

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

ACID DISSOCIATION BEHAVIOR OF 2, 3- AND 2, 3, 9,10-METHYL- OR CYCLOHEXYL-SUBSTITUTED CYCLAMS, THEIR COMPLEXATION BEHAVIOR WITH COPPER(II) AND THE AXIAL SOLVENT SPECTRUM OF THEIR COMPLEXES INTERACTION EFFECT ON THE LIGAND-FIELD

Yoshiki Moriguchi^a; Kazunori Sakata^b; Kazuya Kobiro^c; Yoshito Tobe^d

^a Department of Chemistry, Fukuoka University of Education, Fukuoka, Japan ^b Faculty of Engineering, Kyushu Institute of Technology, Fukuoka, Japan ^c Niihama National College of Technology, Ehime, Japan ^d Department of Chemistry Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan

To cite this Article Moriguchi, Yoshiki, Sakata, Kazunori, Kobiro, Kazuya and Tobe, Yoshito (1997) 'ACID DISSOCIATION BEHAVIOR OF 2, 3- AND 2, 3, 9,10-METHYL- OR CYCLOHEXYL-SUBSTITUTED CYCLAMS, THEIR COMPLEXATION BEHAVIOR WITH COPPER(II) AND THE AXIAL SOLVENT SPECTRUM OF THEIR COMPLEXES INTERACTION EFFECT ON THE LIGAND-FIELD', *Journal of Coordination Chemistry*, 42: 1, 143 – 155

To link to this Article: DOI: 10.1080/00958979708045287

URL: <http://dx.doi.org/10.1080/00958979708045287>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

ACID DISSOCIATION BEHAVIOR OF 2, 3- AND 2, 3, 9, 10-METHYL- OR CYCLOHEXYL-SUBSTITUTED CYCLAMS, THEIR COMPLEXATION BEHAVIOR WITH COPPER(II) AND THE AXIAL SOLVENT INTERACTION EFFECT ON THE LIGAND-FIELD SPECTRUM OF THEIR COMPLEXES

YOSHIKI MORIGUCHI^{a,*}, KAZUNORI SAKATA^b,
KAZUYA KOBIRO^c and YOSHITO TOBE^d

^a*Department of Chemistry, Fukuoka University of Education, Munakata, Fukuoka 811-41, Japan;* ^b*Faculty of Engineering, Kyushu Institute of Technology, Tobata, Kitakyushu, Fukuoka 804, Japan;* ^c*Niihama National College of Technology, Niihama, Ehime 792, Japan;* ^d*Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan*

(Received 11 June 1996; Revised 19 August 1996; In final form 6 November 1996)

Stability constants of Cu(II)-complexes for 1, 4, 8, 11-tetra-azacyclotetradecane (cyclam) analogs with periphery substituted [14]aneN₄-ring, 2, 3-tetramethyl-, 2, 3, 9, 10-octamethyl-, 2, 3-cyclohexyl, and 2, 3, 9, 10-dicyclohexyl-cyclams have been determined at 25°C in aqueous solution. The UV-Vis absorption spectra of their complexes, ([Cu(L)](ClO₄)₂), were measured in water and some typical organic solvents (methanol, acetone, propylene carbonate, formamide, N, N-dimethylformamide, and dimethylsulfoxide). A good linear relationship was found between the stability constant (logK_{CuL}) and the difference between the wavenumber of maximum absorption in water and in the organic solvents ($\Delta\lambda_{max}^{-1}$ (W-S)). The value of logK_{CuL} at $\Delta\lambda_{max}^{-1}$ (W-S) = 0 not only shows a linear relation to solvent parameters, donor number and dielectric constant, but also to the enthalpy of transfer of ClO₄⁻ from water to the organic solvents. The value is proposed as a new solvent parameter 'K_λ-value' to be used as an index for solvent-effects on Cu(II)-complexes of cyclam analogs. The increasing order of the new parameter (log scale) is as follows; DMF(27.24)>DMSO(27.14)>FA(26.82)>MeOH(26.27)>PC(25.75)>AC(24.71). Another meaning of the new parameter is assumed from connection of the potentiometric data with spectrometric data. The solvent effects on stability and the UV-Vis spectra are assumed to be caused by perturbation of the D_{4h} or axially-elongated ligand field through axial approach of solvent to the Cu(II)-complexes and by formation of a solvent-separated ion pair between a solvated Cu(II)-complex cation and counter anion (ClO₄⁻).

