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The Structure of Bis-2,2',N,N' Bipyridylamine Copper(II) Chloride Tetra Hydrate

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The crystal and molecular structure of bis-2,2', N,N'-bipyridylamine copper(II) chloride tetrahydrate has been determined by three-dimensional X-ray analysis and refined by least-squares methods to conventional residuals of $R = 0.081$ *and* $R_w = 0.096$. *The lattice parameters are* $a = 12.556(6)$, $b = 28.002(7)$, $c = 6.997(4)$ Å *and* $\beta = 99.98(6)^\circ$. *The space group is* $P2_1/a$ *with four molecular units per unit cell. A total of 5049 unique data with* $|F_o| \geqslant 3\sigma F$ *were used in the structure determination. The copper ion is pentacoordinate with a chloride ion and two pyridyl nitrogen atoms from different bipyridylamine ligands occupying the equatorial positions of a distorted trigonal bipyramid. The remaining two pyridyl nitrogen atoms occupy the axial positions.*

Introduction

The somewhat flexible bipyridylamine molecule has been found to coordinate to transition metal ions in different coordination geometries [1–3]. For most d^9 complexes, exact octahedral coordination *via* three bipyridylamine ligands is unlikely because of distortions resulting from forces of the Jahn-Teller type. It is of interest to look at geometries of complexes containing chloride ligands along with bipyridylamine ligands to investigate differences between these and the above referenced complexes containing more bulky ions. This paper presents the results of the structure determination for one such complex and illustrates the relative flexibility of this ligand.

Synthesis

Reagent grade copper(II) chloride and bipyridylamine in 1:2 stoichiometric amounts were dissolved in water. Upon standing, dark green rectangular crystals of the title compound formed and were used for the structure determination without further treatment.

Structure Solution

The crystal chosen for the lattice constant determination and the intensity measurements was of rectangular shape with approximate dimensions of 0.15 × 0.15 × 0.25 mm. The air-stable crystal was mounted on a glass fiber with epoxy glue and placed on a four-circle automated diffractometer previously described [4]. The orientation matrix and lattice constant determinations were accomplished by the procedure described earlier [5]. The values for the lattice constants, obtained from the settings of nine high angle, centered reflections, are a = 12.556(6), b = 28.002(7), c = 6.997(4) Å, and β = 99.98(6)°. Oscillation photographs indicated monoclinic symmetry and the space group was subsequently determined to be $P2_1/a$. Monochromated molybdenum K_α radiation was used throughout all phases of the data collection process (λ = 0.70954 Å). Intensity data were collected at ambient temperature to a 2θ maximum of 50°. Only the data that satisfied the condition $|F_o| > 3\sigma F$ were considered observed. However it was noted that the intensities rapidly decreased with increasing theta and there were relatively few observed data above 2θ = 45°. Lorentz and polarization effects were adjusted for in the data reduction process. The effects of absorption were assumed to be negligible (μ = 12.0 cm^{-1} and transmission coefficients are estimated to vary by less than 10%). The standard deviation of a reflection was computed according to

$$\sigma_I = C_T + K_t C_B + (0.03C_T)^2 + (0.03C_B)^2$$

where C_T and C_B represent total and background counts and K_t is a counting time factor.

The copper atom was located from a sharpened Patterson map and the two chlorine atoms were

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TABLE I. Positional Parameters for the Non-Hydrogen Atoms ($\times 10^4$).

