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THE CRYSTAL STRUCTURE OF THE BROWN FORM OF BIS(N-CYCLOHEXYLSALICYLALDIMINATO)COPPER(II)

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The crystal structure of brown form of bis(N-cyclohexylsalicylaldiminato)copper(II) has been determined by the X-ray diffraction method. The coordination of the copper(II) ion is square planar, with Cu-N=2.034Å and Cu-O=1.896Å. The molecule is bent, or stepped, so that the perpendicular distance between the salicylaldimine planes is 1.28Å.

The authors(S.Y and A.T) have recently succeeded in isolating two forms of bis(N-cyclohexylsalicylaldiminato)copper(II), one being brown(Form I) and the other green(Form II)[1]. The brown crystal of Form I melts at 165-166°C, and then crystallizes in the green Form II. The green crystal of Form II melts at 176-177°C. The crystal structure of Form I has been determined.

The crystals of Form I are triclinic, with cell dimensions of

$a=12.035$, $b=7.810$, $c=6.475$Å, $\alpha=104.86$, $\beta=102.06$, $\gamma=97.67°$;
$\rho_m=1.37$, $\rho_c=1.379 \mathrm{g.cm^{-3}}$.

The intensities of 1629 independent reflections were measured on a Rigaku-Denki four-circle X-ray diffractometer with Cu-Kα radiation by the θ-2θ scan technique. There is one molecule in the unit cell. The space group was assumed to be $P\bar{1}$, which was confirmed by the following structure determination. The approximate structure was obtained by the heavy-atom method. Several cycles of block-diagonal least-squares refinement, with anisotropic thermal parameters, brought the R-value to 0.097. Subsequently the hydrogen atoms were located from a difference synthesis and further refinement with the inclusion of these atoms reduced R to 0.037.

Table 1 lists the atomic coordinates. The bond lengths and angles do not significantly differ from normal values as shown Fig.1. Intramolecular distances which appear noteworthy are those of 2.32Å between the H(8) or H(8') atom of the cyclohexyl group and the oxygen atom of the opposite ligand. The molecule is centrosymmetric and the coordination around the copper(II) ion is therefore exaxtly planar. This result is different from the tetrahedral configuration, as deduced from the study of the absorption spectra[2]. The salicylaldimine group is planar within experimental accuracy. Each salicylaldimine group makes an angle of 153.5° with the coordination plane. The molecule is bent or stepped, so that the perpendicular distance between the salicylaldimine planes is 1.28Å.

Table 1. The final atomic coordinates

Atom	x	y	z	Atom	x	y	z
Cu	0.0	0.0	0.0	H(1)	0.072	0.273	-0.405
O	0.1587	0.1074	0.1286	H(3)	0.257	0.283	-0.423
N	-0.0075	0.1506	-0.2147	H(4)	0.456	0.304	-0.267
C(1)	0.0830	0.2109	-0.2706	H(5)	0.521	0.231	0.077
C(2)	0.2006	0.2036	-0.1739	H(6)	0.376	0.142	0.255
C(3)	0.2862	0.2586	-0.2772	H(8)	-0.176	0.057	-0.381
C(4)	0.4010	0.2658	-0.1887	H(91)	-0.114	0.426	-0.075
C(5)	0.4344	0.2231	0.0073	H(92)	-0.162	0.243	-0.004
C(6)	0.3527	0.1698	0.1121	H(101)	-0.312	0.403	-0.093
C(7)	0.2337	0.1581	0.0228	H(102)	-0.340	0.199	-0.259
C(8)	-0.1225	0.1843	-0.3132	H(111)	-0.256	0.522	-0.360
C(9)	-0.1651	0.3024	-0.1285	H(112)	-0.386	0.399	-0.480
C(10)	-0.2901	0.3197	-0.2167	H(121)	-0.256	0.336	-0.719
C(11)	-0.3005	0.3936	-0.4145	H(122)	-0.302	0.154	-0.659
C(12)	-0.2538	0.2802	-0.5948	H(131)	-0.078	0.385	-0.449
C(13)	-0.1280	0.2670	-0.5034	H(132)	-0.100	0.188	-0.619

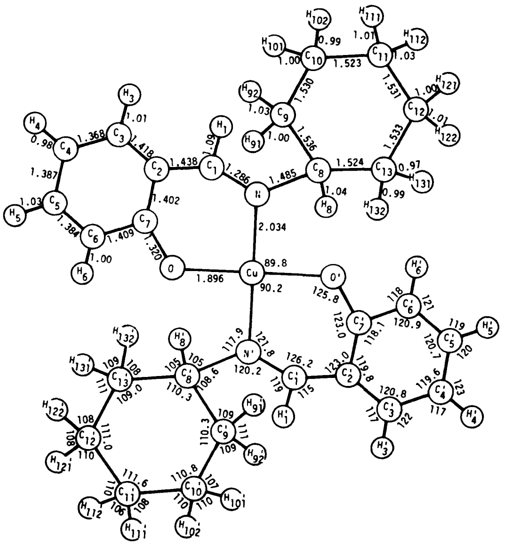

Fig.1. Interatomic distances and angles

Estimated standard deviations are:

0.002Å	for	Cu-O, Cu-N
0.004Å	for	O-C, N-C
0.004~0.005Å	for	C-C
0.03~0.04Å	for	C-H
0.1°	for	O-Cu-N, O'-Cu-N
0.2°	for	Cu-N-C, Cu-O-C_7
0.3~0.4°	for	C-C-C
2°	for	C-C-H
3°	for	H-C-H bond angles.

The cyclohexyl group twists around the N-C(8) or N'-C(8') bond to reduce the steric strain. The plane through C(9),C(10),C(12), and C(13) atoms in the cyclohexyl group, therefore, makes an angle of 51.2° with the coordination plane. There are no intermolecular distances less than 3.62Å except for hydrogen atoms in the crystal structure.

References

1) A.Takeuchi and S.Yamada, to be published.
2) S.Yamada and H.Nishikawa, Bull.Chem.Soc.Jpn.,36,755(1963).

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