Thermodynamic Study of Copper Complexes of *N*-(2-aminoethyl)morpholine

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Protonation constants and formation constants for the copper(II) complexes of *N*-(2-aminoethyl)morpholine were determined by potentiometric titration at low ionic strength.

ALL PROCEDURES, except purification of the amine, have been described previously (*1*). *N*-(2-aminoethyl)-morpholine (Jefferson Chemical Co., Inc., Austin, Tex.) was distilled at 202° C. at atmospheric pressure [reported (*3*) 204.5° C. at 768 mm. of Hg]. Solutions prepared from this product had neutral equivalents of 130.1, 130.2, and 130.1 (calcd.: 130.14).

Table I. Protonation Constants and Formation Constants of Copper(II) Ion with *N*-(2-aminoethyl)Morpholine

Ion		10° C.	20° C.	30° C.	40° C.
H^+	log K_1	9.56 ± 0.02	9.39 ± 0.04	9.15 ± 0.04	8.94 ± 0.02
	log K_2	4.29 ± 0.03	4.62 ± 0.10	4.06 ± 0.11	4.13 ± 0.16
Cu^{+2}	log K_1	6.84 ± 0.02	6.74 ± 0.18	6.56 ± 0.18	6.44 ± 0.07
	log K_2	5.41 ± 0.07	5.32 ± 0.17	5.30 ± 0.09	5.33 ± 0.04

RESULTS AND DISCUSSION

Logarithms of formation constants with hydrogen ion and copper(II) ion are assembled in Table I. The 95% confidence intervals are indicated with each value. Thermodynamic functions are assembled in Table II. No constants were calculable for Ni, Co(II), Zn, or Cd because of formation of precipitates.

Table III lists for comparison amines of similar structure. The small differences in the constants determined here and those reported by Hares *et. al.* (*2*) are not unexpected, mainly because of the difference in ionic strength and perhaps also the differences in calculation method employed.

The amine studied is a diamine somewhat similar to 1,2-ethanediamine. The lower protonation constants than those for 1,2-ethanediamine are to be expected. A somewhat lower first protonation constant might be expected simply because of the statistical effect of having only one primary amine group. The second constant is much lower, because the tertiary nitrogen is much less basic. Formation constants with copper are vastly lower because of steric hindrance and lower base strength of the tertiary amine.

Better comparison with the morpholine derivative are the unsymmetrically substituted ethanediamines, but data are not available from low ionic strength media, and direct comparisons cannot be made. For the dialkyl compounds, the reported formation constants are higher because of higher basicity.

Both *N*-(2-aminoethyl)pyrrolidine and *N*-(2-aminoethyl)-piperidine are more basic than *N*-(2-aminoethyl)-morpholine and hence better coordinating agents. The inductive effect of the electronegative oxygen atom would seem to be the cause of the lower base strength of the tertiary nitrogen atom of the latter.

Protonation constants cannot be compared with the nitrogen-containing ring compound. It is the secondary nitrogen which is protonated in *N*-(2-aminoethyl)-piperazine, and the tertiary nitrogen has so low a base strength that it was not determinable. Formation constants for the oxygen-containing compound are higher, presumably because of the higher base strength of the tertiary nitrogen atom of the morpholine derivative. The low base strength of the tertiary nitrogen atom of the piperazine derivative remains low while coordination takes place, since the secondary nitrogen atom remains protonated during this process.

