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CRYSTAL STRUCTURE OF (ETHYLENEDIAMINE-TETRAACETATO)NICKEL(II) BIS(ETHYLENEDIAMINE)CUPRATE DIHYDRATE

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We report an x-ray structure analysis of $(\text{NiA})(\text{Cuen}_2) \cdot 2\text{H}_2\text{O}$ (diffractometer, λMo , 2807 reflections, heavy-atom method, anisotropic refinement, $R = 0.037$). The structure consists of $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ cations, $[(\text{NiA})_2\text{Cu}(\text{en})_2]^{2-}$ trinuclear anions, and water molecules. In the centrosymmetric cation the square coordination of the Cu atom by the 4N of two bidentate cyclic en ligands is expanded to tetragonal bipyramidal by two water molecules; $\text{Cu}-\text{H}_2\text{O}$ is 2.635 and $\text{Cu}-\text{N}$ 2.010 Å. In the anion the Cu atom lies at a center of symmetry and is bonded to two en ligands in the same way, while the Ni atom is octahedrally coordinated by the hexadentate A ligand; one of its carboxylate O atoms bonded to Ni expands the square coordination of Cu to octahedral; $\text{Cu}-\text{O}_{\text{br}}$ is 2.376 Å, i.e., the bridging oxygens join the apices of the octahedra into a trinuclear associate; $\text{Cu}-\text{O}-\text{Ni}$ is 118° , the average $\text{Cu}-\text{N}$ distances are 2.040, $\text{Ni}-\text{N}$ 2.075, and $\text{Ni}-\text{O}$ 2.055 Å. The anions are linked by a system of hydrogen bonds involving a water molecule.

At the present time there is much interest in mixed polynuclear complexes derived from universal complexing reagents (complexons). The structures of single crystals of such compounds have not been examined.

Here we report an x-ray structure analysis of the complex $(\text{NiA})(\text{Cuen}_2) \cdot 2\text{H}_2\text{O}$ (I), where A is ethylenediaminetetraacetate $[\text{C}_2\text{H}_4\text{N}_2(\text{CH}_2\text{COO})_4]^{4-}$ and en is ethylenediamine, which we synthesized by reaction of basic nickel and copper carbonates with ethylenediaminetetraacetic acid followed by addition of ethylenediamine.

The literature has nothing on the interactions of $(\text{Men}_2)^{2+}$ and $(\text{MA})^{2-}$ ions.

EXPERIMENTAL AND STRUCTURE SOLUTION

The monoclinic crystals of $\text{NiCuC}_{14}\text{H}_{28}\text{O}_8\text{N}_6 \cdot 2\text{H}_2\text{O}$ had $a = 8.468(1)$, $b = 21.752(2)$, $c = 12.598(1)$ Å, $\beta = 104.79(1)^\circ$, $V = 2243.7$ Å³, $M = 566.7$, $d_{\text{calc}} = 1.677$ g/cm³, $Z = 4$, space group $\text{P}2_1/c$.

We used a single crystal of dimensions $0.14 \times 0.30 \times 0.75$ mm and a CAD4-SDP-t55 automatic system ($\lambda\text{Mo K}\alpha$, graphite monochromator, ω scan, $\Delta\omega = 0.70 + 0.35 \tan \theta$, measurable counter aperture $\text{APT} = 1.00 + 0.70 \tan \theta$, the variable absorption was compensated by making corrections for the acicular shape of the crystal with automatically chosen optimum azimuthal angles ψ). We collected 4204 reflections in the

