

Metal Chelates of Hydrazo- β -Diketone Ligands. Chelating Tendencies of 2-Carboxyphenylhydrazodibenzoylmethane and 2-Carboxyphenylhydrazothienoyltrifluoroacetone.

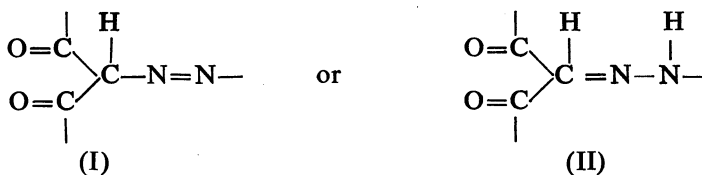
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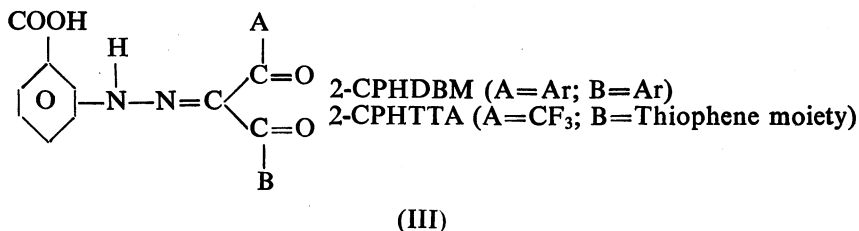
The acid-base properties of 2-carboxyphenylhydrazodibenzoylmethane (2-CPHDBM) and 2-carboxyphenylhydrazothienoyltrifluoroacetone (2-CPHTTA) and their equilibria with transition and lanthanide ions in 75% (v/v) dioxanwater solvent at 30°C have been investigated by pH titrimetry. The application of the theoretical equation derived by Irving and Rossotti indicates that the coordination modes of 2-CPHDBM and 2-CPHTTA toward the transition and lanthanide ions are the same. The stability constants for transition and lanthanide ion complexes with respect to the organic ligands follow the order: 2-CPHTTA > 2-CPHDBM.

INTRODUCTION

A reaction between diazonium salt and β -diketone species take place through the active methylene group to give ligands with chromophoric group I and II respectively.



The hydrazo structure (II) was substantiated by Yashiharu¹. The binding characteristics of ligands (II) have been studied. In some cases, auxiliary strong coordinating groups such as carboxylate^{2,3} or hydroxy^{4,5} groups have been incorporated. In the present communication the acid-base equilibrium and metal-ion chelating tendencies of two of the representative phenylhydrazo- β -diketones viz. 2-carboxyphenylhydrazodibenzoylmethane (2-CPHDBM) and 2-carboxyphenylhydrazothienoyltrifluoroacetone (2-CPHTTA) which are shown in III, is described.



EXPERIMENTAL

The ligands were synthesized by coupling diazonium salt of 2-amino benzoic acid with dibenzoylmethane or thienoyltrifluoroacetone in sodium acetate medium. The pure materials were obtained after crystallization several times from aqueous dioxan and methanol for 2-CPHDBM and 2-CPHTTA respectively. The elemental analysis for 2-CPHDBM: found for $C_{22}H_{16}O_4N_2$: C 70.76, H 4.25, N 7.45; calculated: C 70.87, H 4.30, N 7.53. 2-CPHTTA: found for $C_{15}H_9O_4N_2F_3S$: C 48.45, H 2.4, N 7.46, F 15.15, S 8.49; calculated: C 48.65, H 2.43, N 7.57, F 15.41, S 8.65.

The nitrate salts of the divalent and trivalent lanthanide metal ions were prepared and standardized as described previously². Dioxan was purified distilled prior to each use as described elsewhere². The base was carbonate free KOH kept under nitrogen atmosphere and standardized against primary standard potassium-hydrogen phthalate.

