chamber to prove that the α-activities present were AcX and its daughters and no others. The absence of RdAc α-particles was specifically verified. From these data, with proper allowance for the 1.2% α-branching[10,11] of Ac^{227} and for decay since time of separation, etc., it was possible to calculate the chemical yield of AcK. This yield was quantitative within the experimental error of 5%.

B. **Preparation of Fr^{221}.**—The 4.8 minute isotope of Fr^{221} may be isolated from its 10 day parent Ac^{225} which in turn is isolated from the decay products of U^{233} or is prepared by the cyclotron bombardment of thorium. The shortness of the half-life requires that the isolation procedure be as brief as possible. If one first carefully purifies the actinium parent, the number of possible contaminating radioactivities is quite limited and a single precipitation of silicotungstic acid and a single hydrochloric acid wash give a nearly quantitative separation of the Fr^{221} from its parent. If one can tolerate a small amount of inert solid matter in the final francium solution, the ethyl ether method of separating the bulk of the free silicotungstic acid may be used and the total elapsed time for the isolation of Fr^{221} can be cut to 10 minutes.

C. **Isolation of Radioisotopes of Cesium.**—The main defect of the silicotungstic acid method is that no separation of francium from fission product cesium is obtained. It might be hoped that some heteropoly acid could be found which would carry francium without also carrying cesium.

This quantitative coisolation of cesium, however, suggests that the method may have wide applicability in radiochemical and nuclear chemical studies involving the isotopes of cesium. With the exception of those applications in which the chemical yield must be determined by weighing a cesium compound, this new procedure would appear to be superior to any cesium radiochemical isolation procedure previously published. In particular in the study of cesium radioisotopes in a β-ray spectrometer or mass spectrograph where a weightless sample is desirable or absolutely essential, it should be particularly applicable. It might also prove useful as part of a procedure for the isolation of the valuable isotope, Cs^{137}, from aged fission product wastes.

(10) M. Perey, *J. chim. phys.*, **43**, 153, 269 (1946).

(11) S. Peterson and A. Ghiorso, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper 19.10 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).

Discussion

A word might be said concerning the coprecipitation behavior which forms the basis of the carrier-free method since at first sight it seems rather strange that a cation should coprecipitate so well with a free acid. It is felt that a reasonable explanation lies in the unusual isomorphism displayed by the salts of the heteropoly acids and the corresponding free acids. Borotungstic acid is isomorphous with ammonium borotungstate,[12] silicotungstic acid with lithium silicotungstate[13] and phosphotungstic acid with sodium phosphotungstate.[14] Even more surprising is the fact that the alkaline earth salts of some heteropoly acids are also isomorphous with the free acids.[15] With this isomorphism and the known low solubility of cesium silicotungstate, it is not surprising that trace amounts of francium and cesium coprecipitate so well with free silicotungstic acid. Presumably other ions such as Rb^+, Ba^{++} and Ra^{++} do not coprecipitate because of the higher solubility of the corresponding salts.

Other heteropoly acids may be substituted for silicotungstic acid but none of those so far studied in a preliminary way are to be preferred. Phosphotungstic acid, for example, will carry cesium from a concentrated hydrochloric acid solution.

(12) H. Copaux, *Bull. soc. chim. France*, **3**, 101 (1908) (IV).

(13) H. Copaux, *Bull. soc. franc. mineral.*, **29**, 77 (1906).

(14) M. Sobolew, *Z. anorg. Chem.*, **12**, 16 (1896).

(15) W. Hückel, "Structural Chemistry of Inorganic Compounds," Elsevier Publishing Co., Inc., Amsterdam, 1950, p. 185.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. LOUIS UNIVERSITY]

Metal–Amino Acid Complexes. II. Polarographic and Potentiometric Studies on Complex Formation between Copper(II) and Amino Acid Ion[1,2]

BY NORMAN C. LI[2a] AND EDWARD DOODY

RECEIVED DECEMBER 20, 1951

Polarographic studies on the copper(II) complexes of glutamate, phenylalaninate, threoninate, serinate, arginine and lysine are made and the stability of the complexes decreases in the order given. The ratio of amino acid to copper in each of the complexes is 2 to 1, and this ratio is in agreement with potentiometric data. Further potentiometric results are presented on interaction between copper(II) and serine, arginine hydrochloride, argininate, lysinate, biglutamate and methioninate. Interpretation of the results on the basis of the molecular structures of the amino acids is given.