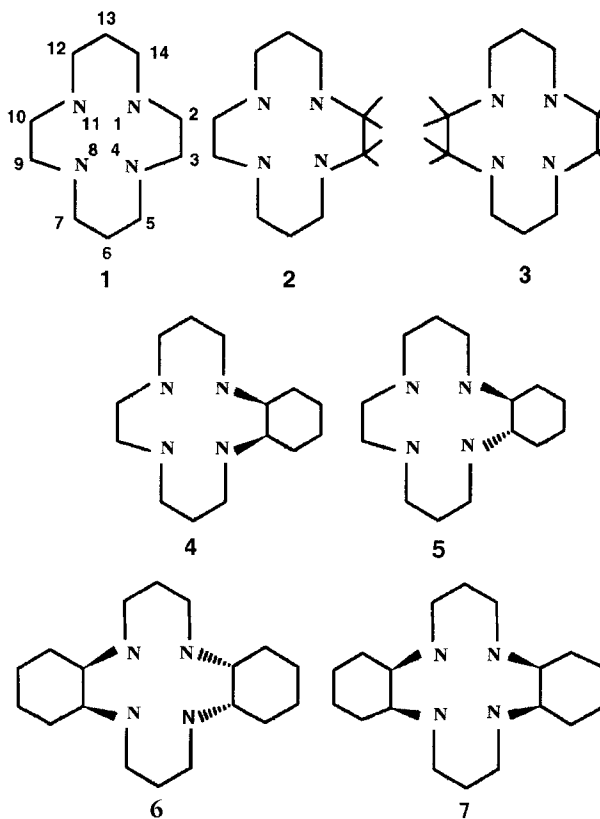
Keywords: cyclam analogs; copper complexes; stability constant; electronic spectra; solvent effect; solvent parameter

* Author for correspondence.

INTRODUCTION

In a previous paper,¹ we reported on the acid dissociation behavior and complexation with Ni(II), Cu(II), and Zn(II) for two conformers of *cis-anti-cis-* and *cis-syn-cis-* 2, 3, 9, 10-dicyclohexylcyclams (Cy₂cyclam(P) and (N), **6** and **7**) which are substituted by a cyclohexyl group at the 2, 3, 9, 10-positions of 1,4,8,11-tetraazacyclotetradecane(cyclam, **1**), and discussed the conformational, basicity and macrocyclic effects caused by substitution of the cyclohexyl group on the periphery of a cyclam-ring, [14]aneN₄.

In this paper, from results of the acid dissociation behavior, the complexation with Cu(II), and the solvent effect on the UV-Vis absorption spectra for the cyclam analogs shown in Scheme 1; 2, 3-tetramethyl (Me₄cyclam, **2**), 2, 3, 9, 10-octamethyl (Me₈cyclam, **3**), 2, 3-cyclohexyl (*cis-* and *trans*-Cycyclams, **4** and **5**) cyclams, and ligands (**6**, **7**), we report the effects for substitution of



SCHEME 1

methyl and cyclohexyl groups on the ligand basicity and ligand field. These 2, 3, 9, 10-substituted cyclams are favorable for systematic investigation of the substitution effect on four nitrogen atoms of the [14]aneN₄-ring because it is expected that the ligand-field symmetry which is formed between a metal and four nitrogen atoms of these Cu(II)-complexes is moderately and continuously changeable from D_{4h} to axial-elongated D_{4h} by the solvent interaction without essential change from square-planar to octahedral or square-pyramidal geometries as observed in the Ni(II)-complexes.²⁻³ On the other hand, 6, 13-substituted cyclams⁴ have considerable distance between the substituent group and nitrogen, and 5, 7, 12, 14-substituted cyclams⁴ have effects not readily compared to the 6, 13-position. Besides, these ligands which have substituent groups on the propylene chain of the [14]aneN₄-ring have a more complicated substituent effect on the ligand-field of the Cu(II)-complex because of increasing conformers and lower symmetry with longer chain-length from methylene to propylene. Furthermore, 1, 4, 8, 11-substituted cyclam⁵ is not as useful because the basicity and symmetry are much affected by direct substitution on nitrogen.

EXPERIMENTAL

Materials and Reagents

Six ligands with methyl- or cyclohexyl-substituted cyclams, **2-7**, were prepared in the same manner as previously report.^{1-3, 6} Cyclam was purchased in a free-base form (99% purity) from Aldrich Chem. Co. and was used without further purification. Cu(II) complexes of these ligands(L) were prepared by modification of the Korybut-Daszkiewicz method as follows;⁷ A methanol solution of the Cu(II) perchlorate was slowly added dropwise into a methanol solution of each ligand in a mini-flask with a reflux-condenser under heating at 50–60°C until the copper was equimolar. After cooling the mixture in a refrigerator overnight, the crystalline products were filtered and recrystallized from methanol as [Cu(L)](ClO₄)₂

L = 1: dark purple needless, *Anal.* Calcd. for C₁₀H₂₄N₄O₈Cl₂Cu(%) :C, 25.93; H, 5.23; N, 12.10. Found: C, 26.06; H, 5.06; N, 11.99.

L = 2: purple, *Anal.* Calcd. for C₁₄H₃₂N₄O₈Cl₂Cu(%) : C, 32.38 ; H, 6.22; N, 10.79. Found: C, 32.46; H, 6.35; N, 10.97

L = 3: reddish brick, *Anal.* Calcd. for C₁₈H₄₀N₄O₈ Cl₂Cu(%) :C, 37.56; H, 7.01; N, 9.74. Found: C, 37.58; H, 6.87; N, 9.55.

L = 4: reddish brick fine, *Anal.* Calcd. for C₁₄H₃₀N₄O₈Cl₂Cu(%) :C, 32.50; H, 5.85; N, 10.84. Found: C, 32.72; H, 5.85;N, 10.28.

