Table IV. ^{113}Cd NMR of Cd(bpy)$_2$X$_2$ Species (0 ppm[a] = 0.1 M Cd(ClO$_4$)$_2$ in D$_2$O)

compd	solution	CP/MAS solid (Hw, ppm)[b]
1. Cd(bpy)$_2$-(NO$_3$)$_2$·$^1/_2$H$_2$O	+66 (4) (DMF)[c] +172 (5) (D$_2$O)	+123 (13), 51 (12)
2. Cd(bpy)$_2$Cl$_2$	*d*	+250 (46)
3. Cd(bpy)$_2$Br$_2$	*d*	+185 (28)
4. Cd(bpy)$_2$I$_2$	*d*	*d*
5. Cd(bpy)$_2$(NCS)$_2$	+122 (5) (Me$_2$SO)[c]	+216 (24)

[a] Positive values represent greater deshielding than the standard. [b] Hw = half-width of resonance at half peak height. [c] Concentration range 1. = 56–125 mM with 4 ppm variation 5. = 77–118 mM with 5 ppm variation. [d] No ^{113}Cd NMR signal observed, due to solubility problems or simply not observable in solid state experiments.

50 ppm shift from the +123 ppm signal is due to the second water molecule in the coordination polyhedron replacing the oxygen of nitrate in the NO$_3$H$_2$OCdN$_4$ONO$_2$ coordination of the crystallographic Cd(1). The second signal in the CP/MAAs ^{113}Cd NMR at +51 ppm is then due to the CdN$_4$O$_2$ [Cd(2)] bound to the pyridyl nitrogen and the oxygen of the nitrate groups. This is also consistent with our observations[54] that oxygen atoms of nitrate groups coordinated to Cd tend to make the ^{113}Cd nucleus more shielded. It is also in line with our postulate that poorer electron donors (certainly nitrate oxygen is one) will shield the ^{113}Cd nucleus relative to better donors. This is, in this case, nitrate oxygen compared to water oxygen.

The relative positions of the ^{113}Cd NMR isotropic chemical shifts in Table IV can be understood in these same terms. The model we propose in order to understand the isotropic ^{113}Cd chemical shift is the following. The most shielded ^{113}Cd nucleus is the gaseous bare Cd^{2+} ion with an electronic configuration Kr(4d)^{10}(5s)^0. Any chemical bonding will involve mixing of these orbitals with ligand orbitals, whether it be d or inner shell sp, and will only deshield the ^{113}Cd nucleus. Therefore, it is not unreasonable to view the chemical shifts in Table IV in terms of a CdN$_4$X$_2$ octahedron; the best classical chemical bond (Cd–X) is that of N$_4$Cd–Cl$_2$, followed by N$_4$Cd–(NCS)$_2$, N$_4$Cd–Br$_2$, N$_4$Cd–(OH$_2$)$_2$, N$_4$Cd(OH$_2$)-(ONO$_2$), and N$_4$Cd–(ONO$_2$) with chemical shifts of +250, +216, +185, +172, +123, and +51 ppm, respectively.

It is unfortunate that the ^{113}Cd NMR of the Cd(bpy)$_2$I$_2$ was not observed either in solution or in the solid state. We do not believe the Cd(bpy)(NCS)$_2$ ^{113}Cd NMR spectrum observed in Me$_2$SO is meaningful relative to the above model because of the solution properties of Me$_2$SO. It is interesting to note from a ^{113}Cd NMR utilization point of view that the unexpected isocyanate structure is clearly established by the ^{113}Cd NMR CP/MAS solid-state results.

Acknowledgment. We wish to thank the PHS for research support via Grant GM-27721 and the NSF-supported regional NMR centers at the University of South Carolina (Grant CHE 78-18723) and Colorado State University (Grant CHE 78-18581) for their help, discussions, and assistance with the ^{113}Cd NMR data.

Registry No. A, 81521-32-6; B, 88801-78-9; Cd(bpy)$_2$Br$_2$, 77130-38-2; Cd(bpy)$_2$I$_2$, 56270-76-9; Cd(bpy)$_2$Cl$_2$, 77139-24-3; Cd(bpy)$_2$(OH$_2$)$_2$, 88801-79-0; ^{113}Cd, 14336-66-4.

Supplementary Material Available: Listings of anisotropic temperature factors, hydrogen atom coordinates and distances, angles involving hydrogen atoms, and observed and calculated structure factors and a packing figure of A (48 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of the Imidazolate-Bridged Dicopper(II) Ion in Two Binucleating Macrocycles

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Received July 26, 1983

The synthesis and structural characterization of complexes containing the imidazolate-bridged dicopper(II) core bound within two different binucleating macrocyclic ligands are reported. The ligands used in this study were 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane (macrocycle A) and 1,4,7,13,16,19-hexaazacyclotetracosane (macrocycle A′). Imidazolate-bridged dicopper complexes form readily upon addition of 1 equiv of imidazole (imH) and 1 equiv of sodium hydroxide to an aqueous solution of the ligand and 2 equiv of copper(II) perchlorate. Crystals suitable for X-ray diffraction experiments were best obtained upon addition of a fifth ligand (L = imH or 1-methylimidazole (MeIm)) to give pentacoordinate copper atoms. Insertion of the [Cu$_2$(im)L$_2$]$^{3+}$ unit into the macrocyclic ligand cavity results in distorted trigonal bipyramidal geometries for the two copper centers, with Cu–N bond lengths ranging from 1.95 to 2.26 Å. The complex [Cu$_2$(im)(imH)$_2$$\subset$A](ClO$_4$)$_3$ crystallizes in the monoclinic system, space group *C*2/*c*, with a = 15.008 (3) Å, b = 10.186 (2) Å, c = 26.062 (3) Å, β = 100.48 (1)°, and Z = 4. For [Cu$_2$(im)(1-MeIm)$_2$$\subset$A′](ClO$_4$)$_3$, X-ray studies revealed orthorhombic symmetry, space group *Pnma*, with a = 16.670 (4) Å, b = 28.112 (18) Å, c = 9.195 (9) Å and Z = 4.

