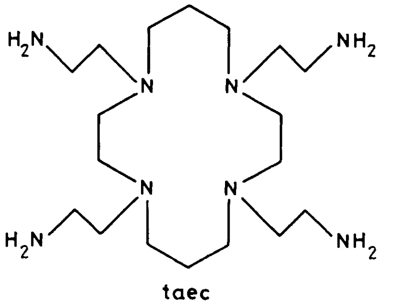
Synthesis, Crystal Structure, and Quasi-reversible Dioxygen Binding of $[Cu_2(tpmc)]X_2$ [tpmc = 1,4,8,11-Tetrakis(2′-pyridylmethyl)-1,4,8,11-tetra-azacyclotetradecane; X = ClO_4, PF_6, or CF_3SO_3]‡

Eiji Asato, Shinji Hashimoto, Naohide Matsumoto, and Sigeo Kida*,†
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka 812, Japan, and Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

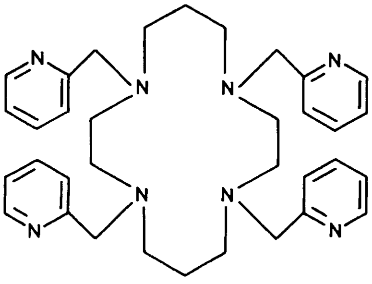
Dicopper(I) complexes of tpmc [1,4,8,11-tetrakis(2′-pyridylmethyl)-1,4,8,11-tetra-azacyclotetradecane] have been synthesized. The complexes reacted with dioxygen at low temperature (below −60 °C) to form two species of adduct quasi-reversibly, which were characterized by Resonance Raman spectra ($^{16}O-^{16}O$ stretching at 820 and 771 cm^{-1} and $Cu-^{16}O$ stretching at 529 and 491 cm^{-1} which shifted to lower energy when $^{18}O_2$ was substituted for $^{16}O_2$). From an acetone solution of the dioxygen adducts bis(pyridine-2-carboxylato)copper(II) was isolated. The molecular structure of the dicopper(I) complex $[Cu_2(tpmc)][CF_3SO_3]_2$ was determined by *X*-ray diffraction analysis. The complex crystallizes in the monoclinic space group $P2_1/n$ with a = 14.341(4), b = 15.392(4), and c = 9.700(2) Å, β = 93.95(2)°, and Z = 2, and the structure was refined to R = 0.055 and R' = 0.058. The complex cation has a centre of symmetry and each copper atom is co-ordinated by one nitrogen of the macrocyclic ring and two pendant pyridyl nitrogens forming a distorted trigonal plane with a Cu ··· Cu separation of 6.739(2) Å.

Haemocyanins are copper-containing metalloproteins, which bind and transport dioxygen in the haemolymph of molluscs and arthropods, containing two copper ions in their active centre.[1–4] Recent *X*-ray structural studies on a deoxyhaemocyanin (spiny lobster *Panulirus interruptus*) indicated that three imidazole groups co-ordinate to each copper(I) ion with no endogenous protein-derived bridging ligand, which had been proposed before, the distance between the two copper atoms being 3.8 ± 0.4 Å.[5] The copper(I) centre reacts with dioxygen to give oxyhaemocyanin, in which the two copper atoms are separated[6] by *ca.* 3.6 Å and bridged by a peroxide anion with a *cis-OO′* fashion.[7]

Based on the above information, many chemists have attempted to prepare a model compound which mimics the structure and the function of haemocyanin.[8] The general strategy to obtain a stable Cu_2-O_2 complex was to design chelating ligands which bind two copper atoms at an appropriate distance such that a peroxide ion is bound to both coppers. However, in most cases, formation of a stable Cu_2-O_2 unit could not be achieved, because a $Cu^{II}{}_2-O_2$ unit which is formed in the initial stage of reaction with O_2 is generally attacked by another dinuclear unit $Cu^{I}{}_2$, resulting in irreversible dioxygen reduction with O–O bond cleavage.[9] In some cases the co-ordinated dinucleating ligand undergoes oxidation by the activated O_2. Therefore, in order to stabilize a $Cu^{II}-O_2-Cu^{II}$ unit and to suppress the above-mentioned undesirable concomitant reactions the binding site of O_2 must be in an aprotic environment so as to suppress the transfer of bound O_2 as a protonated superoxide or peroxide ion, and to protect it sterically from further attack by another copper(I) unit. Further, in order to cause reversible dioxygen binding with Cu^I, the Cu^I-Cu^{II} redox potential of the copper(I) precursor should be high enough to allow the back reaction. Flexibility of the dinucleating ligand may also be an important factor, since the co-ordination geometry preferred by Cu^I differs from that of Cu^{II}.



