Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1184). Services for accessing these data are described at the back of the journal.

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A Dimeric Copper(II) 4-Chlorophenoxyisobutyrate Adduct with Methanol and a Monomeric Copper(II) 4-Chlorophenoxyisobutyrate Adduct with Pyridine

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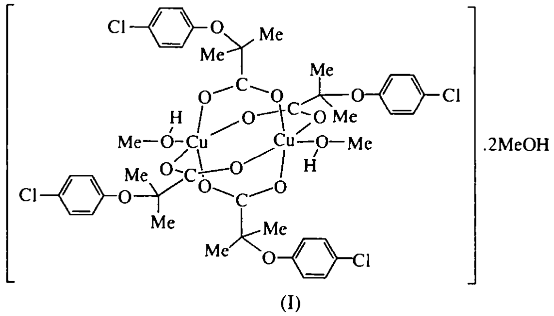
Abstract

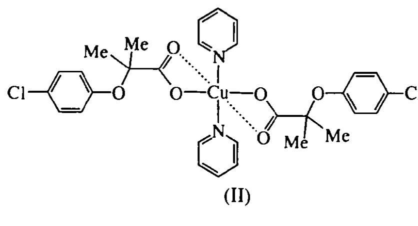
In the crystal structure of tetrakis(μ-4-chlorophenoxyisobutyrato-O,O')di(methanol-O)dicopper(II) dimethanol solvate, $[\mathrm{Cu(pciba)_2(CH_3OH)}]_2.2\mathrm{CH_3OH}$ (pcibaH is 4-chlorophenoxyisobutyric acid, $\mathrm{C_{10}H_{11}ClO_3}$), there is a dinuclear $\mathrm{Cu^{II}}$ complex which has a typical cage structure with a Cu···Cu distance of 2.6437 (4) Å. The magnetic $-2J$ value is $360\,\mathrm{cm^{-1}}$ ($H = -2JS_1.S_2$). In the crystal structure of *trans*-bis(4-chlorophenoxyisobutyrato-O,O')dipyridinecopper(II), $[\mathrm{Cu(pciba)_2(C_5H_5N)_2}]$, the monomeric $\mathrm{Cu^{II}}$ complex has a distorted octahedral coordination.

Comment

The dimeric title compound, (I), has a center of symmetry. The Cu1—O4 bond length is 1.991 (2) Å, which is *ca* 0.02 Å longer than the other Cu1—O(carboxyl) bonds as a result of the hydrogen bond between the O4 atom and crystal methanol (O11). The dimeric copper(II) complexes related by translation along **c** are connected by two hydrogen-bond bridges, Cu1—O4···H11—O11···H10$^{\rm i}$—O10$^{\rm i}$—Cu$^{\rm i}$ and Cu1—O10—H10···O11$^{\rm i}$—H11$^{\rm i}$···O4$^{\rm i}$—Cu$^{\rm i}$ [symmetry code: (i) $1-x$, $-y$, $-1-z$]. Several kinds of dimeric copper(II) phenoxyalkanoates have been prepared and their crystal structures published (Reck & Jaehnig, 1979; Smith *et al.*, 1985; Mak *et al.*, 1987). However, their magnetic data were not reported. In this study, the magnetic susceptibility of (I) was measured using the Faraday method over a temperature range of 80–300 K, and the $-2J$ and g values were determined to be $360\,\mathrm{cm^{-1}}$ and 2.22, respectively, with the mole fraction of the monomeric $\mathrm{Cu^{II}}$ impurity being 1.3%. It was assumed that crystal methanol molecules were lost from the crystals under reduced pressure. The $-2J$ value is comparable with those of $[\mathrm{Cu(Ph_2MeCCOO)_2(EtOH)}]_2.\mathrm{EtOH}$ ($-2J = 347\,\mathrm{cm^{-1}}$; Steward *et al.*, 1996) and $[\mathrm{Cu(PhMe_2CCOO)_2(H_2O)}]_2$ ($-2J = 348\,\mathrm{cm^{-1}}$; Fujita *et al.*, 1993). This indicates that there is a negligible influence on the antiferromagnetic interaction when a phenyl group is replaced by a phenoxy group bonded at the α-carbon of the bridging carboxylate ions.

