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Enantiomeric bis(μ-*N*,*N*′-hexamethylenedisalicylaldiminato)dicopper(II) complexes

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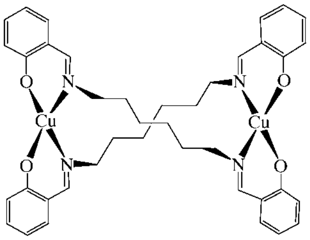
The title dimeric complex, bis{μ-2,2′-[hexane-1,6-diylbis(nitrilomethylidyne)]diphenolato-1:2κ^4*O*,*N*:*N*′,*O*′}dicopper(II), [$Cu_2(C_{20}H_{22}N_2O_2)_2$], has been investigated by single-crystal X-ray diffraction, by thermogravimetric analysis and differential scanning calorimetry, and also by FT–IR spectroscopy. Different synthetic and crystallization procedures gave crystals which were quite different in appearance, and it was initially thought that these were different polymorphic forms. Subsequent structure determination showed, in fact, serendipitous preparation of crystals in the $P4_1$ space group by one method and in space group $P4_3$ by the other. In these enantiomorphic structures, the Cu atoms have a distorted flattened tetrahedral coordination, with Cu—N and Cu—O distances in the ranges 1.954 (4)–1.983 (4) and 1.887 (4)–1.903 (4) Å, respectively.

Comment

Although copper(II) and nickel(II) complexes with Schiff base ligands containing bridging aliphatic chains containing two, three or four methylene groups have been the subject of several crystallographic investigations (Freiburg *et al.*, 1980; Akhtar, 1981; Akhtar & Drew, 1982; Drew *et al.*, 1985; Yao *et al.*, 1997), less work has been performed on homologous compounds containing longer bridging chains (Martin *et al.*, 1978; Kitajima *et al.*, 1986). The aliphatic chain length can have a pronounced influence on the coordination polyhedron of the metal ion, and also on intermolecular oligomerization and polymerization in the solid state and in solution.

Previous work (Duggal & Agarwala, 1988) carried out on the complex of copper(II) with *N*,*N*′-hexamethylenebis(salicylaldimine) concluded, on the basis of IR and diffuse-reflectance spectroscopy measurements, that the complex should be monomeric, with the Cu^{II} ion in a *cis*-square-planar environment. We concluded that it would be interesting to examine the folding of the rather long polymethylene chain in such a compound, so the title complex was prepared and crystallized using a diffusion reaction technique, to give (I), or by evaporation of a dioxane solution of the complex, to give (II). The results obtained by the present structure determinations are not in agreement with the structure proposed previously by Duggal & Agarwala (1988). The title complex was found to be dimeric in the solid state, with anions of *N*,*N*′-hexamethylenebis(salicylaldimine) functioning as bridging bis-bidentate ligands.



(I)

One set of crystals of the title copper complex was grown by evaporation from a dioxane solution, and the compound obtained, (II), was found to crystallize in space group $P4_3$. However, crystals obtained by slow interdiffusion of a basic methanolic *N*,*N*′-hexamethylenebis(salicylaldimine) solution and a copper(II) nitrate solution, (I), exhibited space group $P4_1$. Structure determination from room-temperature data

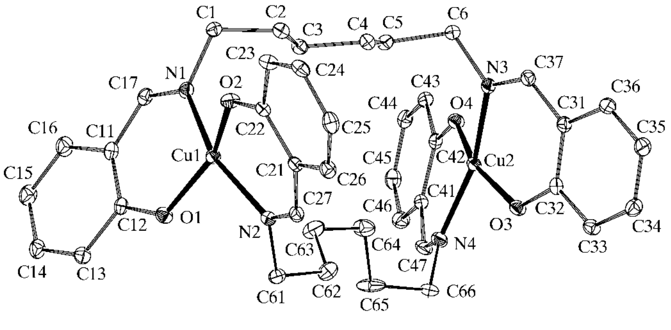


Figure 1
A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 10% probability level and H atoms have been omitted.

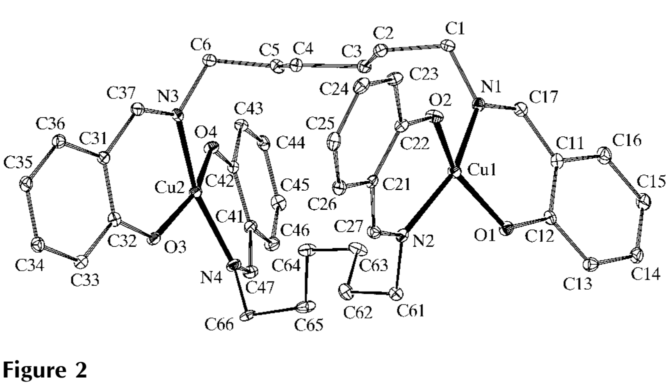


Figure 2
A view of (II) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 10% probability level and H atoms have been omitted.

