

## Unusual Affinities of Monovalent Anions to Dicopper(II) Complexes with $N,N',N'',N'''$ -Tetrakis(2-aminoethyl)-tetra-azacycloalkanes

EIJI ASATO, KAZUKIKO OZUTSUMI, SHIN-ICHI ISHIGURO, SIGEO KIDA\*

Okazaki National Institutes, Institute for Molecular Science, Myodaiji, Okazaki 444 (Japan)

and ICHIRO MURASE

Laboratory of Chemistry, College of General Education, Kyushu University 01, Ropponmatsu, Fukuoka 810 (Japan)

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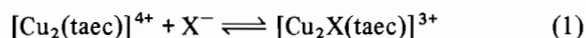
### Abstract

The equilibrium constants for  $[\text{Cu}_2\text{L}]^{4+} + \text{X}^- = [\text{Cu}_2\text{XL}]^{3+}$  were determined spectrophotometrically in aqueous solution at 25 °C, where L represents the title ligands and X denotes Cl, Br, I and  $\text{CH}_3\text{COO}^-$ . The formation constants of  $[\text{Cu}_2\text{XL}]^{3+}$  thus obtained were unusually large compared to those of common copper(II) complexes with Cu–X bonds, and decrease in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{CH}_3\text{COO}^-$  for a given L, and  $\text{taec} > \text{taep} > \text{taeh}$  for a given  $\text{X}^-$ . The origin of the surprisingly high stabilities was discussed.

### Introduction

Recently, Kida *et al.* have shown that  $N,N',N'',N'''$ -tetrakis(2-aminoethyl)-1,4,8,11-tetra-azacyclotetradecane (abbreviated as taec) acts as an octadentate ligand to form dinuclear complexes with various transition metal(II) ions [1–5]. These complexes exhibited unusual features in various aspects. Among them the most conspicuous feature is the very high stability of the Cu–X linkage in  $[\text{Cu}_2\text{X}(\text{taec})]^{3+}$  in aqueous solution [2] compared to those of  $[\text{CuX}]^+$ , where  $\text{X}^-$  denotes a monovalent anion such as  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{NO}_2^-$ , etc.

The equilibrium constants  $K$  for the reactions



were determined spectrophotometrically by Evers *et al.* [6] and Kida *et al.* [2], independently. Although their results were significantly different

due to the different experimental conditions, the formation constants obtained by both workers were very much larger ( $10^3$ – $10^4$  times) than those of Cu–X bonds of ordinary copper(II) complexes [7, 8].

Murase *et al.* prepared analogous ligands with a 15-membered tetra-azamacrocyclic and with a 16-membered one [9]. Accordingly, in this study, in order to see the effect of expanding the macrocyclic ring, the formation constants ( $K$ ) of the reactions were determined



$$K = [\text{Cu}_2\text{XL}^{3+}]/[\text{Cu}_2\text{L}^{4+}][\text{X}^-] \quad (3)$$

where L denotes taec, taep ( $N,N',N'',N'''$ -tetrakis(2-aminoethyl)-1,4,8,12-tetra-azacyclopentadecane) [9] and taeh ( $N,N',N'',N'''$ -tetrakis(2-aminoethyl)-1,5,9,13-tetra-azacyclohexadecane) [9] illustrated in Fig. 1.

Since the method and apparatus of the measurements have been much improved from our previous one [2], the present study can provide more accurate data which may enable us to discuss the origin of such surprisingly high stabilities of the Cu–X linkage.

### Experimental

#### Materials

$[\text{Cu}_2(\text{taec})](\text{ClO}_4)_4$  [1],  $[\text{Cu}_2(\text{taep})](\text{ClO}_4)_4$  [9], and  $[\text{Cu}_2(\text{taeh})](\text{ClO}_4)_4$  [9] were prepared by the procedures reported previously. The other reagents (guaranteed grade) were commercially obtained.

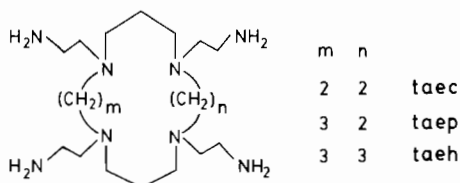


Fig. 1. The octa-amine ligands and their abbreviations.

