Refinement

Refinement on F
$R = 0.042$
$wR = 0.036$
$S = 1.117$
5333 reflections
343 parameters
H atoms not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Pd(1)—Cl(1)	2.297 (1)	P(1)—C(3)	1.813 (4)
Pd(1)—Cl(2)	2.400 (1)	P(1)—C(9)	1.795 (4)
Pd(1)—P(1)	2.209 (1)	P(2)—C(16)	1.821 (4)
Pd(1)—N(1)	2.049 (3)	P(2)—C(17)	1.809 (4)
Pd(2)—Cl(3)	2.289 (1)	P(2)—C(23)	1.803 (5)
Pd(2)—Cl(4)	2.366 (1)	N(1)—C(1)	1.479 (5)
Pd(2)—P(2)	2.201 (1)	N(2)—C(15)	1.468 (6)
Pd(2)—N(2)	2.056 (3)	C(1)—C(2)	1.511 (6)
P(1)—C(2)	1.831 (4)	C(15)—C(16)	1.468 (7)
Cl(1)—Pd(1)—Cl(2)	96.27 (5)	C(2)—P(1)—C(3)	106.0 (2)
Cl(1)—Pd(1)—P(1)	91.97 (5)	C(2)—P(1)—C(9)	107.6 (2)
Cl(1)—Pd(1)—N(1)	176.87 (9)	C(3)—P(1)—C(9)	107.1 (2)
Cl(2)—Pd(1)—P(1)	171.74 (4)	Pd(2)—P(2)—C(16)	100.6 (2)
Cl(2)—Pd(1)—N(1)	86.80 (9)	Pd(2)—P(2)—C(17)	115.2 (1)
P(1)—Pd(1)—N(1)	84.96 (9)	Pd(2)—P(2)—C(23)	117.4 (2)
Cl(3)—Pd(2)—Cl(4)	93.23 (4)	C(16)—P(2)—C(17)	109.5 (2)
Cl(3)—Pd(2)—P(2)	92.53 (4)	C(16)—P(2)—C(23)	107.0 (2)
Cl(3)—Pd(2)—N(2)	176.44 (10)	C(17)—P(2)—C(23)	106.6 (2)
Cl(4)—Pd(2)—P(2)	173.94 (4)	Pd(1)—N(1)—C(1)	116.3 (3)
Cl(4)—Pd(2)—N(2)	89.25 (10)	Pd(2)—N(2)—C(15)	116.6 (3)
P(2)—Pd(2)—N(2)	85.07 (10)	N(1)—C(1)—C(2)	108.9 (3)
Pd(1)—P(1)—C(2)	100.9 (1)	P(1)—C(2)—C(1)	106.4 (3)
Pd(1)—P(1)—C(3)	112.9 (1)	N(2)—C(15)—C(16)	111.9 (4)
Pd(1)—P(1)—C(9)	121.1 (2)	P(2)—C(16)—C(15)	108.5 (3)
N(1)—C(1)—C(2)—P(1)	51.6 (4)		
N(2)—C(15)—C(16)—P(2)	−45.8 (5)		
C(2)—P(1)—C(3)—C(4)	−133.5 (4)		
C(16)—P(2)—C(17)—C(22)	155.5 (4)		
C(2)—P(1)—C(3)—C(8)	45.0 (4)		
C(16)—P(2)—C(17)—C(18)	−24.7 (5)		
C(2)—P(1)—C(9)—C(10)	−136.1 (5)		
C(16)—P(2)—C(23)—C(24)	119.0 (5)		
C(2)—P(1)—C(9)—C(14)	43.8 (6)		
C(16)—P(2)—C(23)—C(28)	−65.1 (5)		

Data were corrected only for Lorentz–polarization and absorption effects, and equivalent reflections were averaged. Reflections with $I < 0.5\sigma(I)$ were subsequently disregarded. The structure was solved by Patterson methods and expanded by Fourier difference syntheses. H atoms were located in a difference map. Their positions were not refined and their displacement parameters U_{iso} set as $1.2U_{eq}$ of the attached C atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985, 1992). Program(s) used to solve structure: *PATTY* in *DIRDIF*92 (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

