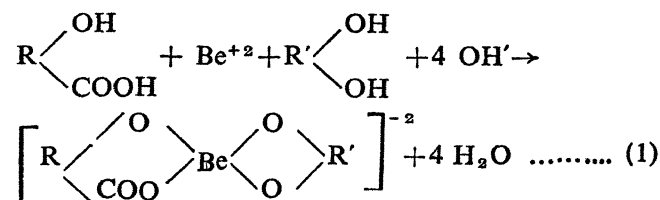


1 shows only one inflection at $m=1$ which is due to neutralisation of one of the two phenolic-OH groups

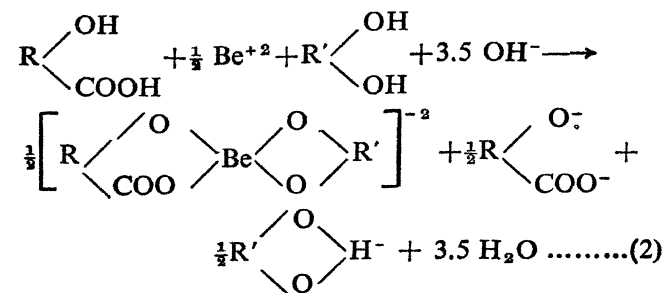
of CTA ($R' \begin{matrix} \text{OH} \\ \diagdown \\ \diagup \\ \text{OH} \end{matrix}$). The second phenolic -OH is not neutralised due to the formation of intramolecular H-bonding⁷. Curve 2 shows two inflections at $m=1$ and $m=2$ which indicate the neutralisation of -COOH and -OH groups of DNS ($R \begin{matrix} \text{OH} \\ \diagdown \\ \diagup \\ \text{COOH} \end{matrix}$).

When 1 : 1 mixture of these ligands is titrated against a standard alkali, two inflections at $m=1$ and $m=3$ (Curve 3) are observed which confirms the above neutralisation patterns. When equimolar concentration of Be is added to a 1 : 1 mixture of these ligands, an inflection at $m=4$ (Curve 4) is observed which reveals the formation of a 1 : 1 : 1 mixed anion salt as under



The formation of such a salt is confirmed by the observation that on titration with an alkali a 1 : 1 : $\frac{1}{2}$, DNS, CTA, Be mixture shows an inflection at $m=3.5$.

The reaction may be represented as follows :



The formation of this salt appears to justify the 4-fold coordination requirements of the sp^3 hybridised Be.

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References

1. D. D. PERRIN, I. G. SAYCO and V. S. SHARMA, *J. Chem. Soc.*, 1967, **11**, 1755.
2. P. R. SHUKLA and GOPAL NARAIN, *J. Indian Chem. Soc.*, 1967, **44**, 552.
3. G. K. CHATURVEDI and J. P. TANDON, *Zeit. Naturforsch.*, 1970, **25**, 26.
4. R. C. SHARMA, S. S. DHINDSA and D. N. BHARGAV, *Monatshefte für chemie*, 1978, **109**, 333.
5. S. S. DUBE and S. S. DHINDSA, *Z. Naturforsch.*, 1969, **246b**, 967.
6. R. C. MEHROTRA, V. D. GUPTA and C. K. SHARMA, *J. Indian Chem. Soc.*, 1973, **50**, 207.
7. R. WAKE, H. MIYATE and TOEIK, *Bull. Chem. Soc. Japan.*, 1968, **41**, 1452.

Stepwise Stability Constants and Thermodynamic Functions of Mn(II), Zn(II) and Cd(II) Complexes with 2-Hydroxy-5-chlorobenzophenone-*o*-tolil (HCBOT)

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In continuation of our previous communications^{2,3} herein, we describe potentiometric studies on chelates of 2-hydroxy-5-chlorobenzophenone-*o*-tolil (HCBOT) with Mn(II), Zn(II) and Cd(II) in 60% v/v dioxan water media at $\mu = 0.1M$ at 25°, 30° and 35°.

Experimental

The expanded scale pH meter of systronic with a wide range (0.01 pH glass electrode and a calomel reference electrode was used for pH measurements.