Introduction

The metalloenzyme bovine erythrocyte superoxide dismutase (BESOD) has been the subject of extensive research.[2,3] Its structure has been determined by X-ray crystallography.[4] Each of the two identical subunits contains an imidazolate-(histidine-) bridged bimetallic active site incorporating one

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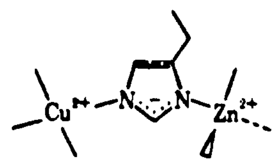
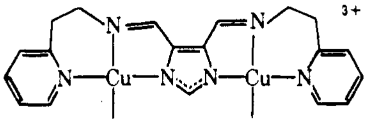
0020-1669/84/1323-1004$01.50/0

zinc(II) and one copper(II) atom:



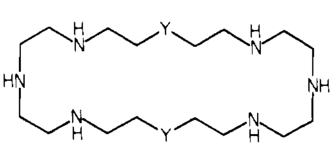
The proposed biological function[5] of BESOD is to scavenge the superoxide (O_2^-) ion, believed to be a toxic byproduct of oxygen metabolism, although this view has been challenged.[6] Numerous studies of the enzyme, its derivatives with other metals, and model compounds have been undertaken. Of particular interest is the catalytically active four-copper form of the protein (Cu_2Cu_2SOD), in which the zinc atoms have been replaced by copper.[7-9] Antiferromagnetic coupling of the two copper atoms in each subunit through the imidazolate bridge results in characteristic features in the electron spin resonance (ESR) spectrum, providing a sensitive indicator of the bridged, binuclear copper(II) center.

As models for the Cu_2Cu_2SOD active site, a number of imidazolate-bridged dicopper complexes have been prepared and characterized.[10,11] Simple complexes such as $[Cu_2(TMDT)_2(im)]^{3+}$[12] proved to be insufficient as models because their imidazolate bridge in aqueous solution is stable only over a very narrow pH range (8.0 < pH < 9.5).[10c,d] Below pH 8, the imidazolate group becomes protonated, breaking the bridge, while above pH 9.5 hydroxide ion competes with imidazolate binding. The bridge in $[Cu_2bpim]^{3+}$, where the imidazolate ion is incorporated into a chelating ligand, remains intact down to pH 4.5.[10d,12] The magnetic and structural properties of this complex, however, are sufficiently different from those of Cu_2Cu_2SOD[10d,e] to render it unsuitable as a model for Cu_2Cu_2SOD.



Cu_2bpim^{3+}

In order to obtain imidazolate-bridged dicopper(II) complexes that more faithfully mimic the solution, magnetic, and structural properties of Cu_2Cu_2SOD, we decided to use the macrocyclic amine ligands A and A′. The choice of these ligands was based on a study of the structure of the $[Cu_2(TMDT)_2(im)]^{3+}$ cation,[12] from which it was apparent that a binucleating macrocycle containing five-atom linker chains would nicely encapsulate the $[Cu_2im]^{3+}$ unit. Here we report the synthesis and structural characterization of imidazolate-bridged dicopper(II) complexes of macrocycles A and A′. A subsequent paper will describe their solution chemistry and magnetic properties.[13] Some preliminary results of this work have been previously communicated.[14]



macrocycle A, Y = O
macrocycle A′, Y = CH_2

Experimental Section

General Procedures. Macrocycles A and A′ were prepared as previously described.[14,15] Other reagents were commercially available and were used without further purification, except for 1-methylimidazole, which was vacuum distilled. Solution electronic spectra were recorded with a Varian 118C UV-visible spectrophotometer using matched 1-cm path length quartz cells.

Syntheses. $[Cu_2(im)(imH)_2\subset A](ClO_4)_3$. A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (110 mg, 297 μmol) in 1.0 mL of methanol was added dropwise to a stirred solution of macrocycle A (5.0 mL of a 29 mM methanolic solution). To the resulting deep blue solution was added 2.0 mL of a 75 mM methanolic solution of imidazole, followed by 0.145 mL of 1.0 M sodium hydroxide. A small amount of precipitate formed, which mostly dissolved upon addition of 1.0 mL of a 290 mM methanolic solution of imidazole. The filtered solution was allowed to crystallize by slow evaporation, producing deep blue crystals in 84% yield. Owing to the small amount of material made, no chemical analysis was performed on this compound. Its identity was established by X-ray crystallography (vide infra).

A similar route to this complex using $Cu(NO_3)_2\cdot 3H_2O$ as the starting material was described previously.[14a] Unit cell determinations of a number of crystals established that the bulk material made by both methods had the same composition.

$[Cu_2(im)\subset A'](ClO_4)_3\cdot H_2O$. To a stirred solution of macrocycle A′ (200 mg, 584 μmol) in 10.0 mL of methanol was added dropwise 5.0 mL of a 235 mM methanolic solution of $Cu(ClO_4)_2\cdot 6H_2O$. During the first half of the addition, a light blue precipitate formed which redissolved as the rest of the copper was added. After 5 min, 2.0 mL of 290 mM methanolic imidazole was added, followed by addition of 0.585 mL of 1.0 M aqueous sodium hydroxide. The methanol was removed by careful distillation at atmospheric pressure. The resulting blue solid was dissolved in 55 mL of hot water and allowed to cool slowly, which resulted in a 77% yield of blue crystals. Analytical data were reported previously.[14b] Absorption spectrum: λ_{max} 582, 271 nm.

