

**Chelating Behaviour of Substituted 3-Arylhydrazo-
Pentane-2,4-Dione Part VIII
The Stabilities of Complexes of Lanthanide Ions With
2-, 3-, 4- and 2-Sulphonic(4-Methyl) Phenylhydrazo-
Pentane-2,4-Dione Ligands**

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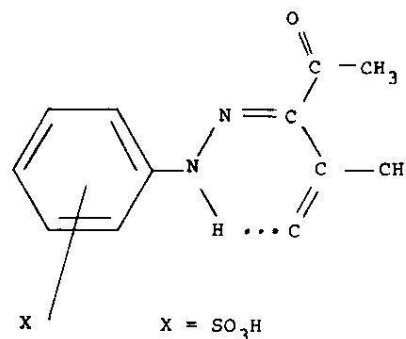
Summary: The stability constants have been determined for the reaction products of 2-, 3-, 4-, and 2-sulphonic (4-methyl)phenylhydrazo-pentan-2, 4-dione (2-SPHA, 3-SPHA, 4-SPHA and 2-S(4-Me)PHA) ligands with trivalent lanthanide ions. The measurements have been made at constant temperature 30°C and ionic strength 0.1 M in aqueous medium. Plotting $\log \beta_2$ (overall stability constant) against the atomic number of the lanthanide elements showed linear relationship from La to Eu with change in stability of 0.12, 0.24, 0.26 and 0.1 for 2-, 3-, 4- and 2-S(4-Me)PHA ligands respectively. After Gd, the stability remains nearly constant. The effect of substitution of sulphonic groups was discussed. The relation between $\log \beta_2$ and the pK's values of the organic ligands was also investigated.

Introduction

Varieties of ligands have been studied for complex formation with trivalent lanthanide ions [1,2] and involved the use of wide range techniques, and ionic media. The simple carboxylate, the hydroxy carboxylate and the amino polycarboxylate have been investigated [3]. The stability constants of acetylacetonates have been reported [4,5] and thermodynamic parameters have been measured [6]. However, a very interested tridentate water soluble organic ligands (sulphonic phenylhydrazo-acetylacetone SPHA) were prepared from coupling the diazonium salts of sulphonic anilines and acetylacetone in sodium acetate medium [7].

In the present investigation, the stability constants of chelate compounds between lanthanide ions and

2-, 3-, 4-, and 2-S(4-Me)PHA ligands are calculated. Also the relation between the $\log \beta_2$ (overall stability) and the atomic number of the lanthanide ion is studied.



Experimental

The exact concentration of lanthanide nitrates [8], acid form of the

organic ligands and all the other reagents were prepared as mentioned previously [9]. Also the pH-metric titrations were repeated at least twice and agreement between pH-readings was usually with ± 0.03 . In order to calculate the stability constants, it was also necessary to include the acid dissociation constants pK_1 and pK_2 for 2-,3-,4- and 2-S (4-Me) PHA ligands which are calculated previously [9] and the values obtained are 2.14, 10.96; 2.22, 10.6; 2.5, 10.70 and 2.40, 11.00 respectively. The stability constants of the formed complexes were calculated as mentioned before.

Results and Discussion

The trivalent lanthanide ion and organic ligand mixture of ratio 1:2 was titrated and a sharp inflection was obtained at $m = 2$ (where $m =$ mole of base per mole of ligand) indicating presence of 1:2 type complex. Moreover, the titration mixtures of some selected lanthanide ions and organic ligand in 1:10 ratio, were shown in Fig.1 that the inflection was obtained at $m = 2$, confirming that the 1:2 complex is the higher complex formed. The buffer zone obtained at $pH=8.0$, may be attributed to the presence of hydroxo complex and not to the hydroxide of the metal as no precipitate was observed during the titration.

