where M = Ni, $n = 4$; M = Fe, $n = 5$; M = Mo, $n = 6$.

The Mössbauer spectrum of the iron complex $Fe(CO)_3$(bicars) has provided some information about the electronic properties of this new ligand. The isomer shift of +0.18 mm/sec is typical of low-valent iron species. The strongly electron-donating properties of the ligand are reflected in the negative shift compared to $Fe(CO)_5$.[12] The isomer shift of $Fe(CO)_3$(bicars), +0.18 mm/sec, compares favorably with the value of +0.16 mm/sec[13] reported for $((C_6H_5)_3P)_2Fe(CO)_3$,[14] which suggests that these two ligands may be similar in their bonding properties.

The complex $Ni(CO)_2$(bicars) exhibits two strong infrared absorptions which may be easily attributed to the carbonyl stretching modes at 2027 and 1968 cm^{-1}. These frequencies are about 20–30 cm^{-1} higher than those for the comparable complex containing diarsine as a ligand, $Ni(CO)_2[o\text{-}C_6H_4(As(CH_3)_2)_2]$. This suggests that the ligand containing the carborane framework may back-accept electron density to a greater extent that the more conventional arsine ligand. A similar observation about phosphine ligands has also been mentioned by Rohrscheid and Holm.[2]

It is interesting to note that the Mössbauer and ir data confirm the fact that *o*-carborane possesses the ability to serve as both electron donor and acceptor, already chemically established.[15]

The ^{11}B nmr spectrum of the ligand bicars may be explained in terms of selective overlapping of the expected four doublets.[16,17] The higher degree of resolution in the ^{11}B spectrum of bicars over that of *o*-carborane[18] suggests an increased differentiation in the types of borons in the molecule. This change in environment about the carbon atoms may be due to the presence of the $As(CH_3)_2$ groups.

In addition to the position of carbonyl absorptions, the number of absorptions also adumbrates steric properties of the ligand bicars. Group theory suggests that the C_{2v} octahedral complex containing four carbonyl groups and a bidentate ligand, for example, $Mo(CO)_4[o\text{-}C_6H_4(AsCH_3)_2]$, should exhibit four infrared-active carbonyl vibrations. This has been observed by Nyholm.[19] If the ligand would cause the octahedral complex to be distorted to C_{4v} symmetry with the four carbonyl groups occupying the same plane, four carbonyl absorptions would still be expected. If the distortion were less than above, but still significant, the distorted octahedron thus produced would show seven infrared-active absorptions ($3A_1 + 2B_1 + 2B_2$). The complex $Mo(CO)_4$(bicars) does indeed show seven bands attributable to carbonyl absorptions at 2020, 2015 (sh), 1994, 1953, 1946, 1940, and 1875 cm^{-1}, suggesting that a distortion of this type may occur. The complex $Fe(CO)_3$(bicars) also exhibits five rather than the four infrared bands expected in the carbonyl region for C_{3v} symmetry ($2A_1 + 2E$). This increase in the number of bands may also reflect a distortion of some type which lowers the symmetry of the complex.

We are currently employing epr data in conjunction with Mössbauer information in order to elucidate more fully the nature of the electronic properties of the ligand in some selected iron complexes. The results of this work will be published in the future.

Acknowledgment.—Generous support of this work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. The authors wish to thank Dr. P. G. Rasmussen of the University of Michigan for obtaining the Mössbauer spectrum. The authors also are deeply indebted to Mr. F. Parker and Dr. R. W. Parry of the University of Michigan for obtaining the ^{11}B nmr spectrum. We also appreciate the many helpful discussions with Mr. R. Sterry, Monmouth College.

---

[12] L. M. Epstein, *J. Chem. Phys.*, **36**, 2731 (1962).

[13] This value was obtained by correcting the value cited for the difference in standard employed.

[14] R. L. Collins and R. Pettit, *J. Am. Chem. Soc.*, **85**, 2332 (1963).

[15] M. F. Hawthorne, T. E. Berry, and P. A. Wegner, *ibid.*, **87**, 4746 (1968).

[16] R. L. Piling, F. N. Tebbe, M. F. Hawthorne, and E. A. Pier, *Proc. Chem. Soc.*, 402 (1964).

[17] G. D. Vickers, H. Agahigian, E. A. Pier, and H. Schroeder, *Inorg. Chem.*, **5**, 693 (1966).

[18] H. Schroeder, T. L. Heying, and J. B. Reines, *ibid.*, **2**, 1092 (1965).

