two complexes. Examination of Dreiding models reveals that on imidazole coordination CH-2′ projects out toward the C-terminus peptide residue and its chemical shift would be influenced by whether the carboxylate is bound or free. The CH-1 and CH_2-4 resonances for the two histidyl peptide complexes have very similar chemical shifts as expected for the structures given in Figure 1.

The acid dissociation constant for the pyrrole hydrogen, NH-1, of imidazole has been reported to be in the range 14.2–14.5.[24] The acidity of the pyrrole hydrogen increases upon complexation of a metal ion at N-3. Cobalt(II) lowers the pK_a from that of unbound ligand by about 2 logarithmic units, copper(II) by 1 more logarithmic unit, and palladium(II) by almost another logarithmic unit.[24] Coordination to cobalt(III) lowers the pK_a of imidazole and its derivatives by almost 4 logarithmic units, and values fall in the range 10.0–10.8.[25–28] The pK_a values determined for the pyrrole hydrogens of [Co(NH$_3$)(H$_{-2}$HisGG)] and [Co(NH$_3$)$_2$-(H$_{-2}$HisGG)] at 298 K, 10.73 ± 0.04 and 10.69 ± 0.04, respectively, provide strong evidence that the imidazole side chain is coordinated in both L-His-Gly-Gly complexes. If it was unbound, pK_a values of approximately 5.5 and 14 would have been expected for NH-3$^+$ and NH-1, respectively.[1,2]

Potentiometric titration of [Co(NH$_3$)$_2$(H$_{-2}$HisGG)] with acid at 298 K gave a pK_a value of 4.34 ± 0.04 for the free carboxylate group. For the free tripeptide, a value of 3.17 is reported for the pK_a of the carboxylate group.[1] As the charge on the free tripeptide changes from 1+ to 2+ on protonation of the carboxylate group while the charge on the complex changes from 0 to 1+, the decreased acidity of the carboxylate group of the complex is to be expected. Enright determined the pK_a^D of the carboxylate group of [Co(NH$_3$)$_3$(H$_{-2}$GGG)], which also has zero charge, by ^{1}H NMR titration and reports a value of 4.15.[11] The difference between this value and the value observed for [Co(NH$_3$)$_2$-(H$_{-2}$HisGG)] is of a magnitude similar to the difference in the

pK_a values for the protonation and deuteration of the free carboxylate group of [Co(NH$_3$)$_2$(H$_{-2}$GGHis)] (0.24 logarithmic unit).[20]

The microanalysis of fraction 1 from the reaction of L-His-Gly-Gly with the "peroxo dimer" is consistent with a superoxide-bridged binuclear cobalt(III) complex with the peptide. It has an ESR spectrum consistent with this. The $g = 2.01$ signal is consistent with a free radical such as the superoxide group. Values for mononuclear cobalt(III) superoxide complexes have been reported in the range 2.013–2.036.[29–31] The low value of the cobalt hyperfine coupling constant for the superoxide resonance is consistent with formulation as a cobalt(III) complex.[32,33] The majority of cobalt(III) superoxide complexes are stable only in nonaqueous solvents at low temperature. Similar complexes with other non-histidyl tripeptides have not been isolated. Thus the observation of such a species under the present conditions is extremely unusual. However, a similar complex has been isolated with Gly-L-His-Gly.[19] They are unstable as would be expected for such superoxide species, being decomposed by dinitrogen to yield a cobalt(II) complex. Attempts at detailed characterization were not successful. For example, ^{1}H and ^{13}C spectra of the complexes showed extremely broad resonances.

Coordination of imidazole in one of the apical positions of a cobalt(III) complex of a quadridentate ligand is known to stabilize coordination of a superoxide in the other apical position.[33,34] The same reason is possible for the stabilization of the superoxide complexes of the histidyl peptides reported here.

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Reactions of Molybdenum(V) Tetraphenylporphyrins with Superoxide. Mechanism of the Reactions and the Characterization of an Isolated Dioxygen Complex[1]

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The mechanism of the reactions of Mo^{V}O(TPP)X (TPP = 5,10,15,20-tetraphenylporphyrin; X = Br, Cl, NCS) with superoxide ion O$_2^-$ in aprotic solvents under anaerobic conditions has been stoichiometrically elucidated. The complex Mo^{V}O(TPP)X is reduced by O$_2^-$ to Mo^{IV}O(TPP) in dichloromethane containing 1% (v/v) dimethyl sulfoxide at 25 °C via an intermediate, complex 1. Complex 1 is stable in solution at –80 °C but is converted into Mo^{IV}O(TPP) at room temperature. Complex 1, a new dioxygen complex of molybdenum tetraphenylporphyrin, was isolated. The chemical formula of complex 1 is ascertained to be [18-crown-6-K][Mo^{V}O(TPP)(O$_2^{2-}$)] where the dioxygen binds side-on with the electronic configuration of peroxide. The structure and oxidation state of the molybdenum–dioxygen unit in the dioxygen complex are maintained in aprotic media over the temperature range between –80 and –20 °C.

Introduction

Dioxygen complexes of metalloporphyrins have been of great interest in relation to the elucidation of the mechanism of transport and storage of dioxygen by hemoglobin and myoglobin,[2] of ac-

tivation of dioxygen by cytochrome P-450,[3] and of four-electron reduction of dioxygen by cytochrome oxidase[4] in vivo. Dioxygen adducts formed by the reactions of molecular dioxygen with iron(II),[5–11] cobalt(II),[12–14] chromium(II),[15] ruthenium(II),[16]
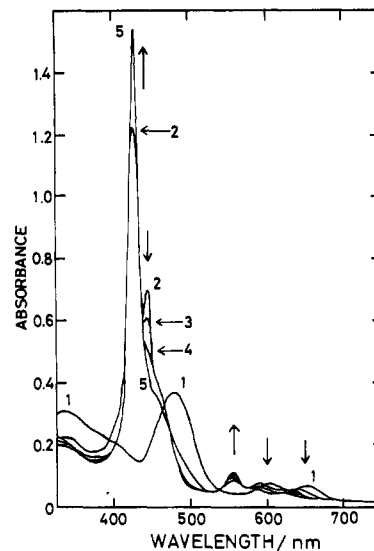
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rhodium(II),[17] titanium(III),[18] and manganese(II)[19] porphyrins have been reported. The dioxygen ligands of these complexes and oxyhemoglobin etc., except the manganese complex, are considered to adopt the electronic configuration of superoxide with end-on bonding.[5] In the manganese complex, dioxygen is suggested to bind side-on with a peroxide formulation.[19] Peroxo complexes are also formed by irreversible reactions of metalloporphyrins and peroxide ion. Examples are peroxotitanium(IV) porphyrins[20] and diperoxomolybdenum(VI) porphyrin.[21] Recently, Valentine et al.[22,23] reported the formation of new dioxygen complexes $[Fe^{III}(porph)(O_2^{2-})]^-$ produced in the reaction of $Fe^{III}(porph)Cl$ with O_2^- ion in a molar ratio of 1:2. These new dioxygen complexes have an oxidation level different from that of hemoglobin models but are of interest as models of intermediates in the oxygen activation cycles of cytochrome P-450 and cytochrome oxidase.[23,24] Our preliminary studies showed that oxomolybdenum(V) tetraphenylporphyrins $Mo^VO(TPP)X$ were reduced by O_2^- to Mo^{IV}-$O(TPP)$ in aprotic media via an intermediate that was thought to be a dioxygen complex.[25] In the present paper, the detailed mechanism of the reactions of $Mo^VO(TPP)X$ with O_2^- and the isolation and characterization of the dioxygen complex of oxomolybdenum tetraphenylporphyrin are reported.

