C3—N1—C7	120.6 (3)	N1—C3—S1	113.5 (2)
C4—N1—C7	113.1 (3)	N1—C3—S2	124.5 (3)
C14—N2—C8	117.8 (2)	S1—C3—S2	122.0 (2)
O1—C1—O2	126.7 (3)		

In (I), phenyl groups were refined as rigid hexagons. The morpholinyl rings are somewhat disordered and restraints had to be applied. The N—C and O—C distances were *DFIX*ed (*DFIX* in *SHELXL*97; Sheldrick, 1997*a*) at 1.45±0.01 Å, whereas the C—C distances were *DFIX*ed at 1.54±0.02 Å; additionally, C22···C24 = C47···C49 = 2.51±0.02 Å and C23···C25 = C48···C50 = 2.37±0.02 Å.

For both compounds, data collection: *CAD*-4/*PC* (Kretschmar, 1994). Cell refinement: *CAD*-4 *Manual* (Enraf–Nonius, 1988) for (I); *CELDIM* in *CAD*-4 *Manual* for (II). For both compounds, data reduction: *XCAD*4 (Harms, 1997); program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structures: *SHELXL*97; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1237). Services for accessing these data are described at the back of the journal.

References

Enraf-Nonius (1988). *CAD*-4 *Manual*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.

Harms, K. (1997). *XCAD*4. *Program for the Lp Correction of Nonius CAD-4 Diffractometer Data*. University of Marburg, Germany.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kretschmar, M. (1994). *CAD*-4/*PC*. Version 1.5c. PC Version of *CAD*-4 *Software* (Version 5.0). University of Tübingen, Germany.

Kumar Das, V. G., Chen, W., Ng, S. W. & Mak, T. C. W. (1977). *J. Organomet. Chem.* **322**, 33–47.

Lo, K. M., Kumar Das, V. G. & Ng, S. W. (1999). *Acta Cryst.* **C55**. Submitted.

Nachmias, G. (1952). *Ann. Chim. (Paris)*, **7**, 584–631.

Ng, S. W. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 73–75.

Ng, S. W. (1996*a*). *Acta Cryst.* **C52**, 181–183.

Ng, S. W. (1996*b*). *Main Group Met. Chem.* **19**, 113–120.

Ng, S. W. (1997*a*). *Acta Cryst.* **C53**, 779–781.

Ng, S. W. (1997*b*). *Z. Kristallogr.* **212**, 279–281.

Ng, S. W., Chen, W. & Kumar Das, V. G. (1988). *J. Organomet. Chem.* **345**, 59–61.

Ng, S. W. & Kumar Das, V. G. (1991). *J. Organomet. Chem.* **409**, 143–156.

Ng, S. W. & Kumar Das, V. G. (1995*a*). *Acta Cryst.* **C51**, 2489–2491.

Ng, S. W. & Kumar Das, V. G. (1995*b*). *Main Group Met. Chem.* **18**, 309–314.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Pluijgers, C. W. & van der Kerk, G. J. M. (1961). *Recueil*, **90**, 1089–1100.

Sheldrick, G. M. (1997*a*). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXS*97. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Tiekink, E. R. T. (1991). *Appl. Organomet. Chem.* **5**, 1–23.

Tiekink, E. R. T. (1994). *Trends Organomet. Chem.* **1**, 71–115.

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A dimeric copper(II) bis(4-chlorophenoxy)acetate adduct with dimethylformamide

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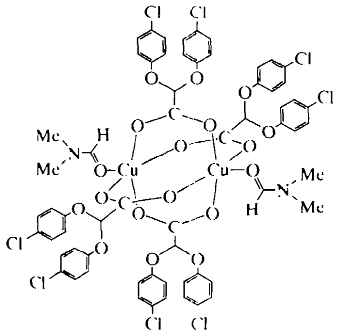
Abstract

The crystal structure of tetrakis[μ-bis(4-chlorophenoxy)acetato-*O*:*O'*]bis[(dimethylformamide-*O*)copper(II)], $[Cu(bpca)_2(dmf)]_2$ [bpca is bis(4-chlorophenoxy)acetate, $C_{14}H_9Cl_2O_4$; dmf is dimethylformamide, C_3H_7NO], consists of a dinuclear Cu^{II} complex which has a typical cage structure, with a Cu···Cu distance of 2.685 (1) Å. The magnetic $-2J$ value is 361 cm^{-1} ($H = -2JS_1.S_2$).

Comment

The dinuclear title complex, (I), has a center of symmetry, and the conformations of the two independent bpca ligands [bpcaH is bis(4-chlorophenoxy)acetic acid] are different. The PhO—C—C(O)—O torsion angle is 55.1 (5)° for one bpca ligand (O4—C2—C1—O2) and −8.2 (5)° for the other (O8—C16—C15—O5). The planes of the two phenoxy groups in each of the bpca moieties are almost perpendicular to each other, the dihedral angles being 85.8 (3) and 89.8 (3)°. However, the ring-to-ring dihedral angle of the phenoxy groups is 59.7° in the crystals of bpcaH (Smith & Kennard, 1981).



