(MXBA)][ClO_4]$_2$ and [Cu_2(MXPNB)][ClO_4]$_2$ complexes, respectively. Steric factors may also be important in these displacement reactions, since accommodation of imidazole rings within the copper coordination spheres may cause excessive crowding with the various phenyl residues of the ligands.

In conclusion, the present investigation shows that by proper choice of the residues to be conjugated with the xylyl frame I it is possible to obtain stable binuclear copper(I) complexes with nitrogen donor ligands. The metal centers of these systems can come in close proximity by proper conformational arrangement of the flexible xylyl side chains,[13b,14b,d] though in the absence of structural determinations, only magnetic studies on the copper(II) analogues can give an estimate of the metal–metal interaction. Binding of the various functional groups of the ligand to copper(I) can, however, be conveniently deduced by careful examination of their IR and NMR spectra. Besides the donor groups of the ligands, the binuclear copper(I) complexes described here have other coordination sites available. These can be filled by solvent molecules or binding to external ligands such as carbon monoxide or imidazole. This is an important requisite in model studies based on binuclear copper(I) systems such as those derived from I, where small differences in structure or donor set can produce significant changes in reactivity.

Acknowledgment. The authors thank the Italian MPI for financial support, the Italian CNR for instrumentation facilities, and M. Bonfã for recording the proton NMR spectra.

Registry No. II (Z = NO_2), 86260-99-3; [Cu_2(MXPNB)][ClO_4]$_2$, 86261-01-0; [Cu_2(MXBA)][ClO_4]$_2$, 86261-03-2; [Cu_2(MXPNB)(CO)$_2$][ClO_4]$_2$, 86261-05-4; [Cu_2(MXBA)(CO)$_2$][ClO_4]$_2$, 86261-07-6; [Cu_2(MXPNB)(Im)$_2$][ClO_4]$_2$, 86261-09-8; [Cu_2(MXBA)(Im)$_2$][ClO_4]$_2$, 86261-11-2; α,α'-bis(diphthaloyldiethylenetriamino)-*m*-xylene, 86260-97-1; 1,3-bis[(bis(2-aminoethyl)amino)methyl]benzene hexahydrochloride, 86260-98-2; diphthaloyldiethylenetriamine, 63563-83-7; α,α'-dibromo-*m*-xylene, 626-15-3; *p*-nitrobenzaldehyde, 555-16-8; benzaldehyde, 100-52-7; tetrakis(acetonitrile)copper(I) perchlorate, 14057-91-1.

Notes

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Fluxional Behavior of a Pseudo-Jahn–Teller Complex: X-ray Crystal Structure of [Cu(bpy)$_2$(ONO)][NO_3] at 165 and 296 K

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Received August 18, 1982

The first crystal structure of a [Cu(bpy or phen)$_2$(OXO)]Y complex (bpy = 2,2′-bipyridyl, phen = 1,10-phenanthroline and OXO$^-$ = a bidentate ligand) to be reported was that of [Cu(bpy)$_2$(ONO)][NO_3].[2] The stereochemistry of the [Cu(bpy)$_2$(ONO)]$^+$ cation was classified as cis-distorted octahedral, with one nitrogen atom from each bpy ligand axial and the other two nitrogen atoms and both nitrito oxygen atoms equatorial. However, a recent analysis[3] of the crystal structures and temperature dependence of the ESR spectra of a series of [Cu(phen)$_2$(CH_3CO_2)][Y] "cation-distortion isomers" (Y = $BF_4\cdot 2H_2O$, $ClO_4\cdot 2H_2O$, ClO_4, and BF_4) suggests that the molecules are fluxional and that the purported cis-distorted octahedral geometry is not a genuine *static* stereochemistry of Cu(II) complexes in general.[4,5] The apparent fluxionality of these pseudo-Jahn–Teller (PJT) complexes was explained in terms of a potential energy surface involving two thermally accessible minima; the crystallographically observed geometries are thus statistical means weighted according to the relative thermal populations of the two minima.[5] To help establish whether indeed the cis-octahedral CuN_4O_2 chromophore is fluxional, we have determined the structure of [Cu(bpy)$_2$(ONO)][NO_3] at low temperature (165 K) and have repeated the determination at room temperature. Pertinent crystallographic results, a brief exposition of the distortional behavior in terms of a PJT formalism, and a simple derivation relating the energy difference between conformers to the observed distortions from C_2 symmetry are presented.

