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Structural Characterization of Bis[dichloroaquo(pyridine *N*-oxide)copper(II)]

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The crystal and molecular structure of bis[dichloroaquo(pyridine *N*-oxide)copper(II)], $[Cu(pyO)(H_2O)Cl_2]_2$, has been determined from three-dimensional x-ray data collected by counter methods. The material crystallizes in the space group $P\bar{1}$ of the triclinic system with one dimeric formula unit in a cell of dimensions $a = 7.976$ (2), $b = 9.469$ (3), $c = 5.906$ (1) Å; $\alpha = 81.02$ (2), $\beta = 96.38$ (2), and $\gamma = 98.77$ (3)°. The observed and calculated densities are 1.88 and 1.899 g cm^{-3}, respectively. Least-squares refinement of the structure based on 2335 independent reflections has led to an R factor (on F) of 0.051. The structure consists of oxygen-bridged dimers with a Cu–Cu' separation of 3.272 (1) Å and a Cu–O–Cu' angle of 109.4 (1)°. The coordination about the copper atoms is tetragonal pyramidal with two chlorine and two oxygen atoms forming the base and a water oxygen atom at the apex. The observed magnetic and conductivity properties of the complex are readily understood in the light of the observed structure.

Introduction

A number of 1:1 and 2:1 complexes of pyridine *N*-oxide and copper halides have been prepared and characterized.[1-9] The abnormally low room-temperature magnetic moments of these complexes suggested a dimeric or polymeric structure with the bridging oxygen atoms of the pyridine *N*-oxide ligands providing a pathway for a superexchange mechanism. Subsequent structure determinations indicated that the 2:1 complexes $[Cu(pyO)_2Cl_2]_2$ and $[Cu(pyO)_2Br_2]_2$ are dimeric[8,9] with one pyridine *N*-oxide ligand acting as a bridge and the other as a monodentate ligand. In $[Cu(pyO)_2Cl_2]_2$ the coordination at the copper atom is tetragonal pyramidal[9] with the terminal pyridine *N*-oxide ligand in the apical position; in $[Cu(pyO)_2Br_2]_2$ the coordination at the copper atom is trigonal bipyramidal[8] with the terminal pyridine *N*-oxide ligand in an equatorial position.

In the 1:1 complexes $[Cu(pyO)Cl_2]_x$ and $[Cu(pyO)Br_2]_x$, the geometry around the copper is tetragonal pyramidal with the pyridine *N*-oxide ligand bridging two copper atoms, but the apical position is now occupied by a distant halide atom from an adjacent dimer, forming infinite chains of dimers.[6,7]

The complexes $[Cu(pyO)_2Cl_2]_2$, $[Cu(pyO)Cl_2]_x$, and $[Cu(pyO)Br_2]_x$, which have similar geometries at the copper centers, show[10] a correlation between the Cu–O–Cu bridging angle, ϕ, and the singlet–triplet splitting, $2J$, which is like that reported for hydroxo-bridged copper dimers, namely, that as ϕ increases $2J$ decreases.[11]

Kokoszka and coworkers have determined the magnetic[12,13] and conductometric[14] properties of the complex dichloroaquo(pyridine *N*-oxide)copper(II), $Cu(pyO)(H_2O)Cl_2$, which they proposed should be of the 2:1 structure type with a water molecule replacing the nonbridging pyridine *N*-oxide ligand. The large negative $2J$ value of -885 cm^{-1} is almost identical with the value[15] of -880 cm^{-1} reported for $[Cu(pyO)_2Cl_2]_2$, which suggests that the complexes may have very similar geometries. However, the unusually high conductivity[14] of the aquo complex suggests that there may be an additional pathway for magnetic exchange. In order to investigate this possibility and to further our understanding of the relationship between the structural and magnetic properties of copper(II) complexes, we have undertaken a complete three-dimensional analysis of the crystal structure of $[Cu(pyO)(H_2O)Cl_2]_2$.