Atom	x	y	z
Cu	8581.5(7)[a]	1388.7(3)	3401.6(10)
Cl1	3548(2)	1384.8(9)	3749(4)
Cl2	9622(2)	1341(1)	6501(5)
N1	9447(5)	846(2)	2597(9)
C1	10482(6)	884(3)	2453(10)
C2	11128(7)	479(4)	2412(10)
C3	10694(8)	36(4)	2451(10)
C4	9601(8)	−9(3)	2555(10)
C5	9017(7)	402(3)	2620(10)
N3	10970(5)	1325(2)	2384(10)
C6	10528(6)	1761(3)	1765(10)
C7	11206(7)	2098(3)	1082(10)
C8	10784(8)	2528(3)	418(10)
C9	9706(8)	2624(3)	390(10)
C10	9097(7)	2281(3)	1112(10)
N2	9497(5)	1856(2)	1812(10)
N4	7338(5)	1253(2)	1204(9)
C11	6310(6)	1247(3)	1471(10)
C12	5453(7)	1077(3)	61(10)
C13	5715(8)	924(4)	−1685(10)
C14	6775(8)	948(4)	−2017(10)
C15	7541(6)	1114(3)	−548(10)
N6	6040(4)	1426(2)	3171(9)
N6	6559(6)	1808(3)	4226(10)
N5	7610(5)	1869(2)	4337(10)
C17	8063(6)	2260(3)	5294(10)
C18	7483(8)	2593(3)	6114(10)
C19	6392(7)	2522(3)	6038(10)
C20	5915(6)	2116(3)	5128(10)
O1	6293(6)	214(3)	3850(10)
O2	4043(6)	329(2)	2954(10)
O3	2665(7)	6209(3)	2467(10)
O4	1885(6)	5318(3)	930(10)

[a] In this and succeeding tables numbers in parentheses indicate standard deviations in the least significant figures.

located from the electron density map phased by the copper atom. The light atoms belonging to the bipyridylamine ligands were readily found and the oxygen atoms of the water molecules were located from a difference map computed from a model containing the other non-hydrogen atoms in the structure. Refinement was then carried out using a block diagonal least-squares procedure [6]. Anisotropic thermal parameters were used for all the non-hydrogen atoms and the quantity minimized was $\Sigma\omega(\|F_o| - |F_c\|)^2$. At this stage hydrogen atoms were included for the pyridyl rings assuming 1.00 Å C–H distances and 120° bond angles. The hydrogen atom positions were not refined. Atomic scattering factors for the non-hydrogen atoms were those of Hanson *et al.* [7]. Chlorine and copper scattering factors were modified using real and imaginary correction terms [8]. The hydrogen atom scattering factor terms were those of Stewart [9]. The final residual index after a full matrix least squares refinement cycle was $R = 0.081$ with the corresponding $R_w = 0.096$, where

$$R = \frac{\Sigma(\|F_o| - |F_c\|)}{\Sigma|F_o|}$$

and

$$R_w = \frac{\Sigma\omega(\|F_o| - |F_c\|)}{\Sigma\omega|F_o|}$$

The shift in any parameters after this cycle was less than one standard deviation.

Discussion

Atom positional parameters for the non-hydrogen atoms are given in Table I. The anisotropic thermal parameters and the positional parameters for the hydrogen atoms are given as supplementary material. Selected bond distances and angles for the complex are given in Table II. Although the geometry of the ligands about the copper does not closely fit any idealized geometry, it can be best treated as a distorted trigonal bipyramid with the chlorine atom (Cl2) occupying an equatorial position and N2 and N4, the two nitrogen atoms from different bipyridylamine ligands, occupying the remaining equatorial sites (Figs. 1 and 2). The axial nitrogen atoms (N1

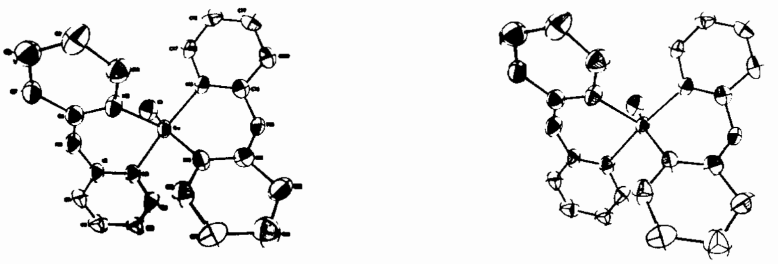

Fig. 1. A stereoscopic view of bis-2,2',N,N' bipyridylamine copper(II) chloride showing the non-hydrogen atoms using 50% probability ellipsoids.

