

**Chelating Behaviour of Substituted 3-Arylhydrazo-  
Pentane -2,4-dione. Part VII. Stability Constants  
of Chelates of Divalent Transition Metals with  
2-, 3-, 4- and 2-Sulphonic (4-methyl) Phenyl-  
hydrazo-Pentane-2,4-dione**

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**Summary:** The dissociation constants for 2-, 3-, 4- and 2-sulphonic (4-methyl) phenylhydrazo acetylacetonate ligands, as well as the stability constants for chelates of these ligands with divalent metal ions Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II), have been calculated pH-metrically. The first dissociation constant for SO<sub>3</sub>H group was found to be strong. The difference between the values of both  $pK_1$  and  $pK_2$  for the various ligands were found to be small. The stability constants for chelates containing 1:1 and 2:1 ratio have been calculated and compared with the stability constants of acetylacetonate itself. These differences may be attributed to the lower basicity of the sulfonated ligands and to the different nature of the ligands. The relation between  $1/2 \log B$  (overall stability constant) of the chelate compounds and both electronegativity ( $X_m$ ) and second ionization potential (2nd Ip) was discussed.

## Introduction

The  $\beta$ -diketones are well known as chelating agents as are many azo compounds [1]. The stability constants of several complexes of  $\beta$ -diketones with transition metals were reported [2]. However the combination between these two classes of complexing compounds form new interesting compounds, which act as very good tridentate ligands. Recently some of these compounds such as phenyl-azo-acetylacetonate and its o-, m-, and p-carboxy derivatives [3a] were prepared and used as complexing agents for some transition metals. The spectroscopic [3b] and polarographic behaviours of such ligands were also investigated.

In the present investigation the dissociation constants of the organic ligands as well as the stability constants of the metal ions Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II) are calculated. The relationship between the overall stability constants and both electronegativity and second ionization potential are also shown.

## Experimental

The organic ligands used in this work were synthesized by coupling the diazonium salt of 2-, 3-, 4- and 2-sulphonic (4-methyl) aniline with acetylacetonate in presence of sodium acetate [4]. The yellow crude material

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Table-1: Elemental analysis of the sodium salt of organic ligands

Formula	Found				Calculated				Ref.
	C	H	N	S	C	H	N	S	
2-SPHA $C_{11}H_{11}N_2O_5Na$	43.43	3.6	9.25	10.6	43.14	3.60	9.15	10.45	-
3-SPHA $C_{11}H_{11}N_2O_5Na \cdot H_2O$	40.59	3.79	8.80	10.5	40.74	4.10	8.64	10.45	5
4-SPHA $C_{11}H_{11}N_2O_5Na \cdot H_2O$	40.40	4.10	8.70	10.6	40.74	4.10	8.64	10.45	5
5-S(4-Mc)PHA $C_{12}H_{13}N_2O_5Na \cdot H_2O$	43.00	4.3	8.39	10.1	42.60	4.43	8.28	9.47	5

was crystallized several times in methanol or ethanol. The solid organic ligand was found to be the sodium salt of the acid [5] Table 1. An aliquot portion of sodium salt was passed on to a column containing strong acidic cation exchanger resin (Merck) to separate the acid from the ligand. The concentration of the metal ion was determined by titration with standard EDTA, using the suitable indicator [6]. The standard potassium hydroxide solution was prepared from the solid hydroxide (Merck) in carbon dioxide free bidistilled water [6]. The pH-metric titrations were carried out at  $30^\circ + 0.2^\circ \text{C}$  and constant ionic strength 0.1 M as mentioned previously [7]. Conductivity water was used in all measurements of conductance by conductance bridge model RC-16 & 2, RC-21 6B2 Beckman instruments.

The dissociation constants of the ligands were calculated as mentioned previously [7]. In pH-metric regions below 4.0 and above 10.0, the corrected values of  $[H^+]$  and  $[OH^-]$  were calculated in order to refine the results [8]. Also the hydrogen ion activity was calculated from hydrogen ion concentration. The stability constants of the chelate compounds were calculated as mentioned before [7].