Experimental Section

Bright green crystals of $[Cu(pyO)(H_2O)Cl_2]_2$ were prepared by the following method. Pyridine *N*-oxide was added dropwise to a concentrated solution of $CuCl_2{\cdot}2H_2O$ in approximately 50 ml of hot ethanol until a yellow-green precipitate formed. Water was then added dropwise until the precipitate redissolved. Crystals were obtained from the filtered solution after standing for a few days.

On the basis of precession and Weissenberg photographs, the crystals were assigned to the triclinic system. No systematic absences were observed, which implies that the space group is either $P1$ or $P\bar{1}$. The latter space group was chosen and subsequent refinement of the structure indicated that this choice is the correct one. The cell constants, obtained by the least-squares method of Busing and Levy,[16] are $a = 7.976$ (2), $b = 9.469$ (3), $c = 5.906$ (1) Å; $\alpha = 81.02$ (2), $\beta = 96.38$ (2), and $\gamma = 98.77$ (3)°. A density of 1.899 g cm^{-3}

Table I. Positional Parameters ($\times 10^4$)[a] for $[Cu(pyO)(H_2O)Cl_2]_2$

Atom	*x*	*y*	*z*
Cu	1480 (1)	876 (1)	−1596 (1)
Cl(1)	3482 (1)	−14 (1)	−3029 (1)
Cl(2)	1486 (1)	2896 (1)	−4078 (1)
OB	−674 (3)	1022 (2)	−276 (4)
OW	3198 (3)	1781 (3)	1465 (4)
N	−1546 (3)	2168 (2)	−719 (4)
C(1)	−2661 (4)	2268 (3)	−2566 (5)
C(2)	−3589 (5)	3393 (5)	−3003 (8)
C(3)	−3360 (6)	4413 (4)	−1576 (9)
C(4)	−2221 (6)	4292 (4)	306 (8)
C(5)	−1296 (4)	3130 (4)	768 (6)
HW(1)	312 (10)	181 (8)	232 (13)
HW(2)	422 (7)	148 (5)	152 (9)
H(1)	−282	156	−357
H(2)	−439	346	−432
H(3)	−398	522	−189
H(4)	−205	500	133
H(5)	−52	302	209

[a] Positional parameters for hydrogen are $\times 10^3$.

calculated for one dimeric unit in the cell agrees well with the value of 1.88 g cm^{-3} obtained by flotation in chloroform and iodomethane.

Diffraction data were collected using a Picker four-circle automatic diffractometer equipped with a graphite monochromator with the wavelength assumed as $\lambda(Mo\ K\alpha_1)$ 0.7093 Å. A parallelepiped-shaped crystal with faces (010), $(0\bar{1}0)$, (100), $(\bar{1}00)$, (001), and $(00\bar{1})$ was chosen for data collection. The separations between opposite pairs of faces were as follows: (010) and $(0\bar{1}0)$, 0.037 cm; (100) and $(\bar{1}00)$, 0.040 cm; (001) and $(00\bar{1})$, 0.129 cm. The crystal was mounted on a glass fiber roughly normal to the (001) planes and in this orientation intensity data were collected. The mosaicity of the crystal was examined by means of the narrow-source, open-counter, ω-scan technique; the ω scans were much wider than we would normally consider desirable, but since they were single, the crystal was judged to be acceptable. Twelve reflections, accurately centered through a narrow vertical slit at a takeoff angle of 1.0°, formed the basis for the least-squares refinement of cell parameters and orientation using the logic documented by Busing and Levy[16] for the PDP-8/L computer.

Intensity data were collected at a takeoff angle of 2.0°; at this angle the peak intensity for a typical strong reflection was about 85% of the maximum value as a function of takeoff angle. The counter aperture was 5.0 mm high by 5.0 mm wide and was positioned 32 cm from the crystal. The data were collected by the θ–2θ scan technique at a scan rate of 1°/min. To allow for the presence of both $K\alpha_1$ and $K\alpha_2$ radiations, the scan range was from 1.25° below the calculated $K\alpha_1$ peak position to 1.25° above the calculated $K\alpha_2$ peak position. Stationary-counter, stationary-crystal background counts of 20 sec were taken at each end of the scan.