TABLE II(a). Selected Bond Distances.

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Cu	C12	2.334(4)	C7	C8	1.36(1)
Cu	N1	2.004(6)	C8	C9	1.38(1)
Cu	N2	2.172(6)	C9	C10	1.38(1)
Cu	N4	2.028(6)	N4	C11	1.34(1)
Cu	N5	2.001(6)	N4	C15	1.352(9)
N1	C1	1.32(1)	C11	N6	1.386(9)
N1	C5	1.36(1)	C11	C12	1.41(1)
C1	C2	1.40(1)	C12	C13	1.39(1)
C1	N3	1.38(1)	C13	C14	1.39(1)
C2	C3	1.356(15)	C14	C15	1.36(1)
C3	C4	1.39(1)	N6	C16	1.40(1)
C4	C5	1.37(1)	N5	C16	1.32(1)
N3	C6	1.38(1)	N5	C17	1.36(1)
N2	C6	1.33(1)	C16	C20	1.40(1)
N2	C10	1.35(1)	C20	C19	1.39(1)
C6	C7	1.41(1)	C19	C18	1.38(1)
			C18	C17	1.37(1)

TABLE II (b). Selected Bond Angles.

Atom 1	Atom 2	Atom 3	Angle °	Atom 1	Atom 2	Atom 3	Angle °
Cl2	Cu	N1	88.5(2)	N2	C10	C9	123.5(8)
Cl2	Cu	N2	104.4(2)	C6	C7	C8	119.0(8)
Cl2	Cu	N4	158.0(2)	C7	C8	C9	120.0(8)
Cl2	Cu	N5	90.5(2)	C8	C9	C10	117.8(8)
N1	Cu	N2	87.2(2)	C6	N2	C10	118.1(7)
N1	Cu	N4	91.7(2)	N4	C11	N6	120.1(6)
N1	Cu	N5	173.0(2)	N4	C11	C12	123.0(6)
N2	Cu	N4	97.5(2)	N6	C11	C12	116.9(6)
N2	Cu	N5	99.7(2)	C11	C12	C13	116.9(8)
N4	Cu	N5	86.6(2)	C12	C13	C14	120.7(8)
Cu	N1	C1	123.3(5)	C13	C14	C15	117.5(7)
Cu	N1	C5	117.0(5)	N4	C15	C14	124.2(7)
Cu	N2	C6	119.8(5)	C11	N4	C15	117.5(6)
Cu	N2	C10	121.4(5)	N6	C16	N5	120.1(7)
Cu	N4	C11	122.1(5)	N6	C16	C20	117.2(6)
Cu	N4	C15	120.0(5)	N5	C16	C20	122.8(7)
Cu	N5	C16	123.6(5)	N5	C17	C18	123.3(7)
Cu	N5	C17	118.5(5)	C16	N5	C17	117.6(6)
N1	C1	C2	121.3(8)	C17	C18	C19	118.9(8)
N1	C1	N3	121.3(7)	C18	C19	C20	119.0(7)
C2	C1	N3	117.4(7)	C19	C20	C16	118.2(7)
C1	N1	C5	118.1(7)				
C1	C2	C3	120.2(8)				
C2	C3	C4	119.2(9)				
C3	C4	C5	117.6(8)				
C4	C5	N1	123.6(8)				
N2	C6	N3	120.7(7)				
N3	C6	C7	117.8(7)				
N2	C6	C7	121.5(7)				

and N5) are tipped slightly toward the equatorial nitrogen atom of the molecule to which each is connected. The average N–N distance between pyridyl nitrogen atoms within a molecule is 2.824(9) Å which agrees with the 2.80 Å distance reported for the similar structure di[iodobis-(2,2′-bipyridylamine)]

TABLE III. Least Squares Planes.

