

COMPLEXES OF MERCAPTOETHYLAMINETRIACETIC ACID IN SOLUTION*

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The complexes of mercaptoethylaminetriacetic acid with 24 cations of the transition and non-transition metals were studied in aqueous solution. The composition, the stability constants and the electronic spectra of these complexes were determined by potentiometric, polarographic and spectrophotometric methods. The stability constant trends and the interpretation of the electronic spectra have enabled certain conclusions concerning the molecular structure of the studied complexes to be drawn. Depending on the kind of central atom, the ligand behaves as tetradentate (through three carboxyls and the nitrogen with Mg, Ca, Sr, Ba, V^{2+} , Cr, Mn^{2+} , Sc, Y, lanthanoids) or pentadentate (three carboxyls, sulphur and nitrogen with Co, Ni, Cu, Pb). Water molecules complete the coordination sphere of the metal to form a distorted octahedral configuration.

The preparation and acid-base behaviour of mercaptoethylaminetriacetic acid, $HOOCCH_2SCH_2CH_2N(CH_2COOH)_2 = H_3M$, were studied in a previous paper in this series¹. The ligand, as a structural analogue of ethylenediaminetetraacetic acid, can exhibit specific complexation ability towards certain cations, both from the point of view of the kind of donor atoms and because of their advantageous steric arrangement. Therefore, the topic of the present paper is the determination of the behaviour of the ligand towards various types of metal cations in aqueous solutions, thus completing the older qualitative data cited in the previous paper¹.

EXPERIMENTAL

Chemicals and Instruments

The preparation of H_3M has been described in a previous communication in this series¹. Solutions of metal perchlorates were prepared by dissolution of the metal oxides, hydroxides or carbonates in a slight excess of dilute perchloric acid. Ferrous perchlorate was prepared by reaction of ferrous sulphate with the equivalent amount of a barium perchlorate solution in an inert atmosphere and by filtration. Crystalline sulphates $VSO_4 \cdot 7 H_2O$ and $CrSO_4 \cdot 5 H_2O$ were obtained by electrolytic reduction of $VOSO_4$ and $Cr_2(SO_4)_3$ solutions on a mercury cathode and by crystallization from aqueous ethanol in the absence of air. Other chemicals employed were *p.a.* substances from the firms Lachema and Merck.

* Part III in the series Compounds Structurally Related to Complexone; Part II: This Journal 39, 2724 (1974).

The instrumentation is largely described in the first paper in this series². Polarographic measurements were carried out on a Radiometer PO-4 instrument with a dropping mercury electrode. The mercury drop constants in a medium of 0.1M-NaClO₄ + 0.005% gelatine were $m = 2.45 \text{ mg s}^{-1}$; $t = 3.85 \text{ s}$. The potentiometric and polarographic measurements were performed at $25 \pm 0.1^\circ\text{C}$ and spectrophotometric measurements at $25 \pm 1^\circ\text{C}$. The calculations were carried out on an IBM 370/135 computer.

Analytical Methods

The ligand concentration in the stock solutions was determined alkalimetrically and bromometrically¹. The perchlorate solutions were analyzed for their metal contents using standard complexometric and gravimetric methods. The concentration of excess perchloric acid in these solutions was determined by the Gran method³.

The Composition of the Complexes

The composition of the complexes was determined spectrophotometrically employing the Job method. Suitable wavelengths were found from orientative measurements of changes in the metal ion spectra on addition of excess ligand (or *vice versa*) in an acetate buffer medium of pH 5.

Determination of the Stability Constants

A) *Analysis of titration curves.* Solutions containing $4 \cdot 10^{-3}\text{M-H}_3\text{M}$ and various concentrations of metal perchlorates ($1 \cdot 10^{-3}$ to $8 \cdot 10^{-3}\text{M}$) in 0.1M-NaClO₄ were titrated with a 0.1M carbonate-free sodium hydroxide standard solution in a pure nitrogen atmosphere. The pH values were measured with a precision of ± 0.01 pH unit and the titration curves were always reproduced at least twice, with a maximum deviation of 0.03 pH units. With divalent chromium the titration curves were measured point-by-point by preparing solutions containing all the component except chromium(II) sulphate and various amounts of sodium hydroxide, to which the chromium(II) salt was added immediately before the measurement. The pH values became stable within 1–2 minutes and after c. 5 min a decrease occurred due to reduction of water by the chromium(II) complex.