Experimental Section

Materials. The complexes $Mo^VO(TPP)X$ (X = Br, Cl, NCS) and $Mo^{IV}O(TPP)$ were synthesized according to previously described methods.[25,26] Dichloromethane and chloroform were distilled, passed through a basic alumina column (Woelm, activity grade I, basic) to remove stabilizers,[27] dried over 4-Å molecular sieves, and redistilled under Ar immediately before use. Hexane was dried over 4-Å molecular sieves and distilled under Ar. Dimethyl sulfoxide (Me_2SO) was kept over CaH_2 for several days, distilled at 37 °C under reduced pressure, and stored under an Ar atmosphere. The solvents were degassed by several freeze–thaw-evacuate cycles before use. KO_2 (ICN Pharmaceuticals) and 18-crown-6 (Nippon Soda) were used without further purification. To dissolve KO_2 in Me_2SO under an Ar atmosphere, 18-crown-6 was used.[28] The concentration of O_2^- was determined by photometric titration with iodine immediately before use.[29] $K^{18}O_2$ was prepared by the method in the literature.[30] Dioxygen gas (Nippon Sanso, pure oxygen B, >99.9%) was

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Figure 1. Spectral change in the reaction of $Mo^VO(TPP)Br$ with O_2^- in 1% (v/v) Me_2SO–CH_2Cl_2 at 25 °C for (1) $[Mo^VO(TPP)Me_2SO]Br$, and (2) 40 s, (3) 4 min 25 s, (4) 19 min 40 s, and (5) 117 min 40 s after the addition of O_2^-. The initial concentrations are $[Mo^VO(TPP)Br]_0 = 7.86 \times 10^{-6}$ M and $[O_2^-]_0 = 2.16 \times 10^{-4}$ M.
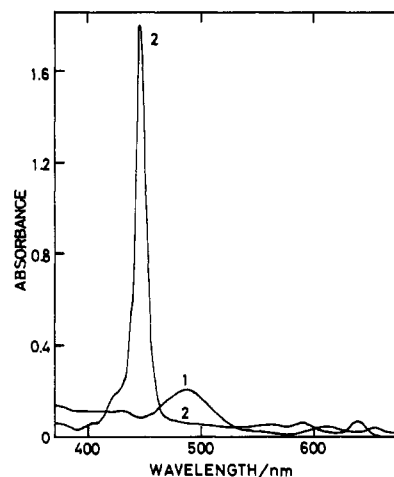
Figure 2. Visible absorption spectra in 1% (v/v) Me_2SO–CH_2Cl_2 at −72 °C of $[Mo^VO(TPP)Me_2SO]Br$ (1) and of complex **1** formed by the reaction of $Mo^VO(TPP)Br$ with O_2^- (2). The initial concentrations are $[Mo^VO(TPP)Br]_0 = 4.83 \times 10^{-6}$ M and $[O_2^-]_0 = 9.13 \times 10^{-5}$ M.

used without further purification. All manipulations to prepare the sample solutions were performed in an Ar atmosphere or under anaerobic conditions unless otherwise specified.

Measurements. Electronic spectra were recorded on a Hitachi spectrophotometer Model 808. The measurements at low temperatures were performed by dipping an optical cell in a vacuum bottle with two optical windows filled with dry ice–ethanol. Infrared spectra were recorded on a Hitachi 270-50 spectrophotometer. A JASCO low-temperature IR cell thermostated by a Lauda Kryo-Star 80D device was used for the measurements of IR spectra at low temperatures. ^{1}H NMR spectra were measured with a JEOL JNM-FX 100PFT spectrometer. ESR spectra were recorded on a JEOL JES-FE1X spectrometer operating at 100-kHz modulation. A Hitachi RMU-6 mass spectrometer was used to detect the gas evolved in the reaction of $Mo^VO(TPP)X$ with O_2^-. A Shimadzu inductively coupled plasma quantorecorder, Model ICPQ 1000, and a Hitachi 170-50 atomic absorption spectrophotometer were used for the elemental analyses of molybdenum and potassium, respectively.

Results and Discussion

Electronic Spectral Change. The electronic spectrum of a dichloromethane solution of $Mo^VO(TPP)Br$ at 25 °C has a Soret band, a β band, and an α band at 511, 639, and 685 nm, respectively.[31] In a dichloromethane solution containing 1% (v/v)

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Table I. Absorption Maxima in the Visible Region[a]

complex	λ_{max}/nm ($\epsilon/10^4$ M^{-1} cm^{-1})						
$[Mo^VO(TPP)(O_2{}^{2-})]^-$ (1)	422 (sh)	445 (35.3)	565 (0.95)	586 (1.29)	604 (0.78)	635 (1.47)	
$Mo^{IV}O(TPP)Me_2SO$ (2)	429 (sh)	444 (34.3)	573 (1.47)		614 (0.85)		

[a] In 2% (v/v) $Me_2SO-CH_2Cl_2$ at -72 °C.

Me_2SO, the absorption peaks of these bands shift to 477, 604, and 648 nm, respectively. This spectral shift is ascribed to the formation of the dimethyl sulfoxide complex, $[Mo^VO(TPP)-Me_2SO]Br$.[31] By the addition of a large excess of O_2^- to a solution of $Mo^VO(TPP)Br$, the absorbances of these peaks of $[Mo^VO-(TPP)Me_2SO]Br$ rapidly decrease with the appearance of two new peaks at 445 and 428 nm (Figure 1). The new peak at 445 nm inversely begins to decrease slowly with time ($t_{1/2}$ = ca. 10 min) with increasing absorbance at 428 nm. The final spectrum of the reaction mixture agrees with the spectrum of the complex $Mo^{IV}O(TPP)$.[25] The spectrum characterized by the absorption peak at 445 nm can be ascribed to that of a reaction intermediate, which is temporarily termed as complex 1. The spectral change in the course of the reaction indicates that the complex $Mo^{IV}O-(TPP)$ is formed through two pathways; a slow reaction path via the formation of complex 1 and a fast reaction path without the formation of complex 1.