Experimental Section

The synthesis of [Cu(bpy)$_2$(ONO)][NO_3] (**1**) has been previously reported.[6] A single crystal of **1**, a parallelepiped with dimensions 0.23 × 0.17 × 0.14 mm, was selected for X-ray diffraction study and was mounted approximately along its longest dimension. An Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation and equipped with an ultrastable refrigeration-type concentric stream low-temperature device was used for preliminary experiments and for the measurement of diffraction intensities at both temperatures. Cell constants and data acquisition procedures are summarized in Table I. The formulas used to derive the intensity and its standard deviation were $I_{raw} = (K/\mathrm{NPI})(C - 2B)$ and $\sigma(I_o) = [(\sigma(I_{raw}))^2 + (pI_{raw})^2]^{1/2}(Lp)^{-1}$, where $\sigma(I_{raw}) = (K/\mathrm{NPI})(C + 4B)^{1/2}$, K = (20.1166)(attenuator constant), NPI = scan speed parameter, C = total integrated count, B = total background count, p = a factor used to downweight intense reflections (0.05), and Lp = Lorentz–polarization factor.[7] The raw intensity data were corrected for Lorentz–polarization effects ($I_o = I_{raw}/Lp$) but not for absorption (μ(Mo Kα) = 11.3 cm^{-1}). The weights of the 2921 (165 K) and 2142 (296 K) observations ($I_o > 2\sigma(I_o)$) used in the least-squares refinements were equal to $[\sigma(F_o)]^{-2}$. Scattering factors for the atoms were taken from ref 8a and corrected for anomalous dispersion.[8b]

Positional coordinates from the original room-temperature determination,[2] which was based on visually estimated intensity data, were used as starting coordinates. Several cycles of full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms led to the final error indices:[9] R = 0.046, R_w = 0.076, esd =

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(1) (a) Texas A&M University. (b) Present address: Chemistry Department, University of Puerto Rico, Rio Piedras, Puerto Rico 00931. (c) University College, Cork.

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(7) All calculations were carried out on a PDP 11/60 computer at the Molecular Structure Corp., College Station, TX, with the Enraf-Nonius structure determination package with local modifications.

(8) (a) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71–102. (b) *Ibid.*, p 149.

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Table I. Experimental Details of the X-ray Diffraction Study of $[Cu(bpy)_2(ONO)][NO_3]$ at 165 and 296 K

(A) Crystal Parameters[a]

T, K	165	296
a, Å	11.217 (2)	11.225 (2)
b, Å	11.936 (5)	12.035 (5)
c, Å	14.969 (3)	15.109 (5)
β, deg	99.14 (2)	99.55 (2)
V, Å^3	1979 (2)	2013 (2)
d_{calcd}, g cm^{-3}	1.624	1.597

formula	$CuC_{20}H_{16}N_6O_5$	space group	$P2_1/n$
fw	483.93	*Z*	4
cryst syst	monoclinic		

(B) Measurement of Intensity Data

instrument	Enraf-Nonius CAD4, κ-geometry diffractometer
radiation	Mo Kα (λ($α_1$) = 0.709 26, λ($α_2$) = 0.713 54 Å), graphite monochromatized
takeoff angle, deg	2.8
scan tech	θ–2θ
scan width, deg	variable; $\Delta\omega = 0.7 + 0.34 \tan\theta$
scan rate, deg min^{-1}	variable; 2.24–20.12 in ω(165 K); 2.01–20.12 in ω(296 K)
scan range, deg	$0 < 2\theta < 50$
prescan rejection limit	reflcns obeying $[\sigma(I)/I]_{pre} \geq 2.0$ considered unobserved and not rescanned
prescan acceptance limit	reflcns obeying $[\sigma(I)/I]_{pre} \leq 0.02$ considered observed but not rescanned
max counting time, s	27 (165 K), 31 (296 K)
bkgd measurements	moving crystal-moving detector; 25% added to scan width at both ends of each scan
std reflcns	three reflcns measd after every 2200 s (165 K) and 4000 s (296 K); 6.5% decay observed for the 165 K data for which an anisotropic decay correction was applied; no discernible decrease obsd for the 296 K data
no. of (+*h*, +*k*, ±*l*) data	3477 (165 K) and 3535 (296 K) nonspace group extinguished

[a] Determined from a least-squares treatment of the angular coordinates of 25 independent high-angle reflections.