During data treatment, the titration curves were first recalculated to give the \bar{n} vs $-\log [M^{3-}]$ function using the program of Romary, Donnelly and Andrews⁴. This function served as a check on whether mononuclear complexes only are formed in the solution⁵ and for preliminary estimation of the stability constants. These rough values were then refined using the statistical SCOGS program⁶, taking into account mixed protonized complexes whenever their existence was indicated during the calculation.

B) *Redox potential measurement.* Solutions containing equimolar concentrations of divalent and trivalent cations of a transition metal (always $1 \cdot 10^{-3}\text{M}$) and excess ligand were brought to a desired pH using HClO₄ or NaOH solutions. The potential was measured in a cell without liquid junction consisting of a bright platinum-silver

chloride electrode pair. The background electrolyte had the composition (0.018M-Na₃M + 0.01M-NaCl). In the calculation of the stability constant for the oxidized form of a complex, the stability constant of the reduced form (known from the titration curves) and the redox potential value (extrapolated to 1M ligand concentration) were employed, in the pH region in which the redox potential was independent of the pH. The Peters formula then assumes the form

$$E = E'_0 + \frac{RT}{nF} \ln \frac{[\text{Me}^{\text{III}}\text{M}]}{[\text{Me}^{\text{II}}\text{M}^-]} + \frac{RT}{nF} \ln \frac{\beta_{\text{Me}^{\text{II}}\text{M}^-}}{\beta_{\text{Me}^{\text{III}}\text{M}}},$$

where E'_0 is the formal redox potential for the $\text{Me}^{3+}/\text{Me}^{2+}$ system under the given conditions, i.e. 25°C and $I = 0.1$ (ref.⁷).

C) *The shift in the half-wave potential during complex formation.* The method was applied to complexes CrM and CuM^- . Solutions containing $1 \cdot 10^{-3}\text{M}$ metal perchlorate and increasing concentrations of the ligand in an acetate buffer of pH 5 ($I = 0.1$) were, with chromium, first boiled for fifteen minutes and then allowed to equilibrate overnight. Then the polarographic waves corresponding to the reduction to CrM^- or to metallic copper were recorded. The waves were reversible and

TABLE I

The Conditions Under Which the Job Plots Were Obtained

Cation	Total concentration mol l ⁻¹	λ nm
V ²⁺	0.02	480
Cr ²⁺	0.02	640
Cr ³⁺	0.01	400, 575
Mn ²⁺	0.5	418
Mn ³⁺	0.002	470
Fe ²⁺	0.1	835, 1 120
Fe ³⁺	0.0001	270
Co ²⁺	0.005	260
	0.02	495
Ni ²⁺	0.001	247
	0.02	610
Cu ²⁺	0.0005	245
	0.01	780
Pb ²⁺	0.0002	250
Zn ²⁺	0.005	240
Cd ²⁺	0.005	240

were independent of the ligand concentration for all ligand to metal ratios higher than 1 : 1. From their half-wave potentials, shifted with respect to the $\text{Cr}^{3+}/\text{Cr}^{2+}$ and Cu^{2+}/Cu systems, the stability constants for the chromium(III) and copper(II) complexes were calculated in the usual way⁸. The waves of the cobalt(III) and iron(III) complexes were irreversible and the wave of the cobalt complex was, moreover, located at too positive a potential to be evaluated.

D) *Competition of metals in complexes.* In this method was utilized the fact that the CuM^- complex yields a polarographic wave that is readily distinguishable from the Cu^{2+} wave in an acetate buffer of pH 5 and $I = 0.1$. Solutions containing