## Results and Discussion

During the pH-metric titrations of 1:1 and 2:1 ligand to metal, (Fig. 1 represents titration curves of Ni(II) organic ligand mixture as an example), a steep inflection appeared in the titration curve at  $m$  values equal to one and two ( $m$  = moles of base added per mole of metal ion) which may be due to the formation of 1:1 and 2:1 complexes. Buffer zones in the titration curves also appeared at  $m = 1-2$  in case of 1:1 and at  $m = 2-4$  in case of 2:1 titration. These buffer zones may be attributed to the formation of hydroxo-complexes. The formation of metal hydroxide, is excluded due to the fact that metal hydroxide is not formed at pH less than 8.00 under that condition. (Fig. 1 curve 5).

Various conductometric titrations of ligands in the presence and in the absence of metal ions including 1:1, 2:1, 3:1 ligand to metal ratios using 0.04 M. KOH as a titrant are illustrated in Fig.2. The titration curve of 1:1 ratio showed a broken line at  $m = 2$  in case of Cu(II), which agrees with the inflection at  $m = 2$  in pH-metric titration. The other divalent ions showed a broken line at  $m = 1$ , confirming the pH-metric results. Also a

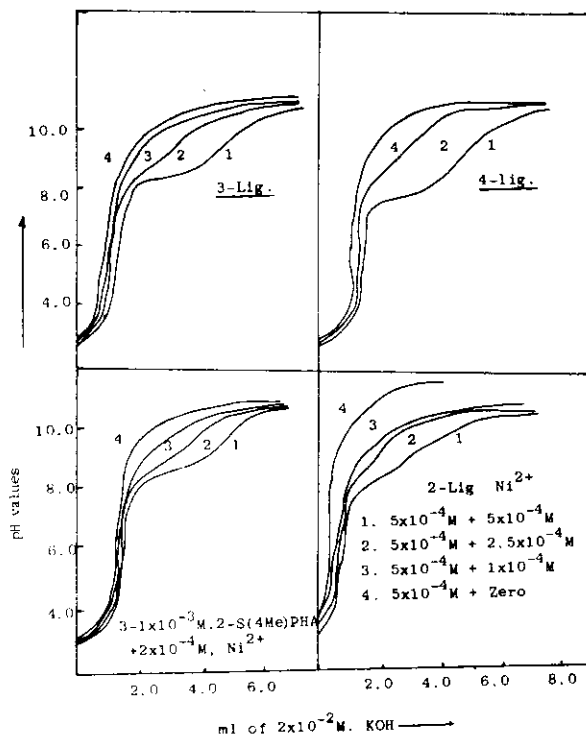


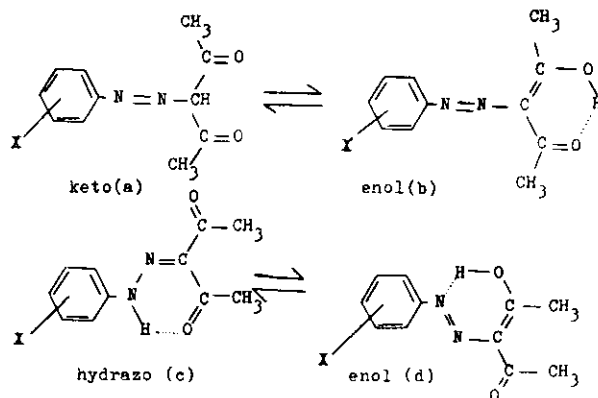
Fig.1: pH-metric titrations of 30 ml. mixture of 2-,3-,4-,2-S(4-Me)PHA ligands and Nickel ion at 30°C: [Lig.] [Ni<sup>2+</sup>] [Lig] [Ni<sup>2+</sup>]

1.  $1.0 \times 10^{-3}$  M +  $1.0 \times 10^{-3}$  M.  $3.1.0 \times 10^{-3}$  +  $1.0 \times 10^{-4}$  M
2.  $1.0 \times 10^{-3}$  M +  $0.5 \times 10^{-3}$  M  $4.1.) \times 10^{-3}$  + Zero

buffer zone was obtained at  $m = 1-2$ , indicating the presence of hydroxo complex. Further more, the titration of 2:1 and 3:1 ligand to metal ratio gives a break at  $m = 2$ , confirming that 2:1 ratio is the higher complex formed.