The protonation constants of ligands and stability constants of complexes were determined in 75%(v/v) dioxan-water and ionic strength of 0.10 M (KNO_3). The potentiometric measurements were carried out using Beckman SSR 2 pH-meter fitted with a combination glass-calomel electrode. The electrode was calibrated with standard buffer of pH 4.01 and 7.00. In basic media borax solution (0.01M) served as a standard buffer of pH 9.17. Correction for hydrogen ion activity in solutions of 0.10M ionic strength and 75% (v/v) dioxan-water was obtained by using⁶ activity coefficient 1.906. pK^H values for the free ligands were calculated from the titration curves as described elsewhere⁷. The values of the stability constants were obtained by titrating volumes of 1 : 2 molar ratio of M : L with standard (CO_2 -free) potassium hydroxide in 75% (v/v) dioxan-water. In all measurements, the ligand concentration was kept at 0.005M, the temperature was maintained at 30°C, and ionic strength of the reaction medium was kept constant by the addition of appropriate amount of potassium nitrate. The data were processed by using program based on the SIMPLEX algorithm and written by us as described previously⁷. The relative standard deviations were estimated from the calculated values of the stability constants obtained from three to four experiments.

RESULTS AND DISCUSSION

Figures 1 and 2 show representative plots for the titration curves of 2-CPHDBM and 2-CPHTTA in absence and presence of divalent metal ions. The curves for the free ligands give two separate buffer regions. The first one is between $a = 0$ and $a = 1$ ($a =$ number of moles of base added per mole of ligand present) followed by strong inflection point at $a = 1$ due to the complete neutralization of the carboxylate group (K_1^H). The second one is noticed at higher-pH values between $a = 1$ and $a = 2$ with weak

inflection at $a = 2$, due to the complete dissociation of the hydrazo group (K_2^H). This behaviour indicates that 2-CPHDBM or 2-CPHTTA acts as diprotic ligand. The liberation of two protons on titrating the ligands in

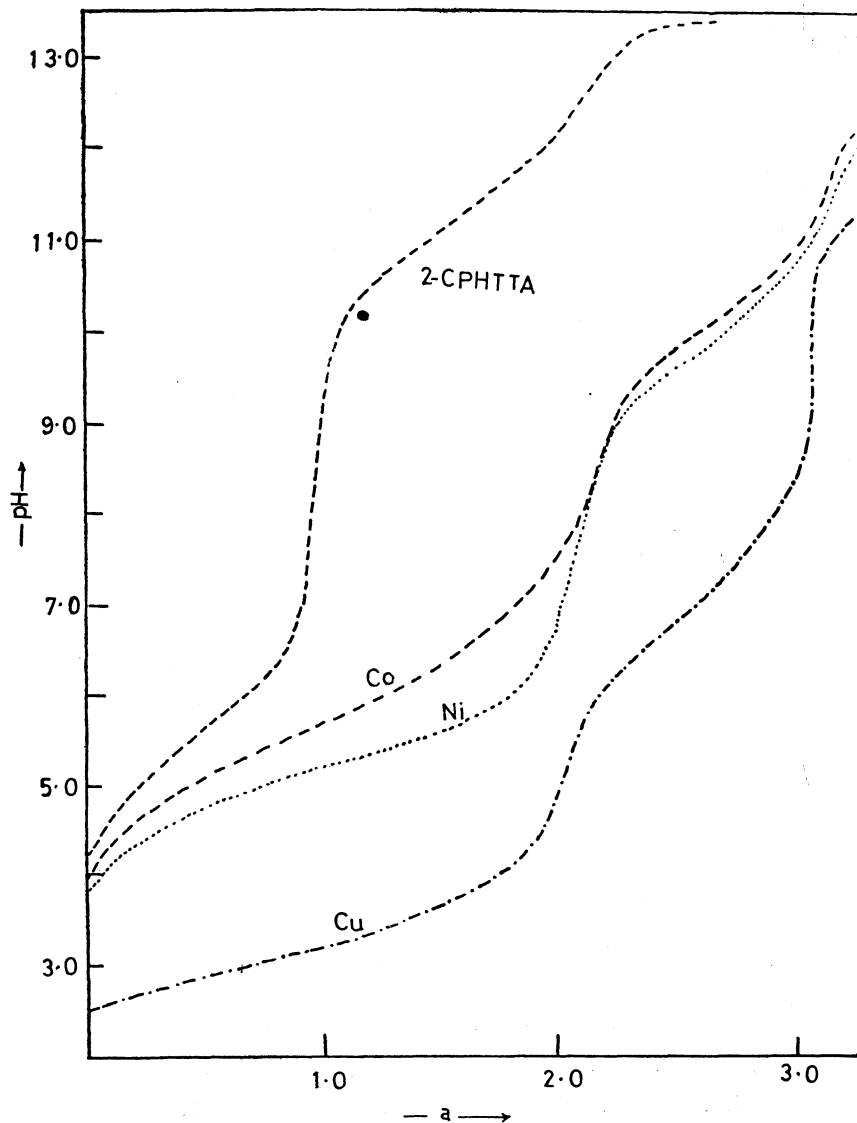


Fig. 1 Potentiometric equilibrium curves for 1 : 2 molar ratios of metal ions of to 2-CPHTTA; a = moles of base added per mole of ligand; concentration is 0.0025M in metal ion

