

**References**

- ZOLUTUKHIN, V. K., GALANETS, Z. G. & GUBARENKO, V. K., *Zh. neorg. Khim.*, **16** (1971), 2655; *Chem. Abstr.*, **76** (1972), 287.
- PICKERING, W. F. & MILLER, J. W., *J. Proc. R. Soc. N.S.W. XCII* (1958), 73.
- CANNAN, R. K. & KIBRICK, A., *J. Am. chem. Soc.*, **60** (1938), 2314.
- PATNAIK, R. K. & PANI, S., *J. Indian chem. Soc.*, **34** (1957), 673.
- TRIPATHY, K. K. & PATNAIK, R. K., *Chem. Abstr.*, **80** (1974), 305.
- TRIPATHY, K. K. & PATNAIK, R. K., *Indian J. Chem.*, **5** (1967), 511.
- PATNAIK, R. K. & PANI, S., *Indian J. Chem.*, **6** (1968), 658.
- TRIPATHY, K. K. & PATNAIK, R. K., *J. inorg. nucl. Chem.*, **35** (1973), 1050.
- KOSTROMINA, N. A., *Russ. J. inorg. Chem.*, **5** (1960), 46, *Chem. Abstr.*, **55** (1961), 4230.

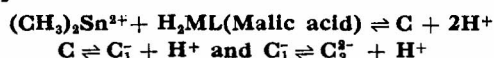
**Malate Complex of Dimethyltin**

NIRADA KUMARI MOHANTY &amp; R. K. PATNAIK

 Department of Chemistry, Regional Engineering College  
Rourkela 8

Received 12 November 1974; accepted 14 August 1975

**Dimethyltin reacts with malic acid at low pH forming a neutral complex which behaves as a dibasic acid and dissociates to complexes  $C_1^-$  and  $C_2^{2-}$  at higher pH range. The equilibrium constants of the reactions**

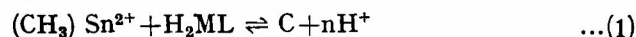


are found to be  $6.02 \times 10^{-7}$ ,  $1.606 \times 10^{-5}$  and  $1.55 \times 10^{-8}$  respectively by pH metric titrations.

**WE** report in this note the results of our studies on the malate complex of dimethyltin.

The ionic strength was kept constant in all the experiments at 0.1M by the addition of potassium chloride. Dimethyltin dichloride solution was prepared by dissolving a known amount of dimethyltin dichloride in a known amount of hydrochloric acid solution. The acid was neutralized by KOH after the addition of malate ligand. All the titrations were carried out under nitrogen atmosphere and at  $31^\circ \pm 0.5^\circ$ .

The number of protons liberated in the systems containing dimethyltin and malate in the ratios of 1:1.25 and 1:5 is the same indicating the formation of a 1:1 type of complex. The reaction between the dimethyltin ion and malic acid can be represented as



where  $H_2ML$  stands for malic acid and C denotes the dimethyltin malate complex. The charge on the complex C is not shown to avoid complexity in subject treatment. The equilibrium constant of the reaction can be evaluated from Eq. 2.

$$K = \frac{[C][H^+]^n}{[(CH_3)_2Sn^{2+}][H_2ML]} \quad \dots(2)$$

It can be shown on the basis of earlier studies on tartrate and citrate complexes of some metals<sup>1-5</sup>

that

$$\frac{\Delta[NaOH] - a/b\Delta[ML]}{[C]} = n - a/b \quad \dots(3)$$

where

$$a = \frac{k_1}{[H^+]} + \frac{2 \cdot k_1 k_2}{[H^+]^2}; \quad b = 1 + \frac{k_1}{[H^+]} + \frac{k_1 k_2}{[H^+]^2}$$

$k_1, k_2$  are the first and second dissociation constants of malic acid respectively. The values of  $k_1$  and  $k_2$  are  $5.5 \times 10^{-4}$  and  $2.1 \times 10^{-5}$  respectively. When the formation of the complex is complete,  $[C] = [(CH_3)_2SnCl_2]$ .

The values of  $\Delta[NaOH], -\Delta[ML], [(CH_3)_2SnCl_2]$  and then  $n$  were calculated at different pH values as done earlier. The values of  $n$  are found to be more than 2 and 3 at and above pH 4.0 and pH 6.6 respectively.  $[C]$  was calculated at pH less than 4.0 by Eq. 3, assuming the value of  $n$  to be 2. The values of  $K$  were calculated and are  $6.43 \times 10^{-7}$ ,  $6.03 \times 10^{-7}$ ,  $5.42 \times 10^{-7}$ ,  $6.23 \times 10^{-7}$  and  $5.98 \times 10^{-7}$  at pH 3.0, 3.1, 3.2, 3.3 and 3.4 respectively.