2.351 (165 K); $R = 0.046$, $R_w = 0.053$, esd = 1.298 (296 K). The largest shift in a positional or thermal parameter in the final cycle of least squares was less than 80% of its esd for both refinements. Final difference Fourier syntheses showed no excursions above background. Supplementary material includes final positional and thermal parameters (Tables S1 and S2), bond distances and angles (Tables S3 and S4), and observed and calculated structure factors (Tables S5 and S6).

Discussion

The structure of $[Cu(bpy)_2(ONO)][NO_3]$ (**1**) is shown in Figure 1. Table II gives the metal–ligand bond lengths for **1** for $[Zn(bpy)_2(ONO)][NO_3]$ (**2**),[10] an orbitally nondegenerate d^{10} complex whose crystal is isostructural with **1**, and for $[Cu(bpy)_2(ONO)][BF_4]$ (**3**),[10] a cation-distortion isomer of **1**.

A Cu(II) complex with D_3 symmetry such as $[Cu(bpy)_3]^{2+}$ has an ^{2}E electronic ground state and is susceptible to Jahn–Teller distortion.[11] If one of the bpy groups is replaced by a chelating nitrito group, the resulting molecular symmetry is C_2 and the electronic degeneracy is lifted: the ^{2}E term splits into a ^{2}A ground state and a ^{2}B excited state.[6] Nevertheless, $[Cu(bpy)_2(ONO)]^+$ will be unstable with respect to pseudo-Jahn–Teller distortion if (i) the splitting of the ^{2}A and ^{2}B states in the undistorted complex (2Δ) is sufficiently small and (ii) the vibronic coupling constant, $\langle ^2A|H_i|^2B\rangle$, is nonzero, which requires the vibrational mode(s) coupling the ^{2}A and ^{2}B electronic states to have b symmetry. Thus, an isolated $[Cu(bpy)_2(ONO)]^+$ cation is unsusceptible to distortion unless a vibronic coupling of the ^{2}A and ^{2}B electronic states occurs, in which case *static C_2 symmetry cannot be retained*.[12]

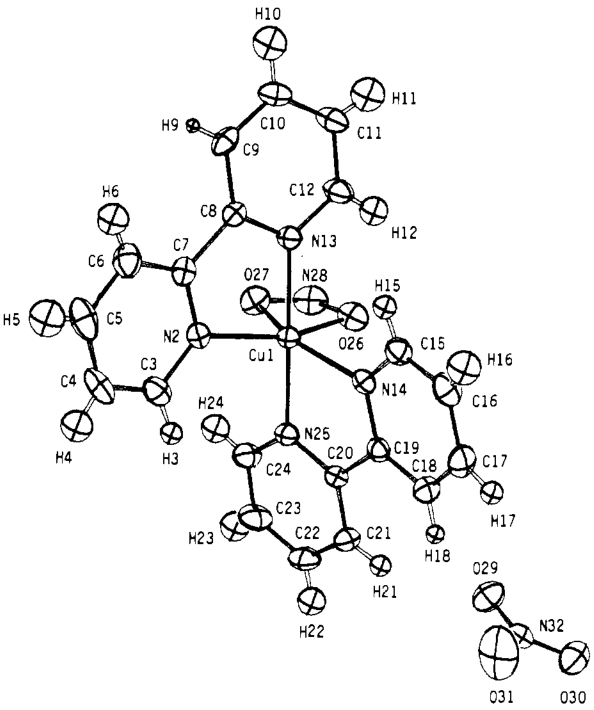

Figure 1. ORTEP drawing of the molecular structure of $[Cu(bpy)_2(ONO)][NO_3]$ (**1**) at 296 K. Ellipsoids of 25% probability are shown. Copper–ligand bond distances are given in Table II.

