Bis(benzoato-O,O')bis(nicotinamide-N)copper(II)

Ivan Leban,[a]* Primož Šegedin[a] and Karl Gruber[b]

[a]*Department of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, PO Box 537, 61001 Ljubljana, Slovenia, and* [b]*Institut für Physikalische Chemie, Karl-Franzens-Universität Graz, Heinrichstraße 28, A-8010 Graz, Austria. E-mail: ivan.leban@uni-lj.si*

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Abstract

The title compound, $[Cu(C_7H_5O_2)_2(C_6H_6N_2O)_2]$, belongs to the family of neutral copper(II) monomeric carboxylato complexes. The Cu^{II} ion lies on a twofold axis and the two bidentate benzoate groups form the equatorial plane. The Cu—O distances are 2.180 (3) and 2.209 (3) Å. The two nicotinamide moieties are bonded in axial positions [Cu—N 2.007 (3) Å], thus completing the distorted octahedral coordination around Cu^{II}. The amide groups of the two *trans* nicotinamide molecules are *cis* with respect to each other.

Comment

There are only a few examples of structure determinations of copper(II) complexes having nicotinamide as a ligand (Hoang, Valach & Melnik, 1993, and references therein). (Carboxylato)copper(II) complexes having a different coordination mode are of interest from both a biological and a chemical point of view (Bergant, Petrič, Pohleven, Reberšek & Šegedin, 1994; Melnik, 1982; Kato & Muto, 1988). We report herein the crystal structure of the monomeric complex $[Cu(benz)_2(nia)_2]$ [where benz is benzoate ($C_7H_5O_2^-$) and nia is nicotinamide ($C_6H_6N_2O$)], (I).

(I)
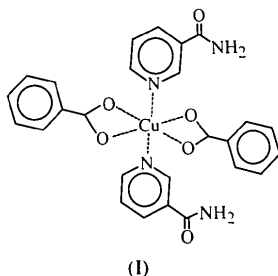
$[Cu(benz)_2(nia)_2]$ is a neutral monomeric octahedral complex of Cu^{II}, with an equatorial arrangement of the four benzoate O atoms and with the two nicotinamide molecules coordinated in axial positions. The equatorial Cu—O distances [2.180 (3) and 2.209 (3) Å] are quite different from those found for the sim-

ilar complex bis(salicylato)bis(nicotinamide)copper(II) [1.935 (6) and 2.609 (6) Å; Hoang, Valach & Melnik, 1993]. The axial Cu—N distance of 2.007 (3) Å is close to the value of 1.994 (7) Å observed for the compound cited above. Since the Cu ion is located on the twofold axis along **b**, the amide groups of the nicotinamide molecules were found to be *cis* with respect to each other, which is in contrast to the *trans* arrangement usually found when the complex possesses a centre of symmetry (Figs. 1 and 2). The monomeric $[Cu(benz)_2(nia)_2]$ complex units are linked together *via* N—H$\cdots$O hydrogen bonds. Only the two H atoms of the amide group are involved in these single nearly linear hydrogen bonds [N21$\cdots$O12^i 2.904 (5) Å and N21—H10$\cdots$O12^i 170.4 (2)°; N21$\cdots$O21^{ii} 2.769 (4) Å and N21—H11$\cdots$O21^{ii} 152.9 (3)°; symmetry codes: (i) $1-x, 1-y, -z$; (ii) $x, 1-y, \frac{1}{2}+z$]. There are no other unusual close intermolecular contacts.
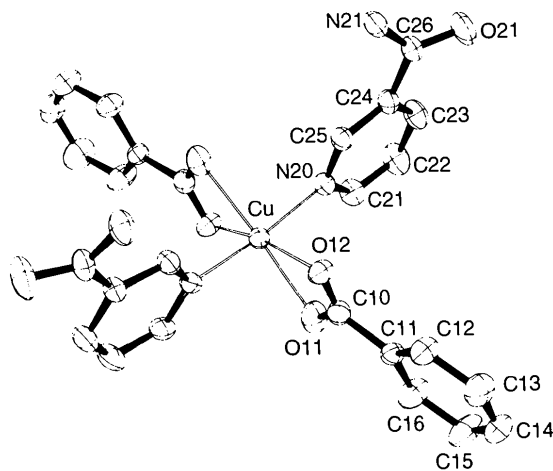