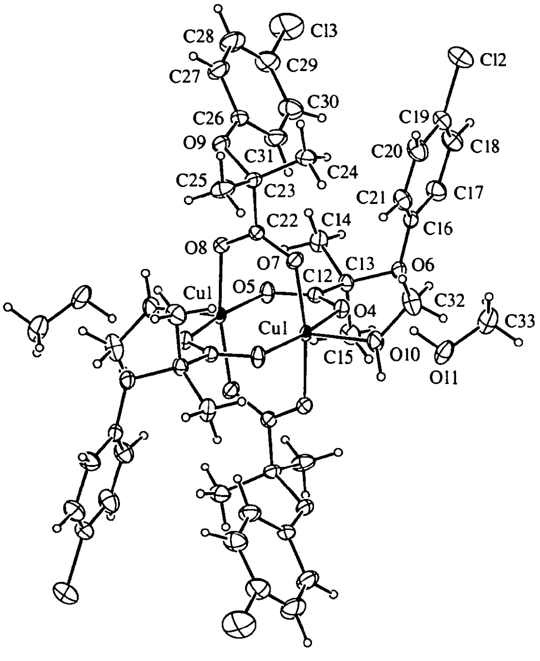


(I)

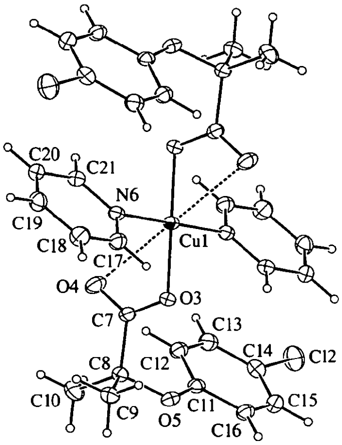


(II)

Attempts to prepare the dimeric copper(II) pyridine adduct of pciba yielded only the mononuclear complex (II). The Cu atom lies on a center of inversion and the phenyl ring of pciba is approximately parallel to and stacked with one of the intramolecular pyridine rings, with the shortest C···C distance being 3.467 (3) Å. The carboxylate group forms an asymmetric chelate ring with the Cu atom, and the Cu—O bond lengths are 1.963 (2) and 2.683 (1) Å. A similar (4+2)-coordination of Cu^{II} was reported for $[Cu(Ph_3CCOO)_2(2,6\text{-}C_5H_3NMe_2)_2]$, where the Cu—O distances are 1.936 (3) and 2.825 (4) Å (Fujita *et al.*, 1993).



(*a*)



(*b*)

Fig. 1. The molecular structures of (*a*) (I) and (*b*) (II), with displacement ellipsoids at the 20% probability level. H atoms are represented by circles of radius 0.1 Å.

Experimental

For the preparation of (I), pcibaH (537 mg, 2.5 mmol) and $CuCO_3.Cu(OH)_2.H_2O$ (150 mg, 0.63 mmol) were suspended in aqueous ethanol (1:1, 40 ml). The solution was stirred for 70 min at room temperature and then evaporated to dryness. The green residue was dissolved in methanol (20 ml) to yield a green solution, from which the crystals of (I) were grown. When pyridine was added to the methanol solution, the colour changed from green to purple and crystals of (II) were obtained. The crystal specimen of (I) was sealed in a capillary with the mother liquor to avoid efflorescence.

Compound (I)

Crystal data

$[Cu_2(C_{10}H_{10}ClO_3)_4(CH_4O)_2].2CH_3OH$
$M_r = 1109.82$
Triclinic
$P\overline{1}$
$a = 9.672\ (1)$ Å
$b = 15.698\ (2)$ Å
$c = 9.040\ (2)$ Å
$\alpha = 104.48\ (1)°$
$\beta = 105.07\ (1)°$
$\gamma = 88.53\ (1)°$
$V = 1282.1\ (3)$ Å^3
$Z = 1$
$D_x = 1.437$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10\text{–}15°$
$\mu = 1.102$ mm^{-1}
$T = 297$ K
Plate
0.7 × 0.5 × 0.1 mm
Light green

Data collection

Rigaku AFC-5 diffractometer
$\theta\text{–}2\theta$ scans
Absorption correction: by integration (Coppens, Leiserowitz & Rabinovich, 1965)
$T_{min} = 0.590$, $T_{max} = 0.895$
6248 measured reflections
5897 independent reflections

4680 reflections with $|F_o| > 3\sigma(|F_o|)$
$R_{int} = 0.014$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 12$
$k = -20 \rightarrow 20$
$l = -11 \rightarrow 11$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.046$
$wR = 0.042$
$S = 1.15$
4680 reflections
298 parameters
H atoms riding
$w = 1/[\sigma^2(F) + 0.000225F^2]$

$(\Delta/\sigma)_{max} = 0.04$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °) for (I)*