L = 5: purple fine needles, *Anal.* Calcd. for $C_{14}H_{30}N_4O_8Cl_2Cu$ (%) :C, 32.50; H, 5.85, N, 10.84. Found: C, 32.38; H, 6.00; N, 10.77

L = 6, 7: same materials in previous reports.¹⁻²

Measurements of Acid Dissociation and Stability Constants

Acid dissociation constants of ligands, **2** – **5**, and stability constants of their Cu(II) complexes were determined by pH-metric titration at 25°C as previously report.¹⁻⁶ The results are shown in Table I.

Measurement of Electronic Spectra

Electronic absorption spectra of the complexes were recorded in the wavelength region of 250 to 900nm (11000 – 40000cm^{-1}) on a Hitachi U-2000 double beam spectrophotometer for water and organic solutions at room temperature. The commercial GR-grade, 'Dotite Spectro-sol' organic solvents, methanol(MeOH), acetone (AC), propylene carbonate(PC), formamide(FA), N,N-dimethyl-formamide(DMF), and dimethylsulfoxide(DMSO) were used without further purification. The spectrum of the Cu(II) complex of cyclam is shown in Figure 1 as an example. The wavenumbers of maximum absorption with $\log \epsilon$ 1.6–2.3 in water are assigned to *d-d* ligand-field transition (Table II).

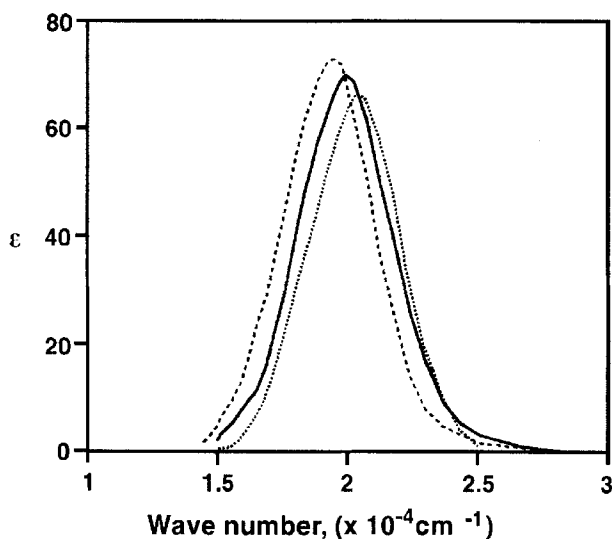


FIGURE 1 UV-Vis absorption spectra of a Cu(II)-cyclam complex in some solvents. (—), in water; (...), in AC; (---), in DMF.

TABLE I Acid dissociation constants of 2, 3- and 2, 3, 9, 10-methyl and -cyclohexyl substituted cyclams, and stability constants of their copper(II) complexes $[\text{Cu}(\text{L})](\text{ClO}_4)_2$, at 25°C, 0.1M KNO_3 aqueous solution

Ligand L	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}	ΔpK_{a34}	pK_{a34} (av)	$\log K_{\text{Cul}}$	Ref
1 cyclam	~1	2.3	10.57	11.49	0.92	11.03	26.52	1
2 Me ₄ cyclam	~1	3.7	10.19	12.21	2.02	11.20	26.68	This work
3 Me ₈ cyclam	~1	2.2		precipitate		(11.1) ^{*1}	(26.6) ^{*2}	This work
4 cis-Cycyclam	~1	3.2	9.99	11.38	1.39	10.69	26.04	This work
5 trs-Cycyclam	~1	2.4	10.64	11.21	0.57	10.93	26.27	This work
6 Cy ₂ cyclam (P)	~1	1.7	10.41	10.95	0.54	10.68	26.46	1
7 Cy ₂ cyclam (N)	~1	1.5	10.37	11.31	0.94	10.84	27.08	1

$$\Delta pK_{a34} = pK_{a4} - pK_{a3}, pK_{a34}(\text{av}) = (pK_{a3} + pK_{a4})/2$$

*¹ Estimated from interpolation of linear relation in Figure 3, refer to text

*² Estimated from interpolation of linear relation in Figure 4, refer to text

TABLE II The stability constants of 2, 3- and 2, 3, 9, 10-methyl or -cyclohexyl substituted cyclams with copper (II) at 25°C in 0.1M KNO_3 aqueous solution wavenumber for maximum absorption of their copper (II) complexes, $[\text{Cu}(\text{L})](\text{ClO}_4)_2$, in water and organic solvents