[19] C. C. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2582 (1961).

Contribution from the Department of Chemistry,
State University of New York at Buffalo,
Buffalo, New York 14214

Thermodynamics of Ion Association. XVIII. Copper Complexes of Tetraglycine[1]

By G. H. Nancollas and D. J. Poulton

Received July 22, 1968

Recently,[2] a potentiometric and calorimetric study was made of copper diglycine and triglycine complexes, systems of particular interest because of their biological importance in enzyme reactions.

In solutions of higher pH, evidence for multichelated structures similar to those in the solid state[3–6] has usually been based upon the results of potentiometric, kinetic, and spectral measurements.[7–12] At lower pH

---

[1] Supported by National Science Foundation Grant No. GP-6042.

[2] A. P. Brunetti, M. C. Lim, and G. H. Nancollas, *J. Am. Chem. Soc.*, **90**, 5120 (1968).

[3] H. C. Freeman, J. C. Schoone, and J. G. Sime, *Acta Cryst.*, **18**, 381 (1965).

[4] H. C. Freeman, G. Robinson, and J. C. Schoone, *ibid.*, **17**, 719 (1964).

[5] B. Strandberg, I. Linqvist, and R. Rosenstein, *Z. Krist.*, **116**, 266 (1961).

[6] H. C. Freeman, "The Biochemistry of Copper," J. Peisack, P. Aisen, and W. E. Blumberg, Ed., Academic Press, New York, N. Y., 1966, p 77.

[7] S. P. Datta and B. R. Rabin, *Trans. Faraday Soc.*, **52**, 1123 (1956).

[8] B. R. Rabin, *Trans. Faraday Soc.*, **52**, 1130 (1956).

[9] C. B. Murphy and A. E. Martell, *J. Biol. Chem.*, **226**, 37 (1957).

[10] M. K. Kim and A. E. Martell, *J. Am. Chem. Soc.*, **85**, 3080 (1963).

[11] M. K. Kim and A. E. Martell, *Biochemistry*, **3**, 1169 (1964).

[12] M. K. Kim and A. E. Martell, *J. Am. Chem. Soc.*, **88**, 914 (1966).

and prior to peptide proton elimination, however, there has been a considerable amount of discussion concerning the nature of the ligand atoms bound to the metal. From studies of the effects of substituents upon the stabilities of a number of copper peptide complexes, Rabin[8] has proposed the nonparticipation of the peptide nitrogen atoms under such conditions. The results of previous di- and triglycine studies add strong support to this suggestion.[2] In the present work thermodynamic functions have been obtained for the corresponding copper tetraglycine species in order to provide more information concerning their structures in solution.

Experimental Section

The preparation of materials and experimental techniques have been described previously.[2] Tetraglycine obtained from Nutritional Biochemicals Corp. was used without further purification. Solutions of 1–5 × 10^{-3} M tetraglycine with or without an equimolar quantity of copper perchlorate were titrated potentiometrically and calorimetrically at 25 ± 0.02° with carbonate-free sodium hydroxide. Additional calorimetric titrations were made by adding perchloric acid to a mixture of tetraglycine, copper perchlorate, and sodium hydroxide.

Results and Discussion

Equilibria in the tetraglycine solutions may be represented by the reactions

$$H_2GGGG^+ \rightleftharpoons H^+ + HGGGG^{\pm} \qquad k_1 \qquad (1)$$

$$HGGGG^{\pm} \rightleftharpoons H^+ + GGGG^- \qquad k_2 \qquad (2)$$

$$Cu^{2+} + GGGG^- \rightleftharpoons CuGGGG^+ \qquad K_1 \qquad (3)$$

$$CuGGGG^+ \rightleftharpoons CuA + H^+ \qquad k'_a \qquad (4)$$

$$CuA \rightleftharpoons CuB^- + H^+ \qquad k'_b \qquad (5)$$

$$CuB^- \rightleftharpoons CuC^{2-} + H^+ \qquad k'_c \qquad (6)$$

In these equations, CuA, $CuB,^-$ and CuC^{2-} represent the successively deprotonated complexes of Cu^{2+} and the tetraglycine anion, $GGGG^-$ ($GGGG^- = HA^- = H_2B^- = H_3C^-$).

Thermodynamic functions were first determined for reactions 1 and 2 at a constant ionic strength, I = 0.10 M. Concentrations of ionic species were calculated in the usual way from potentiometric data,[13] and dissociation constants representing the results of at least 30 titration points are given in Table I together with the standard deviations; the agreement with literature data[12,14] is seen to be good.