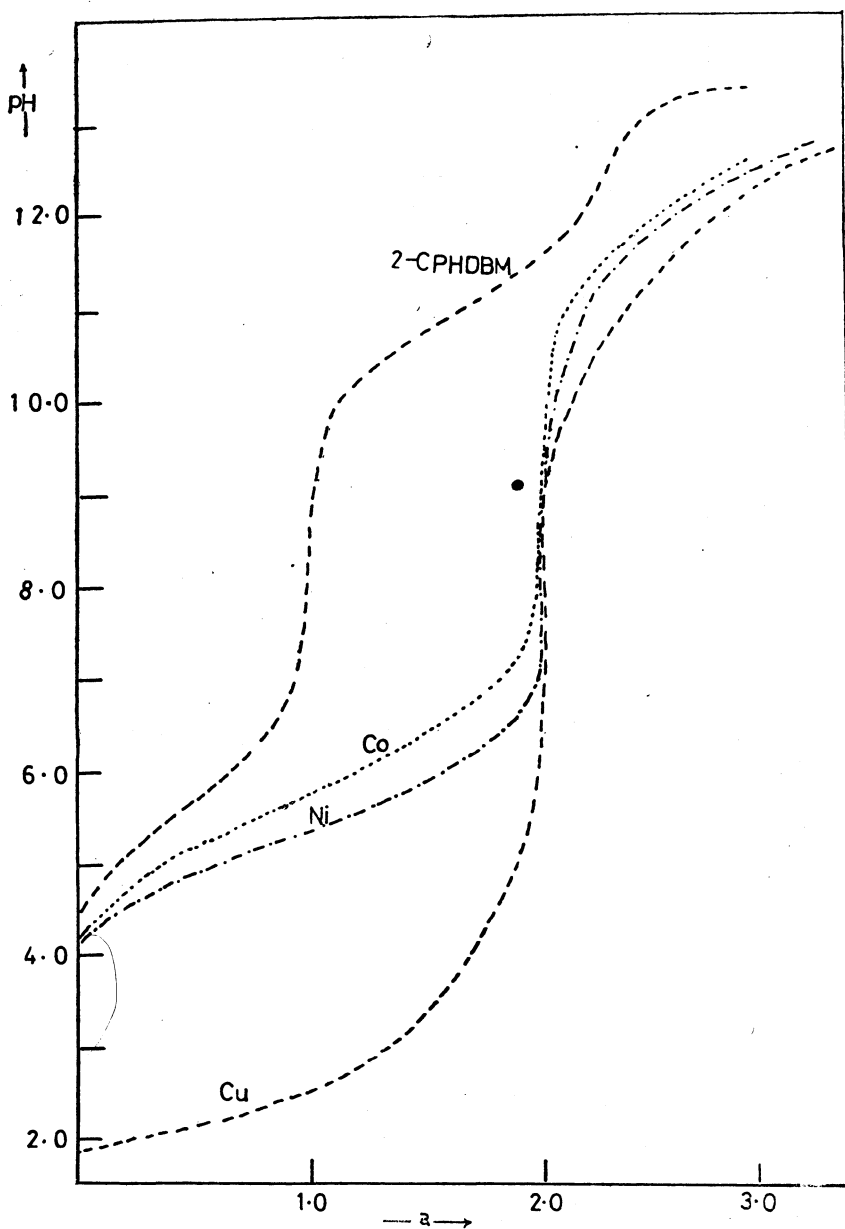


Fig. 2 Potentiometric equilibrium curves for 1:2 molar ratios of metal ions to 2-CPHDBM; concentration is 0.0025M in metal ion

the presence of various metal ions support the diprotic nature of these ligands. The titration curves of 2-CPHDBM and 2-CPHTTA complexes of Cu(II), Ni(II) and Co(II) show the presence of long buffer region from $a = 0$ to $a = 2$ due to the formation of bis-chelates represented by the