$[Cu_2(im)(MeIm)_2\subset A'](ClO_4)_3$. To a solution of $[Cu_2(im)\subset A'](ClO_4)_3\cdot H_2O$ (22.6 mg, 26 μmol) in 1.5 mL of water was added 0.495 mL of 0.107 M aqueous 1-methylimidazole. Crystals were grown by slow evaporation, and their composition was determined by solution of the X-ray crystal structure. The unit cell was obtained for several of the platelike crystals to determine that the bulk of the material was the same as the crystal used for data collection.

X-ray Studies. Collection and Reduction of X-ray Data for $[Cu_2(im)(imH)_2\subset A](ClO_4)_3$. Crystals suitable for single-crystal X-ray analysis were obtained by slow evaporation of a methanolic solution of the complex containing excess sodium perchlorate. The crystal used for the study was a diamond-shaped platelet bounded by six faces: (001) and $(00\bar{1})$, 0.06 mm apart, and the two pairs (110), $(\bar{1}\bar{1}0)$ and $(1\bar{1}0)$, $(\bar{1}10)$, both 0.18 mm apart. Preliminary precession and Weissenberg photographs using copper $K\bar{\alpha}$ radiation (λ = 1.5418 Å) showed the space group to be either $C2/c$ (No. 15, C_{2h}^6) or Cc (No. 9, C_s^4).[16] Data collection and reduction followed the usual procedures

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(12) Ligand abbreviations: TMDT = 1,1′,7,7′-tetramethyldiethylenetriamine; im = imidazolate anion; imH = imidazole; MeIm = 1-methylimidazole; A = 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane; A′ = 1,4,7,13,16,19-hexaazacyclotetracosane; bpim = 4,5-bis[((2-(2-pyridyl)ethyl)imino)methyl]imidazolate; tren = tris(2-aminoethyl)amine.

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Table I. Experimental Details of the X-ray Diffraction Studies of $[Cu_2(im)(imH)_2\subset A](ClO_4)_3$ (**1**) and $[Cu_2(im)(MeIm)_2\subset A'](ClO_4)_3$ (**2**)

(A) Crystal Parameters[a] at 26 °C

	1	2		1	2
a, Å	15.008 (3)	16.670 (4)	space group	*C*2/*c*	*Pnma*
b, Å	10.186 (2)	28.112 (18)	*Z*	4	4
c, Å	26.062 (3)	9.195 (9)	ρ(calcd), g cm^{-3}	1.654	1.540
β, deg	100.48 (1)		ρ(obsd),[b] g cm^{-3}	1.68 (1)	1.55 (1)
V, Å^3	3917.7	4308.8	mol wt	975.2	999.3

(B) Measurement of Intensity Data

instrument: Enraf-Nonius CAD-4F κ-geometry diffractometer

radiation: Mo Kα (λ_{α_1} = 0.7093 Å, $\lambda_{\bar{\alpha}}$ = 0.710 73 Å), graphite monochromatized

bkgd measmt: moving cryst-moving detector; 25% added to scan width at both ends of each scan

	1	2
takeoff angle, deg	2.0	2.0
stds, measd every 1 h of X-ray exposure time[c]	(400), (110), (024)	$(\bar{2},11,0)$, $(\bar{5}2\bar{1})$, $(0,\overline{16},0)$
no. of reflcns colled excluding syst absences	4636 [4° ≤ 2θ ≤ 50° (+*h*,+*k*,±*l*)]	4259 [3° ≤ 2θ ≤ 50° (+*h*,+*k*,+*l*)]

(C) Treatment of Intensity Data[d]

	1	2
μ, cm^{-1}	13.7	12.4
transmission factor range[e]	0.76–0.92	0.64–0.90
averaging, R_{av}	0.019	
no. of reflcns after averaging	3436	3843
obsd unique data [$F_O > 4\sigma(F_O)$]	1632	912

[a] From a least-squares fit to the setting angles of 25 reflections with $2\theta > 30°$. [b] By suspension in $CHCl_3/CHBr_3$. [c] Compound **1** showed only random, statistical fluctuations. [d] F_O and $\sigma(F_O)$ were corrected for background, attenuator, and Lorentz-polarization effects of X-radiation as described previously (see ref 17). [e] Performed with the Wehe–Busing–Levy ORABS program.

adopted in our laboratory,[17] details of which are given in Table I.

Determination and Refinement of the Structure of $[Cu_2(im)(imH)_2\subset A](ClO_4)_3$. The structure was solved in the space group *C*2/*c* by using conventional heavy-atom methods.[18] The position of the copper atom was calculated from the Patterson map. All other non-hydrogen atoms were found on subsequent difference Fourier maps following least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions, with C–H = 0.95 Å and N–H = 0.87 Å. Hydrogen atom H131, attached to the C2 carbon atom of the bridging imidazolate, was fixed on the twofold axis. The positions of the amine hydrogen atoms were also fixed. The remaining hydrogen atoms were permitted to ride on the carbon atoms to which they were attached. The group temperature factor for these hydrogens was allowed to refine and converged at *U* = 0.108 (11) Å^2.

