The Crystal Structure of Bis(N^1-isopropyl-2-methyl-1,2-propanediamine)copper(II) Perchlorate. Coordination and Conformation of the N^1-Isopropyl-2-methyl-1,2-propanediamine Molecule*

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The title compound $[Cu(C_7H_{18}N_2)_2(ClO_4)_2]$ crystallizes in the orthorhombic space group *Pbca* (No. 61) with cell dimensions a = 11.406(3), b = 13.761(4), c = 15.113(4) Å and Z = 4. A four-coordinated copper(II) atom lies at the centre of symmetry, with Cu–N (primary) and Cu–N (secondary) distances of 1.996(6) and 2.039(5) Å, respectively. Oxygen atoms of the symmetry-related perchlorate ions lie in the apical positions at a distance of 2.805(6) Å from the copper(II) atom. The separate ions are linked by very weak hydrogen bonds and van der Waals forces. The structure was refined to the weighted R_w value of 0.052 for 1142 reflections.

Earlier conformational studies on sixteen transition metal compounds containing the N^1-isopropyl-2-methyl-1,2-propanediamine (NPDA) ligand[1–10] have been continued with the study of the title compound. The coordination sphere in this new compound is square-coplanar with a centre of symmetry not found before. Two other complexes with square-coplanar coordination spheres, viz. bis(NPDA)copper(II) malonate trihydrate[1] and bis(NPDA)nickel(II) perchlorate,[10] have a pseudo two-fold axis perpendicular to the coordination plane, with the central atom deviating from the plane.

The secondary nitrogen atom of NPDA is chiral when coordinated and the conformation of the amine molecule depends on the configuration of this asymmetric atom.[1] The coordination number of the central atom – copper(II) in most of the compounds studied, zinc(II)[9] in one compound and nickel(II)[10] in another – is usually five, but can also be four or six. The coordination geometry of the central atom varies between square-coplanar, trigonal-bipyramidal and square-pyramidal to square-bipyramidal, with different distortions.

NPDA is an unsymmetrically C- and N-substituted ethylenediamine derivative. It forms a bidentate five-membered unsymmetrically puckered chelate ring having either a δ or λ conformation, and in bischelates either δδ(λλ) or δλ(λδ).[§] Thus, the complexes have either a pseudo C_2-axis perpendicular to the basal plane or a real or pseudo centre of symmetry at the central atom. Most of the studied mixed ligand complexes containing NPDA have a mono- or dicarboxylate ion as counterion. In bis complexes the anion is usually coordinated at the apical position, but in some cases (e.g. malonate or hydrogencarbonate ion)[1] it is uncoordinated and forms a hydrogen bonded network between complex units.

[§]The nomenclature used is that of Ref. 11.

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Table 1. Crystal data and details of data collection for bis(NPDA)copper(II) perchlorate.

Crystal data		Data collection	
a/Å	11.406(3)	Diffractometer	Nicolet P3
b/Å	13.761(4)	2θ range/°	5–50
c/Å	15.113(4)	Scan speed/° min^{-1}	2.0–29.3
V/Å^3	2372(1)	Scan type	ω
Z	4	Total refl. meas.	2092
M_r	522.90	Obsd. refl. $I > 2\sigma(I)$	1142
D_c/g cm^{-3}	1.464	Temperature/°C	25±1
D_m/g cm^{-3}	1.46	Variables	188
F(000)	1100		
Space group	*Pbca* (No. 61)		
λ(Mo*K*α)/Å			
(graphite monochr.)	0.7107		
μ(Mo*K*α)/cm^{-1}	11.9		
Crystal size/mm	0.3×0.3×0.4		

Experimental

Bis(NPDA)copper(II) perchlorate $[Cu(C_7H_{18}N_2)_2(ClO_4)_2]$ was crystallized from a mixture of copper(II) perchlorate, NPDA and malic acid titrated with sodium hydroxide, adjusted to I = 0.5 M with $NaClO_4$. Red violet crystals were formed within a few days. Crystal data and details concerning data collection are given in Table 1. Two test reflections, (111) and (204), were monitored after every 60 reflections and showed no decay of the crystal. The data were corrected for Lorentz and polarization effects but not for absorption.