equilibrium: $M^{z+} + 2H_2L \rightleftharpoons ML_2^{(z-4)+} + 4H^+$. The curves for 2-CPHTTA complexes give additional buffer region between $a = 2$ and $a = 3$ probably due to the formation of hydroxo complex: $[ML_2(OH)_2]^{(z-6)+}$. The log of the formation constants of the divalent and trivalent metal ion complexes with the different ligands are presented in Table I. Values of $\log K_2$ for the bis chelates of Zn(II)-, Mn(II)-, Cd(II)- and Ln-2-CPHTTA are not included in Table I because of the tendency of these species to hydrolyse in the region of its formation.

Figure 3 shows the correlation of $\log K_1$ and $\sum pK^H$ for Sm(III) with a number of 2-carboxy- and 2-hydroxyphenylhydrazo- β -diketone ligands. $\sum pK^H$ and $\log K_1$ values for 2-carboxyphenylhydrazomalononitrile(2-CPHMN), 2-carboxyphenylhydrazodimedone(2-CPHD), 2-hydroxyphenylhydrazodimedone(2-HPHD), 2-carboxyphenylhydrazo-*para*-chloro-acetoacetanilide(2-CPH-p-Cl-AAA) and 2-carboxyphenylhydrazo-*para*-methoxy-acetoacetanilide(2-CPH-p-OCH₃-AAA) were obtained from reported work^{2-4,8}. Sm(III) was used for this comparison as it represents

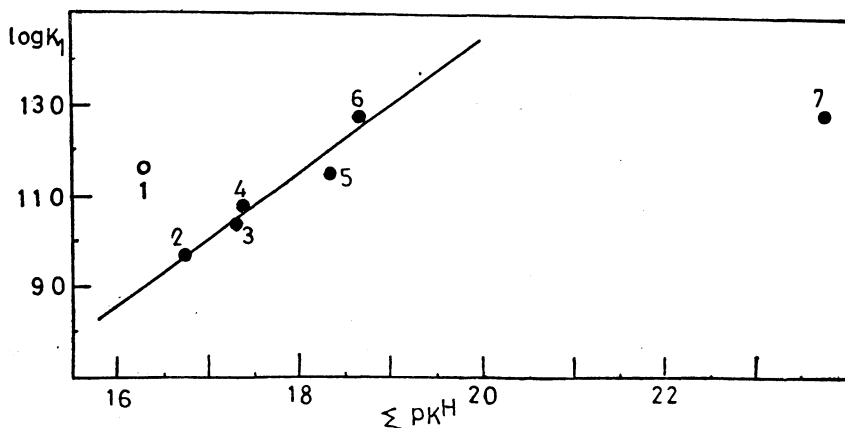


Fig. 3 Relationship between the values of $\log K_1$ for Sm(III) complexes 2-CPHMN(1); 2-CPHDBM(2); 2-CPHTTA(3); 2-CPH-p-Cl-AAA(4) 2-CPHD(5); 2-CPH-p-OCH₃-AAA(6); 2-HPHD(7)

the average behaviour. The correlation in Fig. 3 has been noticed for many metal-ligand systems and reflects the strongly ionic nature of the bonding of the complex. Structural effects can perturb the correlation as in cases of 2-CPHMN and 2-HPHD complexes. The extra stabilization (the $\log K_1$ is above the straight line) of the Sm(III)-2-HPHD complex is attributed to the difference in the basicity of hydroxyl and carboxy groups. In addition to a shorter Ln-O distance in 2-HPHD compared to the more flexible Ln-O distance in carboxylate type. The deviation of Sm(III)-2-CPHMN from the line could be due to the bidentate nature (O,N) of 2-CPHMN⁸ compared to the tridentate character of the other ligands^{2,5}.

In case of 2-CPHMN the coordination sites are carboxylate oxygen and hydrazo nitrogen while in the other ligands the sites are carboxylate or hydroxy oxygen, hydrazo nitrogen and ketonic oxygen.

