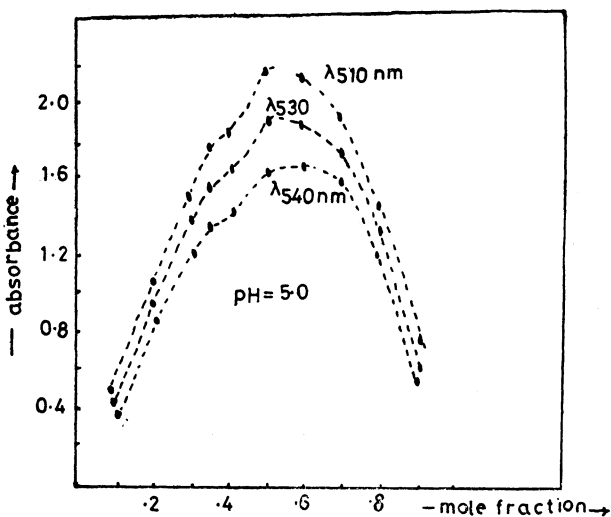
$$C_L = [L^{2-}]\{1 + K_1^H[H^+] + K_1^H K_2^H [H^+]^2\} \quad (5)$$

C_L is the total ligand concentration.

The absorption spectra of Lu-DC-4-Me-PHD mixture at the optimum pH(6.5) with an M : L ratio lower than one change significantly with the amount of ligand added (the ligand solution at pH 6.5 is taken as reference). The band maximum moving to longer wavelength with respect to the free ligand (Fig. 1a), whereas the band shape tends to resemble that of the corresponding O, N-chelates of d-transition elements⁸. Above M : L concentration = 1, further increase of the ligand concentration cause change of either the intensity or the position of the band. Above M : L concentration = 2, the increase of the ligand concentration does not change either the intensity or the position of the band. Similar behaviour is obtained in the case of DC-4-Me-PHD-Sm and DC-4-Me-PHD-



(a)



(b)

Fig. 2(a) Molar ratio method for Sm(III)-, Lu(III)-, and $\text{UO}_2(\text{II})$ -DC-4-Me-PHD systems.

(b) Job's method for $\text{UO}_2(\text{II})$ -DC-4-Me-PHD system.

UO_2 systems, except that in the case of the latter the increase of the ligand concentration causes a change in the intensity of the band only (Fig. 1c). This behaviour indicates 1:1 and 1:2 complexes are formed at these optimum pH values. This was substantiated by the comparison of absorption vs. pH plot with mole fractions α_{ML} and α_{ML_2} (obtained from pH-

metric data) vs. pH plot. Such comparison indicates that both 1 : 1 and 1 : 2 complex types were formed at pH values up to 6.5, 6.0 and 4.8 for Sm(III), Lu(III) and UO_2 (II) respectively. In addition to that the molar ratio and Job's methods indicate the formation of 1 : 1 and 1 : 2 complexes at the optimum pH values. As is clear from Fig. 3, the complexes exhibit weak absorbance up to pH 4.5, 4.5 and 3.0 for Sm, Lu and UO_2 complexes respectively, then rapidly increases until it reaches a maximum, then