Structure determination and refinement

The non-hydrogen atom positions of the structure were determined by the Patterson method using SHELXS-86,[12] and use of the Fourier methods of XTAL83[13] gave the hydrogen atom positions. Atomic scattering factors were those included in the program systems. Refinement was carried out with the full-matrix least-squares methods of XTAL83. Refinement of positional parameters and isotropic temperature parameters for non-hydrogen atoms converged to the R-value of 0.11, and refinement of positional parameters for all atoms and anisotropic temperature parameters for non-hydrogen atoms, with fixed isotropic temperature parameters of U = 0.07 Å for hydrogen atoms, converged to an R-value of 0.067 ($R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$) and a weighted R_w-value of 0.052 $\{R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F)\}$ for 1142 observed reflections $[I > 2\sigma(I)]$. The average shift/error in the last cycle was 0.36. Lists of structure factors and anisotropic temperature parameters are obtainable from the author on request.

Results and discussion

The structure is shown in an ORTEP drawing, with atomic labelling, in Fig. 1 (ORTEP is included in the XTAL83 program system). Fractional atomic coordinates with e.s.d.'s and equivalent isotropic temperature parameters are tabulated in Table 2, and bond lengths and angles with e.s.d.'s for non-hydrogen atoms in Table 3.

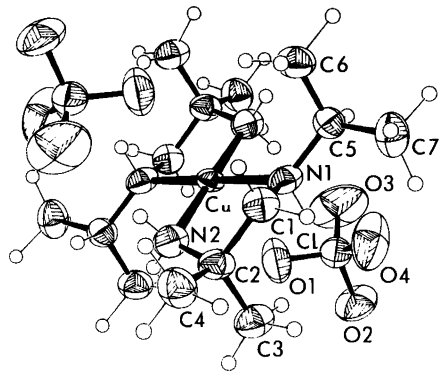

Fig. 1. ORTEP drawing of bis(NPDA)copper(II) perchlorate showing the atomic labelling of non-hydrogen atoms.

Table 2. Atomic positional parameters of bis(NPDA)copper(II) perchlorate, with e.s.d.'s and equivalent isotropic temperature parameters of the form $U_{eq} = 1/3\,\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \vec{a}_i \cdot \vec{a}_j$ with fixed values for hydrogen atoms.

Atom	*x*	*y*	*z*	U_{eq}/Å^2
Cu	0.5000(0)	0.5000(0)	0.0000(0)	0.035
N1	0.5458(5)	0.4933(4)	0.1303(4)	0.051
N2	0.6540(5)	0.5669(4)	−0.0149(4)	0.054
C1	0.6769(6)	0.5066(6)	0.1329(4)	0.054
C2	0.7123(7)	0.5897(5)	0.0727(4)	0.051
C3	0.6655(7)	0.6877(5)	0.1033(5)	0.062
C4	0.8467(7)	0.5924(6)	0.0626(5)	0.064
C5	0.4999(7)	0.4141(5)	0.1891(4)	0.052
C6	0.5395(7)	0.3152(5)	0.1597(5)	0.062
C7	0.5283(7)	0.4304(6)	0.2867(5)	0.069
Cl	0.2860(2)	0.6654(2)	0.1221(1)	0.061
O1	0.3649(5)	0.6622(5)	0.0474(4)	0.090
O2	0.2482(6)	0.7623(4)	0.1380(4)	0.090
O3	0.1917(6)	0.6048(6)	0.1060(6)	0.166
O4	0.3504(6)	0.6310(5)	0.1968(4)	0.124
H1	0.527(5)	0.555(4)	0.147(4)	0.070
H2	0.624(5)	0.617(5)	−0.057(4)	0.070
H3	0.695(5)	0.520(4)	−0.037(4)	0.070
H4	0.705(5)	0.519(5)	0.205(4)	0.070
H5	0.709(5)	0.443(4)	0.118(4)	0.070
H6	0.562(5)	0.687(4)	0.107(4)	0.070
H7	0.694(5)	0.691(4)	0.171(4)	0.070
H8	0.673(5)	0.754(5)	0.065(4)	0.070
H9	0.879(5)	0.651(4)	0.016(4)	0.070
H10	0.870(5)	0.613(5)	0.128(4)	0.070
H11	0.876(5)	0.529(4)	0.034(4)	0.070
H12	0.394(5)	0.419(4)	0.190(4)	0.070
H13	0.631(5)	0.308(4)	0.169(4)	0.070
H14	0.529(5)	0.311(4)	0.082(4)	0.070
H15	0.495(5)	0.252(5)	0.201(4)	0.070
H16	0.618(5)	0.415(4)	0.306(4)	0.070
H17	0.526(5)	0.504(5)	0.314(4)	0.070
H18	0.446(5)	0.382(4)	0.328(4)	0.070