As part of a general program on complex formation between metallic and amino acid ions, this paper presents the results on the glutamate, phenylalaninate, threoninate, serinate, arginine, lysine and methioninate complexes of copper(II), using the methods of polarography and potentiometry. Complex formation between copper(II) and the unsubstituted neutral amino acids, glycine and alanine, as well as an acidic amino acid, aspartic acid, have been investigated[2–4]; however, quantitative results on the nature and stability of the copper(II) complexes of the amino acids presented in this paper have not yet been reported in the literature. The ultimate purpose of this study is to facilitate the elucidation of the more complicated systems in which the heavy metal ions interact with proteins and enzymes, inasmuch as these substances are largely composed of amino acids.

Results

Reagent quality chemicals were used without further purification. The preparation and analyses of solutions, together with the apparatus

(1) This paper represents a part of the dissertation to be submitted by Brother Edward Doody to the Graduate School of St. Louis University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented in part before the 12th International Congress of Pure and Applied Chemistry, New York, September, 1951.

(2) Paper I in this series: N. C. Li and E. Doody, THIS JOURNAL, **72**, 1891 (1950).

(2a) Department of Chemistry, Duquesne University, Pittsburgh, 19, Pa.

(3) R. M. Keefer, THIS JOURNAL, **68**, 2329 (1946).

(4) H. A. Laitinen, E. I. Onstott, J. C. Bailar, Jr., and S. Swann, Jr., *ibid.*, **71**, 1550 (1949).

used for polarographic and potentiometric measurements, have already been described.[2] The polarographic half-wave potentials were reproducible to ±2 mv. The *p*H of the solutions used for the polarographic studies and for the determination of *pK* of the amino acids was obtained with a Leeds and Northrup *p*H meter, assembly number 7661, and the *p*H values were accurate to 0.02 *p*H unit.

The polarographic results for the phenylalaninate threoninate, serinate, arginine, lysine and glutamate complexes of copper(II) at 25.0° are listed in Table I. As a maximum suppressor we again used a mixture of methyl red (0.025%) and brom cresol green (0.12%) and we have put into solution a buffer in order to prevent the depletion of hydrogen ion concentration at the dropping electrode surface. All the complexes investigated are reduced directly to the amalgam and the electrode reactions are reversible as shown by the values of $(E_{3/4} - E_{1/4})$, where $E_{3/4}$ and $E_{1/4}$ are the values of $E_{d.e.}$ at $i = (3/4)i_d$ and $i = (1/4)\ i_d$, respectively. The methioninate complex of copper(II) was not determined polarographically because of the formation of a precipitate which interferes with the analyses.

TABLE I

HALF-WAVE POTENTIAL AS FUNCTION OF *p*H AND TEST FOR REVERSIBILITY OF ELECTRODE REACTIONS

Indifferent electrolyte 0.06 *M* KH_2PO_4 plus KOH; 5×10^{-4} *M* $Cu(NO_3)_2$; and 0.04 *M* solutions of:

*p*H	$-E_{1/2}$ *vs.* S.C.E.	$E_{3/4} - E_{1/4}$	*p*H	$-E_{1/2}$ *vs.* S.C.E.	$E_{3/4} - E_{1/4}$
(A) Potassium phenylalaninate			(B) Potassium threoninate		
6.92	0.204	0.030	6.99	0.214	0.031
7.04	.211	.030	7.09	.220	.032
7.28	.226	.032	7.35	.233	.033
7.39	.232	.033	7.74	.258	.032
7.85	.260	.033	8.28	.286	.031
			8.45	.297	.033
(C) Potassium serinate			(D) Arginine		
7.03	0.206	0.030			
7.08	.209	.032	6.97	0.185	0.031
7.45	.230	.034	7.04	.189	.031
7.88	.258	.034	7.20	.198	.030
			7.59	.219	.032
(E) Lysine			8.30	.264	.030
6.89	0.181	0.031			
7.02	.189	.028	(F) Potassium glutamate		
7.15	.194	.031			
7.33	.204	.028	7.02	0.192	0.030
7.41	.210	.031	7.16	.200	.028
8.51	.274	.029	7.60	.226	.033
			8.52	.280	.031
(G) Potassium glycinate					
7.08	0.193	0.033			
7.16	.198	.030			
7.37	.210	.029			
7.78	.234	.031			
8.57	.281	.029			

