

SOME METAL CHELATES OF *o*-MERCAPTOBENZOIC ACID

R. RAMAMANI AND SP. SHANMUGANATHAN

Department of Chemistry, Pachaiyappa's College, Madras-30

THE stepwise stability constants of the chelates of *o*-mercaptobenzoic acid with zinc (II), nickel (II), cobalt (II), iron (II), and manganese (II) have been determined in 45% (v/v) aqueous alcohol at 30°, 40° and 50° C. at an ionic strength of 0.15. The thermodynamic functions ΔF° , ΔH° and ΔS° have also been evaluated at these temperatures. The behaviour of iron (III) and copper (II) towards *o*-mercaptobenzoic acid has also been studied. This investigation was undertaken in order to obtain more information on the manner in which the mercaptide sulphur complexes with divalent metal ions and to make comparisons with the corresponding oxygen compounds. The Calvin¹-Bjerrum² potentiometric titration technique has been used to study the behaviour of Zn(II), Ni(II), Co(II), Fe(II) and Mn(II) with *o*-mercaptobenzoic acid. Previous work on the chelate stabilities of mercaptoacetic acid,³ β -mercaptopropionic acid,⁴ mercaptosuccinic acid,⁵ 6-mercaptapurine⁶ and thioxine⁷ have shown that the Zn(II) complex is more stable than the corresponding Ni(II) complex. In addition, these mercaptans tend to reduce Cu(II) to Cu(I). The present study reveals that *o*-mercaptobenzoic acid behaves in a similar manner towards these metal ions.

The general procedure employed for the determination of chelate formation constants was to titrate a mixture of the ligand and mineral acid to which sufficient sodium perchlorate had been added to maintain a constant ionic strength of 0.15 in the presence and absence of the metal, with standard sodium hydroxide solution and determine the pH of the solution after each addition. The ratio of the ligand to metal was varied from 1:1 to 1:6. All solutions were titrated in an atmosphere of nitrogen. All metals were added as perchlorates. *o*-Mercaptobenzoic acid (Evans Chemetics product) was purified as described by Allen and Mackay.⁸ Aqueous alcohol (45% v/v) has been used for all titrations. The ionisation constant of the mercapto group of *o*-mercaptobenzoic acid was determined spectrophotometrically and that of the carboxyl group potentiometrically using the same ionic strength. Values of the formation function \bar{n} and the negative log of the free ligand concentration pL and log K have been calculated

using the method of Bjerrum² as modified by Calvin and Wilson,¹ and the free energy of complex formation from $\Delta F^\circ = -RT \ln K$, the ligational enthalpy from

$$\Delta H^\circ = \frac{2.303 RT_1 T_2 (\log K_2 - \log K_1)}{(T_2 - T_1)}$$

and entropy from

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T}$$

The titration curves in the presence of metal ions reveal the overall stoichiometry of the reactions between these ions and *o*-mercaptobenzoic acid. The titration curves of *o*-mercaptobenzoic acid in the presence of metal ions correspond to a stoichiometry of 1:1 and 2:1 *o*-mercaptobenzoic acid to metal. Conductometric studies also indicate the presence of these two chelates. Ni(II) forms dark violet, Zn(II) colourless, Mn(II) yellowish-brown, Co(II) dark-brown, Fe(II) green, and Fe(II) blue chelates. Table I gives the stepwise formation constants log K_1 and log K_2 for these five metals at 30°, 40° and 50° C. together with ΔF° , ΔH° and ΔS° values at these three temperatures. From the values given in Table I it is seen that the stabilities of the complexes conform to the Irving-Williams Series⁹ Mn < Fe < Co < Ni < Zn. Log K_1 for *o*-mercaptobenzoic acid chelates is greater than the corresponding values for salicylic¹⁰ and anthranilic¹¹ acids. In this connection it is noteworthy that Sidgwick¹² has compared the relative donor properties of oxygen and sulphur and showed that, in general, the donor properties of sulphur are dependent, to a larger extent, on the acceptor properties of the metal. On the other hand, according to Sidgwick, oxygen and nitrogen may be considered quite similar with respect to their tendency to complex with metal ions. Therefore, it is not surprising that the *o*-mercaptobenzoic acid Zn(II)-chelate is more stable than the salicylic acid and anthranilic acid Zn(II)-chelates, nor is the fact that there is a reversal in the order of stabilities between the corresponding Ni(II) and Zn(II)-chelates of mercapto and aminobenzoic acids, since Zn(II) would appear to accept sulphur as the donor atom more readily than would nitrogen. It is suggested that this may be attributed to a steric effect, since the sulphur atom is bigger than the nitrogen atom.