taec



tpmc

Recently, Kida and co-workers[10a,b] reported that a dinuclear copper(II) complex $[Cu_2(taec)][ClO_4]_4$ reacts with various anions X^- in aqueous solution to form X-bridged complexes $[Cu_2X(taec)][ClO_4]_3$, where taec denotes 1,4,8,11-tetrakis(2′-aminoethyl)-1,4,8,11-tetra-azacyclotetradecane and X = F, Cl, Br, I, CH_3CO_2, NO_2, NCO, N_3, *etc.*[10] The formation constants of $[Cu_2X(taec)]^{3+}$ from $[Cu_2(taec)]^{4+}$ and X^- are extremely large compared to those for the X^--Cu^{II} complex formation from $Cu^{2+}(aq)$.[10c] If X^- is peroxide ion, the situation is reminiscent of the active site of haemocyanins. However, the copper(I) complex of taec $[Cu_2(taec)][ClO_4]_2$ was irreversibly air-oxidized in acetonitrile–dichloromethane (1:1) even at low

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† *Present address:* Kyushu University.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

temperature (below −60 °C) to give a hydroxo-bridged dicopper(II) complex $[Cu_2(OH)(taec)][ClO_4]_3 \cdot H_2O$.[11] Our recent investigation[12] on tpmc complexes [tpmc = 1,4,8,11-tetrakis(2′-pyridylmethyl)-1,4,8,11-tetra-azacyclotetradecane] showed that dinuclear Cu^{II}–tpmc complexes $[Cu_2X(tpmc)]^{3+}$ also have a hydrophobic cavity which is surrounded by aprotic and bulkier pyridylmethyl pendant arms. It is expected that substitution of pyridines for the alkylamines of the taec copper(II) complex gives rise to a considerable positive shift in the Cu^I–Cu^{II} redox potential, since pyridine is generally a weaker donor than alkylamines. Furthermore, the Cu^{II}–Cu^{II} separation [3.712(1) Å] found[12] in the μ-hydroxo complex $[Cu_2(OH)(tpmc)][ClO_4]_3 \cdot 2H_2O$ is very close to that of oxyhaemocyanin. These facts prompted us to investigate the reactivity of dioxygen with the dinuclear copper(I) tpmc complex as a model for haemocyanins. This paper describes the preparation and structure of a dinuclear copper(I) complex with tpmc as the precursor of the Cu_2–O_2 complex, and the reaction of dioxygen with the copper(I) complex.

Experimental

Preparation.—The ligand tpmc was prepared using the method of Alcock *et al.*[13] The crude product was recrystallized from ethanol–acetonitrile (1:5). The starting materials $[Cu(CH_3CN)_4]X$ ($X = ClO_4$, PF_6, or CF_3SO_3) were prepared by the general method.[14] Synthesis and isolation of copper(I) complexes were carried out in an argon atmosphere by use of the Schlenk technique. Solvents used for the synthesis were distilled in an argon atmosphere prior to use.

$[Cu_2(tpmc)][ClO_4]_2$ (**1**). To a suspension of $[Cu(CH_3CN)_4]ClO_4$ (327 mg, 1 mmol) in acetonitrile (15 cm^3) was added tpmc (283 mg, 0.5 mmol) with stirring. When the mixture was heated at about 60 °C with stirring it gradually changed to a transparent brownish yellow solution, which was concentrated until crystals began to appear and filtered. Yellow prisms were separated from the filtrate upon cooling in a refrigerator. Yield: 105 mg (47%) (Found: C, 45.90; H, 5.00; Cu, 14.20; N, 12.70. Calc. for $C_{34}H_{44}Cl_2Cu_2N_8O_8$: C, 45.85; H, 5.00; Cu, 14.25; N, 12.60%).

$[Cu_2(tpmc)][PF_6]_2$ (**2**). This compound was obtained by a method similar to that for (**1**) except that $[Cu(CH_3CN)_4]PF_6$ was used instead of the perchlorate. Orange prisms were separated from the acetonitrile solution, but they became a yellow powder *in vacuo* in 24 h, probably due to loss of solvent of crystallization. Yield: 45% (Found: C, 41.50; H, 4.55; Cu, 12.75; N, 11.60. Calc. for $C_{34}H_{44}Cu_2F_{12}N_8P_2$: C, 41.60; H, 4.50; Cu, 12.95; N, 11.40%).

$[Cu_2(tpmc)][CF_3SO_3]_2$ (**3**). This compound was obtained as yellow prismatic crystals by a method similar to that for (**1**) except that $[Cu(CH_3CN)_4]CF_3SO_3$ was used instead of the perchlorate. Yield: 38% (Found: C, 43.65; H, 4.50; Cu, 12.90; N, 11.30. Calc. for $C_{36}H_{44}Cu_2F_6N_8O_6S_2$: C, 43.70; H, 4.50; Cu, 12.85; N, 11.30%).