TABLE II
The Stability Constants of the Complexes

Cation	Method, log β (3σ)			Residual ml
	β_1	β_1^{H}	β_2 [β_1^{OH}]	
Mg^{2+}	A 3.49 (0.10)	A 1.6 (0.6)		0.012
Ca^{2+}	A 4.56 (0.06)	A 1.75 (0.35)		0.013
Sr^{2+}	A 3.39 (0.09)	^a		0.028
Ba^{2+}	A 3.10 (0.02)	^a		0.015
Zn^{2+}	A 10.92 (0.02)	A 3.05 (0.07)		0.044
Cd^{2+}	A 9.25 (0.03)	A 2.93 (0.13)		0.061
Pb^{2+}	A 10.75 (0.05)	A 3.09 (0.23)		0.047
V^{2+}	A 7.21 (0.08)	A 1.7 (0.5)		0.081
Cr^{2+}	A 8.23 (0.05)	A 1.9 (0.5)		0.078
Cr^{3+}	C 12.0 (0.3)	A 3.08 (0.11) ^b	[A 6.12 (0.10) ^b]	
Mn^{2+}	A 6.71 (0.02)	A 1.52 (0.08)		0.016
Fe^{2+}	A 8.94 (0.03)	A 2.11 (0.18)		0.072
Fe^{3+}	B 13.3 (0.4)	A 3.02 (0.12) ^b	[A 7.01 (0.09) ^b]	
Co^{2+}	A 11.06 (0.03)	A 3.08 (0.09)		0.054
Co^{3+}	B 30.9 (0.4)	^a		
Ni^{2+}	D 13.07 (0.08)	A 3.14 (0.08) ^b		
Cu^{2+}	D 13.61 (0.07) ^c	A 3.79 (0.10) ^b		
	C 13.8 (0.3)			
Sc^{3+}	A 11.51 (0.13)	A 2.94 (0.21)	A 16.83 (0.19)	0.054
Y^{3+}	A 8.36 (0.02)	A 2.63 (0.17)	A 11.72 (0.08)	0.032
La^{3+}	A 7.59 (0.04)	A 2.60 (0.07)	A 11.31 (0.11)	0.045
Ce^{3+}	A 8.07 (0.02)	A 2.47 (0.05)	A 12.05 (0.06)	0.028
Pr^{3+}	A 8.14 (0.02)	A 2.53 (0.07)	A 12.14 (0.09)	0.037
Nd^{3+}	A 8.25 (0.04)	A 2.66 (0.10)	A 12.17 (0.15)	0.065

^a Unrecordable; ^b obtained from titration of MeM with perchloric acid or with sodium hydroxide; ^c competition with cobalt(II) cation.

TABLE III

The Electronic Spectra of the Complexes

Complex	Maximum, cm^{-1} (ϵ_M)	Assignment
VM^-	13 400 (28) 20 800 (37) 41 500 sh (220)	${}^4\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$ ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{2g}$ CT (ligand)
CrM^-	15 600 (35) 16 200 sh } 42 000 sh (250)	${}^5\text{T}_{2g} \leftarrow {}^5\text{E}_g$ CT (ligand)
CrM	17 400 (74) 25 200 (72) 42 000 sh (290)	${}^4\text{T}_{2g} \leftarrow {}^4\text{A}_{2g}$ ${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{2g}$ ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{A}_{2g} + \text{CT (ligand)}$
MnM^-	18 000 (0.11) 22 600 sh 24 100 (0.19) 26 900 (0.07)	${}^4\text{T}_{1g}(\text{G}) \leftarrow {}^6\text{A}_{1g}$ ${}^4\text{T}_{2g}(\text{G}) \leftarrow {}^6\text{A}_{1g}$ ${}^4\text{A}_{1g}, {}^4\text{E}_g(\text{G}) \leftarrow {}^6\text{A}_{1g}$ ${}^4\text{T}_{2g}(\text{D}) \leftarrow {}^6\text{A}_{1g}$
MnM	20 300 (420) 21 200 sh }	${}^5\text{T}_{2g} \leftarrow {}^5\text{E}_g$
FeM^-	8 620 (8.2) 11 800 (6.1) 41 500 (300)	${}^5\text{E}_g \leftarrow {}^5\text{T}_{2g}$ CT (ligand)
FeM	18 500 (6.6) 21 100 (11.7) 37 000 (5 800)	spin-forbidden transitions CT ligand \rightarrow metal
CoM^-	8 800 (9.5) 19 500 (26) 20 300 (27) 32 300 sh (600) 41 700 (850) }	${}^4\text{T}_{2g} \leftarrow {}^4\text{T}_{1g}(\text{F})$ ${}^4\text{A}_{2g} \leftarrow {}^4\text{T}_{1g}(\text{F})$ ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ CT (S \rightarrow Co) CT (ligand \rightarrow metal) + CT (ligand)
CoM	17 900 (330) 25 800 (300) 32 000 (850) 41 700 (17 100)	${}^1\text{T}_{1g} \leftarrow {}^1\text{A}_{1g}$ ${}^1\text{T}_{2g} \leftarrow {}^1\text{A}_{1g}$ CT (S \rightarrow Co) CT (ligand \rightarrow metal)

