Relation between Structure and Spectra of Pseudo-tetrahedral Copper(II) Complexes. Crystal Structure of Bis(di-2-pyridylamido)copper(II)

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The copper(II) complex of the deprotonated form of di-2-pyridylamine has been prepared by treating the ligand with freshly prepared copper(II) hydroxide, and the crystal structure determined. Crystal data: Monoclinic, space group $C2/c$, a = 14.691(6), b = 12.256(9), c = 11.945(2) Å, β = 124.24(3)°, and Z = 4. The final R value was 0.039 for 1 052 independent, observed reflections. The copper atom environment is pseudo-tetrahedral with a dihedral angle of 58.8° between the two CuN_2 ligand planes. It is demonstrated that the observed molecular structure and the ligand field spectra in the literature are in good agreement. The extent of distortion from pure tetrahedral geometry in a series of related copper bis(bidentate ligand) complexes, as estimated from ligand-field spectra, correlates very well with the observed crystallographic dihedral angle values. This structural result is now available for calibration of the electronic and e.s.r. spectral data for small-molecule pseudo-tetrahedral copper(II) complexes and the presumed four-co-ordinated Type I ' blue ' copper protein sites.

THERE has been considerable interest in the relationship of the magnetic, spectroscopic, and structural properties of pseudo-tetrahedral copper(II) complexes.[1-22] Much work has also been devoted to the relation between the structures and magnetic and spectroscopic properties of di-2-pyridylamine (Hbipyam) [20,21,23-29] complexes of bivalent transition metals, particularly copper(II),[20,21,26-32] nickel(II) [26-33] palladium(II),[34] cobalt(II),[35] and iron(II).[36] A variety of stereochemical arrangements has been inferred for the cobalt, iron, and nickel complexes including trinuclear and polynuclear nickel(II) derivatives. Gouge and Geldard [20] have examined $[Cu(Hbipyam)_2]^{2+}$, $[Cu(bipyam)_2]^0$, and a series of other copper(II) complexes with stereochemically similar ligands, which produce a pseudo-tetrahedral metal environment. Their work can then be used with the known structure of $[Cu(Hbipyam)_2][ClO_4]_2$ [31] to calibrate the spectra of the various copper complexes in terms of distortion from regular tetrahedral symmetry. The accuracy of this $[Cu(Hbipyam)_2][ClO_4]_2$ structure is limited (R = 0.094), presumably due to some disorder in the perchlorate groups. The structure of $[Pd(bipyam)_2]$, which has also been reported,[35] is no help in this regard because the molecule is strained in a way which would not be possible in a copper(II) complex, in order to obtain a square-planar palladium environment with consequent extreme distortion of the ligands. We have therefore undertaken the structure determination of suitable pseudo-tetrahedral copper(II) chelates to determine whether the distortion from tetrahedral geometry, as expressed by a single parameter, the dihedral angle between ligands, can be correlated adequately with the distortion effects perceived in the crystal field spectra; and if such a correlation is experimentally verified, whether it is linear or not.

EXPERIMENTAL

Preparation of the Complex.—To a solution of di-2-pyridylamine (0.873 g) in distilled benzene (75 cm³) was added $Cu[OH]_2$ (0.200 g), freshly prepared by precipitation from a $CuCl_2$ solution using aqueous K[OH]. The mixture was heated at reflux for 50 h (during which time it turned dark green), cooled, and filtered, and the filtrate concentrated to a volume of about 15 cm³ on a rotary evaporator. Absolute diethyl ether was added to the remaining solution, and the solution stood in the refrigerator overnight. The resulting fine black crystals were filtered off and recrystallized from benzene–ether (1 : 1), m.p. 215—216 °C (decomp. 218 °C).

