*Contribution from the Department of General and Inorganic Chemistry University of Ghent, Ghent, Belgium*

# Polymeric Complexes Between Nickel(II) and 2-mercaptoethanol and 3-mercapto-1,2-propanediol

**H.F. De Brabander, L.C. Van Poucke and Z. Eeckhaut**

*Received October 5, 1971*

*The complexes between nickel(II) and 2-mercaptoethanol(MEL) and 3-mercapto-1,2-propanediol(MPD) were studied in aqueous solution by a pH-metrical method, at 25° C and in 0.5 M $KNO_3$. According to Sillén's theory the complex formation can be represented by a "core + links" system $B\,(A_2B)_n$, where B means the metal ion and A the ligand. At any rate n tends to very high values. It is possible that with an excess of the ligand, complexes with formula $(BA_2)_n$ are formed. Theoretically n can take values form zero to infinite. In practice no difference can be found between an infinite value of n and very high values. So the mechanism can be represented by a chain polymeric structure. The reduced stability constants of the system were found by comparing experimental data with theoretical curves.*

## Introduction

Several reports have been dealt with on the preparation of nickel mercaptides. In some investigations brown insoluble powders were obtained, which were described as highly polymeric. In other cases a hexameric compound was found. Hexameric $Ni^{II}$ complexes of methyl mercaptan, ethyl mercaptan and 1-propanethiol were prepared by Woodward, Dahl, Abel and Crosse[1]. Gould and Taylor[2,3] prepared also the hexameric $Ni^{II}$ complexes of 2-mercaptoethanol and 1-mercapto-2-propanol. X-ray diffraction shows that the hexameric complex has a crown structure, with six metal ions forming a ring and linked by twelve mercaptide ions. On the other hand species of a highly polymeric structure were precipitated from an aqueous solution of nickel chloride in the presence of an excess of ethyl mercaptan and ammonia by Manchot and Kaess[4]. Similar nickel mercaptide complexes were prepared by Jensen[5] and by Hayter and Humiec[6]. Only a few investigations have been carried out on the aqueous soluble complexes between $Ni^{II}$ and mercaptide ions. Gould and Taylor[3] reported in a brief communication that they have found parallel formation curves, which could be explained by the formation of a single complex with formula $(BA_2)_n$ in agreement with the solute complex, they prepared. It should be interesting whether the hexameric or the complexes with a higher degree of polymerisation are formed with 2-mercaptoethanol and especially with 3-mercapto-1,2-propanediol, which gives very good water soluble complexes.

## Experimental

*Reagents*: Both mercaptans were FLUKA p.a. and were redestilled before use. Aqueous solutions of the mercaptans were prepared with oxygen-free water and regularly flushed with pure nitrogen gas. Only freshly prepared solutions were used for the measurements. A stock solution of nickel nitrate (BAKER a.r.) 0.2 *M* was made and standardized gravimetrically as bis (dimethylglyoximato)-nickel[13]. In order to keep the activity coefficients as constant as possible all solutions were prepared in 0.5 *M* $KNO_3$. Before use all solutions were flushed with pure nitrogen gas.

*Measurements*: The titration procedure of the nickel (II) complexes with 2-mercaptoethanol has been described before[7]. Five titrations were performed with total metal ion concentration 0.008 *M*, 0.004 *M*, 0.002 *M*, 0.001 *M*, 0.0005 *M*; the initial ligand concentration was five times the total metal ion concentration. The system was assumed to have reached equilibrium when the measured pH value was constant for at least 10 minutes. The reaction rate of the complex formation for the system nickel(II), 3-mercapto-1,2-propanediol is too low for direct titration. Therefore a series of volumetric flasks of 50 ml was prepared, containing constant metal ion concentration and constant total ligand concentration but increasing amounts of base. From each volumetric flask of this series 25 ml was transferred into the corresponding number of another series and diluted to 50 ml with 0.5 *M* $KNO_3$ So a second series was obtained, where the metal ion concentration was half that of the first series, and so on. A constant pH value was obtained after one hour, and no change was observed within a period of one day. The pH was measured with a Radiometer pHM4 using a glass electrode type C, and a saturated

---

[1] Woodward P., Dahl L.F., Abel E.W., and Crosse B.C., *J. Am. Chem. Soc.*, *87*, 5251 (1965).
[2] Gould R.O. and Taylor R.M., *Proceedings 9ICCC*, 303 (1966).
[3] Gould R.O. and Taylor R.M., *Chem. Ind.* (*London*), 378 (1966).
[4] Manchot W. and Kaess F., *Ber.*, *60*, 2175 (1927).
[5] Jensen K.A., *Z. Anorg. Allgem. Chem.*, *252*, 227 (1944).
[6] Hayter R.G. and Humiec F.S., *J. Inorg. Nucl. Chem.*, *26*, 807 (1969).

