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Crystallographic report

Benzilate of diaquabis(ethylenediamine)copper(II) dihydrate and benzilate of aquabenzylatobis(ethylenediamine)copper(II)

Rosa Carballo*, Berta Covelo, Emilia García-Martínez and Ezequiel M. Vázquez-López

Departamento de Química Inorgánica, Facultad de Química, Edificio de Ciencias Experimentales, Universidad de Vigo, E-36310 Vigo, Galicia, Spain

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Compounds $[Cu(en)_2(OH_2)_2](HB)_2\cdot 2H_2O$ (1) and $[Cu(HB)(en)_2(OH_2)](HB)$ (2) (HB = benzilate; en = ethylenediamine) present the Cu(II) atom coordinated by different N_4O_2 donor sets, with 4 + 2 and 4 + 1 + 1 coordination geometries, respectively. In compound 1 the Cu(II) atom is located on a centre of inversion. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: copper; ethylenediamine complexes; benzilic acid; crystal structure

COMMENT

The title compounds $[Cu(en)_2(OH_2)_2](HB)_2\cdot 2H_2O$ (**1**) and $[Cu(HB)(en)_2(OH_2)](HB)$ (**2**) (HB = benzilate; en = ethylenediamine) are a contribution to the study of the chemistry of divalent metals complexes containing N-ligands and benzilic acid[1–3] because it is known that amine coordination compounds of copper(II) are active catalysts.[4] In **1**, the copper(II) atom lies on a crystallographic centre of inversion and the two benzilate molecules are monoanionic counterions. In the cation of **1** (Fig. 1) the oxygen atoms of two water molecules lying in axial positions, Cu–O = 2.653(5) Å, complete the elongated octahedral coordination sphere (4 + 2 coordination geometry). In the cation of **2** (Fig. 2) one benzilate molecule at a Cu–O distance of 2.725(5) Å creates an unsymmetrical tetragonal bipyramidal arrangement (4 + 1 + 1) about the Cu(II) atom. In compounds **1** and **2** the five-membered chelate ring bond angles of 84.81(18)° for **1** and 83.9(2) and 84.2(3)° for **2** are normal for ethylenediamine copper(II) complexes.[5] In both cases, the hydrogen bonds create a two-dimensional network.

*Correspondence to: Rosa Carballo, Departamento de Química Inorgánica, Facultad de Química, Edificio de Ciencias Experimentales, Universidad de Vigo, E-36310 Vigo, Galicia, Spain.
E-mail: rcrial@uvigo.es
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EXPERIMENTAL

Synthesis

A solution of benzilic acid (1 mmol) and ethylenediamine (1 mmol) in ethanol (20 ml) was slowly added to a suspension of $CuCO_3\cdot Cu(OH)_2\cdot 0.5H_2O$ (0.5 mmol) in water (20 ml). The mixture was refluxed for 1 h and stirred for several days, resulting in a purple solution. Concentration of the solution obtained in a sand bath (40 °C) afforded a solid composed of two kinds of crystals, **1** (purple) and **2** (blue), **1** being the major product. The pure products of **1** and **2** were obtained by manual separation. In these conditions the synthesis was repeated reproducibly, always with a very low yield for **2**. When the reaction occurs in acetonitrile, an unexpected product forms owing to the uptake of carbon dioxide from air: $[Cu(en)_2(H_2O)_2]$ $(OOCNHCH_2CH_2NHCOO)$.[6] Data for **1**: yield 25%, m. p., 220 °C, IR (KBr, cm^{-1}) ν(OH) + ν(NH): 3330vs, 3272s, 3146m, 3085m; ν_{asym}(OCO), 1615vs; ν_{sym}(OCO), 1352s; ν(CO), 1162m. Anal. found: C, 54.5; H, 6.8; N, 8.2. Calc. for $C_{32}H_{46}N_4O_{10}Cu$: C, 54.1; H, 6.5; N, 7.9. Data for **2**: yield <5% (it was possible to get some crystals for X-ray diffraction).

Crystallography

Intensity data for **1** and **2** were collected at 293 K on a Bruker SMART CCD diffractometer for a purple crystal $0.07 \times 0.12 \times 0.24\ mm^3$ (**1**) and for a blue crystal $0.29 \times 0.15 \times 0.05\ mm^3$ (**2**). **1**, $C_{32}H_{46}N_4O_{10}Cu$, M = 710.27, triclinic, P-1, $a = 7.4987(13)$, $b = 10.9857(18)$, $c = 11.1135(19)$ Å, $\alpha = 91.166(4)$, $\beta = 90.395(4)$, $\gamma = 109.429(4)°$, $V = 863.1(3)$ Å^3, $Z = 1$; 3599 unique data ($\theta_{max} = 28.0°$), $R = 0.073$ (1298 data with $I > 2\sigma(I)$), $wR = 0.184$ (all data), $\rho_{max} = 0.51$ e.Å^{-3}. **2**. $C_{32}H_{40}N_4O_7Cu$, $M = 656.22$, monoclinic, $P2_1/c$, $a = 24.052(4)$, $b = 9.9357(19)$, $c = 12.984(2)$ Å,