In the pH range 4.0-6.4,  $n$  is between 2 and 3. Hence, the neutral complex C dissociates according to Eq. 4.



It can be shown<sup>5</sup> that

$$K_1 = \frac{(n-2)[H^+]}{(3-n)} \quad \dots(5)$$

The values of equilibrium constant  $K_1$  calculated using Eq. 5 are  $1.06 \times 10^{-5}$ ,  $2.23 \times 10^{-5}$ ,  $2.01 \times 10^{-5}$ ,  $1.66 \times 10^{-5}$ ,  $1.50 \times 10^{-5}$  and  $1.68 \times 10^{-5}$  at pH 4.0, 4.4, 4.6, 4.8, 5.0 and 5.2 respectively. The mean value of  $K_1$  is  $1.606 \times 10^{-5}$ .

At higher pH (>6.6), the complex  $C_1^-$  dissociates to  $C_2^{2-}$  and  $H^+$  according to Eq. 6.



Similarly it can be shown that

$$K_2 = \frac{(n-3)[H^+]}{(4-n)} \quad \dots(7)$$

The values of  $K_2$  were calculated and are  $1.66 \times 10^{-8}$ ,  $1.21 \times 10^{-8}$ ,  $2.03 \times 10^{-8}$  and  $1.29 \times 10^{-8}$  at pH 6.6, 6.8, 7.8 and 8.0 respectively. Mean value of  $K_2$  thus obtained is  $1.55 \times 10^{-8}$ .

The amount of acid liberated is same in the system containing dimethyltin and sodium malate in the ratios of 1:1.25 and 1:5 indicating the formation of 1:1 complex. At pH values of 8.0, 8.5 and 9.0, in the titration of system containing dimethyltin and sodium malate in the ratio 1:5, the number of protons liberated per g atom of dimethyltin is 1.55, 1.6 and 1.7 respectively. In the titration of system containing dimethyltin and malic acid in the ratio 1:1.25, it is found that the complexes C and  $C_1^-$  exist in the pH range 3.8-6.4.

Therefore,  $[(CH_3)_2SnCl_2] = [C] + [C_1^-]$

It can be shown as before that

$$[ML] - [M] = x[HML^-] \quad \dots(8)$$

where

$$x = 1 + \frac{k_2}{[H^+]} + \frac{[H^+]}{k_1}$$

and

$$[C_1] = [\text{NaOH}] + Y[\text{HML}^-] + [\text{H}^+] \quad \dots(9)$$

where

$$Y = 1 + 2 \frac{[\text{H}^+]}{k_1}$$

$[\text{HML}_2]$  and  $[C_1]$  were calculated using Eqs. 8 and 9 respectively. Concentration of the complex C is obtained by subtracting  $[C_1]$  from  $[(\text{CH}_3)_2\text{SnCl}_2]$ .  $K_1$  was calculated according to Eq. 7 and the values are  $3.95 \times 10^{-5}$ ,  $1.35 \times 10^{-5}$  and  $1.01 \times 10^{-5}$  at pH 5.8, 5.9 and 6.0 respectively. The mean value of  $K_1$  thus obtained is  $2.1 \times 10^{-5}$ , which is in agreement with the value obtained earlier ( $1.606 \times 10^{-5}$ ).

In the pH range 6.4-9.0, both  $C_1^-$  and  $C_2^{2-}$  complexes exist as shown by the titration of system containing dimethyltin and malic acid in the ratio 1:1.25. Hence, it can be shown that<sup>2,3</sup>

$$[\text{ML}] = [(\text{CH}_3)_2\text{SnCl}_2] + x[\text{HML}^-] \quad \dots(10)$$

and

$$[C_2^{2-}] = [\text{NaOH}] + Y[\text{HML}^-] + [\text{H}^+] - [(\text{CH}_3)_2\text{SnCl}_2] \quad \dots(11)$$

$[\text{HML}^-]$  and  $[C_2^{2-}]$  were calculated using Eqs. 10 and 11 respectively.  $[C_1^-]$  was calculated by subtracting  $[C_2^{2-}]$  from the total metal concentration. The mean value of  $K_2$  thus obtained is  $1.98 \times 10^{-8}$  which is in close agreement with the value obtained earlier ( $1.55 \times 10^{-8}$ ).

Thanks are due to the Ministry of Education, Government of India, for the award of a scholarship to one of the authors (N.K.M.). The authors are thankful to BSIR, Orissa, also for giving financial assistance.