Ligand(L)	$\log K_{\text{Cul}}$	$\lambda_{\text{max}}^{-1}$ ($\times 10^{-4} \text{cm}^{-1}$)	water	PC	AC	MeOH	FA	DMF	DMSO
1 cyclam	26.52	1.984	2.024	2.024	2.024	2.000	1.953	1.946	1.938
2 Me ₄ cyclam	26.68	1.980	2.033	2.037	2.004	2.004	1.965	1.946	1.946
3 Me ₈ cyclam (26.6) [*]		1.980	2.045	2.049	2.000	2.000	1.957	1.938	1.946
4 cis-Cycyclam	26.04	1.965	2.020	2.020	1.980	1.980	1.946	1.919	1.931
5 trs-Cycyclam	26.27	1.972	2.004	2.016	1.980	1.980	—	1.912	1.919
6 Cy ₂ cyclam(P)	26.46	1.969	2.016	2.012	1.980	1.980	1.931	1.916	1.923
7 Cy ₂ cyclam(N)	27.08	1.980	2.028	2.016	2.004	2.004	1.946	1.946	1.972
Donor number (D_N)		18.0	15.1	17.0	19.0	19.0	24	26.0	29.8
Acceptor number (A_N)		54.8	18.3	12.5	41.3	41.3	39.8	16.0	19.3
Dielectric constant (D_C)		78.54	64.4	20.7	32.6	32.6	11.1	36.71	46.6

* Predicted from interpolation of linear relation in Figure 4, refer to text. PC propylene carbonate; AC acetone; MeOH methanol; FA formamide; DMF dimethylformamide; DMSO dimethylsulfoxide

RESULTS AND DISCUSSION

Acid Dissociation Behavior

As shown in Table I, four acid dissociation steps are observed for all 2, 3- and 2, 3, 9, 10- methyl or cyclohexyl substituted cyclams. These are largely split into two groups with a jump between the second and third steps. The behavior of the ligands is similar to that of cyclam, and is explained by two of the four dissociative protons on $H_4[14]aneN_4^{4+}$, are tightly fixed inside the ring by hydrogen bonding and the other two protons are on the outside of the ring.⁸ Each dissociation constant of the ligands, however, shifts to a certain extent by substituting a methyl or cyclohexyl group into a cyclam-ring.

We use two parameters, $\Delta pK_{a_{34}}$ and $pK_{a_{34(av)}}$, to discuss effects of the substituting group on the ligand basicity and the ring deformation. The magnitude of $\Delta pK_{a_{34}}$ which is the difference between third- and fourth-dissociation constants may measure the ring deformation which is likely to relate to the relative conformation of the four nitrogens on a cyclam ring. The magnitude of $pK_{a_{34(av)}}$ which is the average of third- and fourth-dissociation constants may measure ligand basicity of the cyclam analogs, which may relate to induced-effects of methyl and cyclohexyl groups on the four nitrogens of the cyclam analogs. From the results shown in Table I and Figure 2, values of $pK_{a_{34(av)}}$ for the methyl-substituted cyclams are greater than that for cyclam and the values for

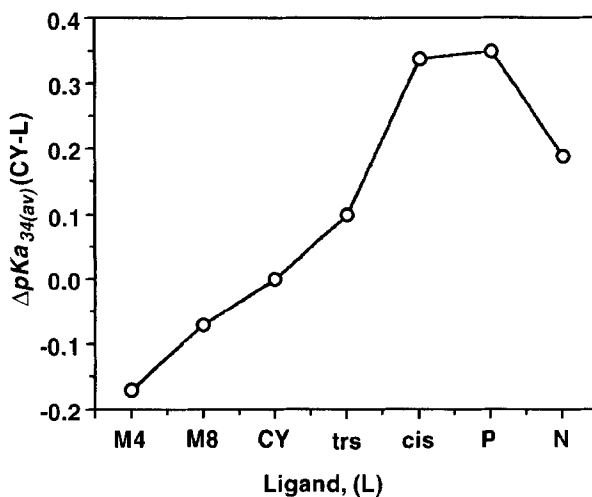


FIGURE 2 Substitution effects of methyl and cyclohexyl on the ligand basicity of cyclam $\Delta pK_{a_{34(av)}}(CY-L) = \Delta pK_{a_{34(av)}}(CY) - \Delta pK_{a_{34(av)}}(L)$ Ligand **M4**, Me₄ cyclam; **M8**, Me₈ cyclam; **CY**, cyclam; **cis**, *cis*-Cycyclam; **trs**, *trans*-Cycyclam; **P**, Cy₂ cyclam(P); **N**, Cy₂ cyclam(N).

cyclohexyl-substituted cyclam are smaller than that for cyclam. The cyclohexyl group and heightened by modification of the methyl group in spite of the little difference in basicity between n-hexylamine(10.63) and cyclohexylamine(10.61). On the other hand, values of ΔpK_{a34} for ligands **5** and **6** are smaller than that for cyclam, and the values for ligands **2** and **4** are greater than that for cyclam. These differences do not always depend on the kind of substituted group, methyl or cyclohexyl, and there are great differences in ligands, **4**, **5**, and **6**, **7** with the same cyclohexyl group. These results seem to show that formation of hydrogen bonds between third- and fourth-dissociative protons and two of four nitrogens depend on the conformation of the nitrogens on a cyclam ring.

