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Complexes of 15,15′-Trimethylenebis(1,4,7,10,13-pentaazacyclohexadecane-14,16-dione) with Bivalent Metal Ions. Complexation Equilibria in an Aqueous Solution

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With polarographic and potentiometric methods, the complexation equilibria of 15,15′-trimethylenebis-(1,4,7,10,13-pentaazacyclohexadecane-14,16-dione) [abbreviated to bis(dioxo[16]aneN_5)] with Cu^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} ions were investigated systematically. It was found that bis(dioxo[16]aneN_5) reacts with Cu^{2+} ion affording a 2 : 1 ratio binuclear complex, designated Cu_2L^{4+} or $[Cu_2H_{-4}L]^{\circ}$, but in the reactions with Cd^{2+}, Hg^{2+}, and Pb^{2+} ions it forms 1 : 1 ratio complexes, ML^{2+}. Comparison of formation constants for the complexes of the latter bivalent metal ions with those of the parent 1,4,7,10,13-pentaazacyclohexadecane-14,16-dione [abbreviated to dioxo[16]aneN_5] showed that the attachment of the second dioxo[16]aneN_5 moiety always enhances the complexation ability of the dioxo[16]aneN_5 ligand considerably, suggesting the formation of sandwich-type complexes, where the metal(II) ion is located between the two cyclic pentaamine moieties.

Generally, macrocyclic dioxopolyamines have the novel properties of saturated macrocyclic polyamines blended with oligopeptide features. 1, 4, 7, 10, 13-Pentaazacyclohexadecane-14,16-dione (hereafter abbreviated to dioxo[16]aneN_5) depicted in Fig. 1 accomodates Ni^{2+} and Cu^{2+} ions in its macrocyclic N_5 cavity with simultaneous dissociation of the two amide protons to afford 1 : 1 ratio complexes designated $[MH_{-2}L]^{\circ}$.[1,2] It was also discovered that at neutral pH it accomodates one or two protons within its macrocyclic cavity and acts as inorganic and organic receptors.[3,4] In our previous paper,[4] we have synthesized a new ditopic anion receptor molecule, 15,15′-trimethylenebis(1,4,7,10, 13-pentaazacyclohexadecane-14,16-dione) (hereafter abbreviated to bis(dioxo[16]aneN_5)), which is comprised of two identical dioxo[16]aneN_5 moieties linked with a trimethylene chain (Fig. 1), and studied its anion association behavior. Its complexing ability as an anion receptor was found to be an order of magnitude greater than that of the parent monomacrocycle, invoking a ditopic type of interaction between two dioxo[16]aneN_5 moieties. To understand more precisely the ligating properties of the newly synthesized ditopic ligand, bis(dioxo[16]aneN_5), I planned to investigate its complexation equilibria with bivalent metal ions, Cu^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}, using polarographic and potentiometric methods in this report. It was found that in the reaction with copper(II) ion, bis(dioxo[16]aneN_5) forms a binuclear complex designated Cu_2L^{4+} or $[Cu_2H_{-4}L]^{\circ}$, but in the reactions with Cd^{2+}, Hg^{2+}, and Pb^{2+} ions it forms solely 1 : 1 ratio complexes, ML^{2+}. As was observed in its anion association reaction, the 1 : 1 ratio Cd(II), Hg(II), and Pb(II) complexes had an increased thermodynamic stability, relative to their parent dioxo-[16]aneN_5 complexes. It might also be an indication for the ditopic type of interaction between two dioxo[16]-aneN_5 moieties, suggesting the formation of sandwich-type complexes, where the metal(II) ion is located between two dioxo[16]aneN_5 moieties.

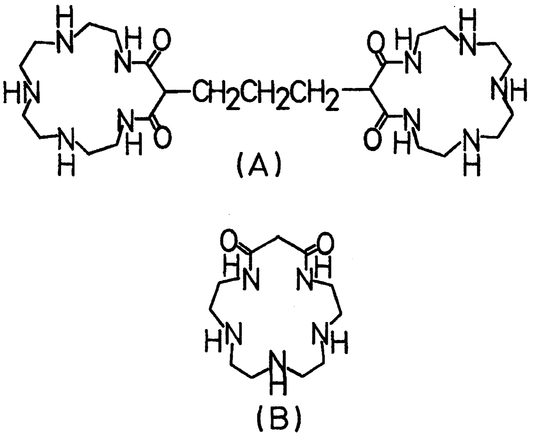

Fig. 1. Ligand used in the present investigation. (A) Bis(dioxo[16]aneN_5), (B) Dioxo[16]aneN_5.

Experimental

The macrocyclic dioxo[16]aneN_5 ligands used in this study (Fig. 1) were prepared according to the methods described in the literature.[3,4] The logarithmic protonation constants of bis(dioxo[16]aneN_5)[4] used in the analysis of experimental data were 9.38, 9.37, 8.58, 6.90, <2, and <2, and those of the parent dioxo[16]aneN$_5$,[4] 9.10, 8.47, and ca. 2 (ionic strength 0.20 mol dm^{-3} and 25 °C).