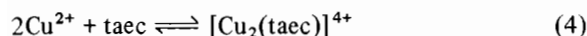
\*Author to whom correspondence should be addressed. Present addresses: E.A. and S.K., Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Fukuoka 812, Japan; S.I., Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuda, Nagatsuda, Midori-ku, Yokohama 227, Japan; K.O., Department of Chemistry, University of Tsukuba, Sakura, Ibaraki 305, Japan.

### Measurements

Electronic spectra were measured with a Shimadzu multipurpose spectrophotometer MPS-2000 equipped with an NEC PC-9801 vm computer which records data in 1 nm intervals over the wavelength range 300–850 nm. A flow cell with a pathlength of 1 cm was connected to a titration vessel through Teflon and glass tubes. An aqueous solution of  $[\text{Cu}_2\text{L}](\text{ClO}_4)_4$  (L = taec, taep and taeh) was placed in the vessel and titrated with an aqueous NaX (X = Cl, Br, I and  $\text{CH}_3\text{COO}$ ) solution ( $30 \text{ mmol dm}^{-3}$ ). Spectrophotometric data at selected 44 wavelengths over the 450–750 nm range were employed for the least-squares calculations.

### Analysis of the Data

According to Evers *et al.* [6], the equilibrium constant for



is extremely large compared to those for (1), hence the dissociation of  $[\text{Cu}_2\text{L}]^{4+}$  was neglected throughout the present calculations.

The absorbance  $A_{ij}$  observed at the  $i$ th titration point at a given wavelength  $\lambda_j$  is described by using the formation constant  $K$  of (3) and molar extinction coefficient  $\epsilon_n(\lambda_j)$  of  $[\text{Cu}_2\text{XL}]^{3+}$  as

$$A_{ij} = \epsilon_n(\lambda_j)Km_i x_i + \epsilon_M(\lambda_j)m_i + \epsilon_X(\lambda_j)x_i \quad (5)$$

where  $m$  and  $x$  represent the concentrations for  $[\text{Cu}_2\text{L}]^{4+}$  and  $\text{X}^-$ , respectively, and  $\epsilon_M$  and  $\epsilon_X$  are molar extinction coefficient for  $[\text{Cu}_2\text{L}]^{4+}$  and  $\text{X}^-$ , respectively.  $\epsilon_M$  could be readily determined experimentally and  $\epsilon_X$  is zero for all the anions used in this study over the range of the measurements. The total concentrations of the copper complexes  $C_M$  and the anion ligand  $C_X$  are given as

$$C_{Mi} = m_i + Km_i x_i \quad (6)$$

$$C_{Xi} = x_i + Km_i x_i \quad (7)$$

By utilizing the relations (6) and (7),  $A_{ij}$  can be expressed as a function of  $K$  and  $\epsilon_n(\lambda_j)$ . Thus,  $K$  and  $\epsilon_n(\lambda_j)$  can be determined by least-squares calculations.

### Results and Discussion

Coordination modes of copper(II) taec complexes can be classified into two types as shown in Fig. 2; type 1 being found for  $[\text{Cu}_2(\text{taec})](\text{ClO}_4)_4$  and type 2 for  $[\text{Cu}_2\text{X}(\text{taec})](\text{ClO}_4)_3$  (X = Cl, Br, I, etc.) [1–5]. It is almost certain that the  $[\text{Cu}_2\text{X}(\text{taec})]^{3+}$  complex in solution has the same coordination mode as in the crystal, since the frequencies of d–d absorption maxima are practically the same for solid and solution. However, the band maximum of  $[\text{Cu}_2-$

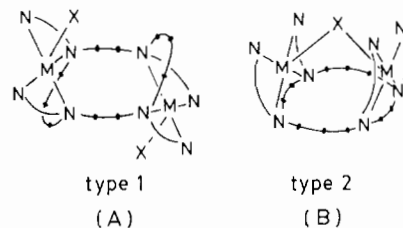


Fig. 2. Coordination modes of taec complexes.

