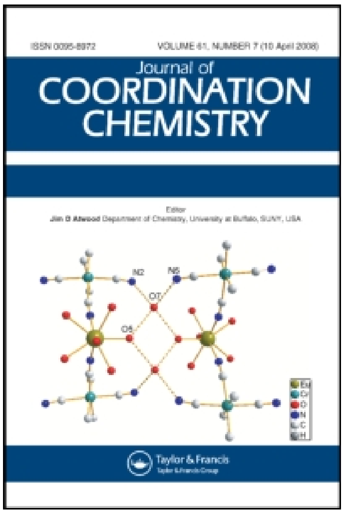

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Kumari, Madhu and Narain, L.(1982) 'EQUILIBRIA OF COMPLEXATION OF Cd(II), Co(II), Cu(II), Mn(II), Ni(II), AND Pb(II) WITH SULPHADIAZENE', Journal of Coordination Chemistry, 12: 1, 49 — 52

To link to this Article: DOI: 10.1080/00958978208075841

URL: http://dx.doi.org/10.1080/00958978208075841

J. Coord. Chem., 1982, Vol. 12, pp. 49–52
0095-8972/82/1201-0049$06.50/0

EQUILIBRIA OF COMPLEXATION OF Cd(II), Co(II), Cu(II), Mn(II), Ni(II), AND Pb(II) WITH SULPHADIAZENE

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(*Received December 12, 1981*)

pH-Metric studies of the Coordination complexes of sulphadiazene with Cd(II), Co(II), Cu(II), Mn(II), Ni(II) and Pb(II) have been made. The acid dissociation constant of sulphadiazene and the stability constants of the chelates have been determined. The thermodynamic parameters of the complexes have been calculated.

INTRODUCTION

Since sulpha drugs are amongst the very important and potent synthetic bacteriostatic compounds, studies of their metal chelates have much physiological relevance. The first studies on the complexation of sulpha drugs with metal ions were conductometric and spectrophotometric.[1–4] The metal chelates of sulpha drugs have been found to be more potent bacteriostatic than the drugs themselves.[5,6] Some pH-metric studies on related compounds have also been reported.[7] Some pH-metric and polarographic studies on the metal ion complexes of Sulphadiazene, Sulphathiazole and Sulphacetamide have already been reported from this laboratory.[8–11] The present communication described the pH-metric studies on the complexes of sulphadiazene with Cd(II), Co(II), Cu(II), Mn(II), Ni(II), and Pb(II).

EXPERIMENTS AND RESULTS

Studies were made on a Philips pH-meter (pR-9405). Metal nitrate solutions were prepared and standardised by the usual methods. From the point of view of the solubility of Sulphadiazene the systems were maintained in 65% aqueous Dimethyl Sulphoxide. The necessary ionic strength was maintained with KNO_3.

Determination of the Practical Acid Dissociation Constant of the Ligand (SDZ)

Structurally SDZ is a monobasic acid. In order to calculate the stability constants of the metal chelates, it is essential to have the prior knowledge of the practical acid dissociation constant of the ligand. It was determined by Bjerrum pH-metric titration.[12] 10 ml solution containing SDZ (0.0067 M) and KNO_3 (0.1 M) in 65% aqueous DMSO was titrated with 0.01 M KOH in 65% aqueous DMSO. $\bar{n}_H$ values were calculated and plotted against pH. $\log K_H$ was determined as being the value of pH corresponding to $\bar{n}_H = 0.5$.

Determination of the Stability Constants of the Complexes

These were also determined by Bjerrum method.[12] The following two solutions were subjected to pH-metric titration with 0.01 M KOH in 65% aqueous DMSO.

TABLE I

$\log K_{H}^{25^\circ} = 8.37 \qquad \log K_{H}^{30^\circ} = 8.16$

		Bjerrum method			Fonnin and Majorova method				
System	Temperature	$\log k_1$ ($= \log \beta_1$)	$\log K_2$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$	$-\Delta G$ K.Cal/Mole	$-\Delta H$ K.Cal/Mole	$-\Delta S$ Cal./deg./Mole
Cd-SDZ	25°	3.82	2.64	6.46	3.65	6.77	9.10	119.00	368.8
	30°	3.24	2.01	5.25	3.44	5.45	7.20		
Co-SDZ	25°	2.99	1.38	4.37	3.38	4.48	5.90	89.25	279.5
	30°	2.42	0.90	3.32	2.66	3.92	4.60		
Cu-SDZ	25°	4.51	3.55	8.06	4.41	8.57	11.0	115.30	349.9
	30°	4.01	2.71	6.72	3.84	6.76	9.3		
Mn-SDZ	25°	3.51	2.49	6.00	3.45	6.28	8.2	110.32	342.8
	30°	3.30	1.90	5.23	3.65	5.57	6.4		
Ni-SDZ	25°	3.75	2.67	6.42	3.81	6.71	8.7	62.80	181.5
	30°	3.35	2.33	5.68	3.39	5.83	7.8		
Pb-SDZ	25°	3.63	3.09	6.72	3.65	6.46	9.1	49.60	135.8
	30°	3.35	2.74	6.09	3.15	5.63	8.4		

Solution 1 10 ml solution containing HNO_3 (0.004 M), SDZ (0.0067 M), and KNO_3 (0.1 M) in 65% aqueous DMSO.

Solution 2 10 ml solution containing HNO_3 (0.004 M), SDZ (0.0067 M), metal ion (0.0015 M) and KNO_3 (0.1 M) in 65% aqueous DMSO.

