Structural Studies in Metal–Purpurate Complexes. Part 9.[1] Crystal Structure of Bis(purpurato)copper(II) 'Octahydrate' *

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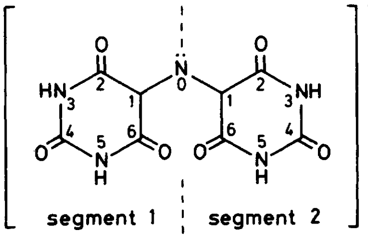
The crystal structure of a new hydrate phase of bis(purpurato)copper(II), $CuL_2 \cdot \approx 7.6H_2O$ (L = purpurate, $C_8H_4N_5O_6^-$), has been determined by single-crystal *X*-ray diffraction methods at 295 K, being refined by least squares to a residual of 0.052 for 2 124 'observed' reflections. Crystals are triclinic, space group $P\bar{1}$, with a = 12.187(4), b = 11.889(5), c = 10.447(3) Å, α = 73.57(3), β = 83.72(3), γ = 75.09(2)°, and Z = 2. Each of the purpurate ligands is symmetrically co-ordinated to the copper atom in a tridentate manner, but in consequence of Jahn–Teller distortion, considerable differences are found between them; for one ligand Cu–N is 1.973(6) and Cu–O 2.023(7), 2.029(7) Å, while for the other, Cu–N is 2.021(5) and Cu–O 2.289(5), 2.303(5) Å.

In the previous papers in this series, the structural and bonding properties of a wide variety of crystalline metal–purpurate complexes have been explored in detail [' purpurate ' = $C_8H_4N_5O_6^-$ (= L), (I)].



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Among the complexes studied, bis(purpurato)-copper(II) pentahydrate, $CuL_2 \cdot 5H_2O$, was of considerable interest.[2] The complex was found to crystallize as pseudo-tetragonal capped blocks and was assigned to the orthorhombic space group *Fddd*; the copper atom occupied a site of symmetry *222* so that only one-half of one ligand, *i.e.* a quarter of the molecule, was crystallographically independent. The copper atom was found to have a highly anisotropic thermal ellipsoid, the anisotropy not being reflected in the ellipsoids of the neighbouring ligand atoms; attempts to refine the copper atom as a pair of independent sites in a lower symmetry space group were successful in lowering *R* significantly.

At the time, the existence of a different copper(II) purpurate phase, ' very fine elongated flakes,' was recorded, but our inability to obtain sufficiently large crystals of this complex, hampered in handling also by its ready efflorescence, precluded further studies in this system. Recently, we have been successful in capturing in a capillary a crystal of the complex of sufficient size to enable a structure solution to be obtained; the result is of interest in the context of the above anomaly and in regard to the nature of the Jahn–Teller effect in complexes of symmetrical oligodentate ligand systems and is reported in this paper.

EXPERIMENTAL

Crystal Data.—$C_{16}H_8CuN_{10}O_{12} \cdot 7.6H_2O$, M = 725.2, Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 12.187(4), b = 11.889(5), c = 10.447(3) Å, α = 73.57(3), β = 83.72(3), γ = 75.09(2)°, U = 1 401.9(9) Å^3, D_c = 1.72 g cm^{-3}, (Z = 2), $F(000)$ = 750, monochromatic Mo-K_α radiation, λ = 0.7106$_9$ Å, μ = 8.8 cm^{-1}, specimen size: 0.45 × 0.18 × 0.04 mm, T = 295 K.

Structure Determination.—A unique data set was measured using a Syntex $P2_1$ four-circle diffractometer in a conventional θ—2θ scan mode yielding 3 697 independent reflections within the limit $2\theta < 45°$; of these 2 124 with $I > 3\sigma(I)$ were considered ' observed ' and used in the least-squares refinement after absorption correction and solution of the structure by the heavy-atom method. 9 × 9 Block-diagonal least squares was used; anisotropic thermal parameters were refined for the non-hydrogen atoms. For one of the water molecules, refinement of the population led to a value significantly less than 1; although U_{ij} for some of the others was very high, the population refined to near unity and was held as such in the final cycles. Hydrogen atoms were located for the water molecules in difference maps and constrained at fixed positions with $U_H = 1.5\ U_{ii}$ (parent O); ligand hydrogens were located geometrically and constrained at $U_H = 1.25\ U_{ii}$ (parent atom). At convergence, R and R' were 0.052 and 0.059, reflection weights being $[\sigma^2(F_o) + 0.0005\ (F_o)^2]^{-1}$. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[3] Computation was carried out using the ' *X*-RAY '76 ' program system,[4] implemented on a Perkin-Elmer 3240 computer. Material deposited as Supplementary Publication No. SUP 23204 (15 pp.) † comprises structure-factor amplitudes, thermal parameters, and hydrogen parameters. Atom numbering for ligands ' a ', ' b ' follows that defined previously (see above). Non-hydrogen atom co-ordinates are given in Table 1.