$(\text{taec})](\text{ClO}_4)_4$  in crystal form suffers a considerable red shift ( $19.2 \rightarrow 17.7 \times 10^3 \text{ cm}^{-1}$ ) when the crystals are dissolved in water, hence it is not clear whether the cation takes the type 1 or type 2 coordination mode in aqueous solution. Since no time dependence was detected in the spectra, the conversion of  $[\text{Cu}_2(\text{taec})]^{4+}$  into  $[\text{Cu}_2\text{X}(\text{taec})]^{3+}$  should be facile in aqueous solution. This suggests that both species adopt the same coordination mode (trimethylene-bridging structure like type 2), because the transformation from type 1 to type 2 requires a serious rearrangement of coordination bonds and ligand conformation. Thus, it is likely that the transformation occurs in the process of dissolution of  $[\text{Cu}_2(\text{taec})](\text{ClO}_4)_4$ .

Figures 3 and 4 show the electronic spectra obtained by titrating  $[\text{Cu}_2(\text{taec})](\text{ClO}_4)_4$  and  $[\text{Cu}_2-$

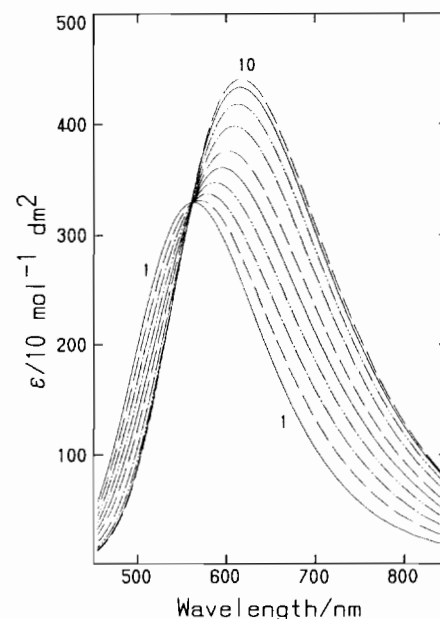


Fig. 3. Absorption spectra of  $[\text{Cu}_2(\text{taec})](\text{ClO}_4)_4$  in aqueous solution (containing  $\text{NaClO}_4$  ( $30 \text{ mmol dm}^{-3}$ )), when titrated with  $\text{NaCl}$  solution.  $C_X/C_M$  of each solution 0 (1), 0.122 (2), 0.244 (3), 0.365 (4), 0.487 (5), 0.609 (6), 0.812 (7), 1.421 (8), 4.059 (9), or 8.113 (10), where  $C_X$  and  $C_M$  represent the total concentrations of the anion and complex cations, respectively, and the number in parentheses refers to the absorption curve in the Fig.

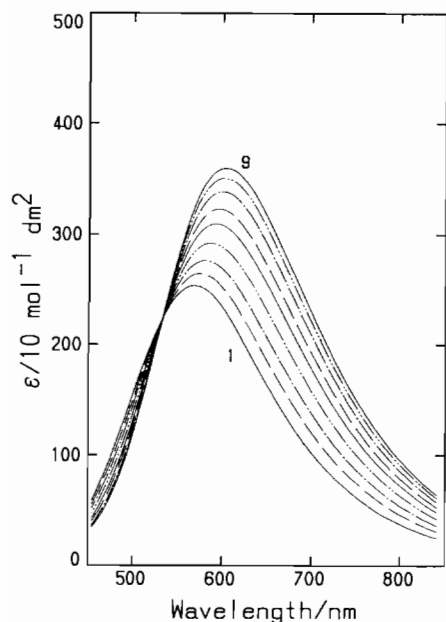


Fig. 4. Absorption spectra of  $[\text{Cu}_2(\text{taep})](\text{ClO}_4)_4$  in aqueous solution (containing  $\text{NaClO}_4$  ( $30 \text{ mmol dm}^{-3}$ )), when titrated with  $\text{NaCl}$  solution.  $C_X/C_M$  of each solution is 0 (1), 0.162 (2), 0.324 (3), 0.539 (4), 0.809 (5), 1.079 (6), 1.618 (7), 2.695 (8), or 5.319 (9), where  $C_X$  and  $C_M$  represent the total concentrations of the anion and complex cations, respectively, and the number in parentheses refer to the absorption curve in the Fig.