Complexation Behavior and Electronic Spectra

As shown in Table I and Figure 3, although slight differences in stability constants of the Cu(II)-complexes exist for ligands, **1-7**, there is a good linear relation to the ligand basicity, $pK_{a34(av)}$, except for ligands **6** and **7**. These results show that the ring framework of cyclam ([14]aneN₄-ring) is firm and affected little by periphery modification around the ring because the ring-size is favorable for Cu(II) coordination. The stability constant, however, is linearly sensitive to the nitrogen basicity change by substituent group. The stability constants for complexes of ligands **6** and **7** are much larger than the constants predicted their ligand basicities (Figure 3). This may be based on the macrocyclic effect accompanied by symmetric conformation of two cyclohexyl-rings.¹

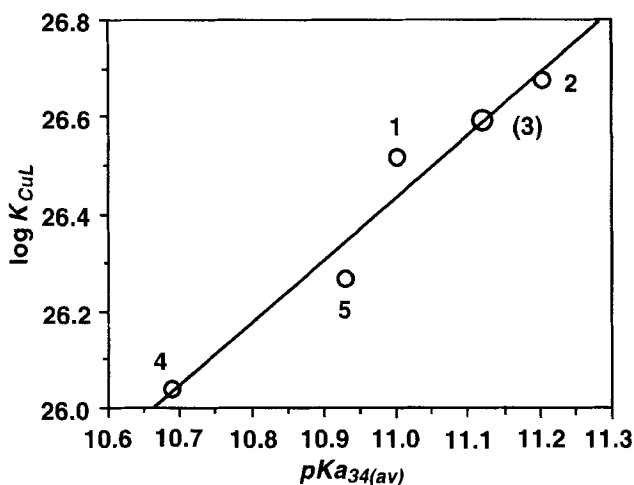


FIGURE 3 Linear relation between basicity of ligands, $pK_{a34(av)}$ and stability constants of their Cu(II)-complexes **1**, cyclam; **2**, Me₂cyclam; **3**, Me₃cyclam; **4**, cis-Cycyclam; **5**, trs-Cycyclam.

The wavenumbers for maximum absorption of these complexes in the electronic spectrum were determined in water and some typical organic solvents. These values are shown in Table II with solvent parameters, donor numbers (D_N) and dielectric constants (D_C). As shown in Figure 4, the stability constants of the complexes in water have a good linear relationship to the difference in wavenumber of maximum absorption in water and in organic solvent ($\Delta\lambda_{\max}^{-1}(W-S)$). The wavenumber shift in pyridine deviates because of the high coordination ability of the solvent. The absorption in ethanol is hard to detect because of poor solubility for the complexes. Using these results, unknown stability constants for Cu(II)-complexes of 2, 3- and 2, 3, 9, 10-substituted cyclams can be predicted by the linear relation in Figure 4 using electronic spectral data of the Cu(II)-complexes. Furthermore, ligand basicity ($pK_{a34(av)}$) is also predictable from interpolation of a straight line in Figure 3 by using the stability constant of the complex. For example, although the value of $\log K_{CuL}$ for ligand **3** cannot be determined because pK_{a3} and pK_{a4} obscured by precipitation during the pH-titration, the values of $\log K_{CuL}$ and $pK_{a34(av)}$ are predicted to be 26.6 and 11.1 from interpolation in Figure 4 and in Figure 3, respectively.

Since each of these absorptions is assigned to a ligand-field band which overlaps with three components of the $d-d$ ($d_{xz} - d_{x^2-y^2}$, $d_{z^2} - d_{x^2-y^2}$, $d_{yz} - d_{x^2-y^2}$) in D_{4h} symmetry,⁹ these linear relations are assumed to be brought

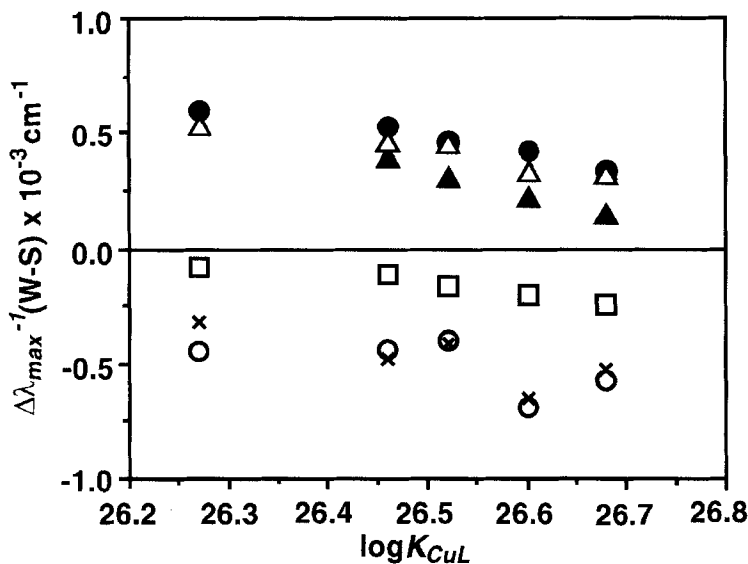


FIGURE 4 Linear relation between the stability constants of the Cu(II)-complexes and the shift difference of maximum absorption wavenumber between water and organic solvent $\Delta\lambda_{\max}^{-1}(W-S) = \Delta\lambda_{\max}^{-1}(W) - \Delta\lambda_{\max}^{-1}(S)$ (●)AC; (□)MeOH; (▲)FA; (△)DMSO; (●)DMF; (x)PC.