Table II. Molecular Geometries for $[M(bpy)_2(ONO)][Y]$ Complexes (M = Cu, Zn) (Å)

	$[Cu(bpy)_2(ONO)][NO_3]$ (**1**)[a]		$[Zn(bpy)_2(ONO)][NO_3]$ (**2**)[b]	$[Cu(bpy)_2(ONO)][BF_4]$ (**3**)[b]
	165 K	296 K	298 K	298 K
M-N(13)	1.984 (2)	1.980 (3)	2.129 (9)	1.990 (5)
M-N(25)	1.989 (2)	1.988 (3)	2.151 (9)	2.004 (5)
M-N(2)	2.071 (2)	2.074 (4)	2.076 (9)	2.052 (5)
M-N(14)	2.098 (2)	2.085 (4)	2.092 (9)	2.142 (5)
M-O(26)	2.204 (3)	2.230 (5)	2.223 (9)	2.117 (6)
M-O(27)	2.351 (3)	2.320 (5)	2.217 (8)	2.462 (6)
δ°[c]	0.18 (1)	0.11 (1)	0.04 (2)	0.45 (1)

[a] This work. [b] Reference 10. [c] δ° (Å) = {[M-N(25)] − [M-N(13)]} + {[M-N(14)] − [M-N(2)]} + {[M-O(27)] − [M-O(26)]}.

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(9) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/[\sigma(F_o^2)]^2$. The unweighted and weighted residuals are defined as $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The error in an observation of unit weight (esd) is $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

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(12) Öpik and Pryce[13] and Bersuker[14,15] have shown that the adiabatic potential energy for pseudodegenerate electronic states in the harmonic first-order model approximation is given by $E_\pm(S) = 1/2KS^2 \pm (\Delta^2 + a^2S^2)^{1/2}$, where $E_\pm$ is the energy for the upper (+) and lower (−) potential curves (assuming a two-dimensional surface), K is the effective force constant of the active vibronic mode with symmetry coordinate S, 2Δ is the splitting of the two nondegenerate states at $S = 0$, and a is the vibronic coupling constant. If $\Delta > a^2/K$, then both curves are parabolas and the molecule is stable with respect to distortion; otherwise, the potential surface will have equivalent minima (isolated molecule) at $S^m = \pm(a^2/K^2 - \Delta^2/a^2)^{1/2}$, and distortion away from the symmetrical geometry will be spontaneous. Also, distortion via a HOMO–LUMO interaction between the $3d_{z^2}$ and 4s orbitals in the $[Cu(bpy\ or\ phen)_2(OXO)][Y]$ systems, which has been implicated in certain six-coordinate Cu(II) complexes,[16] would *preserve* C_2 symmetry and must be judged as insignificant according to the crystallographic results reported herein.

The potential energy surface for the electronic ^{2}A and ^{2}B states in a [Cu(bpy or phen)$_2$(OXO)][Y] complex is shown in Figure 2 as a function of the distortion coordinate S(b) of the active b mode.[13-15] The form of this mode is shown below the minima and is based on the consistent patterns of distortion from C_2 symmetry observed in 12 such complexes.[17] When the *average* site symmetry of the complex is C_2, the ground-state minima are equivalent (solid curve); otherwise, they are nonequivalent (dotted curve) and are separated in energy by ΔE. A maximum in the ^{2}A curve occurs at $S(\text{b}) = 0$, i.e. for an undistorted complex with static C_2 symmetry.[18]

The proposed model of two thermally accessible potential energy minima separated in energy by ΔE suggests that the observed geometries of [Cu(bpy or phen)$_2$(OXO)][Y] complexes are not only statistical means weighted according to the relative thermal populations of the two minima but also temperature dependent. In fact, it is possible to derive an equation relating the energy difference between the conformers (ΔE) to the observed δ° values (Table II); it is solvable if the structure has been determined at two or more temperatures. Boltzmann statistics indicate $n_\tau{}^A = n_\tau{}^B \exp(\Delta E/RT)$, where $n_\tau{}^A$ and $n_\tau{}^B$ are the relative thermal populations of minima "A" and "B". The δ° values are weighted according to $\delta^\circ = n_\tau{}^A\delta^m - n_\tau{}^B\delta^m$, where δ^m is the maximum value of δ° corresponding to the purely static case. [With this weighting scheme it is implicitly assumed that the degree of distortion from C_2 symmetry is identical for both conformers (i.e., the minima are symmetrically disposed about $S = 0$) even though they are energetically nonequivalent because of intracrystalline forces.[19]] Inserting this equation into the Boltzmann equation and rearranging give $\Delta E = RT \ln [(\delta^\circ + \delta^m)/(\delta^m - \delta^\circ)]$. A series of structure determinations at various temperatures (including that at liquid helium, which allows δ^m to be obtained directly) enable ΔE to be determined accurately from a linear least-squares fit of ln K vs. T^{-1}, where $K = (\delta^\circ + \delta^m)/(\delta^m - \delta^\circ) = n^A/n^B$.[19] If δ^m cannot be obtained directly, it can be determined less accurately in an iterative fashion using the equation $T_2/T_1 = \{\ln [(\delta^\circ{}_1 + \delta^m)/(\delta^m - \delta^\circ{}_1)]\}\{\ln [(\delta^\circ{}_2 + \delta^m)/(\delta^m - \delta^\circ{}_2)]\}^{-1}$ (assuming ΔE is temperature independent and cooperative forces are negligible), where $\delta^\circ{}_1$ and $\delta^\circ{}_2$ are the δ° values at T_1 and T_2; knowing δ^m allows ΔE to be determined. Preliminary results obtained for **1** from the values in Table II are $\delta^m = 0.31$ Å and $\Delta E =$ ca. 155 cm^{-1}. Our ΔE value is comparable to the following ΔE values determined from the temperature dependence of ESR g values for various six-coordinate Cu(II) complexes: 75 cm^{-1} for a [Cu(H$_2$O)$_6$]$^{2+}$ complex doped into a zinc (Tutton's) host crystal,[19] ca. 400 ± 100 cm^{-1} for Ni(prp)$_2$enCu(hfa)$_2$((prp)$_2$en = 2-hydroxypropiophenone iminato, hfa = hexafluoroacetylacetonato),[20] and ca. 200 and 100 cm^{-1} for [Cu(tach)$_2$][ClO$_4$]$_2$ and [Cu(tach)$_2$][NO$_3$]$_2$, respectively (tach = *cis,cis*-1,3,5-triaminocyclohexane).[21]