In most of the experiments reported in this paper, the hydrogen ion concentration of the solution is much greater than the dissociation constant, K_2, of the amino acid. In order to calculate the number of groups, p, coördinated to each copper(II) ion and the concentration dissociation constant, K_c, of the complex, therefore, we may use the equation given by Li and Doody[2] and by Laitinen, *et al.*[4] This equation may be rearranged to give

$$(E_{1/2})_c = p\ 0.0296(pK\text{-}p\text{H}) + 0.0296 \log k_c - p\ 0.0296 \log C_{AH} + (E_{1/2})_s \quad (1)$$

In this equation $(E_{1/2})_c$ is the half-wave potential of the complex metal ion; $(E_{1/2})_s$ is the half-wave potential of the simple copper(II) ion for which Laitinen and co-workers' value[4] of +0.016 v. was used; C_{AH} is the analytical concentration of the free amino acid and was obtained by subtracting the concentration of the amino acid combined with copper(II) ion (assumed CuA_2) from the total amino acid concentration in the solution. The apparent ionization constant, pK_2 (NH_3^+), of the amino acid was determined by a method similar to that described by Li and Doody,[2] and the values are listed in Table II. Values of pK_2 reported by Cohn and Edsall,[5] Keefer[3] and by Vestling and Warner[6] are included for reference. The agreement is excellent. An additional determination of the pK_2 of arginine was made by potentiometric *p*H titration of 0.100 *M* arginine monohydrochloride with 0.109 *M* KOH. The titration curve obtained is similar to that given by Birch and Harris[7] and the value of pK_2 corresponds exactly with the value given in Table II. A similar titration of lysine monohydrochloride with KOH gives no definite break in the curve and an estimate of pK_2 from the curve gives a value of 8.92, compared to value of 8.95 reported by Cohn and Edsall.[5]

TABLE II

CALCULATED CONSTANTS FOR THE AMINO ACIDS AND THEIR COMPLEXES

	pK_2	pK_2, previously reported	p	$K_c \times 10^{16}$
Phenylalanine	9.13	9.13 [5]	1.99	2.2
Threonine	9.00	9.00 [6]	1.99	2.9
Serine	9.14	9.15 [5]	1.99	2.9
Arginine	9.04	9.04 [5]	2.01	18
Lysine		8.95 [5]	2.01	25
Glutamic acid		9.67 [5]	2.00	0.72
Glycine		9.69 [3]	2.00	0.79

Since the dissociation of the NH_3^+ group in the amino acids studied is small it is evident from equation (1) that the half-wave potential of the complex metal ion is a linear function of $(pK_2 - p\text{H})$, with a slope of p 0.0296. Plots of $(pK_2 - p\text{H})$ *vs.* $E_{1/2}$ are shown in Fig. 1 and the values of p calculated from the slopes are given in Table II, column 4. The results show that for each of the amino acids studied, the formula of the complex is CuA_2. Again from equation (1) we see that by extending the linear plot in the region where $(pK_2 - p\text{H}) > 1.0$, to zero ordinate, where $(pK_2 - p\text{H}) = 0$, the limiting value of $(E_{1/2})_c$ becomes equal to 0.0296 log $K_c - p$ 0.0296 log $C_{AH} + (E_{1/2})_s$, from which the values of K_c, can be obtained. The dissociation constants thus obtained are listed in Table II.

In order to indicate the accuracy of this novel

(5) E. J. Cohn and J. T.-Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corp., New York, N. Y., 1943, pp. 84–85.

(6) C. S. Vestling and D. T. Warner, *J. Biol. Chem.*, **144**, 689 (1942).

(7) T. W. Birch and L. J. Harris, *Biochem. J.*, **24**, 570 (1930).

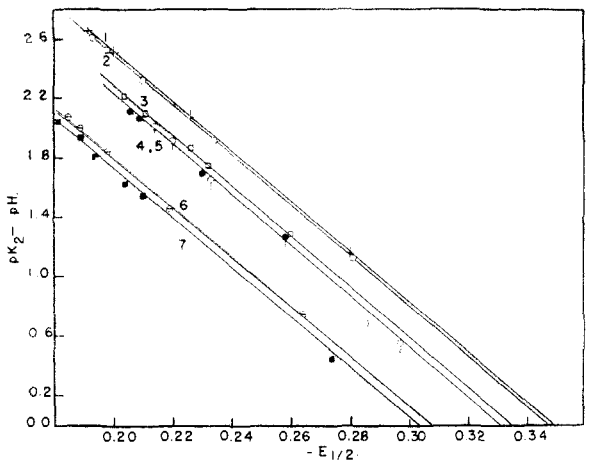


Fig. 1.—Change of half-wave potential with $(pK_2 - pH)$: 1, glutamate, +; 2, glycinate, O; 3, phenylalaninate, □; 4, threoninate, ♀; 5, serinate, ●; 6, arginine, ⊖; 7, lysine, ■.