Crystal Data for $[Cu(bipyam)_2]$.—$C_{20}H_{16}CuN_6$, M = 404, Monoclinic, space group $C2/c$, a = 14.691(6), b = 12.256(9), c = 11.945(2) Å, β = 124.24(3)°, U = 1 778 Å³, D_m = 1.48 g cm⁻³, Z = 4, D_c = 1.51 g cm⁻³, $F(000)$ = 828, μ(Mo-K_α) = 13.0 cm⁻¹, λ(Mo-K_α) = 0.710 69 Å, crystal dimensions (distances in mm of faces from centroid) 0.09 (110), 0.09 ($\bar{1}\bar{1}0$), 0.085 ($1\bar{1}0$), 0.085 ($\bar{1}10$), 0.20 ($\bar{1}01$), 0.20 (101); maximum and minimum transmission coefficients 0.89 and 0.71 respectively.

Cell dimensions and space-group data were obtained by standard methods on an Enraf–Nonius four-circle CAD-4 diffractometer. The θ—2θ scan technique was used, as previously described,[37] to record the intensities for all non-equivalent reflections for which $1 < 2\theta < 46°$. Scan widths were calculated as $(A + B\tan\theta)$, where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to K_{α_1}–K_{α_2} splitting. The values of A and B were 0.60 and 0.35° respectively.

The intensities of four standard reflections, monitored at 100-reflection intervals, showed no greater fluctuations than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz and polarization effects, and for absorption. Of the 1 224 independent intensities, there were 1 052 with $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[38] These data were used in the final refinement of the structural parameters.

Structure Determination.—From a three-dimensional Patterson function calculated from all data and the unit-cell size, it seemed likely that the metal atom should lie on a two-fold symmetry axis. The position of the copper atom from the Patterson function phased the reflections sufficiently well to permit location of the remaining non-hydrogen atoms from Fourier-difference functions. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Further Fourier-difference functions

permitted location of all the hydrogen atoms, which were included in the refinement for three cycles of least squares and then held fixed. The model converged with $R = 0.039$, and $R' = 0.049$. A structure factor with all observed and unobserved reflections included (no refinement) gave $R = 0.048$; on this basis it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the

TABLE 1

Positional parameters and their estimated standard deviations

Atom	x	y	z
Cu	0.000 0(0)	0.124 24(7)	0.250 0(0)
N(1)	0.093 9(2)	0.023 4(3)	0.232 0(3)
N(1′)	−0.013 2(3)	0.226 1(3)	0.115 6(3)
N(2)	0.103 2(2)	0.128 0(3)	0.067 8(3)
C(2)	0.131 3(3)	0.042 9(4)	0.151 0(4)
C(3)	0.204 2(3)	−0.034 7(4)	0.153 8(4)
C(4)	0.238 3(3)	−0.124 0(4)	0.234 5(4)
C(5)	0.200 9(3)	−0.140 9(4)	0.317 6(4)
C(6)	0.130 1(3)	−0.066 6(4)	0.312 1(4)
C(2′)	0.035 0(3)	0.210 2(4)	0.046 5(4)
C(3′)	0.012 6(3)	0.287 4(4)	−0.054 6(4)
C(4′)	−0.065 7(4)	0.372 0(4)	−0.087 2(5)
C(5′)	−0.107 2(4)	0.385 0(4)	−0.018 3(5)
C(6′)	−0.082 6(4)	0.313 0(5)	0.079 9(5)
H(3)	0.231(3)	−0.022(4)	0.105(4)
H(4)	0.284(3)	−0.177(4)	0.235(4)
H(5)	0.221(3)	−0.206(3)	0.368(4)
H(6)	0.098(3)	−0.079(4)	0.359(4)
H(3′)	0.057(3)	0.276(4)	−0.094(4)
H(4′)	−0.068(4)	0.421(4)	−0.147(5)
H(5′)	−0.144(3)	0.443(5)	−0.032(5)
H(6′)	−0.116(4)	0.318(5)	0.131(5)

results. A final Fourier-difference function was featureless. The principal programs used are as previously described.[37] Tables of the observed and calculated structure factors, thermal parameters, and least-squares planes are available as Supplementary Publication No. SUP 22886 (8 pp.).*

