J. Coord. Chem.
1974, Vol. 3, pp. 301-306

P1974-01

POLYMERIC COMPLEXES BETWEEN CADMIUM (II) AND 2-MERCAPTOETHANOL AND 3-MERCAPTO-1,2-PROPANEDIOL

H. F. DE BRABANDER and L. C. VAN POUCKE†

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

(Received March 29, 1973; in final form July 9, 1973)

The complex formation between Cd(II) and 2-mercaptoethanol (MEL) and 3-mercapto-1, 2-propanediol (MPD) was studied by a pH-method at 25°C and in 0.5 M KNO_3. The best representation of the complex formation is the 'core + links' series $B(A_5B_3)_n$, B being the metal ion and A the ligand; n tends to relatively high values. The reduced stability constants were found by comparing experimental data with theoretical curves.

INTRODUCTION

Studies of the complex formation of Cd(II) in aqueous solution with ligands containing a mercapto-group are rather scarce. In addition there is a considerable disagreement among the published results. Li and Manning[1] e.g. investigated the system Cd(II) -2-aminoethanethiol and found two mononuclear species BA and BA_2; Felder, *et al.*[2], however proposed for the same system a complex BA and a protonated complex HBA. From a small number of polarographic measurements Saxena and Gupta[3] detected four mononuclear complexes in the Cd(II)-3-mercaptopropionic acid system. On the other hand Strickler[4] reported that the structure of the crystalline salts isolated from the Cd(II)-2-mercaptoethanol system are built up from decanuclear cations $(B_{10}A_{16})^{4+}$. Therefore it is not unlikely that also in queous solution polynuclear complexes are formed as in the case of Zn(H) and N(II)[5,6]. Polynuclear complexes are sometimes overlooked, especially when the total metal ion concentration is not varied over a sufficiently wide concentration range. In this paper the results are dealt with of a study of the Cd(II) complexes of 2-mercaptoethanol (MEL) and 3-mercapto-1, 2-propanediol (MPD). MEL was chosen in order to compare the composition of the solid complexes with that of the complexes in solution. As it turned out that in a certain concentration range a precipitate was formed, another ligand MPD was investigated giving more soluble complexes.

EXPERIMENTAL

Reagents

A stock solution of cadmium nitrate (Baker) was standardized gravimetrically as $CdNH_4PO_4 \cdot H_2O$[7]. Solutions of both ligands (Fluka p.a.) were prepared as indicated in an earlier paper[5]. The ionic stength was kept at 0.5 by means of potassium nitrate.

Apparatus and Measurements

The titration procedure for studying polynuclear complexes has been described elsewhere[5,6]. Five titrations were performed with a total metal concentration of respectively 0.016 M, 0.008 M, 0.004 M, 0.002 M and 0.001 M. The initial ligand concentration was five times the total metal ion concentration. The pH was measured with a digital Radiometer pHM52 equipped with a glass electrode type C and a saturated calomelelectrode as reference. The electrodes were standardized against 0.01 M borax buffer according to Bates[8]. All measurements were carried out at 25.0 ± 0.1°C.

For the calculations a number of computer programs were written in Fortran IV. Short programs and programs needing a plot equipment were executed on an IBM 360/30 computer. Larger programs were run on a Siemens 4004/150.

---

†Present Address: L. C. Van Poucke, Limburgs Universitair Centrum, Universitaire Campus, B3610 Diepenbeek, Belgium.

RESULTS

The symbols are the same as in the papers of Sillén[9,10,11]. They are listed below.

B : total concentration of Cd(II).

b : concentration of free Cd(II).

A : total ligand concentration.

h_i: concentration of the protonated ligand H_ia.

a : concentration of free ligand.

h ; activity of the hydrogen ion.

C_{Base} : concentration of added base.

Z : average number of ligand bound per Cd(II).

t ; number of ligands in a link.

n : variable integer : number of links in a 'core + links' complex.

$\bar{n}$: average number of links in a 'core + links' complex.

K_{Hi} : mixed protonation constant of the ligand defined

$$K_{Hi} = h_i a / h \cdot h_{i-1} a$$

β_n : overall stability constant for a complex with n links, defined as

$$\beta_n = (B(A_tB)_n)/b^{n+1} \cdot a^{nt}$$

$\log F = \log (B/b)$

$u = a^t b$

$y = Z/t$

$x = t \log a + \log B$

N : maximum number of hydrogen ions that the ligand can take up.

