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Chelation Behaviour of Lanthanons with *o*-Arsonodibenzoylmethanephenylhydrazone

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Summary. The chelate formation reaction of La(III), Pr(III), Nd(III), Gd(III), Ho(III), and Er(III) with *o*-arsonodibenzoylmethanephenylhydrazone has been investigated potentiometrically and conductometrically in 40% (*v*/*v*) aqueous ethanol, ionic strength 0.1 *M*. The order of stability constants was found to be La < Pr < Nd > Gd < Ho < Er. The chelates formed have 1 : 1 and 1 : 2 stoichiometries ($M^{3+} : L$). The complexes have been isolated in solid state and have been characterized on the basis of elemental analysis and IR data. Coordination occurs through – NH of the hydrazo and – OH of the arsonic groups.

Keywords. Stability constants; *o*-Arsonodibenzoylmethanephenylhydrazone; Lanthanides.

Chelierungsverhalten von Lanthaniden mit *o*-Arsonodibenzoylmethanphenylhydrazon

Zusammenfassung. Die Reaktion der Chelatbildung von La(III), Pr(III), Nd(III), Gd(III), Ho(III) und Er(III) mit *o*-Arsonodibenzoylmethanphenylhydrazon wurde potentiometrisch und konduktometrisch in 40% (*v*/*v*) wäßrigem Ethanol bei einer Ionenstärke von 0.1 *M* untersucht. Die Reihung der Stabilitätskonstanten war La < Pr < Nd > Gd < Ho < Er. Die Chelate haben 1 : 1 und 1 : 2 Stöchiometrien ($M^{3+} : L$). Die Komplexe wurden im Festzustand isoliert und mittels Elementaranalyse und IR-Spektroskopie charakterisiert. Die Koordinierung erfolgt über – NH der Hydrazo- und – OH der Arsongruppe.

Introduction

The arylhydrazones of dibenzoylmethane are of interest because of their biological activity [1, 2] and dyeing properties for a variety of fabrics [3]. They have been used as analytical reagents; values of stability constants of some transition metal complexes have been reported [4, 5]. A survey of literature reveals that no work has been done on the lanthanide complexes of *o*-arsonodibenzoylmethanephenylhydrazone. Pichen et al. [6] investigated the structure and physical properties in solutions of compounds obtained from condensation of aryldiazonium salts with carbanions of β-diketones. Recently, the successive stability constants (log K_1 and log K_2) of the complexes of some benzoylacetonearylhydrazone and dibenzoylmethanearylhydrazone derivatives with La(III) ion have been determined potentiometrically [7].

The present article deals with the evaluation of the ionization constant of *o*-arsonodibenzoylmethanephenylhydrazone and stability constants of its complexes with some lanthanons. The structure of the solid complexes was also ivestigated by elemental and IR spectroscopy.

Experimental Part

o-Arsonodibenzoylmethanephenylhydrazone (**1**) was prepared by coupling of dibenzoylmethane and *o*-arsonophenyldiazonium salt as previously reported in the presence of sodium acetate as a weak base [8, 9]. The resulting solution was acidified with dilute (1 : 1) HCl. The product was filtered and recrystallized from ethanol to constant melting point. The purity of the resulting compound was confirmed by elemetal analysis (m.p. 212°C): calc. C 55.76, H 3.96, N 6.19; found C 54.60, H 4.20, N 6.30%.

Stock dye solution (0.001 *M*) was prepared in absolute ethanol. 0.01 *M* solutions of $Ln(ClO_4)_3$ [*Ln* = La(III), Pr(III), Nd(III), Gd(III), Ho(III) and Er(III)] were prepared in distilled water and standardized with *EDTA* [10] using Arsenazo I as indicator, then a 0.001 *M* solution was prepared by accurate dilution. Solutions of 0.107 *M* perchloric acid; 0.305 *M* NaOH and 1 *M* sodium perchlorate were also prepared.

Three mixtures were prepared [11] as follows:

(a) 5 ml 0.107 *M* $HClO_4$ + 4.5 ml 1 *M* $NaClO_4$ + 20 ml ethanol; the volume was made up to 50 ml with distilled water.

(b) 5 ml 0.107 *M* $HClO_4$ + 4.5 ml 1 *M* $NaClO_4$ + 20 ml 10^{-3} *M* ethanolic solution of **1**; the volume was made up to 50 ml.