TABLE III
(Continued)

Complex	Maximum, cm^{-1} (ϵ_M)	Assignment
NiM^-	9 720 (28) 16 400 (11) 25 600 (25) 40 800 (1 700)	${}^3\text{T}_{2g} \leftarrow {}^3\text{A}_{2g}$ ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}$ ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}$ CT (ligand \rightarrow metal)
CuM^-	12 800 (44) composite 30 300 sh (430) } 41 600 (3 800) }	CT (S \rightarrow Cu) CT (ligand \rightarrow metal)
PbM^-	40 400 (7 800)	CT (ligand \rightarrow metal)

various concentrations of cupric perchlorate, the ligand and another metal perchlorate were prepared. Equilibrium was established in these solutions after several days (Co^{2+}) or weeks (Ni^{2+}) at 25°C . The Cu^{2+} and CuM^- waves were then recorded. From the heights of these waves the concentrations of all free and complex ions were calculated and, after correction for the presence of the acetate complexes⁹, the stability constants were obtained.

Electronic Spectra

Solutions for the measurement of electronic spectra were made from appropriate perchlorates, sulphates or acetates and the ligand at a pH and component concentration such that only a single complex was formed in the solution. These regions were apparent from the distribution diagrams calculated using the SCOGS program output. The solution of the cobalt(III) complex was prepared from $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ (ref.¹⁰) and that of the manganese(III) complex from manganese(III) acetate in a medium of 50% acetic acid (in water manganese(III) is instantaneously reduced to divalent manganese). The spectra were measured in a range of $5000\text{--}50000\text{ cm}^{-1}$.

RESULTS

The Composition of the Complexes

It has been found spectrophotometrically that only 1 : 1 complexes are formed at pH 5 with all cations exhibiting changes in the spectra on mixing with the ligand.

Table I specifies the wavelengths and concentrations at which the measurements were carried out. The values for Zn^{2+} and Cd^{2+} correspond to a decrease of the intensity of the ligand band at 240 nm.

The Stability Constants

Table II summarizes the determined stability constants. The values correspond to a temperature of 25°C and an ionic strength of 0.1 (mostly NaClO_4 except for method B, where the majority of the "inert salt" concentration consisted of Na_3M). The given errors represent 3σ . The stability constants are defined as follows (the charges have been omitted):

$$\beta_1 = \frac{[\text{MeM}]}{[\text{Me}][\text{M}]}, \quad \beta_2 = \frac{[\text{MeM}_2]}{[\text{Me}][\text{M}]^2}$$

$$\beta_1^{\text{H}} = \frac{[\text{MeHM}]}{[\text{Me}][\text{HM}]}, \quad \beta_1^{\text{OH}} = \frac{[\text{MeMOH}]}{[\text{MeM}][\text{OH}]}$$

Electronic Spectra

Maxima present in the electronic spectra of the complexes and their assignment are given in Table III. The other complexes studied exhibit spectra identical with the sum of the spectra of the metal cation and of the ligand, except for Zn^{2+} and Cd^{2+} , which decrease the intensity of the ligand band at 42000 cm^{-1} .

DISCUSSION

The main question in determining the kind of bonding in the studied complexes is determination of which ligand atoms are coordinated. From this point of view it is convenient to consider the ligand as substituted iminodiacetic acid of the $\text{R}-\text{N}(\text{CH}_2\text{COOH})_2$ type, where R is $-\text{CH}_2\text{CH}_2\text{SCH}_2\text{COOH}$. Substances of this type were described in detail by Schwarzenbach and coworkers¹¹. A number of conclusions concerning the ligand bonding to the metals studied can be drawn when the stability constants reported for some of these derivatives and corrected to 25°C are compared with those for the complexes of mercaptoethylaminetriacetic acid.