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TABLE 1. Coordinates of Nonhydrogen Atoms ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
Cu(1)	1/2	0	1/2	C(1)	7809(20)	378(7)	4348(13)
Cu(2)	0	1/2	1/2	C(2)	6633(18)	879(7)	3927(13)
Ni	3057(2)	1450(7)	5751(1)	C(3)	2734(18)	4662(7)	4210(13)
O(1)	4806(9)	786(4)	6269(6)	C(4)	2042(18)	4069(7)	4537(14)
O(2)	6233(9)	407(4)	7843(7)	C(5)	3604(21)	2390(6)	7334(10)
O(3)	4314(9)	1894(4)	4800(6)	C(6)	2431(19)	2661(6)	6314(10)
O(4)	6334(8)	2552(5)	4873(8)	C(7)	5288(20)	1438(6)	7848(9)
O(5)	1420(10)	1209(4)	4288(7)	C(8)	5478(14)	830(6)	7285(10)
O(6)	-435(9)	1685(6)	2861(8)	C(9)	5942(14)	2191(6)	6575(10)
O(7)	1693(11)	1042(4)	5688(7)	C(10)	5488(11)	2225(6)	5315(10)
O(8)	-758(11)	1100(5)	7025(8)	C(11)	805(17)	2277(6)	4477(10)
O(W1)	1755(14)	6438(5)	4272(8)	C(12)	657(17)	1673(7)	3812(10)
O(W2)	1105(20)	4506(6)	6959(10)	C(13)	107(13)	1950(6)	6175(11)
N(1)	7467(12)	112(5)	5341(9)	C(14)	371(20)	1310(6)	6661(9)
N(2)	4939(11)	646(5)	3813(9)				
N(3)	2272(13)	5166(5)	4859(9)				
N(4)	265(10)	4162(5)	4392(9)				
N(5)	4646(12)	1919(4)	7026(8)				
N(6)	1414(10)	2165(5)	5665(8)				

TABLE 2. Coordinates of Hydrogen Atoms ($\times 10^3$)

Atom	x	y	z	Atom	x	y	z
H(1)O(W1)	179(7)	674(3)	467(4)	H(1)C(3)	234(6)	475(2)	343(4)
H(2)O(W1)	123(7)	644(3)	345(4)	H(2)C(3)	400(7)	456(3)	445(4)
H(1)O(W2)	30(7)	475(3)	713(4)	H(1)C(4)	263(7)	401(3)	536(4)
H(2)O(W2)	111(7)	416(3)	750(4)	H(2)C(4)	224(7)	369(3)	410(4)
H(1)N(1)	783(7)	44(2)	598(4)	H(1)C(5)	307(7)	219(3)	780(4)
H(2)N(1)	794(6)	-19(2)	561(4)	H(2)C(5)	419(7)	273(3)	784(4)
H(1)N(2)	437(7)	100(2)	397(4)	H(1)C(6)	175(7)	296(3)	654(4)
H(2)N(2)	460(7)	44(3)	325(4)	H(2)C(6)	300(7)	285(3)	584(4)
H(1)N(3)	297(7)	522(3)	566(4)	H(1)C(7)	449(7)	139(2)	833(4)
H(2)N(3)	227(7)	557(3)	452(4)	H(2)C(7)	608(7)	152(3)	824(4)
H(1)N(4)	-33(7)	423(3)	362(4)	H(1)C(9)	696(7)	192(3)	675(4)
H(2)N(4)	-8(7)	391(3)	480(5)	H(2)C(9)	618(7)	262(3)	684(4)
H(1)C(1)	775(7)	-1(3)	375(4)	H(1)C(11)	160(7)	257(3)	427(4)
H(2)C(1)	877(7)	56(3)	448(4)	H(2)C(11)	-19(7)	245(3)	431(4)
H(1)C(2)	664(7)	103(3)	325(4)	H(1)C(13)	-83(7)	194(3)	564(4)
H(2)C(2)	682(7)	123(3)	451(4)	H(2)C(13)	0(7)	227(3)	674(4)

range $\theta \leq 25^\circ$, 2807 of which had $I > 3\sigma$. Intensity data were processed and structure calculations were carried out with the ENX-SDP system on a PDP-11/t55 minicomputer.