$(\text{taep})(\text{ClO}_4)_4$  solution, respectively, with an  $\text{NaCl}$  solution for example. In each system, the presence of an isobestic point implies that only two species of chromophores, i.e.  $[\text{Cu}_2\text{L}]^{4+}$  and  $[\text{Cu}_2\text{ClL}]^{3+}$  ( $\text{L} = \text{taec}, \text{taep}$ ) exist in solution. From these experimental data the formation constants were obtained by the method described in the previous section, and are listed in Table 1. The extinction coefficients of  $[\text{Cu}_2\text{XL}]^{3+}$  can be calculated from the measured

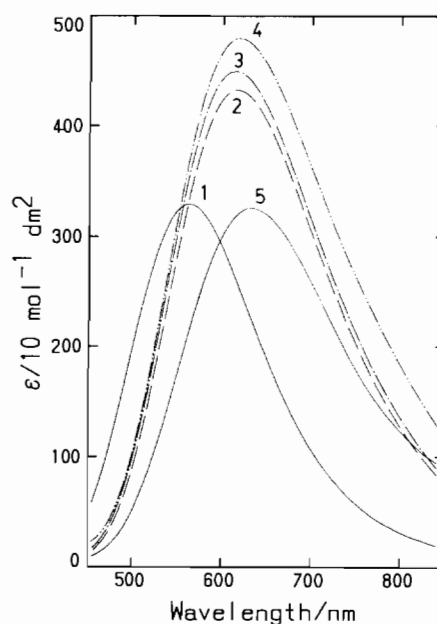


Fig. 5. Absorption spectra of  $[\text{Cu}_2(\text{taec})\text{X}]^{3+}$  estimated from the measured absorption data and the formation constants obtained in this study, where  $\text{X} = \text{Cl}$  (2),  $\text{Br}$  (3),  $\text{I}$  (4) and  $\text{CH}_3\text{COO}$  (5), where the number in parentheses refers to the absorption curves in the Fig. The spectrum of  $[\text{Cu}_2(\text{taec})]^{4+}$  (1) is also cited for comparison.

absorption data and the formation constants obtained here. The absorption spectra of  $[\text{Cu}_2\text{XL}]^{3+}$  ( $\text{L} = \text{taec}$  and  $\text{taep}$ ) cited in Figs. 5 and 6 were drawn in this way.

In the cases of  $\text{L} = \text{taec}$  and  $\text{taep}$ , in order to suppress the change in ionic strength, all measurements were carried out on solutions containing  $30 \text{ mmol dm}^{-3}$   $\text{NaClO}_4$ , which is 10–30 times more than the complex species. No higher perchlorate concentration was feasible, because addition of perchlorate greatly reduces the solubility of the

TABLE 1. Equilibrium constants  $K$  ( $\text{mol}^{-1} \text{dm}^3$ ) for  $[\text{Cu}_2\text{L}]^{4+} + \text{X}^- \rightleftharpoons [\text{Cu}_2\text{XL}]^{3+}$

Complex	Anion	$\log K^a$	$N^b$	$U^c$	$R^d$
$[\text{Cu}_2(\text{taec})](\text{ClO}_4)_4$	Cl	4.465(0.035)	1540	0.0930	2.09
	Cl*	5.113(0.078)	1364	0.1408	2.80
	Br	4.485(0.019)	2244	0.1583	1.88
	I	3.871(0.007)	1672	0.0436	1.48
	$\text{CH}_3\text{COO}$	2.117(0.002)	1584	0.0016	0.53
$[\text{Cu}_2(\text{taep})](\text{ClO}_4)_4$	Cl	3.223(0.005)	1672	0.0372	0.88
	Br	3.245(0.006)	1496	0.0398	0.97
	I	2.760(0.003)	1628	0.0288	0.80
	$\text{CH}_3\text{COO}$	1.346(0.037)	2068	0.0361	1.15
$[\text{Cu}_2(\text{taeh})](\text{ClO}_4)_4$	Cl*	2.574(0.002)	1980	0.0019	0.47
	Br*	2.592(0.005)	1804	0.0055	0.78
	I*	2.186(0.006)	1804	0.0072	0.92

<sup>a</sup>Values in parentheses refer to standard deviations. <sup>b</sup>The number of data points. <sup>c</sup>Error-square sum. <sup>d</sup>The Hamilton  $R$  factor. Starred items: measurement were carried out without adding  $\text{NaClO}_4$ .