(c) 5 ml 0.107 *M* $HClO_4$ + 4.5 ml 1 *M* $Ln(ClO_4)_3$; the volume was made up to 50 ml.

The above three mixtures were titrated potentiometrically against 0.305 *M* NaOH using a *pH*-meter (Schott Mainz Model CG 801 digital Ionalyzer) at 27 ± 0.1°C. The correction factor for converting the *pH*-meter reading in 40% (*v*/*v*) ethanol-water to *pH* values, amounts to 0.15 [12], and the *pH* versus volume of NaOH curves were plotted accordingly. The $\bar{n}_A$, $\bar{n}$ and *pL* values were calculated using the equations described by Irving and Rossotti [13].

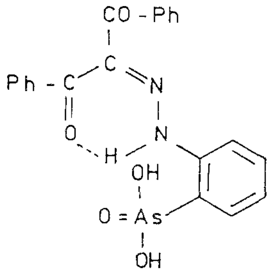
Conductometric titrations were performed using a PTI 18 digital conductivity meter at a frequency of 2 kHz.

The solid complexes were prepared by reacting 1 : 1 and 1 : 2 stoichiometric proportions of La(III), Pr(III), Ho(III), and Er(III) and ligand **1**. The hot mixture was stirred and left for 30 min on a steam bath, then dilute ammonium hydroxide solution was added dropwisely with stirring. At *pH* values ranging from 8 to 9.50, the solid complexes were precipitated, collected and washed with cold ethanol, 1 : 1 and 1 : 2 complexes were obtained in all cases, characterized on the basis of microanalysis and IR spectrum (using the KBr technique with the aid of a PYE UNICAM SP 3-300 spectrophotometer).

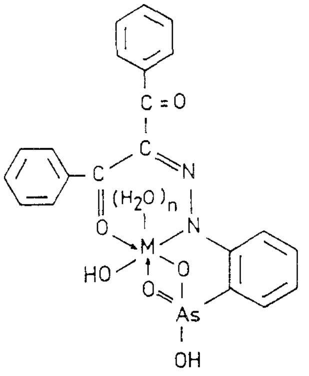
Results and Discussion

In the present work the *pK* values of ligand **1** have been evaluated by calculating $\bar{n}_A$ at various *pH* from the acid and ligand titration curves. The formation curves ($\bar{n}_A$ against *pH*) for the proton-ligand system are found to be extended between 0 to 3 on the $\bar{n}_A$ scale, this indicates that the ligand has three dissociable protons, the values 3.75 and 9.00 being assigned to the ionization of the two protons of the arsonic acid groups. The value, 11.30 is due to the ionization of the −NH group in the hydrazone moiety.

The formation curves of the complexes were obtained by plotting the average number of ligands attached per metal ion ($\bar{n}$) versus the free ligand exponent (*pL*). The $\bar{n}$ values (0–2) indicates the formation of 1 : 1 and 1 : 2 (*M* : *L*) complexes. The stability constants were computed by interpolation at half $\bar{n}$ values and are listed in Table 1.

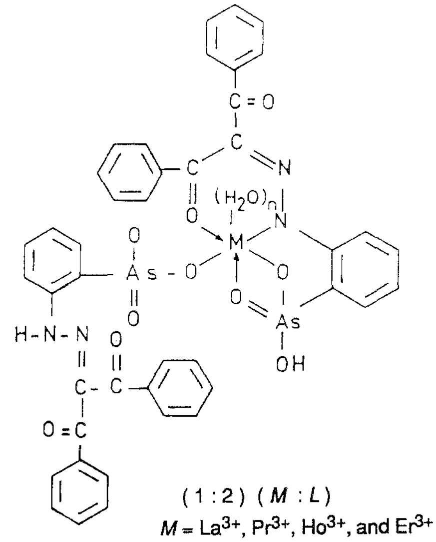


1: *o*-Arsono*DBMPH*



(1 : 1) (*M* : *L*)
M = La^{3+}, Pr^{3+}, Ho^{3+}, and Er^{3+}
n = 0, 1 or 2

2



(1 : 2) (*M* : *L*)
M = La^{3+}, Pr^{3+}, Ho^{3+}, and Er^{3+}
n = 0 or 4

3

Table 1. Stability constants of lanthanon complexes with *o*-arsano*DBMPH* at $\mu = 0.1$ *M* $NaClO_4$ and 27 ± 0.1°C