We solved the structure by the heavy-atom method and refined it in the isotropic approximation with the weighting scheme $w_1 = 1/\sigma(F_1^2)$, and then in the anisotropic approximation. We then located all 32 hydrogen atoms by difference synthesis. We refined the positions of the nonhydrogen atoms in five full-matrix anisotropic cycles and then carried out three cycles of refinement of the coordinates of the hydrogen atoms with fixed thermal parameter $B_{\text{iso}} = 5 \text{ \AA}^2$. The final $R = 0.037$, $R_w = 0.040$, with extinction coefficient $E = 4.0 \times 10^{-8}$.

The coordinates of the nonhydrogen atoms and the hydrogen atoms are collected in Tables 1 and 2.* Bond lengths and angles appear in Tables 3 and 4. The O-H, N-H, and C-H interatomic distances are in the range 0.74-1.12 Å ($\delta \approx 0.04 \text{ \AA}$) and the bond angles involving hydrogen atoms in the range 98.6-120° ($\delta \approx 2.0^\circ$).

* Tables of the thermal factors can be obtained from the authors.

TABLE 3. Interatomic Distances d, Å

Bond	d	Bond	d
NiA		N(6)—C(6)	1,488(5)
Ni—O(1)	2,052(2)	C(5)—C(6)	1,528(5)
Ni—O(3)	2,038(2)	N(5) ... N(6)	2,884(4)
Ni—O(5)	2,070(2)	N(5) ... O(1)	2,658(3)
Ni—O(7)	2,053(3)	N(5) ... O(3)	2,747(3)
Ni—N(5)	2,080(3)	N(6) ... O(5)	2,708(4)
Ni—N(6)	2,070(3)	N(6) ... O(7)	2,743(4)
O(1)—C(8)	1,264(4)	Cu(en) ₂	
C(8)—C(7)	1,528(5)	Cu(1)—O(1)	2,376(2)
C(7)—N(5)	1,475(4)	Cu(1)—N(1)	2,037(3)
C(8)—O(2)	1,233(4)	Cu(1)—N(2)	2,044(3)
O(3)—C(10)	1,264(4)	N(1)—C(1)	1,473(5)
C(10)—C(9)	1,536(5)	C(1)—C(2)	1,481(6)
C(9)—N(5)	1,482(4)	C(2)—N(2)	1,493(5)
C(10)—O(4)	1,238(4)	Cu(2)—N(3)	2,009(3)
O(5)—C(12)	1,261(4)	Cu(2)—N(4)	2,011(3)
C(12)—C(11)	1,542(5)	Cu(2)—O(W2)	2,635(3)
C(10)—N(6)	1,474(4)	N(3)—C(3)	1,478(5)
C(5)—N(5)	1,467(4)	C(3)—C(4)	1,517(6)
C(12)—O(6)	1,221(4)	C(4)—N(4)	1,483(5)
O(7)—C(14)	1,254(4)	Ni ... Cu(1)	3,788(0)
C(14)—C(13)	1,515(5)	N(1) ... N(2)	2,745(4)
C(13)—N(6)	1,490(4)	N(3) ... N(4)	2,796(4)
C(14)—O(8)	1,248(4)		

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

In the structure of I the Ni atom, which lies in a general position, is octahedrally coordinated by 4O and 2N of the A ligand, forming the usual five five-membered chelate rings, four glycinate and one ethylenediamine (Fig. 1). The Cu(1) and Cu(2) atoms are crystallographically inequivalent and occupy two special positions, i.e., there are two systems of centers; both Cu atoms are coordinated by two en ligands forming two five-membered chelate rings. Thus four N atoms form a square plane around each Cu atom. The water molecules expand the square coordination of the Cu(2) atom to a highly elongated tetragonal bipyramid with a Cu(2)—O(W2) axial bond of 2.635 Å. The square of 4 N around Cu(1) is expanded to a tetragonal bipyramid by O(1) of one of the acetate groups of ligand A, which acts as a bridge linking the Ni and Cu polyhedra. It is noteworthy that the coordination of the Cu atom involves not the carbonyl but the carboxylate O atom of the acetate group bonded to Ni.

As a result trinuclear centrosymmetric associates consisting of the central Cu(1)(en)₂ complex and two outer NiA complexes are formed.