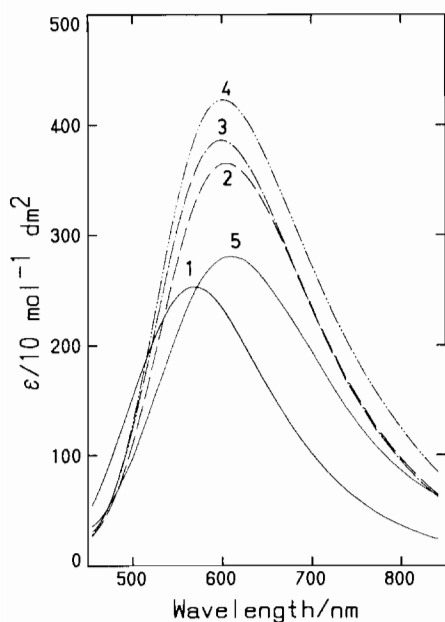


Fig. 6. Absorption spectra of  $[\text{Cu}_2(\text{taep})\text{X}]^{3+}$  estimated from the measured absorption data and the formation constants obtained in this study, where X = Cl (2), Br (3), I (4) and  $\text{CH}_3\text{COO}$  (5), where the number in parentheses refers to the absorption curves in the Fig. The spectrum of  $[\text{Cu}_2(\text{taep})]^{4+}$  (1) is also cited for comparison.

complexes. In the case of the taeh complexes, the solubilities become very low when an excess of  $\text{ClO}_4^-$  is added, hence the measurements were carried out without  $\text{NaClO}_4$ . Therefore, the direct comparison of these data to those of the taec and taep complexes would not be justified. Accordingly, the measurements were carried out on the  $[\text{Cu}_2\text{Cl}(\text{taec})](\text{ClO}_4)_3$  solutions without ionic-strength buffer to estimate the effect of the presence of ionic-strength buffer, and the result is given in Table 1. Thus, taking the effect of  $\text{ClO}_4^-$  into consideration, we may conclude that the formation constants  $K$  of (2) are in the order  $\text{taeh} < \text{taep} < \text{taec}$ , i.e. the larger the macrocycle the lower the formation constants.

The  $K$  values for the taec complexes reported by Evers *et al.* [6] are approximately 1/10 smaller than those obtained in this work. Such a discrepancy should be attributed to the difference in coordinating abilities between  $\text{NO}_3^-$  and  $\text{ClO}_4^-$  which were added as ionic-strength buffers, respectively. In both cases, there is no doubt that the formation constants obtained are surprisingly large ( $10^3$ – $10^4$  times) compared to those of ordinary  $\text{Cu}(\text{II})$ –X complexes [7]. Martell and coworkers reported a considerably high formation constant of macrocyclic copper(II) cryptate complexes with  $\text{Cl}^-$  [8]. However, the presently obtained value for  $\text{Cl}^-$  is even higher than their value.

Such unusually high stabilities may originate from various factors such as (i) bonding of  $\text{X}^-$  to both copper(II) ions, forming an 'inverse chelate ring', (ii) the fact that sixth coordination of the copper ion is sterically hindered by the methylene chains of the ligand, (iii) hydrogen bonding of  $\text{X}^-$  with the amino hydrogen of the ligand, (iv) the hydrophobic environment around  $\text{X}^-$  within  $[\text{Cu}_2\text{XL}]^{3+}$ . All these factors may contribute to the enhanced stabilities of  $[\text{Cu}_2\text{XL}]^{3+}$ .