$k_0 = \beta_1/k$: indication for facility of formation of the first complex.

$k = \beta_{n+1}/\beta_n$: relation between two succeeding links : indication for facility of adding a new link.

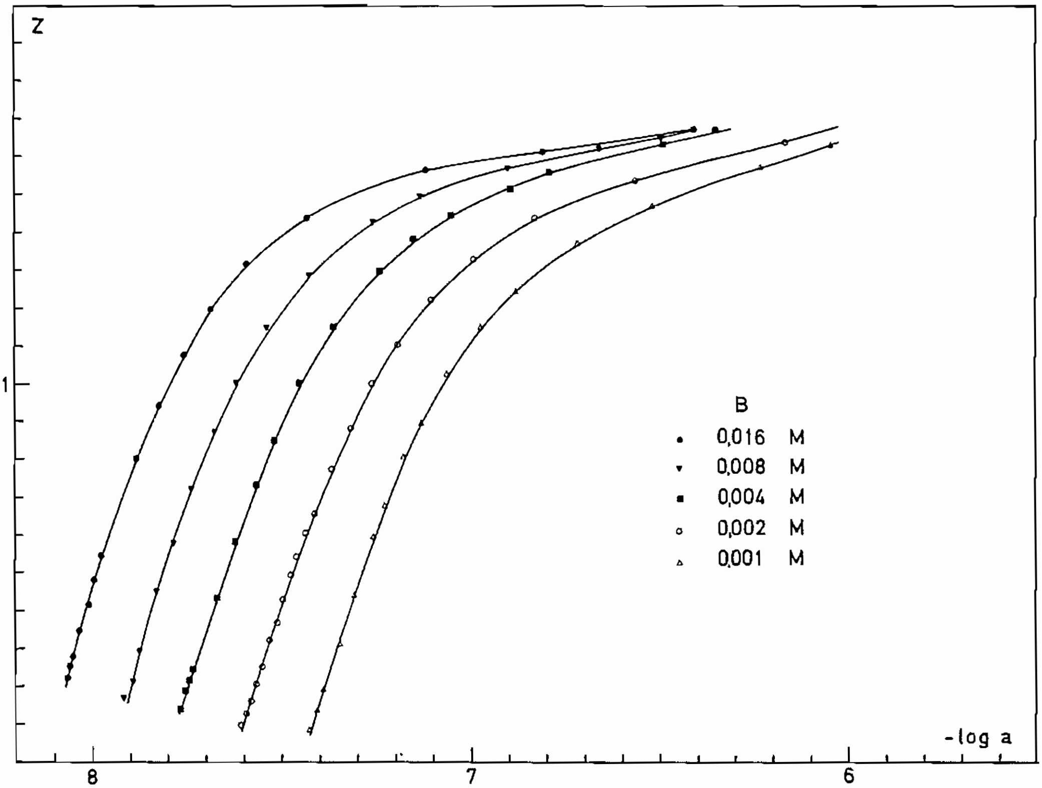

FIGURE 1 The formation curves of the system cadmium(II) and 2-mercaptoethanol.