TABLE I

DISSOCIATION CONSTANTS OF TETRAGLYCINE AT 25°

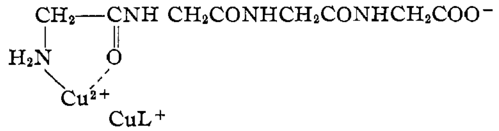
Temp, °C	I, M	pk_1	pk_2	Ref
25.0	0.10	3.17 ± 0.03	7.88 ± 0.02	This work
24.9	0.10 (KNO_3)	3.24	7.89	12
25	0.16	3.25	7.98	14

Potentiometric titrations in the presence of copper ions yielded the equilibrium constants given in Table II. In view of the different experimental conditions used, the agreement between the different sets of results is very satisfactory.

Calorimetric titrations were made by the addition of perchloric acid to solutions containing 1:1 mixtures of copper perchlorate and tetraglycine at a concentration of 2–4 × 10^{-3} M and sodium perchlorate at a total ionic strength of 0.10 M. The heats of ionization of tetraglycine were obtained by adding perchloric acid (for the first ionization) or sodium hydroxide (for the second ionization) to solutions of 3–6 × 10^{-3} M tetraglycine containing sodium perchlorate at an ionic strength of 0.10 M. The separation of the experimental heat changes, Q_{exptl}, into heats for the various reactions in the copper–tetraglycine system was not as simple as for the di- and triglycines owing to the fact that several reactions occur simultaneously. It was possible to obtain Q_6 for reaction 6 directly as this reaction predominates at a somewhat higher pH (8.5–10) than the other three reactions (pH 5–8). Thus ΔH_6 was calculated from $\Delta H_6 = Q_6/\Delta[CuC^{2-}]$, and its contribution in the lower pH range was subtracted from the experimental heat change.

Enthalpy changes for reactions 3–5 were obtained by a reiterative procedure involving a graphical solution, and thermodynamic functions are given Table III. The larger uncertainties in the experimental enthalpy changes for the tetraglycine system as compared with the other copper polyglycines[2] are occasioned by the larger number of equilibria all occurring within closely overlapping ranges of pH. This is especially the case for reactions 3 and 4.

The enthalpy change for the formation of $CuGGGG^+$ is strikingly similar to the values[2] for the formation of CuG^+, $CuGG,^+$ and $CuGGG^+$. The substantial decrease in stability of all of the cationic polyglycine complexes as compared with copper monoglycinate is entirely due to the much less positive entropy changes. The data strongly suggest that the bidentate structures proposed for the di- and triglycine complexes[2] may also be applicable in the monotetraglycinate case. For all three systems in the lower range of pH, the ligand molecules appear to be bound to the copper ion in bidentate structures similar to that for the copper monoglycine itself. It is likely that the structures in solution resemble those in the solid state[3,4,6] in which the copper is bound to the terminal $-NH_2$ and to the oxygen of the first peptide group (I) in a five-membered ring.



CuL$^+$

I

The essentially electrostatic character of the Cu–O bond will account for a ΔH value closely similar to that for CuG^+ formation. The entropy data are also entirely consistent with structures such as that proposed in I in which the charged carboxyl group is not bound to the copper ion. The resulting charge separa-

---

(13) G. H. Nancollas, "Interactions in Electrolyte Solutions," Elsevier Publishing Co., Amsterdam, 1966.

(14) W. L. Kolthun, R. H. Roth, and F. R. N. Gurd, *J. Biol. Chem.*, **238**, 124 (1963).

TABLE II

COPPER TETRAGLYCINE EQUILIBRIUM CONSTANTS[a]

Log K_1	pk'_a	pk'_b	pk'_c	I, M	Temp, °C	Ref
5.13 ± 0.02	5.41 ± 0.02	6.81 ± 0.02	9.15 ± 0.05	0.10 ($NaClO_4$)	25.0	This work
5.4	5.6	6.77	9.0	0.10 (KNO_3)	24.9	12
4.93	5.45	6.91	9.23	0.16	25	14

[a] For detailed methods of calculation, order Document No. NAPS-00186 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. Remit $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