Hence the crystal consists of [Cu(2)(en)₂(H₂O)₂]²⁺ cations, [(NiA)₂Cu(1)(en)₂]²⁻ trinuclear anions, and water molecules; consequently, the structural formula of the compound should be written as [Cu(en)₂(H₂O)₂][NiA—Cu(en)₂—NiA] · 2H₂O.

In addition to the en ring E the NiA complex incorporates two G and two R glycinate rings (in terms of Hoard's symbolism [1]) (Fig. 1). The equatorial plane of the octahedron contains O(3), O(5), O(7), and N(5); their maximum deviation from the mean plane is 0.078 Å. The nickel atom lies 0.13 Å out of the plane. The axial positions are occupied by N(6) and O(1).

As we have mentioned, the O(1) atom bridges the Ni and Cu(1) atoms, and the three octahedra in the trinuclear anion are linked at their common apices O(1) and O(1)^b into a centrosymmetric associate. The Ni—O(1)—Cu(1) angle is 117.5°, while the dihedral angle between the equatorial planes of the Cu and Ni polyhedra is 46.8°; consequently, the associate has a zigzag shape with Ni...Cu(1) distance 3.788 Å.

Thus the A ligand has a twisted shape, coordinating on one metal atom through all six active atoms. In the two nickel complexes examined earlier — Ni(H₂A) · H₂O (II) [2] and Ni₃(HA)₂ · 10H₂O (III) [3] — A is a pentadentate ligand; one acetate group is not involved in coordination and the sixth site in the Ni octahedron is occupied by a water molecule.

In the structure of I three acetate groups are monodentate while the fourth bridges via a single atom. This mode of coordination is quite rare in complexes of A. In those A complexes that contain associates or chains of polyhedra of the same metal atom, the acetate group most often acts as a bidentate bridge by means of coordination by the O carbonyl atom, as for example in Zn₂A · 6H₂O [4], Cu₂A · 4H₂O [5], and Mn₃(HA)₂ · 10H₂O [6].

TABLE 4. Bond Angles ω (deg)

Angle	ω	Angle	ω
NiA			
O(1)NiO(3)	94,46(10)	NiO(4)C(8)	111,79(22)
O(1)NiN(5)	80,05(10)	O(1)C(8)C(7)	117,43(31)
O(1)NiN(6)	164,95(10)	O(1)C(8)O(2)	123,73(33)
O(1)NiO(7)	88,79(10)	C(7)C(8)O(2)	118,82(31)
O(1)NiO(5)	111,69(9)	C(8)C(7)N(5)	110,63(27)
O(3)NiN(5)	83,68(10)	NiN(5)C(7)	104,13(20)
O(3)NiN(6)	93,35(10)	NiO(3)C(10)	115,34(22)
O(3)NiO(7)	176,74(10)	O(3)C(10)C(9)	117,39(31)
O(3)NiO(5)	85,88(10)	O(3)C(10)O(4)	124,41(33)
O(5)NiN(5)	164,90(10)	C(9)C(10)O(4)	118,11(32)
O(5)NiO(7)	93,16(10)	C(10)C(9)N(5)	113,62(29)
O(5)NiN(6)	81,69(10)	NiN(5)C(9)	107,20(20)
O(7)NiN(5)	96,66(10)	NiO(5)C(12)	111,22(22)
O(7)NiN(6)	83,43(10)	O(5)C(12)C(11)	117,82(31)
N(5)NiN(6)	88,05(11)	O(5)C(12)O(6)	124,60(37)
NiN(5)C(5)	103,41(21)	C(11)C(12)O(6)	117,51(37)
N(5)C(5)C(6)	110,66(30)	C(12)C(11)N(6)	111,41(30)
C(5)C(6)N(6)	110,05(29)	NiN(6)C(11)	103,52(21)
NiN(6)C(6)	103,23(21)	NiO(7)C(14)	114,40(22)
C(5)N(5)C(7)	116,66(27)	O(7)C(14)C(13)	118,42(32)
C(5)N(5)C(9)	112,16(28)	O(7)C(14)O(8)	125,65(35)
C(7)N(5)C(9)	112,09(27)	C(13)C(14)O(8)	115,91(35)
C(6)N(6)C(13)	112,34(28)	C(14)C(13)N(6)	114,44(31)
C(6)N(6)C(11)	116,19(29)	NiN(6)C(13)	107,77(22)
C(11)N(6)C(13)	112,58(28)		
Cu(en) ₂			
Cu(1)O(1)Ni	117,45(10)	C(2)N(2)Cu(1)	108,58(24)
O(1)Cu(1)N(1)	90,86(10)	O(W2)Cu(2)N(4)	86,56(12)
O(1)Cu(1)N(2)	90,24(10)	N(3)Cu(2)N(4)	85,80(13)
N(1)Cu(1)N(2)	84,56(13)	Cu(2)N(3)C(3)	108,09(24)
Cu(1)N(1)C(1)	106,35(24)	N(3)C(3)C(4)	107,78(33)
N(1)C(1)C(2)	109,44(35)	C(3)C(4)N(4)	107,42(35)
C(1)C(2)N(2)	109,09(33)	Cu(2)N(4)C(4)	106,63(25)
O(W2)Cu(2)N(3)	87,88(12)		

