Talanta, Vol. 23, pp. 405–407. Pergamon Press, 1976. Printed in Great Britain

ANALYTICAL DATA

A POTENTIOMETRIC STUDY OF THE COMPLEXES FORMED BETWEEN Ni(II) AND Zn(II) AND 3-MERCAPTOPROPIONIC ACID

H. F. DE BRABANDER*, H. S. CREYF, A. M. GOEMINNE and
L. C. VAN POUCKE†

Department of General and Inorganic Chemistry, University of Ghent, Ghent, Belgium

(*Received* 11 *March* 1975. *Revised* 28 *August* 1975. *Accepted* 3 *September* 1975)

In earlier investigations[1–4] the complexation of the metal ions Ni^{2+} and Zn^{2+} with the following thiols as ligands was studied: 2-mercaptoethanol (MEL), 3-mercapto-1,2-propanediol (MPD), thioglycollic acid (TGA) and thiolactic acid (TLA).

Not much work has been done on the complexation of 3-mercaptopropionic acid (3-MPA). Saxena and Gupta[5,6] studied the Ni^{2+} and Cd^{2+} complexes of this ligand and found only mononuclear complexes. This is not surprising, taking into account that the range of total metal ion concentration used was rather restricted. In the present work the complexation of Ni^{2+} and Zn^{2+} with 3-mercaptopropionic acid is studied over a large concentration range. This ligand is interesting for comparison of the results with those obtained for TGA and TLA, since the carboxyl group is substituted in the β-position relative to the $-SH$ group.

EXPERIMENTAL

Apparatus

A digital pH-meter "Radiometer pHM52" was used, equipped with a G 202 C glass electrode and a saturated calomel electrode as reference. The glass electrode was standardized with an NBS standard 0·01*M* borax buffer, pH 9·18 at 25°.[7] All solutions were kept at 25°.

Reagents

Stock solutions (0·2*M*) of nickel and zinc nitrate were prepared and standardized as before.[1,2] 3-Mercaptopropionic acid (3-MPA) was obtained from Fluka and redistilled just before use. Aqueous solutions of 3-MPA are stable for a long period if they are prepared with oxygen-free water and regularly flushed with pure nitrogen.[9] All solutions were made up to an ionic strength of 0·5 with potassium nitrate (Merck *p.a.*) to keep the activity coefficients as constant as possible.

Procedure

The titration procedure for zinc was as described before.[1] The total metal ion concentration was varied from 0·001 to 0·016*M*. The initial ligand concentration was five times the total metal ion concentration. The reaction of nickel(II) with 3-MPA was too slow for direct titration. Therefore a series of 50-ml volumetric flasks was prepared, containing solutions with constant total metal ion and ligand concentrations but increasing amounts of base. A 25-ml aliquot of each solution was diluted to 50-ml with 0·5*M* potassium nitrate, giving a second series with half the original total metal ion concentration. A constant pH-value was obtained after 1 hour.

Calculations

The calculations were performed with a number of computer programs written in FORTRAN IV. All programs were executed on a Siemens 4004/150 computer.

RESULTS AND MATHEMATICAL TREATMENT

The symbols used are those listed earlier,[3] except that B represents Ni^{2+} or Zn^{2+} (and *B* the total metal ion concentration), A represents 3-MPA (and *A* the total ligand concentration).

The protonation constants log K_{Hi} of the carboxylate and mercapto group of 3-mercaptopropionic acid (3-MPA) were calculated by a method described by Thiers, Van Poucke and Herman[9] and found to be 4·16 and 10·10 respectively.

With a general computer program ZPAF the formation functions $Z(pa)_B$ were calculated as before.[3] A proportionality factor described before[10] was used to calculate $[H^+]$ from the activity of the hydrogen ion.