by two factors; (1) the metal-to-nitrogen distance in a planar complex, $[\text{Cu}(\text{L})]^{2+}$ affecting the ligand-field strength, and (2) the effect of solvent-complex interaction on axial elongation in D_{4h} symmetry. This may be supported from results of that the wave number shift from water to organic solvents, $\Delta\lambda_{\text{max}}^{-1}(\text{W-S})$, which not only tends to depend linearly on the stability constant, but also on the donor number (D_N) and the dielectric constant (D_C) as shown in Figures 5 and 6. A similar linearity between shift of maximum wavenumber and donor number has been reported $[\text{VO}(\text{acac})_2]$ by Selbin. It is expected that a solvent molecule adds to the sixth position and alters the magnitude of axial perturbation based on the oxygen at the position *trans* to the solvent molecule.¹⁰ As shown in Scheme 2, the dielectric constant and donor number are assumed to affect solvent-separated ion pair formation among a complex ion ($[\text{Cu}(\text{L})]^{2+}$), solvent molecule(S), and counter ion (ClO_4^-). Therefore, higher dielectric constant of solvent causes easier ion-pair dissociation between the complex cation and counter anion. For a solvent approach to a complex cation, on the other hand, higher donor number of solvent

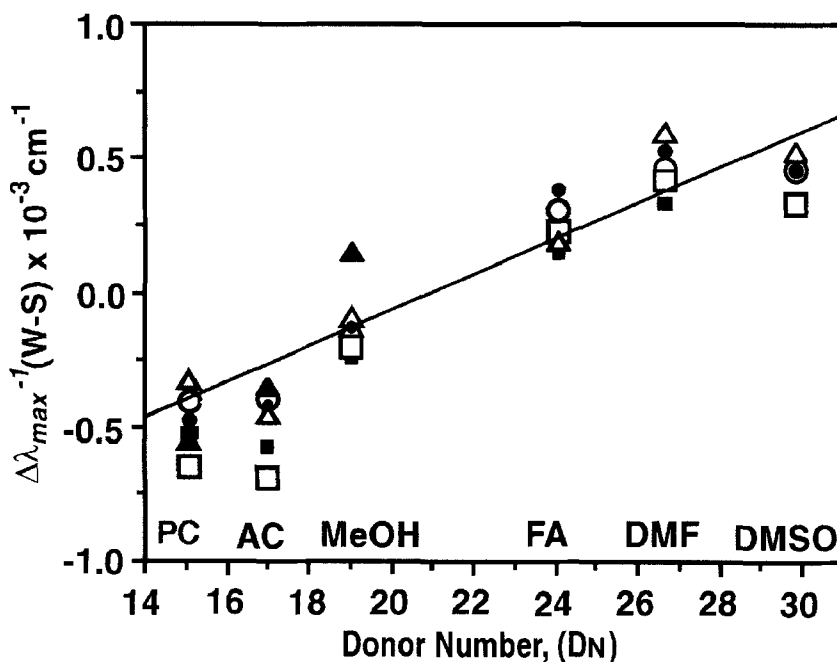


FIGURE 5 Dependence of the shift difference of maximum absorption wavenumber between water and organic solvents on donor number (D_N) of the organic solvent. A line is plotted in the case for cyclam. (O) cyclam; (■) Me_4cyclam ; (□) Me_8cyclam ; (▲) *cis*-Cycyclam; (Δ) *trans*-Cycyclam; (●) $\text{Cy}_2\text{cyclam(P)}$.

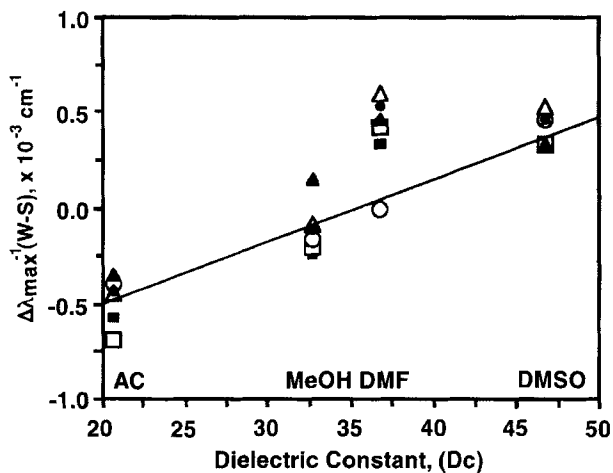
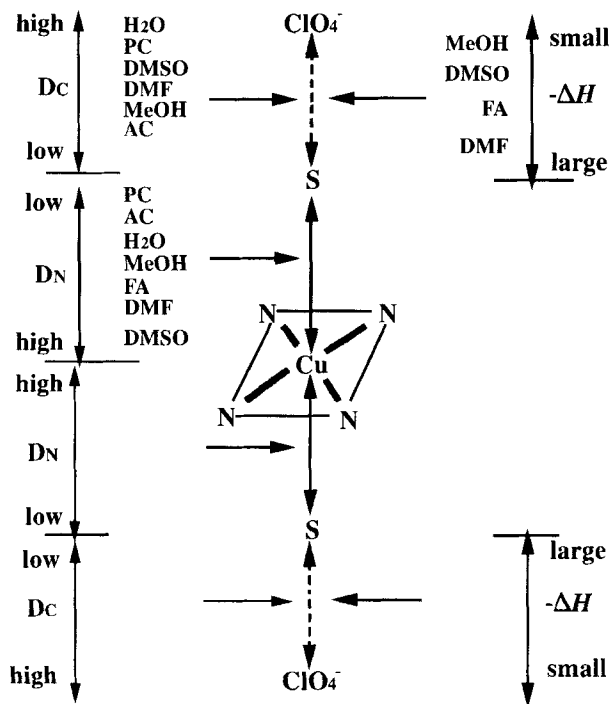


