Inorganica Chimica Acta, 11 (1974) 31–32

Formation Constants of Some 1:1 and 2:1 2,3-Dihydroxy-2-Methylpropanoato and 2,3-Dihydroxy-2-Methylbutanoato Complex Species of Divalent Transition Metals

J. E. POWELL and S. KULPRATHIPANJA

Ames Laboratory–USAEC, and Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.

Received March 13, 1974

Stability constants of the complex species formed between Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) and the anions of 2,3-dihydroxy-2-methylpropanoic acid and 2,3-dihydroxy-2-methylbutanoic acid were determined at an ionic strength of 0.100 (KNO_3) and 25° C.

Introduction

Data on the formation of complex species by divalent transition metals with monohydroxycarboxylates (glycolate, lactate, β-hydroxypropionate and α-hydroxyisobutyrate) have been reported previously.[1–4] However, because of the commercial unavailability of dihydroxycarboxylic acids, such as 2,3-dihydroxy-2-methylpropanoic acid (DHMP) and 2,3-dihydroxy-2-methylbutanoic acid (DHMB), it is not surprising that the stability constants of species formed between the anion of these two acids and divalent transition metals have not yet appeared in the literature. Due to the recent efficient syntheses and isolation of these two dihydroxycarboxylic acids using ion-exclusion and ion-exchange techniques in this laboratory,[5,6] it became possible to investigate the characteristics of 1:1 and 2:1 DHMP and DHMB complexes of some divalent transition metals. The stabilities of the DHMP and DHMB complexes of divalent cobalt, nickel, copper, zinc and cadmium at $\mu = 0.100$ (KNO_3) and 25°C are reported here, and possible molecular structures are discussed. For comparison purposes, the stabilities of the 1:1 and 2:1 α-hydroxyisobutyrate (HIB) complex species of divalent copper were also investigated at the same ionic strength and temperature.

Experimental

DHMP and DHMB were prepared as described previously,[5,6] and HIB (Aldrich Chemical Co. Inc.) was purified by recrystallizing it from hot carbon tetrachloride solution. Buffer solutions ($\sim 0.1M$ total ligand) were then prepared by partially neutralizing standard solutions of these three acids with standard CO_2-free potassium hydroxide. The free acid concentration in each buffer was confirmed by subsequent titration of aliquots with standard base. Divalent transition metals nitrate (Baker Analyzed Reagent) solutions ($\sim 0.1M$) were standardized by passing aliquots through a well-washed hydrogen-form cation exchanger and titrating the effluent and rinsing with standard base. Different volumes of buffer were added to a series of 25, 100-ml, volumetric flasks together with 2.00 ml of standard divalent transition metal nitrate solution, and a constant ionic strength of 0.100 was maintained in all cases by adding calculated volumes of standard (*ca.* $1M$) potassium nitrate solution prior to dilution to volume. All solutions were equilibrated overnight in a 25.0° C water bath, and the pH_c of each was determined to 0.001 units by means of a Beckman Research pH Meter or Corning Model 101 Digital Electrometer, equipped with glass and saturated calomel electrodes.

The conditional ionization constants of the DHMP, DHMB and HIB acids were determined as slightly varying parameters *vs.* ligand anion concentration at fixed ionic strength of 0.100 (KNO_3) at 25.0°C, by measuring the pH_c values of similar series of buffer solutions to which no metal ion was added. The least squares values of K_a were found to be 1.60×10^{-4}, 2.65×10^{-4} and 3.06×10^{-4} for the HIB, DHMP and DHMB acids, respectively.

Computation of the formation constants was performed with the IBM 360/50 computer system at Iowa State University, using a version of the computational techniques of Sullivan, Rydberg and Miller.[7] The primary change was the inclusion of statements to allow selection of a proper K_a in each instance by an iterative process from a relationship of the type $K_a = A + B[A^-]$.

Results and Discussion

The first and second successive formation constants, their ratios, and the maximum n̄ achieved in each

TABLE I. Step Formation Constants of 1 : 1 and 1 : 2 Chelate Species (at 25° C; $\mu = 0.1$).

Metal	DHMB	($K_a = 3.06 \times 10^{-4}$)			DHMP	($K_a = 2.65 \times 10^{-4}$)			HIB	($K_a = 1.60 \times 10^{-4}$)		
	K_1	K_2	K_1/K_2	max. $\bar{n}$	K_1	K_2	K_1/K_2	max. $\bar{n}$	K_1	K_2	K_1/K_2	max. $\bar{n}$
Co	38.8±0.7	17.2± 6.7	2.3	0.57	41.5±0.2	5.8±11.7	7.1	0.49				
Ni	64.0±0.2	17.3± 1.8	3.7	0.85	66.1±0.2	8.9± 8.2	7.4	0.60				
Cu	414.0±0.2	47.4± 1.1	8.8	1.26	429.0±0.2	45.8± 0.7	9.4	1.35	660.0±0.2	62.8±1.0	10.5	1.2
Zn	56.9±0.6	22.0± 4.8	2.6	0.78	58.3±1.0	5.6±20.0	10.4	0.69				
Cd	41.5±0.1	27.9±10.5	1.5	0.86	42.5±0.3	22.6± 4.1	1.9	0.92				

determination are presented in Table I. For both dihydroxy ligands (DHMP and DHMB) the sequence of increasing formation constants proved to be the same: $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+} > Cd^{2+}$, in agreement with the well-known Irving–Williams series.[8,9]