RESULTS AND DISCUSSION

The structure determination establishes the complex to be a hydrate of bis(purpurato)copper(II); the complex species present comprises copper co-ordinated by a pair of purpurate ligands with no water molecules in the

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* Purpuric acid is 5-(hexahydro-2,4,6-trioxo-5-pyrimidinylimino)pyrimidine-2,4,6-($1H$,$3H$,$5H$)-trione.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 1

Non-hydrogen atom co-ordinates

	Ligand ' a '			Ligand ' b '		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
N(0)	0.066 5(5)	0.222 2(6)	0.234 0(6)	0.396 3(5)	0.056 2(5)	0.245 0(6)
C(11)	0.029 0(6)	0.268 7(7)	0.337 3(7)	0.427 8(5)	−0.041 2(6)	0.345 3(7)
C(12)	0.119 5(6)	0.263 6(7)	0.420 5(8)	0.334 4(6)	−0.089 3(7)	0.421 0(8)
O(12)	0.221 9(4)	0.216 1(5)	0.392 0(5)	0.234 1(4)	−0.045 1(5)	0.389 7(6)
N(13)	0.092 4(5)	0.310 2(6)	0.525 0(6)	0.362 6(5)	−0.188 6(6)	0.526 7(6)
C(14)	−0.018 3(6)	0.364 4(8)	0.560 5(8)	0.469 2(6)	−0.236 2(8)	0.576 7(8)
O(14)	−0.036 4(5)	0.414 0(6)	0.650 8(6)	0.487 7(5)	−0.320 6(6)	0.678 2(7)
N(15)	−0.102 6(5)	0.354 4(6)	0.490 7(6)	0.552 9(5)	−0.181 2(6)	0.510 3(6)
C(16)	−0.088 6(6)	0.301 3(7)	0.387 7(8)	0.539 8(6)	−0.081 6(6)	0.400 2(7)
O(16)	−0.168 9(4)	0.276 7(5)	0.348 1(5)	0.617 0(4)	−0.030 0(5)	0.365 3(5)
C(21)	0.017 2(6)	0.219 6(7)	0.127 5(7)	0.461 2(6)	0.105 9(7)	0.145 1(7)
C(22)	0.090 7(6)	0.138 5(7)	0.053 9(8)	0.408 3(6)	0.229 1(7)	0.067 0(8)
O(22)	0.190 3(4)	0.085 1(5)	0.087 0(5)	0.311 9(4)	0.282 6(5)	0.096 5(6)
N(23)	0.047 8(5)	0.123 5(6)	−0.052 0(7)	0.471 3(6)	0.279 8(6)	−0.036 2(8)
C(24)	−0.060 3(7)	0.185 0(8)	−0.099 1(8)	0.573 9(8)	0.223 2(9)	−0.082 5(12)
O(24)	−0.096 1(5)	0.164 3(6)	−0.192 8(7)	0.621 5(7)	0.273 5(8)	−0.181 1(11)
N(25)	−0.121 1(5)	0.271 0(6)	−0.038 0(7)	0.618 6(5)	0.107 1(6)	−0.013 3(7)
C(26)	−0.087 0(6)	0.299 5(7)	0.067 2(8)	0.566 8(6)	0.038 3(7)	0.094 4(8)
O(26)	−0.136 4(4)	0.392 3(5)	0.099 5(6)	0.605 0(4)	−0.069 7(5)	0.132 5(5)
Cu	0.229 09(8)	0.138 97(10)	0.240 73(11)			
Water molecule oxygen atoms						
O(1)	0.822 9(5)	0.023 0(6)	0.211 3(6)			
O(2)	0.745 3(5)	0.713 1(6)	0.292 7(7)			
O(3)	−0.005 1(5)	0.949 1(6)	0.398 4(7)			
O(4)	0.903 2(7)	0.605 0(7)	0.129 2(8)			
O(5)	0.323 1(7)	0.560 6(9)	0.415 9(9)			
O(6)	0.626 1(7)	0.485 2(8)	0.167 7(13)			
O(7)	0.284 8(12)	0.515 2(10)	0.170 2(15)			
O(8)	0.560 1(15)	0.590 1(15)	0.385 4(16)	[population: 0.60(2)]		