The pH-metric titrations were done with a Mettler automatic titrator,[5,6] under a nitrogen or an argon atmosphere at 25±0.1 °C. In the titration 0.100_0 mol dm^{-3} carbonate-free tetraethylammonium hydroxide ((C$_2$H$_5$)$_4$NOH, TEAOH) solution and 50 ml test solutions of ionic strength I=0.20 mol dm^{-3} (NaNO$_3$) containing $1.00_0\times10^{-3}$ mol dm^{-3} ligand (as L·3HCl (L=dioxo[16]aneN$_5$)) or as L·6HCl (L=bis(dioxo[16]aneN$_5$)) were used. Three titrations were done for each system. The apparatuses and experimental procedures used for the polarographic measurements are the same as those used in the study of the Hg(II)–macrocyclic polyamine complexation.[5] For all the polarographic measurements, 3.0×10^{-2} mol dm^{-3} borate buffer solutions of ionic strength I=0.20 mol dm^{-3} containing 2.0×10^{-4} mol dm^{-3} ligand was used. However, this buffer had practically no effect on the half-wave potentials of anodic dissolution waves.

Visible spectra were recorded on a Hitachi spectrometer 124.

The values of $-\log\,[\mathrm{H}^+]$ used for the calculation of formation constants were estimated by applying a correction of -0.13 pH unit to the pH readings.[5]

Results and Discussion

Complexation Measurement by Anodic Polarography. As in the case of the parent dioxo[16]aneN$_5$, at a dropping mercury electrode bis(dioxo[16]aneN$_5$) in a borate buffer solution gave a well-defined single anodic wave of a diffusion-controlled nature, the height of which was nearly equal to that due to the parent dioxo[16]aneN$_5$. The reversibility of the electrode process was measured by the a.c. polarographic method.[7] The summit potential was nearly equal to the corresponding d.c. half-wave potential, and the value indicating the degree of reversibility, $I_{\mathrm{ac}}/i_1\cdot n\cdot t_{\mathrm{d}}$ (K) was nearly equal to that of the cathodic wave of Cd^{2+} ion in 0.20 mol dm^{-3} KNO$_3$ solution. Here, I_{ac}, i_1, t_{d}, and n, respectively, denote the a.c. peak height, d.c. diffusion current, drop time in seconds (s), and the number of electrons involved in the electrode reaction. Thus, I could conclude that the electrode process for the anodic wave due to the uncomplexed bis(dioxo[16]aneN$_5$) is ideally reversible in a polarographic sense. Accordingly, I investigated the complexation equilibrium between the mercury(II) ion and bis(dioxo[16]aneN$_5$) ligand using the conventional d.c. polarographic method.

Plots of $\log\,[i/(i_1-i)]$ against d.c. potential, E, invariably gave a straight line having reciprocal slopes of 29 to 31 mV over the entire pH range covered, suggesting a two-electron reversible oxidation of mercury and the formation of mercury(II) complex. As mentioned by Reilley et al.,[8] the ethylenediamine-N,N,N',N'-tetraacetate anion (EDTA^{4-} ion, L$'^{4-}$) also gives a single well-defined anodic wave at DME. As Fig. 2 shows, plots of antilog A calculated with the aid of Eq. 1a (Eq. 5 in Ref. 9) against the reciprocal of hydrogen-ion concentration, $[\mathrm{H}^+]^{-1}$, afforded a straight line with an intercept of finite value. Here, $\Delta E_{1/2}$ is the half-wave potential difference between EDTA^{4-} ion[8,10] and bis(dioxo[16]aneN$_5$) systems,

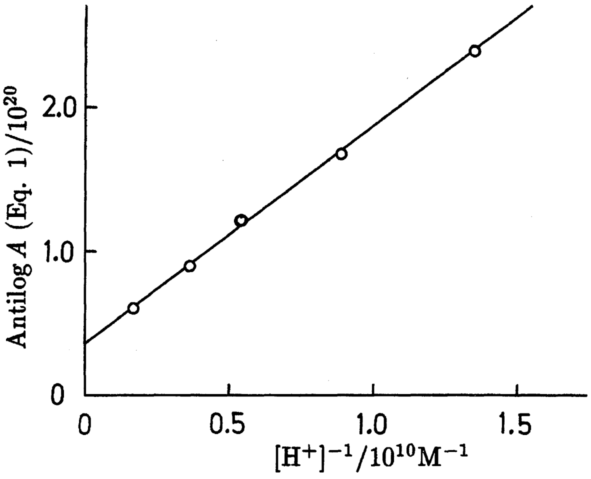

Fig. 2. Plots of antilog A (Eq. 1) against the reciprocal of hydrogen ion concentration, $[\mathrm{H}^+]^{-1}$. Bis(dioxo[16]aneN$_5$): 0.20 mmol dm^{-3}, Borate buffer: 0.030 mol dm^{-3}, I=0.20 mol dm^{-3}, 25 °C.

$$\mathrm{Antilog}\,A = \mathrm{Antilog}\,\Big(\frac{\Delta E_{1/2}}{0.0296} + \log K_{\mathrm{HgL}'} + \log\,(\alpha_{\mathrm{H}})_{\mathrm{L}} - \log\,(\alpha_{\mathrm{H}})_{\mathrm{L}'}\Big) \qquad (1a)$$