#### References

1. DAS, H. K., MOHAPATRA, G., MOHAPATRA, S., PATNAIK, R. K. & PANI, S., *Proceedings of the symposium on the chemistry of coordination compounds, Agra, Part III* (1959), 102.
2. TRIPATHY, K. K. & PATNAIK, R. K., *Indian J. Chem.*, **4** (1967), 511.
3. TRIPATHY, K. K. & PATNAIK, R. K., *J. inorg. nucl. Chem.*, **35** (1973), 1050.
4. TRIPATHY, K. K. & PATNAIK, R. K., *Acta chim. hung.*, **79** (1973), 279.
5. PATNAIK, R. K. & PANI, S., *J. Indian chem. Soc.*, **34** (1957), 675.

### Stability Constants of Zirconyl Chelates with Substituted Azobenzenes

P. T. JOSEPH & G. DEVADASAN

Industrial Research Laboratory, Trivandrum 19

Received 21 June 1975; accepted 14 August 1975

Synthesis of 3-formyl-4-hydroxy-3'-nitroazobenzene (FH3'NB) and 3-formyl-4-hydroxy-4'-nitroazobenzene (FH4'NB) and determination of their proton-ligand stability constants and metal-ligand stability constants of their ZrO(II) complexes have been studied in 60% (w/w) ethanol-water solution at  $28 \pm 0.1^\circ$  using Calvin-Bjerrum titration technique. It is found that FH3'NB has a stronger chelating tendency than FH4'NB but both of these are lesser chelating agents than 3-formyl-4-hydroxyazobenzene (FHB).

In this note we report the synthesis of 3-formyl-4-hydroxy-3'-nitroazobenzene (FH3'NB) and 3-formyl-4-hydroxy-4'-nitroazobenzene (FH4'NB) and the effect of nitro substituents on the stability of the chelates of these ligands with zirconium as determined by Calvin-Bjerrum potentiometric titration technique.

The ligands were synthesized from *m*-nitroaniline or *p*-nitroaniline and salicylaldehyde of AR grade according to a procedure similar to that reported earlier<sup>1</sup>. FH3'NB (Found: C, 57.25; H, 3.21; N, 15.42 reqd: C, 57.55; H, 3.32; N, 15.50%) and FH4'NB (Found: C, 57.34; H, 3.19; N, 15.38 reqd: C, 57.55; H, 3.32; N, 15.50%) are yellowish brown and reddish brown crystalline solids melting at  $156^\circ \pm 1.5^\circ$  and  $195^\circ \pm 1.5^\circ$  respectively. The molecular weights of FH3'NB and FH4'NB were found to be 271.9 and 272.5 respectively.

All the reagents used were of AR quality. Zirconyl chloride solution was prepared in doubly distilled water and standardized gravimetrically as mandelate.

A Systronic pH meter type 322 (accuracy  $\pm 0.05$  units) was used for pH measurements. Titrations were carried out in 60% (w/w) ethanol-water mixture at  $28^\circ \pm 0.1^\circ$ . Adequate amount of potassium nitrate solution (1M) was added to keep the ionic strength constant at 0.2M. Corrections in pH values were made according to the method of Bates<sup>2</sup>.

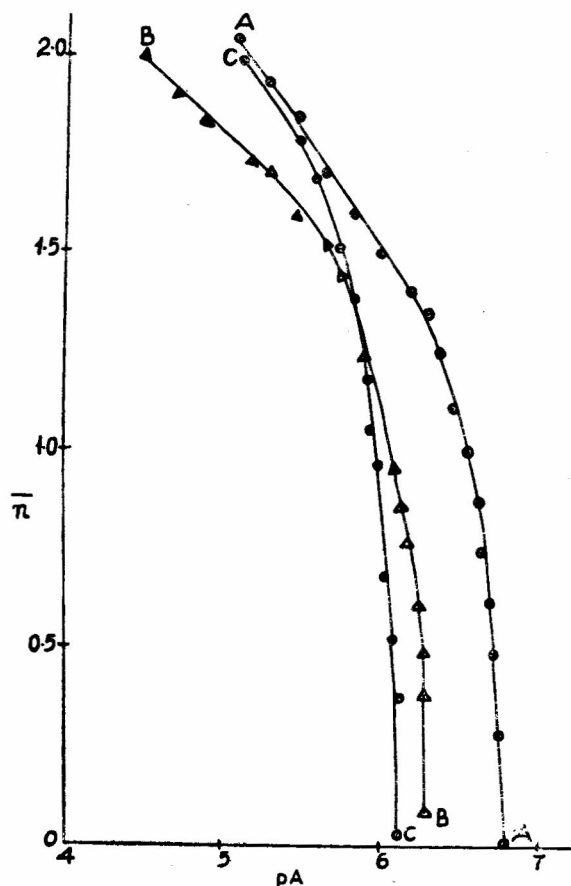


Fig. 1 — Formation curves of ZrO(II) complexes [A, ZrO(II) — FHB; B, ZrO(II) — FH3'NB; C, ZrO(II) — FH4'NB]