In I the Ni-N distances are 2.080 and 2.070 Å, i.e., rather less than the 2.16 Å in $\text{Ni}_3(\text{HA})_2 \cdot 10\text{H}_2\text{O}$ [3]. The Ni-O distances are 2.052 and 2.070 Å in the G rings and 2.039 and 2.053 Å in the R rings (Table 3), i.e., the difference in the distances in the G rings relative to the R rings of ~ 0.1 Å in III and 0.07 Å in II does not occur here [2]. Moreover the involvement of O(1) in bonding with Cu(1) does not reduce the covalence of the Ni-O(1) bond (2.052 Å).

The angular distortions of the Ni octahedron are the inevitable consequence of the formation of five chelate rings fused at two points. All the L-Ni-L intrachelate angles (L is ligand) are in the range 80-88°, i.e., less than 90°, while all the extrachelate angles are greater than 90°, except for O(3)-Ni-N(5), 83.68°, and O(3)-Ni-O(5), 85.88° (Table 4).

The N-C and C-C distances in the E, G, and R rings are 1.467-1.490 Å and 1.515-1.542 Å respectively (Table 3), which are normal for sp^3 hybridization of these atoms; the C-O distances are almost equal, though the carbonyl bond (average 1.235 Å) is slightly shorter than the carboxylate (average 1.261 Å). Similar distances have been found in, for example, $\text{Na}_2[(\text{H}_2\text{O})\text{MnA}] \cdot 5\text{H}_2\text{O}$ (average 1.255 Å) [7] and II (average 1.253 Å) [2]. The inequivalence of the C-O bonds is more clearly apparent in III (1.19 and 1.32 Å). Stezowski et al. [7] considered that slight differences among the C-O bond lengths typify weak complexes while Porai-Koshits et al. [3] believed them due to ionic or pseudoionic states.

The conformation of the A ligand is E, G/R, i.e., it is normal for octahedral coordination. The en ring E