A unique data set having $2\theta(Mo) < 60°$ was gathered, a total of 2586 intensities being recorded. The intensities of three standard reflections, measured after every 100 reflections, showed no systematic decline as a function of exposure time.

Data processing was carried out using the method of Corfield et al.[17] After correction for background, the intensities were assigned standard deviations according to the formula

$$\sigma(I) = (C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2)^{1/2}$$

and the value of p was selected as 0.045. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects and for absorption factors. The absorption coefficient for this compound for Mo $K\alpha$ radiation is 31.70 cm^{-1}, and for the crystal chosen the transmission coefficients ranged from 0.280 to 0.412. Of the 2586 data collected, 2340 were greater than 3 times their estimated standard deviations. Only these data were used in the structure analysis and refinement.[18]

Solution and Refinement of Structure

The position of the copper atom was determined from a three-dimensional Patterson function, and two cycles of least-squares refinement were run on this position. All least-squares refinements were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$, and the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. In calculations of F_c the atomic scattering factors for Cu, Cl, and N were from Cromer and Waber,[19] those for O and C from Ibers,[20] and those for H from Stewart, Davidson, and Simpson.[21] The effects of the anomalous dispersion of Cu and Cl were included in the calculations of F_c;[22] the values of $\Delta f'$ and $\Delta f''$ for Cu were taken from Cromer and Liberman[23] and those from Cl from Cromer.[24]

The remaining nonhydrogen atoms were located in subsequent difference Fourier maps. Isotropic least-squares refinement of these atoms led to values of the conventional agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ of 0.154 and 0.213, respectively. Two further cycles of least squares in which the atoms were assigned variable anisotropic thermal parameters reduced R_1 and R_2 to 0.053 and 0.075.

The two water hydrogen atoms were located in a subsequent difference Fourier map. Attempts to locate the pyridine *N*-oxide hydrogen atoms were unsuccessful so they were placed in calculated positions with C–H distances of 0.95 Å[25] and were not refined. Two cycles of least squares in which the water hydrogen atoms were assigned variable isotropic thermal parameters led to values of 0.050 and 0.069 for R_1 and R_2, respectively.

The value of R_2 showed some dependence on sin θ, so the weighting scheme was modified by dividing the weights w for reflections with $2\theta < 20°$ by 2.00 and those for reflections with $20° < 2\theta < 30°$ by 1.37. In every case in which we have used our graphite monochromator and Mo radiation a similar correction has been necessary.[26] The final values of F_o and F_c suggested that no correction for secondary extinction was necessary. The final values of R_1 and R_2 were 0.051 and 0.067. In the final cycle of least-squares refinement, no parameter underwent a shift in excess of 10% of its estimated standard deviation, which is taken as evidence that the refinement had converged.

The positional and thermal parameters derived from the final least-squares cycle are given in Tables I and II. A compilation of

Table II. Thermal Parameters (U_{ij} in $Å^2$) for $[Cu(pyO)(H_2O)Cl_2]_2$[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	345 (2)	357 (2)	227 (2)	87 (1)	117 (1)	12 (1)
Cl(1)	407 (3)	468 (4)	333 (3)	83 (3)	168 (2)	−87 (3)
Cl(2)	496 (4)	402 (3)	278 (3)	63 (3)	83 (2)	54 (2)
OB	420 (10)	356 (10)	476 (11)	177 (8)	242 (9)	112 (8)
OW	501 (12)	595 (14)	256 (10)	139 (10)	31 (9)	−73 (9)
N	323 (9)	288 (9)	295 (9)	47 (7)	66 (7)	−19 (7)
C(1)	476 (14)	430 (14)	342 (13)	48 (12)	−33 (11)	−76 (11)
C(2)	540 (18)	659 (23)	594 (22)	218 (17)	−55 (17)	78 (18)
C(3)	657 (21)	454 (18)	843 (30)	278 (16)	332 (21)	142 (18)
C(4)	850 (27)	423 (17)	760 (26)	−32 (17)	412 (23)	−285 (18)
C(5)	506 (13)	528 (17)	369 (14)	−29 (13)	49 (12)	−181 (13)
HW(1)	10 (3)					
HW(2)	6 (1)					
H(1)	9					
H(2)	9					
H(3)	9					
H(4)	9					
H(5)	9					

[a] Anisotropic thermal parameters are $\times 10^4$; isotropic thermal parameters, $\times 10^2$.