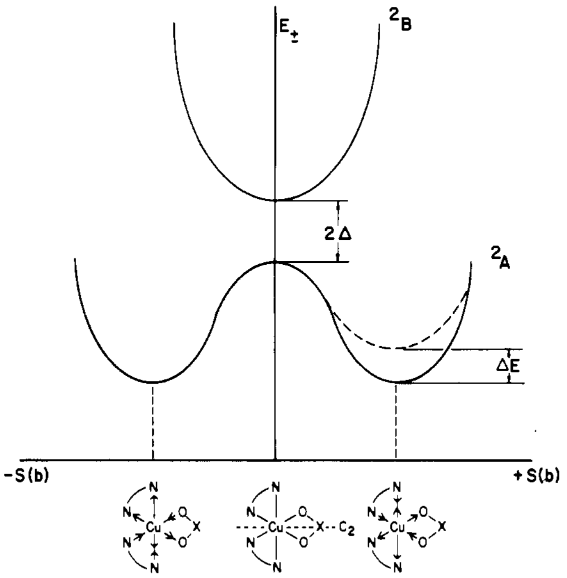

Figure 2. Proposed potential energy surface for the pseudodegenerate electronic ^{2}A ground and ^{2}B excited states in a [Cu(bpy or phen)$_2$(OXO)][Y] complex as a function of the distortion coordinate S(b) of the PJT-active b mode.[13-15] If the *average* site symmetry of a complex is C_2, the ground-state minima are equivalent (solid curve); otherwise, they are nonequivalent (dotted curve). The preliminary ΔE value for **1** is ca. 155 cm^{-1}.

The δ^m value is closely related to the Jahn-Teller (JT) radius, R_{JT}. The R_{JT} values determined for an assortment of JT Cu(II) complexes have a remarkably small spread, clustering at ca. 0.32 (3) Å.[21] Although the δ^m value for **1**, 0.31 (1) Å, is smaller, much larger values are predicted for other [Cu(bpy or phen)$_2$(OXO)][Y] systems. For example, the δ° value (partly static) for [Cu(bpy)$_2$(CH$_3$CO$_2$)][BF$_4$] is 1.0 (1) Å at 298 K.[22] Larger PJT distortions, vis-à-vis JT, are consistent with Bersuker's "vibronic amplification rule":[14] a small perturbation such as replacing a bpy group with a nitrito group in [Cu(bpy)$_3$]$^{2+}$ may be vibronically amplified, resulting in large distortions. The magnitude of the distortions will vary considerably (as evidenced by the structural differences between **1** and **3**) because ΔE is very sensitive to differences in crystal-packing forces etc. (the "plasticity effect"[15]).