Plane 1 (plane determined by atoms N1, C1, C2, C3, C4, C5)

$0.05666\ X - 0.00076\ Y + 0.99839\ Z - 2.4279 = 0$

Atom	Distance from LS plane (Å)
N1	0.0115
C1	−0.0132
C2	0.0060
C3	0.0026
C4	−0.0042
C5	−0.0027
amine nitrogen N2	−0.0264

Plane 2 (plane determined by atoms N3, C6, C7, C8, C9, C10)

$0.08249\ X + 0.38964\ Y + 0.91726\ Z - 4.12333 = 0$

Atom	Distance from LS plane (Å)
N3	0.0132
C6	−0.0132
C7	0.0000
C8	0.0126
C9	−0.0125
C10	−0.0002
amine nitrogen N2	−0.0585

Plane 3 (plane determined by atoms N4, C11, C12, C13, C14, C15)

$-0.08977\ X + 0.92935\ Y - 0.35812\ Z - 2.1711 = 0$

Atom	Distance from LS plane (Å)
N4	−0.0207
C11	0.0152
C12	0.0025
C13	−0.0144
C14	0.0088
C15	0.0086
amine nitrogen N6	0.1109

Plane 4 (plane determined by atoms N5, C16, C17, C18, C19, C20)

$0.03825\ X - 0.51760\ Y + 0.85476\ Z - 0.18817 = 0$

Atom	Distance from LS plane (Å)
N5	0.0023
C16	−0.0240
C17	0.0172
C18	−0.0138
C19	−0.0075
C20	0.0258
amine nitrogen N6	−0.1117

Plane 5 (plane determined by atoms Cu, C12, N2, N4)

$-0.54815\ X + 0.78772\ Y + 0.28111\ Z + 1.96822 = 0$

Atom	Distance from LS plane (Å)
Cu	0.0023
C12	−0.0040
N2	−0.0016
N4	−0.0045

copper(II) iodide perchlorate [2]. The copper–chlorine bond length (2.334(4) Å) is almost midway between the equatorial distance (2.391(1) Å) and the axial distance (2.296(1) Å) found in the regular trigonal bipyramid structure of $CuCl_5^{3-}$ [10]. This is likely due to an inherent difference in bonding in a complex where the metal ion is attached to five ionic ligands and one where the metal ion is attached to one ionic ligand and two-bidentate, neutral molecules.

Although the Cu–Cl distance is a reasonable one, the N–Cu–C equatorial angles as found were certainly unexpected. With a N–Cu–N angle in this plane of 97.5°, one might expect angles of ~131° for those equatorial angles involving chlorine; instead angles of 104.4 and 158° were found. The reason for such a difference is difficult to assess. Although it could be due to crystal packing forces or hydrogen bonding effects, nearest neighbor contacts do not seem to support such a large deviation. It is also interesting to note that in the di[iodobis(2,2′-bipyridylamine)] copper(II) iodine perchlorate complex, as illustrated in Fig. 3, such distortions were also found, albeit to a lesser degree than in the present study. The occurrence of a smaller displacement in the iodide case would be commensurate with the latter's larger radius however. It is interesting to speculate that the angular differences that have been observed could be due to allow energy barrier for distortion between trigonal bipyramidal and square pyramidal geometry [11, 12].

The greater flexibility of the bipyridylamine ligand as compared to the bipyridyl ligand results in a wider variety of possible coordination geometries.