Fig. 1. *ORTEP*II (Johnson, 1971) view of the title complex with the atomic numbering scheme and anisotropic displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity.
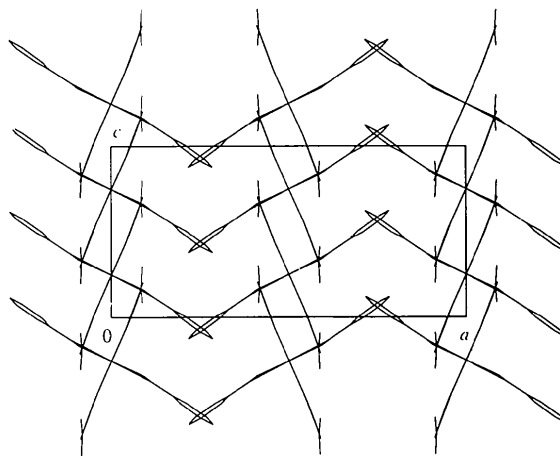

Fig. 2. *PLUTON* drawing (Spek, 1991) of the crystal packing viewed along the *b* direction.

C22	0.5797 (2)	0.8481 (4)	−0.1548 (4)	0.0710 (13)
C23	0.5885 (2)	0.7500 (4)	−0.2045 (4)	0.0645 (12)
C24	0.5743 (2)	0.6670 (3)	−0.1195 (3)	0.0470 (8)
C25	0.5503 (2)	0.6873 (3)	0.0126 (3)	0.0438 (8)
C26	0.5832 (2)	0.5605 (3)	−0.1758 (4)	0.0540 (10)
O21	0.5864 (2)	0.5467 (3)	−0.3012 (3)	0.0848 (11)
N21	0.5867 (2)	0.4840 (3)	−0.0862 (3)	0.0602 (9)

Experimental

Crystals suitable for X-ray diffraction analysis were obtained when metallic copper was added to a toluene solution of sodium benzoate and nicotinamide (molar ratio 1:1). Crystals proved to be stable in air.

Crystal data

[Cu(C$_7$H$_5$O$_2$)$_2$(C$_6$H$_6$N$_2$O)$_2$]
$M_r = 550.02$
Orthorhombic
Pbcn
$a = 20.054$ (4) Å
$b = 13.005$ (3) Å
$c = 9.611$ (2) Å
$V = 2506.6$ (9) Å^3
$Z = 4$
$D_x = 1.457$ Mg m^{-3}
$D_m = 1.46$ (2) Mg m^{-3}
D_m measured by flotation in chloroform/*n*-heptane

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9$–$11°$
$\mu = 0.920$ mm^{-1}
$T = 293$ (2) K
Prismatic
$0.38 \times 0.36 \times 0.32$ mm
Blue

Data collection

Stoe diffractometer
ω scans (fixed step of 1.2°)
Absorption correction:
refined from ΔF (*XABS2*; Parkin, Moezzi & Hope, 1995)
$T_{min} = 0.77$, $T_{max} = 0.97$
3412 measured reflections
3412 independent reflections

1979 observed reflections
$[I > 2\sigma(I)]$
$\theta_{max} = 30.01°$
$h = 0 \rightarrow 28$
$k = -18 \rightarrow 0$
$l = 0 \rightarrow 12$
3 standard reflections
monitored every 400 reflections
intensity decay: 2.6%

Refinement

Refinement on F^2
$R(F) = 0.0531$
$wR(F^2) = 0.1785$
$S = 1.074$
3387 reflections
168 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 1.4233P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.004$
$\Delta\rho_{max} = 0.363$ e Å^{-3}
$\Delta\rho_{min} = -0.487$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Cu	1/2	0.80079 (4)	1/4	0.0388 (2)
O11	0.42140 (14)	0.8987 (3)	0.1664 (3)	0.0729 (9)
O12	0.40862 (14)	0.7324 (3)	0.1611 (3)	0.0645 (8)
C10	0.3887 (2)	0.8213 (4)	0.1292 (4)	0.0547 (10)
C11	0.3269 (2)	0.8335 (3)	0.0447 (3)	0.0429 (8)
C12	0.2902 (2)	0.7496 (3)	0.0034 (5)	0.0586 (10)
C13	0.2344 (2)	0.7615 (4)	−0.0799 (5)	0.0739 (13)
C14	0.2159 (2)	0.8561 (4)	−0.1227 (5)	0.0750 (14)
C15	0.2509 (2)	0.9404 (4)	−0.0837 (6)	0.091 (2)
C16	0.3068 (2)	0.9290 (3)	0.0013 (6)	0.0742 (13)
N20	0.54077 (14)	0.7827 (2)	0.0608 (3)	0.0423 (7)
C21	0.5557 (2)	0.8621 (3)	−0.0227 (4)	0.0547 (10)