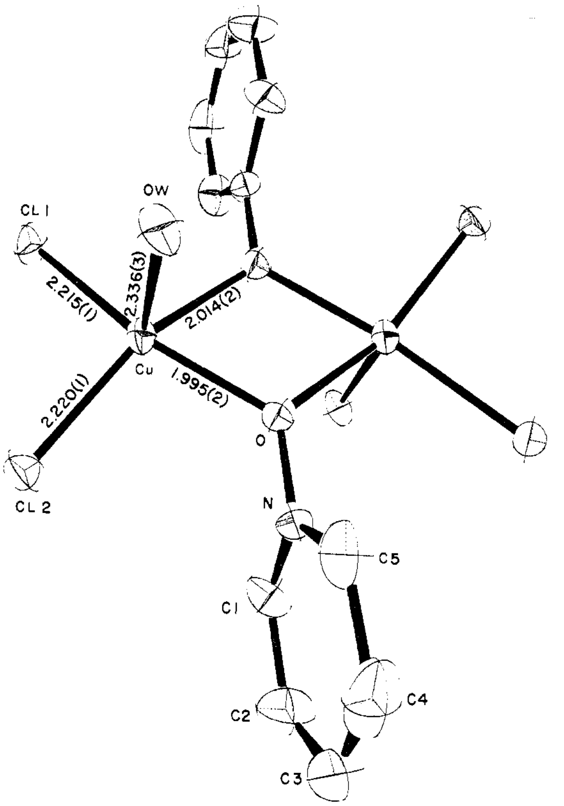

Figure 1. View of the $[Cu(pyO)(H_2O)Cl_2]_2$ dimeric unit. Hydrogen atoms have been omitted for clarity.

Table III. Structural and Magnetic Properties of Aromatic *N*-Oxide–Copper(II) Dimers

Complex	Cu–O–Cu, deg	Cu···Cu, Å	$2J$, cm^{-1}	Ref
$[Cu(pyO)Br_2]_2$[a]	110.1	3.244		7
$[Cu(pyO)_2Cl_2]_2$	110.0	3.306	−880	9, 15
$[Cu(pyO)Cl_2]_2$[a]	107.8	3.25	−720	4-6, 15
$[Cu(pyO)_2Br_2]_2$	107.7	3.375	−242	8, 15
$[Cu(4\text{-}PhpyO)Cl_2]_2 \cdot H_2O$	109.5	3.260	−1027	30, 31
$[Cu(pyO)(DMSO)Cl_2]_2$	109.2	3.342		32, 33
$[Cu(4\text{-}MepyO)_2Cl_2]_2$	109.0	3.348		34
$[Cu(pyO)(H_2O)Cl_2]_2$	109.4	3.272	−885	12, 13, this work

[a] In view of the weakness of the out-of-plane interaction in these polymeric complexes, their magnetic properties may be discussed in terms of a dimeric model.