$K_{\mathrm{HgL}'}=[\mathrm{HgL}'^{2-}]/[\mathrm{Hg}^{2+}][\mathrm{L}'^{4-}]$, $(\alpha_{\mathrm{H}})_{\mathrm{L}'}$ denotes the (α_{H}) value for the EDTA^{4-} ion given previously,[8,10] $(\alpha_{\mathrm{H}})_{\mathrm{L}}$ that for the bis(dioxo[16]aneN$_5$) expressed as $1+K_1[\mathrm{H}^+]+\cdots+K_1K_2\cdots K_6\times[\mathrm{H}^+]^6$, and K_i the i-th protonation constant of bis(dioxo[16]aneN$_5$) (L). As was discussed in connection with the anodic polarography of the polyamino polycarboxylic macrocycle system,[9] all the above findings evidently suggest that under these experimental conditions, the bis(dioxo[16]aneN$_5$) ligand forms solely 1 : 1 ratio complex with mercury(II) ion and the electrode process is expressed by Eq. 2, with a corresponding half-wave potential, $(E_{1/2})_{\mathrm{L}}$, given by Eq. 3. Here, $K_{\mathrm{HgL}}=[\mathrm{HgL}^{2+}]/[\mathrm{Hg}^{2+}][\mathrm{L}]$

$$\mathrm{Hg}+\mathrm{H}_i\mathrm{L}^{i+} \rightleftharpoons \begin{cases} \mathrm{HgL}^{2+}+i\mathrm{H}^+ + 2\mathrm{e}^- \\ [\mathrm{HgH}_{-1}\mathrm{L}]^+ + (i+1)\mathrm{H}^+ + 2\mathrm{e}^- \end{cases} \qquad (2)$$

$$(E_{1/2})_{\mathrm{L}}=\varepsilon^{\circ}_{\mathrm{Hg}} - 0.0296[\log f_{\mathrm{Hg}^{2+}} + \log\,(K_{\mathrm{HgL}} + K_{\mathrm{HgH}_{-1}\mathrm{L}}/[\mathrm{H}^+]) - \log\,(\alpha_{\mathrm{H}})_{\mathrm{L}}] \qquad (3)$$

$$\mathrm{Antilog\,A} = K_{\mathrm{HgL}} + K_{\mathrm{HgH}_{-1}\mathrm{L}}/[\mathrm{H}^+] \qquad (1b)$$

and $\mathrm{K}_{\mathrm{HgH}_{-1}\mathrm{L}}=[\mathrm{HgH}_{-1}\mathrm{L}^+][\mathrm{H}^+]/[\mathrm{Hg}^{2+}][\mathrm{L}]$. All other symbols used in Eq. 3 have their usual meanings.[9] In terms of the Eq. 3 antilog A in Eq. 1a can be equated with $K_{\mathrm{HgL}}+\mathrm{K}_{\mathrm{HgH}_{-1}\mathrm{L}}/[\mathrm{H}^+]$ (Eq. 1b).

The pH dependence of the half-wave potential of the bis(dioxo[16]aneN$_5$) system can also be explained in terms of the formation of a mixed complex, [HgL(OH)]$^+$, instead of [HgH$_{-1}$L]$^+$. In this case $K_{\mathrm{HgH_{-1}L}}$ in Eqs. 1b and 3 should be replaced by $K_{\mathrm{HgL(OH)}}K_{\mathrm{w}}$. Here, $K_{\mathrm{HgL(OH)}}=[\mathrm{HgL(OH)}^+]/[\mathrm{Hg}^{2+}][\mathrm{L}][\mathrm{OH}^-]$ and $K_{\mathrm{w}}=[\mathrm{H}^+][\mathrm{OH}^-]$. In considering the fact that the parent dioxo[16]aneN_5 forms $[\mathrm{HgH_{-1}L}]^+$ where mercury(II) ion coordinates to dioxo[16]aneN_5 ligand through amino nitrogen atoms and one deprotonated amide nitrogen atom, one cannot rule out the possibility of $[\mathrm{HgH_{-1}L}]^+$ formation. To discover the exact formula of the mercury(II)–bis(dioxo[16]aneN_5) complex formed at the mercury electrode surface by an X-ray crystal study, I tried to isolate the mercury(II)–bis(dioxo[16]aneN_5) complex crystals from the mercury(II)–bis(dioxo[16]aneN_5 equimolar mixture solution of pH's higher than 10.5, but failed.

Calculation for the formation of binuclear mercury(II) complex, $\mathrm{Hg_2L^{4+}}$, and that for the formation of mercury(I) complex were also made. However, the theoretical equations derived for the formations of these complexes did not fit the experimental data.

Thus, the $\log K_{\mathrm{HgL}}$ was estimated to be $3.6_0\times10^{19}$ from the intercept of the straight line in Fig. 2.