[7] De Brabander, H.F., Van Poucke, L.C., and Eeckhaut, Z., *Inorg. Chim. Acta*, *5*, 473 (1971).

calomel electrode as reference. The glass electrode was standardized against 0.01 *M* borax buffer according to BATES[8]. All measurements were carried out at 25° C.

## Results

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

B: total concentration of $Ni^{2+}$
b: concentration of free $Ni^{2+}$
A: total concentration of ligand
ha: concentration of protonated ligand
ha: concentration of free ligand
h: activity of the hydrogen ion
$C_{base}$: concentration of base added
Z: average number of ligands bound per $Ni^{2+}$—ion
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
$K_a$: mixed acidity constant of ligand, defined as $K_a=\frac{h\,.\,a}{ha}$
$K_n$: overall stability constant for a complex with n links, defined as

$$K_n=\frac{(B(A_2B)_n)}{b^{n+1}a^{2n}}$$

$\log F=\log\frac{B}{b}$
$u=a^tb$
$y=\frac{Z}{t}$
$x=t\log a+\log B$
$k_o=\frac{K_1}{k}$ indication for facility of formation of the first complex

$k=\frac{K_{n+1}}{K_n}$: relation between two succeeding links, indication for facility of adding a new link.

The acidity constants of MEL and MPD were calculated by a method of Thiers, Van Poucke and Herman[12] and were found to be $3.23\ 10^{-10}$ and $3.77.10^{-10}$. As shown in an earlier paper[7] the formation curves were calculated from equations:

$$Z=\frac{A-(A-C_{base})\frac{h+\bar{K_a}}{h}}{B} \qquad (1)$$

$$a=(A-C_{base})\frac{K_a}{h} \qquad (2)$$

The formation curves are shown in Figure 1 and Figure 2. As can be seen from the figures a family of parallel curves are obtained in each case. According to Sillèn[9,10,11] systems which give such curves are polynuclear and form a so called "core + links" system of general formula $B(A_tB)_n$. The value of t may be found from the spacing of the curves with the aid of the relation:

$$t=-\left(\frac{\partial\log B}{\partial\log a}\right)_Z \qquad (3)$$

In both cases t was found to be two.

The correctness of the factor t was checked by calculating the curves y(x). If t is correct, all y(x)

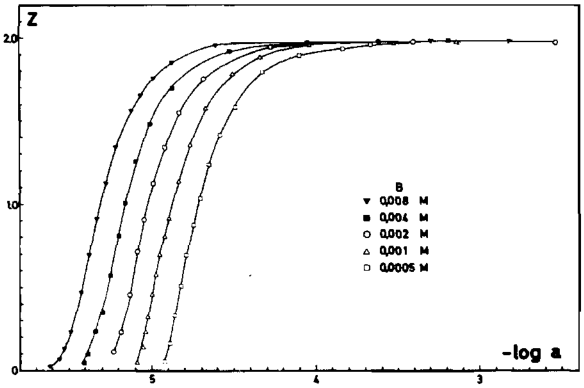


Figure 1. The formation curves of the system nickel(II) and 2-mercaptoethanol.

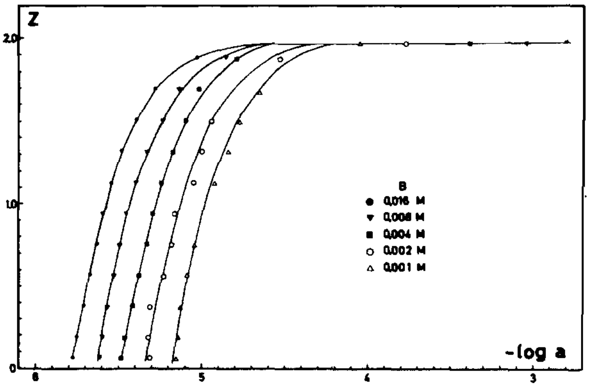


Figure 2: The formation curves of the system nickel(II) and 3-mercapto-1,2-propanediol.