FIGURE 6 Dependence of the shift difference of maximum absorption wavenumber between water and organic solvents on dielectric constants (D_C) of organic solvent. A line is plotted in the case for cyclam. (O) cyclam; (■) Me_4 cyclam; (□) Me_8 cyclam; (▲) *cis*-Cyclclam; (Δ) *trans*-Cyclclam; (●) Cy_2 cyclam(P).



Scheme 2

causes a stronger interaction between a metal on the complex and the solvent molecules in the axial position. We assume that these solvent effects bring about the wavenumber shift on the electronic spectrum. As shown in Figure 4, the wavenumber shifts from water to organic solvents ($\Delta\lambda_{max}^{-1}(W-S)$) show red-shift in dimethylsulfoxide and dimethylformamide, and blue-shift in acetone and propylene carbonate, respectively. In methanol, there are small red- and blue-shifts. When a fifth or sixth ligand coordinates to axial position of a square-planar Cu(II)-ammine complex, a large red-shift has been observed in the main *d-d* absorption band, which is well known as the penta-ammine effect.¹¹⁻¹² Therefore, dimethylsulfoxide and dimethylformamide molecules show stronger interaction for close approach to the axial position of the Cu(II)-complex than water. On the other hand, acetone shows weaker interaction than water, and methanol shows an interaction comparable to water. The fact that the wavenumber maximum in these solvents depends linearly on the stability constant of the complex in water and tends to shift to low wavenumber (red-shift) with decreasing stability constants, suggests that lower stability of the complex results from the stronger axial interaction between a Cu(II) complex and solvent molecule.

As shown in Table II, the effects of periphery substituents on cyclam analogs on the wavenumber maximum of their Cu(II) complexes tend to be blue-shift for methyl and red-shifted for cyclohexyl except ligand 7 in each solvent. The results seem to show a more effective ring-conformation and ligand-field on the approach of axial solvent by substituting cyclohexyl.

We propose a new parameter ' $\log K_{\lambda}(S)_0$ ' to indicate the effect of solvent on the transferred complex from water to non-aqueous solvents. We call the parameter ' K_{λ} -value', which is the value of $\log K_{CuL}$ obtained from interpolating or extrapolating intersection each line in Figure 4 to $\Delta\lambda_{max}^{-1}(W-S) = 0$. This parameter is distinguishable from other optical scales such as Z - and E_T -values,¹³⁻¹⁴ which arise from a charge-transfer band based on intramolecular interaction in an ion-pair. The physical meaning of the new parameter is the limiting stability constant for which the complex maintains the spectrochemical situation in the organic solvent as in water against the solvent-complex interaction through axial approach. In other words this parameter is the imaginary isostability constant in water by transferring the Cu(II)-complex from organic solvent to water without any spectrochemical shift. The increasing order of $\log K_{\lambda}(S)_0$ is as follows; DMF(27.24)>DMSO(27.14)>FA(26.82)> MeOH(26.27)>PC(25.75) >AC(24.71). This order is almost parallel to increasing orders of D_N and D_C for the solvents shown in Table II. For example, when the stability constant of a complex is 26.27 in water, it may be able to keep same situation in MeOH as in water by interaction between a complex and MeOH molecule, however, it may be not able to do so in DMF and DMSO because of lower $\log K_{\lambda}(S)_0$.

The values of $\Delta\lambda_{\max}^{-1}(\text{W-S})$ show linear dependence on enthalpies of transfer of ClO_4^- from water to organic solvents,¹⁵⁻¹⁷ as shown in Figure 7. The linear dependence is especially good among DMF, DMSO, FA and MeOH. More exothermic solvents cause larger shifts for $\Delta\lambda_{\max}^{-1}(\text{W-S})$, *i.e.*, more exothermic solvation for ClO_4^- allows easier approach of solvent (S) to a complex ($[\text{Cu}(\text{L})]^{2+}$), and formation of solvent-separated ion pair ($[\text{Cu}(\text{L})]^{2+} \cdot (\text{S})_m \cdot (\text{ClO}_4^-)_n$, where $m, n=1$ or 2) as shown in Scheme 2. These results suggest that effects of solvent on M—N bond character of $[\text{Cu}(\text{L})]^{2+}$ by axial-interaction and ion pair-association of solvated complex bring about the spectrochemical shift through ligand-field perturbation with M—N bond stretching or axial elongation. Therefore, dissociation of ClO_4^- from an ion-pair and approach of solvent to the complex are assumed to depend on the solvation enthalpy of ClO_4^- and the stability constant of the complex, $[\text{Cu}(\text{L})]^{2+}$, respectively. Properly speaking, the free energy transfer accompanied by the entropy contribution should be used rather than the enthalpy of transfer in order to show the linear relation described above. The free energy and entropy data for organic solvents, however, require more explanation than we can detail in this report.