The results of the crystal structure determination of **1** at 165 and 296 K have been discussed in terms of a potential energy surface consisting of two nonequivalent, thermally accessible minima. According to the model, the observed distortions from C_2 symmetry should increase with decreasing

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(17) The pattern of continuous distortion from C_2 symmetry observed in a series of [Cu(bpy or phen)$_2$(OXO)][Y] complexes is that as a pair of trans Cu–O$_{eq}$ and Cu–N$_{eq}$ bonds lengthen, the other pair concomitantly shorten. (In fact, a plot of Δ(Cu–N)$_{eq}$ vs. Δ(Cu–O)$_{eq}$ is nearly linear; see Figure 2 of ref 10.) Furthermore, the Cu–N$_{ax}$ bonds become slightly unequal; the nitrogen atoms in the shorter Cu–N$_{ax}$ bonds always belong to the same bpy (or phen) ligands as do the in-plane nitrogen atoms in the shorter Cu–N$_{eq}$ bonds (see Table II and Tables 1 and 6 of ref 3 and 10).

(18) The amplitude and anisotropy of the thermal motions of the acetato oxygen atoms in a series of [Cu(phen)$_2$(CH$_3$CO$_2$)][Y] complexes (Y = BF$_4$·2H$_2$O, ClO$_4$·2H$_2$O, ClO$_4$, and BF$_4$) increase as the complexes become more symmetric; concomitantly, the angles between the major axes of the oxygen thermal ellipsoids and the Cu–O bond vectors decrease.[3] For example, the angles between the major axes of the oxygen thermal ellipsoids and the Cu–O bonds in the "symmetric" BF$_4$·2H$_2$O and ClO$_4$·2H$_2$O complexes (both $P2/c$, $Z = 2$) are only 13 and 7°, respectively, while in the asymmetric BF$_4$ complex ($P\bar{1}$, $\delta^\circ = 0.84$ (1) Å), they are 42 and 54°. Increasing vibrational amplitudes with increasing symmetry is evident by the trend in the rms values (Å) of the oxygen thermal ellipsoids in these complexes: 0.42, 0.26, 0.23, and 0.41, 0.27, 0.24 in BF$_4$·2H$_2$O and ClO$_4$·2H$_2$O, respectively, and 0.36, 0.29, 0.21 and 0.24, 0.23, 0.21 in BF$_4$. A marked temperature dependence of the ESR spectra for only the "symmetric" and nearly symmetric BF$_4$·2H$_2$O, ClO$_4$·2H$_2$O, and ClO$_4$ complexes was also noted. These facts are consistent with a fluxional complex lacking *static* C_2 symmetry; the fluxionality increases as ΔE decreases. Thus, the structure of [Cu(phen)$_2$(CH$_3$CO$_2$)][BF$_4$]·2H$_2$O, in which Cu(II) lies on a crystallographic C_2 axis, consists of two interconverting *asymmetric* structures associated with two equivalent energy wells, and the complex has average C_2 symmetry.

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temperature, a result of depopulating the higher energy well; this is consistent with the experimental results and strongly implies that the cis-octahedral CuN_4O_2 chromophore is fluxional. The fact that the $\delta°$ values of **1** are greater than those of **2**, a d^{10} complex whose crystal is isostructural, indicates that the "driving force" governing the distortional behavior is vibronic in origin and is not related to crystal-packing forces etc. (Cooperative forces in **1** are also unimportant: the electronic reflectance and ESR spectra for Cu(II)-doped **2** show no discernible variations from 0.1–100% copper doping.[5]) The derivation presented allows ΔE to be easily determined from X-ray diffraction experiments performed at different temperatures, and it seemingly repudiates the notion that "X-ray analysis thus provides information about the preferred conformations of molecules although it has nothing to say about the energy differences between the conformations or the energy barriers that separate them. This information has to be obtained by other methods."[23]

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE-81-14613). We also wish to thank the Molecular Structure Corp. College Station, TX, for their help in obtaining the room and liquid-nitrogen data sets and for the use of their computing facilities and Richard E. Marsh, California Institute of Technology, for his very useful comments.

Registry No. 1, 23578-78-1.

Supplementary Material Available: Tables of final positional and thermal parameters (Tables S1 and S2), bond distances and angles (Tables S3 and S4), and observed and calculated structure factors (Tables S5 and S6) (32 pages). Ordering information is given on any current masthead page.