Moreover the solid complexes of both 4-SPHA and 2-S (4-Me) PHA ligands with divalent metal ions Cu, Ni, Co, Mn, and Cd are investigated. The elemental analysis and i.r. spectra of the solid complexes confirmed 2:1 composition of the complexes [5]. The structural formula of the organic ligands were investigated previously [3b,5,9]. The organic ligands may

have the following general tautomeric structure representing the keto, enol and hydrazo forms:



The hydrazo structure, in which hydrogen is bonded to one of the carbonyl groups of acetylacetone is the more stable form. It is confirmed by polarography [10] and spectroscopy [3b,9,11].

The slight differences in values of  $pK_2$ , Table 2, of the studied ligands (7c) may be due to the different position occupied by  $-SO_3H$  group. The  $pK_1$  for the ligands are highly acidic due to the strong dissociation of  $-SO_3H$  group. The slight increase in acidity value of ortho-derivative (2-SPHA) is attributed to the inductive and resonance effects. However the para-derivative (4-SPHA) is the weakest since  $-SO_3H$  group shows more resonance with azo group. The difference between  $pK_1$  values for 2- and 2- S(4-Me) PHA arises from the presence of methyl group which act as electron repelling one (7c).

The ligands used in the present study have the same end groups of  $\beta$ -diketone and differing in the position of sulphonic group. The stability constants of the formed complexes between transition metals and these ligands are summarized in

Table-2: Ionization constants of 2-, 3-, 4- and 2-S (4-Me)PHA ligands at constant ionic strength 0.1 M and at T = 30°C (7c).

Ionization constant	Organic ligands			
	2-SPHA	3-SPHA	4-SPHA	2-S(4Me)PHA
PK <sub>1</sub>	2.14±0.01	2.22±0.01	2.50±0.02	2.40±0.02
PK <sub>2</sub>	10.96±0.02	10.60±0.02	10.70±0.02	11.00±0.01

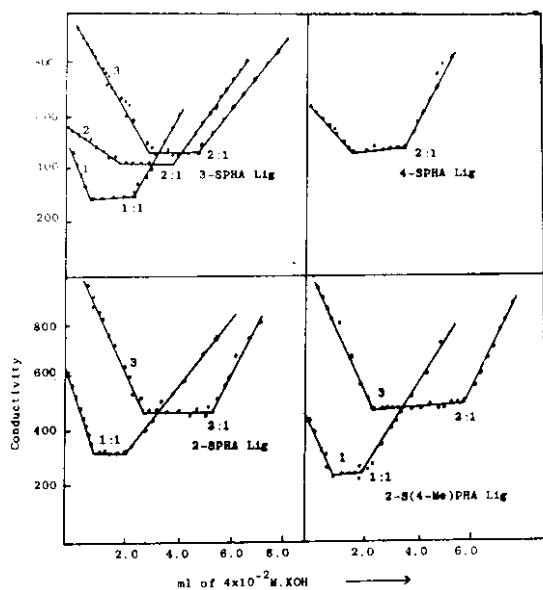


Fig.2: Conductometric titrations of 40 ml of mixture ligands and Ni<sup>2+</sup> ion using 4x10<sup>-2</sup> M. KOH as titrant:

- [Ligand] 1x10<sup>-3</sup> M. + [Ni<sup>2+</sup>] 1x10<sup>-3</sup> M.
- [Ligand] 2x10<sup>-3</sup> M. + [Ni<sup>2+</sup>] 1x10<sup>-3</sup> M.
- [Ligand] 3x10<sup>-3</sup> M. + [Ni<sup>2+</sup>] 1x10<sup>-3</sup> M.

Table 3. The stabilities of metal complexes increased in the order 4-SPHA < 3-SPHA < 2-S(4Me)PHA < 2-SPHA ligand. This is due to the shift of the sulphonic group from 4 to 2 position in phenyl ring. On the other hand, the presence of methyl group in 2-S (4-Me)PHA ligand causes a decrease in the stability compared with 2-SPHA, which can be attributed to

the electron repelling effect of methyl group.