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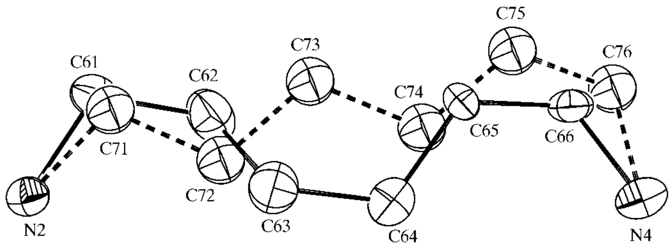

Figure 3
A view of the two disordered hexamethylene chains in (I). Displacement ellipsoids are drawn at the 30% probability level. The corresponding view for (II) is very similar.

indicated that the molecular geometries were the same in both crystals, the only difference being the direction of the polar axis.

Space-group determinations and data collection were performed on several crystals from each set at room temperature, and the Flack data (Flack, 1983) were always consistent with space group $P4_1$ for the diffusion-grown and $P4_3$ for the dioxane-grown crystals. However, the data collected at room temperature indicated the existence of disorder in one of the bridging aliphatic chains of the dimeric complex molecule. The final structure determinations reported here were undertaken using low-temperature data, which enabled the resolution of the disorder (see *Experimental*).

The molecular geometries in both (I) (Fig. 1) and (II) (Fig. 2) are identical. The Cu^{II} ions in the dimers are coordinated in the form of very flattened tetrahedra, with the N- and O-donor atoms in a *trans* arrangement around each Cu^{II} centre. There is similar significant disorder in one of the two hexamethylene chains in each compound; a view of the pair of disordered chains in (I) is shown in Fig. 3.

The distance between the two Cu^{II} centres in the dimer is 7.7019 (8) Å in (I) and 7.7186 (8) Å in (II). The degree of the distortion of the metal coordination tetrahedron can be expressed by the dihedral angle between the corresponding O—Cu—N planes; in (I), this is 35.0 (2)° for atom Cu1 and 23.3 (2)° for Cu2, and in (II), the angle is 34.5 (2)° for Cu1 and 23.6 (2)° for Cu2. These values fall in the range of previously reported angles in similar complexes (Bear *et al.*, 1970; Elder & Hill, 1979). Details of the bond lengths at the Cu atoms are given in Tables 1 and 2. The molecular dimensions in both complexes are all in accordance with values previously reported for copper(II) salicylaldiminates (Bhadbhade & Srinivas, 1993; Kani *et al.*, 1998).

The reasons for the observed dependence of the orientation of the polar axis on crystallization conditions are, as yet, unclear.

Experimental

The Schiff base ligand *N*,*N*′-hexamethylenebis(salicylaldimine) was prepared by the condensation of salicylaldehyde with 1,6-diaminohexane in the molar ratio 2:1 in methanol. The yellow product so obtained was identified by FT–IR, and ^1H and ^{13}C NMR spectroscopy. The copper(II) complex was obtained as a brown powder by slow simultaneous dropwise addition of ethanol solutions of the Schiff base (containing an equimolar amount of triethylamine) and copper(II) nitrate trihydrate into a small volume of ethanol. The concentrations of the reactants varied from 0.05 to 0.10 mol dm^{-3}. It was observed that the rate of addition, as well as the concentration of the reacting solutions, strongly influenced the nature of the product. Higher addition rates and reagent concentrations favoured the formation of green precipitates of unknown composition. The title compound was separated from the insoluble products by extraction with chloroform and subsequent precipitation with *n*-hexane or diethyl ether. The compound was crystallized by evaporation of a dioxane solution, giving red crystals of (II) in the shape of bicapped tetragonal prisms. As the compound dissolved in dioxane tends to decompose, yielding an insoluble green precipitate (of currently unknown composition), another method of preparation of the compound, by slow diffusion of solutions of the Schiff base and copper(II) nitrate, was used. As a result, long red needle-like crystals of (I) were obtained. As mentioned above, we initially considered that the crystals of (I) and (II) might be polymorphs, but the present X-ray structure determinations establish that the different preparation and crystallization conditions have instead yielded crystals of the same compound in enantiomorphic space groups, *i.e.* (I) in $P4_1$ and (II) in $P4_3$. The differential scanning calorimetry measurements, performed in an inert gas flow atmosphere (Ar, 200 cm^3 min^{-1}) over the temperature range 298–873 K using aluminium crucibles, revealed a weak exothermic change at 499 K, followed by melting combined with decomposition at 587 K, for both crystal forms. The thermogravimetric analyses, made in an oxygen gas flow atmosphere (200 cm^3 min^{-1}) over the temperature range 298–873 K, gave the expected copper content of 15.73% (calculated copper content 16.38%) in both crystal forms and confirmed the chemical composition.