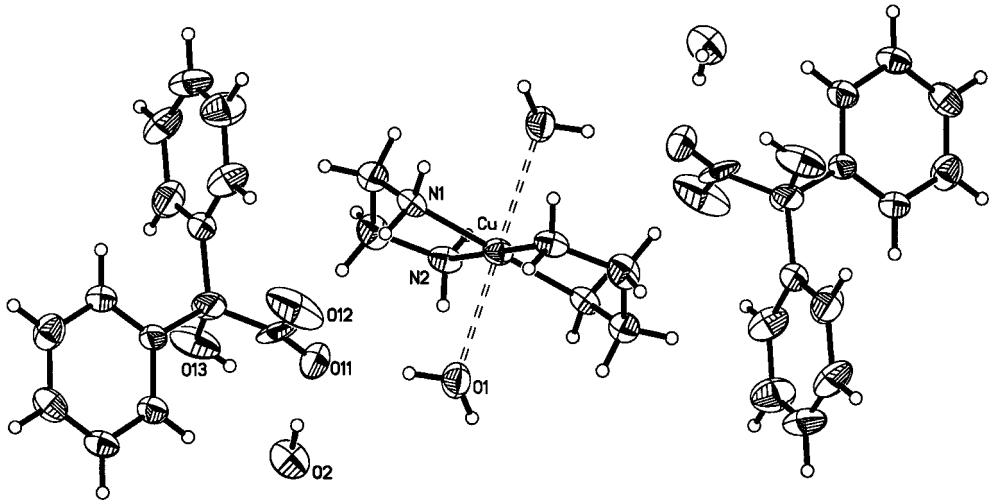

Figure 1. Molecular structure of compound **1**. Key geometric parameters: Cu–N1 2.009(4), Cu–N2 2.017(4), Cu–O1 2.653(5) Å; N1–Cu–N2 84.81(18), N1–Cu–N2^{i} 95.19(18), N1–Cu–O1 94.57(17), N1^{i}–Cu–O1 85.43(16), N2–Cu–O1 90.91(16), N2^{i}–Cu–O1 89.09(16)°. Symmetry operation: $i = -x + 2, -y + 1, -z$.

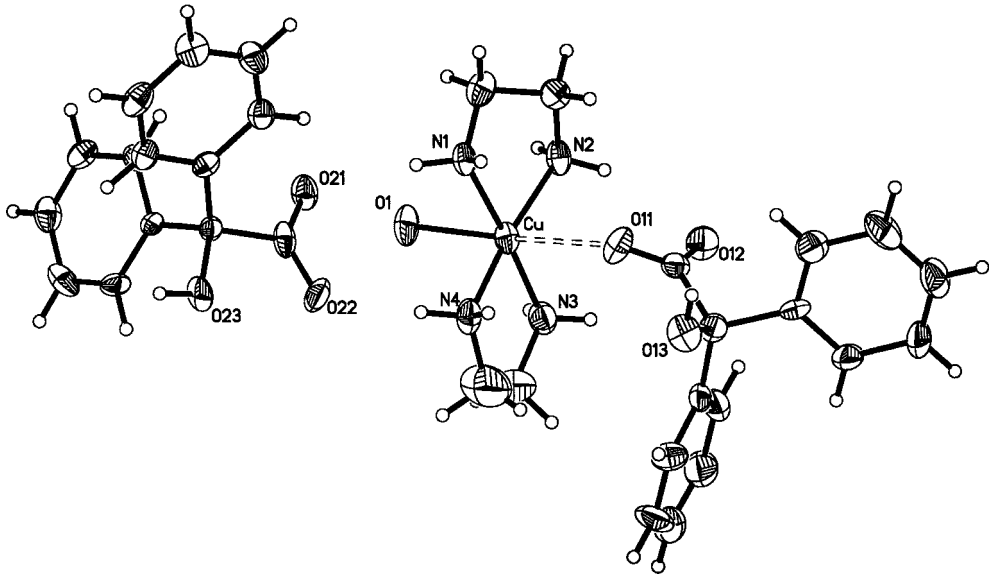

Figure 2. Molecular structure of compound **2**. Key geometric parameters: Cu–N1 1.973(6), Cu–N4 1.986(6), Cu–N3 1.992(6), Cu–N2 2.007(5), Cu–O1 2.336(4), Cu–O11 2.725(5) Å; N1–Cu–N4 95.2(3), N1–Cu–N3 175.6(2), N4–Cu–N3 84.2(3), N1–Cu–N2 83.9(2), N4–Cu–N2 170.3(2), N3–Cu–N2 97.3(2), N1–Cu–O1 85.52(19), N4–Cu–O1 97.5(2), N3–Cu–O1 90.2(2), N2–Cu–O1 92.0(2), N1–Cu–O11 90.12(19), N4–Cu–O11 82.2(2), N3–Cu–O11 94.2(2), N2–Cu–O11 88.21(19), O1–Cu–O11 175.58(17)°.

$\beta = 95.631(8)°$, $V = 3087.9(9)$ Å^3, $Z = 4$; 6806 unique data ($\theta_{max} = 28.1°$), $R = 0.071$ (1800 data with $I > 2\sigma(I)$), $wR = 0.171$ (all data), $\rho_{max} = 0.48$ e.Å^{-3}. Programs used: SAINT, SHELXS97, SHELXL97 and PLATON. CCDC deposition numbers: 245740 and 245741.

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REFERENCES

1. Carballo R, Covelo B, Balboa S, Castiñeiras A, Niclós J. *Z. Anorg. Allg. Chem.* 2001; **627**: 948.
2. Carballo R, Covelo B, García-Martínez E, Vázquez-López EM, Castiñeiras A. *Appl. Organometal. Chem.* 2004; **18**: 201.
3. Carballo R, Castiñeiras A, Covelo B, García-Martínez E, Niclós J, Vázquez-López EM. *Polyhedron* 2004; **23**: 1505.
4. Baesjou PJ, Driessen WL, Reedijk J, Spek AL. *Inorg. Chim. Acta* 2000; **306**: 237.
5. Melník M, Kabesová M, Macásková L, Holloway CE. *J. Coord. Chem.* 1998; **45**: 31.
6. Kovbasyuk LA, Fritsky IO, Kokozay VN, Iskenderov TS. *Polyhedron* 1997; **16**: 1723.