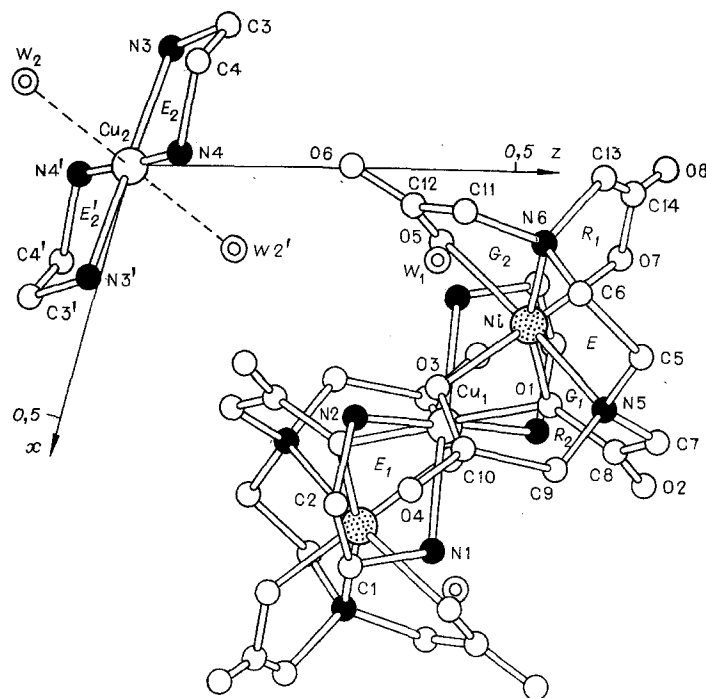


Fig. 1. Independent part of the structure.

(Fig. 1) is nonplanar and has the normal gauche structure with almost symmetrical deviations of the C(5) and C(6) atoms from the N(5)NiN(6) plane (-0.34 and 0.36 Å respectively). The N(5)–C(5)–C(6)–N(6) torsion angle is 58.0° . The G and R rings are also nonplanar. If we take the sum of the interior angles as a criterion of ring strain, the G_1 and G_2 rings (sum of the angles 524.03 and 525.66° respectively) are considerably strained by comparison with R_1 and R_2 (sums close to 540 – 538.42 and 537.23° respectively), i.e., the G_1 and G_2 rings are more puckered than the R_1 and R_2 rings. In the G_1 and G_2 rings the folding along the N...O axis (35.1 and 32.6°) is greater than that along the C...O axis (12.9 and 9.9°), whereas in the R_1 and R_2 rings it is the same, 9.6 and 8.4° along the N...O axis and 10.3 and 9.6° along the C...O axis.

The four C–COO units are almost planar, but in each of them the tendency of the C atoms of the methylene groups to deviate from the plane of the COO fragment is clearly apparent. The dihedral angles between the mean planes are 6.8° for the G_1 and G_2 rings and 94.3° for the R_1 and R_2 rings. The G_1 and G_2 rings are tilted through 23.5 and 23.8° and the R_1 and R_2 rings through 85.1 and 79.3° relative to the N(5)–NiN(6) plane.

The bis(ethylenediamine) complexes of Cu(1) and Cu(2) in I are centrosymmetric and the en fragment in them is a bidentate chelating ligand. The Cu–N distances in the E_1 ring (2.037 and 2.044 Å) are slightly longer than those in the E_2 ring (2.009 and 2.011 Å). These bond lengths are within the range known for en complexes of copper – 2.049 and 2.040 Å in (Tmen) $_2$ (glutarato)Cu [8], 1.991 and 2.074 Å in [Cu(Dmen)Cl $_2$] $_2$ [9], and 2.025 and 2.024 Å in Cu(Tmen)(SO $_4$) · 3H $_2$ O [10] (Tmen is tetramethylethylenediamine, Dmen is dimethylethylenediamine).

The N–C distances in the E_1 and E_2 rings are 1.473 – 1.493 and the C–C are 1.481 and 1.517 Å respectively, i.e., slightly less than normal in the E_1 ring, but even shorter C–C distances have been encountered among structurally studied en complexes, such as 1.373 Å in Cu(Tmen)(SO $_4$) · 3H $_2$ O [10].

In the Cu(1) tetragonal bipyramid the Cu(1)–O(1) axial bond (2.376 Å) involving the bridging oxygen is perpendicular to the equatorial plane –O(1)–Cu(1)–N(1) is 90.86 and O(1)–Cu(1)–N(2) 90.24° . In the Cu(2) polyhedron the Cu–O(W2) bond (2.635 Å) involving the oxygen of the water molecule is slightly tilted toward the equatorial plane –O(W2)–Cu(2)–N(3) 87.88 and O(W2)–Cu(2)–N(4) 86.56° . The weakening of the Cu(2)–O(W2) axial bond is the usual indication of the Jahn–Teller effect in copper complexes. Others have found Cu–O distances of the same order in, for example, Cu(en) $_2$ (ClO $_4$) $_2$ (2.61 Å) [11] and Cu[(en) $_2$](Acac) · 2H $_2$ O [12].