When a large excess of O_2^- is added to the dichloromethane solution of $Mo^VO(TPP)Br$ containing 1% (v/v) Me_2SO at -72 °C, complex 1 is formed and is stable in solution (Figure 2). Namely, no formation of $Mo^{IV}O(TPP)$ is observed. The spectrum of the solution of complex 1 keeps the same shape over the temperature range from -72 to 0 °C, excepting a decrease of absorbance in the whole visible region by ca. 17%. For a further rise in the temperature from 0 to 25 °C, the absorption peaks due to complex 1 decrease with the appearance of the peaks of the spectrum of $Mo^{IV}O(TPP)$. This change from complex 1 to $Mo^{IV}O(TPP)$ exhibits isosbestic points at 436, 460, 512, 532, and 563 nm. The apparent rate constant of this reaction was determined to be 2.2×10^{-4} s^{-1} at 25 °C under the conditions described in the caption of Figure 2. Complex 1 is also formed by the addition of solid KO_2 to a dichloromethane solution of $Mo^VO-(TPP)Br$ containing 18-crown-6 without Me_2SO at low temperature, indicating that the formation of complex 1 does not always require the solvent Me_2SO.

When the concentration of O_2^- is lower than that of $Mo^VO-(TPP)Br$, a new complex, hereafter referred to as complex 2, is immediately formed at -72 °C provided that the solution contains 1% (v/v) Me_2SO. The absorption spectrum of complex 2 has absorption bands at 444, 573, and 614 nm and is discriminated from that of complex 1, which has absorption bands at 445, 565, 586, 604, and 635 nm. Complex 2 is completely converted to $Mo^{IV}O(TPP)$ as the solution is warmed to room temperature. This reaction proceeds reversibly to form complex 2 as the solution is again cooled to -72 °C. However, $Mo^{IV}O(TPP)$ is formed even at -72 °C at very low concentrations of Me_2SO (0.001% (v/v)): the formation of complex 2 is not observed. Complexes 1 and 2 are eventually clarified to be $[Mo^VO(TPP)(O_2{}^{2-})]^-$ and $Mo^{IV}O(TPP)Me_2SO$, respectively, as described below. The electronic spectral data of complexes 1 and 2 are summarized in Table I.

Stoichiometry for the Reaction of $Mo^VO(TPP)X$ with O_2^-. The change in the absorbances at 445 and 635 nm were followed titrimetrically by adding O_2^- solution to the $Mo^VO(TPP)NCS$ solution to determine the stoichiometries of the formation reactions of complexes 1 and 2 at -72 °C. The concentration of Me_2SO in the reaction system was held in the range 2.0–2.1% (v/v) during the titration. Although the solution of $Mo^VO(TPP)NCS$ initially contained a few percent of $[Mo^VO(TPP)Me_2SO]NCS$,[31] no significant influence on the spectral confirmation of complexes 1 and 2 was observed. Upon addition of O_2^-, complex 2 was formed first and then was transformed into complex 1 by the further addition of O_2^-. The stoichiometries in the reactions of $Mo^VO-(TPP)X$ with O_2^- to form complexes of 2 and 1 were determined to be $Mo^VO(TPP)X:O_2^- = 1:1$ and 1:2, respectively (Figure 3).
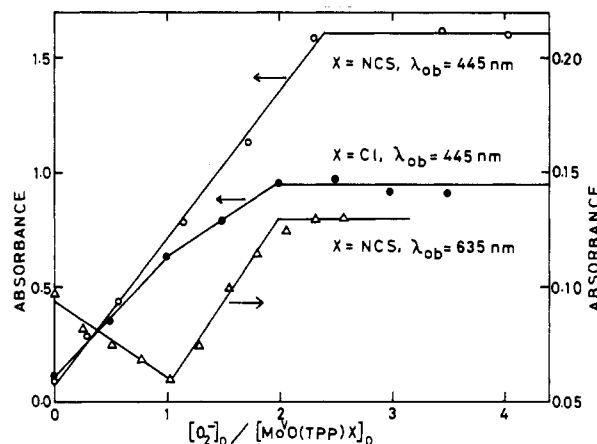
Figure 3. Molar ratio method for the reaction of $Mo^VO(TPP)X$ (X = Cl, NCS) with O_2^- in 2.0–2.1% (v/v) $Me_2SO-CH_2Cl_2$ at -72 °C.

When the reaction system contains a very small amount of Me_2SO (<0.001% (v/v)) at -72 °C, $Mo^{IV}O(TPP)$ is formed by the addition of an equimolar amount of O_2^- and complex 1 by a twofold amount of O_2^-. The formation of these complexes is expressed as follows.

$$Mo^VO(TPP)X \xrightarrow[2\% \ Me_2SO]{1 \ equiv \ of \ O_2^-} 2 \xrightarrow{1 \ equiv \ of \ O_2^-} 1 \qquad (1)$$

$$Mo^VO(TPP)X \xrightarrow{1 \ equiv \ of \ O_2^-} Mo^{IV}O(TPP) \xrightarrow{1 \ equiv \ of \ O_2^-} 1 \qquad (2)$$
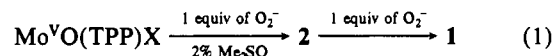
Stoichiometry for the Reaction of $Mo^{IV}O(TPP)$ with Me_2SO. The electronic spectrum of $Mo^{IV}O(TPP)$ in neat dichloromethane at -72 °C is essentially the same as that of the complex at room temperature. By the successive addition of Me_2SO to the solution at -72 °C, the absorption peaks at 428 and 554 nm due to $Mo^{IV}O(TPP)$ are lowered with increase in the absorbances at 444, 573, and 614 nm. The final spectrum coincides with that of complex 2. Isosbestic points appear at 398, 435, 542, and 560 nm. The stoichiometry of the reaction was determined to be n = 1 by the plot of log ($[Mo^{IV}O(TPP)(Me_2SO)_n]/[Mo^{IV}O(TPP)]$) vs. log $[Me_2SO]$ (Figure 4), indicating the formation of $Mo^{IV}O-(TPP)Me_2SO$.[32]

$$Mo^{IV}O(TPP) + Me_2SO \underset{}{\overset{K}{\rightleftharpoons}} Mo^{IV}O(TPP)Me_2SO \qquad (3)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \textbf{2}$$
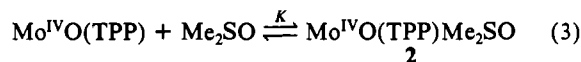
The formation constant, K, was determined to be 48 M^{-1} at -72 °C. In the solution containing 2% (v/v) Me_2SO at low temperatures, $Mo^{IV}O(TPP)$ is solvated in the form of $Mo^{IV}O-(TPP)Me_2SO$ and reacts with O_2^- to give complex 1 with a 1:1 stoichiometry.