Complexation Measurement by Potentiometry. Under these experimental conditions, the complexation reactions of bis(dioxo[16]aneN_5) with $\mathrm{Cu^{2+}}$, $\mathrm{Cd^{2+}}$, and $\mathrm{Pb^{2+}}$ ions proceeded very rapidly. Hence, I used a conventional pH-metric titration to measure their complexation equilibria. As illustrated by the curves in Fig. 3, titration curves for the equimolar mixture solutions of bis(dioxo[16]aneN_5) ligand in its fully protonated form ($\mathrm{H_6L^{6+}}$) and $\mathrm{Cd^{2+}}$ or $\mathrm{Pb^{2+}}$ ion invariably gave one break at $a=6$, indicating the formation of a 1 : 1 ratio complex, $\mathrm{ML^{2+}}$. Here, a (titration point) denotes the number of moles of base ($(\mathrm{C_2H_5})_4\mathrm{NOH}$) added per mole of ligand present. The pH-metric titration data for the Cd(II) and Pb(II) systems were found to fit successfully with the theoretical Eq. 4 derived for the formation of 1 : 1 ratio mononuclear complex, $\mathrm{ML^{2+}}$, of hexaazacyclooctadecane in a equimolar metal(II)–ligand mixture solution,[11] where the formation of 1 : 1 $\mathrm{OH^-}$ complex, $[\mathrm{M(OH)}]^+$, should be taken into account. Plots of $[(6-R)(\alpha_{\mathrm{H}})_{\mathrm{L}}-\beta_{\mathrm{H}}][(\alpha-RC_{\mathrm{L}})(\alpha_{\mathrm{H}})_{\mathrm{L}}-\beta_{\mathrm{H}}C_{\mathrm{L}}]$ against $(6C_{\mathrm{L}}-\alpha)^2(\alpha_{\mathrm{H}})_{\mathrm{L}}/(1+K^{\mathrm{OH}}[\mathrm{OH}^-])$ gave a straight line passing through the point of origin. Meanings of the symbols used in Eq. 4 are as follows.

$$K_{\mathrm{ML}}\frac{(6C_{\mathrm{L}}-\alpha)^2(\alpha_{\mathrm{H}})_{\mathrm{L}}}{1+K^{\mathrm{OH}}[\mathrm{OH}^-]}=[(6-R)(\alpha_{\mathrm{H}})_{\mathrm{L}}-\beta_{\mathrm{H}}]$$
$$[(\alpha-RC_{\mathrm{L}})(\alpha_{\mathrm{H}})_{\mathrm{L}}-\beta_{\mathrm{H}}C_{\mathrm{H}}] \quad (4)$$

$$K_{\mathrm{ML}}=[\mathrm{ML^{2+}}]/[\mathrm{M^{2+}}][\mathrm{L}]$$

C_{L}: the analytical concentration of bis(dioxo[16]aneN_5)

$$\alpha=aC_{\mathrm{L}}+[\mathrm{H}^+]-[\mathrm{OH}^-]$$

$$\beta_{\mathrm{H}}=6+5K_1[\mathrm{H}^+]+4K_1K_2[\mathrm{H}^+]^2+\cdots$$
$$+K_1K_2K_3K_4K_5[\mathrm{H}^+]^5$$

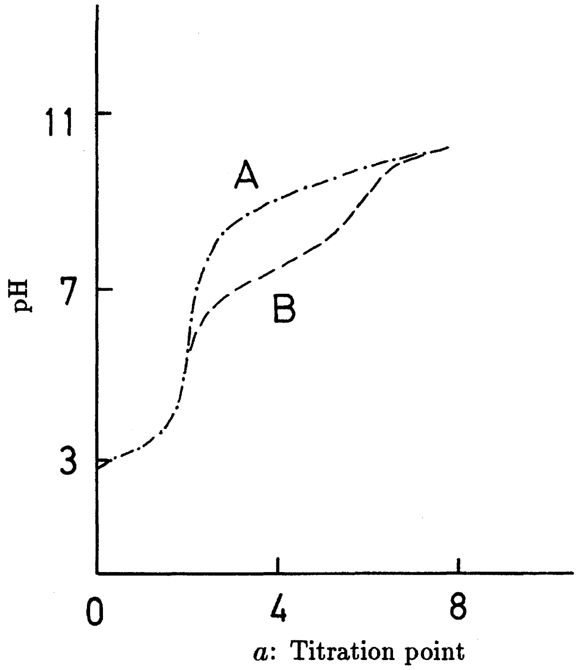

Fig. 3. Titration curves for the lead(II)–bis(dioxo[16]aneN_5) system. I=0.20 mol dm^{-3}, 25 °C, Bis(dioxo[16]aneN_5) ($\mathrm{H_6L^{6+}}$): 1.00 mmol dm^{-3}. (A) in the absence of lead(II) ion, (B) in the presence of 1.00 mmol dm^{-3} lead(II)ion.

$$K^{\mathrm{OH}}=[\mathrm{M(OH)}^+]/[\mathrm{M^{2+}}][\mathrm{OH}^-], R$$
$$=K^{\mathrm{OH}}[\mathrm{OH}^-]/(1+K^{\mathrm{OH}}[\mathrm{OH}^-])$$