The formation curves for the Zn^{2+}/3-MPA complex all crossed at a value $Z = \pm 1{\cdot}45$, forming a real or pseudo cross-over point. From graphical analysis of the formation curves[11,12] it appeared that a mixture of mononuclear complexes BA, BA_2 and a "core + links" series $B(A_6B)_n$ with $n_{max} = 3$ was very probable. To find out which complexes were really present the computer program PNUC was used.[4]

This program is based on minimization of the function *U* related to the difference between calculated and experimental *Z*-values:

$$U = \Sigma\,(Z_{cal} - Z_{exp})^2 \tag{1}$$

The standard deviation of *Z* is given by

$$\sigma^2(Z) = U_{min}/(n_{exp} - n_{par}) \tag{2}$$

where n_{exp} is the number of experimental points and n_{par} is the number of complexes. This calculation is repeated for different complex compositions, and the set of complexes that is really present will give the lowest values of U_{min} and $\sigma(Z)$.

The calculation is started with guessed stability constants. Bad guesses can ruin the calculation. If the guess for a certain stability constant is too low, its contribution to *U* is negligible and the constant remains unchanged during the calculation. The best guesses are 3–5 log β units higher than the finally obtained results.

---

* Present address: Laboratory of Chemical Analysis of Food from Animal Origin, Casinoplein, 24 B-9000 Ghent, Belgium.

† Present address: Department of Chemistry, Limburgs Universitair Centrum, B-3610 Diepenbeek, Belgium.

Input values for a complex B_QA_P can be calculated[13] from

$$\log \beta_{Q,P}\,(\text{guessed}) = 2{\cdot}1\,(Q-1) + P\,pa \qquad (3)$$

where pa is the value of $-\log a$ for $B = 0{\cdot}016$ and $Z = 0{\cdot}5$.

The distribution of complexes ($\alpha_{q,p}$) was calculated from

$$\alpha_{q,p} = \frac{100\,q\beta_{q,p}\,b^q a^p}{B} \qquad (4)$$

The results for the zinc system are given in Table 1. The possible complexes are BA, BA_2, B_2A_2, B_3A_4 and B_4A_6. The complexes BA and B_2A_2 are rejected and the system Zn^{2+}/3-MPA can be represented by the formation of the complexes BA_2, B_3A_4 and B_4A_6.

The formation curves for the Ni/3-MPA system are shown in Fig. 1. The "core + links" theory could not be applied. As there is no "cross-over" point a mixture of poly- and mononuclear complexes is not very probable. Below $Z = 0{\cdot}7$ the spacing of the curves points to a "core + links" series $(A_2B)_n$, also found for other Ni^{2+} thiol complexes.[2–4] For $Z > 0{\cdot}7$ the spacing changes and all formation curves tend to a value of $Z_{max} = 2$, so complexes with a ligand/metal ratio of 2 are very probable. This system was also treated with the program PNUC, starting with two complexes B_3A_4 and B_3A_6, and adding sequentially all complexes with less than seven metal ions and a ligand/metal ratio < 2. The mononuclear complexes BA, BA_2, BA_3 and the polymeric complexes $(BA_2)_n$ with $n = 1$–9 were also tested. The complexes were accepted or rejected as described elsewhere.[4] The lowest value for U_{min} and $\sigma^2(Z)$ was found for a mixture of complexes B_5A_{10}, B_6A_{12}, B_6A_9 and B_6A_{11}. As can be seen from Table 2 the predominant species are B_6A_{12} and B_6A_9.

Table 1. Stability constants for 3-MPA/Zn^{2+} complexes from treatment with PNUC

System	$\log \beta_{q,p}$	$\alpha_{q,p_{max}}$	present	U_{min}	$\sigma^2(z)$
BA	3·44	<0·1	−	0·02553	$0{\cdot}61 \times 10^{-3}$
BA_2	12·18	97	+		
B_2A_2	11·95	<0·1	−		
B_3A_4	30·40	32	+		
B_4A_6	45·59	40	+		
BA_2	12·18	97	+	0·02718	$0{\cdot}63 \times 10^{-3}$
B_2A_2	11·95	<0·1	−		
B_3A_4	30·47	32	+		
B_4A_6	45·45	40	+		
BA	3·44	<0·1	−	0·02555	$0{\cdot}59 \times 10^{-3}$
BA_2	12·18	97	+		
B_3A_4	30·40	32	+		
B_4A_6	45·59	40	+		
BA_2	12·18	97	+	0·02539	$0{\cdot}58 \times 10^{-3}$
B_3A_4	30·40	32	+		
B_4A_6	45·59	40	+		