(I)

In this study, the magnetic susceptibility of the title complex was measured using the Faraday method over the temperature range 80–300 K, and the $-2J$ and g values were determined to be 361 cm^{-1} and 2.26, respectively, with a mole fraction of monomeric Cu^{II} impurity of 2.4%. The $-2J$ value is comparable with those of $[Cu(pciba)_2(CH_3OH)]_2 \cdot 2CH_3OH$ (pcibaH is 4-chlorophenoxyisobutyric acid, $C_{10}H_{11}ClO_3$; $-2J$ = 360 cm^{-1}; Kani *et al.*, 1998) and $[Cu(Ph_2MeCCOO)_2(EtOH)]_2 \cdot EtOH$ ($-2J$ = 347 cm^{-1}; Steward *et al.*, 1996). It is confirmed that there is a negligible influence of the antiferromagnetic interaction caused by the replacement of two phenyl groups with two phenoxy groups bonded at the α-carbon of the bridging carboxylate ions. In contrast, the copper(II) benzoylformates show abnormally strong spin-exchange interaction; $-2J$ = 648 cm^{-1} for $[Cu(PhCOCOO)_2(py)]_2$ (py is pyridine; Harada *et al.*, 1997).

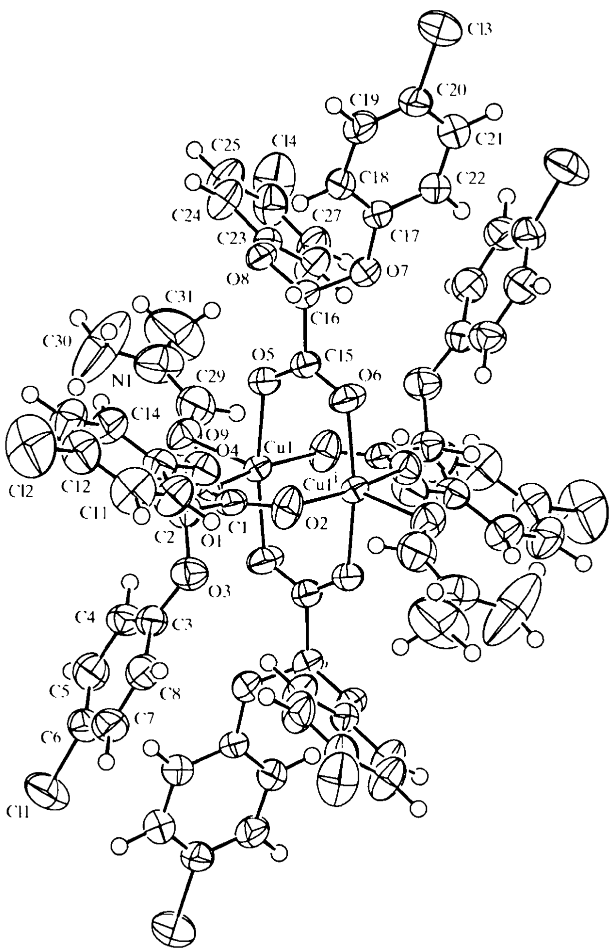


Fig. 1. The molecular structure of (I), with displacement ellipsoids at the 50% probability level. H atoms are represented by circles of arbitrary size.

Experimental

Bis(4-chlorophenoxy)acetic acid (626 mg, 2.0 mmol) and $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ (120 mg, 0.5 mmol) were suspended in aqueous methanol (1:1, 40 ml). The solution was stirred for 4 h at room temperature and then filtered. The green residue was dissolved in dimethylformamide (20 ml) to yield a dark-green solution, from which green crystals were grown.

Crystal data

$[Cu_2(C_{14}H_9Cl_2O_4)_4(C_3H_7NO)_2]$
M_r = 1521.8
Monoclinic
$P2_1/n$
a = 10.115 (3) Å
b = 10.757 (4) Å
c = 30.986 (4) Å
β = 96.24 (2)°
V = 3351 (1) Å^3
Z = 2
D_x = 1.508 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 14.8–15.0°
μ = 1.024 mm^{-1}
T = 297 K
Prism
0.70 × 0.60 × 0.30 mm
Dark green

Data collection

Rigaku AFC-5*R* diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.616, T_{max} = 0.736
10 267 measured reflections
9762 independent reflections

6184 reflections with $I > 1.5\sigma(I)$
R_{int} = 0.027
θ_{max} = 30°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 15$
$l = -44 \rightarrow 44$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
R = 0.065
$wR(F)$ = 0.062
S = 1.795
6184 reflections
415 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o) + 0.00031|F_o|^2]$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu1···Cu1^i	2.685 (1)	Cl3—C20	1.743 (4)
Cu1—O1	1.951 (3)	Cl4—C26	1.747 (5)
Cu1—O2^i	1.967 (3)	O1—C1	1.248 (5)
Cu1—O5	1.982 (3)	O2—C1	1.238 (5)
Cu1—O6^i	1.971 (3)	O5—C15	1.232 (4)
Cu1—O9	2.115 (3)	O6—C15	1.251 (4)
Cl1—C6	1.726 (5)	O9—C29	1.253 (6)
Cl2—C12	1.738 (4)		
O1—Cu1—O2^i	166.6 (1)	Cu1^i—O6—C15	121.5 (3)
O5—Cu1—O6^i	166.5 (1)	Cu1—O9—C29	120.5 (3)
Cu1—O1—C1	121.1 (3)	O1—C1—O2	127.4 (4)
Cu1^i—O2—C1	124.6 (3)	O5—C15—O6	127.7 (3)
Cu1—O5—C15	124.0 (2)		

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

The positions of all the H atoms were calculated geometrically $[U(H) = 1.2U_{eq}(C)]$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction:

TEXSAN (Molecular Structure Corporation/Rigaku Corporation, 1998). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1053). Services for accessing these data are described at the back of the journal.

