metal-organic compounds

Two dimeric Cu^{II} benzoate derivatives solvated with acetonitrile

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The title compounds, tetrakis(μ-benzoato-O:O')bis(2,6-diaminopyridine)-1κN,2κN-dicopper(II)–acetonitrile (1/2), [Cu$_2$(C$_7$H$_5$O$_2$)$_4$(C$_5$H$_7$N$_3$)$_2$]·2C$_2$H$_3$N, (I), and bis(acetonitrile)-1κN,2κN-tetrakis(μ-benzoato-O:O')dicopper(II)–acetonitrile (1/1.5), [Cu$_2$(C$_7$H$_5$O$_2$)$_4$(C$_2$H$_3$N)$_2$]·1.5C$_2$H$_3$N, (II), crystallize as acetonitrile solvates exhibiting different stability. They have similar molecular structures with discrete dimeric units located at crystallographic inversion centres. The copper ions are bridged by four benzoate groups and neutral N-donor ligands, *viz.* 2,6-diaminopyridine in (I) and acetonitrile in (II), are coordinated at apical positions. The diverse stability is probably due to hydrogen-bond interactions of the solvated acetonitrile molecules with neighbouring dimers in compound (I).

Comment

Copper carboxylate complexes have properties of importance in various areas and accordingly have been extensively studied (Sundberg *et al.*, 1996, and references therein). In this series, mononuclear, dinuclear and polymeric complexes are known. In a continuation of our research on metal carboxylates with increased fungicidal activity, two dimeric Cu^{II} benzoates with 2,6-diaminopyridine and acetonitrile as axially coordinated ligands were prepared. Both compounds crystallize as acetonitrile solvates with markedly different stability. While compound (I) is stable in air, crystals of compound (II) decompose rapidly when taken from the mother liquor. In this context, the crystal structures of the title compounds are presented here.

In the unit cell, two crystallographically independent dimeric units are present in both structures, with an inversion centre located between the copper ions. The Cu atom is five-coordinated in a square-pyramidal fashion: four equatorial O atoms belong to bridging carboxyl groups and the N atom at the apical position belongs to 2,6-diaminopyridine in (I) (Fig. 1) and to acetonitrile in (II) (Fig. 2). Geometrical parameters are comparable to the values reported previously for similar types of compounds (Speier *et al.*, 1989; Kawata *et al.*, 1992; Leban *et al.*, 1997; Marsh, 1999). As reported by Sundberg *et al.* (1996), the longer the Cu···Cu distance within the dimer, the higher the Cu out-of-plane deviation. The Cu···Cu

(I)

(II)
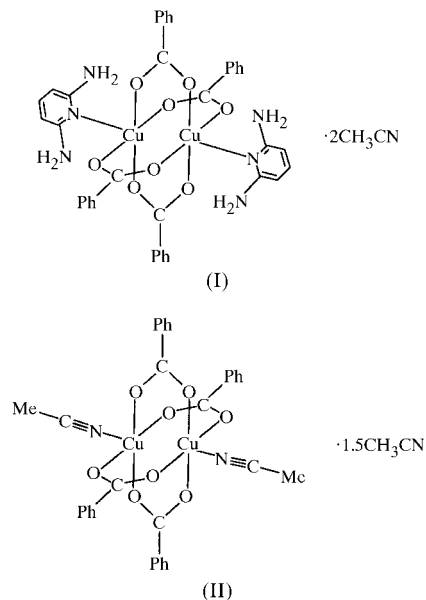
separations for (I) are 2.711 (1) and 2.713 (1) Å, with deviations of copper from the basal plane of 0.244 (2) Å for both dimeric units. In compound (II), the corresponding values are 2.6323 (5) and 2.6202 (5) Å for the Cu···Cu separations, and 0.1958 (7) and 0.1901 (6) Å for out-of-plane displacement.
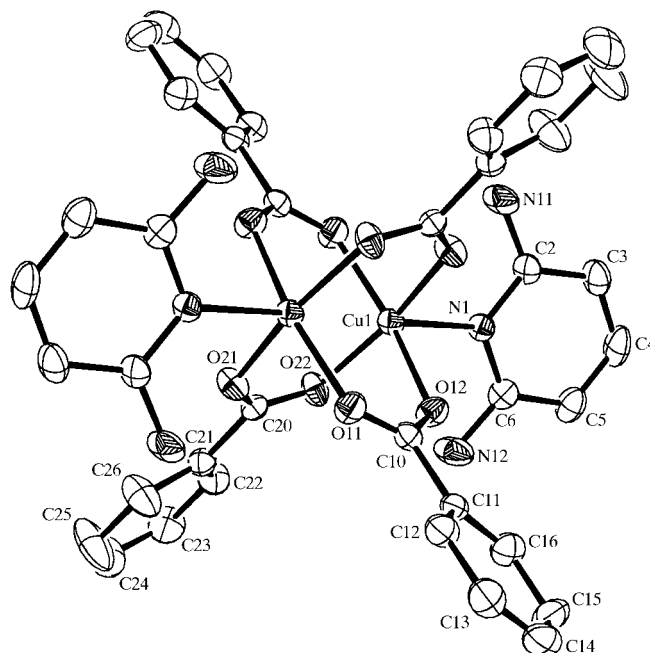