Elemental Analyses.—Carbon, hydrogen, and nitrogen analyses were carried out at the Chemical Material Center, Institute for Molecular Science and at the Elemental Analysis Service Center, Kyushu University. Copper analysis was carried out with a Seiko STS-7000 plasma spectrometer and with a Shimadzu AA-680 atomic absorption flame spectrometer.

X-Ray Diffraction Analysis.—Diffraction data were obtained on a Rigaku Denki AFC-5 four-circle diffractometer with graphite-monochromatized Mo-K_α radiation ($\lambda = 0.710\,73$ Å) at ambient temperature (20 ± 1 °C). Pertinent crystallographic parameters are summarized in Table 1. The crystal of $[Cu_2(tpmc)][CF_3SO_3]_2$ (**3**) used for analysis was covered with Nujol to prevent gradual air oxidation. The intensities of standard reflections showed no decay during measurement. Reflection data were corrected for Lorentz polarization effects but not for absorption.

The structure was solved by the standard heavy-atom method. Refinements were carried out by the block-diagonal least-squares method, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. All hydrogen atoms were located on the Fourier difference map, and the atomic parameters were refined isotropically. The atomic scattering factors were taken from ref. 15. The calculations were carried out on the FACOM-M 780 computer at the Computer Center of Kyushu University, by the use of the UNICS III program system.[16,17] Positional parameters of non-hydrogen atoms are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Proton N.M.R. Spectra.—Spectra were measured on a JEOL JML GX-400 Fourier-transform n.m.r. spectrometer in CD_3CN (400 MHz), tetramethylsilane being used as an internal standard.

Low-temperature U.V.–Visible Spectra.—U.v.–visible spectra were obtained at −85 °C in acetone by using a JASCO UVIDEC-610 C spectrophotometer equipped with an OXFORD CF 1204 cryostat. The cryostat was connected with an OXFORD 3120 thermocontroller which controlled the temperature of the sample solution by flushing of nitrogen gas evolved from liquid nitrogen. The spectrum of the solvent alone was measured under the same conditions as those used for measurement of the sample solution, and used as the baseline for the spectra of the latter.

The sample solution was prepared under an argon atmosphere using the Schlenk technique. The weighed solid sample (**2**) was dissolved in acetone and transferred to a quartz cell equipped with a long three-way tap placed outside the cryostat. The cell was placed in the cryostat and cooled to −85 °C. After thermal equilibrium had been attained (30 min) the spectrum was recorded. Oxygenation of the chilled solution was effected by bubbling dry oxygen using a syringe needle through the three-way tap. In order to maintain the low temperature the rate of bubbling must be slow. After recording the spectrum of the resultant reddish brown solution (dioxygen complex), the oxygen molecule was removed by argon gas bubbling (5 min) using a syringe needle connected with an argon gas bomb. Since the bubbling gave rise to an elevation of temperature, it took *ca.* 20 min to reattain thermal equilibrium (−85 °C). Then the spectrum was recorded, and the process repeated several times.

Resonance Raman Spectra.—Complex (**2**) was dissolved in degassed ethyl acetate–dimethylformamide (1:1) in a Schlenk tube under an argon atmosphere. The solution (*ca.* 5 mmol) was transferred under an argon atmosphere to a cylindrical cell and cooled to −90 °C in a ethanol–liquid nitrogen bath. After thermal equilibration, the argon flow was stopped and oxygen gas was injected into the solution. The cell was placed in a Dewar vessel filled with a mixture of ethanol and liquid nitrogen (−90 °C). The sample was spun in the cylindrical cell at 1 000 revolutions min^{-1} to prevent decomposition by the laser light. Resonance Raman spectra were measured with the excitation line at 488.0 nm of an NEC GLG 3200 argon-ion laser and the scattered light was detected with a diode monochromator. The accumulation time was about 3 min and 1 pixel corresponds to 1 cm^{-1}. The spectrometer was calibrated with indene and the accuracy of the peak wavenumber is 1 cm^{-1}. An isotopic experiment was carried out by using commercial $^{18}O_2$ (CEA-ORIS Bureau Des Isotopes Stables).

