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Notes

Contribution from the Department of Chemistry,
Kinki University, Kowakae, Higashi-Osaka 577, Japan

Synthesis of the Novel Infinite-Sheet and -Chain Copper(I) Complex Polymers $\{[Cu(C_4H_4N_2)_{3/2}(CH_3CN)](PF_6)\cdot 0.5C_3H_6O\}_\infty$ and $\{[Cu_2(C_8H_{12}N_2)_3](ClO_4)_2\}_\infty$ and Their X-ray Crystal Structures

Susumu Kitagawa,* Megumu Munakata, and Tadashi Tanimura

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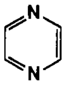
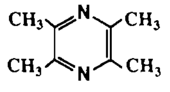
Crystalline polymers having copper complex units provide not only novel structures and geometries[1] but also interesting properties.[2,3] On the synthetic point of view, there is sparse literature, which has elucidated the relationship between the polymer and monomer structures, toward rational synthesis of copper complex polymers in the single crystal phase. This work concerns the discovery and the structural characterization of one- and two-dimensional copper(I) polymers, whose structures are controlled by the modification of linking ligands.

Pyrazine (pz) is well-known to act as a linking ligand, especially in low-dimensional compounds, and many infinite-chain copper(II) compounds have been synthesized.[4] Surprisingly, there are few infinite-chain copper(I) compounds. The objectives in this work are, thus, to build up new crystal structures of copper(I) polymer compounds containing pyrazines. The ligands used here are pyrazine and tetramethylpyrazine (Me_4pz).



pyrazine(pz)



tetramethylpyrazine(Me_4pz)

Experimental Section

All operations were carried out under an atmosphere of argon by using the standard Schlenk techniques. Solvents were dried and deoxygenated by using the standard methods prior to use.

Safety Notes. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of materials should be prepared, and these should be handled with great caution.

Preparation of $\{[Cu(pz)_{3/2}(CH_3CN)](PF_6)\cdot 0.5C_3H_6O\}_\infty$ (1). An acetone (5 mL) solution of pz (0.15 mmol) was added to $[Cu(CH_3CN)_4]PF_6$ (0.05 mmol), and the mixture was stirred for ca. 2 min. After filtration, the yellow filtrate was sealed in a glass tube, which was kept at 5 °C for 10 days. Orange single crystals of **1** were obtained (yield 14.7%).[5] The crystals are thermally unstable, and decomposition occurs when the crystals are taken from the mother liquor.

Table I. Crystallographic Data for $\{[Cu(pyrazine)_{3/2}(CH_3CN)](PF_6)\cdot 0.5C_3H_6O\}_\infty$ (**1**) and $\{[Cu_2(tetramethylpyrazine)_3](ClO_4)_2\}_\infty$ (**2**)

formula	$CuPF_6O_{0.5}N_4C_{9.5}H_{12}$ (**1**)	$Cu_2Cl_2O_8N_6C_{24}H_{36}$ (**2**)
fw	398.74	734.58
a, Å	9.048 (1)	15.641 (8)
b, Å	11.705 (6)	16.009 (7)
c, Å	8.543 (4)	12.108 (9)
α, deg	112.36 (4)	
β, deg	99.66 (6)	
γ, deg	65.04 (5)	
V, Å^3	759 (1)	3032 (3)
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$Pbcn$
Z	2	4
ρ_{calc}, g/cm^3	1.745	1.609
μ(Cu Kα), cm^{-1}	37.04	38.42
λ, Å	1.541 78	1.541 78
temp, °C	23	23
R^a	0.059	0.065
$R_w{}^a$	0.077	0.079

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2}$.