method of calculating K_c, studies were made of the copper(II) glycinate complex and the results are included in Tables I and II and Fig. 1. The dissociation constant obtained, 7.9×10^{-16}, is in excellent agreement with the values 7.4 and 7.9×10^{-16}, respectively, reported by Keefer[3] and Laitinen and his co-workers.[4]

In a few experiments with lysine, we added hydrochloric acid purposely in order to decrease the pH of the solutions. The resulting half-wave potentials were decreased to values which fall on the $(pK_2 - pH)$ *vs.* $E_{1/2}$ plot for the lysine complex in Fig. 1. The change of half-wave potential with pH is thus a reversible phenomenon.

From Table II we see that the concentration dissociation constants of the copper(II) phenylalaninate, threoninate and serinate complexes are larger than that of the glycinate complex. The presence of the phenyl group in phenylalanine and the hydroxyl group in threonine and serine, both groups being electron-attracting, would be expected to increase the acid strength of the NH_3^+ group, as shown by the smaller pK_2 values of these three amino acids as compared to that of glycine. The basic strength, with its tendency to share its electron pair with a copper(II) ion in the formation of the chelate, of the amino group in the phenylalaninate, threoninate and serinate complexes is therefore decreased, with a consequent decrease in stability of the complexes. The threoninate and serinate complexes are slightly less stable than the phenylalaninate and the reason may lie in the tendency for intramolecular hydrogen bond formation between the hydroxyl and amino groups in threonine and serine, which must be in direct competition with the chelation of the amino group with the copper(II) ion. This additional factor in increasing the dissociation constant of the complex is absent in the phenylalaninate.

The structure of arginine, Ar^{+-}, may be written[8]

$$H_2N\text{-}C(=NH_2^+)\text{—}NH\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH(NH_2)\,COO^- \quad (2)$$

An examination of a model for arginine reveals that the long chain of the molecule may be folded in such a manner that the positively charged ($=NH_2^+$) group is adjacent to the α-amino. If the chelation with copper involves the carboxylate and the α-amino groups, as is generally assumed, the copper(II) cation is repelled by the adjacent positive charge, resulting in a lesser degree of complex formation. The larger value for the dissociation constant of the copper(II) arginine complex thus appears reasonable.

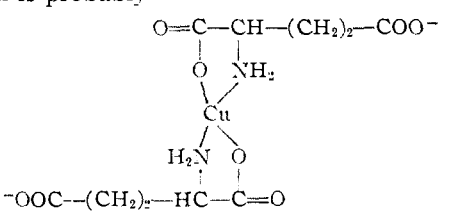
Among the amino acids investigated in this paper the lysine complex is the most unstable. Lysine may exist in the two dipolar isoelectric forms

$$H_3N\text{—}(CH_2)_4\text{—}CHNH_3^+\text{—}COO^- \quad (A)$$

$$^+H_3N\text{—}(CH_2)_4\text{—}CHNH_2\text{—}COO^- \quad (B)$$

and the ratio of A to B in solution is about 1 to 5.6, according to Cohn and Edsall.[8] Structure A, in which the α-amino group is absent, would be expected to contribute to the instability of the lysine complex.

A marked increase in the formation of complex of copper(II) with glutamate ion is observed. The complex is probably



(3)

If one considers the statistical effect of having two carboxylate groups in each glutamate ion available to the cation, one would expect the glutamate complex to be more stable than the glycinate. However chelation of copper(II) with the amino and the γ-carboxylate groups would introduce a seven-membered ring and the resulting decrease in stability somewhat nullifies the statistical effect. In the copper(II)-aspartate complex, investigated by Li and Doody,[2] chelation of copper with the amino and the β-carboxylate groups introduces a six-membered ring, so that the aspartate complex is more stable than the glutamate.

The potentiometric titration of serinate with copper is shown in Fig. 2, curve 1, and the ratio of serinate ion to copper, p, is 1.99. In a reverse titration of copper with serinate the same ratio was obtained. These results confirm the polarographic data on the formula of the complex.