TABLE III

THERMODYNAMIC FUNCTIONS AT 25° AND $I = 0.10\ M$

Reacn no.	Reacn	ΔG, kcal mol^{-1}	ΔH, kcal mol^{-1}	ΔS, cal deg^{-1} mol^{-1}
1	$H_2GGGG^+ \rightleftharpoons HGGGG + H^+$	4.33 ± 0.02	$+0.18 \pm 0.1$	-13.9 ± 0.3
2	$HGGGG \rightleftharpoons GGGG^- + H^+$	10.75 ± 0.02	$+10.40 \pm 0.02$	-1.2 ± 0.1
3	$Cu^{2+} + GGGG^- \rightleftharpoons CuGGGG^+$	-7.00 ± 0.02	-6.0 ± 0.6	$+3.3 \pm 2.0$
4	$CuGGGG^+ \rightleftharpoons CuA + H^+$	7.38 ± 0.02	$+7.5 \pm 0.8$	$+0.4 \pm 3$
5	$CuA \rightleftharpoons CuB^- + H^+$	9.28 ± 0.02	$+6.6 \pm 0.3$	-9.0 ± 1.0
6	$CuB^- \rightleftharpoons CuC^{2-} + H^+$	12.49 ± 0.05	$+8.9 \pm 0.3$	-12.0 ± 1.2

tion and retention of a degree of solvent orientation contrast the much more effective charge neutralization in CuG^+ in which the copper ion is bound to the carboxyl group. In the latter complex the short-bond formation in the xy plane of coordination would also be expected to produce a greater degree of tetragonal distortion of the octahedral symmetry and freeing of the axial water molecules.[15] At higher pH, it is seen (Table III) that, as with the di- and triglycines, the labilization of the peptide hydrogen atoms as compared with the ligand molecule (reaction 2) is predominantly an enthalpy effect; the ΔH value for reaction 4 is less endothermic than that for reaction 2.

Thermodynamic functions for successive proton dissociation from H_2GGGG^+ are seen to be closely similar to the corresponding tri- and diglycine reactions.[2] The considerably more negative ΔS for reaction 1 as compared with reaction 2 is a consequence of the appreciable solvent-ordering properties of the zwitterion HGGGG, especially at the $-NH_3^+$, and also the greater internal structure of HGGGG as compared with $GGGG^-$. Removal of a proton from the zwitterion is more difficult than from the positive ion H_2GGGG^+ and this is reflected in the more endothermic enthalpy change for reaction 2 as compared with that for reaction 1. In the former, the fields associated with an anion and a cation have to be created.

In reaction 4, a proton dissociates from $CuGGGG^+$ which, by structure I, retains a degree of solvent-ordering properties. The entropy decrease predicted from changes in solvent structure will thus be moderately small. The positive contribution to ΔS resulting from the increased number of species will be compensated to some extent by the loss in freedom of the tetraglycine molecule as the multichelated CuA is formed from I. In reaction 5 the creation of the fields associated with the oppositely charged ions CuB^- and H^+ is characterized once more by an appreciable negative entropy change. Taking into account the experimental uncertainties, ΔH for reaction 5 is similar to that for reaction 4 in which the proton is removed from a positively charged ion. On the basis purely of electrostatic effects, ΔH_5 might have been expected to be more positive than ΔH_4. However, these reactions reflect not only the proton separation but also the breaking of a Cu–O, the making of Cu–N bonds, and concomitant structural rearrangement. For reaction 6, in which the proton is removed from a uninegative ion in the formation of CuC^{2-} and H^+, the additional work required is reflected in the more endothermic ΔH term.

---

[15] A. McAuley, G. H. Nancollas, and K. Torrance, *Inorg. Chem.*, **6**, 136 (1967).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF UTAH, SALT LAKE CITY, UTAH 84112

Kinetics of Aqueous Scandium(III) Perchlorate Hydrolysis and Dimerization[1]

BY DAVID L. COLE, LARRY D. RICH, JEFFREY D. OWEN,
AND EDWARD M. EYRING

Received August 5, 1968

From the number and length of chemical relaxations observed in aqueous solutions of a trivalent metal perchlorate one can deduce the minimum number of hydrolysis and polymerization equilibria present and their respective rates. We report here such a relaxation method investigation of dilute aqueous scandium(III) perchlorate.

Experimental Section

American Potash and Chemical Corp. scandium oxide was dissolved in excess perchloric acid, and crystals of scandium(III) perchlorate appeared on cooling from perchloric acid and water.[2]

---

[1] (a) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research under Grant AF-AFOSR-476-66. (b) Presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

[2] M. Kilpatrick and L. Pokras, *J. Electrochem. Soc.*, **100**, 85 (1953).