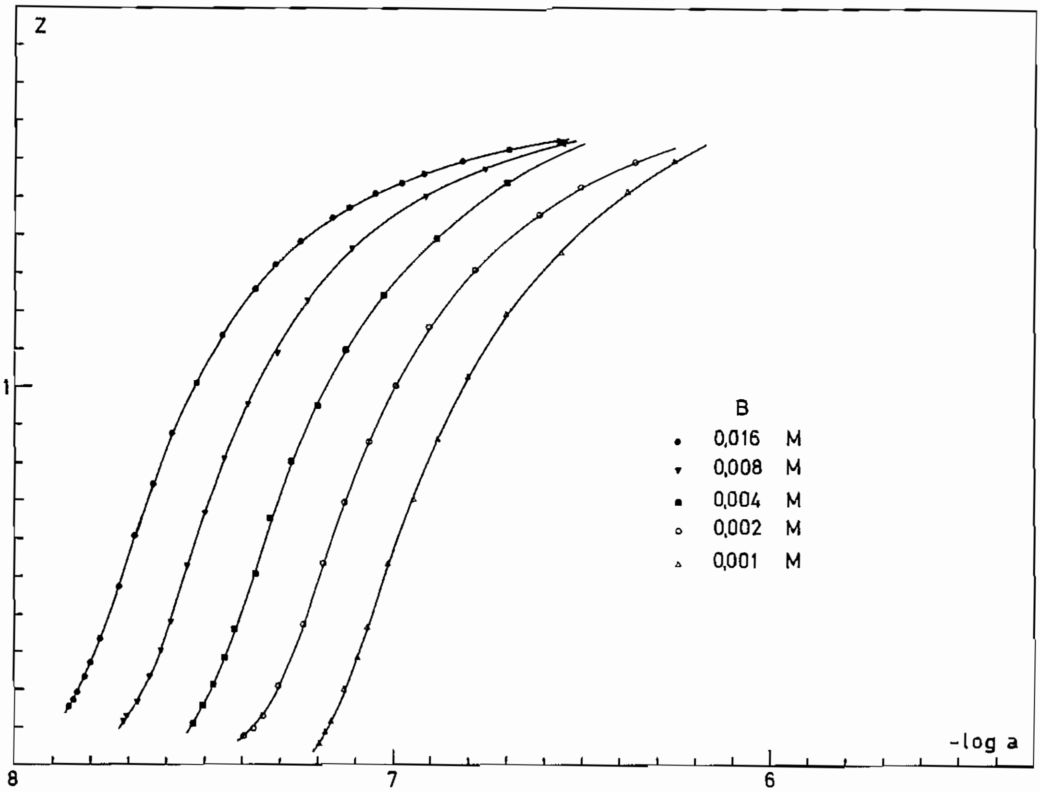

FIGURE 2 The formation curves of the system cadmium(II) and 3-mercapto-1,2-propanediol.

The logarithms of the protonation constants K_{Hi} for MEL and MPD were determined previously[5] as 9.49 and 9.43 respectively.

For the calculation of the formation function a general computer program ZPAF was written. By means of Eqs. (1) and (2) the formation function can be calculated, even when the ligands are polybasic acids.

$$a = \frac{N.A - C_{base} - (H^+) + (OH^-)}{\sum_{n=1}^{N} n.h.^n \prod_{i=1}^{n} K_{Hi}} \qquad (1)$$

$$Z = (A - a(1 + \sum_{n=1}^{N} h^n . \prod_{i=1}^{n} K_{Hi}))/B \qquad (2)$$

The values of h were obtained from pH measurements. The method of standardization described above will shift the pH scale with a constant and unknown value. But since the protonation constants have been determined in the same circumstances this will not affect the a and Z values as can be seen from Eqs. (1) and (2). The concentration of hydrogen ions (H^+) can be calculated from experimentally obtained h values using a proportionality factor reported by Goeminne[12]. As the pH range was limited to 8.5 the term (OH^-) in Eq. (1) may be neglected. Thus the formation function Z(a) can be calculated from Eqs. (1) and (2). The computer programme was so designed that the Z and a values can be printed out, can be plotted giving a family of formation curves and can be punched on cards for further use. Unlike the earlier papers[5,6] protonation constants were used instead of acidity constants in Eqs. (1) and (2). This was done to provide conformity with the stability constants of metal ion complexes. It was found that Eqs. (1) and (2) using protonation constants become less intricate, easier to programme, especially when exponent underflow or overflow must be avoided.

For both ligands, as illustrated in Figures 1 and 2, a family of equidistant curves was obtained. According to Sillén[9] the complexes are polynuclear and can be represented by a 'core + links' series $B(A_tB)_n$. The value of t was determined by a plot of log B versus log a at constant values of Z. For each value of Z a straight line was obtained with a slope of 1.66. Using this value for t, the y(x) curves were calculated. As can be seen from Figures 3 and 4 all points fall on one single curve. It follows that the general formula for this 'core + links' can be represented by $B(A_{5/3}B)_n$; n must be a multiple of 3. The maximum value of n can be calculated[5,10] from the limit value of y using Eq. (3).