Table II. Fractional Atomic Coordinates for Complex **1**[a]

atom	x/a	y/b	z/c	B_{eq},[b] Å^2
Cu(1)	0.1018 (1)	0.16267 (8)	0.4018 (1)	4.75 (6)
P(1)	0.3529 (3)	0.2813 (2)	0.9973 (2)	6.1 (1)
F(1)	0.357 (1)	0.297 (1)	0.829 (1)	18 (1)
F(2)	0.336 (1)	0.248 (1)	1.147 (1)	14.1 (7)
F(3)*	0.193 (2)	0.266 (3)	0.927 (2)	18 (2)
F(4)*	0.273 (2)	0.423 (1)	1.125 (2)	16 (1)
F(5)*	0.513 (2)	0.306 (3)	1.062 (2)	17 (2)
F(6)*	0.463 (3)	0.142 (2)	0.902 (2)	21 (1)
F(7)*	0.177 (3)	0.406 (2)	1.012 (3)	8 (1)
F(8)*	0.393 (6)	0.396 (2)	1.031 (6)	14 (3)
F(9)*	0.511 (4)	0.202 (7)	1.013 (7)	19 (4)
F(10)*	0.257 (7)	0.200 (5)	0.964 (5)	14 (4)
O(1)*	0.632 (2)	0.310 (2)	0.444 (2)	11 (1)
N(1)	0.3380 (6)	0.0640 (4)	0.4539 (5)	3.8 (3)
N(2)	0.0387 (6)	0.0707 (4)	0.1619 (6)	3.9 (3)
N(3)	0.0466 (6)	0.3629 (4)	0.4593 (6)	3.8 (2)
N(4)	−0.0366 (8)	0.1761 (7)	0.5780 (8)	6.2 (4)
C(1)	0.3829 (7)	−0.0285 (6)	0.5287 (8)	4.5 (3)
C(2)	0.4586 (8)	0.0888 (6)	0.4264 (8)	4.6 (4)
C(3)	−0.1027 (7)	0.0572 (6)	0.1258 (8)	4.5 (3)
C(4)	0.1415 (7)	0.0133 (6)	0.0345 (8)	4.3 (3)
C(5)	0.0349 (8)	0.4431 (6)	0.6154 (7)	4.3 (3)
C(6)	0.0127 (8)	0.4184 (6)	0.3413 (7)	4.4 (3)
C(7)	−0.111 (1)	0.2178 (7)	0.693 (1)	5.2 (4)
C(8)	−0.207 (1)	0.2746 (8)	0.842 (1)	7.7 (6)
C(9)*	0.550 (2)	0.424 (2)	0.470 (2)	6.5 (9)
C(10)	0.599 (1)	0.507 (1)	0.418 (2)	11 (1)

[a] The $PF_6{}^-$ anion and the acetone are disordered. Starred atoms were refined at the site occupancies as follows: 0.75 for F(3), F(4), F(5), and F(6), while 0.25 for F(7), F(8), F(9), and F(10). In the case of acetone, O(1) and C(9) have a half-occupancy. Their relationship is mentioned in the text. All other atoms without stars are refined at full occupancies. [b] B values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Preparation of $\{[Cu_2(Me_4pz)_3](ClO_4)_2\}_\infty$ (2). An acetone (3 mL) solution of Me_4pz (0.75 mmol) was added to an acetone (2 mL) solution

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(5) A similar complex is also obtained from $Cu(ClO_4)_2\cdot 6H_2O$/copper wire/ethylene. The orange microcrystals are not suitable for X-ray diffraction measurements.