A linear relationship between the acidity of the donor group ($\log K_a$) and the chelate stability ($\log K$) has been found to hold for much of the data found in the literature. Thus, the weaker the acidity of the carboxyl donor group, the more stable the chelate compound should be. The data in this investigation agree with these past observations; that is, the values of formation constants increase in the sequence DHMB < DHMP < HIB, and the acidity values of the acids considered change in the reverse order.

Because of the Jahn–Teller effect in the d^9 configuration of divalent copper, the tetragonally distorted octahedron (in which two *trans* metal–ligand distances are greater than the other four) is the most common structure. The crystal structure of diaquobis(HIB)copper(II) is an example of this, having two waters in *trans* positions and two bidentate HIB ligands which form *trans*-chelate rings in a square planar configuration.[10] Let us apply Bjerrum's statistical ratio theory[11] for this system. The ratio of the successive formation constants (K_1/K_2), or the total effect (T), is equal to the product of the statistical term (S), the ligand repulsion effect (E) and the "rest" effects (R). The S term is calculated, using the configuration of diaquobis(HIB)copper(II), to be 8. Because small ligands are involved in this system, steric hindrance can be ignored (this is shown by the linear relationship of $\log K_a$ and $\log K$ mentioned above), so R equals about 1. E values (calculated using these assumptions) are then 1.10, 1.18 and 1.31 for DHMB, DHMP and HIB, respectively. Manning[12] summarized the formation constant data on divalent copper chelates, from Powell[13] and Fronaeus,[14] and found the E value was 1.75 for acetate. One can see then that E increases in the sequence: DHMB < DHMP < HIB < acetate, with the inductive effects on these ligands changing in the reverse sequence. This is reasonable, because the E value is determined principally by the magnitude of the effective negative charge on the carboxyl group. K_1/K_2 values of 8.8 for DHMB, 9.4 for DHMP and 10.5 for HIB, therefore, do not appear unreasonable, if one assumes that the $Cu(DHMB)_2$, $Cu(DHMP)_2$ and $Cu(HIB)_2$ species in solution all have the tetragonally distorted octahedron configuration (for which S equals 8) in agreement with the crystal structure of diaquobis(HIB)copper(II) mentioned above.

No safe conclusions with regard to coordination geometry can be drawn in the cases of the DHMB and DHMP complexes of Co, Ni, Zn, and Cd. In our experiments, the maximum $\bar{n}$ achieved was less than 1 in these cases, thus the standard deviations for the K_2 values in Table I are prohibitively large.

References

1 I. Filipović, T. Matusinović, B. Mayer, I. Piljac, B. Buch–Dragutinović and A. Bujak, *Croat. Chem. Acta, 42,* 541 (1970).
2 I. Filipović, I. Piljac, A. Medved, S. Savić, A. Bujak, B. Buch–Dragutinović and B. Mayer, *Croat. Chem. Acta, 40,* 131 (1968).
3 Z. Warnke and E. Kwiatkowski, *Roczniki Chem., 47,* 467 (1973).
4 H. Thun, W. Guns and F. Verbeek, *Anal. Chim. Acta, 37,* 332 (1967).
5 J.E. Powell, H.R. Burkholder and J.L. Farrell, *J. Chromatogr., 57,* 309 (1971).
6 J.E. Powell, S. Kulprathipanja, D.A. Johnson and H.R. Burkholder, *J. Chromatogr., 74,* 265 (1972).
7 J.C. Sullivan, J. Rydberg and W.F. Miller, *Acta. Chem. Scand., 13,* 2023 (1959).
8 H. Irving and R.J.P. Williams, *Nature, 162,* 746 (1948).
9 H. Irving and R.J.P. Williams, *J. Chem. Soc.,* 3192 (1953).
10 C.K. Prout, R.A. Armstrong, J.R. Carruthers, J.G. Forrest, P. Murray–Rust and F.J.C. Rossotti, *J. Chem. Soc., A11,* 2791 (1968).
11 J. Bjerrum, "*Metal Ammine Formation in Aqueous Solution*", Haase, Copenhagen, 1941.
12 P.G. Manning, *Can. J. Chem., 43,* 3258 (1965).
13 R.S. Kolat and J.E. Powell, *Inorg. Chem., 1,* 293 (1962).
14 S. Fronaeus, *Ph. D. Thesis,* Gleerupska University, Lund, Sweden, 1948.