As a general trend, the chelate stability of divalent metal ions and the studied sulphonated ligands can be arranged in the following order Cu > Ni > Zn > Co > Mn Cd. This order

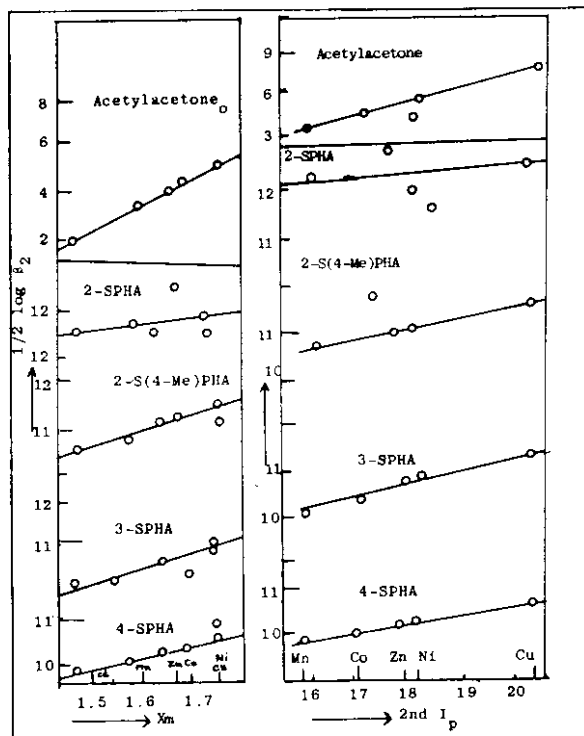


Fig.3: Plot of  $1/2 \log K_2$  for several bivalent metal ions with 2-, 3-, 4- and 2-S(4-Me)PHA vs. the electronegativity ( $\chi_m$ ) and second ionization potential ( $2nd I_p$ ) of the respective metal ion at 30°C.

Table-3:  $\log \beta$  (overall stability) values of the complexes of divalent metal ions with sulphonic organic ligands at  $\mu = 0.1$  and  $T=30^\circ\text{C}$ .

metal ion	$\log \beta$ (overall stability)				Ac Ac[14]
	4-SPHA	3-SPHA	2-S(4-Me)PHA	2-SPHA	
Cu(II)	21.47+0.01	22.01+0.08	22.80+0.06	23.83+0.03	15.16
Ni(II)	21.02+0.02	21.87+0.04	22.41+0.07	23.50+0.05	10.77
Co(II)	20.38+0.02	20.80+0.02	22.04+0.03	-	9.57
Zn(II)	20.68+0.03	21.79+0.04	22.41+0.02	23.28+0.04	9.02
Mn(II)	20.21+0.02	20.62+0.03	21.92+0.04	23.84+0.05	7.35
Cd(II)	19.84+0.05	20.21+0.02	21.40+0.05	23.25+0.03	6.72

is in good agreement with that obtained previously in literature [13]. Also the order of stability of the studied complexes is the same order of stability for metal acetylacetonate [14] complexes.

The Zn(II) and Cd(II) chelates are observed to have about the same order of stability and one cannot predict with certainty which will be more stable with particular ligand. The order with acetylacetonate is  $\text{Zn} > \text{Cd}$ , but Irving [13] reports that salicylaldehyde complex of Cd(II) is more stable. A possible explanation for this lack of predictability lies in the fact that two opposing effects are present. In going from Zn(II) to Cd(II) the ionic radius increases by  $0.2^\circ\text{A}$ , and therefore Zn(II) to be more stable, while the atomic number has increased by 18 units in Cd(II) the latter effect was result in a more stable Cd (II) complex. Apparently these two opposing effects are so balanced that compounds of similar stability result in

most instances. In the present study the order of stability is  $\text{Zn(II)} > \text{Cd(II)}$  which is in agreement with acetylacetonate complexes [14].

Mellor et al. [15] have stated that the hydrated cations are obtained only with highly electronegative donor atoms (oxygen, nitrogen). The IR spectra of the solid complexes showed the sharing of nitrogen of azo group in chelation process [3b,5] in the form of hydrazo structure.

In Fig 3, the electronegativities ( $x_m$ ) and second ionization potentials (2nd Ip) of metal ions were plotted against  $1/2 \log \beta$  (overall stability of complexes). Straight lines are obtained for all the cases. From this figure, the stability decreases in the following order:  $\text{Cu} > \text{Ni} > \text{Zn} > \text{Co} > \text{Mn} > \text{Cd}$ . This trend indicates that the stability of chelate compounds increases with the increase of electronegativity of metal ion. Since the electronegativity

of oxygen is 3.5 according to Pauling [16] scale, while the values for majority of metal ions were much lower the covalent character of the bonds between metal ions and chelating agents which coordinate through oxygen, also increases with the metal ion electronegativity.

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