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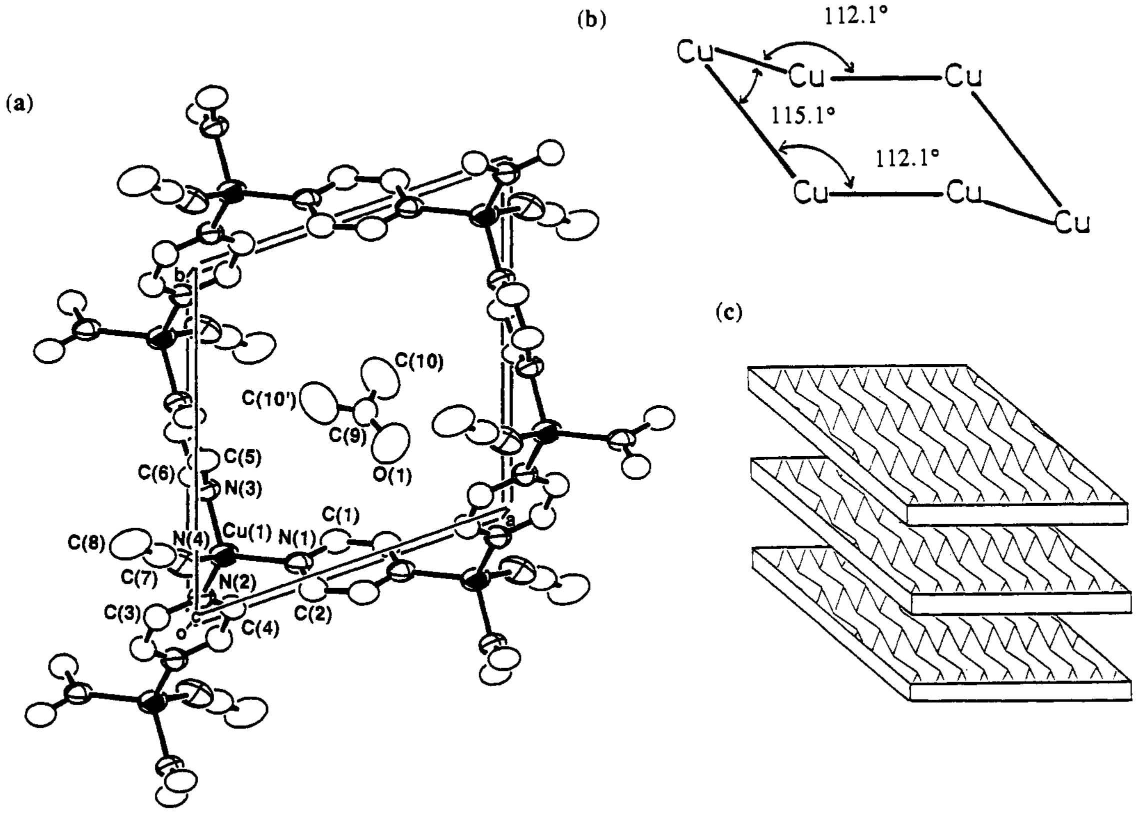

Figure 1. (a) Crystal structure of **1** projected down the *c* axis. Acetone is disordered on a crystallographic inversion center and one of the two models is depicted in the cavity. (b) Hexanuclear copper unit forming a chair-like structure. (c) Schematic array of infinite sheets.

Table III. Fractional Atomic Coordinates for Complex **2**

atom	x/a	y/b	z/c	B_{eq},[a] Å^2
Cu(1)	1	0.1034 (1)	3/4	2.94 (8)
Cu(2)	1	0.5211 (1)	3/4	5.0 (1)
Cl(1)	0.3356 (2)	0.1182 (2)	0.5178 (3)	5.8 (2)
O(1)	0.3160 (6)	0.1250 (7)	0.6308 (8)	9.5 (7)
O(2)	0.2746 (7)	0.0600 (7)	0.4692 (9)	10.5 (7)
O(3)	0.4158 (6)	0.083 (1)	0.5044 (9)	13 (1)
O(4)	0.325 (1)	0.1925 (6)	0.464 (1)	12.6 (9)
N(1)	1	0.2306 (6)	3/4	2.5 (4)
N(2)	1	0.4025 (6)	3/4	3.6 (5)
N(3)	0.9984 (5)	0.0410 (4)	0.6013 (6)	2.7 (3)
N(4)	1	0.6396 (6)	3/4	3.5 (5)
N(5)	1	0.8103 (7)	3/4	4.2 (5)
C(1)	1.0710 (5)	0.2736 (5)	0.7225 (6)	2.5 (4)
C(2)	1.0711 (6)	0.3596 (5)	0.7247 (7)	3.0 (4)
C(3)	1.1505 (6)	0.2257 (6)	0.6941 (8)	3.5 (5)
C(4)	1.1501 (7)	0.4097 (6)	0.701 (1)	4.3 (5)
C(5)	0.9349 (6)	0.0521 (5)	0.5273 (8)	2.9 (4)
C(6)	1.0631 (5)	−0.0102 (5)	0.5758 (7)	2.5 (4)
C(7)	0.8628 (7)	0.1084 (7)	0.556 (1)	4.9 (6)
C(8)	1.1327 (6)	−0.0232 (6)	0.6586 (8)	3.6 (5)
C(9)	1.0506 (6)	0.6819 (6)	0.8196 (8)	3.3 (5)
C(10)	1.0490 (6)	0.7677 (6)	0.8206 (9)	3.9 (5)
C(11)	1.1065 (7)	0.6322 (7)	0.894 (1)	4.8 (6)
C(12)	1.1012 (8)	0.8183 (7)	0.902 (1)	5.9 (7)