Titration curves for the 1.00 mmol dm^{-3} bis(dioxo[16]aneN_5) ($\mathrm{H_6L^{6+}}$) solutions containing a large excess of lead(II) or cadmium(II) ions also gave one break at the titration point $a=6$, but its pH buffer region appeared at pH's where no $\mathrm{M(OH)^+}$ is formed. Experimental data obtained in this titration fitted well with Eq. 2 in Ref. 11, which was applied to the formation of a 1 : 1 ratio cadmium(II) complex of macrocyclic hexaamine (1,4,7,10,13,16-hexaazacyclo-octadecane, [18]aneN_6) in the presence of a large excess of cadmium(II) ions. Plots of $\alpha(\alpha_{\mathrm{H}})_{\mathrm{L}}-\beta_{\mathrm{H}}C_{\mathrm{L}}$ against $(6C_{\mathrm{L}}-\alpha)$ afforded a straight line passing through the point of origin, and its slope was exactly equal to the product of the slope of the straight line obtained by plotting $[(6-R)(\alpha_{\mathrm{H}})_{\mathrm{L}}-\beta_{\mathrm{H}})][(\alpha-RC_{\mathrm{L}})(\alpha_{\mathrm{H}})_{\mathrm{L}}-\beta_{\mathrm{H}}C_{\mathrm{L}})]$ against $(6C_{\mathrm{L}}-\alpha)^2(\alpha_{\mathrm{H}})_{\mathrm{L}}/(1+K^{\mathrm{OH}}[\mathrm{OH}^-])$ and the metal(II) ion concentration. All these findings collected in the pH-metric titrations clearly indicate that cadmium(II) and lead(II) ion form solely 1 : 1 ratio complexes, $\mathrm{ML^{2+}}$, with bis(dioxo[16]aneN_5). Thus, I measured the K_{ML} values for cadmium(II) and lead(II) complexes from gradients of the linear relation between $[(6-R)(\alpha_{\mathrm{H}})_{\mathrm{L}}-\beta_{\mathrm{H}})][(\alpha-RC_{\mathrm{L}})\times(\alpha_{\mathrm{H}})_{\mathrm{L}}-\beta_{\mathrm{H}}C_{\mathrm{L}})]$ and $(6C_{\mathrm{L}}-\alpha)^2(\alpha_{\mathrm{H}})_{\mathrm{L}}/(1+K^{\mathrm{OH}}[\mathrm{OH}^-])$, and listed them in Table 1. K^{OH} values used for the cadmium(II) and lead(II) systems[12] were $10^{4.1}$ and $10^{6.0}$, respectively. In a similar way I tried to measure the complex formation constants,

Table 1. Formation Constants$^{a)}$ I=0.20 mol dm^{-3}, 25 °C

Metal(II) ion	Ligand	K_{ML} (K^2_{ML})	$K_{\mathrm{MH_{-2}L}}$ ($K^2_{\mathrm{MH_{-2}L}}$)	$K_{\mathrm{M_2L}}$	$K_{\mathrm{M_2H_{-4}L}}$
Cu(II)	Dioxo[16]aneN$_5$	$(9.8\pm0.1)\times10^{11}$ 5)	$(1.6\pm0.5)\times;10^{-2}$ 5)	—	—
		$((9.6\pm0.2)\times10^{23})$	$((2.8\pm1.6)\times10^{-4})$	—	—
	Bis(dioxo[16]aneN$_5$)	—	—	$(1.1_2\pm0.1_1)\times10^{24}$	$(2.6_4\pm0.2_7)\times10^{-4}$
Cd(II)	Dioxo[16]aneN$_5$	—	—	—	—
	Bis(dioxo[16]aneN$_5$)	$(3.3_7\pm0.5_1)\times10^{7}$	—	—	—
Hg(II)	Dioxo[16]aneN$_5$	$(4.6_0\pm1.3_8)\times10^{18}$	—	—	—
	Bis(dioxo[16]aneN$_5$)	$(3.6_0\pm0.9_0)\times10^{19}$	—	—	—
Pb(II)	Dioxo[16]aneN$_5$	$(2.1_2\pm0.3_1)\times10^{6}$	—	—	—
	Bis(dioxo[16]aneN$_5$)	$(3.0_3\pm0.3_5)\times10^{8}$	—	—	—

a) Confidence limits at 95% confidence level (each for three experimental runs) are given. — means no determination.

K_{ML} (=$[\mathrm{ML}^{2+}]/[\mathrm{M}^{2+}][\mathrm{L}]$), for cadmium(II) and lead(II) complexes of parent dioxo[16]aneN$_5$. The K_{PbL} was calculated from the slope of the linear relation between $[(3-R)(\alpha_{\mathrm{H}})_{\mathrm{L}}-\beta_{\mathrm{H}}][(\alpha-RC_{\mathrm{L}})(\alpha_{\mathrm{H}})_{\mathrm{L}}-\beta_{\mathrm{H}}C_{\mathrm{L}}]$ and $(3C_{\mathrm{L}}-\alpha)^2\times(\alpha_{\mathrm{H}})_{\mathrm{L}}/(1+K^{\mathrm{OH}}[\mathrm{OH}^-])$ and listed in Table 1. In the cadmium(II) system, a reliable measurement was disturbed by the formation of $\mathrm{Cd(OH)_2}$ precipitation and the formation constant, K_{CdL}, could not be calculated.