I wish to thank Alan Kennedy for assistance in data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1349). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 310–313

catena-Poly[[tetrakis(μ-3,5-dinitrobenzoato-*O*:*O*′)dicopper(II)]bis[(μ-3,5-dinitrobenzoato-*O*:*O*′)(methanol-*O*)copper(II)]]†

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Abstract

The title complex, $[Cu_3\{(NO_2)_2C_6H_3COO\}_6(CH_3OH)_2]_n$, is a linear polymeric chain with the dinitrobenzoate ions forming all bridges. The chain is linked across $Cu(CH_3OH)_2$ units on symmetry centres and includes fourfold bridged pairs of Cu atoms with a Cu···Cu separation of 2.616 (2) Å. The latter Cu atoms are five-coordinated, surrounded by square pyramids of

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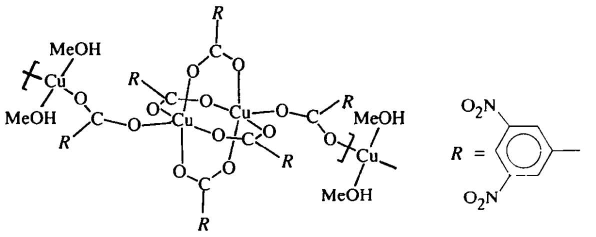
† Alternative name: *catena*-poly[[pentakis(μ-3,5-dinitrobenzoato)-1:2κ^8*O*:*O*′;2:3κ^2*O*:*O*′-dimethanol-3κ^2*O*-tricopper(II)]-μ-(3,5-dinitrobenzoato)-1κ*O*:κ*O*′].

carboxylate O atoms, each with a long apical Cu—O distance of 2.169 (2) Å and four short basal Cu—O distances in the range 1.951 (3)–1.959 (2) Å. The coordination in the $Cu(CH_3OH)_2$ unit is completed by two carboxylate O atoms to give a square-planar arrangement, with Cu—O distances of 1.933 (2) and 1.937 (2) Å.

Comment

3,5-Dinitrobenzoic acid is used for the preparation of amoxycillin and flucloxacillin (Amin *et al.*, 1994), but the anion can also serve as a ligand in metal complexes. IR studies of the Zn^{II}, Cd^{II} and Hg^{II} compounds indicate that the carboxylate groups coordinate the metal ions in a bidentate or bridging fashion (Odunola, 1993). The benzoate ions act as bidentate ligands also in copper compounds, *e.g.* $[Cu(C_6H_5COO)_2(C_5H_5N)]_2$ (Usubaliev *et al.*, 1980), $[Cu(C_6H_5COO)_2(py)]_2$ (Speier & Fulop, 1989) and $[Cu_2(C_6H_5COO)_4(C_{10}H_{14}N_2O)_2]$ (Hökelek *et al.*, 1995). The structure of the title compound (a copper complex of 3,5-dinitrobenzoate and methanol ligands), (I), was determined to further investigate the complex formation properties of the benzoate ligand.



(I)

The structure of (I) comprises linear polymeric chains formed by two Cu1 atoms bridged both to each other by four benzoate ligands and to Cu2 atoms on symmetry centres by fifth and sixth benzoate ligands (Fig. 1). The coordination polyhedron about the Cu1 atom is a square pyramid, with the Cu1 atom displaced by 0.203 (1) Å towards the centroid of the pyramid and the apical Cu1—O7 distance slightly longer than the basal Cu1—O distances to O1, O2, O13 and O14 (Table 1). The Cu2 atom is coordinated by two carboxylate and two methanol O atoms in a square-planar arrangement. The Cu2—O and basal Cu1—O distances, as well as the O—Cu—O angles, are in good agreement with values reported for other copper complexes, *e.g.* $[Cu_2(CH_3CO_2)_4(pyrazine)]$