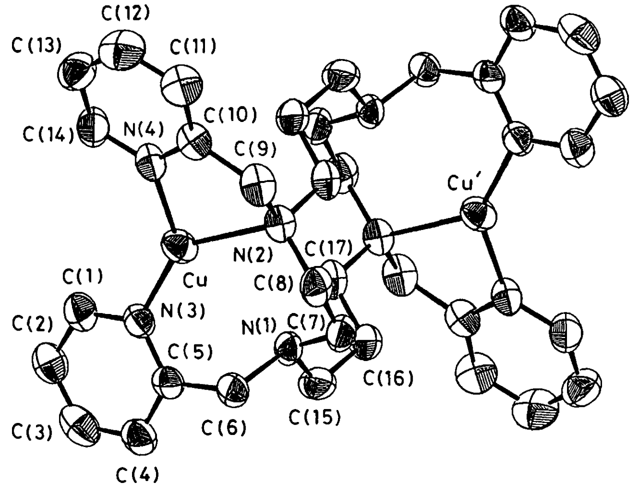

Figure 1. Structure and numbering system for $[Cu_2(tpmc)]^{2+}$

Table 1. Crystal data and data collection details for $[Cu_2(tpmc)][CF_3SO_3]_2$

Formula	$C_{36}H_{44}Cu_2N_8O_6S_2$
M	990.01
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	14.341(4)
b/Å	15.392(4)
c/Å	9.700(2)
β/°	93.95(2)
U/Å^3	2 136.1(9)
Z	2
D_c/g cm^{-3}	1.538
Crystal size/mm	0.30 × 0.30 × 0.40
μ(Mo-K_α)/cm^{-1}	11.68
F(000)	1 016
Scan mode	θ—2θ
Scan width/°	1.2 + 0.35 tanθ
2θ range/°	2.5—50
Collection region	$+h, +k, \pm l$
No. of reflections collected	3 664
No. of unique data [$\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$]	2 577
No. of variables	360
R	0.055
R′	0.058
Weighting scheme	*w* = 1
Largest peak on Fourier difference map/e Å^{-3}	0.78

X-Band E.S.R. Spectrum.—The spectrum was recorded on a JEOL JES-FE-3X spectrometer at liquid-nitrogen temperature, using diphenylpicrylhydrazyl (dpph) as a standard marker. The sample solution was prepared as follows. Complex (**3**) was dissolved in degassed acetone under an argon atmosphere in a Schlenk tube. The solution was transferred under an argon atmosphere to an e.s.r. tube, and cooled to −90 °C in an ethanol–liquid nitrogen bath. Dry oxygen gas was injected into the solution using a syringe needle, and the e.s.r. tube was placed in a Dewar vessel filled with liquid nitrogen. After the solution had been cooled to liquid-nitrogen temperature, the spectrum was recorded.

Measurements of Oxygen Uptake.—The complex $[Cu_2(tpmc)][CF_3SO_3]_2$ (2.13 g, 2.15 mmol) was dissolved in dimethylformamide–acetone (1 : 1, 40 cm^3) and kept at −85 °C in a liquid nitrogen–ethanol bath. To this solution was introduced dioxygen (uptake 83.2 cm^3); a blank solution absorbed 43.5 cm^3. Thus, the net uptake was 39.7 cm^3, which corresponds to 3/4 of the copper(I) complex on a molar basis. Measurements at −60 °C gave the same result. The details of the apparatus and procedure may be obtained from the author (S. K.) upon request.

Table 2. Fractional positional parameters (× 10^5) of non-hydrogen atoms for $[Cu_2(tpmc)][CF_3SO_3]_2$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Cu	17 015(6)	14 928(5)	−2 224(8)
N(1)	8 737(34)	6 523(30)	22 013(49)
N(2)	18 958(32)	668(30)	−1 940(52)
N(3)	12 942(35)	23 675(30)	10 177(50)
N(4)	23 827(35)	14 016(31)	−19 238(51)
C(1)	10 764(49)	31 701(41)	5 465(69)
C(2)	8 008(51)	38 241(43)	13 836(74)
C(3)	7 396(49)	36 481(47)	27 452(77)
C(4)	9 572(47)	28 334(44)	32 696(68)
C(5)	12 368(40)	22 037(39)	23 650(60)
C(6)	15 202(43)	13 091(39)	28 288(61)
C(7)	13 199(48)	−2 017(40)	21 852(64)
C(8)	21 077(46)	−2 639(39)	12 268(67)
C(9)	27 491(43)	−198(41)	−9 705(71)
C(10)	28 103(40)	6 402(40)	−21 028(64)
C(11)	33 273(48)	4 827(48)	−32 095(75)
C(12)	34 031(49)	11 182(56)	−41 818(76)
C(13)	29 642(53)	19 080(51)	−40 124(71)
C(14)	24 694(51)	20 244(43)	−28 881(71)
C(15)	154(49)	6 395(47)	29 586(65)
C(16)	−7 838(46)	1 136(42)	22 972(65)
C(17)	−11 094(43)	4 351(38)	8 929(66)
S	47 325(14)	13 760(11)	17 757(18)
F(1)	46 473(54)	30 188(33)	11 218(66)
F(2)	46 261(49)	27 743(33)	32 410(61)
F(3)	34 361(39)	25 571(46)	19 325(99)
O(1)	43 830(64)	11 683(49)	4 165(67)
O(2)	43 585(64)	9 297(37)	28 448(74)
O(3)	57 145(39)	14 932(41)	18 956(73)
C(18)	43 349(57)	24 729(53)	20 109(94)

Table 3. Selected interatomic distances (Å) and angles (°) for $[Cu_2(tpmc)][CF_3SO_3]_2$ with e.s.ds in parentheses