The overall stability constants $\log \beta_2$ for 1:1 and 1:2 complexes formed between lanthanide ions and the organic ligands (2-,3-,4-and 2-S(4-Me) PHA) are given in Table 1. The error limits were calculated by subjecting the data to a least squares analysis and the standard deviation of an individual run was deduced. Overall stability constant ($\log \beta$) is the only constant obtainable, since 1:2 complex is being formed even at the start of

titration [10] and it can be easily calculated as mentioned previously [8].

Grenthe confirmed that the hydrolysis of the central metal atom, which seriously affected the accuracy of stability constants, is strongly suppressed by strongly complexing with acetylacetone. Hence the complexing ability of the studied ligands in the present work are more than that of acetylacetone itself as shown from their stability values in Table 1, therefore no problem of this kind arises in the present investigation.

The trivalent rare earth ions form a unique series for a study of the influence of the size of the central ion on the properties of the coordination compounds. If the metal ligand

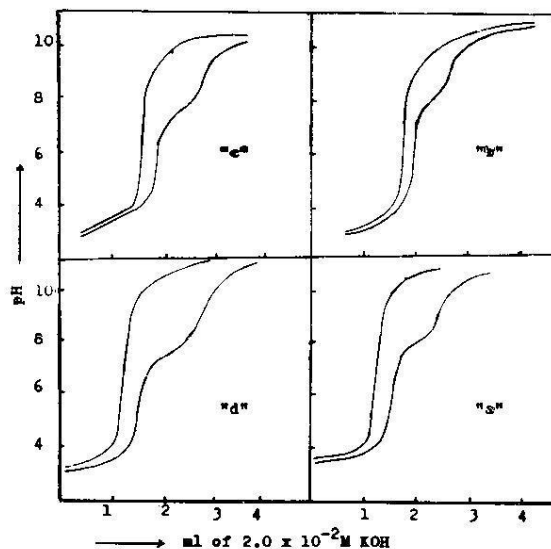


Fig.1: pH-metric titration of 30 ml mixture of:

- a- 1.0×10^{-3} M. 2-SPHA + 2.0×10^{-4} M. Dy(III)
- b- 1.0×10^{-3} M. 3-SPHA + 1.0×10^{-4} M. Gd(III)
- c- 1.0×10^{-3} M. 4-SPHA + 2×10^{-4} M. La(III)
- d- 1.0×10^{-3} M. 2-S(4-Me)PHA + 2×10^{-4} M. Gd(III)

Table-1: Log β_2 values for the reaction of trivalent rare earth ions with organic ligands at T=30°C and ionic strength 0.1 M

Metal ion	Log β_2 at $\mu = 0.1$ M and T = 30°C				
	2-SPHA	2-S(4Me)PHA	3-SPHA	4-SPHA	Ac.Ac. ⁴
La ³⁺	23.34±0.05	22.26±0.06	20.64±0.30	20.51±0.07	8.41
Pr ³⁺	23.76±0.05	22.59±0.04	21.47±0.04	21.21±0.03	9.20
Nd ³⁺	23.86±0.01	22.91±0.07	21.88±0.05	21.70±0.06	9.40
Sm ³⁺	24.03±0.11	23.01±0.03	21.91±0.05	21.78±0.04	10.05
Eu ³⁺	23.77±0.07	23.01±0.03	22.12±0.04	21.95±0.02	10.35
Gd ³⁺	24.27±0.09	23.06±0.04	22.18±0.03	22.08±0.02	10.38
Tb ³⁺	24.19±0.07	23.26±0.03	21.99±0.05	21.94±0.09	10.63
Dy ³⁺	24.26±0.05	23.42±0.03	22.12±0.03	22.04±0.04	10.70
Ho ³⁺	23.94±0.06	23.52±0.06	21.98±0.03	21.87±0.02	10.73
Er ³⁺	24.86±0.06	23.74±0.06	21.98±0.04	21.83±0.03	10.85
Tm ³⁺	25.13±0.08	23.75±0.03	22.11±0.03	21.85±0.02	10.85
Yb ³⁺	24.83±0.07	24.03±0.10	22.00±0.03	22.06±0.03	11.04
Lu ³⁺	24.92±0.05	24.21±0.04	22.23±0.07	22.18±0.02	11.00