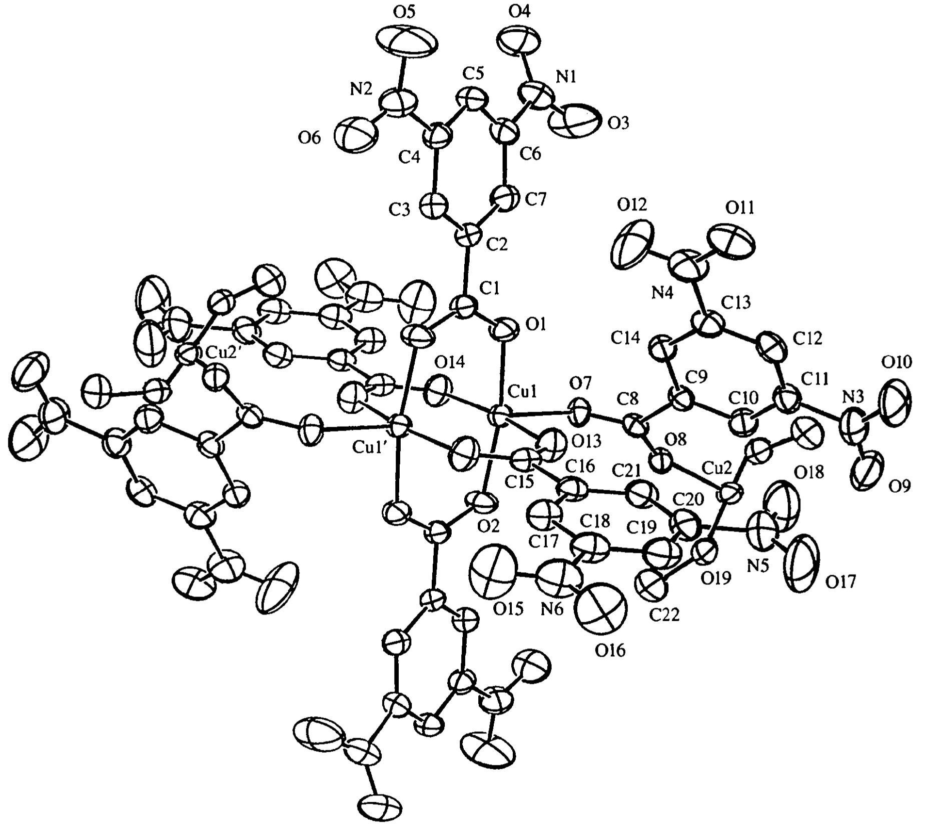


Fig. 1. An *ORTEP* (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

(Morosin *et al.*, 1975), $[Cu(C_6H_5CO_2)_2(py)]_2$ (Speier & Fulop, 1989), $[Cu(C_7H_5O_2)_2(C_{10}H_{14}N_2O)_2]$ (Hökelek *et al.*, 1996) and $[Cu(C_7H_4O_4N)_2(C_{10}H_{14}N_2O)_2(H_2O)_2]$ (Hökelek *et al.*, 1997).

The Cu1···Cu1($-x$, $1-y$, $-z$) distance is rather short, 2.616 (2) Å, as in similar copper–benzoate compounds (Usubaliev *et al.*, 1980; Speier & Fulop, 1989; van Niekerk & Schoening, 1953; Hökelek *et al.*, 1995). The metallic Cu—Cu bond length is 2.55 Å (Lee, 1986) so there might be a weak orbital interaction between the two Cu1 atoms.

Experimental

An aqueous solution of $NaHCO_3$ was added to hot 3,5-dinitrobenzoic acid in distilled water. After mixing by magnetic stirring for 30 min, a solution of Cu^{II} acetate was added and the reaction mixture refluxed for a further 24 h at 333 K. The reaction mixture was filtered and set aside for crystallization at ambient temperature for one month. Suitable deep-blue crystals were obtained by recrystallization from methanol.