Table IV. Internuclear Distances (Å) in $[Cu(pyO)(H_2O)Cl_2]_2$

Cu–Cu′	3.272 (1)	N–C(1)	1.330 (3)
Cu–Cl(1)	2.215 (1)	C(1)–C(2)	1.364 (5)
Cu–Cl(2)	2.220 (1)	C(2)–C(3)	1.358 (7)
Cu–OB	1.995 (2)	C(3)–C(4)	1.357 (7)
Cu–OB′	2.014 (2)	C(4)–C(5)	1.391 (6)
Cu–OW	2.336 (3)	C(5)–N	1.341 (4)
OB–N	1.352 (3)		

Table V. Internuclear Angles (deg) in $[Cu(pyO)(H_2O)Cl_2]_2$

Cu–OB–Cu′	109.4 (1)	Cu–OB–N	125.7 (2)
OB–Cu–OB′	70.6 (1)	Cu′–OB–N	124.7 (2)
OB–Cu–Cl(2)	96.0 (1)	N–C(1)–C(2)	119.6 (3)
Cl(2)–Cu–Cl(1)	97.33 (3)	C(1)–C(2)–C(3)	120.2 (3)
Cl(1)–Cu–OB′	93.3 (1)	C(2)–C(3)–C(4)	119.5 (3)
OW–Cu–OB	93.2 (1)	C(3)–C(4)–C(5)	120.2 (3)
OW–Cu–OB′	94.4 (1)	C(4)–C(5)–N	118.0 (3)
OW–Cu–Cl(1)	97.1 (1)	OB–N–C(1)	118.8 (2)
OW–Cu–Cl(2)	99.3 (1)	OB–N–C(5)	118.6 (2)

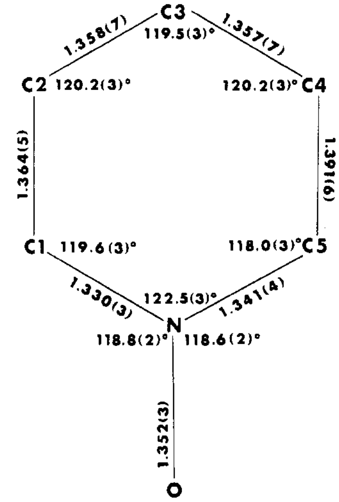

Figure 2. Bond distances and angles in the pyridine *N*-oxide ligand.

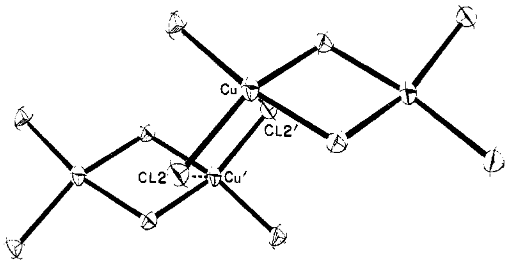

Figure 3. Possible out-of-plane Cu–Cl–Cu′–Cl′ interaction in $[Cu(pyO)(H_2O)Cl_2]_2$.

observed and calculated structure factors is available.[27] A final difference Fourier synthesis showed electron density of up to 1.1 e Å^{-3} in the vicinity of the copper atom but no geometrically meaningful features.

Discussion

The complex consists of dimeric $[Cu(pyO)(H_2O)Cl_2]_2$ units; the structure of the dimer is shown in Figure 1. The geometry around the copper atom is best described as tetragonal pyramidal with Cl(1), Cl(2), OB, and OB′ forming the base and OW occupying the apical position. The basal atoms are almost coplanar, with Cl(2) and OB′ lying only 0.02 and 0.03 Å, respectively, below the best least-squares plane through the four atoms and Cl(1) and OB lying only 0.02 and 0.03 Å, respectively, above it. The copper atom lies 0.23 Å above the plane, i.e., toward the apical OW atom; this is normal for tetragonal pyramidal[28] complexes. The Cu–OW distance of 2.336 (3) Å is quite short for axial coordination to copper.[29]

The bridging Cu–OB–Cu′–OB′ unit is strictly planar, there being a crystallographic inversion center in the middle of the dimer. A comparison of the bridging geometry and magnetic properties with those of other known pyridine *N*-oxide halide complexes is given in Table III. The Cu–O–Cu′ angle of 109.4 (1)° and the Cu–Cu′ separation of 3.272 (1) Å both fall in the ranges observed for these other complexes.[4-9,15,30-34] The bond lengths and angles observed for the dimer are given in Tables IV and V. The Cu–O bridges are roughly symmetric, and the Cu–O distances of 1.995 (2) and 2.014 (2) Å are similar to those in other complexes of this type.[4-9] The Cu–Cl distances of 2.215 (1) and 2.220 (1) Å are normal.[35,36]