primary co-ordination sphere. The complex species contains no crystallographically imposed symmetry elements, and together with the solvent molecules makes up the asymmetric unit. The number of solvent molecules in question is not precisely integral; thermal motion on some is very high and the population of one has refined to less than unity. In view of the mounting of a wet crystal in the capillary and the stability of the standard reflections during data collection, it appears unlikely that the non-stoicheiometry of the hydration is a consequence of ' decomposition,' *i.e.* loss of solvent. The degree of hydration accordingly is assigned as ' about 7 + 0.6 '. None of the water atoms co-ordinates to the copper (Figure 1).

While the molecule possesses no crystallographically imposed symmetry, nevertheless its internal geometry corresponds quite well to an internal symmetry of *2*, the two-fold axis passing through the copper atom and the central nitrogen atom of each ligand; the symmetry about the copper atom might be regarded as slightly higher, being ' *mm* '. Within each ligand the internal geometry and that involving the metal is consistent between each half; however, the two ligands differ considerably in their individual mode of interaction with the metal, ligand ' a ' being much more tightly bound than ligand ' b '. In consequence, the geometry of ligand ' b ', differing most significantly from that of ' a ' in terms of the angles about the co-ordinating atoms, more nearly resembles that of the free ion than that of ligand ' a ' in some respects (see below) (Table 2).

Whereas copper(II) environments have been well studied in an environment of unidentate ligands, in the context of which the usual ' square-planar ' geometry is found, with any contacts in the remaining two ' octahedral ' co-ordination sites being usually long and quite diverse, studies of symmetrical systems involving two tridentate or three bidentate symmetrical ligands, where the potential exists for six-co-ordination, are relatively few. In the tris(bidentate) situation, structure determinations have been carried out on the tris(ethane-1,2-diamine)-,[5] tris(2,2′-bipyridyl)-, and tris(1,10-phenanthroline)-copper(II) [6] systems, all cases exhibiting the presence of two long Cu–N bonds *trans* to each other. In the bis(tridentate) situation, the structure of bis(2,2′:6′,2″-terpyridyl)copper(II) nitrate has been examined.[7] The copper atom lies on a crystallographic two-fold symmetry axis as do the central nitrogen atoms of the tridentate ligands. The Cu–N (central) distances differ slightly, being 1.965(5) and 2.012(5) Å. The Cu–N (distal) distances of the second ligand are longer than those of the first, being 2.228(4), *cf.* 2.085(4) Å. The copper atom co-ordination environment is thus pseudo-square planar with in-plane Cu–N distances ranging from 1.965(5) to 2.085(4) Å, while the long Cu–N bonds ' *trans* ' to each other are 2.228(4) Å. The two ligands are thus inequivalent, one being much more tightly bound than the other.

The results of the previous study of the pentahydrate of bis(purpurato)copper(II) have been outlined above; with a pair of equivalent ligands disposed about a copper