In the titration of 1.00 mmol dm^{-3} bis(dioxo[16]aneN$_5$)(in its fully-protonated form, $\mathrm{H_6L^{6+}}$) solution containing equimolar copper(II) ion, the titration curve had two breaks. One occurred at $a=4$ and the other at $a=6$. On the other hand, in the titration of 1.00 mmol dm^{-3} bis(dioxo[16]aneN$_5$)($\mathrm{H_6L^{6+}}$) solution containing 2.00 mmol dm^{-3} copper(II) ion, the titration curve also had two breaks, but the 1st one appeared at a=6 and the 2nd one at a=10 (Fig. 4). Furthermore, it was found that these two mixture solutions gave quite similar visible spectra, but the molar absorbance of the former solution was exactly half the magnitude of that of the latter solution. As in the case of copper(II)–dioxo[16]aneN$_5$ system, the $\lambda_{\max}$ for the blue complex formed at the 1st buffer region (5.0>pH>4.0) occurred at 610 nm and that for the violet complex formed at the 2nd buffer region (7.5>pH>6.5) at 562 nm. Spectral data of copper(II) complexes obtained were listed in Table 2. In the light of the fact that K_5 and K_6 of bis(dioxo[16]aneN$_5$) were very small, all these findings clearly suggest that with copper(II) ion, the bis(dioxo[16]aneN$_5$) ligand forms solely binuclear complexes in which two dioxo[16]aneN$_5$ moieties of ligand encapsulate one copper(II) ion each, that is to say, at the 1st pH buffer region $\mathrm{Cu_2L^{4+}}$ is formed and at the 2nd buffer region ionization of the four hydrogens of amide groups occurs with concurrent formation of $[\mathrm{Cu_2H_{-4}L}]^{\circ}$.

If bis(dioxo[16]aneN$_5$) ligand forms only a binuclear complex, $\mathrm{Cu_2L^{4+}}$, in its C_{L} mol dm^{-3} (in a fully-protonated form, $\mathrm{H_6L^{6+}}$) solution containing $2C_{\mathrm{L}}$ mol dm^{-3} copper(II) ion, the sum of the hydrogen and $\mathrm{(C_2H_5)_4N^+}$ ion concentrations subtracted by the hydroxide ion concentration, $[\mathrm{OH}^-]$, at the titration point a is given by relation 5. The total concentrations of copper(II) ion

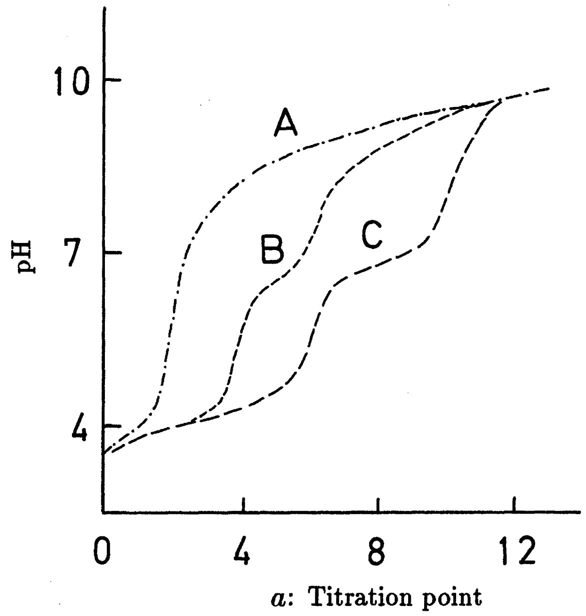

Fig. 4. Titration curves for the copper(II)–bis(dioxo[16]aneN$_5$) system. I=0.20 mol dm^{-3}, 25 °C, Bis(dioxo[16]aneN$_5$) ($\mathrm{H_6L^{6+}}$): 1.00 mmol dm^{-3}. (A) in the absence of copper(II) ion, (B) in the presence of 1.00 mmol dm^{-3} copper(II) ion, (C) in the presence of 2.00 mmol dm^{-3} copper(II) ion.

Table 2. Electronic Spectral Data of Copper(II) Complexes

Ligand	pH	$\lambda_{\max}$ nm	$\varepsilon_{\max}$	Remarks
Dioxo[16]aneN$_5$	7.00	610	1.21×10^2	Blue
	10.04	560	1.12×10^2	Violet
Bis(dioxo[16]aneN$_5$)	5.40	610	2.41×10^2	Blue
	10.05	562	2.25×10^2	Violet

and ligand, C_{Cu} and C_L, and the formation constant of Cu_2L^{4+}, K_{Cu_2L}, are given by 6, 7, and 8, respectively. Here, $[L]_f$ denotes the concentration of uncomplexed bis(dioxo[16]aneN$_5$) and is given by Eq. 9.

$$\begin{aligned}\alpha &= aC_L + [H^+] - [OH^-] \\ &= 6[L] + 5[HL^+] + 4[H_2L^{2+}] + 3[H_3L^{3+}] \\ &\quad +2[H_4L^{4+}] + [H_5L^{5+}] + 6[Cu_2L^{4+}]\end{aligned} \tag{5}$$

$$C_{Cu} = 2C_L = [Cu^{2+}] + 2[Cu_2L^{4+}] \tag{6}$$

$$C_L = [L]_f + [Cu_2L^{4+}] \tag{7}$$

$$K_{Cu_2L} = \frac{[Cu_2L^{4+}]}{[Cu^{2+}]^2[L]} \tag{8}$$

$$\begin{aligned}[L]_f = [L] + [HL^+] + [H_2L^{2+}] + [H_3L^{3+}] + [H_4L^{4+}] \\ +[H_5L^{5+}] + [H_6L^{6+}]\end{aligned} \tag{9}$$