The residual indices[19] converged at $R_1 = 0.0737$ and $R_2 = 0.0794$. The function minimized in the least squares was $\sum w(|F_o| - |F_c|)^2$, where $w = \kappa/[\sigma^2(F_o) + 0.0004F_o^2]$ and κ was allowed to refine and converged at 3.545.[18] A total of 274 variable parameters was used to fit 1632 reflections above background. Neutral-atom scattering factors for non-hydrogen atoms and corrections for anomalous dispersion effects were obtained from ref 20. Scattering factors for the hydrogen atoms were those of Stewart et al.[21] In the final cycle of refinement, no variable shifted by more than 0.002σ.

Table II. Positional Parameters for $[Cu_2(im)(imH)_2\subset A](ClO_4)_3$[a]

ATOM	X	Y	Z
Cu	0.43843(9)	-0.04706(15)	0.35055(5)
N11	0.4850(6)	0.0227(8)	0.2898(3)
C13	0.5000	-0.0473(16)	0.2500
C15	0.4877(8)	0.1515(11)	0.2745(4)
N1	0.3195(6)	-0.1132(9)	0.3007(4)
C2	0.2616(8)	-0.1738(13)	0.3325(4)
C3	0.3173(8)	-0.2416(13)	0.3771(5)
N4	0.3823(6)	-0.1424(10)	0.4048(4)
C5	0.4547(10)	-0.1983(13)	0.4458(5)
C6	0.5264(9)	-0.2530(15)	0.4217(5)
N7	0.5648(7)	-0.1534(11)	0.3891(4)
C8	0.6272(9)	-0.2054(13)	0.3622(5)
C9	0.6895(8)	-0.1059(14)	0.3452(5)
O10	0.7362(5)	-0.1706(8)	0.3102(3)
C11	0.7905(9)	-0.0895(13)	0.2841(5)
C12	0.2712(8)	-0.0188(14)	0.2622(5)
N21	0.4598(8)	0.1324(11)	0.3933(3)
C22	0.3980(10)	0.2049(17)	0.4090(6)
N23	0.4317(14)	0.3154(16)	0.4276(5)
C24	0.5247(14)	0.3148(18)	0.4229(6)
C25	0.5366(10)	0.2021(16)	0.4018(5)
Cℓ1	0.0000	-0.0617(5)	0.7500
O11	0.0514(6)	0.0183(10)	0.7886(4)
O12	-0.0612(5)	-0.1461(9)	0.7728(3)
Cℓ2	0.2397(3)	0.0031(5)	0.99645(16)
O21	0.1735(9)	0.0159(11)	1.0211(4)
O22	0.2162(7)	0.0038(10)	0.9437(4)
O23	0.3259(10)	0.0094(17)	1.0157(6)
O24	0.2477(16)	-0.1644(18)	1.0062(8)
O25	0.2531(18)	0.175(2)	0.9992(11)

[a] Atoms are labeled as shown in Figure 1. Numbers in parentheses are estimated standard deviations in the last significant digit(s).

The largest peak on the final difference Fourier map was 0.51 e Å^{-3}. The average $w\Delta^2$ for groups of data sectioned according to parity group, $|F_o|$, $(\sin\theta)/\lambda$, $|h|$, $|k|$, or $|l|$, showed reasonable consistency, and the weighting scheme was considered to be satisfactory.

One perchlorate anion was disordered over two positions. Attempts to refine an ordered structure in space group *Cc* did not improve the model and, due to the small number of data above background, were abandoned.

Collection and Reduction of X-ray Data for $[Cu_2(im)(MeIm)_2\subset A'](ClO_4)_3$. Weakly diffracting crystals that were acceptable but not optimal for X-ray analysis were obtained by slow evaporation of an aqueous solution of the complex. A plate bounded by (010) and $(0\bar{1}0)$, 0.08 mm apart, (001) and $(00\bar{1})$, 0.26 mm apart, and (100) and $(\bar{1}00)$, 0.36 mm apart, was used. Further details of the data collection and reduction are given in Table I.

Determination and Refinement of the Structure of $[Cu_2(im)(MeIm)_2\subset A'](ClO_4)_3$. Preliminary examination of the diffractometer data showed the space group to be either *Pnma* (No. 62, D_{2h}^{16}) or $Pn2_1a$ (No. 33, C_{2v}^{9}) in a nonstandard setting.[16] Since the data set was quite weak, the refinement was initially carried out in the centrosymmetric space group *Pnma*. A Patterson map was used to calculate the position of the copper atom, and the remaining non-hydrogen atoms were found on subsequent difference Fourier maps following least-squares refinement. Because of the paucity of data, only the copper and chlorine atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined as discussed above. The hydrogen atom group temperature factor refined to *U* = 0.153 (27) Å^2.

The reliability indices converged at $R_1 = 0.124$ and $R_2 = 0.137$, for 135 variable parameters. These unusually high values are due to the poor quality of the crystals; only 912 reflections had $F > 4\sigma(F_o)$. During the final cycle of least-squares refinement, the parameters associated with rotation about the C–N bond for the methyl group attached to the imidazole shifted by 0.8σ, while most of the remaining variables shifted by less than 0.1σ.

On the final difference Fourier map, the largest peak was 0.86 e Å^{-3}. The variance of $w\Delta^2$, sectioned as described above, showed reasonable consistency, and the weighting scheme, for which κ converged at 3.60, was considered to be satisfactory.