Isolation of Complex 1. The following manipulations were performed in a dry dioxygen atmosphere. KO_2 powder (200 mg) was added to a dichloromethane solution (50 cm^3) containing $Mo^VO(TPP)Br$ (480 mg) and 18-crown-6 (360 mg) at -72 °C and the solution was warmed to 0 °C with gentle stirring. When the color of the solution changed from brown to green completely, the solution was again cooled to -72 °C and the residual KO_2 was

(32) The formation of $Mo^{IV}O(TPP)py$ was also confirmed by the spectral change in the reaction of $Mo^{IV}O(TPP)$ with pyridine at -72 °C. The absorption maxima are 447, 577, and 619 nm in 2% (v/v) $py-CH_2Cl_2$. The complex $Mo^{IV}O(TPP)MeTHF$ has absorption maxima at 437, 566, and 606 nm in 2-methyltetrahydrofuran at -72 °C: Imamura, T.; Takahashi, M.; Tanaka, T.; Jin, T.; Fujimoto, M.; Sawamura, S.; Katayama, M. *Inorg. Chem.* **1984**, *23*, 3752.

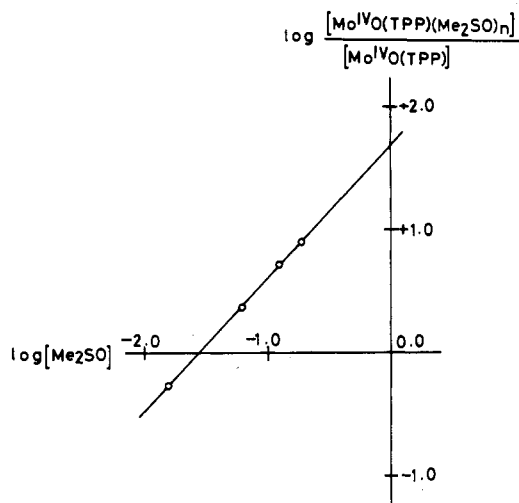**Figure 4.** log ([$Mo^{IV}O(TPP)(Me_2SO)_n$]/[$Mo^{IV}O(TPP)$]) vs. log [Me_2SO] plot for the reaction of $Mo^{IV}O(TPP)$ with Me_2SO in CH_2Cl_2 at -72 °C.

removed by filtration at low temperature. Hexane (150 cm^3) was added to the filtrate at -72 °C to precipitate the desired complex. The product was collected by filtration below -20 °C and recrystallized four times from a mixture of dichloromethane and hexane at -72 °C. The complex dried in vacuo was stored in an Ar atmosphere. Anal. Calcd for [18-crown-6-K][MoO-(TPP)(O$_2$)]·$^1/_2$C$_6$H$_{14}$ (C$_{59}$H$_{59}$O$_9$N$_4$KMo):[33] C, 64.24; H, 5.39; N, 5.08; K, 3.54; Mo, 8.70. Found: C, 63.68; H, 4.72; N, 5.42; K, 3.9; Mo, 8.70.

Electronic Spectra. The electronic spectrum of complex 1 dissolved in dichloromethane at -72 °C is identical with that of complex 1 observed in the reaction mixture of $Mo^VO(TPP)Br$ with a large excess of O_2^- in dichloromethane containing 1% (v/v) Me_2SO (Figure 2). The spectral feature of complex 1 dissolved in dichloromethane is retained in the temperature range between -72 and -20 °C. When the temperature is higher than -20 °C, $Mo^{IV}O(TPP)$ is formed in the solution. On the other hand, complex 1 formed in the presence of a large excess of O_2^- is stable in the solution even at 0 °C. The result suggests that the presence of an excess of O_2^- prevents the shift of equilibrium 4 to the right-hand side.

$$[Mo^VO(TPP)(O_2{}^{2-})]^- \rightleftharpoons Mo^{IV}O(TPP) + O_2^- \quad (4)$$

Complex 1 in dichloromethane has four absorption peaks at 565, 586, 604, and 635 nm in the Q-band region, whereas $Mo^VO(TPP)X$ has the two peaks of α and β.[26] The split of the Q-bands is thought to be a reflection of the decrease in the symmetry of the complex by the side-on coordination of the peroxide group. A similar split of the Q-bands into four has been observed in the electronic spectra of [$Fe^{III}(TPP)(O_2{}^{2-})$]$^-$ [22,23] and Mn^{IV}-(TPP)(O$_2{}^{2-}$).[19]

Infrared Spectra. The coordination of peroxide ligand to the central molybdenum of complex 1 was proved by the infrared spectroscopy. The IR spectrum of complex 1 (KBr pellet) is shown in Figure 5. The stretchings at 876, 521,[34] and 490 cm^{-1} shift respectively to 821, 486, and 466 cm^{-1} for complex 1 synthesized by using K^{18}O$_2$ instead of K^{16}O$_2$. The shifts of the band at 876 assigned to $\nu(^{16}O-^{16}O)$ and of the bands at 521 and 490 cm^{-1} assigned to $\nu(Mo-^{16}O)$ identify that the dioxygen ligand coordinates side-on to the central molybdenum atom and has the formal electronic configuration of peroxide, $O_2{}^{2-}$. When the dioxygen ligand coordinates end-on to a metal atom as O_2^-, the O–O stretching may be observed in the range 1100–1200 cm^{-1}.[5,35]

Figure 5. Infrared spectra of complex 1, [18-crown-6-K]-[Mo^VO-(TPP)(O$_2{}^{2-}$)]·$^1/_2$C$_6$H$_{14}$ (KBr pellet).