[a] B values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

containing a reduced intermediate from $Cu(ClO_4)_2{\cdot}6H_2O$ (0.12 mmol)/copper wire,[6] and the mixture was stirred for 5 min under ethylene to give the colorless solution. The ethylene atmosphere was replaced with an argon atmosphere. The reaction solution was filtered, and the resultant colorless filtrate was sealed in a glass tube. Within 2 days stable colorless crystals of **2** were obtained at 25 °C (yield 46.9%).

Table IV. Selected Bond Distances (Å) and Angles (deg) for **1** and **2**

		Compound **1**			
Cu(1)–N(1)	2.022 (5)	Cu(1)–N(2)	2.033 (5)	Cu(1)–N(3)	2.050 (5)
Cu(1)–N(4)	2.035 (7)	N(4)–C(7)	1.110 (9)	C(7)–C(8)	1.44 (1)
C(9)–C(10′)	1.52 (2)	C(9)–O(1)	1.17 (2)		
N(1)–Cu(1)–N(2)	111.7 (2)	N(1)–Cu(1)–N(3)	111.5 (2)		
N(1)–Cu(1)–N(4)	107.7 (2)	N(2)–Cu(1)–N(3)	113.7 (2)		
N(2)–Cu(1)–N(4)	112.1 (2)	N(3)–Cu(1)–N(4)	99.4 (2)		
N(4)–C(7)–C(8)	178.8 (7)	Cu(1)–N(4)–C(7)	160.5 (6)		
O(1)–C(9)–C(10′)	120 (2)	C(10)–C(9)–C(10′)	118 (1)		
		Compound **2**			
Cu(1)–N(1)	2.04 (1)	Cu(1)–N(3)	2.059 (7)		
Cu(2)–N(2)	1.90 (1)	Cu(2)–N(4)	1.90 (1)		
N(1)–Cu(1)–N(3)	119.0 (2)	N(3)–Cu(1)–N(3′)	122.0 (4)		
N(2)–Cu(2)–N(4)	180				

X-ray Data Collection, Structure Solution, and Refinement. A Rigaku AFC6S diffractometer was used for the measurement of the data for **1** and **2**. In the case of **1**, the 2199 unique data observed ($I > 3\sigma(I)$) were collected with the use of the $\omega/2\theta$ scanning technique and graphite-monochromated Cu Kα radiation. The pertinent data are summarized in Table I. The structure was solved by MITHRIL.[7] After anisotropic least-squares refinement for the copper/pyrazine/PF_6^- moiety without hydrogen atoms, significant peaks in the difference electron density maps were observed both around the PF_6^- anion and in the cavity of each hexanuclear Cu core, which could be occupied by the F atoms of the PF_6^- and an acetone, respectively. (1) The PF_6^- anion is disordered with the site occupancies of 3:1 for equatorial F(2), F(3), F(4), and F(5) vs F(6), F(7), F(8), and F(9), whereas those for the two axial F(1) and F(2) are 1. The minor model is the anion which rotates ca. 55° from another major model around the F(1)–P(1)–F(2) axis. (2) The acetone is disordered about a crystallographic inversion center. The atoms O(1) and C(9) were refined at half-occupancies, and the atom C(10) was refined at full occupancy. The significance of these schemes is verified by stable refinement. Finally, all hydrogen atoms were located in the difference Fourier map, but their parameters were not refined. Residuals at convergence $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.059$ and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2} = 0.077$.