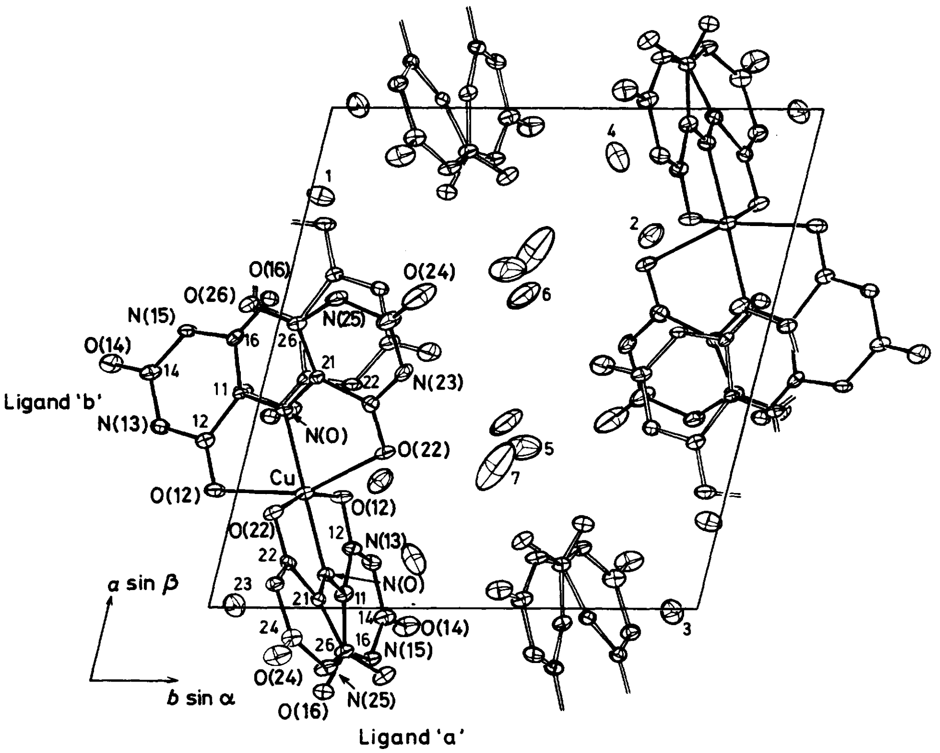


FIGURE 1 Unit-cell contents projected down *c*; thermal ellipsoids are shown at the 20% level for the non-hydrogen atoms. Section labelling for the ligands is given and the fully populated water oxygen atoms are included, labelled 1—7

TABLE 2

Ligand geometries

Segment *n*	Ligand a		Ligand b		'Free' ligand
	1	2	1	2	
(*a*) Distances/Å					
N(0)–C(*n*1)	1.334(11)	1.333(11)	1.326(8)	1.332(9)	1.33_0
C(*n*1)–C(*n*2)	1.456(12)	1.465(11)	1.460(10)	1.477(10)	1.45_8
C(*n*1)–C(*n*6)	1.465(10)	1.458(10)	1.449(10)	1.464(10)	1.45_4
C(*n*2)–O(*n*2)	1.272(8)	1.252(8)	1.240(9)	1.236(9)	1.23_1
C(*n*6)–O(*n*6)	1.232(11)	1.232(10)	1.220(10)	1.211(9)	1.22_8
C(*n*2)–N(*n*3)	1.333(11)	1.348(12)	1.367(9)	1.343(10)	1.38_1
C(*n*6)–N(*n*5)	1.369(12)	1.371(13)	1.387(9)	1.386(10)	1.39_4
N(*n*3)–C(*n*4)	1.397(9)	1.399(10)	1.372(10)	1.368(12)	1.35_9
N(*n*5)–C(*n*4)	1.370(12)	1.371(11)	1.370(10)	1.364(11)	1.36_1
C(*n*4)–O(*n*4)	1.220(12)	1.222(13)	1.232(9)	1.206(14)	1.23_0
O(16) · · · O(26)	2.614(7)		2.632(9)		2.62_2
(*b*) Angles/°					
C(11)–N(0)–C(21)	133.5(6)		128.0(6)		$128._3$
N(0)–C(*n*1)–C(*n*2)	113.4(6)	112.2(6)	114.7(6)	115.3(6)	$114._4$
N(0)–C(*n*1)–C(*n*6)	127.6(8)	128.2(7)	124.1(7)	123.8(6)	$126._4$
C(*n*1)–C(*n*2)–O(*n*2)	119.8(8)	121.7(8)	122.2(6)	121.5(7)	$125._7$
C(*n*1)–C(*n*6)–O(*n*6)	123.7(8)	123.1(9)	125.7(6)	125.5(7)	$125._3$
O(*n*2)–C(*n*2)–N(*n*3)	121.5(7)	120.6(7)	120.9(7)	122.2(6)	$117._8$
O(*n*6)–C(*n*6)–N(*n*5)	121.4(7)	121.3(7)	119.1(6)	120.2(7)	$118._5$
C(*n*1)–C(*n*2)–N(*n*3)	118.7(6)	117.7(6)	116.9(6)	116.3(6)	$116._3$
C(*n*1)–C(*n*6)–N(*n*5)	114.7(7)	115.3(7)	114.8(6)	114.1(6)	$116._0$
C(*n*2)–N(*n*3)–C(*n*4)	124.0(7)	123.8(7)	124.8(7)	125.7(7)	$125._7$
C(*n*6)–N(*n*5)–C(*n*4)	126.7(6)	126.0(7)	126.5(7)	126.3(7)	$125._4$
N(*n*3)–C(*n*4)–O(*n*4)	120.8(8)	120.8(8)	121.8(7)	121.3(9)	$121._8$
N(*n*5)–C(*n*4)–O(*n*4)	123.5(7)	122.5(7)	121.9(7)	121.9(9)	$121._8$
N(*n*3)–C(*n*4)–N(*n*5)	115.7(8)	116.7(8)	116.2(6)	116.8(8)	$116._4$
C(*n*2)–C(*n*1)–C(*n*6)	117.9(7)	118.7(7)	119.4(6)	119.6(6)	$118._1$
Cu–N(0)–C(*n*1)	113.3(5)	113.2(5)	116.5(4)	115.6(4)	
Cu–O(*n*2)–C(*n*2)	110.5(6)	109.6(5)	106.7(5)	106.5(5)	