Table II. IR Spectral Data

complex	$\nu_{O-O}/$cm^{-1}	$\nu_{M-O}/$cm^{-1}	
[18-crown-6-K][$Mo^VO(TPP)(O_2{}^{2-})$][a]	876	521	490
[18-crown-6-K][$Mo^VO(TPP)(^{18}O_2{}^{2-})$][a]	821	486	466
$Mo^{VI}(TTP)(O_2{}^{2-})_2$[b]	964		
$Ti^{IV}(TPP)(O_2{}^{2-})$[c]	895	635	595
$Ti^{IV}(OEP)(O_2{}^{2-})$[c]	895	645	600
[$Fe^{III}(OEP)(O_2{}^{2-})$]$^-$[d]	806		
$K_2Mo^{VI}OCl_4(O_2{}^{2-})$[e]	940	585	530
$K_2Mo^{VI}OF_4(O_2{}^{2-})$[f]	933	599	565

[a] KBr pellet. [b] From ref 21 (CH$_2$Cl$_2$ solution). [c] From ref 20 (CsI pellet). [d] From ref 23 (Me$_2$SO solution). [e] From ref 36a (KBr pellet). [f] From ref 36b (Nujol mull).

The bands at 521 and 490 cm^{-1} ascribed to the Mo–O stretchings may be attributed to the symmetric and antisymmetric vibrations. The presence of these three vibrational modes at 876, 521, and 490 cm^{-1} for the Mo(O$_2$) group suggests an isosceles triangular geometry.[36,37] The Mo=O stretching vibration is observed at 903 cm^{-1}. This value is close to those of the Mo=O stretchings in oxomolybdenum(V) porphyrin complexes that have alkoxo or μ-oxo ligands coordinating through the O atom; the Mo=O stretchings in $Mo^VO(TPP)OC_2H_5$ and [$Mo^VO(TPP)$]$_2$O are 901 and 905 cm^{-1}, respectively.[38] All other peaks of complex 1 are attributed to [18-crown-6-K]$^+$ and the Mo–TPP moiety. IR data are listed in Table II.

In chloroform, the Mo=O and the O–O stretchings of complex 1 are at 890 and 871 cm^{-1}, respectively, over the temperature range between -60 and -20 °C. The Mo–O stretchings were not observed in chloroform by the overlap with the solvent spectrum; however they were observed at 527[34] and 487 cm^{-1} in dichloromethane in the temperature range between -80 and -20 °C. These results reveal no change in the structure of complex 1 in solution over the temperature range from -80 to -20 °C.

When the dichoromethane solution of complex 1 was warmed to room temperature, the intensity of the Mo–O stretching at 487

(33) As described in NMR section, the complex contains a small amount of 18-crown-6 species as impurities (<5%).

(34) Molybdenum(V,IV) tetraphenylporphyrins have some stretching around 525 cm^{-1}. The bands at 521 cm^{-1} (KBr pellet) and at 527 cm^{-1} (CH$_2$Cl$_2$ solution) overlap with the stretching.
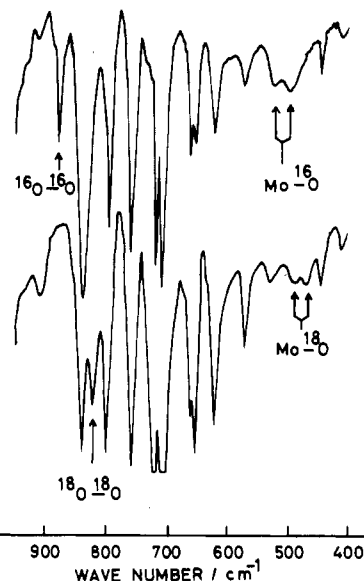
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Table III. ^{1}H NMR Chemical Shifts^a in CD_2Cl_2

| compd | temp/°C | pyrrole β-H | phenyl | | crown ether |
			ortho H	meta,para H	
[18-crown-6-K][Mo^{V}O(TPP)(O$_2{}^{2-}$)]	-80	9.02	8.32	7.84	c
		8.89			
	-40	8.92	8.46	7.85	3.29
	-20	8.91	8.21	7.84	3.25
	+25^b	8.86	8.18	7.81	3.56
Mo^{IV}O(TPP)	+25	8.93	8.18	7.80	
[18-crown-6-K]Cl	-80				3.62
	-20				3.65
18-crown-6	-80				3.59
	-20				3.60

^{a} The chemical shifts are reported in ppm downfield from internal Me$_4$Si. ^{b} The NMR spectrum was measured at 25 °C after complex 1 in CD_2Cl_2 solution was completely converted to Mo^{IV}O(TPP) at room temperature. ^{c} The value of the chemical shift was not obtained because of the broadening spectrum.
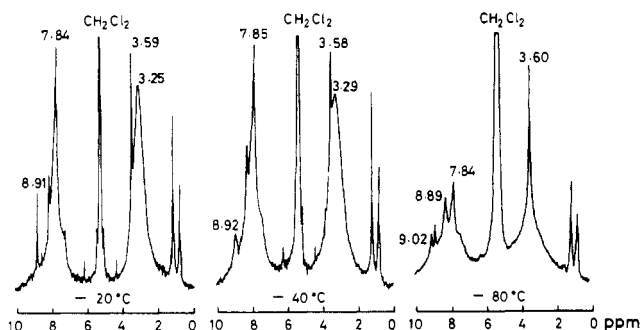
Figure 6. ^{1}H NMR spectra of complex 1 in CD_2Cl_2.

cm^{-1} decreased with the lapse of time. The intensities of the Mo=O and the O—O stretchings in chloroform also decrease with time at room temperature with the appearance of a new band at 895 cm^{-1}. This wave number is in agreement with that of the Mo=O stretching band of the separately prepared Mo^{IV}O(TPP) specimen.