As is clear from Table 1 the stability constants ($\log K_1$) for the divalent and lanthanide ion complexes with respect to the organic ligands follow the order: 2-CPHTTA > 2-CPHDBM which is same as the basicity (ΣpK^H) order of the ligands. This indicates that the basicity of the

TABLE 1
EQUILIBRIUM CONSTANTS* FOR THE INTERACTION OF 2-CPHDBM
AND 2-CPHTTA WITH METAL IONS. ALL MEASUREMENTS AT
 $\mu = 0.1 \text{ M KNO}_3$; 30°C AND 75% (v/v) DIOXAN-WATER

Cation	2-CPHTTA		2-CPHDBM	
	$pK_1^H = 5.97 \pm 0.01$	$pK_2^H = 11.38 \pm 0.03$	$pK_1^H = 5.98 \pm 0.02$	$pK_2^H = 10.77 \pm 0.03$
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
Cu ²⁺	13.57	12.27	14.25**	
Ni ²⁺	9.32	8.40	8.67	7.52
Co ²⁺	8.47	7.40	7.72	6.70
Zn ²⁺	7.95		7.35	6.66
Mn ²⁺	6.95		6.22	5.32
Cd ²⁺	6.65		6.02	5.90
La ³⁺	9.35		8.75	7.17
Ce ³⁺	9.85		9.25	7.49
Pr ³⁺	9.96		9.32	7.62
Nd ³⁺	10.07		9.50	7.75
Sm ³⁺	10.37		9.81	8.02
Eu ³⁺	10.55		9.93	8.22
Gd ³⁺	10.36		9.75	8.17
Tb ³⁺	10.20		9.52	7.75
Dy ³⁺	10.07		9.48	7.87
Ho ³⁺	10.25		9.65	8.19
Er ³⁺	10.42		9.84	8.57
Tm ³⁺	10.62		10.25	8.87
Yb ³⁺	11.03		10.51	9.19
Lu ³⁺	10.89		10.34	8.93

**Spectrophotometric method

* $\pm (0.04 - 0.08)$

ligands is the only factor that govern the increase of the stability of the complexes. If we consider this the stabilities of the complexes of the same type ($\log K_{MA}$ or $\log K_{MB}$, where A = 2-CPHTTA and B = 2-CPHDBM) formed by a similar pair of ligands H_2A and H_2B , with two different series of metal ions are compared by plotting $\log K_{MA}$ vs. $\log K_{MB}$ (Fig. 4 & 5). For both types of complexes the plots yield two separate lines of equal intercept (0.60) respectively, one for the transition metals and the other for lanthanides. This suggests that the coordination mode of these ligands toward the two series of metal complexes are the same. The value

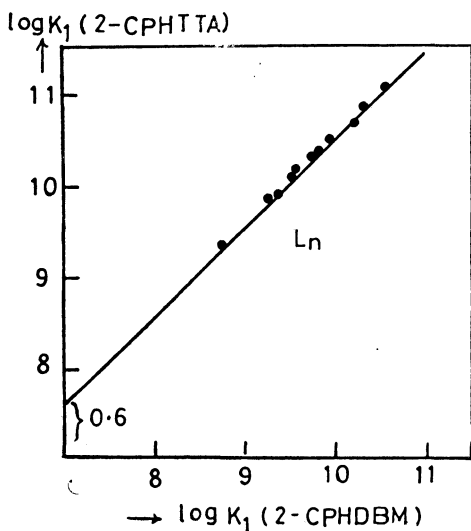


Fig. 4 Relationship between the stability constants for lanthanide complexes

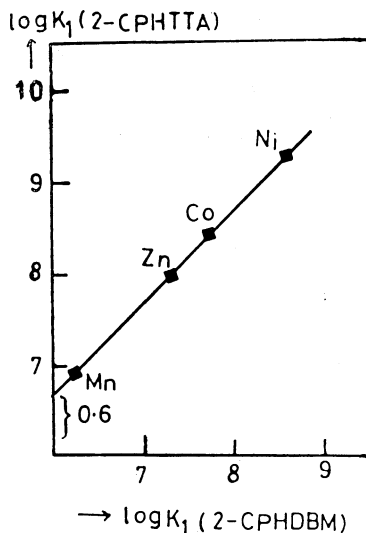


Fig. 5 Relationship between stability constants for some divalent metal complexes