Final non-hydrogen atomic positional parameters for the two crystal structures are given, along with estimated standard deviations, in Tables II and III. Features of the molecular geometry appear in Tables IV and V. Tables S1–S7 report the observed and calculated structure factors, hydrogen atom positional parameters, atomic thermal parameters, and ligand torsion angles.[22]

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(19) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

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Table III. Positional Parameters for $[Cu_2(im)(MeIm)_2\subset A'](ClO_4)_3$[a]

ATOM	X	Y	Z
Cu	0.4031(2)	0.14806(13)	0.1756(5)
N21	0.4442(12)	0.2106(7)	0.227(2)
C22	0.407(3)	0.2500	0.185(5)
C24	0.5204(17)	0.2264(8)	0.281(3)
N31	0.5589(16)	0.0474(10)	0.375(3)
C31	0.602(3)	0.0007(13)	0.380(4)
C32	0.5165(17)	0.0647(10)	0.262(4)
N33	0.4833(14)	0.1081(9)	0.300(3)
C34	0.5131(20)	0.1159(14)	0.430(4)
C35	0.5631(19)	0.0795(12)	0.483(4)
N1	0.424(3)	0.1579(14)	-0.047(5)
C2	0.405(3)	0.102(2)	-0.098(7)
C3	0.329(3)	0.0943(18)	-0.058(5)
N4	0.341(2)	0.0930(12)	0.089(4)
C5	0.261(3)	0.0981(16)	0.178(6)
C6	0.251(3)	0.1157(17)	0.293(6)
N7	0.3016(19)	0.1622(10)	0.309(3)
C8	0.308(4)	0.165(2)	0.447(7)
C9	0.291(4)	0.2061(19)	0.520(7)
C10	0.244(4)	0.2500	0.487(9)
C11	0.489(4)	0.2500	-0.227(7)
C12	0.512(4)	0.2010(20)	-0.147(8)
C13	0.484(6)	0.162(3)	-0.078(12)
Cℓ1	0.2155(8)	0.2500	-0.0311(18)
O11	0.210(4)	0.2500	0.109(9)
O12	0.279(5)	0.2500	-0.083(10)
O13	0.171(4)	0.2102	-0.104(7)
Cℓ2	0.6508(7)	0.0412(4)	0.8771(14)
O21	0.652(3)	0.0113(15)	0.758(7)
O22	0.702(3)	0.0290(14)	0.999(6)
O23	0.643(3)	0.0852(20)	0.854(5)
O24	0.584(4)	0.029(2)	0.916(8)

[a] Atoms are labeled as shown in Figure 2. Estimated standard deviations in the last significant digit(s) are given in parentheses.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $[Cu_2(im)(imH)_2\subset A](ClO_4)_3$[a]

Copper Coordination Chemistry			
Cu-N11	1.976(9)	Cu-N4	2.021(11)
Cu-N21	2.135(11)	Cu-N7	2.256(10)
Cu-N1	2.118(9)		
N11-Cu-N21	94.0(4)	N21-Cu-N4	95.0(4)
N11-Cu-N1	90.2(3)	N21-Cu-N7	98.3(4)
N11-Cu-N4	170.7(4)	N1-Cu-N4	82.2(4)
N11-Cu-N7	98.0(4)	N1-Cu-N7	131.9(4)
N21-Cu-N1	128.5(4)	N4-Cu-N7	83.1(4)
Imidazolate			
N11-C13	1.311(13)	Cu-N11-C15	127.5(7)
N11-C15	1.374(14)	C13-N11-C15	105.8(10)
C15-C15'	1.39(2)	N11-C13-N11	114.2(14)
Cu-N11-C13	125.1(8)	N11-C15-C15'	107.0(6)
Imidazole			
N21-C22	1.30(2)	N23-C24	1.42(3)
N21-C25	1.338(19)	C24-C25	1.30(2)
C22-N23	1.29(2)		
Cu-N21-C22	126.8(10)	C22-N23-C24	106.7(16)
Cu-N21-C25	125.7(10)	N23-C24-C25	104.6(16)
C22-N21-C25	106.7(12)	N21-C25-C24	111.0(15)

[a] Internal ligand bond lengths ranged from 1.374 (18) to 1.558 (17) Å, with angles ranging from 106.5 (11) to 115.7 (10)°. For a complete listing, including values for the perchlorate anions, see ref 24. See footnote to Table II.

Table V. Interatomic Distances (Å) and Angles (deg) for $[Cu_2(im)(MeIm)_2\subset A'](ClO_4)_3$[a]

Copper Coordination Geometry			
Cu-N21	1.95(2)	Cu-N4	2.03(3)
Cu-N33	2.08(3)	Cu-N7	2.13(3)
Cu-N1	2.09(4)		
N21-Cu-N33	97.2(10)	N33-Cu-N4	97.7(12)
N21-Cu-N1	93.6(13)	N33-Cu-N7	107.0(11)
N21-Cu-N4	165.1(12)	N1-Cu-N4	78.5(15)
N21-Cu-N7	88.3(11)	N1-Cu-N7	131.9(15)
N33-Cu-N1	120.2(14)	N4-Cu-N7	87.7(13)
Imidazolate Geometry			
N21-C22	1.33(3)	Cu-N21-C24	132.6(16)
N21-C24	1.43(4)	C22-N21-C24	105(2)
C24-C24'	1.33(5)	N21-C22-N21'	113(3)
Cu-N21-C23	120.9(20)	N21-C24-C24'	1081(12)
Methylimidazole Geometry			
N31-C31	1.50(5)	C32-N33	1.39(4)
N31-C32	1.34(4)	N33-C34	1.31(5)
N31-C35	1.35(5)	C34-C35	1.40(5)
C31-N31-C32	127(3)	Cu-N33-C32	126(2)
C31-N31-C35	123(3)	Cu-N33-C34	130(2)
C32-N31-C35	111(3)	C32-N33-C34	103(3)
N31-C32-N33	110(3)	N33-C34-C35	115(3)
		C34-C35-N31	102(3)

[a] Internal ligand bond lengths ranged from 1.05 (10) to 1.66 (7) Å, with angles ranging from 99 (4) to 145 (7)°. For a complete listing, including values for the perchlorate groups, see ref 24. See footnote to Table III.