Cu1—Cu1^i	2.6437 (4)	O5—C12	1.248 (3)
Cu1—O4	1.991 (2)	O6—C13	1.441 (3)
Cu1—O5^i	1.971 (2)	O6—C16	1.380 (3)
Cu1—O7	1.972 (2)	O7—C22	1.257 (3)
Cu1—O8^i	1.971 (2)	O8—C22	1.249 (3)
Cu1—O10	2.120 (2)	O9—C23	1.446 (3)
Cl2—C19	1.737 (3)	O9—C26	1.375 (3)
Cl3—C29	1.747 (4)	O10—C32	1.412 (4)
O4—C12	1.262 (3)	O11—C33	1.396 (4)

O4—Cu1—O5^i	167.9 (1)	O8^i—Cu1—O10	98.2 (1)
O4—Cu1—O7	89.4 (1)	Cu1—O4—C12	121.5 (2)
O4—Cu1—O8^i	88.5 (1)	Cu1^i—O5—C12	124.8 (2)
O4—Cu1—O10	94.9 (1)	Cu1—O7—C22	125.6 (2)
O5^i—Cu1—O7	90.1 (1)	Cu1^i—O8—C22	120.5 (2)
O5^i—Cu1—O8^i	89.5 (1)	Cu1—O10—C32	127.3 (2)
O5^i—Cu1—O10	97.1 (1)	O4—C12—O5	125.4 (2)
O7—Cu1—O8^i	167.9 (1)	O7—C22—O8	125.8 (2)
O7—Cu1—O10	93.9 (1)		

Symmetry code: (i) $1 - x, -y, -z$.

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O10—H10$\cdots$O11^i	0.959	1.696	2.645 (3)	170
O11—H11$\cdots$O4	0.960	2.015	2.892 (2)	151

Symmetry code: (i) $1 - x, -y, -1 - z$.

Compound (II)

Crystal data

$[Cu(C_{10}H_{10}ClO_3)_2(C_5H_5N)_2]$
$M_r = 649.03$
Monoclinic
$P2_1/n$
$a = 6.728$ (2) Å
$b = 16.958$ (1) Å
$c = 13.388$ (2) Å
$\beta = 101.38$ (2)°
$V = 1497.5$ (5) Å^3
$Z = 2$
$D_x = 1.439$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–15°$
$\mu = 0.953$ mm^{-1}
$T = 299$ K
Prism
0.7 × 0.7 × 0.5 mm
Purple

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: by integration (Coppens, Leiserowitz & Rabinovich, 1965)
$T_{min} = 0.546$, $T_{max} = 0.678$
3815 measured reflections
3429 independent reflections

2674 reflections with $|F_o| > 3\sigma(|F_o|)$
$R_{int} = 0.020$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 22$
$l = -17 \rightarrow 17$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.043$
$wR = 0.048$
$S = 1.34$
2674 reflections
187 parameters
H atoms riding
$w = 1/[\sigma^2(F) + 0.000225F^2]$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Selected geometric parameters (Å, °) for (II)*

Cu1—O3	1.963 (2)	O3—C7	1.273 (3)
Cu1—O4	2.683 (1)	O4—C7	1.230 (3)
Cu1—N6	1.996 (2)	O5—C8	1.446 (3)
Cl2—C14	1.747 (3)	O5—C11	1.370 (3)
O3—Cu1—N6	91.3 (1)	Cu1—O3—C7	107.1 (2)
O4—Cu1—N6	83.2 (2)	O3—C7—O4	124.0 (2)
O3—Cu1—O4	54.2 (2)		

Hydroxyl H atoms of MeOH in (I) were located from difference syntheses. A riding model [O—H and C—H distances of 0.96 Å, and U_{iso}(H) = 0.1 Å^2] was used for all H atoms in (I) and (II).

For both compounds, data collection: *AFC/MSC Diffractometer Control System* (Rigaku Corporation, 1993); cell refinement: *AFC/MSC Diffractometer Control System*; data reduction: local programs; program(s) used to solve structures: *CRYSTAN-GM* (Edwards *et al.*, 1996); program(s) used to refine structures: *CRYSTAN-GM*; molecular graphics: *CRYSTAN-GM*; software used to prepare material for publication: *CRYSTAN-GM*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1037). Services for accessing these data are described at the back of the journal.

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Diaquabis[*N*-(1-naphthyl)-*N*-nitrosohydroxylaminato-*O*,*O'*]cobalt(II)

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Abstract

In the title compound, $[Co(C_{10}H_7N_2O_2)_2(H_2O)_2]$, prepared from neocupferron and $(NH_4)_2[Co(SO_4)_2(H_2O)_6]$, the Co^{II} ion has slightly distorted octahedral coordination defined by six O atoms from the two bidentate ligands and the two water molecules, in a *cis* arrangement [Co—O 2.073 (2)–2.124 (3) Å]. The molecule has crystallographic C_2 symmetry. The plane of the nitrosohydroxylaminato group is twisted out of the plane of the naphthyl ring.

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