It is evident from the absolute stability constant values, which are much larger than with ligands containing only sulphur and carboxyl groups¹², that the stability is determined primarily by the "nitrogen terminal" of the ligand, $-\text{N}(\text{CH}_2\text{COO}^-)_2$. This group has always been found to be tridentate⁷. However, mercaptoethylaminetriacetic acid generally forms more stable complexes than N-alkyliminodiacetic acids¹¹; this increase in the stability is caused by coordination of the "sulphur

terminal", $-\text{SCH}_2\text{COO}^-$. It then becomes important to determine whether this part of the ligand is bound through sulphur alone, through the carboxyl group alone or through both of these functional groups. If the stability constants of the H_3M complexes are compared with those for similar types of complexes, the ligands of which contain only sulphur in the N-substituent (e.g. $\text{CH}_3\text{SCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2$), it can be seen that the general increase in the constants for H_3M indicates that the carboxyl from the $-\text{SCH}_2\text{COO}^-$ group is coordinated in all the studied systems. It is a greater problem to establish the degree to which coordination of sulphur participates in the bonding. No completely analogous ligand is known containing a methylene group instead of sulphur, but nitrilotriacetic acid can be used for the comparison. It can be assumed that, for uncoordinated sulphur, the lengthening of the aliphatic chain by three atoms will result in steric hindrance and the stability of the H_3M complexes will decrease compared with nitrilotriacetic acid. On the other hand, coordination of sulphur must lead to an increase in the stability, as the number of chelate rings increases. When the sulphur-metal interaction is weak, it can be expected that the two effects will compensate one another and it will be difficult to decide on the degree of sulphur coordination.

As has been found in the study of sulphur-containing complexes¹², the affinity towards sulphur is rather specific and the formation of a sulphur-metal bond is manifested not only by an increase in the complex stability, but also as a new charge-transfer band in the UV spectrum.

On the basis of all these criteria, the studied complexes can be divided into three groups according to the ligand-to-metal bonding:

1. Tetradentate ligand (ONO_2): Mg, Ca, Sr, Ba, V^{2+} , Cr, Mn^{2+} , Sc, Y, lanthanoids.
2. Pentadentate ligand (OSNO_2): Co, Ni, Cu, Pb.
3. The ligand-to-metal bonding type cannot be determined: Fe, Zn, Cd.

The trends of the stability constants in the alkaline earth metal series, the lanthanoids and the transition metals are similar to those common with complexone-type ligands. The small increase in the stability of the copper(II) complex compared with the nickel(II) complex is anomalous and worth attention; it can be explained by the low tendency of Cu^{2+} ions to form complexes with coordination numbers higher than 4, due to the Jahn-Teller effect. A similar phenomenon has also been encountered with EDTA and other polydentate ligands. The CuM^- complex probably contains one labile carboxyl-copper bond, since it is probable, by analogy with the structure of complexes of this type^{13,14}, that the sulphur and nitrogen atoms are bound in the equatorial plane of the coordination polyhedron. The weakening of the carboxyl-copper bond causes the proton in the CuHM complex to be significantly more strongly bound than in other species of this type.

The electronic spectra in the $d-d$ transition region can be evaluated using the

Tanabe-Sugano equations with most of the complexes, assuming pseudooctahedral symmetry, which is common with these ligands. In view of the number of metal-to-ligand bonds, additional coordination of 1–2 water molecules in the first coordination sphere must be considered. The Jahn-Teller distortion appears with the d^4 and d^9 configurations, where the spectra cannot be evaluated at all in octahedral symmetry. If the position of the centre of gravity of the composite band is only taken in account, it is not consistent with the spectra of other, less distorted complexes. The value of the Jørgensen parameter¹⁵, f , that characterizes the ligand position in the spectrochemical series, amounts to 1.10 ± 0.02 for most of the cations; for Cr^{2+} it equals 1.16 and for Cu^{2+} and Mn^{3+} , 0.98. The nephelauxetic ratio value was also essentially constant, $\beta = 0.78 \pm 0.03$, provided that it could be calculated from the spectrum.

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