sited at ($\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$), Cu–N, O are 1.931(9), 2.421(6) Å respectively with the two ligands symmetrically chelated. With the copper allowed to refine away from $z = \frac{1}{8}$ to $z = 0.087\,0(13)$, Cu–N becomes 1.954(8) and Cu–O 2.246(8) and 2.621(10) Å, the two ligands now remaining symmetrically chelated, but becoming inequivalent in respect of their Cu–O distances (Figure 2). The dihedral angle between the planes of the two ligand halves is 47.7°; the copper atom deviations are 0.87 Å (ordered model) and 0.20, 0.51 Å (disordered model).

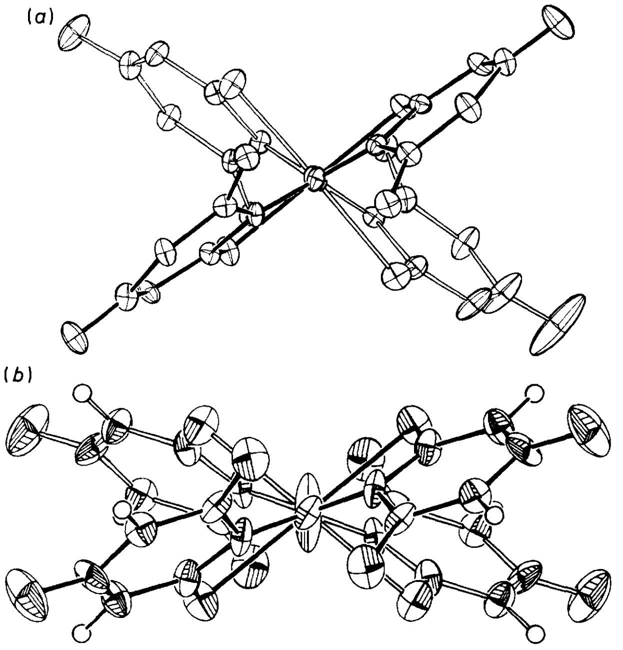
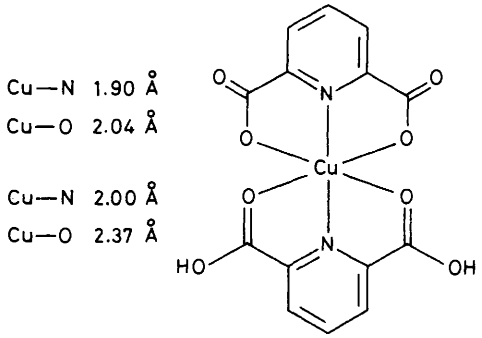


FIGURE 2 (*a*) A single molecule of the complex projected down the short Cu–N bond; (*b*) a similar projection for the complex molecule of the pentahydrate

In the present case, we find a situation more closely related to that of the bis(terpyridyl) species where the copper atom is surrounded by a pair of inequivalent tridentate ligands, one of which is more tightly bound than the other. For ligand 'a', the copper–nitrogen distance [1.973(6) Å] and copper–oxygen distances [2.023(7), 2.029(7) Å] lie in the usual range for copper bound to σ-bonding nitrogen and oxygen ligands (Table 3). The values associated with ligand 'b' are much longer [Cu–N 2.021(5); Cu–O 2.289(5), 2.303(5) Å]. The distortion of the environment about the copper atom from 2*mm* symmetry to, at best, *mm*, corresponds to that expected for a static 'Jahn–Teller' distortion imposed on an environment regarded as approximating potentially to octahedral symmetry. {A similar geometry involving inner nitrogen and outer oxygens in a tridentate ligand has been observed previously in the complex formed with the 'isoelectronic' ligand picolinate(1−), *i.e.* bis[pyridine-2,6-dicarboxylato(1−)]copper(II) trihydrate,[8] although in that case it has also been shown that the complex in reality is as shown below, with the less tightly bound of the two ligands being doubly protonated, so that the two ligands are inequivalent.}