NMR Spectra. The ^{1}H NMR spectra of complex 1 in CD_2Cl_2 at -20, -40, and -80 °C are shown in Figure 6, and the chemical shifts are given in Table III. The signals at 1.25 and 0.88 ppm are attributed to those of hexane contained in the solid sample of complex 1. Integrated intensities of the signals indicate that the isolated compound contains 0.5 molecule of hexane per formula unit of the solid complex. The narrow band around 3.6 ppm is attributed to the free 18-crown-6 or [18-crown-6-K]$^+$ contained as impurities (<5%). The CD_2Cl_2 solutions of 18-crown-6 and [18-crown-6-K]Cl have NMR signals at 3.59 and 3.62 ppm at -20 °C and 3.60 and 3.65 ppm at -80 °C, respectively. The broad signal due to the [18-crown-6-K]$^+$ counterion of complex 1 is observed at 3.25 ppm at -20 °C. However, lowering the temperature to -80 °C causes a conspicuous broadening of the signal. In general, by the formations of ion pairs with paramagnetic anions, the ^{1}H NMR signals of organic cations are expected to be shifted or to be remarkably broadened.[39,40] At -20 °C, the formation of an ion pair of [18-crown-6-K]$^+$ with [Mo^{IV}O-(TPP)(O$_2{}^{2-}$)]$^-$ is indicated by the fact that the signal due to [18-crown-6-K]$^+$ is broadened and shifted to higher field by the influence of the ring current of the porphyrin ring in comparison with that of [18-crown-6-K]Cl in CD_2Cl_2. Thus, the reversible change in the broadness of the signal due to the [18-crown-6-K]$^+$ countercation in the temperature range between -20 and -80 °C may be ascribed to the variation of the strength of the ion pair.
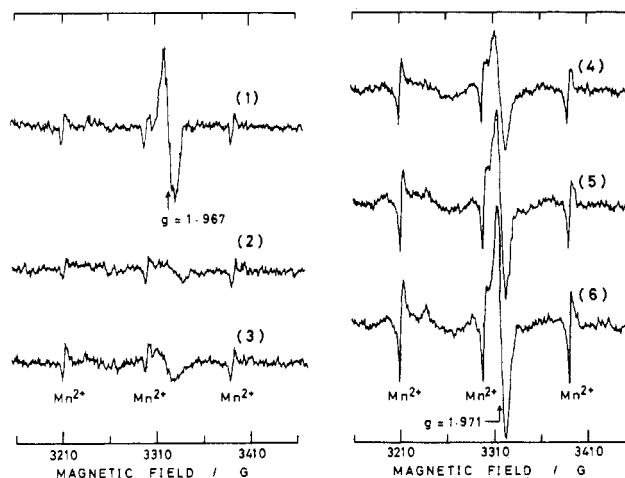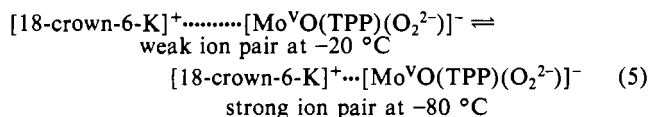
$$[18\text{-crown-6-K}]^+ \cdots\cdots\cdots [Mo^VO(TPP)(O_2{}^{2-})]^- \rightleftharpoons$$
$$\text{weak ion pair at } -20 \text{ °C}$$

$$[18\text{-crown-6-K}]^+ \cdots [Mo^VO(TPP)(O_2{}^{2-})]^- \quad (5)$$
$$\text{strong ion pair at } -80 \text{ °C}$$

Figure 7. ESR spectra of Mo^{V}O(TPP)Br at -65 °C (1) and complex 1 formed by the reaction of Mo^{V}O(TPP)Br with O$_2{}^-$ at -80 (2), -65 (3), -30 (4), -10 (5), and 0 °C (6) in 1% (v/v) Me$_2$SO–CH$_2$Cl$_2$. The initial concentrations are [Mo^{V}O(TPP)Br]$_0$ = 2.12 × 10^{-5} M and [O$_2{}^-$]$_0$ = 4.62 × 10^{-4} M.

The [18-crown-6-K]$^+$ cation of complex 1 at 25 °C gave a narrow NMR signal at 3.56 ppm, which could not be discriminated from the signal of impurities, [18-crown-6-K]$^+$, and/or 18-crown-6. This shift of the signal from 3.25 ppm at -20 °C to 3.56 ppm at 25 °C reflects the formation of the neutral complex, Mo^{IV}O(TPP). Chemical shifts of the NMR signals due to the porphyrin ring of the complex formed in the solution at 25 °C are naturally identical with those of Mo^{IV}O(TPP) in CD_2Cl_2.

The β-protons of the pyrrole moieties in complex 1 give a singlet NMR signal at 8.91 ppm at -20 °C, which is split into two peaks at 9.02 and 8.89 ppm upon cooling to -80 °C. Guilard et al.[20] observed a similar splitting of the NMR signal due to the β-protons of peroxotitanium(IV) tetraphenylporphyrin, Ti^{IV}(TPP)(O$_2{}^{2-}$), in CD_2Cl_2 by decreasing the temperature from -40 to -80 °C and ascribed this behavior to the stereochemical nonrigidity of the peroxide group. The peroxide group of complex 1, [Mo^{V}O-(TPP)(O$_2{}^{2-}$)]$^-$, seems to be rotating in solution.

ESR Measurements. The ESR spectrum of the dichloromethane solution of Mo^{V}O(TPP)Br consists of six weak lines due to ^{95,97}Mo nuclei ($I = {}^5/_2$) and a strong central line ($g = 1.967$) due to ^{92,94,96,98,100}Mo nuclei ($I = 0$), which is split into nine hyperfine lines by the coupling with the four nitrogen atoms of the porphyrin ring.[41] Complex 1 formed by the reaction of Mo^{V}O(TPP)X and a large excess of O$_2{}^-$ in dichloromethane containing 1% (v/v) Me$_2$SO is ESR-silent at -80 °C, but gives an ESR signal ($g = 1.971$) at 0 °C to be ascribed to Mo(V) (d^1) coupled with the four nitrogen atoms of the porphyrin (Figure 7). The intensity of the signal changes reversibly in the tem-

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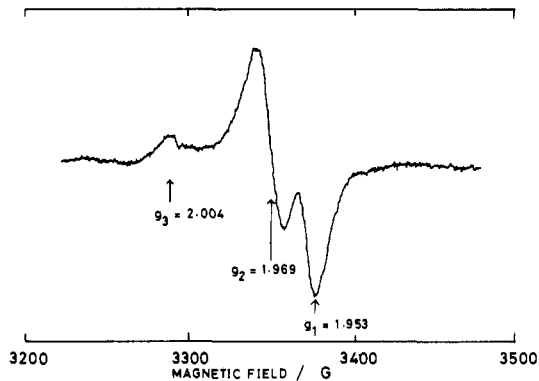
Figure 8. ESR spectrum of complex **1**, [18-crown-6-K][Mo^{V}O-(TPP)(O$_2$$^{2-}$)], in dichloromethane at -150 °C.

Table IV. ESR Parameters of Oxomolybdenum(V) Porphyrin Complexes in Dichloromethane

complex	temp/ °C	g	A_{Mo-N}/ G
Mo^{V}O(TPP)Br^a	25	$\bar{g}$ = 1.967	2.54
	-150	$g_\perp$ = 1.961^b	
[18-crown-6-K][Mo^{V}O(TPP)(O$_2$$^{2-}$)]	-20	$\bar{g}$ = 1.971	2.7
	-150	g_1 = 1.953	
		g_2 = 1.969	
		g_3 = 2.004	

^{a} From ref 41. ^{b} The value of $g_\parallel$ could not be determined because of the overlap with the signal due to ^{95,97}Mo ($I = {}^5/_2$).

perature range between -80 and 0 °C and shows no time dependency at constant temperature. The rise of the temperature of the solution to 25 °C causes the decrease of the intensity of the ESR signal with time due to the formation of Mo^{IV}O(TPP) (diamagnetic).