bond is considered to be purely electrostatic in nature, the strength of the bond should increase linearly with increasing ionic potential Z^2/r , where Z is the charge and (r) is the radius of the ion. In Fig.2, the logarithm of the overall stability constants "log β " of the complexes are plotted as a function of atomic number. Instead of the expected linearly increasing course, a curve is obtained, where only the first part, from lanthanum to europium, increases linearly, the second part gadolinium to lutetium is nearly constant. The differences in

log β_2 between consecutive elements in the first part, La-Gd is 0.12, 0.20, 0.26, 0.15, for 2-,3-,4- and 2-S(4-Me)PHA ligands respectively while the total increase from Tb to Lu is only 0.73, 0.24, 0.24 and 0.85 for the same ligands. The deviation from linearity is not peculiar for the studied ligands, but it is common for most rare earth complexes with multidentate ligands [4,6,12,13]. This behaviour cannot be explained by electrostatic bond theory, but due to the presence of many coordination sites in these ligands, there is a

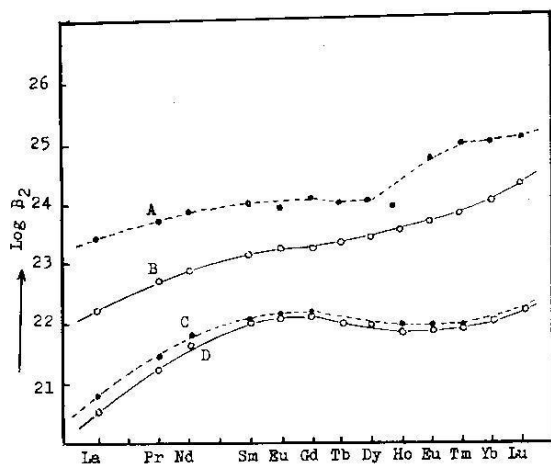


Fig.2: $\text{Log } \beta_2$ as a function of atomic number for various rare earth complexes:

A- 2-SPHA, B- 2-S(4-Me)PHA
C- 3-SPHA, D- 4-SPHA

possibility of change in the number of points of attachment before and after gadolinium [6,12,13].

Literature survey [14-17] showed that lanthanides can form 1:1, 1:2 and 1:3 complex types with β -diketones, while in the present case they form 1:1 and 1:2 types. This may be due to steric effect of the attached groups which hinder the bonding of three molecules of the ligands around the metal ion. The investigation of the solid complexes prepared for the La^{3+} , Nd^{3+} , Pr^{3+} ions with 4-SPHA ligand confirmed that the composition of the complexes are 1:2 metal to ligand ratio [7].

Both 3-SPHA and 4-SPHA ligands gave the same behaviour as well as the values of the stability constants are nearly the same. The small increase in stability values of 3-SPHA than 4-SPHA may be due to the shifting of sulphonic group from 4-to 3-position. The greater stability values of 2-ligands (2-SPHA & 2-S(4-Me)PHA) than the 3-SPHA and 4-SPHA may be due to a greater bonding between the cation and the ligand. This is attributed to the sharing of

sulphonic group in chelation process. Also, the pK_2 of the 2-ligands [9] are higher than those of the 3-and 4-SPHA ligands. These factors would lead to more stable complexes which agree with the obtained values. Also, in case of 2-SPHA ligand, the values of stability constants for lanthanide complexes is higher than in case of 2-S(4-Me)PHA ligand, which may be due to the presence of methyl group. Therefore the increasing order of the stability constants is as following:

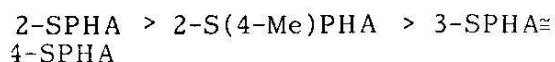


Figure 3, represents a plot of $1/2 \log \beta_2$ for lanthanide complexes vs. the $\Sigma \text{pK}'$ s values of acetylacetone, 2-,3-,4- and 2-S(4-Me)PHA ligands. The points fall on a common line for those compounds which structurally are the same number of water molecular displaced upon complexation.