In the case of **2**, the 1333 unique data observed ($I > 3\sigma(I)$) were collected with the use of the $\omega/2\theta$ scanning technique and graphite-monochromated Cu Kα radiation. The structure was solved by MITHRIL[7]

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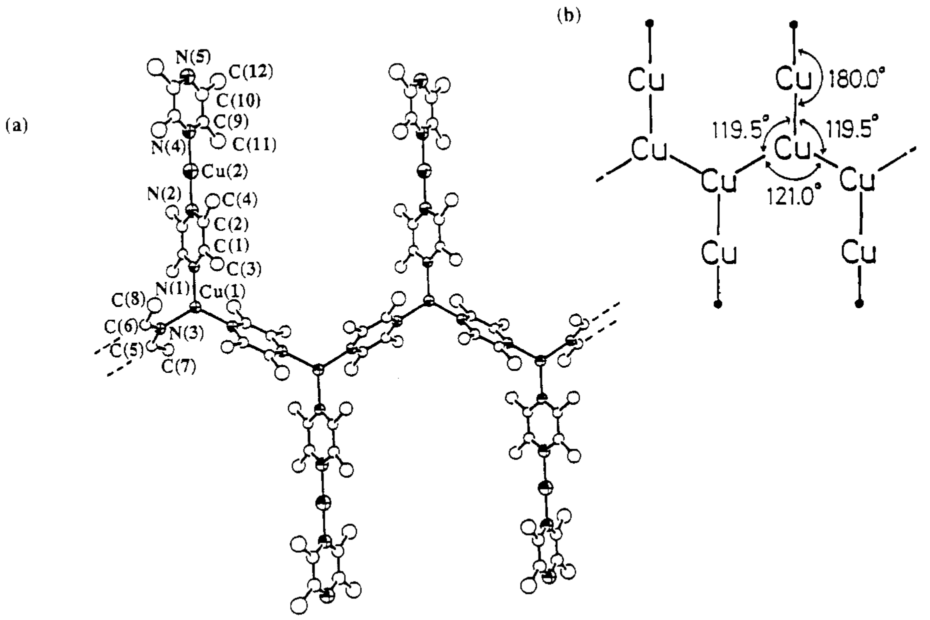

Figure 2. (a) Portion of an infinite chain structure of **2**. (b) Geometries around the copper atoms.

and refined by full-matrix least squares, anisotropically for all non-hydrogen atoms. All the hydrogen atoms were located in a difference Fourier map and introduced as fixed contributors in the final stage of the refinement. The final positional parameters are given in Table III.

Results and Discussion

Figure 1 shows a portion of the cationic infinite two-dimensional sheet of **1** spread out along the *ab* plane (a) and a schematic drawing of the hexanuclear copper unit forming a chair-type cyclohexane-like structure (b). The center of pz sits on the crystallographic inversion center. Bond distances for all Cu–N (2.022 (5)–2.050 (5) Å) are close to those of a typical four-coordinate pyridine complex, $[Cu(py)_4]^+$ (2.05 Å),[8] while the geometry around the copper atom is a distorted tetrahedron, which arises from the unusual coordination of CH_3CN: the Cu(1)–N(4) bond inclines at ca. 10° toward the Cu(1)–N(3) bond (N(3)–Cu(1)–N(4) = 99.4 (2)°). Moreover, CH_3CN is not linearly coordinated to the copper atom with a bent angle of 160.5 (6)°, dissimilar to $[Cu(CH_3CN)_4]^+$ ($174°_{av}$).[9] As observed in $[Cu_2(\mu\text{-dppm})_2(CH_3CN)_4](ClO_4)_2$,[10] where both the linear (173.1 (9)°) and bent (157.4 (9)°) type coordinations of CH_3CN have been found, the Cu–N bond distance of the bent type (2.161 (13) Å) is much longer than another linear type (1.999 (1) Å), whereas complex **1** exhibits a normal bond distance (Cu(1)–N(4) = 2.035 (7) Å) in spite of the bent coordination. These structural characteristics make this copper complex polymer quite unique.

The Cu–Cu distance of the two copper atoms linked by a pz is ca. 6.8 Å, and the mutually-confronted two pyrazines on the sides of the hexagon are parallel to each other, providing a large cavity of hexanuclear copper atoms. Interestingly, as in Figure 1a an acetone molecule is included in each cavity, while the counteranions, PF_6^-, are placed above the sides of cavity. This acetone is not firmly fixed but weakly included in the cavity. This is supported by phenomena that the crystals decompose by losing acetone when taken from mother liquor. The cationic and anionic layers are alternatively arranged. The distance between the nearest-neighbor cationic sheets, interrupted by the PF_6^- anions, is more than 8 Å.