The titration curves drawn from the above data indicates that more protons are liberated when the metal ion is added to the ligand. The excess protons correspond to the complex formed. Consequently at a particular pH, the concentration of the ligand complexed with the metal ion was calculated from the difference in alkali consumed at that pH in the two titrations. Therefrom were calculated the values of $\bar{n}$. The free ligand concentration '*a*' at any pH was calculated with the help of pK_H determined above.

The stability constants of the chelates were then determined with the help of the formation curves obtained by plotting $\bar{n}$ against *pa*.

The data $\bar{n}/a$ were also subjected to Fonnin and Majorova[13] treatment. β_1 was obtained at intercept of the plot $G_l = \bar{n}/a$ against '*a*' intercept of the plot $G_2 = (G_l - \beta_1)/a$ against '*a*' gave the value $2\beta_2 - \beta_1$, whence β_2 was determined. Thermodynamic parameters have also been calculated.

The results of the determination of the practical acid dissociation constant of the ligands are given in Table I and plotted in Figure 1. The formation curves of the complexes are also given in the figure and the stability constants of the complexes determined therefrom are recorded in the table. Thermo-dynamic parameters are also given in the table.

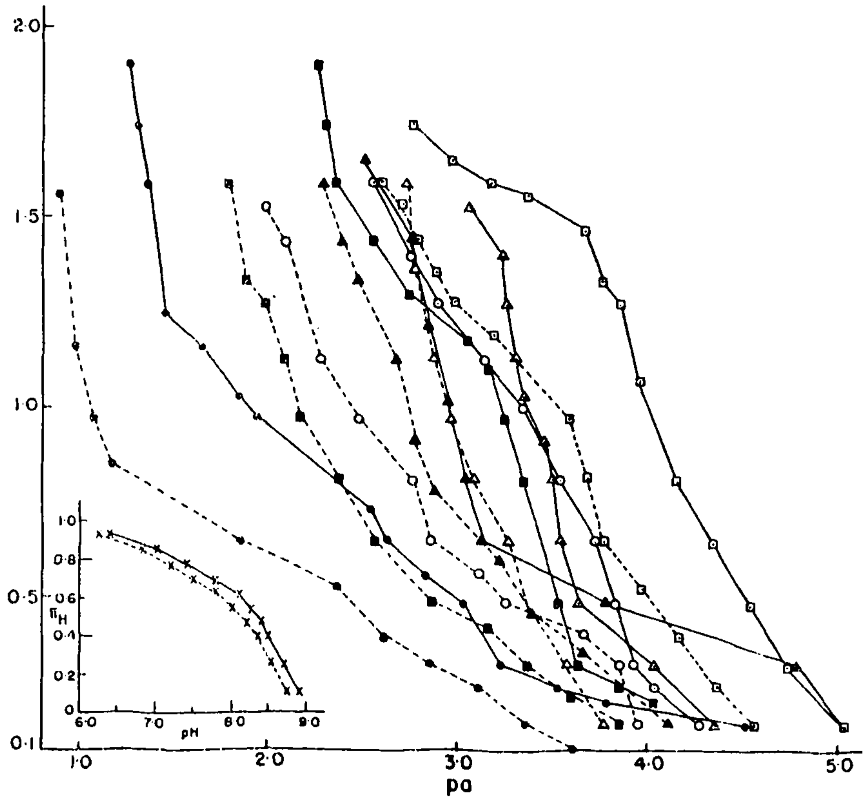
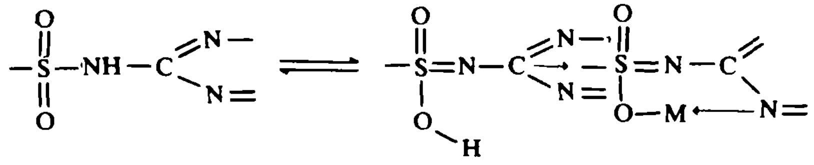


FIGURE 1 Formation curves for the complexes of sulphadiazene. ×, Protonation; ○, Cd(II); ●, Co(II); □, Cu(II); ■, Mn(II); ▲, Ni(II); △, Pb(II); ———, 25°; ------, 30°.

DISCUSSION

The chelating ability of sulpha drugs arises from the acidic hydrogen on the sulfonamide nitrogen and a geometrically suitably placed electron donor atom on the substituent of this nitrogen

Ghosh and Majumdar[14-16] have studied sulphonyl glycin as a complexing agent for metal ions. They have shown that the amide hydrogen becomes more acidic on the formation of metal nitrogen bond but in sulpha drugs the driving force of the deprotonation of the sulphonamide hydrogen may not be the formation of metal and amide-nitrogen bond. Geometrically the metal and amide-nitrogen bond formation is prohibitive in sulpha drugs, since in that case the chelate ring will be stained. Chelation is, therefore, achieved by a tautometric shift of the sulphonamide hydrogen to the sulphonyl oxygen. This alone can explain the chelating ability of sulphonamides when six membered stainless chelate rings are formed.



This is in conformity with Lee[13] infrared studies on copper sulpha drug complexes. He observed a shift of S=O absorption band from 7.62 μ in the sulphonamide to 7.79 μ in the chelate also the C-N vibration at 7.35 μ of the $C-NH-SO_2-$ group is raised to higher energy level, showing that the band becomes parts of a rigid ring (chelate) structure.

ACKNOWLEDGEMENT

The authors are very much indebted to the authorities of M.S.J. College, Bharatpur for providing necessary facilities to work. One of the authors (M.K.) also thanks the U.G.C. for the grant of a J.R.F. to her.

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