The titration of serine, $CH_2OH\text{—}CHNH_3^+COO^-$, with copper, shown in Fig. 2, curve 3, shows no break in the curve. In this case the repulsion of the positively charged NH_3^+ to the copper(II) cation apparently overcomes the affinity of the carboxylate ion for the same cation. From an approximate calculation of the electrical repulsion effect, the serine complex should be very much less stable than the corresponding serinate complex, because additional electrical work is required to bring the copper(II) cation to the NH_3^+ group in serine, whereas no such work is required in the serinate. A complex does form between serine and copper, as evidenced by the deepening of color when solutions containing the two substances are mixed, but the complex is

(8) Reference 5, pp. 103, 104.

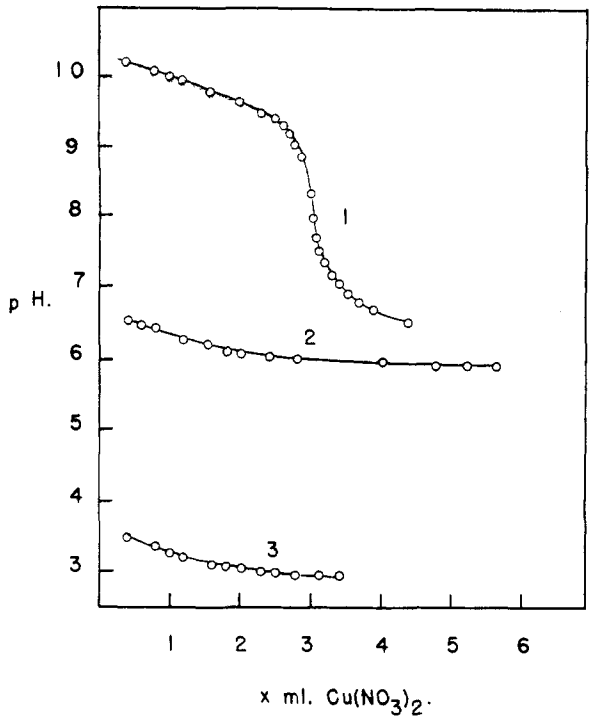


Fig. 2.—Potentiometric titration: curve 1, 22.5 ml. of 0.0333 *M* potassium serinate, dilute to 50 ml., plus *x* ml. of 0.1247 *M* $Cu(NO_3)_2$. p = 1.99; curve 2, 5 ml. of 0.100 *M* potassium acetate, diluted to 50 ml., plus *x* ml. of 0.1334 *M* $Cu(NO_3)_2$; curve 3, 15 ml. of serine 0.05 *M*. diluted to 50 ml., plus *x* ml. of 0.1247 *M* $Cu(NO_3)_2$.

not stable enough to be measured potentiometrically. In order to illustrate this point, we have plotted, in Fig. 2, curve 2, a titration curve of 0.010 *M* potassium acetate with copper(II). The dissociation constant of the $Cu^{++}(CH_3COO^-)$ complex has been reported[9] to be 6.8×10^{-3} and in the 0.010 *M* acetate solution the complex $CuAc^+$ predominates. A complex is present but it dissociates to too great an extent to give a break in the potentiometric titration curve.

The potentiometric titrations of arginine hydrochloride, arginine and argininate with copper are shown in Fig. 3, curves 1, 2, 3, respectively. No endpoint is observed when arginine hydrochloride is used and the reason is evident from the structure for this amino acid

$$H_2N{-}C(=NH_2^+){-}NH(CH_2)_3{-}CH(NH_3^+)COO^- \quad (4)$$

The discussion on the serine complex can be applied here; in this case the repulsion of the positively charged NH_3^+ to the copper(II) cation is enhanced by the positively charged ($=NH_2^+$) group.

The results of potentiometric titrations show that the arginine and argininate complexes are, respectively, $Cu^{++}(Ar^{+-})_2$ and $Cu^{++}(Ar^-)$. The formula of the arginine complex confirms the polarographic data. The argininate complex is not observed polarographically because of the pH range used. At higher pH values the electrode reactions are not reversible.

(9) K. J. Pederson, *Kgl. Danske Videnskab. Selskab., Mat.-fys. Medd.*, **22**, No. 12 (1945). Ref. given by I. M. Klotz, I. L. Faller and J. M. Urquhart, *J. Phys. Colloid Chem.*, **54**, 18 (1950).