Metal ion			For metal ion*	
	log β_1	log β_2	*Z*	1/*r*
La^{3+}	12.78	17.08	57	0.98
Pr^{3+}	13.75	18.10	59	0.99
Nd^{3+}	14.84	19.21	60	1.005
Gd^{3+}	14.20	18.66	64	1.07
Ho^{3+}	16.30	20.90	67	1.12
Er^{3+}	17.35	22.95	68	1.135

* *Z* atomic number; *r* ionic radius (Å)

The stability constants of La(III), Pr(III), Nd(III), Gd(III), Ho(III), and Er(III) with ligand **1** exhibit an increase with increasing atomic number and decreasing ionic radius till Er(III), with something of a break or discontinuity at the Gd(III) ion. The relative increase in stability constants of lanthanons from La-Gd is in agreement with the expected trend of a simple electrostatic model [14]. The situation for heavier lanthanons [Ho(III) and Er(III)] is different and it cannot be explained by the possible existence of crystal field effects [15]. The relative order of stability constants is found to be:

La(III) < Pr(III) < Nd(III) > Gd(III) < Ho(III) < Er(III).

A closer examination of this order of stability in comparison with the results obtained for *EDTA, CDTA, HEDTA*, and *NTA* [16] indicates the similarity in behaviour for lighter lanthanons (La-Gd), while the situation for heavier lanthanons (Gd-Lu) is somewhat different.

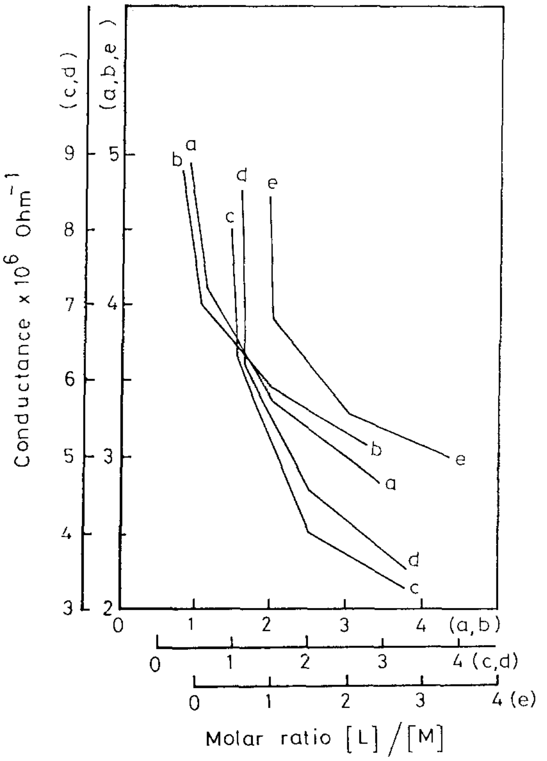


Fig. 1. Conductometric titration curves of 50 ml ($4 \cdot 10^{-5}$ *M*) of *o*-arsono*DBMPH* with 10^{-3} *M* of La (*a*), Nd (*b*), Pr (*c*), Gd (*d*), and Er (*e*) ions

Table 2. Elemental analysis of Ln^{3+} – *o*-arsono*DBMPH* complexes

M:*L*	Formula	C% Calc. (found)	H% Calc. (found)	N% Calc. (found)	*M*% Calc. (found)
1:1	$La(C_{21}H_{16}N_2O_6As)(H_2O)_2$	39.26 (39.70)	3.12 (2.60)	4.36 (4.30)	21.64 (22.00)
1:2	$La(C_{21}H_{15}N_2O_5As)(C_{21}H_{16}N_2O_5As)(H_2O)_4$	45.29 (44.20)	3.50 (3.50)	5.03 (4.88)	12.48 (12.50)
1:1	$Pr(C_{21}H_{15}N_2O_5As)(H_2O)(OH)$	40.27 (41.70)	2.88 (3.20)	4.47 (4.30)	22.51 (22.39)
1:2	$Pr(C_{21}H_{15}N_2O_5As)(C_{21}H_{16}N_2O_5As)(H_2O)_4$	45.21 (46.00)	3.50 (3.55)	5.01 (4.75)	12.64 (12.58)
1:1	$Ho(C_{21}H_{15}N_2O_5As)(OH)$	39.88 (42.00)	2.53 (2.90)	4.43 (4.50)	26.10 (25.98)
1:2	$Ho(C_{21}H_{15}N_2O_5As)(C_{21}H_{16}N_2O_5As)$	47.29 (48.30)	2.91 (3.10)	5.25 (5.45)	15.76 (15.39)
1:1	$Er(C_{21}H_{15}N_2O_5As)(OH)$	39.74 (41.10)	2.52 (2.90)	4.41 (4.70)	26.37 (26.26)
1:2	$Er(C_{21}H_{15}N_2O_5As)(C_{21}H_{16}N_2O_5As)(H_2O)_4$	44.17 (44.60)	3.42 (3.90)	4.91 (4.75)	14.66 (14.66)