RESULTS AND DISCUSSION

Final positional parameters for $[Cu(bipyam)_2]$ are given in Table 1; Tables 2 and 3 contain the bond lengths and angles. The estimated standard deviations were derived from the inverse matrix in the course of least-

TABLE 2

Bond lengths and selected intermolecular distances (Å)

Cu–N(1)	1.952(2)	C(2)–C(3)	1.418(3)
		C(3)–C(4)	1.354(4)
Cu–N(1′)	1.955(2)	C(4)–C(5)	1.395(4)
		C(5)–C(6)	1.356(4)
N(1)–C(2)	1.377(3)	C(2′)–C(3′)	1.419(4)
N(1)–C(6)	1.358(3)	C(3′)–C(4′)	1.348(4)
N(1′)–C(2′)	1.370(3)	C(4′)–C(5′)	1.393(5)
N(1′)–C(6′)	1.367(4)	C(5′)–C(6′)	1.344(4)
N(2)–C(2)	1.335(3)		
N(2)–C(2′)	1.341(3)	C–H (mean)	0.92
N(2) · · · C(6)	3.377(4) [a]		
C(5) · · · C(3′)	3.441(4) [b]		

[a] $x, -y, z - \frac{1}{2}$. [b] $-x, -y, -z$.

squares refinement calculations. Figure 1 is a stereoview of the molecule. The complex consists of well separated, neutral molecules, with no unusually close intermolecular approaches, as shown in the molecular packing diagram, Figure 2. The closest intermolecular distance is 3.377 Å [N(2) · · · C(6)]. The copper environment is four-co-ordinated and pseudo-tetrahedral. This contrasts with the complexes of other transition metals; steric inter-

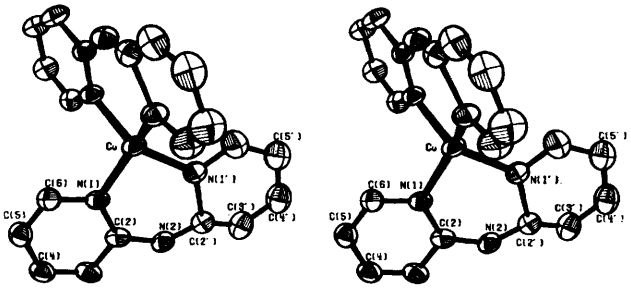

FIGURE 1 Stereoview of the $[Cu(bipyam)_2]$ molecule

actions prevent the possibility of the two bipyam ligands occupying the same plane. In the palladium(II) analogue, $[Pd(bipyam)_2]$, the steric constraints which impose a pseudo-tetrahedral copper(II) geometry in $[Cu(bipyam)_2]$ are insufficient to do the same to the

TABLE 3

Bond angles (°)

N(1)–Cu–N(1) *	101.42(12)	N(1)–C(2)–N(2)	125.4(2)
N(1)–Cu–N(1′)	93.63(8)	N(1)–C(2)–C(3)	117.5(2)
N(1)–Cu–N(1′) *	138.17(8)	N(2)–C(2)–C(3)	117.1(2)
		C(2)–C(3)–C(4)	122.1(2)
		C(3)–C(4)–C(5)	119.4(3)
N(1′)–Cu–N(1′) *	100.67(13)	C(4)–C(5)–C(6)	117.7(3)
Cu–N(1)–C(2)	123.7(2)	N(1)–C(6)–C(5)	124.4(2)
Cu–N(1)–C(6)	117.2(2)	N(1′)–C(2′)–C(5)	125.2(2)
C(2)–N(1)–C(6)	118.9(2)	N(1′)–C(2′)–C(3′)	117.9(2)
Cu–N(1′)–C(2′)	123.9(2)	N(2)–C(2′)–C(3′)	117.0(2)
Cu–N(1′)–C(6′)	117.8(2)	C(2′)–C(3′)–C(4′)	122.3(3)
C(2′)–N(1′)–C(6′)	118.0(2)	C(3′)–C(4′)–C(5′)	118.9(3)
C(2)–N(2)–C(2′)	127.9(2)	C(4′)–C(5′)–C(6′)	118.0(3)
		N(1′)–C(6′)–C(5′)	124.9(3)