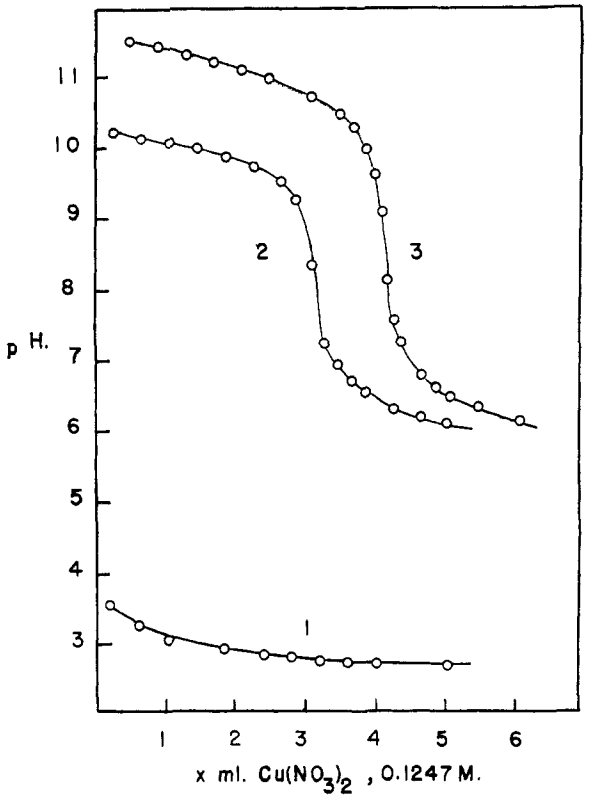


Fig. 3.—Potentiometric titration: curve 1, 7.5 ml. of 0.100 *M* arginine hydrochloride, diluted to 50 ml., plus *x* ml. of $Cu(NO_3)_2$; curve 2, 15 ml. of 0.050 *M* arginine, diluted to 50 ml., plus *x* ml. of $Cu(NO_3)_2$, p = 1.99; curve 3, 10 ml. of 0.050 *M* potassium argininate, diluted to 50 ml., plus *x* ml. of $Cu(NO_3)_2$, p = 1.00.

The potentiometric titration curve of biglutamate, $^-OOC{-}CH{-}NH_3^+(CH_2)_2{-}COO^-$, with copper is similar to that of serine with copper, which is shown in Fig. 2, curve 3. No break is observed and this is as expected due to the presence of the NH_3^+ in the biglutamate.

Potentiometric titration curves for the other amino acid complexes are too numerous to include in this paper. Table III gives the ratio of amino acid ions to copper for the remaining complexes.

TABLE III

POTENTIOMETRIC STUDIES OF RATIOS OF AMINO ACID IONS TO COPPER

$Cu(NO_3)_2$ added to phenylalaninate	2.18[a]
$Cu(NO_3)_2$ added to threoninate	2.18
Threoninate added to $Cu(NO_3)_2$	2.10
$Cu(NO_3)_2$ added to lysine	2.02
$Cu(NO_3)_2$ added to lysinate	1.00
Glutamate added to $Cu(NO_3)_2$	1.98
Methioninate added to $Cu(NO_3)_2$	2.13[a]

[a] Precipitate formed during titration.

With the exception of the lysinate and methioninate which were not studied polarographically, the ratio obtained for the other complexes listed in Table III agrees with that found from polarography. It is interesting to note that the ratios found for the lysine and lysinate complexes from potentiometric studies correspond to those found

for the arginine and argininate complexes, respectively.

Acknowledgment.—The authors wish to express their gratitude to Merck & Co., Inc., for supplying the amino acids used in this research.

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND ORGANIC CHEMISTRY, UNIVERSITY OF SYDNEY]

Sexadentate Chelate Compounds. III[1]

BY FRANCIS P. DWYER, NAIDA S. GILL,[2] ELEONORA C. GYARFAS[2] AND FRANCIS LIONS

RECEIVED OCTOBER 23, 1951

A series of sulfur-containing α,ω-diamines of the general formula $NH_2\cdot(CH_2)_x\cdot S\cdot(CH_2)_y\cdot S\cdot(CH_2)_z\cdot NH_2$, where x, y and z have values of 2 or 3, has been prepared and the bases condensed with salicylaldehyde or 2-hydroxy-1-naphthaldehyde. The resultant Schiff bases behave as sexadentate chelate compounds and can occupy all six coördination positions about a cobalt(III) ion. For certain of them no less than four different unsymmetrical spatial arrangements of the chelate moiety about the central cobalt atom are possible (two pairs of enantiomers) and this capacity has been correlated with the structure of the chelate. Most of the complex salts prepared have been resolved into optical isomers, and the molecular rotations of some of these are extremely high, one of them possessing the highest molecular rotation so far recorded.

