Syntheses and Properties of the Copper(II) Complexes of the Amphoteric Surfactants, *N*-Alkyl-β-alanine

Akio NAKAMURA,* Masakatsu KOSHINUMA,† and Kazuo TAJIMA††
Nagoya Municipal Women's Junior College, Kitachikusa, Chikusa-ku, Nagoya 464
†Laboratory of Chemistry, Faculty of Informatics, Teikyo University of Technology, Uruido, Ichihara-shi, Chiba 290-01
††Department of Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221
(Received July 18, 1989)

Copper(II) complexes of amphoteric surfactants, *N*-alkyl-β-alanine (NAA) (the number of carbon atoms in the alkyl chains: n=2, 4, 6, 8, 10, 12), were synthesized from NAA and copper(II) chloride dihydrate by mixing in aqueous solutions. The properties and structures of these bluish flaky complexes were investigated by elemental analyses, infrared and far-infrared spectroscopy, electronic diffuse reflection spectroscopy, X-ray diffractometry, and thermal analyses. As a result, all of these complexes were found to be composed of one copper(II) ion and two NAA molecules, regardless of the chain length in the alkyl group, ($Cu(NAA)_2 \cdot 2H_2O$), and were also found to have a laminated structure in the crystalline state. A linear relationship was found between the long spacings (d/nm) of the laminated structure and the numbers of carbon atoms (n) in the *N*-alkyl substituents; $d=0.135n+0.62$. From these results it was concluded that copper(II) complex molecules have a trans configuration, and are extended and parallel to the normal line of the laminated planes in the crystal. A multiunilayer model for the molecular arrangement of these copper(II) complexes has been proposed, which is quite different from those so far proposed to explain the long spacings observed for metal soap crystals, lyotropic liquid crystal and so on. Also, the role of the alkyl substituents in complex formation has been indicated.

Amphoteric surfactants of the amino-acid type have recently found wide application because of their excellent characteristics.[1] This type of surfactant is generally known to form stable complexes with transition metal ions. However, these complexes have been neither fully investigated regarding their fundamental properties, nor extensively applied.

Despite the large number of investigations on the metal complexes of amino acids, little is known about either the effect of alkyl substitution on the formation of complexes or on these properties. It is therefore desirable to systematically synthesize a series of metal complexes of the amino-acid type amphoteric surfactants with various lengths of alkyl chains, and to clarify how the chain lengths affect the properties of the resulting complex.

In our previous study[2] we found that *N*-dodecyl-β-alanine (NDA) and copper(II) chloride resulted in the formation of a crystalline complex having the composition 1(Cu):2(NDA) by only simple mixing in a dilute aqueous solution; we therefore suggest that the *N*-alkyl substituents play a significant role in complex formation.

The purpose of the present study is to elucidate the effect of the alkyl chain length on the properties of the copper(II) complexes of *N*-alkyl-β-alanine.

Experimental

Materials. *N*-Alkyl-β-alanine (NAA) (i.e., 3-(alkylammonio)propionate) was used. The number of carbon atoms in the alkyl chain of NAA was 2 (NEtA), 4 (NBuA), 6 (NHeA), 8 (NOA), 10 (NDeA), and 12 (NDA). These homologs, except for NBuA and NHeA, were synthesized from 1-aminoalkane and 3-propanolide (β-propiolactone) in acetonitrile. Details regarding the synthesis and the purification of the materials have been reported elsewhere.[3] Both NBuA and NHeA were especialy available from Wako Pure Chemicals Industry. The copper(II) salt ($CuCl_2 \cdot 2H_2O$) was purified by recrystallization from distilled water.

Elemental Analyses. Copper was analyzed by atomic absorption spectrophotometry with a Hitachi 180-60. Carbon, hydrogen, and nitrogen were simultaneously analyzed by a thermal conductivity method. The chloride contents in the complexes were determined by titrating the complex solution with a standard solution of silver nitrate.