The range of interatomic distances for hydrogen atoms was N–H: 0.85–1.00 Å and C–H: 0.96–1.18 Å with e.s.d.'s of 0.05 Å. A PLUTO[14] drawing of the molecular packing is shown in Fig. 2.

The structure consists of discrete complex cations with the copper ion at the centre of symmetry and two perchlorate ions at a Cu–O1 distance of 2.805(6) Å, which is too long to correspond to a bond. Thus, the coordination sphere of the copper(II) ion is slightly distorted square-coplanar. The distortion is due to the different substituents on the nitrogen atoms.

The possible hydrogen bonds are very weak, as seen from the magnitude of the three shorter N–O distances, varying from 3.097(9) to 3.199(9) Å with the N–H–O angles being from 126(4)° to 134(4)°, respectively. However, the fourth N2–O3($-x, -y, -z$) distances of 3.253(9) Å, with N–H–O angle of 177(4)°, includes the shortest H–O distance of 2.41(5) Å.

The values of 2.039(5) and 1.996(6) Å for the Cu–N1 and Cu–N2 distances, respectively, agree well with the earlier reported values for (NPDA) copper(II) complexes.[1–8] The interatomic distances between copper and the primary nitrogen atom range from 1.973(4) Å in bis(NPDA)copper(II) malonate trihydrate[1] to 2.160(10) Å in bis(NPDA)nitritocopper(II) nitrite,[6] with a mean value of 2.022 Å. Distances from copper to the secondary nitrogen atom vary between 1.998(8)

Table 3. Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses for non-hydrogen atoms of bis(NPDA)copper(II) perchlorate.

Complex cation					
Cu–N1	2.039(5)	N1–Cu–N2	84.5(2)		
Cu–N2	1.996(6)				
N1–C1	1.506(8)	Cu–N1–C1	105.9(4)	N2–C2–C4	110.8(6)
N1–C5	1.502(9)	Cu–N1–C5	121.0(4)	C1–C2–C3	113.1(6)
N2–C2	1.515(9)	Cu–N2–C2	112.5(4)	C1–C2–C4	110.0(6)
C1–C2	1.516(8)	N1–C1–C2	109.9(6)	C3–C2–C4	111.0(6)
C2–C3	1.522(10)	N1–C5–C6	112.1(6)	C6–C5–C7	110.8(6)
C2–C4	1.541(11)	N1–C5–C7	113.0(6)		
C5–C6	1.500(10)	N2–C2–C1	104.6(6)		
C5–C7	1.527(10)	N2–C2–C3	107.2(6)		
Perchlorate ion					
C1–O1	1.446(6)	O1–C1–O2	110.5(4)	O2–C1–O4	109.5(4)
C1–O2	1.421(6)	O1–C1–O3	109.1(4)	O3–C1–O4	109.9(5)
C1–O3	1.383(8)	O1–C1–O4	106.7(4)		
C1–O4	1.428(6)	O2–C1–O3	111.1(4)		

and 2.129(7) Å [both of these values being found in bis(NPDA)nitritocopper(II) nitrite],[6] with a mean of 2.073 Å. The mean values reveal a tendency for Cu–N(prim) to be shorter than Cu–N (sec) (though not in bis(NPDA)nitritocopper(II) nitrite, whose coordination is trigonal-bipyramidal). This tendency has been found in most N-substituted diamines.[15] The shortening effect is about twice that found when methyl is substituted at a nitrogen, though there are exceptions where differences are smaller, as in aqua(*N*-methylethylenediamine)malonatocopper(II).[16]

The values of parameters showing the features of the coordination spheres in some bis(NPDA) copper(II) complexes are listed in Table 4. The distortion of the coordination sphere between square-pyramidal and trigonal-bipyramidal in bis(NPDA)copper(II) complexes is seen in the variation of the N(prim)–Cu–N(prim) angle from 99.1(4)° in trigonal-bipyramidal bis(NPDA)nitritocopper(II) nitrite[6] to 180° in bis(NPDA)disalicylatocopper(II)[5] and in the title compound, with a mean value of 154.3°. The angles vary from much less than the trigonal angle of 120° to the symmetry related angle of 180°.