The ESR spectral change for the isolated complex **1** dissolved in dichloromethane is identical with that observed for complex **1** formed in the reaction mixture of Mo^{V}O(TPP)X with an excess of O$_2$$^-$. The intensity of the ESR signal at constant temperature between -20 and -80 °C is proportional to the concentration of complex **1** over the range between 8.73 × 10^{-3} and 3.24 × 10^{-5} M. The rise of the temperature of the solution above -20 °C causes the formation of Mo^{IV}O(TPP) from complex **1** as well as the system of the reaction mixture.

Complex **1** shows an anisotropic ESR spectrum in a frozen solution of dichloromethane at -150 °C (Figure 8), in contrast with the axial symmetric ESR spectrum of Mo^{V}O(TPP)X.^{42} This anisotropic spectrum reflects the side-on coordination of the dioxygen ligand, which breaks the axial symmetry of the complex. The ESR parameters of complex **1** dissolved in the dichloromethane are summarized in Table IV.

ESR data and the stoichiometry of the reaction of Mo^{V}O(TPP)X with O$_2$$^-$ suggest that complex **1** existing as [Mo^{V}O-(TPP)(O$_2$$^{2-}$)]$^-$ at -20 °C is ESR silent at -80 °C. Three reasons to explain the ESR silence at -80 °C could be adduced.

(a) Complex **1** exists as [Mo^{IV}O(TPP)(O$_2$$^-$)]$^-$ at -80 °C because of the intramolecular electron-transfer reaction

$$[Mo^VO(TPP)(O_2^{2-})]^- \rightleftharpoons [Mo^{IV}O(TPP)(O_2^-)]^- \quad (6)$$
$$\text{at } -20\ °C \qquad\qquad \text{at } -80\ °C$$
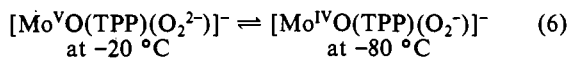
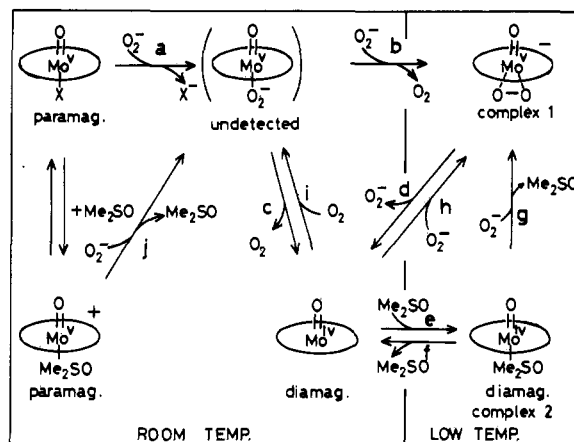(b) Complex **1** dimerizes at -80 °C and shows no ESR signal because of the spin-spin coupling of unpaired electrons on the molybdenum atoms.

$$2[Mo^VO(TPP)(O_2^{2-})]^- \rightleftharpoons [Mo^VO(TPP)(O_2^{2-})]_2^{2-} \quad (7)$$
$$\text{at } -20\ °C \qquad\qquad \text{at } -80\ °C$$
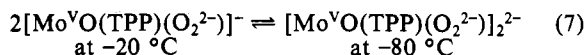
(c) ESR silence of complex **1** at -80 °C arises from a very rapid spin-lattice relaxation induced at low temperature.

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Scheme I

Persistency of the electronic spectrum of complex **1** over the temperature range from -20 to -80 °C denies the possibilities of reasons a and b. The IR data of complex **1** in solution indicated that there is no change in the structure of complex **1** over the temperature range from -80 to -20 °C. Namely, the change in the temperature between -80 and -20 °C causes neither the intramolecular electron transfer (a) nor the monomer-dimer equilibrium (b). Although the complex [Mo^{IV}O(TPP)(O$_2$$^-$)]$^-$ is thought to give an ESR signal due to an unpaired electron on the superoxide anion radical,^{43} no ESR signal due to O$_2$$^-$ is observed at -80 °C, suggesting that the intramolecular electron transfer (a) does not occur. Furthermore, reason b is not in accordance with the fact that the ESR spectral change by the temperature variation is independent of the concentration of complex **1**. These results rule out the possibilities of reactions a and b. In conclusion, only reason c is consistent with the results of IR, electronic, and ESR spectral measurements.^{44} The formation of the strong ion pair between [18-crown-6-K]$^+$ and [Mo^{V}O(TPP)(O$_2$$^{2-}$)]$^-$ occurring at -80 °C was confirmed by NMR measurements. The [18-crown-6-K]$^+$ cation seems to be very efficient for spin relaxation to the solvent by strong ion pair formation. The ESR signal due to molybdenum(V) observed at -20 °C may not be observed at -80 °C by this rapid spin relaxation.

Reaction Mechanism. The reactions of Mo^{V}O(TPP)X with O$_2$$^-$ are illustrated in Scheme I. The complex Mo^{V}O(TPP)X reacts with an excess of O$_2$$^-$ at room temperature through the two competitive pathways, a → b → d and a → c, to form Mo^{IV}O-(TPP). For a low concentration of O$_2$$^-$, the reaction pathway of a → c is predominant. The ratio of the reactions a → b → d to a → c increases with the concentration of O$_2$$^-$ and is estimated to be ca. 0.3 under the conditions of [Mo^{V}O(TPP)Br]$_0$ = 7.86 × 10^{-6} and [O$_2$$^-$]$_0$ = 2.16 × 10^{-4} M at 25 °C.

