

Determination of Stability Constants of $UO_2(II)$ Complexes With Thio Compounds By pH Metry

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The proton-ligand dissociation constant, $\log K_L$ of sodium pentamethylene dithiocarbamate (Pipdte), diethyl dithiocarbamate (Dedte), ammonium pyrrolidine dithiocarbamate (Apdte) and potassium ethyl xanthate (Xanthate) and metal-ligand stability constants $\log K_1$ and $\log K_2$ of their metal complexes with $UO_2(II)$ have been determined in 60% ethanol-water medium at 28°C using Bjerrum Calvin pH titration technique as modified by Irving and Rosotti. The results obtained are compared with the data obtained for the other metal complexes of these ligands studied earlier in these laboratories. It was found that the proton ligand dissociation constants of these structurally similar thio compound and stability constants of their metal complexes decrease in the following order:



INTRODUCTION

The present study is in continuation of our earlier work¹ in these laboratories on proton-ligand dissociation constant, $\log K_L$ of structurally similar thio compounds [sodium pentamethylene dithiocarbamate (Pipdte), diethyl dithiocarbamate (Dedte), ammonium pyrrolidine dithiocarbamate (Apdte) and potassium ethyl xanthate (Xanthate)] stability constants $\log K_1$ and $\log K_2$ of their metal complexes, Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) and catalytic activity² of these ligands with Cr(VI) complexes, From the results (Table 1) it is observed that the dissociation constant of these ligands, stability constants of their metal complexes and catalytic activity are interrelated. As the dissociation constant of these ligands decreases the stability constants and catalytic activity of the corresponding ligand-metal complexes also decrease, The experimental results show that the dissociation constants of the structurally similar thio compounds, stability constants and catalytic activity of their metal complexes decrease in the order of Pipdte > Dedte > Apdte > Xanthate.

An attempt has been made to study the $UO_2(II)$ complexes with the same ligands in order to check the validity of the order obtained

with the complexes already reported¹ in 60% ethanol-water medium at $28^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and 0.05 M (KNO_3) ionic strength. Studies were carried out using Bjerrum-Calvin pH metric method^{3,4} as modified by Irving and Rosotti⁵.

TABLE 1
DISSOCIATION CONSTANTS / STABILITY CONSTANTS / CATALYTIC
ACTIVITY OF STRUCTURALLY SIMILAR THIO COMPOUNDS AND
THEIR METAL COMPLEXES

Name of the ligand	Pipdte	Dedtc	Apdte	Xanthate
1. Dissociation Constant	9.9	9.0	7.5	7.5
2. Stability Constant				
Mn(II)	4.9	4.2	2.1	1.2
Fe(II)	14.0	5.5	2.4	1.9
Co(II)	16.9	8.3	3.5	2.1
Ni(II)	17.8	13.2	6.8	3.4
Cu(II)	19.4	13.7	8.7	4.3
Zn(II)	16.3	10.8	5.5	4.0
3. Catalytic activity				
Cr(VI)	29.0	25.0	20.5	17.0

EXPERIMENTAL

The ligands, Pipdte and Xanthate were prepared by well established methods as reported in the literature^{6,7} Apdte and Dedtc were obtained from S.D. Fine Chem. Pvt. Ltd., Bombay and Loba Chemie Indo Australal Co., Bombay, respectively. The solutions were prepared in double distilled water and ethanol. The solutions of metal ions (0.001 M) and sodium hydroxide (0.1M) were prepared from Glaxo (AnalaR) sample of the salts in CO_2 -free double distilled water and standardised by appropriate methods.

pH measurements were carried out with an Elico (LI-120) digital pH meter. The experimental procedure and the calculations involved were described in our earlier communication¹.

RESULTS AND DISCUSSION

From the formation curves of the proton ligand systems constructed

by plotting $\bar{n}A$ values against pH the dissociation constants of the ligand were obtained as 9.9, 9.0, 7.5 and 7.5 for the ligands Pipdte, Dedtc, Apdte and Xanthate, respectively. Metal-ligand formation constants of the $UO_2(II)$ complexes with these ligands were obtained by applying least square method⁵ to the \bar{n} , P_L data (Table 2).

TABLE 2.
STABILITY CONSTANTS OF $UO_2(II)$ COMPLEXES WITH
THIO COMPOUNDS

S. No.	Thio Compound	log K_1	log K_2	log β_2
1.	Sodium Pentamethylene dithiocarbamate, [Na (Pipdte)]	11.9	10.8	22.7
2.	Diethyl dithiocarbamate, [Dedtc]	9.0	5.7	14.7
3.	Ammonium pyrrolidine dithiocarbamate, [Apdte]	7.4	5.3	12.7
4.	Potassium ethyl Xanthate, [Xanthate]	3.9	3.0	6.9

The results obtained for $UO_2(II)$ complexes with these ligands (Table 2) show that the difference between log K_1 and log K_2 values are small except with Dedtc and ratio of log K_1/K_2 is positive in all cases. Separation factors between first and second formation constants are well within the expected range and the absence of high values in Pipdte, Apdte and Xanthate Complexes indicates that there is little or no steric hindrance in the addition of second ligand molecule.

It is also evident from the data of log K_1 and log K_2 that there is equal tendency for the formation of both ML^+ and ML_2 complexes, whereas a large difference in log K_1 and log K_2 values in the case of $UO_2(II)$ -Dedtc complex indicates the stepwise formation of ML^+ and ML_2 complexes.

From the results in the Table 2 it can be concluded that the overall stability constants of $UO_2(II)$ complexes with structurally similar thio ligands decrease in the order of Pipdte > Dedtc > Apdte > Xanthate as it is observed with the other metal complexes.

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(Received: 7 June 1991; Accepted: 22 February 1992)

AJC-403

Boron Chemistry

**8th INTERNATIONAL MEETING ON BORON CHEMISTRY
(IMBERON—VIII)**

**11-15 July, 1993
TENNESSEE, U.S.A.**

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