DISCUSSION

The complexes formed between Ni^{2+} and 3-MPA are totally different from the Zn^{2+} complexes of 3-MPA, which are analogous with those formed with TLA and TGA.

This different behaviour is not yet understood. From earlier measurements it was found that ligands such as MEL and MPD, containing the –SH group as the only complexing group, form polymeric complexes $B(A_2B)_n$ with high values of n. The implant of a second complexing group on the molecule can block the growth of the polymeric chain. The second group competes with the –SH and after formation of some links it can be energetically favourable to fill up the empty co-ordination places around Ni^{2+} with the second group instead of the –SH group. This may be the reason why complexes higher than B_3A_4 are lacking in the system Ni^{2+}/cysteamine.[1] By analogy with polymer chemistry we could call this a termination reaction, or the second group a "stop" group.

The second group can also confer an extra charge on the complex. This is the case for TGA, TLA and 3-MPA. While the complexes of MEL, MPD and 2-MEA have two positive charges, the complexes of Ni^{2+} with TGA, TLA and 3-MPA receive two negative charges per BA_2 link. High charge on a complex will not be favourable for the stability of that complex.

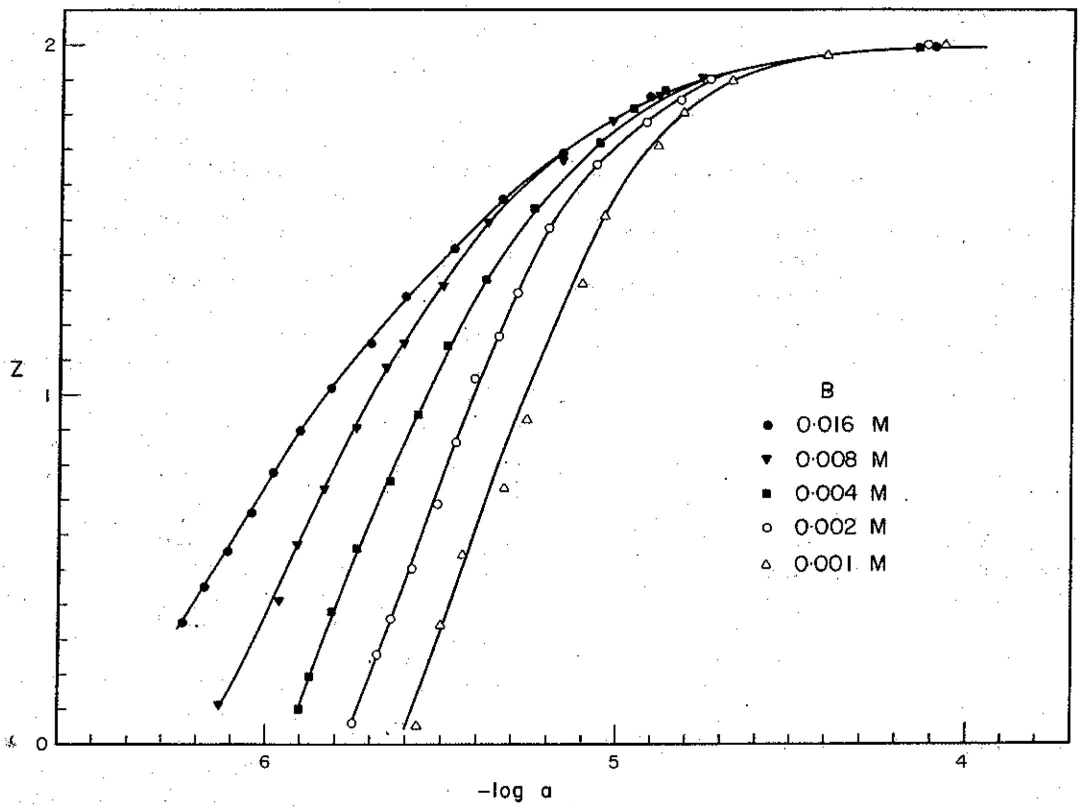

Fig. 1. The formation curves of the system nickel(II)-3MPA.