Cu ⋯ Cu	6.739(2)	Cu ⋯ N(1)	2.999(5)
Cu–N(2)	2.212(5)	Cu–N(3)	1.923(5)
Cu–N(4)	1.980(5)	N(1)–C(6)	1.475(8)
N(1)–C(7)	1.463(8)	N(1)–C(15)	1.476(9)
N(2)–C(8)	1.481(8)	N(2)–C(9)	1.486(8)
N(2)–C(17)	1.491(8)	N(3)–C(1)	1.346(8)
N(3)–C(5)	1.339(8)	N(4)–C(10)	1.340(8)
N(4)–C(14)	1.351(8)	C(1)–C(2)	1.369(8)
C(2)–C(3)	1.357(10)	C(3)–C(4)	1.381(10)
C(4)–C(5)	1.385(9)	C(5)–C(6)	1.496(8)
C(7)–C(8)	1.515(10)	C(9)–C(10)	1.503(9)
C(10)–C(11)	1.368(10)	C(11)–C(12)	1.368(11)
C(12)–C(13)	1.384(11)	C(13)–C(14)	1.353(10)
C(15)–C(16)	1.510(9)	C(16)–C(17)	1.494(9)
N(2)–Cu–N(3)	136.9(2)	N(2)–Cu–N(4)	82.6(2)
N(3)–Cu–N(4)	139.4(2)	C(1)–C(2)–C(3)	118.1(6)
C(2)–C(3)–C(4)	120.8(7)	C(3)–C(4)–C(5)	118.0(6)
N(3)–C(5)–C(4)	121.8(6)	C(1)–N(3)–C(5)	118.4(5)
N(3)–C(1)–C(2)	122.9(6)	N(1)–C(6)–C(5)	110.9(5)
N(1)–C(7)–C(8)	114.1(5)	N(2)–C(8)–C(7)	115.8(5)
N(2)–C(9)–C(10)	113.7(5)	C(10)–C(11)–C(12)	119.2(7)
C(11)–C(12)–C(13)	119.2(7)	C(12)–C(13)–C(14)	118.7(7)
N(4)–C(14)–C(13)	122.8(6)	C(14)–N(4)–C(10)	117.8(6)
N(4)–C(10)–C(11)	122.3(6)	N(1)–C(15)–C(16)	115.5(5)
C(15)–C(16)–C(17)	113.0(5)		

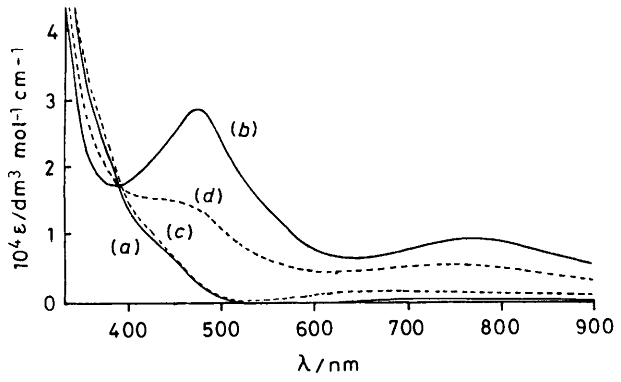

Figure 2. Electronic spectra of $[Cu_2(tpmc)][PF_6]_2$ and its dioxygen adducts in an acetone solution at −85 °C: (*a*) before exposure; (*b*) after exposure to dioxygen; (*c*) after removal of dioxygen by argon bubbling; and (*d*) after repetition of the above cycle

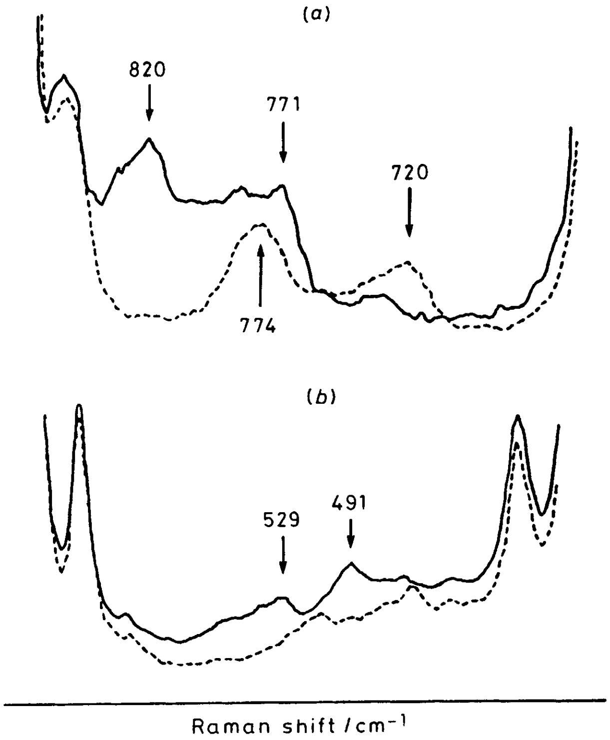

Figure 3. Resonance Raman spectra of dioxygen adducts obtained from $[Cu_2(tpmc)][PF_6]_2$ in a mixture of dimethylformamide and ethyl acetate at −90 °C: (*a*) ν(O–O) and (*b*) ν(Cu–O); ——, $^{16}O_2$; – – – –, $^{18}O_2$