$$y_{\max} = Z_{\max}/t = 1 - 1/(n_{\max} + 1) \qquad (3)$$

$$\bar{n} = y/(1 - y - F^{-1}) \qquad (4)$$

$$\log F = 0.434 + \int_{-\infty}^{x} y dx \qquad (5)$$

Values of $\bar{n}$ in function of y are tabulated in table 1. From this table it is seen that $\bar{n}$ is not constant: more than one complex must be present. Since n becomes rather larger for increasing values of y, it would be interesting to assume an infinite number of complexes and to interpret the y(x) curve in terms of Sillén's[10] hypothesis III. For the addition of new links three possibilities can be considered in hypothesis III: (a) the links are added with the same facility $\beta n + 1/\beta_n = k$ as indicated above, (b) the first links are somewhat more easily added $\beta_{n+1/\beta n}, = k(1 + n^{-1})$, (c) the higher complexes are formed with greater and greater difficulty $\beta_{n+1/\beta n} = k\cdot(1 + n)^{-1}$. Theoretical y(x) curves were calculated, plotted and compared with the experi-

TABLE I
The average number of links in function of y

MEL		MPD	
y	$\bar{n}$	y	$\bar{n}$
0.1	7.98	0.09	5.5
0.310	9.5	0.275	7.2
0.510	11.4	0.390	9.0
0.655	12.9	0.490	10.6
0.765	16.8	0.570	11.1
0.830	17.4	0.640	12.2
0.88	21.4	0.700	13.5
0.910	23.2	0.750	14.9
0.935	28.6	0.795	17.6
0.955	38.9	0.825	17.8
0.970	57.0	0.855	20.3
0.975	66.3	0.875	20.7

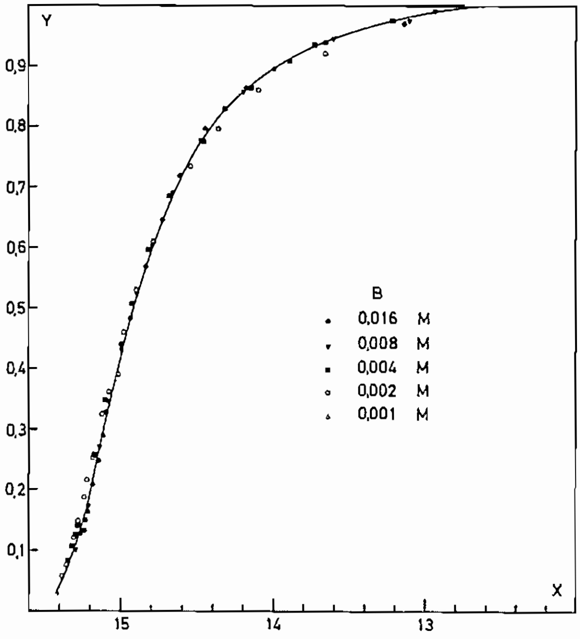

FIGURE 3 The y-x curve of the system cadmium(II) and 2-mercaptoethanol.

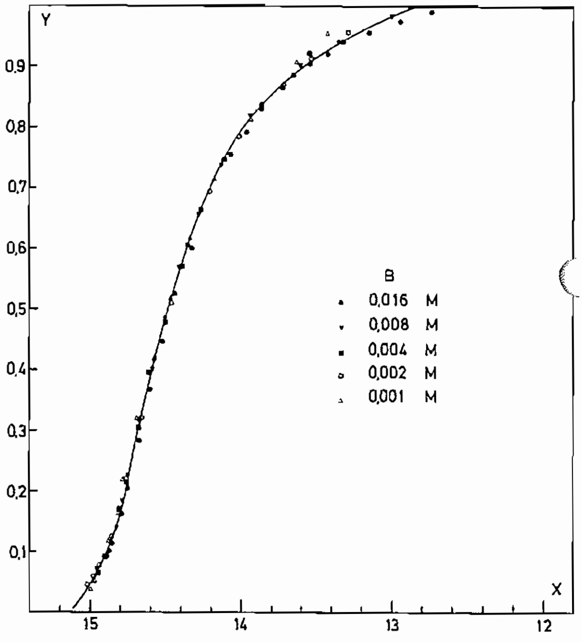

FIGURE 4 The y-x curve of the system cadmium(II) and 3-mercapto-1,2-propanediol.

mental one. In order to avoid all subjective interpretations, the choice between the three possibilities was made using a least squares treatment. The square error sum U is given by Eq. (6).