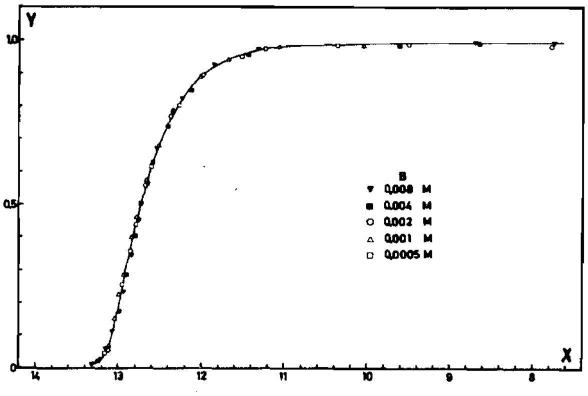


Figure 3. The Y. X curve of the system nickel(II) and 2-mercaptoethanol.

---

(8) Bates R.G., Determination of pH, p. 76, Wiley, New York.
(9) Sillén L.G., *Acta Chem. Scand.*, *8*, 299 (1954).
(10) Sillén L.G., *Acta Chem. Scand.*, *8*, 318 (1954).
(11) B.edermann G. and Sillén L.G., *Acta Chem. Scand.*, *10*, 1011 (1956).
(12) Thiers G.F., Van Poucke L.C., and Herman M.A., *J. Inorg. Nucl. Chem.*, *30*, 1543 (1968).

curves must coincide because both y and x are functions of the same variable u. In Figures 3 and 4 the y(x) curves are shown. Over the whole range this condition has been fulfilled. It can also be seen that y tends to the limit value 1. So all complexes could be represented by the general formula $B(A_2B)_n$, with n very great.

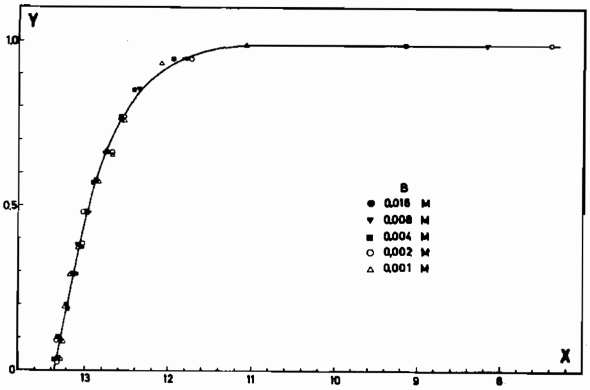


Figure 4. The Y, X curve of the system nickel(II) and 3-mercapto-1,2-propanediol.

Indeed, from[8]

$$y_{max}=\frac{Z_{max}}{t}=1-\frac{1}{n_{max}+1} \qquad (4)$$

it can be seen that if $n_{max}$ tends to infinity the limit value of y is 1.

Of course, for great values of n, the accuracy of the value of $y_{max}$ is too small for the exact determination of $n_{max}$. Thus exact determination of $n_{max}$ is impossible in this way. The only thing we can say is that the n value is very high and thus the complex is a polymer. A test for the proposed formula is the calculation of n, the average number of links in the "core + links" complex. $\bar{n}$ is calculated from the equation:

$$\bar{n}=\frac{y}{1-y-F^{-1}} \qquad (5)$$

where F is given by equation(6):

$$\log F=0.434y+\int_{-\infty}^{x} y\ dx \qquad (6)$$

The results are given in Table I. It can be seen that $\bar{n}$ tends to very large values.

Concerning the great number of complexes present no mathematical method would be able to calculate all stability constants. A certain representation of the reaction mechanism, giving an idea of the values of the stability constants was formulated by Sillén[9]. It is based on the hypothesis that all complexes of the "core + links" system are present in solution and that the addition of a new link can be represented in function of the addition of an earlier one. The system is assumed to be determined by two constants: $k_o$ and k. The first, $k_o$, gives the facility of the formation of the first complex of the "core + links" series, and determines the shape of the formation curve. The second, k, is a measure of the facility of adding a new link and determines the shift of the formation curve. By means of these two parameters all stability constants can be calculated.