At low temperatures, complex **2**, Mo^{IV}O(TPP)Me$_2$SO, is formed through the path a → c → e in 1-2% (v/v) Me$_2$SO solution containing a small amount of O$_2$$^-$ (<1 equiv). The formation of complex **2** is accompanied by the generation of dioxygen gas, which was identified by mass spectrometry. Further addition of O$_2$$^-$ causes the formation of complex **1** from complex **2** by oxidative addition of O$_2$$^-$ through pathway g. Upon addition of a large excess of O$_2$$^-$ at one time to the solution of Mo^{V}O(TPP)X, complex **1** is formed through both the routes a → b and a → c → e → g. The stoichiometries of these two routes used to form complex **1** are the same; Mo^{V}O(TPP)X:O$_2$$^-$ = 1:2. The pathway a → b used to form complex **1** becomes predominant with an increase in the initial concentration of O$_2$$^-$. The formation of complex **1** from Mo^{IV}O(TPP) through route h was confirmed by the spectral change in the course of the reaction of Mo^{IV}O(TPP) with O$_2$$^-$ in

(43) *Superoxide and Superoxide Dismutases*; Michelson, A. M.; McCord, J. M., Fridovich, I., Eds.; Academic: New York, 1977.
(44) In our preliminary study,^{25} ESR silence at -80 °C was thought to be due to the formation of [Mo^{IV}O(TPP)(O$_2$$^-$)]$^-$. But the subsequent detailed studies reveal that complex **1** exists as [Mo^{V}O(TPP)(O$_2$$^{2-}$)]$^-$ even at -80 °C in solution.

dichloromethane containing Me$_2$SO in very low concentrations (<0.001%); the absorbance due to Mo^{IV}O(TPP) decreased with increasing absorption due to complex **1** without the appearance of spectrum of complex **2**.

The complex Mo^{IV}O(TPP) is obtained through reaction paths d and f by warming the solutions of complexes **1** and **2** to room temperature, respectively. Mo^{IV}O(TPP) in solution at room temperature does not react with either O$_2^-$ or O$_2$ but is converted into complex **1** as the O$_2^-$ solution and O$_2$ gas are simultaneously introduced into the reaction system. This observation suggests the presence of the reaction path i → b via the complex Mo^{V}O-(TPP)(O$_2^-$), which was not detected experimentally.

Complex **1**, [Mo^{V}O(TPP)(O$_2^{2-}$)]$^-$, is of the same type as the complexes [Fe^{III}(P)(O$_2^{2-}$)]$^-$ (P = TPP or OEP) formed in the reaction of Fe^{III}(P)Cl with O$_2^-$ in a molar ratio of 1:2.[22,23] Recently the reactions of sulfur with iron and titanium porphyrin peroxo complexes to give sulfate complexes or sulfate were reported.[45]

These peroxo dioxygen complexes are of great interest as mediators in oxygenation reactions and as models of intermediates in oxygen activation cycles of the reactions in vivo.

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Contribution from the Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa, and Laboratory of Chemistry, College of General Education, Kyushu University 01, Ropponmatsu, Chuo-Ku, Fukuoka, Japan

Secondary Anion Binding to the Dicopper(II) Complex of N,N',N'',N'''-Tetrakis(2-aminoethyl)cyclam

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The complexing of Cu^{2+} by the ligand TAEC (N,N',N'',N'''-tetrakis(2-aminoethyl)cyclam) is investigated by potentiometric titration and by UV–visible spectroscopy in 0.5 M NaNO$_3$ at 25 °C. Equilibrium constants for the formation of the species [Cu$_2$(TAEC)]$^{4+}$ and [Cu(TAEC)H$_2$]$^{4+}$ were found to be 32.1 and 18.97 (the latter corresponding to the equilibium Cu^{2+} + LH$_2^{2+}$ ⇌ [CuLH$_2$]$^{4+}$). The complex [Cu$_2$(TAEC)]$^{4+}$ binds secondary anionic ligands, presumably held between the two copper atoms in the complex in a bridging fashion, with log K values for the formation of these secondary complexes being 4.1 for OH$^-$, 3.26 for Br$^-$, 3.57 for Cl$^-$, 4.02 for N$_3^-$, and 2.63 for SCN$^-$. The strength of binding of these secondary ligands is contrasted to that found in other binuclear complexes containing two copper(II) ions and also with mononuclear complexes of copper(II). It is concluded that the bimetallic site increases the strength of binding of secondary ligands by some 2 or 3 orders of magnitude as compared with mononuclear complexes and that the strength of binding in the bimetallic complex may be strongly affected by the coordination geometry around the copper(II) ion.

There is currently considerable interest in ligands that bind two or more metal ions, which arises in part from the possibility that they might act as models for biological systems.[1] There have been several recent reports of thermodynamic studies of macrocyclic ligands that coordinate two metal ions, which are able to coordinate further, secondary, ligands,[2–4] in what has been termed "cascade" binding.[5] Martell et al.[2] thus found that the two copper(II) ions held in the BISTREN molecules (Figure 1) were able to bind a chloride ion with a log K_1 (formation constant) value of 3.55, which is very high in comparison to that reported[6] for a single free Cu^{2+} ion, namely 0.5 log units. At the same time, the binding of hydroxide ion to the two copper(II) ions in BISTREN was extraordinarily high, log K having a value of 11.56, in contrast to the value of 6.7 found for the Cu^{2+} ion itself.[6] Such marked changes in coordinating ability are clearly of interest.

In recent papers[7,8] it was reported that the ligand TAEC (Figure 1) formed complexes in which two copper(II) ions were bound and that[7] binding of bromide ion to these two copper(II) ions appeared to be quite strong. The dicopper(II) complex of TAEC is of interest since structural studies show[7,8] that the copper(II) ions each have four nitrogen donors bound in a planar fashion, so that the secondary ligand, e.g. the bromide ion, must bind to the axial sites on the copper(II) ions, forming a bridge between them. The structure of the monobromo dicopper(II) complex of TAEC has Cu–Br lengths of 2.73 Å to the bridging bromide ion, which can be compared with the shorter Cu–Br lengths of 2.55[9] and 2.52 Å[10] for nonbridging bromides occupying the axial site

Table I. Protonation Constants of the Ligand TAEC[a]

pK_{a1}[b]	10.10 (3)[c]	pK_{a5}	6.08 (7)
pK_{a2}	10.05 (2)	pK_{a6}	4.84 (7)
pK_{a3}	9.41 (4)	pK_{a7}	1.8 (1)
pK_{a4}	9.00 (3)		

[a] Determined by glass-electrode potentiometry, in 0.5 M NaNO$_3$ at 25 °C. TAEC is the ligand N,N',N'',N'''-tetrakis(2-aminoethyl)-cyclam, shown in Figure 1. [b] These are the stepwise constants such that pK_{a1} is the constant for the equilibrium L + H$^+$ ⇌ LH$^+$, pK_{a2} for LH$^+$ + H$^+$ ⇌ LH$_2^{2+}$, and so on. [c] The numbers indicated in parentheses are the estimated errors in the last significant figure shown, which are 3 times the standard deviation indicated by the program.

on copper(II) complexes with square-pyramidal coordination geometry. In contrast, planar coordination of the nitrogen donors to the copper(II) ions in BISTREN is not possible, so that the bridging secondary ligand must occupy the axial sites on what

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