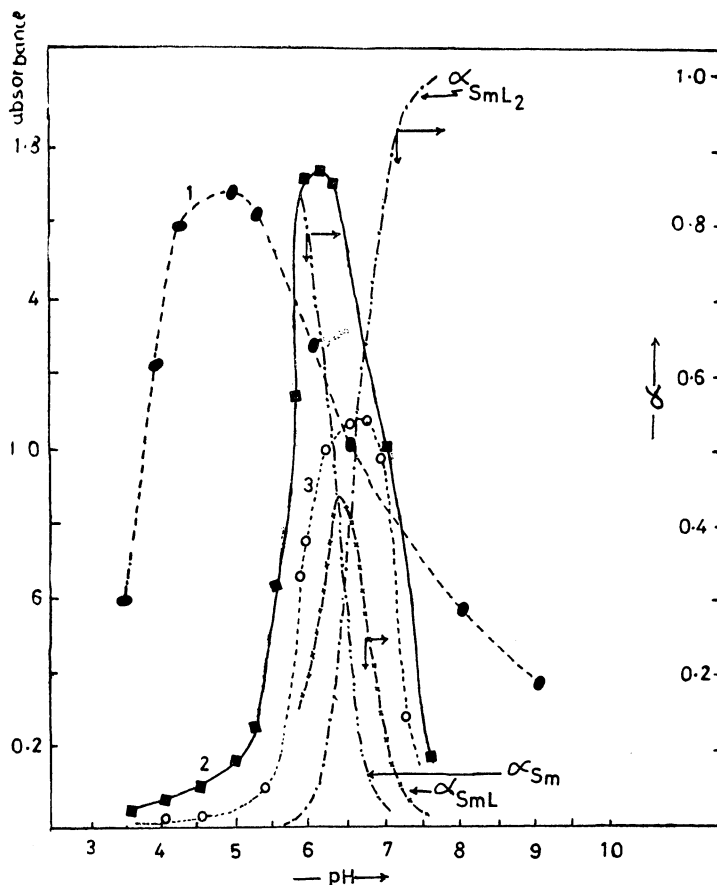


Fig. 3. Absorption-pH and mole fraction-pH plots.

- (1) UO_2 (II)-DC-4-Me-PHD at 510 nm.
- (2) Lu(III)-DC-4-Me-PHD at 510 nm.
- (3) Sm(III)-DC-4-Me-PHD at 520 nm.

decreases again due to the destruction of the complexes upon base hydrolysis. To account for this behaviour, the number of absorbing species in solution were determined applying Coleman *et al.*⁹, graphical method to the different data for Sm(III), Lu(III) and UO_2 (II) complexes at several

wavelengths and at different pH's. Typical plots are given in Fig. 4. The analysis revealed that only one absorbing species exists in moderately acidic region (*ca* pH 3). Increasing the pH to 4.0 (in the case of UO_2) or to 5.0 in the remaining systems to absorbing species were found as indicated by the linear plots shown in Fig. 4. Since the free ligand absorbs