The aromatic ring of the pyridine *N*-oxide ligand is almost exactly planar, the six atoms having a mean distance of 0.005 Å from the best least-squares plane through them; the greatest distance of any atom from the plane is 0.009 Å. The oxygen atom lies 0.02 Å from this plane. The bond lengths and angles, shown in Figure 2, are essentially the same as those found in

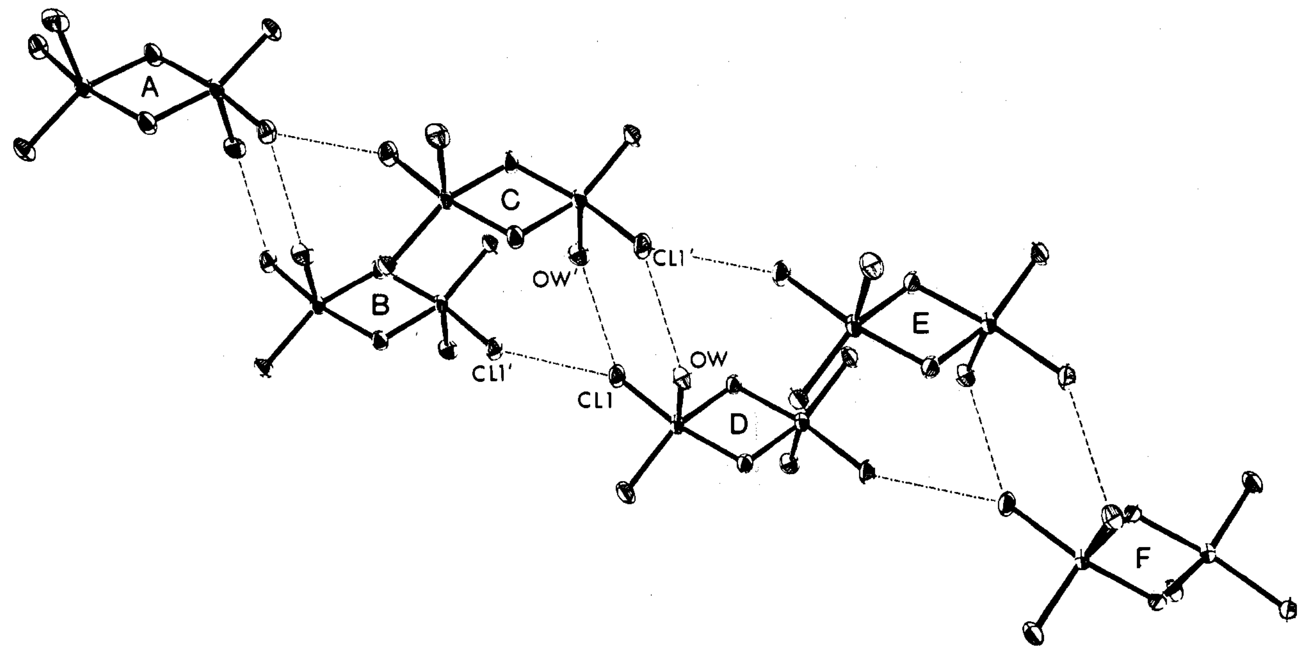

Figure 4. Intermolecular Cu–Cl· · ·Cl–Cu (· · ·) and OW–HW(2)· · ·Cl(1)′ (- - -) interactions. These contacts may provide the pathways which lead to the enhanced electrical conductivity of this material. Molecule E is related to the reference molecule (D) by translation along the crystallographic *c* axis. Molecule C is related to D by translation along the crystallographic *a* axis. Thus, the Cu–Cl· · ·Cl–Cu interactions (i.e., A–C–E and B–D–F) involve translations of −*a*, +*c*; the hydrogen-bonded interactions (i.e., A–B, C–D, E–F) involve translations of −*a*.