Thermal Analysis. Simultaneous TG-DTA measurements were made with a Sinku Riko TGD-7000, and the DSC were measured with a Sinku Riko DSC-7000, using a sample of about 8 mg in each operation with a heating rate of 5 °C min^{-1} in air.

Electronic Diffuse Reflection Spectra. The electronic diffuse reflection spectra were measured from 400 to 850 nm with a Japan Spectroscopic Ubest-50 equipped with a device for diffuse reflection measurements.

Infrared and Far-Infrared Reflection Spectra. The infrared and far-infrared reflection spectra from 200 to 4000 cm^{-1} were measured with a Perkin Elmer FTIR 1800 equipped with a device for diffuse-reflection measurements. In each measurement, scannings were repeated 100 times so as to obtain a high S/N ratio.

Powder X-Ray Diffraction. The measurements were carried out with a Rigaku Denki RAD-rA using Cu $K\alpha$ radiation in the range from 2° to 50° in 2θ.

Syntheses of Complexes. Method (A): Both NAA (10 mmol) and the copper(II) chloride dihydrate (5 mmol) were dissolved in 100 ml of water at about 20 °C; the pH of a mixed solution was adjusted to about 9.0 with an aqueous sodium hydroxide solution (0.1 mol dm^{-3}). The reaction mixture was stirred for 1 h. The resulting precipitate was separated by filtration and thoroughly dried up in a desiccator. Then, a white-bluish precipitate, i.e. the mixture

of the copper(II) complex and the copper(II) hydroxide, was stirred with 50 ml of ethyl alcohol at about 60 °C. After removing the insoluble copper(II) hydroxide by filtration, a deep-blue filtrate was concentrated to a small volume. The resulting bluish, flaky microcrystals were separated by filtration and air-dried. The yield was about 30—60%, increasing as the chain length of NAA increased.

Method (A)′: β-Alanine and the copper(II) chloride dihydrate were mixed in the alkaline solution by the same procedure as Method (A). In this case, however, since the copper(II) complex of β-alanine is highly soluble in water, the resulting complex dissolved in the filtrate. Therefore, after removing the insoluble copper(II) hydroxide by filtration, the complex was precipitated from the concentrated and cooled filtrate, and recrystallized for purification. The yield was about 80%.

Method (B): For the higher homologs (octyl, decyl, or dodecyl) of NAA, an alternative simple method was adopted, since the solubilities of the complexes in an aqueous solution were very low. Precipitation was observed immediately after mixing NAA solutions, ranging in concentration from 5×10^{-4} to 5×10^{-2} mol·dm^{-3}, with an equivalent amount of the copper(II) chloride dihydrate. The solution pH was in the 4.0—5.5 region. The resulting precipitate was filtered out and air-dried. The yield was about 10—50%.

Results and Discussion

Analyses of Complexes. Elemental Analyses: Table 1 shows the results of elemental analyses of the complexes. It was confirmed that all of the copper(II) complexes of NAA have the composition $Cu(NAA)_2\cdot 2H_2O$, regardless of the alkyl chain length and the preparation method. A copper(II) complex of β-alanine, however, has the composition $Cu(\beta\text{-alanine})_2\cdot 4H_2O$, which is the same as that reported.[4]

Thermal Analyses: The results of the thermal gravimetry indicated that the copper(II) complexes of NAA lost weight endothermically by a factor which almost corresponded to the release of two water molecules at 90—120 °C, and started to decompose exothermically at about 170 °C. The weight loss during the first stage may be ascribed to release of two water molecules which coordinate to the copper(II) atom at the two apical positions with a bond length longer than those of the other four donor atoms in the equatorial square around the copper(II) atom. For the copper(II) complex of β-alanine, the presence of the two coordinated water molecules at such positions was reported on the basis of X-ray data, though the other water molecules were also incorpolated in the crystal.[4,5]