An appropriate combination of Eqs. 5, 6, 7, 8, and 9 using the protonation constants of bis(dioxo[16]aneN$_5$) affords the relation 10. Since β_H is nearly equal to $2(\alpha_H)_L$ at pH lower

$$4K_{Cu_2L}(6C_L-\alpha)^3(\alpha_H)_L^2=(6(\alpha_H)_L-\beta_H)^2(\alpha(\alpha_H)_L-\beta_H C_L) \tag{10}$$

than 4.90, Eq. 10 can be simplified to Eq. 11. The Eq. 11

$$K_{Cu_2L}(6C_L - \alpha)^3 = 4(\alpha - 2C_L)(\alpha_H)_L \tag{11}$$

was found to fit well with the experimental data at the 1st pH buffer region. Thus, from the gradient of the straight line between $(\alpha-2C_L)(\alpha_H)_L$ and $(6C_L-\alpha)^3$ given in Fig. 5 the K_{Cu_2L} value could be estimated to be $1.1_2\times10^{24}$.

The equilibrium constant, K^{-4H}, for the quadruple deprotonation reaction of Cu_2L^{4+} given by Eq. 12 can be rewritten as Eq. 13, because the concentrations of Cu_2L^{4+}

$$K^{-4H} = \frac{[Cu_2H_{-4}L^\circ][H^+]^4}{[Cu_2L^{4+}]} \tag{12}$$

$$K^{-4H}\left(\frac{10-a}{a-6}\right) = [H^+]^4 \tag{13}$$

and $[Cu_2H_{-4}L]^\circ$ are given by $(10-a)C_L$ and $(a-6)C_L$, respectively. Although the result was not shown here, Eq. 13 fitted well with the experimental data at the 2nd buffer region of the titration curve. From the slope of the linear line passing through the point of origin, which was obtained by plotting $[H^+]^4$ against $(10-a)/(a-6)$, the K^{-4H} value was found to be $2.3_6\times10^{-28}$. From K_{Cu_2L} and K^{-4H} values thus calculated the $K_{Cu_2H_{-4}L}$ $(=[Cu_2H_{-4}L^\circ][H^+]^4/[Cu^{2+}]^2[L])$ was evaluated to be $2.6_4\times10^{-4}$ with the aid of the relation $K_{Cu_2H_{-4}L}=K_{Cu_2L}K^{-4H}$.

The experimental fact that in the titration of an equimolar copper(II)–bis(dioxo[16]aneN$_5$) mixture solution two breaks occur at $a=4$ and 6 can also be interpreted by assuming the formation of 1:1 ratio complex, CuH_2L^{4+}, in which only one of two dioxo[16]aneN$_5$ moieties of the ligand, binds with copper(II) ion and the remaining dioxo[16]aneN$_5$ moiety is doubly protonated, and subsequent ionization of two hydrogens of the amide groups of dioxo[16]aneN$_5$ moiety bound to the copper(II) ion or dissociation of two hydrogen ions accomodated in the remaining free dioxo[16]aneN$_5$ moiety. If this explanation is rational, the experimental data at the 1st buffer region and those at the 2nd buffer region should obey Eqs. 14 and 15, respectively.

$$\begin{aligned}K_{CuH_2L}\frac{[H^+]^2}{K_1K_2}(4C_L-\alpha)^2(\alpha_H)_L=(\alpha(\alpha_H)_L-\beta_H C_L) \\ (4(\alpha_H)_L-\beta_H)\end{aligned} \tag{14}$$

$$K^{-2H} = \frac{(a-4)[H^+]^2}{(6-a)} \tag{15}$$

Here $K_{CuH_2L}=[CuH_2L^{4+}]/[Cu^{2+}][H_2L^{2+}]$ and K^{-2H} denote the deprotonation constant of CuH_2L^{4+}. However, the experimental data at the 1st buffer region did not fit Eq. 14 derived for the formation of CuH_2L^{4+}, and those at the 2nd buffer region did not fit Eq. 15 for the subsequent deprotonation.

All the equilibrium constants measured in this study are listed in Table 1 and compared with those for the formation reactions of corresponding parent dioxo[16]aneN$_5$ complexes.

As stated above, under these experimental conditions cadmium(II), mercury(II), and lead(II) ions form mononuclear complexes, ML^{2+}, but the copper(II) ion forms blue binuclear complex, Cu_2L^{4+}, at pH lower than 5.0 and violet binuclear complex, $[Cu_2H_{-4}L]^\circ$ at pH higher than 6.0. Generally, in the complexation re-