other (pyridine *N*-oxide)-bridged complexes[4–9] and in free pyridine *N*-oxide.[37] The dihedral angle between the normal to the bridging Cu–OB–Cu′–OB′ plane and the normal to the plane of the pyridine *N*-oxide ring is 79°, a value considerably greater than that of 65.5° for the corresponding[9] dichlorobis(pyridine *N*-oxide)copper(II). Morrow has suggested[9] that the orientation of the pyridine *N*-oxide ring with respect to the bridging plane is determined mainly by intramolecular contacts between the chlorine atoms and atoms in the pyridine *N*-oxide ring. In the present case these separations are as follows: N···Cl(1), 3.136 (2) Å; N···Cl(2), 3.223 (2) Å; Cl(1)···C(5), 3.355 (4) Å; Cl(2)···C(1), 3.461 (4) Å.

There are, as expected, two additional pathways for exchange which could account for the enhanced conductivity of the complex. The first, shown in Figure 3, is an out-of-plane Cu–Cl–Cu–Cl interaction which could be compared to those in $[Cu(tmen)Cl_2]_2$ (tmen = tetramethylethylenediamine),[35] $[Cu(pic)_2Cl_2]_2$ (pic = 2-methylpyridine),[38] and $[Cu(DMG)Cl_2]_2$ (DMG = dimethylglyoxime).[39] The out-of-plane Cu–Cl distance of 4.880 Å, however, is considerably greater than the corresponding distances of 3.147, 3.37, and 2.70 Å in the tmen, pic, and DMG complexes, respectively.[35,38,39] Also, the Cu–Cl–Cu bridging angle of 75.40 (3)° precludes much orbital overlap so we would expect the interaction, if any, to be very small.

The second pathway, and perhaps a more reasonable one, is an intermolecular Cl···Cl contact of 3.535 (2) Å where the Cu–Cl···Cl angle is 154.36 (5)°; this is shown in Figure 4. A similar interaction has been postulated[40] for $[Co(NH_3)_6][CuCl_5]$. The isostructural complex[41] $[Cr(NH_3)_6][CuCl_5]$ has a Cl···Cl contact of 4.11 Å and a Cu–Cl···Cl angle of 144.74°; in the cobalt complex there is an antiferromagnetic transition at 8 K attributed to coupling through the Cl ligands.[40] Hence, the interaction in the present case would be expected to be considerably greater than that in $[Cr(NH_3)_6][CuCl_5]$ since the Cl···Cl contact distance is much shorter in the former complex.

In addition to these two pathways there is a possible O–H···Cl hydrogen-bonding interaction which is also depicted in Figure 4. The Cl(1)–OW′ and Cl(1)′–OW separations of 3.315 Å are greater than the sum of the van der Waals radii of oxygen and chlorine as reported by Pauling[42] (3.20 Å) but similar to that of Bondi[43] (3.32 Å). However, the HW(2)···Cl(1)′ and HW(2)′···Cl(1) separations of 2.470 Å are less than the sum of the reported van der Waals radii of H and Cl, and Hamilton and Ibers[44] have noted that the existence of two such separations, each of which is less than this sum, is a sufficient condition for hydrogen bonding even if the O···Cl distance exceeds the van der Waals sum. These distances and the OW′–HW(2)′–Cl and OW–HW(2)–Cl′ angles of 156° are in the range observed for hydrogen bonds involving chlorine.[45]

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Supplementary Material Available: Listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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Formation and Decomposition of the Oxygen Complex of Ferroprotoporphyrin Bound to the Water-Soluble Polymer Ligand in Aqueous Solution