Table 2. *Selected geometric parameters (Å, °)*

Cu—N20^i	2.007 (3)	C13—C14	1.350 (7)
Cu—N20	2.007 (3)	C14—C15	1.355 (6)
Cu—O11^i	2.180 (3)	C15—C16	1.395 (6)
Cu—O11	2.180 (3)	N20—C25	1.337 (4)
Cu—O12^i	2.209 (3)	N20—C21	1.342 (4)
Cu—O12	2.209 (3)	C21—C22	1.370 (5)
O11—C10	1.253 (5)	C22—C23	1.373 (6)
O12—C10	1.262 (5)	C23—C24	1.383 (5)
C10—C11	1.489 (5)	C24—C25	1.383 (5)
C11—C16	1.371 (5)	C24—C26	1.499 (5)
C11—C12	1.376 (5)	C26—O21	1.219 (4)
C12—C13	1.384 (6)	C26—N21	1.318 (5)
N20^i—Cu—N20	166.5 (2)	C11—C12—C13	120.8 (4)
N20—Cu—O11^i	96.20 (11)	C14—C13—C12	120.1 (4)
N20—Cu—O11	91.66 (12)	C13—C14—C15	120.7 (4)
O11^i—Cu—O11	108.5 (2)	C14—C15—C16	119.5 (4)
O11—Cu—O12^i	167.89 (12)	C11—C16—C15	120.8 (4)
N20^i—Cu—O12	88.01 (11)	C25—N20—C21	118.3 (3)
N20—Cu—O12	86.58 (11)	N20—C21—C22	122.0 (4)
O11^i—Cu—O12	167.89 (11)	C21—C22—C23	119.4 (4)
O11—Cu—O12	59.50 (12)	C22—C23—C24	119.5 (4)
O12^i—Cu—O12	132.5 (2)	C25—C24—C23	117.7 (4)
O11—C10—O12	120.0 (4)	C25—C24—C26	123.3 (3)
O11—C10—C11	120.4 (4)	C23—C24—C26	118.9 (3)
O12—C10—C11	119.6 (4)	N20—C25—C24	123.0 (3)
C16—C11—C12	118.2 (4)	O21—C26—N21	122.2 (4)
C16—C11—C10	120.5 (4)	O21—C26—C24	119.9 (4)
C12—C11—C10	121.2 (4)	N21—C26—C24	117.9 (3)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Space group *Pbcn* (No. 60) was determined from the systematic absences. All H atoms were found in the difference electron density map, but were included in the refinement with calculated positions and isotropic displacement parameters of 1.2 times the U_{eq} value of their respective attached heavy atom. Calculations were performed on a PC 486 computer.

Data collection: local program (Kratky, 1993). Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971) and *PLUTON* (Spek, 1991). Software used to prepare material for publication: *SHELXL*93. Other programs used: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) and the *GX* package (Mallinson & Muir, 1985).

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[(η5-C5Me5)2Mo2(μ-I)4]+[FeI4]−.[(η5-C5Me5)2Mo2I2(μ-I)2(μ-O)]
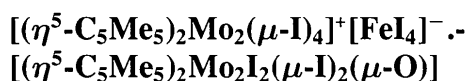
John C. Gordon,[a] Phillip E. Fanwick[b] and Rinaldo Poli[a]

[a]*Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA, and* [b]*Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA. E-mail: rp25@umail.umd.edu*