The ligand 2-hydroxy-5-chlorobenzophenone-*o*-tolil was synthesised by condensing 2-hydroxy-5-chlorobenzophenone with orthotoluidine. It was crystallised from alcohol, m.p. 157°-159°.

All the chemicals used were of B.D.H. AnalaR grade. The potentiometric titration was carried out in an inert atmosphere using carbonate free sodium hydroxide solution and the constant ionic strength was maintained by adding requisite amount of sodium perchlorate solution. The Calvin-Bjerrum pH titration technique^{4,5} as used by Irving and Rossotti¹ has been applied to determine the protonation constants of the ligand and the formation constants of complexes. The log K values were computed by various computational methods as summarised in Table 1.

NOTES

TABLE 1—STABILITY CONSTANTS ON Mn(II), Zn(II) AND Cd(II) CHELATES OF 2-HYDROXY-5-CHLOROBENZOPHENONE *o*-TOLIL AT $\mu = 0.1 M$ IN 60% v/v DIOXANE-WATER MEDIA

Chelates	Temp. °C.	Methods			
		least square	linear-plot	Bjerrum spreading factor method.	
(1)	(2)	(3)	(4)	(5)	
Mn(HCBoT) ₂	25	logK ₁	5.66	5.68	4.08
		logK ₂	4.20	4.13	4.08
		logβ	9.86	9.81	9.74
Mn(HCBoT) ₂	30	logK ₁	5.62	5.63	5.64
		logK ₂	4.04	4.06	4.06
		logβ	9.66	9.69	9.70
Mn(HCBoT) ₂	35	logK ₁	5.47	5.52	5.40
		logK ₂	3.97	3.90	3.98
		logβ	9.44	9.42	9.38
Zn(HCBoT) ₂	25	logK ₁	7.87	7.89	7.90
		logK ₂	5.36	5.37	5.36
		logβ	13.23	13.96	13.26
Zn(HCBoT) ₂	30	logK ₁	7.84	7.75	7.70
		logK ₂	5.21	5.13	5.20
		logβ	12.95	12.88	12.90
Zn(HCBoT) ₂	35	logK ₁	7.59	7.60	7.55
		logK ₂	5.17	5.20	5.25
		logβ	12.76	12.80	12.80
Cd(HCBoT) ₂	25	logK ₁	7.74	7.75	7.70
		logK ₂	5.30	5.27	5.34
		logβ	13.04	13.02	13.04
Cd(HCBoT) ₂	30	logK ₁	7.61	7.61	7.64
		logK ₂	5.15	5.11	5.10
		logβ	12.76	12.72	12.74
Cd(HCBoT) ₂	35	logK ₁	7.43	7.49	7.44
		logK ₂	5.07	5.03	5.08
		logβ	12.50	12.52	12.52
HCBoT	25	logP _{K₁H}	11.01	11.02	11.02
		logP _{K₂H}	3.73	3.73	3.73
		logP _{K₃H}	19.74	14.75	14.75
HCBoT	30	logP _{K₁H}	10.97	10.98	10.97
		logP _{K₂H}	3.68	3.70	3.69
		logP _{K₃H}	14.65	14.68	14.66
HCBoT	35	logP _{K₁H}	10.93	10.94	10.94
		logP _{K₂H}	3.64	3.66	3.65
		logP _{K₃H}	14.57	14.60	14.59

TABLE 2—THERMODYNAMIC PARAMETERS OF Mn(II), Zn(II) AND Cd(II) CHELATES OF 2-HYDROXY-5-CHLOROBENZOPHENONE *o*-TOLIL AT $\mu = 0.1 M$ IN 60% v/v DIOXANE-WATER

Chelate	Temp. °C.	*log β average	-ΔG K cal./mole	-ΔH K cal./mole	-ΔS (e.u.)
Mn(HCBoT) ₂	25	9.86	13.44	16.11	8.96
Mn(HCBoT) ₂	30	9.66	13.40	16.11	8.94
Mn(HCBoT) ₂	35	9.44	13.30	16.11	9.12
Zn(HCBoT) ₂	25	13.23	18.05	19.19	11.21
Zn(HCBoT) ₂	30	12.95	17.95	19.19	11.35
Zn(HCBoT) ₂	35	12.76	17.99	19.19	11.04
Cd(HCBoT) ₂	25	13.04	17.78	21.94	13.96
Cd(HCBoT) ₂	30	12.76	17.70	21.94	13.99
Cd(HCBoT) ₂	35	12.50	17.62	21.94	14.03

The values of the changes in free energy (ΔG) enthalpy (ΔH) and entropy (ΔS) accompanying the metal ligand complex forming reaction have been calculated at 25°, 30° and 35° using the relations—

$$\Delta G = -RT \ln K$$

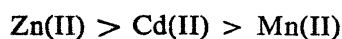
$$\frac{d \log K}{d(1/T)} = \frac{\Delta H}{4.57}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

they are summarised in Table 2.