The effect of factor (i) is obvious, since the energy of the bonding to both copper(II) ions should be at least twice that of a single  $\text{Cu}$ – $\text{X}$  linkage. This should greatly increase the formation constant of (ii). Although an axial  $\text{Cu}(\text{II})$ – $\text{X}$  bond is generally weak due to the Jahn–Teller distortion in six-coordinate complexes, it must be greatly strengthened if the axial ligand in the counter position is eliminated. However, according to the X-ray analyses, the  $\text{Cu}$ – $\text{X}$  bond lengths are in the range of common axial coordination bonds of tetragonal copper(II) complexes [1b, 4b], implying that  $\text{Cu}$ – $\text{X}$  bonds themselves are still not strong enough to account for such remarkably high stabilities. Therefore, one should take account of the environmental effects around the  $\text{Cu}$ – $\text{X}$  bond. Thus, the factors (iii) and (iv) appear to be responsible for the high stability. However, in the course of preparation of this article we have obtained an experimental result which may answer the question of whether (iii) or (iv) is more effective. We have prepared a series of copper complexes of tpmc (*N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetra-azacyclotetradecane) [10]. Similarly to the taec complex,  $[\text{Cu}_2(\text{tpmc})](\text{ClO}_4)_4$  readily binds  $\text{Cl}^-$  forming  $[\text{Cu}_2\text{Cl}(\text{tpmc})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$  whose structure was revealed by X-ray crystal analysis to be similar to  $[\text{Cu}_2\text{X}(\text{taec})](\text{ClO}_4)_3$  [11]. A preliminary spectrophotometric study has shown that the formation constant is in the order of  $10^4$ . Since no amino hydrogen is present in these tpmc complexes, hydrogen bonds cannot contribute to the stability of the  $\text{Cu}$ – $\text{Cl}$  linkage. By analogy with this complex we conclude that factor (iv) may be the important factor for the large formation constants of the present complexes.

As the ring size increases in the order  $\text{taec} < \text{taep} < \text{taeh}$ , the  $\text{Cu}$ – $\text{Cu}$  distance within  $[\text{Cu}_2\text{XL}]^{3+}$  may also increase [12], thereby leading to a significant decrease in the formation constant of  $[\text{Cu}_2\text{XL}]^{3+}$  in the order  $\text{taec} > \text{taep} > \text{taeh}$ . The result can be explained by either factor (i) or (iv). The increase of the  $\text{Cu}$ – $\text{Cu}$  distance brings about the elongation of the  $\text{Cu}$ – $\text{X}$  bond lengths and the decrease in hydrophobicity around the  $\text{Cu}$ – $\text{X}$  bond. In the larger  $[\text{Cu}_2\text{XL}]^{3+}$  cavity, solvent water molecules have access into the cavity so that hydrolysis of the  $\text{Cu}$ – $\text{X}$  bond takes place.

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## References

- 1 (a) I. Murase, M. Mikuriya, H. Sonoda and S. Kida, *J. Chem. Soc., Chem. Commun.*, (1984) 692; (b) I. Murase, M. Mikuriya, H. Sonoda and Y. Fukuda, *J. Chem. Soc., Dalton Trans.*, (1986) 953.
- 2 S. Kida, I. Murase, C. Harada, D. Liao and M. Mikuriya, *Bull. Chem. Soc. Jpn.*, 59 (1986) 2595.
- 3 M. Mikuriya, S. Kida and I. Murase, *J. Chem. Soc., Dalton Trans.*, (1987) 1261.
- 4 (a) M. Mikuriya, S. Kida and I. Murase, *Bull. Chem. Soc. Jpn.*, 60 (1987) 1355; (b) 60 (1987) 1681.
- 5 M. Mikuriya, S. Kida, T. Kohzuma and I. Murase, *Bull. Chem. Soc. Jpn.*, 61 (1988) 2666.
- 6 A. Evers, R. D. Hancock and I. Murase, *Inorg. Chem.*, 25 (1986) 2160.
- 7 L. G. Sillen and A. E. Martell (eds.), *Stability Constants*, The Chemical Society, London, 1978.
- 8 R. J. Motekaitis, A. E. Martell, B. Dietrich and J. M. Lehn, *Inorg. Chem.*, 23 (1984) 1588.
- 9 I. Murase, M. Mikuriya and S. Kida, *Abstr. 12th Int. Symp. Macrocyclic Chemistry, Hiroshima, Japan, 1987*, p. 119.
- 10 S. Kida, E. Asato, H. Toftlund and M. Mikuriya, *26th Int. Symp. Coordination Chemistry, Porto, Portugal, 1988*, Abstr. B11; E. Asato, H. Toftlund, S. Kida, M. Mikuriya and K. S. Murray, *Inorg. Chim. Acta*, 165 (1989) 207.
- 12 M. Mikuriya, S. Kida, I. Murase and I. Ueda, *Abstr. 36th Symp. Coordination Chemistry, Nagoya, Japan, 1986*, p. 299.