Figure 1
The structure of one dimeric unit of (I) with displacement ellipsoids drawn at the 50% probability level.

The main reason for the quite different stability of the two solvates could be ascribed to the hydrogen bonds present in compound (I). Due to the presence of hydrogen donors (amino groups), the extensive hydrogen bonding was expected. Beside the intramolecular N—H···O contacts, the solvated acetonitrile molecules are held in the crystal by N—H···N hydrogen bonds. One acetonitrile molecule is hydrogen bonded to one amino group of 2,6-diaminopyridine [N12···N8 3.139 (9) Å], while the other one is linked to two NH$_2$ groups of different neighbouring dimers [N11···N7 3.2798 Å and N22···N7($-x$ + 2, $-y$ + 1, $-z$) 3.490 (8) Å]. Detailed geometrical parameters for the hydrogen bonds in (I) are presented in Table 2. For compound (II), no classic hydrogen bonds were detected.
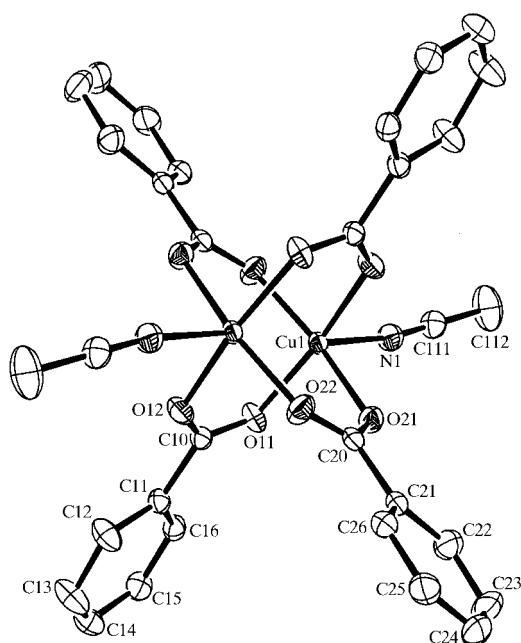

Figure 2
The structure of one dimeric unit of (II) with displacement ellipsoids drawn at the 50% probability level.

Experimental

Complex (I) was obtained by mixing acetonitrile solutions of copper benzoate and 2,6-diaminopyridine in a 1:2 molar ratio. Crystals were deposited at room temperature from the saturated solution. Crystals of compound (II) were obtained from a saturated solution of copper benzoate in acetonitrile after standing in the refrigerator for 2 d.

Compound (I)

Crystal data

[Cu$_2$(C$_7$H$_5$O$_2$)$_4$(C$_5$H$_7$N$_3$)$_2$]·2C$_2$H$_3$N
M_r = 911.92
Triclinic, $P\bar{1}$
a = 10.690 (1) Å
b = 12.822 (3) Å
c = 16.485 (2) Å
α = 85.24 (1)°
β = 71.24 (1)°
γ = 85.87 (1)°
V = 2129.7 (6) Å^3

Z = 2
D_x = 1.422 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 75
  reflections
θ = 8.1–14.6°
μ = 1.06 mm^{-1}
T = 293 (2) K
Prismatic, green
0.40 × 0.19 × 0.11 mm

Data collection

Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: Gaussian
  (*PLATON*; Spek, 1998)
  T_{min} = 0.61, T_{max} = 0.88
8494 measured reflections
8365 independent reflections
4333 reflections with I > 2σ(I)

R_{int} = 0.017
θ_{max} = 26.0°
h = −13 → 0
k = −15 → 15
l = −20 → 19
3 standard reflections
  every 600 reflections
  intensity decay: 17%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.154
S = 0.99
8365 reflections
543 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0852P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.75 e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