Table 3. Important IR bands for Ln^{3+} – *o*-arsono*DBMPH* complexes

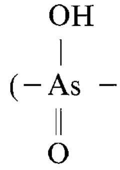
M	$M:L$	γ_{OH}	$\gamma_{C=O}$	$\gamma_{C=O...M}$	δ_{OH}	γ_{OH}	$\gamma_{M=O}+\delta\,(\text{ring})$
La	1:1	3450	1650	1580	1110	850	655
Pr	1:1	3450	1650	1570	1110	840	680
Ho	1:1	3500	1640	1580	1080	850	680
Er	1:1	3500	1650	1570	1090	860	660
La	1:2	3400	1650	1550	1080	870	690
Pr	1:2	3500	1656	1595	1105	840	660
Ho	1:2	3450	1645	1585	1075	870	650
Er	1:2	3400	1650	1590	1080	870	660

The conductometric titration curves (Fig. 1) for the *Ln*-*o*-arsono*DBMPH* show two breaks at molar ratios of 1 : 1 and 1 : 2 indicating the formation of two types of complexes with stoichiometric ratios 1 : 1 and 1 : 2 (metal ion : ligand), which is in accordance with the results obtained from *pH*-metric titrations. The titration curves indicate a gradual increase in the conductance values due to the displacement of protons from the ligand on complex formation.

The solid complexes were prepared as previously mentioned and their purities were examined by elemental analysis, Table 2.

The mode of bonding of the ligand to the Ln^{+3} ions was examined by recording the IR spectra of the complexes and comparing these with that of the ligand. Spectra of the lanthanon chelates of *o*-arsono*DBMPH* are compatible with the structure that would result if the chelated hydrogen of the ligand is replaced by lanthanon ions. Thus, the position of the free carbonyl bands of the ligand is marginally altered in the spectra of their Ln^{+3}-chelates. Instead of the free ligand bands at 1620 cm^{-1} (due to hydrogen bonded carbonyl), the spectra of the *Ln* complexes exhibit another strong band at about 1580 cm^{-1} assignable to $\nu_{C=O\cdots M}$ [17]. In addition to these, metal-oxygen stretching and vibrational modes coupled with ring deformation $\nu_{(M-O)} + \delta_{\text{ring}}$ were observed at about 650 cm^{-1}. The *o*-arsono*DBMPH*-Ln^{3+} complexes exhibit a broad band within the wavenumber range 3500–3400 cm^{-1} which is attributed to the stretching frequency of coordinated water molecules, while the bands observed in the ranges 1075–1110 cm^{-1} and 830–860 cm^{-1} were attributed to δ_{CH} and γ_{OH} respectively of the bonded water molecule, Table 3. In a previous work [7] we have gained a substantial support for the results of the IR spectra by comparing the La^{3+} complexes of some closely related structures (*p*-Cl and *o*-OCH_3 benzoylacetonephenylhydrazone) with those of their ligands.

The NMR spectra of the ligands exhibit a singlet in the range 11–12.70 ppm. This band was assigned to the ionizable proton of the NH group (it disappears after deuteration). The NMR spectra of the 1 : 1 *o*-arsono*DBMPH* did not show the low field signal (NH), thus confirming that the chelated hydrogen is replaced by the Ln^{3+} ion. On the contrary, the NMR spectra of the 1 : 2 complexes show the proton of the NH group in the second ligand molecule.

Furthermore, from the potentiometric results, it was found that one of the hydroxyl groups of the arsonic group  $(-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle O}{\|}}{As}}-OH)$ dissociates first ($pK = 3.75$) and the other dissociates later ($pK = 9.00$), so we came to the conclusion that the hydroxyl group of lower pK value is involved in the chelation, thus the structure of the 1 : 1 and 1 : 2 ($M : L$) complexes may be formulated as **2** and **3**.

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