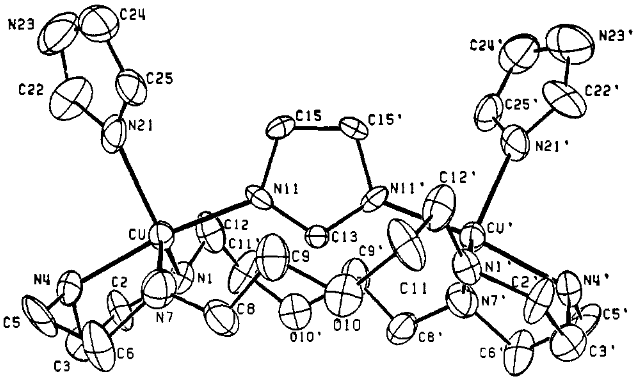

Figure 1. Molecular structure of $[Cu_2(im)(imH)_2\subset A]^{3+}$, depicting the 40% probability thermal ellipsoids. The diagram shows the atom-labeling scheme. The primed atoms are related to the unprimed atoms by a twofold axis through C13.

Results and Discussion

Addition of 2 equiv of cupric ion, 1 equiv of imidazole, and 1 equiv of base to an aqueous or methanolic solution of the hexaaza binucleating macrocycle A or A′ results in formation of the imidazolate-bridged dicopper complex $[Cu_2(im)\subset A]^{3+}$ or $[Cu_2(im)\subset A']^{3+}$. The solution stability of these complexes over a wide pH range has been established.[13,14b,23] The compound $[Cu_2(im)\subset A'](ClO_4)_3{\cdot}H_2O$ could be isolated as a solid and was found to be pure by analytical and magnetic criteria. Although crystals were obtained which had well-developed faces, Weissenberg and precession photographs revealed diffuse reflections between the sharp lattice lines, suggesting disorder or perhaps a superlattice. A complete set of X-ray data was obtained that indicated the space group to be *Pnma* or *Pn*2_1*a*.[16] A Patterson map gave the positions of the copper atoms. Few of the data were above background, however, which, coupled with the probable disorder, made the structure impossible to solve. Further details are available.[24]

When excess imidazole or 1-methylimidazole was present in the reaction mixture, better crystals were obtained. X-ray crystallographic studies, the results of which are discussed below, revealed that for both A and A′ derivatives the two copper atoms are coordinated by the diethylenetriamine poles of the ligands. In addition, an imidazolate anion bridges the two metal ions and the extra imidazoles are also coordinated. As a result, both copper centers are pentacoordinate and have distorted trigonal bipyramidal structures. In related studies employing 24- and 30-membered binucleating Schiff base macrocycles,[25] X-ray structural work revealed square-planar copper coordination geometries with a bridging imidazolate

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occupying an in-plane coordination site on each of the two copper(II) centers. Here it was apparently unnecessary to have additional coordinated imidazole to grow suitable crystals.

$[Cu_2(im)(imH)_2\subset A](ClO_4)_3$. The structure consists of discrete $[Cu_2(im)(imH)_2\subset A]^{3+}$ cations (Figure 1) and perchlorate anions. The cation contains a crystallographically required twofold axis which passes through atom C13 of the bridging imidazolate ring. The geometry around the copper atoms is best described as distorted trigonal bipyramidal, with N11 of the bridging imidazolate and N4 of the macrocycle in the axial positions. The axial Cu–N bond lengths of 1.976 (9) and 2.021 (11) Å (to N11 and N4, respectively) are similar to those observed in other imidazolate-bridged dicopper(II) complexes.[10g] For trigonal-bipyramidal copper(II) complexes with the tren[12] ligand, the average axial Cu–N bond is shorter than the average equatorial bond (2.066 vs. 2.087 Å, respectively).[26] This trend is also observed here, although the equatorial bonds are substantially longer (2.170 Å average). The bond angles also deviate significantly from ideal trigonal-bipyramidal geometry. The N4–Cu–N11 angle is 170.6 (4)° instead of 180°, and the angles between the equatorial ligands are 131.9 (4), 128.5 (4), and 98.3 (4)°, rather than 120°. The (axial)N–Cu–(equatorial)N angles range from 82.2 (4)° for N4–Cu–N1 to 98.0 (4)° for N11–Cu–N7. The copper atom is only 0.14 Å from the plane of the three equatorial nitrogen atoms. The mean plane of N1, N7, N21, and Cu makes an angle of 93° with the mean plane containing N4, Cu, N11, and C13. This value shows that the axis is nearly perpendicular to the equatorial plane. In the nomenclature of Kepert,[27] the geometry corresponds to the T_2 trigonal bipyramidal stereochemistry of a M(tridentate)(unidentate)$_2$ complex, distorted along the pathway toward the S_2 square-pyramidal stereochemistry having N21 as the apical ligand.

The bridging imidazolate ring is nearly planar, with the largest deviation from the mean plane being 0.009 Å. The copper atom is displaced by 0.31 Å toward N1 from the mean plane. The Cu–N11 and Cu′–N11′ vectors form an angle of about 135°. The coordinated imidazole is also planar with a maximum deviation from the plane of 0.004 Å. The copper atom lies 0.26 Å out of this plane. In refining the structure, there was some question as to which atom (C24 or N23) was the pyrrolic nitrogen atom. The N23–O21(perchlorate) contact of 3.04 (2) Å is suggestive of a hydrogen-bonding interaction, while the next shortest contact is between C25 and O22 (3.39 (2) Å). Attempts to refine the structure with the identities of C24 and N23 interchanged or disordered over the two positions led to an increase in the *R* factors.[24] Moreover, comparison with other imidazole structures supports the assignment as made. It has been found that the N1–C5 bond, where N1, C2, N3, C4, and C5 denote the atom labels of an imidazole ring, is longer than the N1–C2 bond, and that C2–N3 is shorter than C4–C5,[10g,28] as observed for this structure.