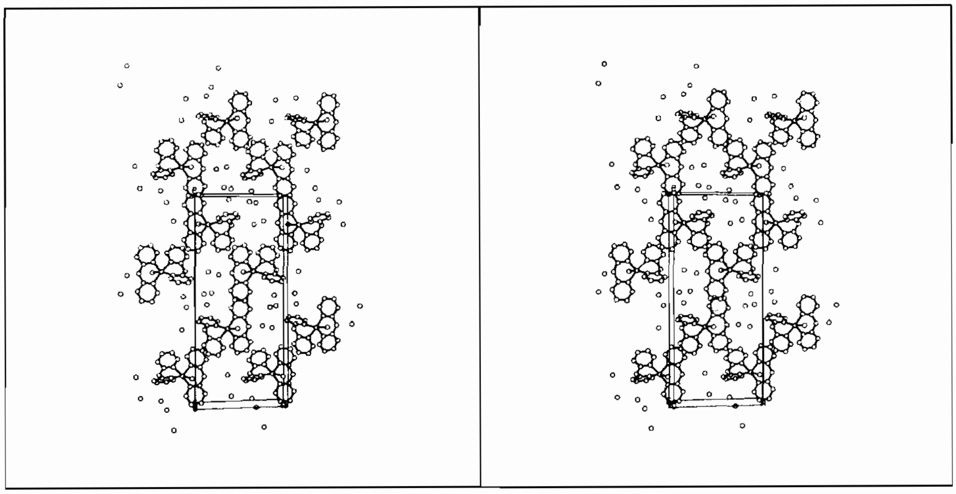

Fig. 2. A stereoscopic view of the unit cell.

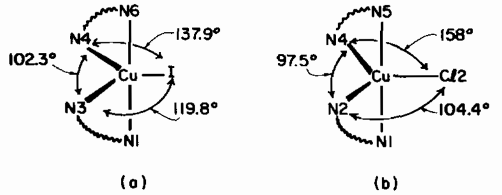

Fig. 3. Equatorial ligand–metal–ligand angles in (a) di[idobis(2,2′-bipyridylamine)] copper(II) iodide perchlorate and (b) this work.

Structures which contain two bidentate ligands of the bipyridyl type commonly assume four or five coordinate geometries. Although steric interactions and Jahn-Teller distortions usually inhibit the formation of octahedral configurations in d^9 metal systems, there are a few cases where such geometries are found for the more flexible ligand systems. For example, the recently reported structure of bis-(O-tricyanoethyleneoate)bis(2,2′,N,N′-bipyridylamine) copper(II) [3] demonstrates that the bipyridylamine ligand can flex enough to allow a *trans* planar coordination. This can be accomplished by, among other things, a twist about the aliphatic amine nitrogen atom bonds.

The relative planarity of bipyridyl ligands has been demonstrated in a number of structures [13]. The largest deviation found of the two rings from a common plane is 10° with most exhibiting deviations of less than 5°. As would be expected, the deviation from relative planarity can be much greater in the bipyridylamine system. As is indicated in Tables III and IV, for a typical series of bipyridylamine complexes, the deviation from planarity can range from 9 to 42°, as compared to 23° found for bipyridylamine itself in the solid state.

TABLE IV. Least Squares Plane Angles in Selected Bipyridylamine Complexes.

Compound	Angles Between Planes	Approximate Symmetry[a]	Reference
Bis-Bipyridylamine Copper(II) Chloride	23° 37½°	D3h	this work
Bis-Bipyridylamine Copper(II)	41.41°	O_h	3
Di[idobis-(2,2′-bipyridylamine)]Copper(II) Iodide Perchlorate	33° 37°	D3h	2
Bis-Bipyridylamine Copper(II) Perchlorate	9.8°	Td	1
Bis-Bipyridylamine Palladium(II)	38.2°	D4h	14
Bipyridylamine	23°	–	15

[a] Refers to the symmetry about the metal atom assuming all ligands are equivalent.

TABLE V. Distances and Angles Indicative of Possible Hydrogen Bonding.

Atom 1	Atom 2	Distance (Å)
O1	O2	2.80
O2	O4	2.76
O3	O4	2.82
O4	O1′	2.73

Atom 1	Atom 2	Atom 3	Angle (°)
O1	O2	O4	117
O2	O4	O3	115
O2	O4	O1′	128
O3	O4	O1′	109
O2	O1	O4′	107

Although the hydrogens on the water molecules were not explicitly located, an examination of the distances and angles involving the water oxygens (Table V) indicates appreciable hydrogen bonding is likely.

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