Enantiomorph (I)

Crystal data

$[Cu_2(C_{20}H_{22}N_2O_2)_2]$
$M_r = 771.81$
Tetragonal, $P4_1$
$a = 13.2963$ (2) Å
$c = 20.6366$ (5) Å
$V = 3648.38$ (12) Å^3
$Z = 4$
$D_x = 1.405$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 4153 reflections
$\theta = 2.9$–$27.5°$
$\mu = 1.21$ mm^{-1}
$T = 150$ (1) K
Needle, red
0.22 × 0.21 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.776$, $T_{max} = 0.794$
20 156 measured reflections

7755 independent reflections
5429 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$
$\theta_{max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -12 \rightarrow 12$
$l = -23 \rightarrow 26$

Table 1
Selected interatomic distances (Å) for (I).

Cu1—O2	1.890 (3)	Cu2—O4	1.895 (3)
Cu1—O1	1.895 (3)	Cu2—O3	1.903 (3)
Cu1—N2	1.959 (4)	Cu2—N4	1.965 (4)
Cu1—N1	1.972 (3)	Cu2—N3	1.980 (4)

Table 2
Selected interatomic distances (Å) for (II).

Cu1—O2	1.887 (4)	Cu2—O4	1.896 (3)
Cu1—O1	1.898 (4)	Cu2—O3	1.903 (3)
Cu1—N2	1.961 (4)	Cu2—N4	1.954 (4)
Cu1—N1	1.979 (4)	Cu2—N3	1.983 (4)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.108$
$S = 1.00$
7755 reflections
470 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}
Absolute structure: Flack (1983), 3489 Friedel pairs
Flack parameter = 0.007 (14)

Enantiomorph (II)

Crystal data

$[Cu_2(C_{20}H_{22}N_2O_2)_2]$
$M_r = 771.81$
Tetragonal, $P4_3$
$a = 13.3288$ (2) Å
$c = 20.5834$ (7) Å
$V = 3656.78$ (15) Å^3
$Z = 4$
$D_x = 1.402$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4153 reflections
$\theta = 2.9$–27.5°
$\mu = 1.21$ mm^{-1}
$T = 150$ (1) K
Prism, red
0.20 × 0.18 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.794$, $T_{\max} = 0.889$
20 308 measured reflections
7763 independent reflections
4824 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.103$
$\theta_{\max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -12 \rightarrow 12$
$l = -26 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.098$
$S = 0.96$
7763 reflections
470 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}
Absolute structure: Flack (1983), 3505 Friedel pairs
Flack parameter = 0.000 (14)

The crystal structure determination of both crystal forms using room-temperature data indicated a hardly resolvable disorder in one of the bridging hexamethylene chains. Therefore, low-temperature diffraction experiments were performed. Crystals of (I) and (II) were significantly different in appearance and both crystallized in the tetragonal system, with space groups of either $P4_1$ or $P4_3$ determined from the systematic absences. $P4_1$ was shown to be correct for (I) and $P4_3$ for (II) from the Flack parameters (Flack, 1983). H atoms were treated as riding, with aromatic C—H = 0.95 Å and aliphatic C—H = 0.99 Å. Both structures were solved independently and it soon became apparent that, in each case, there was essentially identical disorder of one of the $(CH_2)_6$ chains. The occupancies of the major and minor chains were 0.714 (6) and 0.286 (6), respectively, for (I), and 0.747 (6) and 0.253 (6), respectively, for (II). Minor occupancy atoms were assigned an overall $U_{\rm iso}$ value of 0.06 Å^2 and their geometries were restrained to reasonable values *via SHELXL*97 (Sheldrick, 1997) *DFIX* restraints.

For both compounds, data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC, Canada.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1547). Services for accessing these data are described at the back of the journal.

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