0.60 of the intercept is expected from the basicity difference ($\Sigma pK_A^H - \Sigma pK_B^H$) of the ligands. This indicates the validity of the theoretical relationship derived by Irving and Rossotti⁹ between the logarithms of the stability constants for metal complexes of a similar pair ligands A and B:

$$\log K_{MA} = \log K_{MB} + (\log K_{H_2A} - \text{of } \log K_{H_2B})$$

The stability constants ($\log K_1$ and $\log K_2$) for M^{2+} – 2-CPHTTA and M^{2+} – 2-CPHDBM complexes show the following order; $Cu > Ni > Co > Zn > Mn > Cd$. This order is in agreement with that given by William and Irving¹⁰. A number of causes are given for this order among

which the second ionization potential (2nd I_p) and the electronegativity (X_m) of the elements. The increase of 2nd I_p and X_m cause the decrease of electronegativity difference between the metal atom and donor atoms on the ligands, consequently the metal-ligand will be more covalent, and this results into greater stability of the metal chelates.

It should be mentioned here that in the case of Cu(II)-2-CPHDBM system the original pH value of the titration curve (Fig. 2) is 1.87. This indicates that the equilibrium is displaced almost completely towards the chelate giving a curve similar to that of a strong acid titration. The formation of copper chelate is so clearly complete even at low pH, and accordingly, its stability cannot be accurately calculated from potentiometric data. For this reason the value of the stability constant ($\log K_1$) has been determined spectrophotometrically as described previously⁷.

The logarithms of the stability constants $\log K_1$ or $\log K_2$ of Ln(III)-2-CPHTTA and Ln(III)-2-CPHDBM complexes as a function of ionic potential Z^2/r (r = ionic radius) are plotted in Fig. 6. Campbell and

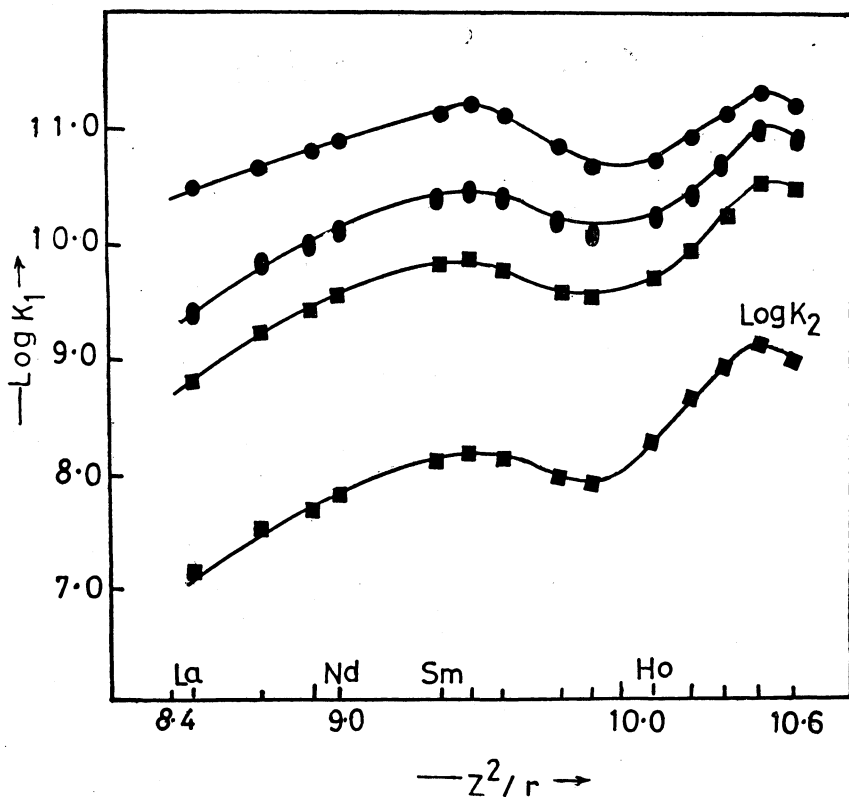


Fig. 6 Plots of $\log K_n$ for the various lanthanide-hydrazo- β -diketone chelates as a function of ionic potential Z^2/r ; $n = 1$ or 2

2-CPHD: 2-CPHTTA; 2-CPHDBM

Moeller¹¹ called attention to smooth linear variation of thermodynamic parameters with ionic potential in absence of structural changes. In our previous^{2-5,7,12,13} and present systems, however, the curves showed distinct discontinuity between lighter (La-Gd) and heavier (Gd-Lu) lanthanides. This behaviour was observed for several complexing systems and were attributed to different degrees of dehydration of lanthanide cations upon complexation^{14,15}.

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