* Position related by two-fold axis.

palladium atom: the large crystal-field stabilization of Pd^{II} enforces a planar metal environment so that gross distortion of the bipyam ligands is required to minimise the steric crowding. The steric problem is apparently avoided in the nickel(II) complex, because it is believed to

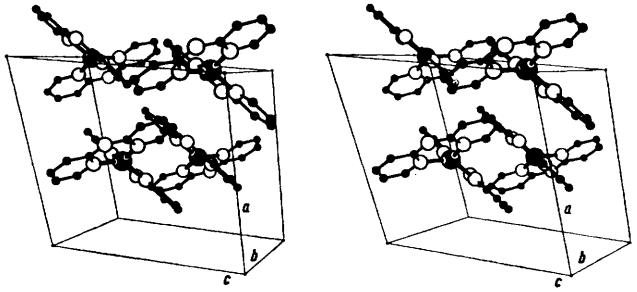

FIGURE 2 Molecular packing in the unit cell of $[Cu(bipyam)_2]$

be polymeric and octahedral, in which case the ligands would already be in different planes.

A convenient way to express the degree of distortion from planar towards tetrahedral geometry, or *vice versa*,

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

is in terms of the dihedral angle, ϕ, between the plane defined by the metal with the two donor atoms of one ligand, and the corresponding plane for the other ligand. Angles of 0 and 90° are then necessary, but not sufficient, conditions for regular square-planar and tetrahedral metal environments respectively. In $[Cu(bipyam)_2]$, $\phi = 58.8°$; the two-fold symmetry axis in the molecule makes the two ligands identical, and therefore ϕ is a good measure of the distortion in this complex.

The ϕ value of 58.8° may be compared with 57.4, 55.6, and 53.8° for $[Cu(bmpa)_2]$,[21] $[Cu(Hbipyam)_2][ClO_4]_2$,[31] and $[Cu(Hppa)_2][ClO_4]_2$ [39] respectively, where Hbmpa = bis(3-methyl-2-pyridyl)amine and Hppa = 2-pyridyl-2-pyrimidinylamine. Some limitations in the applicability of these ϕ values must be mentioned. The accuracy of the crystal structure of $[Cu(Hbipyam)_2][ClO_4]_2$ was limited ($R = 0.094$) by perchlorate disorder.[31] The complex $[Cu(bmpa)_2]$ is unique in this group in having no two-fold crystallographic symmetry axis, and the geometries of the two ligands and their relation to the copper atom are markedly different. Thus the angle ϕ alone is less adequate as an estimator of the degree of distortion in this complex.

Increasing distortion from perfect tetrahedral geometry towards square planar will cause an increase in the crystal-field splitting δ as well as a two-fold splitting of both the upper ^2E and lower $^2T_2$ states. This is well represented by operation on the d-orbital wavefunction with $l_z^2\delta$, corresponding to a flattening of the cube, four of whose vertices form the tetrahedron. In real complexes, especially when ligands behave differently as in $[Cu(bipyam)_2]$, the distortion is not uniaxial, and a further distortion operator $\varepsilon(l^2_+ + l^2_-)$ is needed to simulate the off-diagonal distortion. Now all the degeneracy is removed from the tetrahedral $^2T_2$ ground state, resulting in four d–d transitions which can, in principle, be used to evaluate Δ, δ, and ε provided accurate spectral data are available. For groups of complexes with related bidentate ligands, the parameters each change regularly with increasing distortion, and may be represented by a single parameter, ϕ, the dihedral angle. The value of ϕ gives a direct measure of the flattening of the tetrahedron, while the main off-axial distortion is in the intraligand N–Cu–N angles which should also vary regularly with ϕ.