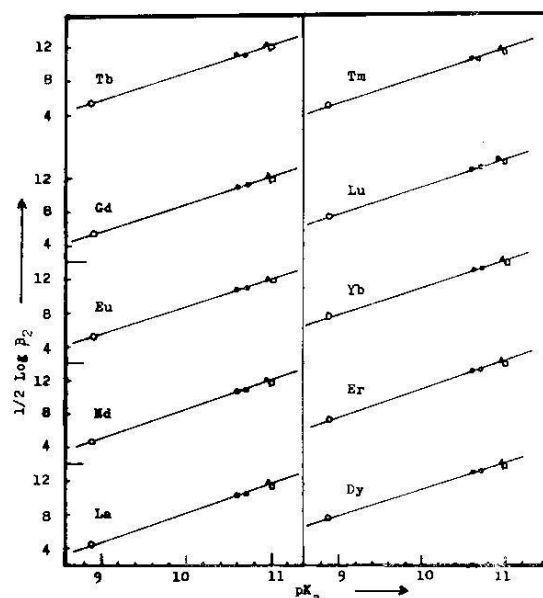


Fig.3: Plot of $1/2 \text{Log } \beta_2$ of rare earth elements vs. pK_2 of acetylacetone, 2-, 3-, 4-, and 2-S(4-Me)PHA ligands at 30°C. Acetylacetone, 2-S(4-Me)PHA, 2-SPHA, 3-SPHA, 4-SPHA

References

1. T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feisterl and W. J. Randall, *Chem. Rev.*, **65**, 1 (1965)
2. G. R. Choppin, XIII Inter. Conf. Coord. Chem. Plenary lecturer, Butterworth, London (1972)
3. Y. Hasegawa and G. R. Choppin, *Inorganic Chem.*, **16**, 2933 (1977)
4. I. Grenthe and W. C. Fernelius, *J. Am. Chem. Soc.*, **82**, 6258 (1960)
5. H. Yoneda, G. R. Choppin, J. L. Bear and J. V. Quagliano, *Inorg. Chem.*, **3**, 1642 (1964)
6. A. Dadgar and G. R. Choppin, *J. Coord. Chem.*, **1**, 179 (1971)
7. G. El-Inany, B. El-Shetary and F. Zidan, *Egypt J. Chem.*, **25**, 301 (1982)
8. A. M. Zahra, B. A. El-Shetary and A. Ismail, *J. Chinese Chem. Soc.*, **27**, 37 (1980)
9. G. El-Inany, A. A. Taha and B. El-Shetary, *Pakistan J. Sci. Ind. Res.*, **25**, 229 (1982)
10. A. Albert and E. P. Serjeant, *"Ionization Constant of Acids and Bases"* Methuen & Co. Ltd. London P. 160-164 (1962)
11. T. Moeller, *private communication*
12. R. Stampfl and G. R. Choppin, *J. Coord. Chem.*, **1**, 173 (1971)
13. G. R. Choppin and J. Groffs, *Inorg. Chem.*, **4**, 1254 (1965)
14. K. K. Davidento and A. A. Jaladkov, *J. Inorg. Chem. (USSR)* **12**, 1195 (1967)
15. N. K. Dutt and P. Bandyopadhyay, *J. Inorg. Nucl. Chem.*, **26**, 729 (1964)
16. G. A. Gutter and G. S. Hammond, *J. Am. Chem. Soc.*, **78**, 5166 (1956)
17. A. S. Berliand, A. E. Bupke and L. E. Martinkeo, *J. Inorg. Chem. (USSR)* **13**, 2106 (1969)
18. L. G. Uitert, G. G. Hass, W. C. Fernelius and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 355 (1953)