The E_1 and E_2 rings are nonplanar and considerably strained; the sums of the interior angles are 518.00 and 524.14° respectively. Like the E rings (sum of the angles 515.4°), they have the gauche conforma-

TABLE 5. Hydrogen Bond Parameters

A ^a —H...B bond*	Distances, Å			Angle (°)
	A ... B	A—H	H ... B	A—H ... B
O(W1)—H(1) ... O(4) ^b	2,777(3)	0,82(4)	2,18(4)	129,1(1,1)
O(W1)—H(2) ... O(6) ^c	2,740(3)	1,02(4)	1,76(4)	161,3(1,1)
O(W2)—H(2) ... O(6) ^c	3,117(3)	1,01(4)	2,25(4)	145,9(1,1)
O(W2)—H(2) ... O(5) ^c	3,270(3)	1,01(4)	2,34(4)	151,7(1,1)
N(1)—H(1) ... O(8) ^d	3,121(4)	1,06(4)	2,10(4)	160,4(1,2)
N(1)—H(2) ... O(5) ^e	3,022(4)	0,80(4)	2,228(4)	155,7(1,2)
N(2)—H(2) ... O(2) ^e	3,086(4)	0,83(4)	2,30(4)	159,2(1,2)
N(2)—H(1) ... O(3) ^a	3,089(4)	0,96(4)	2,21(3)	151,5(1,2)
N(3)—H(2) ... O(W1) ^a	2,868(4)	0,98(4)	1,94(4)	156,8(1,2)
N(3)—H(1) ... O(2) ^f	2,897(4)	1,044(4)	1,89(4)	166,0(1,2)
N(4)—H(1) ... O(8) ^c	2,941(4)	0,99(4)	2,08(4)	145,3(1,2)
N(4)—H(2) ... O(W1) ^g	2,992(4)	0,85(4)	2,19(4)	155,7(1,2)

*Positions of the molecules: a) x, y, z ; b) $\bar{x}, \bar{y}, \bar{z}$; c) $x, \frac{1}{2}-y, \frac{1}{2}+z$; d) $x+1, y, z$; e) $\bar{x}, -y, \bar{z}$; f) $\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z$; g) $-x, \bar{y}, \bar{z}$.

tion, but unlike the E rings the deviations of the carbon atoms to both sides of the NCuN plane are unsymmetrical: 0.507 and -0.143 Å in E₁, 0.270 and -0.444 Å in E₂. The N—C—C—N torsion angles are 51.7° for E₁ and 54.5° for E₂.

The cations and anions are held together by van der Waals forces and H bonds; the hydrogen bond parameters are summarized in Table 5. A considerable contribution to the stabilization of the crystal is made by water molecule W1. Through its two hydrogens it participates in two quite strong O—H...O hydrogen bonds with the O(4) and O(6) carbonyl oxygen atoms of the two NiA complexes and simultaneously through its oxygen it is involved in two N—H...O hydrogen bonds with the two Cu(2)(en)₂²⁺ cations. Water molecule W2, which enters the Cu(2) coordination sphere, forms weaker O(W2)—H...O hydrogen bonds with the oxygen atoms of the G₂ ring.

Apart from these, there is an extensive network of N—H...O hydrogen bonds of length 2.897–3.121 Å in the crystal (Table 5). Thus the hydrogen bonding involves all eight hydrogen atoms of the E₁ and E₂ rings, three of the four hydrogen atoms of the two water molecules, and all the carbonyl and two of the four carboxylate oxygen atoms of the acetate groups.