**Table I.**

| MEL |  | MPD |  |
|---|---|---|---|
| y | $\bar{n}$ | y | $\bar{n}$ |
| 0.03 | 6.32 | 0.21 | 21.06 |
| 0.185 | 7.96 | 0.45 | 19.00 |
| 0.425 | 12.13 | 0.63 | 22.68 |
| 0.525 | 14.20 | 0.745 | 22.52 |
| 0.610 | 16.48 | 0.83 | 29.37 |
| 0.745 | 25.41 | 0.885 | 35.88 |
| 0.835 | 38.31 | 0.92 | 40.96 |
| 0.895 | 62.07 | 0.945 | 51.11 |
| 0.93 | 74.23 | 0.965 | 80.77 |
| 0.95 | 71.27 | 0.97 | 83.30 |
| 0.96 | 87.56 | 0.975 | 93.75 |
| 0.965 | 81.42 | 0.98 | 116.64 |

Three types of hypothesis can be chosen:

*a*) All links are added with the same facility

$K_n=k_ok^n \qquad K_{n+1}\,.\,K_n^{-1}=k$

*b*) The first links are somewhat more easily added.

$K_n=nk_ok^n \qquad K_{n+1}\,.\,K_n^{-1}=k(1+n^{-1})$

*c*) The higher complexes are formed with greater difficulty.

$K_n=\frac{k_ok^n}{n!} \qquad K_{n+1}\,.\,K_n^{-1}=k(1+n)^{-1}$

Calculating theoretical curves and fitting them with the experimental data yields the two parameters $k_o$ and k. Both fitted with hypothesis *a*. The results are given in Table II.

All stability constants can be calculated by equation(7)

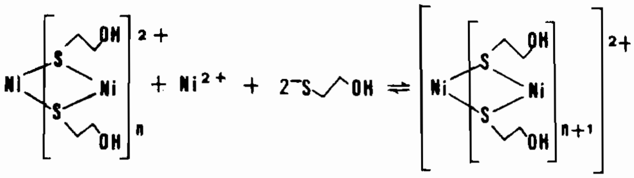
$$\log K_n=\log k_o+n\log k. \qquad (7)$$

**Table II.**

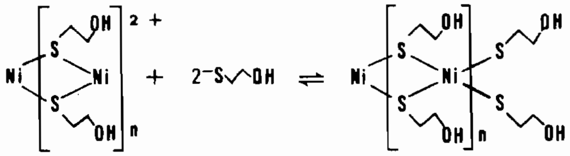
|  | MEL | MPD |
|---|---|---|
| $k_o$ | 0.005 | 0.01 |
| log k | 13.031 | 13.25 |

## Discussion

All authors agree on one thing: nickel forms with mercaptide ions complexes with metal-ligand ratio equal to 1/2. This is again confirmed by the formation curves of Figure 1 and Figure 2. However there are two ways to reach a ratio 1/2, nl. $B(BA_2)_n$ with a high value for n and $BA_2$. According to Sillén's theory a hexomeric complex $(BA_2)_6$ can be considered as a "core + links" system $B(B_1A_{2,4})_5$. In the case of a complex $B(BA_2)_n$ t is equal to 2. A difference of 0.4 for the value of t should correspond with a systematic error of at least 0.12 pH units, what is unacceptable. So one can reject the presence of the hexameric complex in that region where the conditions of the "core + links" hypothesis are fulfilled. Moreover, calculating n for that region, values which are much greater than six are obtained. The final reaction product must be a mixture of polymeric complexes of the general formula $B(BA_2)_n$ or $(BA_2)_n$ with an $n_{max}$ value 50. The reaction mechanism can be represented as follows:



At a high excess of the ligand, a following reaction mechanism is not impossible.



The final complex is uncharged and this is in agreement with the experimental fact that at a high excess of the ligand the $Ni^{II}$ complex of 2-mercaptoethanol is precipitated.

(13) Vogel A.I., « A textbook of quantitative Inorganic Analysis » Longmans, Green and Co, London.