The decomposition of the copper(II) complexes of such amino acids as alanine, valine, and leucine starts at about 220—250 °C,[6] and hydroxyproline at 180—210 °C,[7] after releasing the hydrated water in each complex. Thus, these measurements have proved to be useful in the analysis of hydrated water.[6-8] However, the decomposition temperature seems to be fairly dependent on the nature of the ligands and on the number of the hydrated water. The role of alkyl substituents in the thermal stability for the copper(II)

Table 1. Elemental Analyses of Complexes

Complex	Found (Calcd)[a]/%					
	C	H	N	Cl	Cu	N/Cu
$Cu(\beta\text{-Ala})_2\cdot 4H_2O$[b]	22.7 (23.1)	5.65 (5.77)	8.87 (8.98)	0 (0)	20.2 (20.4)	1.99 (2.00)
$Cu(NEtA)_2\cdot 2H_2O$[c]	36.1 (36.2)	7.18 (7.24)	8.33 (8.44)	0 (0)	19.1 (19.2)	1.98 (2.00)
$Cu(NBuA)_2\cdot 2H_2O$[c]	42.8 (43.3)	8.23 (8.26)	7.15 (7.22)	0 (0)	16.3 (16.4)	1.99 (2.00)
$Cu(NHeA)_2\cdot 2H_2O$[c]	47.2 (48.7)	8.84 (9.02)	6.21 (6.31)	0 (0)	13.8 (14.3)	2.04 (2.00)
$Cu(NOA)_2\cdot 2H_2O$[c]	52.1	10.2	5.53	0	12.7	1.98
$Cu(NOA)_2\cdot 2H_2O$[d]	52.3 (52.8)	10.1 (9.61)	5.55 (5.60)	0 (0)	12.5 (12.7)	2.01 (2.00)
$Cu(NDeA)_2\cdot 2H_2O$[c]	56.0	10.5	4.92	0	11.2	1.99
$Cu(NDeA)_2\cdot 2H_2O$[d]	56.1 (56.2)	10.2 (10.1)	4.95 (5.04)	0 (0)	11.3 (11.4)	1.97 (2.00)
$Cu(NDA)_2\cdot 2H_2O$[c]	58.4	10.4	4.49	0	10.2	2.03
$Cu(NDA)_2\cdot 2H_2O$[d]	58.2 (58.9)	10.4 (10.5)	4.38 (4.58)	0 (0)	10.1 (10.4)	1.97 (2.00)

a) Figures in parentheses are calculated values. b) Synthesized by method (A)′. c) Synthesized by method (A). d) Synthesized by method (B).

complexes of amino acids should be made clear.

Electronic Diffuse Reflection Spectra (EDRS): The copper(II) complexes of NAA are all bluish, flaky microcrystals; the EDRS for all of these complexes showed a maximum absorption band (λ_{MAX}) at 630 nm, regardless of the chain length of the alkyl group in crystals. Since the EDRS exactly reflects the steric configuration,[9] together with such other factors as donor atoms, solvents, etc., all of the copper(II) complexes of NAA are supposed to have the same steric configuration in common.

The copper(II) complex of β-alanine, Cu(β-alanine)$_2$·4H$_2$O, in contrast to the NAA complexes, is deeper blue (λ_{MAX}=660 nm), a prismatic crystal, the configuration of which has been determined to be a trans isomer by three-dimension X-ray analysis.[4] This red shift effect might be caused by the two hydrated water molecules in addition to the two coordinated water molecules. In fact, it was shown for the copper(II) complex of NDeA that the value of λ_{MAX} is also dependent on the presence of water molecules in the vicinity of the copper atom; the removal of the two coordinated water molecules brings about a blue shift (λ_{MAX}: 630 → 570 nm), and the dissolution of the copper(II) complex of NDeA in the micellar solution of NDeA brings about a red shift (λ_{MAX}: 630 → 660 nm).[10] The effects of the coordination, crystallization, or hydration water on the reflection spectra should be reported in near future.