The ligand Me_4pz gives a marked contrast in the crystal structure. Complex **2** is a cationic linear chain polymer (Figure 2), just like a zigzag chain running parallel to the *c* axis. The line of Cu(1)–N(1)–N(2)–Cu(2)–N(4)–N(5) coincides with the crystallographic 2-fold axis. Noteworthy are the different geometries of the two copper atoms: the three-coordinate Cu(1) moiety is similar to the trigonal-planar $[Cu(2\text{-Mepy})_3]^+$,[11] and the two-coordinate Cu(2) shows a perfect linear structure, where Cu(2)–N_{av} = 1.91 Å is close to 1.936 (5) Å of $[Cu(2,6\text{-}Me_2py)_2]^+$.[12] The Cu(1) type forms a linear chain framework, while the Cu(2) type is attached to it just like a pendant, unable to continue to form a cyclohexane framework of copper atoms due to the bulky Me_4pz ligands. All the geometrical constants of **2** produce no significant strains in the lattice, which result in the thermally stable crystals.

Compound **1** gives a band at ca. 400 nm,[13] which is assigned to the Cu $d\pi \rightarrow N\ \pi$ band. The assignment is supported by the fact that copper(I) complexes with pyridines usually have metal-to-ligand charge-transfer bands in the region 300–400 nm.[13] Interestingly, both types of the copper(I) moieties in **2** afford no bands in the visible region and result in colorless crystals.

Concerning the synthesis of the infinite polymer structures with pyrazine, the following are summarized. Firstly, two-dimensional layers are successfully constituted with four-coordinate $Cu(pz)_3L$ units, the fourth position being occupied by the smaller ligand L such as acetonitrile. Secondly, the inclusion of acetone molecules is realized in large hexagonal cavities located in the layers. Lastly, the methyl groups on the substitutable positions of pyrazine give rise to steric constraints, which occur more frequently in closely packed systems. In the case of Me_4pz, the methyl groups prevent the formation of a hexagonal ring unit and give a linear link as a less steric form. Consequently, controlling spatial factors is an important key in building infinite polymeric structures, and the modification of linking ligands by methyl groups is useful for synthesis of crystalline copper(I) polymers.

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Registry No. 1, 139758-81-9; **2**, 139758-83-1.

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Supplementary Material Available: Tables listing crystal data, positional parameters, anisotropic thermal parameters, and complete distances and angles for $\{[\text{Cu}(\text{C}_4\text{H}_4\text{N}_2)_{3/2}(\text{CH}_3\text{CN})](\text{PF}_6)\cdot 0.5\text{C}_3\text{H}_6\text{O}\}_\infty$ and $\{[\text{Cu}_2(\text{C}_8\text{H}_{12}\text{N}_2)_3](\text{ClO}_4)_2\}_\infty$ and a textual presentation of structure solution and refinement details and a molecular figure for $\{[\text{Cu}(\text{C}_4\text{H}_4\text{N}_2)_{3/2}(\text{CH}_3\text{CN})](\text{PF}_6)\cdot 0.5\text{C}_3\text{H}_6\text{O}\}_\infty$ (10 pages); tables of calculated and observed structure factors (11 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Western Ontario,
London, Ontario, Canada N6A 5B7

Ground-State and Optical Spectrum of Metallophthalocyanine Radical Anions from Low-Temperature Magnetic Circular Dichroism Spectroscopy