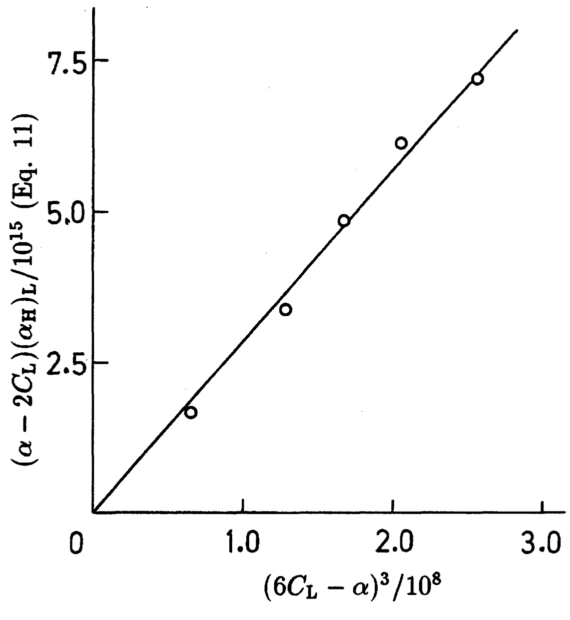

Fig. 5. Plots of $(\alpha-2C_L)(\alpha_H)_L$ against $(6C_L-\alpha)^3$ (Eq. 11). I=0.20 mol dm^{-3}, 25 °C, Bis(dioxo[16]aneN$_5$) (H_6L^{6+}): 1.00 mmol dm^{-3}, Copper(II) ion: 2.00 mmol dm^{-3}.

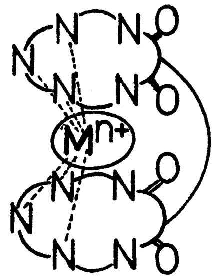

Fig. 6. Proposed model for the 1 : 1 ratio complex, ML^{2+}.

action of dioxopolyamine macrocycles copper(II) ion is successful in promoting the dissociation of amide proton, but cadmium(II), mercury(II), and lead(II) ions are not.[13] The copper(II) ion, the size of which is compatible with the 16-membered polyamine ring size, can be accomodated easily within the cavity of dioxo[16]aneN$_5$ moiety and coordinates firmly to it through amino and amide nitrogen donors, effectively promoting the amide proton dissociation. Thus, each of the dioxo[16]aneN$_5$ moieties would incorporate one copper(II) ion into its cavity hole, forming the binuclear complex, Cu_2L^{4+} or $[Cu_2H_{-4}L]^\circ$. If two dioxo[16]aneN$_5$ moieties in the bis(dioxo[16]aneN$_5$) ligand are noninteracting and react with metal(II) ion independently, it is reasonable to consider that the formation constants of binuclear complexes, $K_{\mathrm{Cu_2L}}$ and $K_{\mathrm{Cu_2H_{-4}L}}$, statistically should be identical with $4K^2_{\mathrm{CuL}}$ and $4K^2_{\mathrm{CuH_{-2}L}}$,[14] respectively. Here, K_{CuL} and $K_{\mathrm{CuH_{-2}L}}$ mean formation constants of corresponding mononuclear complexes of parent dioxo[16]aneN$_5$, CuL^{2+} and $[CuH_{-2}L]^\circ$, respectively. The $K_{\mathrm{Cu_2L}}$ and $K_{\mathrm{Cu_2H_{-4}L}}$ values calculated were compared with $4K^2_{\mathrm{CuL}}$ $4K^2_{\mathrm{CuH_{-2}L}}$ values previously reported.[2] The $K_{\mathrm{Cu_2L}}$ value showed a fairly good agreement with the $4K^2_{\mathrm{CuL}}$ value (3.8×10^{24}) and $K_{\mathrm{Cu_2H_{-4}L}}$ value with the $4K^2_{\mathrm{CuH_{-2}L}}$ value (1.1×10^{-3}). This gives also a strong support to my conclusion that the bis(dioxo[16]aneN$_5$) ligand forms binuclear copper(II) complexes, Cu_2L^{4+} and $[Cu_2H_{-4}L]^\circ$, where two dioxo[16]aneN$_5$ moieties act as noninteracting coordination sites.

On the other hand, cadmium(II) and lead(II) ions, which can scarcely promote the dissociation of an amide proton, might be so large as to fit "exactly" in the cavity hole, and hence, can interact only weakly with donors of the dioxo[16]aneN$_5$ ligand. As mentioned above, the cadmium(II) complex of dioxo[16]aneN$_5$ is not stable enough to be able to prevent the cadmium(II) ion from being precipitated as $Cd(OH)_2$, and the formation constant of lead(II)–dioxo[16]aneN$_5$ complex, K_{PbL}, is only $2.1_2\times10^6$. As shown in Table 1, the trimethylene-bridged bis(dioxo[16]aneN$_5$) can form 1 : 1 ratio complex more stable than that of parent dioxo[16]aneN$_5$, and can effectively prevent the cadmium(II) ion from being precipitated as $Cd(OH)_2$. The fact that bis(dioxo[16]aneN$_5$) forms 1 : 1 ratio cadmium(II) and lead(II) complexes thermodynamically more stable than those of parent dioxo[16]aneN$_5$ can be interpreted by assuming a sandwich structure where metal(II) ion is located between the two dioxo[16]aneN$_5$ moieties. The mercury(II) ion also form a 1 : 1 ratio bis(dioxo[16]aneN$_5$) complex, HgL^{2+}, with a formation constant much larger than that of the parent dioxo[16]aneN$_5$ complex (Table 1). This may also be understood by assuming the formation of a sandwich-type complex. A proposed model for the sandwich type complex, ML^{2+}, is given Fig. 6.

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