Infrared and Far-Infrared Spectra: The spectra of NAA and copper(II) complexes of NAA differ from each other regarding many points as is summarized for the NDeA complex (Table 2). The copper(II) complexes of NAA lack absorption bands at 1655 cm^{-1} and 2355 cm^{-1} due to the $>NH_2^+$ group, and exhibit an absorption band at 3400 cm^{-1} due to coordinated water. Furthermore, in the copper(II) complexes of NAA the absorption band at 864 cm^{-1} due to a gauche mode of -(CH$_2$)$_2$- in the polar group of NAA shifts to a higher frequency (890 cm^{-1}); also, the absorption bands at 1415 cm^{-1} and 1564 cm^{-1} due to the -COO$^-$ of NAA shift to higher frequencies (1431 cm^{-1} and 1570 cm^{-1}). These results furnish spectroscopic evidence for the formation of the complexes of Cu(NAA)$_2$·2H$_2$O.

It has been shown that the absorption spectra in the far-infrared region (200—600 cm^{-1}) should be a criterion of the steric configuration, since this region includes absorption bands attributable to stretching vibrations of Cu-N and Cu-O bonds.[11] For complexes of a cis configuration, the spectra exhibit both asymmetric and symmetric stretching modes for the respective bonds of Cu-N and Cu-O, while for a trans configuration, the spectra exhibit only an asymmetirc stretching mode. These data have been catalogued for copper(II) complexes of such amino acids as glycine, L-alanine, DL-α-aminobutyric acid, DL-proline, and L-isoleucine, whose steric configurations have been elucidated by X-ray crystallography.[12] This criterion was used to predict the cis trans configurations of the copper(II) complexes of several amino acids of previously undetermined steric configurations.[7,12]

The copper(II) complexes of NAA exhibit two common absorption bands which are not observed for NAA alone in the far-infrared region: 350 cm^{-1} and 518 cm^{-1}, which may safely be attributable to the Cu-O and Cu-N asymmetric stretching modes, respectively. Therefore, according to the above criterion, we concluded that these far-infrared spectra are indicative of the trans configuration for the copper(II) complexes of NAA.

Role of Alkyl Chain in Complex Formation. Method (A)′ is similar to the synthetic methods of most copper(II) complexes of amino acids, since the resulting complexes are usually soluble in water rather than in methyl or ethyl alcohol. On the contrary, the copper(II) complexes of NAA are scarcely soluble in water but are fairly soluble in ethyl alcohol. Therefore, for the syntheses of the copper(II) complexes of NAA, method (A)′ was modified into the present method (A). In fact, when microcrystals of the copper(II) complexes of NAA (especially with the *N*-alkyl substituents longer than the hexyl group) were put on the distilled water surface, they neither exhibited any surface pressure nor dissolved into a subphase, at least for several days at a room temperature. Furthermore, the crystals did not become wetted with their own solutions.

Since the coordination of NAA to copper(II) ion is in competition with the protonation of NAA, in either

Table 2. IR and Far-IR Spectra of Cu(NDeA)$_2$·2H$_2$O

Group	NDeA(cm^{-1})	Cu(NDeA)$_2$·2H$_2$O(cm^{-1})	Assignment
Cu-O	—	350	Asym.str.
Cu-N	—	518	Asym.str.
-(CH$_2$)$_2$-[a]	864	890	Gauche
-COO$^-$	1415	1431	Sym.str.
	1564	1570	Asym.str.
$>NH_2^+$	1650	—	Asym.deg.def.
	2355	—	Asym.deg.def.+twisting
-OH[b]	—	3400	Str.

a) In the ammonio-propionate group. b) In the coordinated water molecules.

methods (A) or (A)′, it is necessary to increase the solution pH to the alkaline region so as to assure a high yield of the complex. Because this procedure inevitably results in the formation of a by-product, i.e., copper hydroxide, further purification of the resulting product is required. It is therefore worth noting that, in the cases of NAA with a *N*-alkyl substituent longer than the octyl group, a simple mixing of NAA and copper(II) ion results in a precipitate of the pure complex, even in a weakly acidic aqueous solution.