Table II. Thermodynamic Functions

		Kcal./Mole				Entropy Units	
Ion	Temp., ° C.	ΔF_1^0	ΔF_2^0	ΔH_1^0	ΔH_2^0	ΔS_1^0	ΔS_2^0
H^+	10	12.4	5.6			12	10
	20	12.6	5.8			12	10
	30	12.7	5.7			12	9
	40	12.8	6.0			12	10
	10–40			9.0	2.9		
Cu^{+2}	10	8.9	7.0			17	21
	20	9.0	6.9			17	20
	30	9.0	7.4			17	21
	40	9.2	7.6			17	21
	10–40			4.0	1.1		

Like *N*-(2-aminoethyl)morpholine, 2-picolylamine has primary and tertiary nitrogen atoms. Although somewhat less basic in character than *N*-(2-aminoethyl)morpholine, the picolylamine forms much stronger bonds to metal ions. Steric hindrance of the three groups bonded to a nitrogen atom undoubtedly plays a large part in reducing the chelate stability of the morpholine derivative, and the stabilization of picolylamine by pi bonding (*1*) increases the difference.

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Table III. Comparison of Protonation and Formation Constants with Related Compounds

	T, °C.	Ionic Strength	H^+		Cu^{+2}		Ref.
			Log K_1	Log K_2	Log K_1	Log K_2	
N-(2-aminoethyl)morpholine	30	→0	9.15	4.06	6.56	5.30	
N-(2-aminoethyl)morpholine	30	1.0*M* KNO_3	9.45	4.84	6.60	3.96	(*2*)
N-(2-aminoethyl)piperidine	30	→0	9.89	6.38	7.77	5.83	(*7*)
N-(2-aminoethyl)pyrrolidine	30	→0	9.74	6.56	8.77	6.05	(*7*)
1,2-Ethanediamine	30	→0	9.81	6.79	10.36	8.93	(*5*)
N-(2-aminoethyl)piperazine	30	→0	9.40	8.37	5.49	(3.7)	(*6*)
N,N-dimethyl-1,2-ethanediamine	25	0.1*M* KCl	9.53	6.63	9.23	6.73	(*4*)
N,N-diethyl-1,2-ethanediamine	25	0.1*M* KCl	10.02	7.07	8.17	5.55	(*4*)
2-Picolylamine	30	→0	8.51	3.1	9.45	7.80	(*1*)

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Thermodynamic Functions of Acetylene

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Thermodynamic functions were computed for an ideal gas of C_2H_2 molecules under standard conditions incorporating the effects of anharmonicities, rotational stretching, and vibration-rotation interaction over the temperature range 298° to 6000° K.

BELL AND NIELSEN (*2*) have determined the vibrational fundamentals, the rotational constants, and the 15 first-order anharmonicity terms. Allen, Tidwell, and Plyler (*1*) redetermined some of these. Wiggins, Plyler, and Tidwell (*7*) have recently determined the five vibration-rotation interaction coefficients αi as well as redetermining B_0, D_0, and υ_5. Somewhat different values for the Raman-active vibration-rotation data are given by Stoichieff (*6*). Thermodynamic functions were computed by the Bendix G20 Electronic Data Processing Machine for an ideal gas of C_2H_2 molecules at 1 atm. using a modification of the triatomic molecules program described earlier (*4, 5*). In these calculations, R is 1.98726 cal. per mole degree, the dimensionless factor hc/k is 1.4388, and the Sackur-Tetrode constant K_6 is −7.28353 (*3*). Previous tables for C_2H_2 were based on the rigid rotor-harmonic oscillator (RRHO) approximation. Consideration of the anharmonicities and rotational effects raises C_p^0 (6000° K.) 9.3% beyond the RRHO result.

The separate effects of the anharmonicities, etc., on the free energy function at 6000° K. were also determined as follows:

RRHO part	80.024
Rotational stretch	0.020
Overtone anharmonicities X_{ii}	−0.493
Combination anharmonicities X_{ij}	1.107
Rotation-vibration terms αi	−0.034
Total	80.624

Of course, the other thermodynamic functions are more sensitive to these effects than the free energy function, and at lower temperatures the effects are less in magnitude. The net negative contribution from the X_{ii} terms may seem at first surprising, but is caused by the large negative value of the quantity $-X_{44}/\sigma_{42}$ which corresponds to overtones of the lowest energy, doubly degenerate vibration. Likewise, the net negative contribution from the αi arises from the shortening of the molecule (increase in B) when it