Table 2. Stability constants for Ni^{2+}/3-MPA complexes from treatment with PNUC

System	log $\beta_{q,p}$	$\alpha_{q,p_{\max}}$	present	$U_{\min}$	$\sigma^2(z)$
B_5A_{10}	64·54	16	+	0·2166	$0{\cdot}31 \times 10^{-2}$
B_6A_{12}	78·94	86	+		
B_6A_9	63·58	68	+		
B_6A_{10}	67·80	<4	(±)−		
B_6A_{11}	73·31	12	+		
B_5A_{10}	64·49	16	+	0·2122	$0{\cdot}30 \times 10^{-2}$
B_6A_{12}	78·89	83	+		
B_6A_9	63·58	69	+		
B_6A_{11}	73·60	23	+		
B_6A_{12}	79·03	83	+	0·2135	$0{\cdot}29 \times 10^{-2}$
B_6A_9	63.61	73	+		
B_6A_{11}	73·36	13	+		
B_6A_{12}	79·10	99	+	0·2284	$0{\cdot}31 \times 10^{-2}$
B_6A_9	63·63	82	+		

This could explain the complex formation between Ni^{2+} and 3-MPA. If, in the case of Ni^{2+}, a six-membered chelate, less stable than a five-membered chelate, is not able to stop the growing of the polymeric chain, the formation of higher complexes will be inhibited by the higher charge on the complexes.

Acknowledgement—The authors wish to thank Prof. Dr. Z. Eeckhaut for helpful discussions and W. Lippens for technical assistance.

REFERENCES

1. H. F. de Brabander, L. C. van Poucke and Z. Eeckhaut, *Inorg. Chim. Acta*, 1971, **5**, 473.
2. *Idem, ibid.*, 1972, **6**, 459.
3. *Idem, Anal. Chim. Acta*, 1974, **70**, 401.
4. H. F. de Brabander, A. M. Goeminne and L. C. van Poucke, *J. Inorg. Nucl. Chem.*, 1975, **37**, 799.
5. R. S. Saxena and K. C. Gupta, *J. Indian. Chem. Soc.*, 1969, **46**, 11.
6. *Idem, ibid.*, 1969, **46**, 258.
7. R. G. Bates, *Determination of pH*, p. 76. Wiley, New York, 1964.
8. E. Jacobsen and W. Lund, *Acta Chem. Scand.*, 1965, **19**, 2379.
9. G. F. Thiers, L. C. van Poucke and M. A. Herman, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1543.
10. A. M. Goeminne and Z. Eeckhaut, *ibid.*, 1974, **36**, 357.
11. L. C. van Poucke and H. F. de Brabander, *Talanta*, 1973, **20**, 733.
12. *Idem, ibid.*, 1974, **21**, 279.
13. H. F. de Brabander, unpublished results.

Summary—The composition and stability constants of the complexes formed between Ni^{2+} and Zn^{2+} and 3-mercaptopropionic acid (3-MPA) were studied by a potentiometric method at 25° and in 0·5*M* KNO_3. For the system Zn^{2+}/3-MPA a mixture of the mononuclear complex BA_2 and the polynuclear complexes B_3A_4 and B_4A_6 was found (B means the metal ion and A the ligand). The system Ni^{2+}/3-MPA can be represented by the complexes B_5A_{10}, B_6A_{11}, B_6A_9 and B_6A_{12}. In this series the last two complexes are predominant.