This fact evidently indicates that hydrophobic interactions between the alkyl chains of neighboring molecules in crystals, together with coordination and protonation reactions, play an important role in the promotion of crystalline complex formation. Such hydrophobic interactions have also been observed in the following various kinds of chemical reactions; ion-pair formation between two differently charged ionic surfactants in aqueous solutions,[13] the aminolysis of *p*-nitrophenyl decanoate in an aqueous solution by 1-aminodecane[14] and so on. The role of hydrophobic moieties of NAA, by which the crystalline complex formation is promoted, will be precisely described in a subsequent paper.[15]

An alternative feasible effect of such a side chain as *N*-alkyl substituent is possible to determine steric configurations in the complex. Interesting results have been reported regarding the formation of ternary copper(II) complexes containing two amino acids (e.g. aspartic acid and lysine, etc.). An intramolecular ion pair formation between the two oppositely charged amino acids residues (i.e. two side chains) may be an effective driving force leading to ternary complex formation and to a specific steric configuration.[16] Such a side-chain effect on the steric configuration is also supposed for the copper(II) complex of NAA; the cis configuration suffers from a considerable steric hindrance, i.e., a pair of alkyl chains bonded directly to two nitrogen atoms neighboring in the same side of the planar square spatially exclude each other. Therefore, this reasoning for the trans configuration of the copper(II) complex of NAA is consistent with results regarding the far-infrared spectra described above.

Crystal Structures of Complexes. Figures 1a—1g show X-ray (Cu $K\alpha$ 0.154 nm) diffraction patterns of the copper(II) complexes of NAA and of β-alanine obtained by the powder method. The main peaks observed in each figure can all be assigned to a single long spacing on the basis of the Bragg condition. Figure 2 shows a plot of the long spacing (d nm) against the number of atoms (n) in a hydrocarbon chain of NAA; an empirical relationship was found:

$$d = 0.63 + 0.135n \quad (n = 2—12). \tag{1}$$

The value for the β-alanine complex is shown on the ordinate for the sake of comparison; it is slightly larger

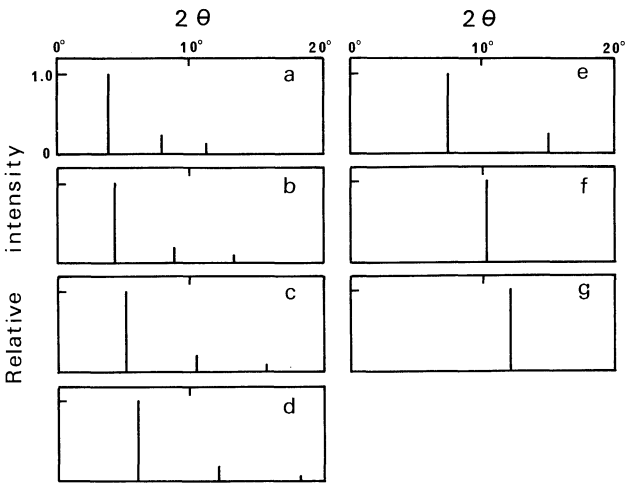

Fig. 1. Powder X-ray diffraction patterns of the copper(II) complexes of NDA (a), NDeA (b), NOA (c), NHeA (d), NBuA (e), NEtA (f) and β-alanine (g).