Recently, Gouge and Geldard [20] proposed an assignment of the four spin-allowed ligand-field transitions in pseudo-tetrahedral bis(bidentate ligand)copper complexes related to $[Cu(bipyam)_2]$. The differences observed in the energies of the proposed d–d transitions suggest differences in ϕ in these complexes. It was proposed that the variation in ϕ correlates with the band positions of the d–d transitions.[20] This parallels the correlation observed between ϕ and the highest-energy d–d transition in tetrachlorocuprate anions with different cations and different copper(II) geometries.[12,40-43] For these anions, the energy of the highest d–d transition varies linearly with the dihedral angle. A similar relationship between band positions and the strengths of antiferromagnetic exchange interactions (J) in some binuclear copper(II) complexes has been explained in terms of the hypothesis that both J values and band energies are shifted by tetrahedral distortion.[44] This was subsequently confirmed by crystal-structure determination.[45-47] A similar trend, in the spectra of a series of N-substituted salicylaldimine and β-diketone complexes of copper(II),[48,49] and in a series of 5,5′-disubstituted bis(dipyrromethene)copper(II) complexes,[50] can be attributed to tetrahedral distortion induced by steric constraints. Figure 3 shows the splitting of the

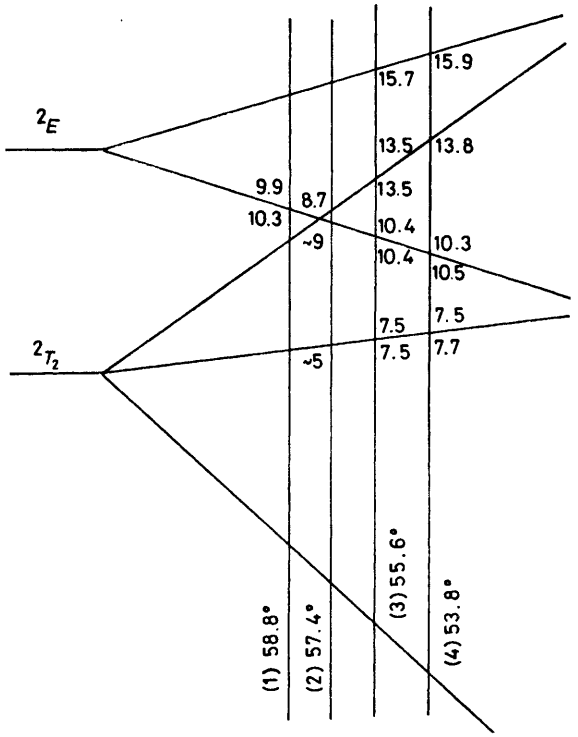

FIGURE 3 Schematic view of level splitting as a function of dihedral angle ϕ. Predicted and observed transition energies [20] in 10^3 cm^{-1}, above and below the lines respectively for the complexes (1) $[Cu(bipyam)_2]$, (2) $[Cu(bmpa)_2]$, (3) $[Cu(Hbipyam)_2][ClO_4]_2$, and (4) $[Cu(Hppa)_2][ClO_4]_2$; dihedral angles are given for (1)—(4)

tetrahedral $^2T_2$ ground state and the ^2E excited state with increasing flattening (decreasing ϕ) of the tetrahedron. The ϕ values and the postulated d–d transitions are indicated on this splitting diagram for four complexes of the CuN_4 series whose structures are now known. When the complexes are arranged in the order indicated by the ϕ values, the sequence is the same as that proposed from the spectra when the ϕ values were unknown.[20] Thus the spectral assignments that have been made are reasonable, and the general correlation suggested for the series appears to be borne out. The crystal structures for the compounds are clearly useful in calibrating literature spectral assignments in terms of the dihedral angles. The structural results are now also available for the calibration of e.s.r. g and $A_{\parallel}$ values, which also show a dependence on tetrahedral distortion of the

copper geometry in small molecules and in the presumed four-co-ordinated Type I ' blue ' copper protein sites.

Support received under an N.S.F. grant is gratefully acknowledged.

[9/1168 *Received*, 23*rd July*, 1979]

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