$$U = \Sigma(y_{exp} - y_{calc.})^2 \qquad (6)$$

y_{calc} was calculated from estimated values of k and k_0, obtained from the graphical analysis and experimental x values. The function U was minimized using the 'variable metric method' described by Davidon[13]. The standard deviation $\sigma(y)$ was calculated from Eq. (7).

$$\sigma(y) = (U_{min}/(n_{exp} - n_{par}))^{1/2} \qquad (7)$$

U_{min} is the value for U at the minimum, n_{exp} the number of experimental points and n_{par} the number of parameters. The hypothesis with the smallest value of $\sigma(y)$ is considered as the 'best' hypothesis. The values of the parameters corresponding with U_{min} are the 'best' parameters. A similar calculation was performed on the corresponding Ni(II) complexes using the data of our earlier investigations[6]. The results of all these calculations are summarized in Table II.

From that table it seems that hypothesis III_a and III_b are almost equally possible. The stability constants calculated according to both hypothesis does not show appreciable differences, except for the lower values $n = 1$ and 2. For n greater than 2, both hypothesis are nearly equivalent. So the stability constants can be calculated from either III_a (8) or III_b (9);

$$\log \beta_n = \log k_0 + n \log k \qquad (8)$$

$$\log \beta_n = \log k_0 + n \log k + \log n \qquad (9)$$

using the appropriate values for k_0 and k.

DISCUSSION

The experimental data of this investigation point to the formation of 'core + links' complexes of type $B(A_5B_3)_n$ with relative high values for n. This is in disagreement with other investigations[1,2,3] in aqueous solution of Cd(II) complexes with ligands containing a mercaptogroup. Comparing with the composition of the crystalline salt[4] a better agreement is obtained: the decanuclearcation $(B_{10}A_{16})^{4+}$ and the complex $B(A_5B_3)_3$ differ only by one ligand molecule. Comparing it with the sfalerite structure of the decanuclear cation it is possible that the link B_3A_5 is formed by a six membered ring with alternating a metal ion and a sulphur atom and two additional ligand molecules bounded with a metal ion of the ring, but still capable of forming a bridge between the ring and one of the other members of the 'core + links' series.

As the complexes of MPD are more soluble than those of MEL the formation curve could be taken up over a wider range. From figure 5 it can be seen that all curves coincide for Z values greater than 1.7. The formation curve shows a slight deflection and tends to a value of about 2.5. As in that region b is neglegible in comparison with B, all complexes will be homonuclear and contain the same number of metal ions. It is possible that the polymeric complex,

TABLE II
Results of the tests of hypothesis III

	Hypothesis	k_0	log k	$\sigma(y)$
Cd(II)/MEL	III_a	$0.2368\ 10^{-1}$	15.205	$0.2168\ 10^{-1}$
	III_b	$0.9752\ 10^{-2}$	15.157	$0.1954\ 10^{-1}$
	III_c	$0.671\ 10^{-4}$	16.145	$0.3494\ 10^{-1}$
Cd(II)/MPD	III_a	$0.2162\ 10^{-1}$	14.769	$0.1234\ 10^{-1}$
	III_b	$0.8132\ 10^{-2}$	14.726	$0.1457\ 10^{-1}$
	III_c	$0.424\ 10^{4}$	15.739	$0.3643\ 10^{-1}$
Ni(II)/MEL	III_a	$0.7475\ 10^{-2}$	13.023	$0.1749\ 10^{-1}$
	III_b	$0.2056\ 10^{-2}$	12.991	$0.1799\ 10^{-1}$
	III_c	$0.226\ 10^{-5}$	14.090	$0.3754\ 10^{-1}$
Ni(II)/MPD	III_a	$0.1863\ 10^{-1}$	13.232	$0.2378\ 10^{-1}$
	III_b	$0.2434\ 10^{-2}$	13.213	$02413\ 10^{-1}$
	III_c	$0.193\ 10^{-4}$	14.226	0.390210^{-1}