Consideration of the geometry of the complex molecule observed in bis(purpurato)copper(II) pentahydrate shows that a pair of superimposed molecules with the present geometry does not provide a satisfactory model for the 'disorder' present in the pentahydrate. As we have already seen, the Cu–O distances are dissimilar while in the present compound, the dihedrals for the two ligands are 24.3 and 39.9°, with the copper atom deviations from each ligand half being 0.27, 0.30 (ligand a) and 0.70, 0.72 Å (ligand b) (Table 4). For the purpurate complexes studied, the above dihedral angle, θ, correlates quite well with the M–O distance, $r_{\text{M-O}}$. Figure 6 of ref. 9 plots these two variables for the 15 compounds of Table 5 of that reference; in that plot, point 10 for the 'ordered' copper pentahydrate complex is a distinct 'outlier.' The present pair of dihedral angles are in much better keeping with the general trend. It is also of interest to note that, whereas terpyridyl appears to be a relatively rigid tridentate ligand, with M–N (central) less than M–N (distal) in all complexes studied, the purpurate ligand is much more flexible: M–N can be much less than M–O as in the present compound (ligand 'a') or greater, as in the iron(II) complex (Fe–N,O 2.21, 2.10 Å), the variation in character being accom-

TABLE 3

Metal atom environment: *r* is Cu–N,O (Å); the other entries in the matrix are the angles (°) subtended at the copper atom by the two relevant ligand atoms

	r	O(a12)	O(a22)	N(b)	O(b12)	O(b22)
N(a)	1.973(6)	81.9(2)	82.3(3)	179.0(7)	104.4(2)	102.1(2)
O(a12)	2.023(7)		164.2(2)	98.2(2)	90.8(2)	91.8(2)
O(a22)	2.029(7)			97.6(2)	93.1(2)	91.5(2)
N(b)	2.021(5)				76.6(2)	76.9(2)
O(b12)	2.289(5)					153.5(2)
O(b22)	2.303(5)					

TABLE 4

Least-squares planes calculated through the C(*n*1,2,4,6)-N(*n*3,5) skeleton of each barbiturate segment (1, 2) of the two ligands (a, b) given in the form $pX + qY + rZ = s$, where the right-hand orthogonal Å frame (X, Y, Z) is defined with X parallel to a, Z in the ac plane. Atom deviations, δ, and σ (defining atoms) are in Å. The angle between the normals to the two barbiturate planes of each ligand is θ°

	Ligand ' a '		Ligand ' b '	
Segment *n*	1	2	1	2
10^4p	2 074	5 724	0 330	6 364
10^4q	9 023	6 979	6 285	3 204
10^4r	−3 780	−4 306	7 771	7 017
s	1.283	1.515	2.651	5.491
σ	0.07	0.06	0.04	0.04
δC(*n*1)	0.09	−0.09	−0.07	0.06
δC(*n*2)	−0.03	0.04	0.05	−0.04
δN(*n*3)	−0.04	0.03	−0.01	0.01
δC(*n*4)	0.06	−0.05	−0.01	0.00
δN(*n*5)	0.01	0.00	0.00	0.02
δC(*n*6)	−0.08	0.07	0.04	−0.05
δN(0)	0.13	−0.13	0.02	−0.03
δO(*n*2)	−0.12	0.18	0.18	−0.14
δO(*n*4)	0.15	−0.11	0.02	−0.03
δO(*n*6)	−0.37	0.36	0.28	−0.27
δCu	−0.27	0.30	0.70	−0.72
θ	24.3		39.9	

modated by changes in non-coplanarity of the two ligand halves.

A final point arises in regard to the thermal parameters of the complex molecule of the present structure. In the pentahydrate, very large thermal anisotropy was probably a foil for either disorder or a dynamic Jahn–Teller effect. In the present structure it is of interest that the more normal thermal ellipsoid of the copper atom nevertheless has a slightly greater amplitude and anisotropy than either of the co-ordinated nitrogen atoms; however, in this case, it appears unlikely that this is a consequence of disorder, since unlike the pentahydrate, in which the largest principal axis of the copper thermal tensor is not directed toward any co-ordinated atom, the largest principal axis of the ellipsoid in the present case lies directed approximately toward the feebly co-ordinated oxygen atoms of ligand ' b '.

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