Cu1—O12	1.963 (3)	Cu2—O32^{ii}	1.961 (3)
Cu1—O11^i	1.968 (3)	Cu2—O31	1.964 (3)
Cu1—O21^i	1.971 (4)	Cu2—O41	1.971 (3)
Cu1—O22	1.975 (3)	Cu2—O42^{ii}	1.974 (4)
Cu1—N1	2.263 (4)	Cu2—N2	2.245 (4)
Cu1—Cu1^i	2.7114 (12)	Cu2—Cu2^{ii}	2.7130 (12)

Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $1 - x, 2 - y, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11A···O11^i	0.86	2.33	3.137 (6)	156
N11—H11A···O21^i	0.86	2.55	2.964 (5)	110
N11—H11B···N7	0.86	2.47	3.279 (8)	157
N12—H12A···O22	0.86	2.12	2.946 (6)	161
N12—H12B···N8	0.86	2.40	3.139 (9)	144
N21—H21A···O32^{ii}	0.86	2.36	3.073 (7)	140
N21—H21A···O41	0.86	2.37	3.000 (6)	130
N22—H22A···O42^{ii}	0.86	2.13	2.871 (7)	144
N22—H22A···O31	0.86	2.52	3.093 (6)	125
N22—H22B···N7^{iii}	0.86	2.69	3.490 (8)	154

Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $1 - x, 2 - y, -z$; (iii) $2 - x, 1 - y, -z$.

Compound (II)

Crystal data

[Cu$_2$(C$_7$H$_5$O$_2$)$_4$(C$_2$H$_3$N)$_2$]·- 1.5C$_2$H$_3$N
M_r = 755.21
Triclinic, $P\bar{1}$
a = 9.8750 (10) Å
b = 10.7070 (10) Å
c = 18.046 (2) Å
α = 75.860 (10)°
β = 79.690 (10)°
γ = 68.280 (10)°
V = 1710.5 (3) Å^3

Z = 2
D_x = 1.466 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 13 906
  reflections
θ = 2.1–26.5°
μ = 1.30 mm^{-1}
T = 150 (2) K
Prismatic, blue
0.22 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
13 906 measured reflections
7102 independent reflections
6315 reflections with I > 2σ(I)

R_{int} = 0.024
θ_{max} = 26.5°
h = −12 → 12
k = −13 → 13
l = −22 → 22

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Table 3
Selected bond lengths (Å) for (II).

Cu1—O11	1.9602 (13)	Cu2—O41^{ii}	1.9542 (12)
Cu1—O22^i	1.9644 (13)	Cu2—O42	1.9615 (12)
Cu1—O12^i	1.9666 (13)	Cu2—O31	1.9616 (13)
Cu1—O21	1.9704 (13)	Cu2—O32^{ii}	1.9737 (13)
Cu1—N1	2.1770 (16)	Cu2—N2	2.1986 (15)
Cu1—Cu1^i	2.6323 (5)	Cu2—Cu2^{ii}	2.6202 (5)

Symmetry codes: (i) $2 - x, -y, 1 - z$; (ii) $2 - x, 1 - y, -z$.

For compound (II), one solvated acetonitrile molecule was found to be disordered through an inversion centre, with a methyl C atom from one disordered molecule and a cyano C atom from the other sharing the same site. H atoms were included at calculated positions in both structures using *SHELXL*97 (Sheldrick, 1997) and refined as a riding model with isotropic displacement parameters taken from the attached heavy atoms and multiplied by 1.2 for aromatic and amino H atoms and by 1.5 for methyl H atoms.

For compound (I), data collection: *CAD*-4 *Software* (Enraf–Nonius, 1994); cell refinement: *PARAM* in *XRAY*76 (Stewart *et al.*, 1976); data reduction: *XCAD*4 (Harms & Wocadlo, 1995). For compound (II), data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*. For both compounds, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

References

Enraf–Nonius (1994). *CAD*-4 *Software*. Version 5.1. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.
Kawata, T., Uekusa, H., Ohba, S., Furukawa, T., Tokii, T., Muto, Y. & Kato, M. (1992). *Acta Cryst.* B**48**, 253–261.
Leban, I., Grgurevič, N., Sieler, J. & Šegedin, P. (1997). *Acta Cryst.* C**53**, 854–856.
Marsh, R. E. (1999). *Acta Cryst.* B**55**, 931–936.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Speier, G. & Fulop, V. (1989). *J. Chem. Soc. Dalton Trans.* pp. 2331–2333.
Spek, A. L. (1998). *PLATON*. Utrecht University, The Netherlands.
Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). *The XRAY*76 *System*. Technical Report TR-446. Computer Science Center, University of Maryland, College Park, Maryland, USA.
Sundberg, M. R., Uggla, R. & Melnik, M. (1996). *Polyhedron*, **15**, 1157–1163.