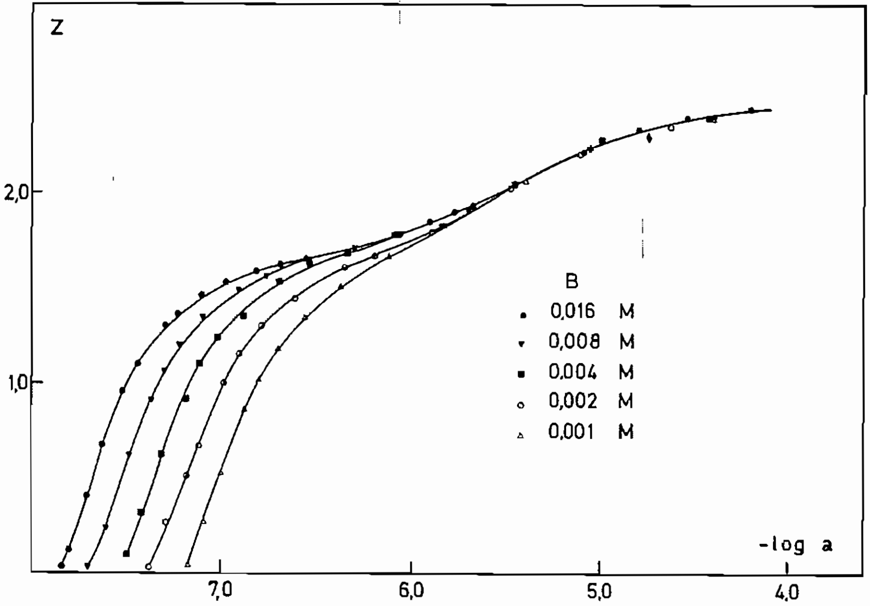

FIGURE 5 The formation curves of the system cadmium(II) and 3-mercapto-1,2-propanediol, taken up over a wider range.

staying in solution, takes up more ligands and finally gives an analogous composition as in the case[5] of Zn(II) which is also a d^{10} ion. In the same region all complexes of MEL/Cd(II) precipitate.

All the metal ions hitherto investigated form with MEL and MPD soluble complexes which can be represented by a 'core + links' system but with a considerable difference concerning the composition in the link: Ni(II) forms $B(A_2B)_n$ complexes[6], Zn(II) $B(A_3B)^5{}_n$ complexes and Cd(II) $B(A_5B_3)_n$ complexes. It seems that the composition is dependent on the electronic structure and polarizing power of the metal ion, factors which influence the bounding distance with the sulphur atoms and the geometrical surrounding of the metal ion by the ligand molecules. These two factors determine in a large degree the structure. It seems that Ni(II) form a chain structure and the Cd(II) and Zn(II) complexes a more pronounced three dimensional structure. In the latter case steric hindrance will be more important and this can be the reason why the MPD complexes are less stable than the MEL complexes as distinct from the Ni(II) complexes where the reverse is found.

ACKNOWLEDGMENT

The authors wish to thank Prof. Dr. Z. Eeckhaut for his helpful discussions.

REFERENCES

1. N. C. Li and R. A. Manning, *J. Amer. Chem. Soc.*, 77, 5225 (1955).
2. E. Felder, C. Rescigno and E. Radice, *Gazetta*, 85, 453 (1955).
3. R. S. Saxena and K. C. Gupta, *J. Indian Chem. Soc.*, 46, 1045 (1969).
4. P. Strickler, *J. Chem. Soc. D.*, 655–56, (1969).
5. H. F. De Brabander, L. C. Van Poucke and Z. Eeckhaut, *Inorg. Chim. Acta*, 5, 473, (1971).
6. H. F. De Brabander, L. C. Van Poucke and Z. Eeckhaut, *Inorg. Chim. Acta*, 6, 459, (1972).
7. A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, (Longmans, Green and Co, London, 1964), p. 493.
8. R. G. Bates, *Determination of pH*, (Wiley, New York, 1964), p. 76.
9. L. G. Sillén, *Acta. Chem. Scand.*, 8, 299, (1954).
10. L. G. Sillén, *Acta. Chem. Scand.*, 8, 318, (1954).
11. G. Biedermann and L. G. Sillén, *Acta. Chem. Scand.*, 10, 1011, (1956).
12. A. M. Goeminne and Z. Eeckhaut, *Bull. Soc. Chim. Belges*, 80, 605–610, (1971).
13. W. C. Davidon, ANL-5990 Physics and Mathematics AEC, Research and Development Report (1966), Argonne National Laboratory.