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Steric and Crystal-Packing Effects on the Molecular Structures of Dimetal(II) Tetrakis(2-oxypyridine) Complexes

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Received November 2, 1982

The anions of 6-methyl-2-hydroxypyridine (Hmhp) and 6-chloro-2-hydroxypyridine (Hchp) form bridged binuclear complexes of the type $M_2(mhp)_4$[2-5] and $M_2(chp)_4$[6,7] with a number of transition metals. Across the series $[Mo_2(mhp)_4]\cdot CH_2Cl_2$,[2] $[Ru_2(mhp)_4]\cdot CH_2Cl_2$,[3] and $[Rh_2(mhp)_4]$,[4] crystal structure determinations have demonstrated a progression toward longer M–M and shorter M–O and M–N bonds. $[Pd_2(mhp)_4]$[5] differs markedly from the Rh dimer only in the M–M separation and angles that depend directly on it. In parallel with this progression is an increase in the mean O–M–M–N torsion angle away from an exactly eclipsed conformation, in the order Mo < Ru < Rh ≈ Pd. We have interpreted this as a direct consequence of intramolecular steric repulsions between methyl groups of the ligands.[3,4] We were, therefore, surprised to see a report of the structure of $[Rh_2(mhp)_4]\cdot H_2O$,[7] in which two crystallographically independent molecules have mean torsion angles of 1.0 and 9.3°, which are respectively lower and higher than any previously observed for $M_2(mhp)_4$ complexes. Furthermore, the mean Rh–Rh bond length of 2.367 (1) Å was interpreted as significantly longer than the 2.359 (1) Å observed in anhydrous $Rh_2(mhp)_4$.[4] This structure raises the question of the effect of crystal-packing forces (the ultimate appeal of crystallographers in search of explanations!) on the molecular structures and, in particular, on the M–M bond lengths and torsional distortions about the M–M bonds in these dimers.

Table I. Crystal Data[a]

	1	2	3
formula	$C_{24}H_{24}N_4O_4Mo_2$	$C_{24}H_{24}N_4O_4Mo_2\cdot CH_3OH$	$C_{24}H_{24}N_4O_4Rh_2\cdot CH_2Cl_2$
cryst color and habit	yellow laths	orange blocks	yellow blocks
fw	624.4	656.4	723.2
cryst size, mm	0.35 × 0.23 × 0.15	0.25 × 0.12 × 0.19	0.19 × 0.35 × 0.50
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	8.865 (1)	8.938 (1)	12.705 (1)
b, Å	10.724 (1)	11.043 (2)	17.240 (1)
c, Å	13.750 (1)	13.903 (2)	12.769 (1)
α, deg	85.69 (1)	94.30 (2)	90
β, deg	77.98 (1)	95.98 (2)	103.58 (1)
γ, deg	77.36 (1)	103.87 (2)	90
V, Å^3	1246.9	1317.9	2718.7
d_{calcd}, g cm^{-3}	1.663	1.654	1.767
Z	2	2	4
μ, cm^{-1}	10.17	9.69	14.31
transmissn factor	[b]	0.746–0.819[c]	0.526–0.613[c]
$2\theta_{max}$, deg	50	55	55
no. of data collcd	4597	6101	6500
no. of data $F > 4\sigma(F)$	2686	3591	5447
no. of refined parameters	319	337	346
g[d]	0.0003	0.0005	0.0005
R[e]	0.028	0.063	0.046
R_w[f]	0.039	0.060	0.062
variance,[g] e	0.98	2.26	1.73
slope[h]	1.34	1.13	1.82
largest peak,[i] e Å^{-3}	0.35	0.81	0.96

[a] Valid for all three data sets: Stoe-Siemens AED diffractometer, Mo Kα radiation, $\lambda = 0.71069$ Å, graphite monochromator; all measurements at room temperature. [b] No absorption corrections. [c] Semiempirical absorption corrections based on intensities measured at various azimuthal angles. [d] Weighting scheme: $w^{-1} = \sigma^2(F) + gF^2$. [e] $R = \Sigma|\Delta|/\Sigma|F_o|$; $\Delta = |F_o| - |F_c|$. [f] $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$. [g] Variance $= (\Sigma w\Delta^2/\Sigma w)^{1/2}$. [h] Slope of normal probability plot. [i] In final difference synthesis.

In the course of our studies of complexes of mhp, we have obtained crystals of two further forms of $Mo_2(mhp)_4$, one as a methanol solvate and the other with no solvent of crystallization. We report here the structures of these and of $[Rh_2(mhp)_4]\cdot CH_2Cl_2$.

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