Crystal data

$[Cu_3(C_7H_3N_2O_6)_6(CH_4O)_2]$
$M_r = 1584.931$
Triclinic
$P\bar{1}$
$a = 11.608\,(1)$ Å
$b = 11.986\,(1)$ Å
$c = 12.775\,(1)$ Å
$\alpha = 73.426\,(7)°$
$\beta = 71.549\,(7)°$
$\gamma = 62.478\,(7)°$
$V = 1474.7\,(2)$ Å^3
$Z = 1$
$D_x = 1.7846$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–18°$
$\mu = 1.540$ mm^{-1}
$T = 298$ K
Block
0.30 × 0.25 × 0.20 mm
Deep blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*MolEN*; Fair, 1990)
$T_{\min} = 0.643$, $T_{\max} = 0.735$
5726 measured reflections
5464 independent reflections
5438 reflections with $F > 0$

$R_{\rm int} = 0.017$
$\theta_{\max} = 26.3°$
$h = 0 \rightarrow 14$
$k = -12 \rightarrow 14$
$l = -14 \rightarrow 15$
3 standard reflections every 250 reflections frequency: 120 min intensity decay: 1%

Refinement

Refinement on F
$R = 0.055$
$wR = 0.070$
$S = 2.31$
5438 reflections
439 parameters
H atoms riding
$w = 1/[\sigma(I)^2 + (0.04F^2)^2]^{1/2}$

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 1.03$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Cu1—O1	1.951 (3)	O6—N2	1.209 (6)
Cu1—O2	1.957 (3)	O7—C8	1.234 (3)
Cu1—O7	2.169 (2)	O8—C8	1.263 (3)
Cu1—O13	1.959 (2)	O9—N3	1.238 (5)
Cu1—O14	1.958 (2)	O10—N3	1.213 (5)
Cu2—O8	1.933 (2)	O11—N4	1.209 (5)
Cu2—O19	1.937 (2)	O12—N4	1.194 (4)
O1—C1	1.248 (3)	O15—N6	1.213 (5)
O3—N1	1.203 (4)	O16—N6	1.192 (5)
O4—N1	1.217 (5)	O17—N5	1.212 (5)
O5—N2	1.210 (6)	O18—N5	1.191 (5)
O1—Cu1—O2	168.6 (1)	Cu1—O13—C15	122.0 (2)
O1—Cu1—O7	97.9 (1)	Cu2—O19—C22	130.8 (2)
O1—Cu1—O13	88.6 (1)	O5—N2—C4	117.3 (4)
O1—Cu1—O14	90.9 (1)	O1—C1—O2^{i}	126.4 (3)
O2—Cu1—O7	93.4 (1)	N1—C6—C5	119.3 (4)
O2—Cu1—O13	89.2 (1)	N1—C6—C7	117.5 (3)
O2—Cu1—O14	89.0 (1)	O7—C8—O8	125.3 (3)
O7—Cu1—O13	95.1 (1)	O7—C8—C9	119.7 (2)
O7—Cu1—O14	96.4 (1)	O8—C8—C9	115.1 (2)
O13—Cu1—O14	168.5 (1)	N3—C11—C10	119.3 (3)
O8—Cu2—O19	92.2 (1)	N3—C11—C12	118.2 (3)
Cu1—O1—C1	122.1 (3)	N4—C13—C12	117.6 (3)
Cu1—O7—C8	136.7 (2)	N4—C13—C14	118.8 (3)
Cu2—O8—C8	132.2 (2)	O13—C15—C16	116.8 (3)

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

H-atom positions were calculated geometrically, with $U_{\rm eq}(H) = 1.3U_{\rm eq}$ of the parent non-H atom. A riding model was used in the refinement.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELX*86 (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1512). Services for accessing these data are described at the back of the journal.

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Bis(2,2′-bipyridine-*N*,*N*′)(isocyanato-*N*)-copper(II) Tricyanomethanide

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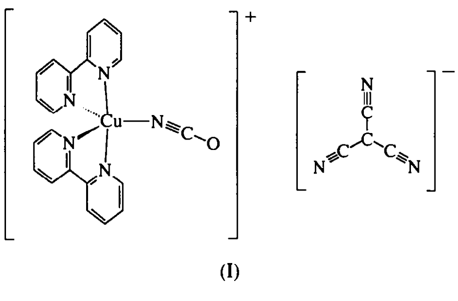
Abstract

The crystal structure of $[Cu(NCO)(C_{10}H_8N_2)_2][C(CN)_3]$ is formed by discrete $[Cu(bipy)_2(NCO)]^+$ cations and $[C(CN)_3]^-$ anions (bipy is 2,2′-bipyridine). The coordination polyhedron of the Cu^{II} atom is a distorted trigonal bipyramid with a CuN_5 chromophore.