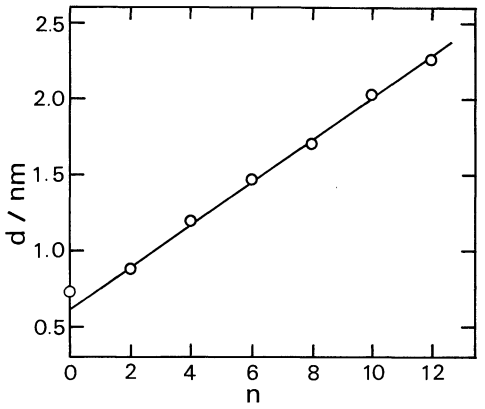

Fig. 2. Long spacing (d) of copper(II) complexes of NAA vs. number of carbon atoms (n) in an alkyl chain of NAA.

than the extrapolated value ($d \rightarrow 0.63$, $n \rightarrow 0$). The long spacing in each system may correspond to the distance between copper(II) atom layers aligned in ordered complex layers with a laminated structure. The increase in the long spacing per $-(CH_2)-$ in the alkyl chain was 0.135 nm, nearly equal to the length of $-(CH_2)-$ (0.125 nm) in crystalline *N*-alkane. This means that the molecules of the copper(II) complexes of NAA are extended and parallel to the normal line of the laminated planes. This result is further evidence for our model regarding the molecular arrangement of the copper(II) complexes of NAA in the crystal state described in a previous paper:[2] The total molecular lenght (L/nm) of the copper(II) complexes with the trans configuration is evaluated from the STS molecular model as:

$$L = 0.60 + 0.125 \times 2n. \tag{2}$$

Therefore, the packing of the complex molecules in

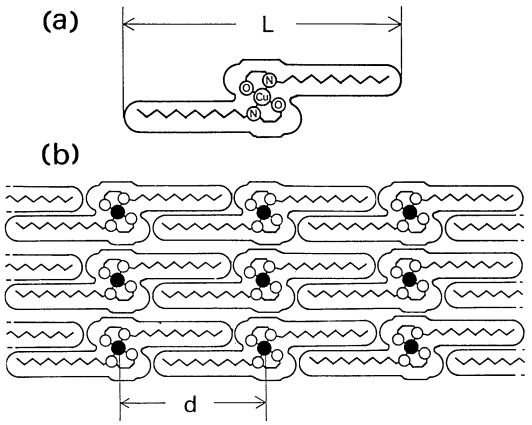

Fig. 3. A model for the copper(II)–NDeA complex molecule; (a), and a model for the molecular packing in the crystals; (b).

the crystal state, e.g. for copper(II)–NDeA complex, can be illustrated as in Fig. 3. The value of the constant term in Eq. 2 may correspond to the size of the polar group of the complex, i.e. roughly the size of the β-alanine complex.

The copper(II) complexes of NAA bear a molecular resemblance to the divalent metal soaps; one molecule is composed of two alkyl chains and one metal ion. Linear relations between the parameters of d and n have been reported for various kinds of metal soaps.[17] However, the long spacing observed in any metal soaps is roughly twice as long as their alkyl chain length. Furthermore, the increase in the long spacing per methylene unit of the alkyl chain is roughly twice as long as the length of $-(CH_2)-$. It is therefore reasonable to presume a multibilayer structure for metal soap crystals, though the precise crystal structure has not yet been experimentally established. In such a structure, the metal soap molecules in adjacent layers are in contact both with tail-to-tail and head-to-head. On the other hand, the molecular arrangement of the copper(II) complex is a multiunilayer structure in which alkyl chains inter-penetrate one another by turn, as shown in Fig. 3. Thus, it is worth noting that the laminated structures of the copper(II) complexes of NAA are quite different from those so far proposed for metal soap crystals, lyotropic liquid crystals, vesicles and so on.