The internal ligand geometry is reasonable, given the limited accuracy of the structure determination. The methylene groups of the linker chains on the macrocyclic ligands are positioned to minimize steric interactions with the bridging imidazolate ligand. In $[Cu_2(im)(imH)_2\subset A](ClO_4)_3$, the chain is extended to nearly its full length between the amine nitrogen and ether oxygen atoms, with torsion angles from N7 through O10 of −159, −169, and −172°.[22] A short contact distance of 3.471 (14) Å is observed between C8 of the chain and N11 of the imidazolate ring. The Cu–N7 bond of 2.256 (10) Å, which is unusually long for an axial Cu–N bond in a diethylenetriamine-type ligand, could not become shorter without decreasing the C8–N11 distance. The chain turns at the ether oxygen atom, the C9–O10–C11–C12′ torsion angle being ~ 80°, to permit binding of N1′ to Cu′. The resulting geometry is quite different from ligand conformations found in other bridged binuclear structures of A and A′.[29]

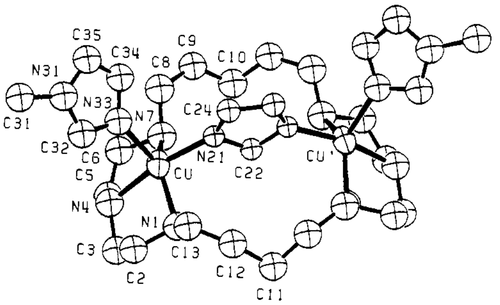

Figure 2. Molecular structure of $[Cu_2(im)(MeIm)_2\subset A']^{3+}$, with arbitrary spheres representing the atomic positions. The primed atoms are related to the unprimed atoms by a mirror plane through C10, C11, and C22.

The perchlorate anion located on the twofold axis (Cl1, O11, O12) is well-behaved, with bond lengths of 1.411 (10) and 1.461 (9) Å for Cl1–O11 and Cl1–O12. The internal angles range from 107.9 (8) to 110.6 (5)°. The other perchlorate is disordered over two positions. Three of the oxygens (O21, O22, and O23) were found to lie in a plane which also contains the Cl atom. Anisotropic refinement showed that the thermal ellipsoids for these four atoms were elongated in the direction perpendicular to the plane, suggesting overlap of two disordered sets of atoms. Two oxygen atoms of half-occupancy (O24 and O25) were located on either side of the plane. The resulting equatorial Cl–O bonds are very short (1.31 Å average), while the axial bonds are very long (1.74 Å). The best description of this arrangement of atoms is interpenetration of two tetrahedral perchlorate anions. Similar disorder was found to occur in the hydroxide-bridged copper complex, $[Cu_2(OH)\subset A](ClO_4)_3$.[30] Efforts to refine such a model for the present structure were unsuccessful, however.

$[Cu_2(im)(MeIm)_2\subset A'](ClO_4)_3$. The paucity of data above background severely limited the refinement and ultimate precision of this structure determination. Many similarties were observed between the geometry of this compound and that of the preceding one, however. The structure consists of discrete $[Cu_2(im)(MeIm)_2\subset A']^{3+}$ cations, shown in Figure 2, and perchlorate anions. The copper atoms are related by a mirror plane perpendicular to the plane of the bridging imidazolate ligand and passing through C10, C11, and C22. The coordination geometry is distorted trigonal bipyramidal, with axial bond lengths of 1.95 (2) Å (Cu–N21) and 2.03 (3) Å (Cu–N4) and a N4–Cu–N21 angle of 165 (1)°. The equatorial bonds are again longer than the axial bonds. The equatorial bond angles range from 107 (1) to 132 (1)°. The imidazolate and 1-methylimidazole rings are both planar, with no deviation greater than 0.06 Å. The perchlorate anions are poorly behaved, with some O–Cl–O angles of less than 100° and Cl–O bond lengths ranging from 1.15 to 1.50 Å. The low precision of the structure determination precludes any further discussion of its geometry.

Comparison with Related Compounds. Structural studies of related nonmacrocyclic complexes revealed the geometry about the copper atoms usually to be square planar or square

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pyramidal.[10] In these cases, however, the axial ligand was not a strong donor such as nitrogen but, rather, a weakly coordinating anion or solvent molecule. Similar results were found for imidazolate-bridged dicopper(II) complexes of large Schiff base macrocycles[25] having only water or perchlorate anions in the axial sites. Trigonal bipyramidal geometry is somewhat unusual for copper(II) complexes unless the ligand system requires it. For example, tren, bipyridine, and *o*-phenanthroline often give trigonal-bipyramidal copper(II) complexes.[27,31] The macrocycles A and A′ were expected to provide square-planar coordination geometries, possibly with weakly bound axial ligands, as found for $[Cu_2(TMDT)_2(im)]^{3+}$. Such is presumably the case for $[Cu_2(im)\subset A'](ClO_4)_3\cdot H_2O$, although the structure could not be determined. Although trigonal-bipyramidal structures occur in the solid state for $[Cu_2(im)(imH)_2\subset A]^{3+}$ and $[Cu_2(im)(MeIm)_2\subset A']^{3+}$, in solution the coordinated imidazoles are most likely replaced by two water molecules to form square-pyramidal copper(II) centers.[13,23]

Acknowledgment. This work was supported at Columbia University by NIH Research Grant No. GM-16449 from the National Institute of General Medical Sciences and by Grant No. CHE 81-09390 from the National Science Foundation.