Comment

In previous papers, we have described structures of compounds containing $[Cu(phen)_2(X)]^+$ cations [phen is 1,10-phenanthroline and X is a pseudohalogenide anion, *i.e.* CN^-, NCS^- or $N(CN)_2^-$] and $[C(CN)_3]^-$ anions (Potočňák *et al.*, 1996*a*,*b*,*c*). Our attempts to prepare a similar compound with $X = NCO^-$ have always resulted in blue needles of $[Cu(phen)(NCO)_2]$, the structure of which is already known (Jin *et al.*, 1991). On the other hand, replacement of phenanthroline with the 2,2′-bipyridine ligand yields $[Cu(bipy)_2(NCO)][C(CN)_3]$, (I), the preparation and crystal structure of which are presented here and compared with related compounds containing the phenanthroline ligand.



(I)

The labeling scheme of one formula unit is shown in Fig. 1. The coordination polyhedron around the Cu atom is a distorted trigonal bipyramid. The Cu atom is five-coordinated by four N atoms of the two bipy molecules and one N atom (in the equatorial plane) of the NCO^- ligand. The tcm^- anion [tcm^- is $C(CN)_3^-$] does not enter the inner coordination sphere. The two out-of-plane Cu—N20 and Cu—N40 bonds in (I) have similar values [2.003 (3) and 1.983 (3) Å, respectively], and are almost collinear [N20—Cu—N40 171.64 (13)°]. The two in-plane Cu—N bonds (Cu—N10 and Cu—N30) have different values [2.158 (3) and 2.054 (3) Å, respectively] and they are longer on average than the out-of-plane Cu—N distances by 0.106 Å. The third in-plane Cu—N5 (N from the NCO^- ligand) bond of 1.949 (4) Å is the shortest bond in the coordination polyhedron. The out-of-plane angles lie within the range 78.26 (13)–96.32 (12)°. All mentioned values of bond distances and angles are comparable with those of the previously published compounds containing phen.

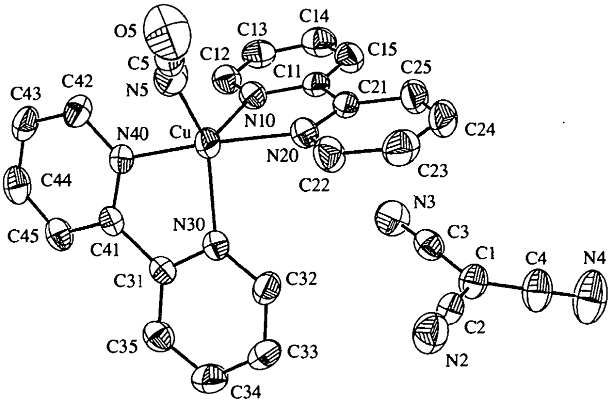


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the formula unit and labeling of atoms. Displacement ellipsoids are plotted at the 40% probability level.

The bond angles in the equatorial plane of (I) differ considerably from the ideal trigonal angle of 120°, with one large angle of 141.7 (2)° (α_1 = N5—Cu—N30) and two small angles of 114.54 (14) (α_2 = N5—Cu—N10) and 103.78 (12)° (α_3 = N30—Cu—N10). Thus, the angle α_3 is narrower than the ideal angle of 120° by 16.22° and there is a difference of 27.16° between α_1 and α_2. According to the criteria of Harrison & Hathaway (1980), the coordination polyhedron around the Cu atom can be best described as distorted trigonal bipyramidal with the square-pyramidal distortion shown by the elongated Cu—N10 equatorial bond. On the other hand, according to the values of the angles α_1, α_2 and α_3 for pentacoordinated compounds with two phen molecules, their coordination polyhedra can be best described as trigonal bipyramidal with near C_{2v} symmetry. The sum of the bond angles in the equatorial