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The complexes formed between iron protoporphyrins (hemes) and partially quaternized poly(4-vinylpyridines) (QPVP's) were analyzed by spectrometry. The coordination number of the axial site of heme iron was determined to be near 1.0 so that the resulting major complexes were five-coordinate pyridine hemichromes or hemochromes. The equilibrium constants of ferri- and ferroprotoporphyrins were 2.60×10^2 and 2.77×10^4 *M*, respectively, and polymer-bound complexes were more stable than the corresponding monomeric analogues. The kinetics of reactions of the QPVP-bound ferroprotoporphyrins with molecular oxygen have been studied as a function of additives such as salt, surface-active agent, and polyelectrolyte. On the basis of the analytical results, it was confirmed that the resulting oxygen complex was a binuclear complex which may be formed successively via a mononuclear complex. The rate of decomposition of an oxygenated ferroprotoporphyrin decreased as a result of binding it to the polymeric ligand. The oxygen complex was consequently found to exist as a stable intermediate even in aqueous solution at room temperature.

Introduction

After Pfeiffer and Tsumaki[1] found that a cobalt–salcomin complex can bind molecular oxygen reversibly in crystalline form, many investigators have been interested in the studies on a reversible oxygen complex. Various types of oxygen complexes of iron, cobalt, and other metals were synthesized. Corwin and his co-workers[2] investigated the interaction between protein-free protoheme and dioxygen in solution and pointed out that the ferrous ion of heme is rapidly oxidized without formation of a detectable oxygen complex in water-containing solution. Calvin[3] reported the results of the reversible oxygen uptake of various cobalt–salcomin complexes in the solid state. Wang[4] and Hatano[5] synthesized a polymer-bound imidazole hemochrome as a model compound of hemoglobin and recognized the polymer effect on retardation of irreversible oxidation. Recently Collman,[6] Baldwin,[7] and Traylor[8] have succeeded in the synthesis of some interesting ferrous complexes which can bind dioxygen reversibly in solution at room temperature. Furthermore, Ibers,[9] Basolo,[10] and Walker[11] have studied the kinetics and thermodynamics of reversible oxygenation of cobalt(II) porphyrins in nonaqueous medium.

However, although many substantial studies have been developed on reversible oxygenation in solution, the study of the formation of an oxygen complex in an aqueous medium near room temperature has not satisfactorily been carried out yet. In this work, we try to stabilize an oxygen complex in a mixture of water and dimethylformamide at room temperature by binding ferroprotoporphyrin to the water-soluble polymeric ligand.

Experimental Section

Materials. Partially quaternized poly(4-vinylpyridine) was prepared according to the following method. Poly(4-vinylpyridine) (8.42 g) was dissolved in 150 ml of methanol and benzyl chloride (10.1 g) was dissolved in 50 ml of methanol. The polymer solution was charged into a four-necked round-bottom flask fitted with a dropping funnel and the benzyl chloride solution was dropped into the former solution from the dropping funnel. Stirred for 12 hr at 60°C, the solution was then condensed up to about 50 ml by evaporation and poured into 1000 ml of ethyl ether. The quaternized poly(4-vinylpyridine) obtained was dissolved in methanol and the solution was poured into ethyl ether. The precipitates were dried in vacuo. The degree of quaternization was determined to be 23.1% by the Volhard method.

Ferriprotoporphyrin chloride (chlorohemin) was extracted from blood by the Willstätter method.[12] Special grade commercial reagents of sodium hydrosulfite ($Na_2S_2O_4$) and sodium lauryl sulfate (NaLS) were used without purification. Distilled water was used through ion-exchange resin before use and the relative resistance of the water was above 10^6 Ω-cm.

Reduction and Oxygenation. Chlorohemin was reduced with $Na_2S_2O_4$ under the following conditions: [chlorohemin] = 2.0×10^{-5} *M*, [$Na_2S_2O_4$] = 2.0×10^{-3} *M*, [QPVP] = 2.0×10^{-2} *M* (a pyridine unit), in DMF–H_2O (1:4) at room temperature under a N_2 atmosphere. The reduction proceeded rapidly under the above conditions with a spectral change in the Soret band from 397 nm (due to a pyridine–hemin complex) to 422 nm (due to a pyridine–heme