References

Harada, A., Tsuchimoto, M., Ohba, S., Iwasawa, K. & Tokii, T. (1997). *Acta Cryst.* B53, 654–661.

Kani, Y., Ohba, S., Matsushima, H. & Tokii, T. (1998). *Acta Cryst.* C54, 193–195.

Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation/Rigaku Corporation (1998). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.9. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA, and Rigaku Corporation, Tokyo, Japan.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.

Smith, G. & Kennard, H. L. (1981). *Acta Cryst.* B37, 1891–1895.

Steward, O. W., Johnston, B. S., Chang, S.-C., Harada, A., Ohba, S., Tokii, T. & Kato, M. (1996). *Bull. Chem. Soc. Jpn*, 69, 3123–3137.

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Dichloro[2,2′-(2,5-dithiahexamethylene)dipyridine-*N*,*N*′,*S*,*S*′]nickel(II)

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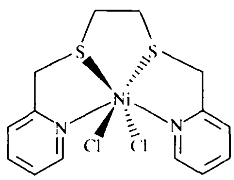
Abstract

The title complex, *cis*-[$NiCl_2(C_{14}H_{16}N_2S_2)$], has twofold crystallographic symmetry and the Ni atom has an octahedral coordination with two *cis* thioether S atoms, two *trans* pyridyl N atoms and two *cis* chloride ions. The main dimensions are Ni—N 2.1078 (16), Ni—S 2.4316 (7) and Ni—Cl 2.3855 (6) Å.

Comment

The identification of nickel complexes capable of generating methane from methyl-coenzyme M has proved to be difficult (Jaun & Pfaltz, 1988) and we recently reported an Ni^{II} compound which has coordinating tendencies towards the coenzyme (Pandiyan *et al.*, 1997*a*). Synthetic model studies of metalloenzymes have been used to illustrate the structural involvement on the biological functions (Stolzenberg & Zhang, 1997; Stolzenberg & Stershic, 1987; Murali *et al.*, 1994; Nishida & Takahashi, 1988; Pandiyan *et al.*, 1992, 1995, 1996, 1997*a*,*b*; Palaniandavar *et al.*, 1995; Drain *et al.*, 1988). The ligand 2,2′-(2,5-dithiahexamethylene)dipyridine (*L*) was synthesized and the spectroscopic biological studies on these complexes are under process in our laboratory.

In the structure of the title compound, (I), the Ni atom lies on a twofold axis of the *Pbcn* space group, while the remaining atoms are in general positions (Fig. 1). The metal center is coordinated by two thioether S atoms, two pyridyl N atoms and two chloride ions. The coordination bond distances and the bond angles are presented in Table 1. The greatest deviation from an idealized octahedral geometry, 12.21 (9)°, is observed for the pyridyl N atoms with Ni1. Atoms S1, $S1^i$, N1 and $N1^i$ are almost coplanar, with a calculated maximum deviation of 0.052 Å for S1 and $S1^i$ [symmetry code (i): $1-x$, y, $\frac{1}{2}-z$]. We can then consider the coordination environment as distorted octahedral with the apical positions occupied by the N atoms. The bite angle N1—Ni1—S1 [81.78 (5)°] is due to the steric hindrance of the five-membered ring formed by Ni1, N1, C3, C2 and S1. On the other hand, the deviation from an idealized geometry [6.00 (3)°] observed for the angle Cl1—Ni1—$Cl1^i$ is rather due to the electronic repulsion of the Cl atoms in a *cis* configuration. Despite a different point



(I)

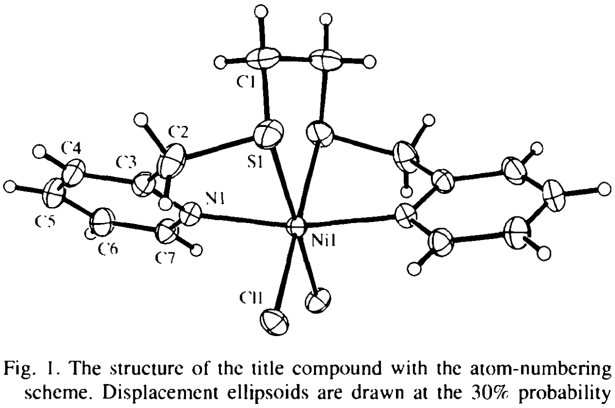


Fig. 1. The structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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