Abstract

The title compound, tetra-μ-iodo-bis[(η5-pentamethyl-cyclopentadienyl)molybdenum](*Mo—Mo*) tetraiodo-ferrate(III) di-μ-iodo-μ-oxo-bis[iodo(η5-pentamethylcyclopentadienyl)molybdenum](*Mo—Mo*), forms as a by-product of the thermal decarbonylation of [(η5-C5Me5)MoI3(CO)2] in tetrahydrofuran. The source of the iron is an impurity in the [(η5-C5Me5)2Mo2(CO)3]2 starting material used to make the triiodide compound. The structure consists of three independent species, namely a [(η5-C5Me5)2Mo2(μ-I)4]+ cation with two pentamethylcyclopentadienylmolybdenum moieties bridged by four iodide ligands, a tetrahedral [FeI4]− anion and a neutral dinuclear species comprising two pentamethylcyclopentadienyliodomolybdenum units bridged by two iodide and an oxo ligand. All three fragments sit on crystallographic mirror planes in the monoclinic space group P21/m.

Comment

The title compound, (I), crystallizes in the monoclinic space group $P2_1/m$ with one half of each moiety in the asymmetric unit. The cation [(η5-C5Me5)2Mo2(μ-I)4]+ (Fig. 1) sits on a mirror plane which passes through atoms Mo(21), Mo(22), I(21), I(22), C(211), C(2111), C(221) and C(2211). The pentamethylcyclopentadienyl groups are η5-bonded to the Mo atoms with Mo—C distances in the range 2.28–2.36 Å. The two metal atoms are at a bonding distance of 2.704 (2) Å from each other and are bridged by four iodide ligands with Mo—I distances in the range 2.735–2.774 Å. The metal–metal distance compares rather well with that observed for the same cation in the triiodide salt [2.718 (3) Å] (Desai, Gordon, Kraatz, Lee, Owens-Waltermire, Poli, Rheingold & White, 1994) as well as with the distance in the reduced neutral complexes [(η5-C5Me5)2Mo2(μ-I)4] [2.708 (3) Å] (Shin & Parkin, 1994) and [(η5-C9H7)2Mo2(μ-I)4] [2.720 (4) Å] (Falvello, Mattamana & Poli, 1995). The Mo—Mo distance for this structural type is not sensitive to the oxidation state because electrons are being pulled from non-bonding orbitals (Green, Green, Mountford & Parkington, 1990). The Mo—I distances are also comparable to, although at the short end of the range of, those reported for the above-mentioned neutral and oxidized dimolybdenum complexes {2.77–2.80 Å for [(η5-C5Me5)2Mo2(μ-I)4]+[I3]−, 2.78–2.80 Å for [(η5-C5Me5)2Mo2(μ-I)4], and 2.80–2.82 Å for [(η5-C9H7)2Mo2(μ-I)4])}, in accord with our assignment of this fragment as a positively charged, Mo$_2^{III,IV}$ species.

(I)
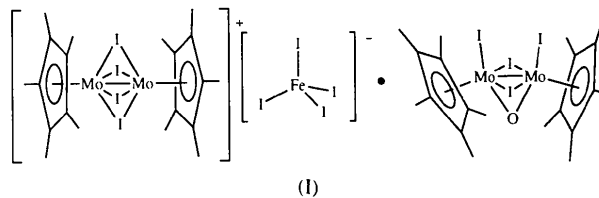
The anion (Fig. 2) sits on a mirror plane which passes through the Fe, I(31) and I(32) atoms. The geometry is close to ideal tetrahedral, the I—Fe—I angles being in the narrow range 107.4 (1)–111.4 (1)°. The Fe—I distances are in the range 2.510 (3)–2.546 (3) Å [average 2.531 (15) Å]. These compare very well with those found for the previously reported structures of [FeI4]− salts, namely (all values are averages over chemically equivalent distances) 2.531 (3) and 2.539 (2) Å for tetragonal and orthorhombic crystals, respectively, of the tetraethyl-ammonium salt (Pohl & Saak, 1985), 2.539 (21) Å for [Fe(CH2O)6][FeI4]2.I2 (Saak & Pohl, 1987), 2.541 (15) Å for [(Me2N)2CSSC(NMe2)2]2+[FeI4−]2 (Bierbach, Saak, Haase & Pohl, 1990), 2.533 (15) Å for [{(η5-C5H5)2Cr2(μ-SCMe3)(μ3-S)2}2Fe]+[FeI4]− (Pasynskii, Eremenko, Stomakhina, Nefedov, Ellert, Yanovsky & Struchkov, 1991) and 2.541 (12) Å for [SbPh4]-