In conclusion, we would like to propose that the Cu(II) complexes of 2, 3- and 2, 3, 9, 10-substituted cyclams are very interesting examples showing the cooperative effects of three solvent parameters (donor number, dielectric constant and solvation enthalpy) on the potentiometric data for solution equilibrium (stability constant) and the spectrometric data for ligand-field perturbation.

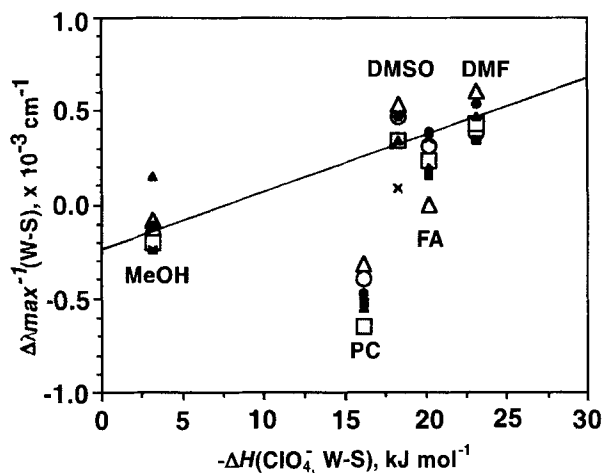


FIGURE 7 Linear relation between wavenumber shift, $\Delta\lambda_{\max}^{-1}(\text{W-S})$, for $[\text{Cu}(\text{L})](\text{ClO}_4)_2$ and the enthalpy of transfer of ClO_4^- from water to some organic solvents. A line is plotted in case for cyclam in MeOH, DMSO, FA, DMF (O)cyclam; (■)Me₄cyclam; (□)Me₈cyclam; (▲)*cis*-Cycyclam; (Δ)*trans*-Cycyclam; (●)Cy₂cyclam(P).

References

- [1] Y. Moriguchi and K. Sakata, *J. Coord. Chem.*, **23**, 321 (1991).
- [2] K. Sakata, S. Wada, N. Sato, M. Krisu, M. Hashimoto and Y. Kato, *Inorg. Chim. Acta*, **119**, 111 (1986).
- [3] K. Kobiro, N. Nakayama, T. Hino, M. Suwa and Y. Tobe, *Inorg. Chem.*, **31**, 676 (1992).
- [4] A.E. Martell and R.M. Smith, *Critical Stability Constants*, Vol. **5** (Plenum Press, New York, 1989), p185.
- [5] R.M. Izatt, K. Pawlak, J.B. Brodshaw, *Chem. Revs.*, **91**, 1738 (1991).
- [6] Y. Moriguchi, Y. Takeuchi, Y. Sato, M. Miyata, K. Kobiro, Y. Tobe and K. Sakata, Presented at the 30th International Conference on Coordination Chemistry, Kyoto, 1994, *Abst.*, PS-524., Y. Moriguchi and Y. Takeuchi, *Bull. Fukuoka Univ. of Education*, **43**, part III, 29 (1994).
- [7] B. Korybut-Daszikiewicz, J. Mrozinski and W. Wojciechowsky, *Bull. Acad. Pol. Sci., Ser. Chim.*, **17**, 411 (1969).
- [8] C. Nave and M.R. Truter, *J. Chem. Soc., Dalton Trans.*, 2351 (1974).
- [9] R.L. Belford, M. Calvin and G. Belford, *J. Phys. Chem.*, **26**, 1165 (1957).
- [10] J. Selbin, *Chem. Revs.*, **65**, 153 (1965).
- [11] J. Bjerrum, C.J. Ballhausen and C.K. Jorgensen, *Acta Chem. Scand.*, **8**, 1275 (1954).
- [12] S. Yamada and S. Miki, *Bull. Chem. Soc. Jpn.*, **36**, 680 (1963).
- [13] E.M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).
- [14] K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, *Liebig Ann. Chem.*, **661**, 1 (1963).
- [15] Y. Marcus, *Ion Solvation*, (John Wiley & Sons Limited, New York 1985), p173.
- [16] H. Ohtaki, *Youeki no Kagaku* in New Chemistry Library Ed. by The Chemical Society of Japan, (Dainippontoshu, Tokyo 1987), p88, 89.
- [17] Y. Moriguchi, K. Sakata, K. Kobiro and Y. Tobe, Presented at the 45th Symposium Coordination Chemistry of Japan, Fukuoka, 1995, *Abst.* 2C16.