It is concluded that with the change in temperature there was no appreciable change in the value of stability constants or which almost remain constant.

The order of stability constants of metal complexes as given below are in good agreement with Irving-Williams order



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References

1. H. IRVING and H. S. ROSSOTTI, *J. Chem. Soc.*, 1953, 3397.
2. Y. Z. PATHAK and G. B. JOSHI, *J. Inst. of Chemists (India)*, 1978, 50, 116.
3. Y. Z. PATHAK and J. B. JOSHI, *J. Indian Chem. Soc.*, 1979, 56, 210.
4. J. BJERRUM "Metal Ammine Formation in Aqueous Solution" P. HAASE and SONS, Copenhagen.
5. CALVIN and K. W. WILSON, *J. Amer. Chem. Soc.*, 1945, 67, 2003.
6. H. IRVING and R. J. P. WILLIAMS, *J. Chem. Soc.*, 1953, 3129.

Mixed Ligand Complexes of Ni(II) with Iminodiacetic Acid (IMDA) as Primary Ligand and Thioglycollic, Thiolactic, Thiomalic Acid and Corresponding Amino Acid as Secondary Ligands

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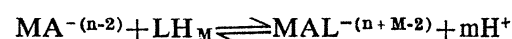
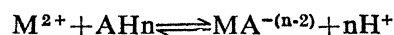
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BHATTACHARYA and co-workers¹⁻⁴ have investigated the mixed ligand system (MAL) involving

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bivalent metal ions like Cu²⁺, Ni²⁺, Zn²⁺ and Histidine. Iminodiacetic acid, nitrilo tri-acetic acid as primary ligands and polyhydroxy phenols or aminoacids as secondary ligands. Various mixed ligand complexes with IMDA⁵ as the primary ligand have been studied. In the present investigation attempt have been made to study the formation constants of the title systems.

IMDA is known to form 1 : 1 complex with Ni(II) at low pH and the complex is stable at higher pH, where the combination of secondary ligand starts. The reaction can be shown as follows :



$$K_{MAL} = \frac{(MAL)}{(MA)(L)}$$

Experimental

All the reagents used were of A. R. quality. Ni(II) perchlorates was prepared from the nickel carbonate and the metal content was determined and checked. All the solutions have been prepared in conductivity water.

Metrohm E 350 A pH meter (accuracy +0.05) was used and the titrations were carried out at 30°, using constant temperature bath (accuracy = 0.1°).

The nature of the curves can be interpreted as done in earlier publications⁶. In the secondary ligand two equivalent extra acid has been added, in order to account for the extra hydrogen ions liberated due to the combination of primary ligand IMDA. n⁻ and P^L can be calculated using same equation as in earlier cases⁷. Precise values of K_{MAL}^{MA} were obtained by using the method of averages⁸; and the values are presented in Table I.

Discussion

It is observed that in case of thioacids the values of mixed ligand formation constants K_{Ni IMDA L}^{Ni IMDA} are lower than K_{Ni L}^{Ni L}. This may be due to the charge repulsion between primary ligand and secondary ligand. In case of thiomalic acid the differences between K_{Ni L}^{Ni L} and K_{Ni IMDA L}^{Ni IMDA} is more because thiomalate ion has three negative charges and has a bigger size resulting in greater electrostatic repulsion.

In case of amino acids, the order of the formation constants of the reaction MA + L is same as in the binary M + L system. This can be explained in terms of their basicities of the secondary ligands⁹⁻¹⁰. However, the values of K_{Ni A L}^{Ni A} are significantly lower than the values of K_{Ni L}^{Ni L}. This can be explained to be due to the charge repulsion between the primary