Results and Discussion

Description of the Structure of $[Cu_2(tpmc)][CF_3SO_3]_2$.—The crystal consists of the dinuclear complex cation $[Cu_2(tpmc)]^{2+}$ and counter anion $CF_3SO_3^-$. A perspective view of $[Cu_2(tpmc)]^{2+}$ with the atom numbering scheme is shown in Figure 1. Selected interatomic bond distances and angles are listed in Table 3. The complex cation has a centre of symmetry midway between the two copper atoms. The co-ordination geometry about each copper atom is best described as a distorted trigonal plane formed by one nitrogen of the macrocycle and two pyridyl nitrogens of pendant groups. The bond distance between the ring nitrogen and the copper [2.212(5) Å] is significantly longer than the other Cu–N distances [1.923(5) and 1.980(5) Å]. The non-co-ordinated ring nitrogen is at the distance of 2.999(5) Å from the copper. The copper atom is displaced by 0.11 Å from the basal plane toward the other copper. The two co-ordination sites do not face each other, unlike in $[Cu_2X(tpmc)]^{3+}$ (X = F, Cl, OH, or NO_3),[12] and the Cu $\cdots$ Cu distance [6.739(2) Å] is significantly longer than those of tpmc copper(II) complexes.

The spherically symmetric d^{10} copper(I) ion adopts co-ordination numbers ranging from two to five. The complex in Figure 1 has trigonal planar geometry as usually found in the case of three-co-ordination. The ring adopts the *trans* IV form,[18] which has not been found in other tpmc complexes or any taec complexes obtained thus far except for $[Cu_2Br_2(tpmc)][ClO_4]_2$ reported by Alcock *et al.*[13] This result shows that tpmc is so flexible as to be adaptable to various co-ordination geometries. Such flexibility of a dinucleating ligand plays an important role in the reactivity of dioxygen with a dinuclear copper(I) complex, because the change in oxidation state ($Cu^I \longrightarrow Cu^{II}$) with oxygenation requires the ligand to change its co-ordination geometry from that favourable for Cu^I to that for Cu^{II}. The complexes (**1**) and (**2**) probably have the same structure as that of (**3**), since their counter anions have only poor donating ability like $CF_3SO_3^-$. The ^1H n.m.r. spectra of these complexes measured in CD_3CN at 25 °C are practically the same, indicating the same structure in solution.

All complexes (**1**)—(**3**) are air-sensitive. When exposed to the atmosphere the crystals changed from yellow to green over several hours, while their solutions are extremely air-sensitive. For example, when an acetone solution of the complexes was exposed to air at room temperature it immediately turned from yellow to dark green. When oxygen gas was introduced to the solution at temperatures below −60 °C a dark reddish brown colour was observed, suggesting the formation of a dioxygen complex.

The reactivity of the copper(I) complex toward dioxygen at low temperature is manifested by the electronic spectra shown in Figure 2. Spectrum (*a*) shows no absorption in the visible region. When the solution was exposed to dioxygen the spectrum changed to (*b*) which has two peaks at $\lambda_{max.}$ = 472 (ε = *ca.* 2 900) and 780 nm (*ca.* 900 dm^3 mol^{-1} cm^{-1}). When argon gas was bubbled for 5 min to remove dioxygen from the solution, the intensities of the absorptions were much decreased, as shown by spectrum (*c*), but not so as to coincide with the original spectrum (*a*). The very broad and weak band centred at *ca.* 670 nm may be assigned to irreversibly oxidized copper(II) species. When oxygen gas was injected into the solution again the two peaks observed in spectrum (*b*) appeared again in spectrum (*d*), but their intensities were about 50% of those of spectrum (*b*). These results indicate that $[Cu_2(tpmc)]^{2+}$ quasi-reversibly forms a dioxygen adduct at low temperature. U.v.–visible spectral evidence for such an oxygenation cycle can be obtained four to five times depending on the conditions. The strong absorption at 472 nm observed in the presence of dioxygen may be assigned to the O_2^{2-}–Cu^{II} ligand-to-metal charge-transfer (l.m.c.t) transition, and the other absorption in the visible region is most likely due to *d–d* transitions of the Cu^{II}.