Consequently, we have concluded that all of the obtained copper(II) complexes of NAA have the trans configuration with respect to the planar square coordination of two nitrogen atoms and two oxygen atoms to the central copper(II) atom on the basis of the following facts: (1) The diffuse reflection spectra in the far-infrared region exhibit only an asymmetric stretching vibration mode for the respective bonds of Cu–O and Cu–N. (2) The observed long spacings for the copper(II) complexes of NAA are well explained in terms of the trans configuration and of the extended conformation of the complex molecule, as shown in Fig. 3. (3) The copper(II) complexes of β-alanine, hitherto reported on the basis of X-ray analyses, have only a trans configuration.[4,5] (4) From the space-filling molecular model, the cis configuration suffers from a considerable steric hindrance.

More precise measurements concerning the three-dimensional crystal structure of the copper(II) complexes of NAA have not been made for the time being due to difficulty in preparing single crystals of suitable size.

References

1) M. J. Rosen, "Surfactants and Interfacial Phenomena," Wiley-Interscience, New York (1978), p. 22.
2) A. Nakamura and K. Tajima, *Bull. Chem. Soc. Jpn.*, **61**, 3807 (1988).
3) T. Okumura, K. Tajima, and T. Sasaki, *Bull. Chem. Soc. Jpn.*, **47**, 1067 (1974).
4) Y. Mitsui, Y. Iitaka, and H. Sakaguchi, *Acta Crystallogr., Sect. B*, **32**, 1634 (1976).
5) K. Tomita, *Bull. Chem. Soc. Jpn.*, **34**, 297 (1961).
6) M. Tomassetti, E. Cardarelli, R. Curini, and G. Dàscenzo, *Thermochim. Acta*, **113**, 243 (1987).
7) Y. Inomata, T. Takeuchi, and T. Moriwaki, *J. Inorg. Chim. Acta*, **68**, 187 (1983).
8) Y. Inomata, T. Inomata, and T. Moriwaki, *Bull. Chem. Soc. Jpn.*, **47**, 818 (1974).
9) T. Yasui and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **39**, 604 (1966); S. H. Laurie, *Aust. J. Chem.*, **20**, 2609 (1967); Y. Inomata, T. Takeuchi, and T. Moriwaki, *Spectrochim Acta, Part A*, **40**, 179 (1984).
10) A. Nakamura, M. Koshinuma, and K. Tajima, to be published.
11) R. A. Condrate and K. Nakamoto, *J. Chem. Phys.*, **42**, 2590 (1965); J. R. Kincaid and K. Nakamoto, *Spectrochim. Acta, Part A*, **32**, 277 (1976); K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed., Jone Wiley & Sons, Inc., New York (1978), p. 305.
12) A. W. Herlinger, S. L. Wenhold, and T. V. Long, II, *J. Am. Chem. Soc.*, **92**, 6474 (1970); A. W. Herlinger and T. V. Long, II, *ibid.*, **92**, 6481 (1970).
13) A. Nakamura, *Bull. Chem. Soc. Jpn.*, **48**, 1720 (1975); D. G. Oakenfull and D. E. Fenwick, *J. Phys. Chem.*, **78**, 1759 (1974).
14) D. G. Oakenfull and D. E. Fenwick, *Aust. J. Chem.*, **26**, 2646 (1973); **27**, 2149 (1974); A. Ben-Naim, "Hydrophobic Interactions," Plenum Press, New York and London (1980), p. 49.
15) A. Nakamura, M. Koshinuma, and K. Tajima, to be published.
16) O. Yamauchi, Y. Nakao, and A. Nakahara, *Bull. Chem. Soc. Jpn.*, **48**, 2572 (1975); T. Sakurai, O. Yamauchi, and A. Nakahara, *ibid.*, **49**, 169 (1976).
17) P. A. Spegt and A. E. Skoulios, *Acta Crystallogr.*, **16**, 301 (1963); **17**, 198 (1964); R. Matsuura, *Nippon Kagaku Zasshi*, **86**, 560 (1965); K. Ogino and T. Saito, *Bull. Chem. Soc. Jpn.*, **50**, 1623 (1977).