The variation deviates from the Berry twist[17] in that in bis(NPDA) complexes the pathway from square-pyramidal to trigonal-bipyramidal is not continuous; rather, there is a change in the conformation of the amine molecule when the N(prim)–Cu–N(prim) angle decreases to less than ca. 140°. There is a smaller variation in the N(sec)–Cu–N(sec) angle, viz. from 161.7(2)° in bis(NPDA)tartratocopper(II) propanol adduct[3]

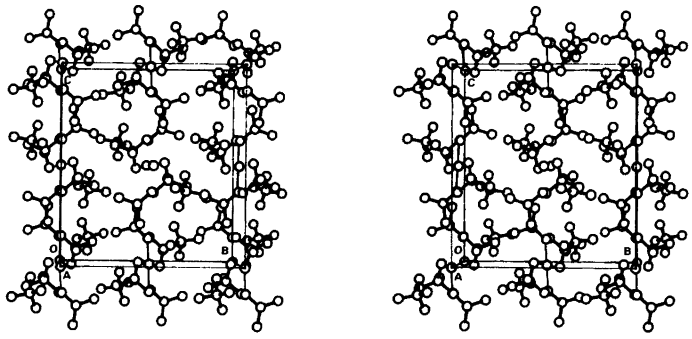

Fig. 2. Stereoscopic PLUTO drawing showing the molecular packing of bis(NPDA)copper(II) perchlorate.

Table 4. Comparison of Cu–N distances (Å), N–Cu–N angles (°) and Cu–L(ax) distances (Å) in some bis(NPDA)copper(II) complexes.

Compound	Cu–N(sec)	Cu–N(prim)	Cu–L(ax)	N(sec)–Cu–N(sec)	N(prim)–Cu–N(prim)	Ref.
Bis(NPDA)-μ-succinato-dicopper(II) succinate octahydrate	2.097 2.113	2.030 2.031	2.162	171.06	153.93	1
Bis(NPDA)copper(II) malonate trihydrate	2.032 2.039	1.973 1.975		171.2	161.7	1
Bis(NPDA)malatocopper(II) dihydrate-methanol	2.067 2.088	2.032 2.009	2.225	166.2	168.8	1
Bis(NPDA)aquacopper(II) bishydrogencarbonate hemihydrate	2.111 2.121	2.010 2.004	2.208	170.2	153.7	1
Bis(NPDA)disalicylato-copper(II)	2.049 2.049	1.989 1.989	2.606 2.606	180.0	180.0	5
Bis(NPDA)lactatocopper(II) lactate monohydrate	2.108 2.099	2.025 2.009	2.157	168.7	153.7	8
Bis(NPDA)copper(II) perchlorate	2.038 2.038	1.996 1.996		180.0	180.0	This work

to 180° in bis(NPDA)disalicylatocopper(II)[5] and in the present compound, with a mean value of 171.0°.

The uncoordinated N^1-isopropyl-2-methyl-1,2-propanediammonium ion has a synclinal conformation with an N–C–C–N torsion angle of 73.7(5)° and a non-bonded N–N distance of 3.139 (8) Å.[18] These values differ markedly from the present values of 51.1(7)° and 2.712(8) Å and the mean values of 51.4° and 2.736 Å, respectively, for the coordinated amine molecule.[1] Coordinated NPDA is unsymmetrically puckered and has a synclinal δ or λ conformation. The δ conformation of the amine corresponds to the *S* configuration at the secondary nitrogen atom, and the λ conformation to the *R* configuration. The conformations in the five-membered Cu–N–C–C–N rings range from unsymmetric envelope, as found in bis(NPDA)lactatocopper(II) lactate monohydrate[8] and bis(NPDA)copper(II) malonate dihydrate,[1] through nearly symmetric skew, in bis(NPDA)tartratocopper(II) propanol adduct,[3] to unsymmetric skew, which is the most common and is the conformation found in all other NPDA complexes so far examined.