Registry No. **1**, 69470-57-1; **2**, 89016-78-4; $[Cu_2(im)\subset A'](ClO_4)_3$, 76096-70-3.

Supplementary Material Available: Tables S1–S7 reporting observed and calculated structure factor amplitudes, hydrogen atom positional parameters, atomic thermal parameters, and ligand torsion angles (17 pages). Ordering information is given on any current masthead page.

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Synthetic, Structural, and Physical Studies of Titanium Complexes of Catechol and 3,5-Di-*tert*-butylcatechol

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Received August 16, 1983

Catechol ligands are found in biologically important metal complexing agents and have a remarkable affinity for metal ions in high oxidation states or with high charge/radius ratios. The coordination chemistry of titanium with catechol (H_2cat) and 3,5-di-*tert*-butylcatechol (H_2DTBC) is described, and the preparation and characterization of several types of complexes are reported. The structures of the representative compounds $[Et_3NH]_2[Ti(cat)_3]$ (**2**) (*Ia*, with a = 9.431 (1) Å, b = 32.634 (4) Å, c = 10.055 (1) Å, and β = 100.07 (1)°; Z = 4; ρ_{calcd} = 1.257, ρ_{obsd} = 1.25 g cm^{-3}; R_w = 3.79%), $K_4[TiO(cat)_2]_2\cdot 9H_2O$ (**4**) (*I*2/*a*, with a = 20.602 (1) Å, b = 6.237 (1) Å, c = 28.099 (2) Å, and β = 102.37 (1)°; Z = 4; ρ_{calcd} = 1.655 g cm^{-3}; R_w = 6.4%), and $[Et_3NH]_2[Ti(DTBC)_2(HDTBC)]_2\cdot 2CHCl_3$ (**5**) ($P\bar{1}$, with a = 14.369 (1) Å, b = 14.617 (1) Å, c = 15.330 (2) Å, α = 62.12 (1)°, β = 81.85 (1)°, and γ = 70.35 (1)°; Z = 1; ρ_{calcd} = 1.154 g cm^{-3}; R_w = 8.7%) have been determined by single-crystal X-ray diffraction. The complex anions of **4** and **5** are dimers with oxo and catecholato oxygen bridging groups, respectively. The $Ti(cat)_3^{2-}$ complex in **2** is pseudooctahedral with an average Ti–O bond length of 1.966 (27) Å. The average trigonal twist angle (0° for trigonal prism, 60° for the octahedron) is 43.5°. Strong hydrogen bonds from the cations to the catecholate oxygens perturb the geometry significantly from the D_3 ideal symmetry. The bis(μ-oxo) dimer $[TiO(cat)_2]_2^{4-}$ in **4** lies on an inversion center with nearly C_{2h} molecular symmetry. The Ti_2O_2 unit has an internal O–Ti–O bond angle of 82° and a Ti–Ti separation of 2.82 Å. The Ti–O catechol bonds trans to the oxide anions are 0.061 Å longer (2.051 (19) Å vs. 1.990 (3) Å) than the cis bonds. In contrast, the $[Ti(DTBC)_2(HDTBC)]_2^{2-}$ anion of **5** is a dimer, which contains both monoanionic and dianionic catecholate ligands, with crystallographic inversion symmetry. The monoanion ($HDTBC^-$) is monodentate, but one of the bidentate dianion ($DTBC^{2-}$) oxygen atoms is coordinated to both metal anions to form a dimeric complex of hexacoordinate Ti(IV). The average Ti–O bridge bonds are longer (2.060 (19) Å vs. 1.887 (2) Å) than the bonds trans to them. The monodentate catechol Ti–O bond distance is 1.936 (2) Å. For each of the structural types infrared and optical spectra are reported. For the $Ti(cat)_3^{2-}$ complex there is a hydrolysis reaction that takes place to form the $[TiO(cat)_2]^{2-}$ dimer above pH 12. The cyclic voltammetry of $Ti(cat)_3^{2-}$ shows a reversible reduction wave corresponding to a standard reduction potential (NHE) of −1.14 V. This remarkable shift of the standard Ti(IV)/Ti(III) reduction potential (0.099 V for $Ti(OH)_2^{2+}/Ti^{3+}$ in acid) is due to the enormous stability of the $Ti(cat)_3^{2-}$ complex.

Introduction

Catechol (1,2-dihydroxybenzene) is a powerful, bidentate chelating agent which has a particular affinity for metal ions that exhibit high oxidation states or high charge to metal ion radius ratios.[1] In biology, catechol functional groups are found in certain siderophores (microbial iron-chelating agents).[2] We have incorporated catechol ligands in the synthesis of sequestering agents that are designed to be specific for iron(III) or actinide(IV) metal ions.[3] This has led us to a general interest in the coordination chemistry of simple catechols. A previous paper reported the solution equilibria and characterization of several vanadium catechol complexes.[4] In this paper the coordination chemistry of catechol and 3,5-di-*tert*-butylcatechol (H_2DTBC) with titanium is explored and the structures of three representative complexes are reported.

In their pioneering study of metal–catecholate chemistry, Rosenheim and co-workers reported the synthesis of $[NH_4]_2[Ti(cat)_3]\cdot H_2O$.[5] A subsequent paper reported the resolution of the anion into its enantiomeric forms.[6] Rosen-

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