TABLE I

Temperature ° C.	Zn (II)	Ni (II)	Co (II)	Fe (II)	Mn (II)
			$\log K_1^\circ$		
30	8.4483	7.0792	6.0264	5.4533	5.0438
40	8.5990	7.3435	6.1951	5.5697	5.1458
50	8.8389	7.6439	6.3475	5.7158	5.2774
			ΔF_1° (Kcal./mole)		
30	-11.71	-9.817	-8.356	-7.561	-6.993
40	-12.32	-10.52	-8.876	-7.980	-7.372
50	-13.07	-11.30	-9.385	-8.450	-7.802
			ΔH_1° (Kcal./mole)		
30-40	6.540	11.48	7.321	5.053	4.427
40-50	11.10	13.90	7.050	6.761	6.088
			ΔS_1° (cal./mole-deg)		
30	60.24	70.31	51.75	41.62	37.70
40	67.55	75.61	51.33	44.39	40.35
50	74.82	78.02	50.90	47.09	42.99
			$\log K_2$		
30	5.9932	4.4559	4.4354	4.4092	4.0531
40	6.2035	4.6404	4.5509	4.4812	4.1845
50	6.2845	4.8032	4.6974	4.6218	4.2800
			ΔF_2° (Kcal./mole)		
30	-8.310	-6.1800	-6.151	-6.115	-5.622
40	-8.888	-6.6460	-6.519	-6.419	-5.995
50	-9.439	-7.101	-6.945	-6.832	-6.327
			ΔH_2° (Kcal./mole)		
30-40	9.126	8.007	4.969	3.125	5.675
40-50	8.389	7.532	6.779	6.504	4.419
			ΔS_2° (cal./mole-deg.)		
30	57.55	46.82	36.70	30.50	37.30
40	56.37	46.05	39.60	35.89	35.27
50	55.20	45.30	42.47	41.30	33.29

The stability constants of the Ni(II)-chelates are consistent with the values reported¹³ already in 50% aqueous dioxane. Nigam and co-workers¹⁴ have reported $\log K_1 = 9.1$ and $\log K_2 = 11.2$ for the Zn(II)-chelate and $\log K_3 = 11.76$ in the case of the Co(II)-chelate.¹⁵ Conductometric and potentiometric titrations in the present work show evidence only for a 1:2 complex. The present values indicate that the order $\log K_1 > \log K_2$ holds good. The ΔF° values are negative and the ΔH° and ΔS° values positive. Thus the heat and entropy changes favour complex formation. The high values of the thermodynamic functions may be attributed to the strength of the metal-sulphur bond.

When copper (II) salt was added to a solution of o-mercaptobenzoic acid previously degassed with nitrogen, a brown precipitate was formed immediately. Copper(II) was reduced to copper(I). Study of the complexes formed by univalent copper with disulphides¹⁶ reveal the formation of the copper(I) complex of the corresponding disulphide.

When Fe(III) salt was added to a solution of o-mercaptobenzoic acid in the presence of dilute sulphuric acid, the solution immediately turned green and then bluish as more iron was

added, with the formation of a precipitate. Attempts to use this reaction for the titrimetric estimation of iron or o-mercaptobenzoic acid were not successful.

1. Calvin, M. and Wilson, K., *J. Amer. Chem. Soc.*, 1945, **67**, 2003.
2. Bjerrum, J., *Metal Ammine Formation in Aqueous Solution*, P. Haase and Son, Copenhagen, 1941.
3. Leising, D. L., *J. Amer. Chem. Soc.*, 1958, **80**, 4180.
4. Fernando, Q. and Freiser, H., *Ibid.*, 1958, **80**, 4929.
5. Cheney, G., Fernando, Q. and Freiser, H., *J. Phys. Chem.*, 1959, **63**, 2055.
6. —, Freiser, H. and Fernando, Q., *J. Amer. Chem. Soc.*, 1959, **81**, 2611.
7. Corsino, A., Fernando, Q. and Freiser, H., *Anal. Chem.*, 1963, **35**, 1424.
8. Allen, C. F. H. and Mackay, D. D., *Organic Syntheses, Collective Volume 2*, Edited by Blatt, A. H., John Wiley and Sons, Inc., New York, 1961 Ed., p. 580.
9. Irving, H. and Williams, R. J. P., *J. Chem. Soc.*, 1953, p. 3192.
10. Perrin, D. D., *Nature*, 1958, **182**, 741.
11. Lumme, P. O., *Suomen Kemistilehti.*, 1958, **31 B**, 232; *Ibid.*, 1960, **33** (2), 25.
12. Sidgwick, N. V., *J. Chem. Soc.*, 1941, p. 433.
13. Larionov, S. V., Shul'man, V. M. and Podol'skaya, L. A., *Zh. Neorgan. Khim.*, 1964, **9** (10), 2333.
14. Kumar, A. N. and Nigam, H. L., *Ind. J. Chem.*, 1967, **5**, 48.
15. —, — and Katyal, M., *J. Prakt. Chem.*, 1966, **33** (3-4), 160.
16. Hemmerich, P., Beinert, H. and Vaungard, J., *Angew. Chem.* 1966, **78**, 449.