The resonance Raman spectra of the dioxygen adduct are shown in Figure 3. When $^{16}O_2$ was used, two Raman peaks were observed at 820 and 771 cm^{-1} (O–O stretching), which shifted to lower frequencies (774 and 720 cm^{-1}) when $^{18}O_2$ was substituted for $^{16}O_2$. Hence, these bands can be assigned to O–O stretching vibrations of dioxygen adducts. The magnitudes of the shifts is in accord with calculated values (773 and 727 cm^{-1}) on the assumption of the above assignment. The results clearly indicate the formation of two species of dioxygen complexes. The bands at 529 and 491 cm^{-1} in the $^{16}O_2$ spectrum may be assigned to the Cu–O stretching vibrations of the two species, since these bands disappeared when $^{18}O_2$ was employed. However, the definite assignment of CuO bands in the $^{18}O_2$ spectrum is difficult because of the presence of several indistinct superposed bands in the region expected for these

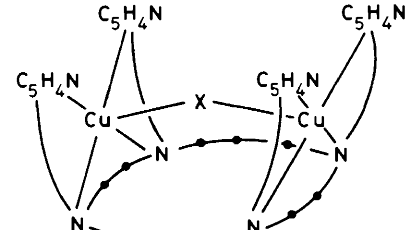

Figure 4. A skeletal structure of $[Cu_2X(tpmc)]^{3+}$

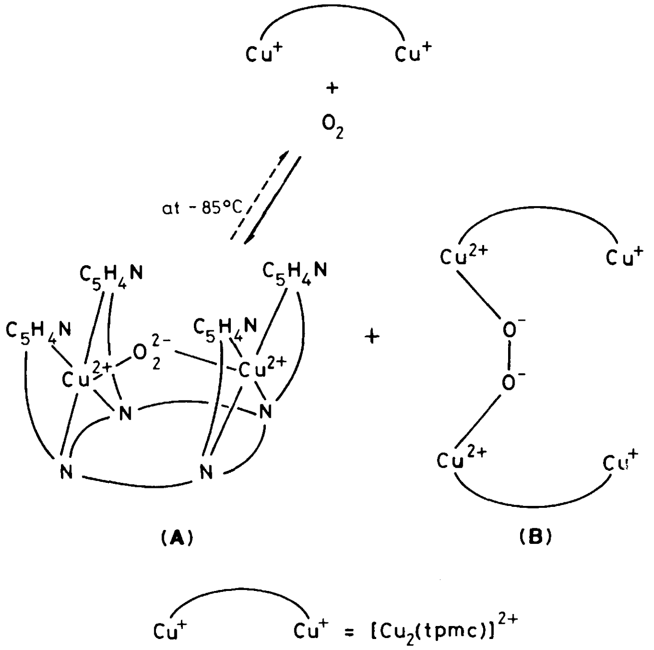

Figure 5. Reaction of $[Cu_2(tpmc)]^{2+}$ with dioxygen and plausible structure of its dioxygen adducts: (**A**) intramolecular peroxo-bridged structure; (**B**) one of the plausible intermolecular peroxo-bridged structures

bands. Judging from the O–O frequencies, the dioxygen in the complexes must be in the form of peroxide. There are several reports on reversible dioxygen binding by copper(I) complexes.[9,19–26] However, only in a few cases, the formation of a Cu^{II}–O_2^{2-}–Cu^{II} unit was detected by means of i.r.[21] and resonance Raman[19] spectroscopies and *X*-ray structure analysis.[26] To our knowledge, the present result is the first example which provides definite evidence for the formation of two species of dioxygen adducts.

Recently, our group prepared several dicopper(II) tpmc complexes with the general formula $[Cu_2X(tpmc)]Y_3$ (X = F, Cl, Br, I, OH, N_3, NO_2, or CH_3CO_2, Y = ClO_4; X = NO_3, Y = PF_6).[12] *X*-Ray analyses and i.r. spectra of these complexes indicated that their skeletal structures are essentially the same, as illustrated in Figure 4. It is noteworthy that four pyridylmethyl pendants and ring methylene groups form an aprotic cavity which can accommodate various anions. Such a cavity seems to be favourable for stabilizing a Cu^{II}–O_2^{2-}–Cu^{II} unit. Accordingly, one of the two dioxygen adducts detected in the solution may be assigned to a complex with the 'intramolecular peroxo-bridged structure,' corresponding to X = O_2^{2-} in Figure 4, where the peroxide anion is surrounded by bulky pyridyl groups which would interfere with further attack by the unreacted dicopper(I) unit. It is difficult to assign the bridging mode of the peroxide anion based on resonance Raman studies only. However, in view of the Cu^{II}–Cu^{II} distances (3.712—4.651 Å) in tpmc complexes with a bridging anion obtained thus far,[12] a μ-*OO′* linkage is most plausible.