The parameters defining the conformational features of coordinated NPDA are shown in Fig. 3, and the values of the parameters for some

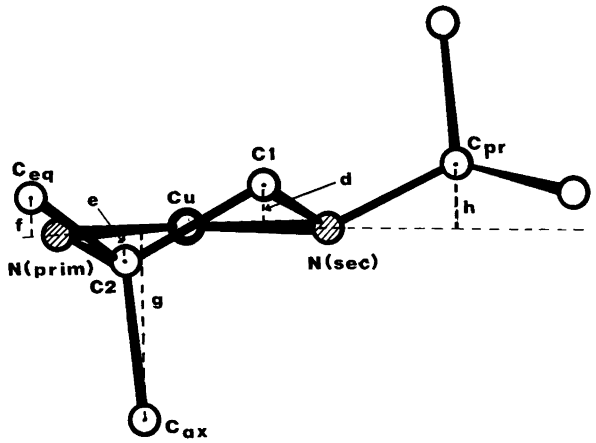

Fig. 3. Schematic view of a coordinated NPDA molecule showing the deviations of atoms C1 (d), C2 (e), C_{eq} (f), C_{ax} (g) and C_{pr} (h) from the NCuN plane. The values of these parameters for some NPDA complexes are listed in Table 4. The conformation of the five-membered chelate ring corresponds to the given coordinates and is unsymmetric skew, designated as λ. The configuration of the secondary nitrogen atom is *R*.

Table 5. Some conformational features of bis(NPDA)copper(II) complexes. Symbols are defined in Fig. 3. The signs (+) and (−) mean above and below the NCuN plane, respectively. τ is the torsion angle N–C–C–N.

Compound	d	e	f	g	h	τ	Ref.
Bis(NPDA)-μ-succinato-dicopper(II)	−0.069	0.596	0.260	2.094	−0.970	50.6	1
succinate octahydrate	−0.121	0.564	0.231	2.066	−0.982	52.3	
Bis(NPDA)copper(II)malonate	0.232	−0.499	−0.146	−1.985	0.862	−55.0	1
trihydrate	−0.032	−0.701	−0.538	−2.162	1.093	−50.0	
Bis(NPDA)malatocopper(II)	−0.254	0.483	0.061	2.007	−0.845	55.8	1
dihydratemethanol	0.365	−0.329	0.296	−1.793	0.622	−50.5	
Bis(NPDA)aquacopper(II)	−0.049	0.630	0.391	2.116	−0.992	52.5	1
bishydrogencarbonate hemihydrate	−0.019	0.659	0.406	2.155	−1.019	51.7	
Bis(NPDA)disalicylatocopper(II)	−0.607	0.008	−0.824	1.455	−0.488	47.8	5
	0.607	−0.008	0.824	−1.455	0.488	−47.8	
Bis(NPDA)lactatocopper(II) lactate	−0.012	−0.667	−0.413	−2.193	0.996	−50.5	8
monohydrate	0.183	−0.529	−0.146	−2.067	1.003	−52.5	
Bis(NPDA)copper(II) perchlorate	0.490	−0.193	0.477	−1.690	0.589	−51.1	This
	−0.490	0.193	−0.477	1.690	−0.589	51.1	work

bis(NPDA)copper(II) complexes are listed in Table 5. As a rule, the atom C1 lies approximately in the NCuN coordination plane and the atom C2 deviates ca. 0.5 Å from the plane. In the present study, however, the deviations are −0.490 and 0.193 Å, respectively, and in bis (NPDA)disalicylatocopper(II) they are −0.607 and 0.008 Å, respectively.[5]

In solution, puckered chelate rings undergo a rapid interconversion between δ and λ conformations. In the case of NPDA a change in the conformation would cause the axial methyl group to approach the isopropyl so closely that it would be possible only if the configuration of the secondary nitrogen atom changed at the same time. However, a change in the chirality cannot take place without breaking the Cu–N bond, and thus the configuration is determined before coordination.

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