John Mack, Scott Kirkby, Edward A. Ough,
and Martin J. Stillman*

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There is considerable current interest in the spectral properties of the anion-radical species of metal porphyrin and phthalocyanine (Pc) complexes.[1-12] Metal porphyrins and phthalocyanines are aromatic, 18-π-electron systems. Intense bands near 350 and 670 nm in the absorption spectrum of neutral phthalocyanines can be explained in terms of three allowed, x/y-polarized π–π^* transitions within the LCAO model developed by Gouterman.[13] The optical data for neutral and ring-oxidized radical-cation species are well-known. We have previously used Gouterman's model as the basis for band assignments of the absorption spectra of the ring-oxidized cation-radical complexes $[\text{MgPc}(-1)]^{\bullet+}$, $[\text{ZnPc}(-1)]^{\bullet+}$ and $[\text{Co}^{\text{III}}\text{OEP}(-1)]^{\bullet 2+}$,[14-19] based on assignments of the absorption and MCD spectra of neutral MPc(−2) species.[19a] However, despite many experimental studies,[20-24] the optical spectra of the ring-reduced, anion-radical species are not well established, and band assignments for these optical spectra have not been described previously. An important first step in the assignment of the bands observed for anion-radical complexes is to establish the degeneracy of the ground and excited states of the ring-reduced molecule.[13]

Magnetic circular dichroism (MCD) spectra have previously provided essential information about ground and excited states for both neutral and ring-oxidized cation-radical complexes of metallophthalocyanines and metalloporphyrins.[14-19] In this paper, we report the first MCD spectrum obtained for a species generated electrochemically in situ in the sample bore of a superconducting magnet and the first low-temperature MCD spectrum for an anion radical of either a phthalocyanine or porphyrin complex. Analysis of these MCD spectral data enables us to extend our earlier assignment of MgPc(−2) and its radical cation to the radical anion. The MCD data provide direct evidence that the ground state of $[\text{Mg}^{\text{II}}\text{Pc}(-3)]^{\bullet-}$ is subject to a Jahn–Teller distortion and is hence orbitally nondegenerate.

The specificity of the MCD technique arises from three highly characteristic spectral features, the $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$ terms.[25] The derivative-shaped $\mathcal{A}$ term is temperature independent and identifies degenerate excited states, while the Gaussian-shaped $\mathcal{C}$ term is highly temperature dependent and identifies an orbitally degenerate ground state.[25] Although not normally of as much utility in the assignment of spectral data of symmetric molecules, the signs of $\mathcal{B}$ terms that arise from mixing between closely related states with x or y polarization can provide definitive data on the structure of the excited states.[26] In this paper, we use the signs of a series of $\mathcal{B}$ terms that arise from coupled pairs of degenerate states split by the Jahn–Teller effect to characterize the spectrum of the phthalocyanine π anion radical.

MgPc provides a suitable starting point for a general study of metallophthalocyanine anion radicals because the complex has D_{4h} symmetry and redox reactions involve only the ligating ring. Several sets of spectral data have previously been reported for $[\text{MgPc}(-3)]^{\bullet-}$ (the anion radical of MgPc), including absorption band maxima and EPR signals for chemically and electrochemically generated species by Clack and Yandle[20] and preliminary absorption and MCD spectra for the chemically reduced $[\text{MgPc}]^{n-}$ (n = 1–4) species by Lindler et al.[21] EPR studies on $[\text{MgPc}(-3)]^{\bullet-}$ at 77 K indicate that the species is monomeric,[21,22-24] unlike the diamagnetic dimer of radical cations that forms at low temperatures.[17]

Experimental Section

Reduction of the ring was carried out in thin-layer spectroelectrochemical cells with designs based on those described by Lever.[27-28] MgPc was synthesized as previously described with a variety of axial ligands.[29-31] Although axial ligation appears to have an effect on the stability of the anion in solution, no major spectral differences have been seen. The initial reduction of [MgPc(−2)] results in a blue shift of the 670-nm band, which is probably caused by the loss of axial ligands.[19b] Initial phthalocyanine concentrations were typically in the 10^{-4} M range. Spectrophotometric grade dimethylformamide (DMF) and dimethylacetamide (DMA) were used as solvents, and tetrapropylammonium perchlorate (TPAP) was used as the supporting electrolyte. The reduction was carried out under the control of a Princeton Applied Research 273 potentiostat/galvanostat. Fixed currents, typically in the 0.1–1.0-μA range, were applied across the spectroelectrochemical cell. $[\text{MgPc}(-3)]^{\bullet-}$ can be formed reversibly with isosbestic spectral changes in the absorption spectrum.[19b] Solutions for low-temperature MCD and absorption

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