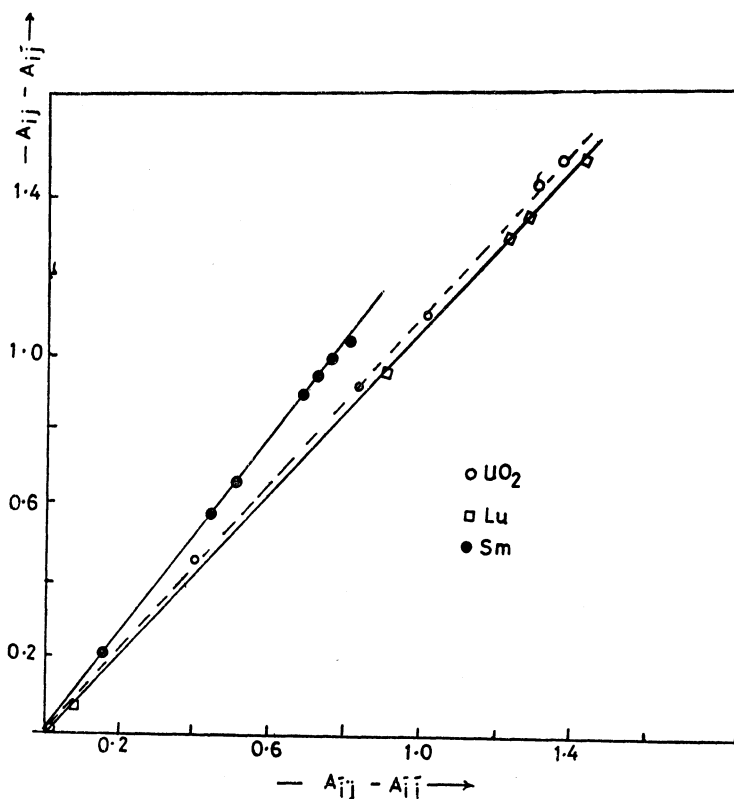


Fig. 4. Coleman *et al.* plots for the different DC-4-Me-PHD chelates

far below this region of the spectrum, perhaps the only possible absorbing species in moderately acidic media is that formed between the metal ions and the acidic ligand, MHL species. At very high acidities protons compete with the metal ions for the available nitrogen donor sites and no complexes are formed, whereas in strong alkaline media, complex hydrolysis might account for the decrease in optical density.

The visible spectra of Sm-, Lu- and UO_2 -DC-4-Me-PHD systems give a very broad band that spread over the range 440–600 nm (fig. 1a, b and c) most of the f-f transitions were obscured by the very broadness of this band. It is probably that this spectral behaviour arise from the coordination of nitrogen atom to lanthanide cation. It has been found in fact

N-coordination causes changes in the band shape and intensity which tend to resemble those of N-protonated form¹⁰.

The analytical and molar conductance data for complexes are presented in Table 1. They analyse for the general formula $[\text{Ln}(\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_3)_2(\text{H}_2\text{O})_2]\text{NO}_3$ where $\text{Ln}=\text{Nd}(\text{III}), \text{Sm}(\text{III}), \text{Yb}(\text{III})$ and $\text{Lu}(\text{III})$ and $[\text{UO}_2(\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_3)(\text{H}_2\text{O})_2]\text{NO}_3$. Molar conductance values for the complexes indicate that they are 1 : 1 electrolytes in DMF.

The IR spectra of all chelates except dioxouranium(II) show similar features. From the structure of the ligand it appears that it can function as a tridentate donor using one phenolic oxygen, one nitrogen of hydrazone group ($-\text{NH}-\text{N}=\text{C}-$) and an oxygen of cyclic $-\text{C}=\text{O}$ group as interaction sites. In the spectra of the ligand two bands are observed at 4140 cm^{-1} and 3400 cm^{-1} can be assigned to ν_{NH} and ν_{OH} respectively^{11,12}. Lowering of ν_{OH} stretch can be attributed to hydrogen bonding^{12,13}. The ν_{NH} stretch remain intact while ν_{OH} band disappears on the spectra of lanthanide ion complexes indicating coordination of phenolic oxygen to the metal ion¹⁴. This is confirmed by the disappearance of δ_{OH} and $\nu_{\text{C}-\text{OH}}$ in the spectra of lanthanide ion complexes¹⁵. The strong bands at 1620 and 1660 cm^{-1} assigned to $\nu_{\text{C}=\text{N}}$ and $\nu_{\text{C}=\text{O}}$ stretch respectively. These groups are shifted or disappeared in the spectra of the complexes indicating the participation of these groups in coordination. The appearance of new bands at 3600–3620 and 3440 cm^{-1} in the spectra of Ln(III) complexes are attributed to $\nu_{\text{asy}}(\text{OH})$ and $\nu_{\text{syn}}(\text{OH})$ of coordinated water molecules.

The spectra of $\text{UO}_2(\text{II})$ chelates significantly different. The ν_{OH} stretch at 3300 cm^{-1} in the spectra of the ligand remains intact while ν_{NH} is absent, indicating bidentate behavior of the ligand. The new strong band at 880 cm^{-1} on the spectra of $\text{UO}_2(\text{II})$ complex could be assigned to $\nu_{\text{asy}}(\text{U}=\text{O})$.

On examining the spectra of the ligand and complexes below 600 cm^{-1} , the new bands at 570–590 and 490–565 cm^{-1} in the spectra of the complexes are tentatively assigned to $\nu_{\text{M}-\text{O}}$ (phenolic) and $\nu_{\text{M}-\text{O}}$ (carbonyl) respectively.

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