The amine groups and the sulfur atoms in diamines of the general formula $NH_2\cdot(CH_2)_x\cdot S\cdot(CH_2)_y\cdot S\cdot(CH_2)_z\cdot NH_2$, where x, y and z have values of two or three, are separated by ethylene or trimethylene bridges; and a convenient nomenclature distinguishing between them designates them simply by a combination of the letters E and T (representing the ethylene or trimethylene bridges). Thus, the base 1,8-diamino-3,6-dithia-octane ($x = y = z = 2$), the metallic derivatives of whose bis-salicylidene and bis-(2-hydroxy-1-naphthylmethylene) condensation products were discussed in Part I,[3] would be designated EEE; 1,9-diamino-3,7-dithianonane ($x, z = 2$; $y = 3$) would be ETE; 1,10-diamino-4,7-dithiadecane ($x, z = 3$; $y = 2$) would be TET, and so on. This paper describes the preparation of sexadentate chelate compounds by condensation of the symmetrical bases ETE, TET and TTT with salicylaldehyde or 2-hydroxy-1-naphthaldehyde and their coördination with cobalt(III) ions. Discussion of the compounds derived from the unsymmetrical bases EET and ETT is reserved for a later paper.

The bases ETE, TET and TTT were prepared by methods exactly similar to that already described[3] for EEE, the appropriate ω-bromo-alkylphthalimide (2 moles) being condensed in alkaline absolute ethanolic solution with the requisite α,ω-dithiol paraffin to the bis-phthalimido derivative of the base, and this being then hydrolyzed by the method of Ing and Manske.[4]

Loss of two protons from a molecule of such a Schiff base as the bis-salicylidene derivative of any one of the bases EEE, ETE, TET or TTT and union of the residue with a cobalt(III) ion leads to formation of a complex ion in which the organic residue is attached through the oxygen, nitrogen and sulfur atoms to the central cobalt atom. The organic residue is thus attached to the metal atom in five successive "chelate loops," and the complex ion may be very clearly formulated in a two-dimensional diagram such as I, the successive chelate loops being numbered from 1 up to 5.

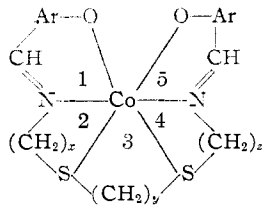


Fig. 1.—I.

Now, it was pointed out in Part I[3] that in the 1,8-bis-(*o*-hydroxyarylideneamino)-3,6-dithiaoctane cobalt(III) salts (from EEE base) the spatial requirements of the sulfur and nitrogen atoms demand a planar arrangement of each of the oxygen–nitrogen–sulfur atom sequences, starting from each end of the sexadentate moiety; and probably, also, substantially, of the 1,2- and 4,5-chelate loops containing them. Lengthening of the chain of carbon atoms between the two sulfur atoms from 2 to 3 (ETE base) would convert chelate loop 3 from a five-membered ring to a six-membered ring but would not be expected to produce any great effect other than, perhaps, some symmetrical buckling in the chelate loop 3; although it should be remembered that coördination compounds derived from the dialkyl ethers of 1,2-dithiol ethane are considerably more stable with their five-membered chelate ring than are any coördination compounds derived from the ethers of α,ω-dithiol paraffins in which the polymethylene chain between the sulfur atoms is longer than ethylene.[5]

In fact, experiment showed that the Schiff bases from ETE behaved normally, or, rather, similarly to those derived from EEE base, yielding characteristic green binary complex cobalt(III) salts comparable to the analogous ones derived from EEE base and capable of resolution into dextro and levo forms.

On the other hand, in the complexes derived from TET and TTT, expansion of the five-membered sulfur- and nitrogen-containing chelate loops 2 and 4 to six-membered chelate loops might be expected to present difficulties in the way of maintenance of

(1) For the previous communication in this series see F. P. Dwyer, F. Lions and D. P. Mellor, THIS JOURNAL, **72**, 5037 (1950).

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