In summary, we note that:

1. Because of the flexibility of the polyhedron, which is typical of Cu complexes [13], there are two types of Cu polyhedra in which the nature of the trans-Cu—O bond differs.
2. On the basis of the bridging function of one of the oxygen atoms of the acetate group, the ligand A can be considered as heptadentate.
3. The structure includes a mode of additional coordination of the acetate group of the A ligand with a second metal atom through the carboxylate oxygen atom, which is rather uncommon in complexes with this ligand.

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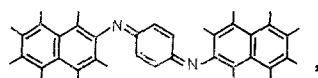
X-RAY STRUCTURE ANALYSIS OF N,N'-DI- β -NAPHTHYL-P-BENZOQUINONE DIIMINE

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X-Ray structure analysis of the crystal and molecular structure of N,N'-di- β -naphthyl-p-benzoquinone diimine, $C_{10}H_7-N=C_6H_4=N-C_{10}H_7$ (diffractometer, 1509 reflections, direct methods, $R = 0.036$) reveals two independent centrosymmetric molecules, I and I', with similar geometrical parameters. The average bond lengths in the quinonoid ring are $C=C$ 1.324 and $C-C$ 1.457 Å and the average $C-C-C$ angle is 115.6° ; the lengths of the $C-N$ and $C=N$ bridges are 1.408 and 1.296 Å respectively, and the CNC bond angle is 122.6° . The molecular configuration is determined by the dihedral angles between the quinonoid and naphthyl rings (45.0° in I and 53.1° in I') and the torsion angles around the $C-N$ and $C=N$ bonds. We compare the structure with that of N,N'-di- β -naphthyl-p-phenylenediamine. The different photoelectric sensitivity of these compounds can probably be related to the different packing of the imino and amino species.

This analysis of the crystal and molecular structure of N,N'-di- β -naphthyl-p-benzoquinone diimine (DNPBDI),



continues our work on a series of model compounds for polyarylenamines, oligomers of heat-resistant polymers with semiconducting properties. Replacement of some of the phenylenamine units in polyphenylenamines by benzoquinone diimine is known to produce higher electrical conductivity in these polymers [1]. Kopylov et al. have examined the correlation between the electrical conductivity of complexes derived from aromatic amines and their chemical and crystal structures [2]. Measurements of the photoelectric properties made in our laboratory by V. M. Vozzhennikov and V. L. Materikin have revealed that the amino compounds N,N'-diphenyl-p-phenylenediamine (DPPPDA) and N,N'-di- β -naphthyl-p-phenylenediamine (DNPPDA) have considerable photoelectric sensitivity, whereas the equivalent imino compounds N,N'-diphenyl-p-benzoquinone diimine (DPPBDI) and DNPBDI display no photoelectric effect. We have already determined the structure of DPPPDA [3] and DNPPDA for comparison with the photoconductivity [4]. We were unable to solve the structure of DPPBDI because of twinning of the crystals. We decided to compare the structures of DNPBDI and DNPPDA as compounds with different photosensitivities.

EXPERIMENTAL AND STRUCTURE DETERMINATION

The single crystals of DNPBDI were dark red lamellar prisms. The x-ray work was carried out on a Syntex P1 automatic diffractometer (λ Mo K_α , graphite monochromator). The triclinic crystals had $a = 19.666(5)$, $b = 6.441(2)$, $c = 7.730(3)$ Å, $\alpha = 93.91(3)$, $\beta = 102.03(3)$, $\gamma = 104.26(2)^\circ$, $V = 920.8(4)$ Å³, $Z = 2$ $C_{26}H_{18}N_2$, $M = 3.58$, $d_{calc} = 1.29$ g/cm³, μ (Mo K_α) = 0.82 cm⁻¹, $F(000) = 376$, space group $P\bar{1}$. The unit-cell parameters were similar to those derived for DNPPDA when an identical mounting was chosen for the crystal. However, we used a mounting different to that adopted for DNPPDA for the work on the DNPBDI crystals. We measured the intensities of 1509 independent reflections from a crystal of dimensions $0.15 \times 0.20 \times 0.06$ mm.

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