As has been discussed for haemocyanin and its model compounds by many workers, the stoicheiometry Cu:O_2 = 2:1 seems to be favourable for the formation of reversible copper–dioxygen adducts.[9] In the present case, however, the dioxygen consumption measurements at −85 °C indicated that dioxygen corresponding to *ca.* 75% of $[Cu_2(tpmc)]^{2+}$ was absorbed, *i.e.* Cu:O_2 = 8:3. Since the measurements at −60 °C showed the same result, the possibility of unsaturation of the dioxygen binding may be small. If one assumes that no dioxygen-free copper is left in the solution, the intramolecular peroxo-bridged species should show a 2:1 stoicheiometry. Thus, in order to be compatible with the above dioxygen consumption, an 'intermolecular peroxo-bridged complex' as depicted in Figure 5 seems to be a plausible candidate for the alternative dioxygen adduct. Recently, Davis *et al.*[27] reported that such an intermolecular peroxo-bridged complex was formed by the reaction of dioxygen with the di-μ-chloro-dicopper(I) complex $[(teen)Cu(\mu\text{-}Cl)_2Cu(teen)]$ in dichloromethane at low temperature, where teen denotes *N,N,N′,N′*-tetraethylethylenediamine. The peroxo complex was stable at temperatures below −40 °C. However, O–O bond cleavage took place to give an oxo-bridged complex above −40 °C. Sorrell and Borovic[28] demonstrated that the dicopper(I) complex $[Cu_2(bpeac)]BF_4$ reacts with dioxygen at low temperature irreversibly, probably forming dimeric or oligomeric μ-oxo species in Cu:O_2 = 4:1 stoicheiometry, where Hbpeac denotes 2,6-bis{[2-(2′-pyrazolyl)ethyl]amino}-*p*-cresol. This apparently implies that two dinuclear units react with one dioxygen resulting in complete reduction of O_2 with O–O bond cleavage. An intermolecular peroxo-bridged complex is likely to exist as an intermediate in Sorrell and Borovic's case also, since their result resembles that of Davis *et al.* Thus, we propose that one of the dioxygen adducts detected in our system is an intramolecular peroxo-bridged complex with reversible dioxygen-binding ability, and the other is an intermolecular peroxo-bridged complex which undergoes concomitant irreversible degradation. Therefore, the total reversibility of dioxygen binding becomes low, being consistent with the low-temperature u.v.–visible spectra shown in Figure 2.

Spectrum (*b*) in Figure 2 shows the two bands at 472 and 780 nm assignable to l.m.c.t. and *d–d* transitions, respectively. There is no indication of splitting of these bands due to the presence of the two species presumed from the resonance Raman study. Probably, the bands of the two species overlap, and are not sharp enough to be observed as separate bands. The two bands observed may correspond to those at 570 (ε = 1 000) and 700 nm (ε = 200 dm^3 mol^{-1} cm^{-1}) of oxy-haemocyanin.[2,4,20b] Very recently, a few model complexes for oxy-haemocyanin were reported by Karlin and co-workers[19,20,26] and Kitajima *et al.*[29] The common structural feature except for $[(CuL)_2O_2]^{2+}$[L = tris(2-pyridylmethyl)amine][26] is that these complexes have N_3 donor sets and no endogenous bridging ligand. In the case of our model complex, the ligand tpmc may function as two sets of N_4 donors for Cu^{II}, because in all the dinuclear Cu^{II}–tpmc complexes obtained thus far tpmc functions as an octadentate ligand as illustrated in Figure 5. The dioxygen adducts generated from $[Cu_2(tpmc)][CF_3SO_3]_2$ in acetone gave e.s.r. signals at *g* = 2.220 (*A* = 176 cm^{-1}) and 2.059, which is common for mononuclear copper(II) with tetragonal co-ordination geometry. However, it is doubtful that the spectrum is that of the dioxygen adducts, because the peroxide ion is supposed to mediate magnetic coupling between two coppers so that an e.s.r. signal is not observable or at least becomes broad with no fine structure. The spectrum obtained here might be due to irreversibly oxidized mononuclear copper(II) species.

The above results lead to the conclusion that our model complex mimics the essential features of the structure and function of haemocyanins, *i.e.* reversible binding of dioxygen to form a peroxide bridge between two copper(II) ions, though the modelling is not perfect as regards the stability, reversibility, u.v.–visible and e.s.r. spectra.

When the acetone solution of dioxygen adducts generated from compound (**1**) or (**3**) at −80 °C was allowed to stand at room temperature, blue needles precipitated in a few hours. The compound was found to be bis(pyridine-2-carboxylato)-copper(II) based on the elemental analysis and comparison of the i.r. spectrum with that of an authentic sample (yield: *ca.* 15% per copper). The blue oxidation product obtained from compound (**2**) could not be characterized. In the reaction giving bis(pyridine-2-carboxylato)copper(II), the activated dioxygen (O_2^{2-}) attacks the pendant groups of the ligand to bring about C–N bond cleavage and oxygenation. Very recently, Karlin *et al.*[30] reported an example of C–N bond cleavage of a chelating ligand co-ordinated to coppers by the activated dioxygen, which is similar to the present case.

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