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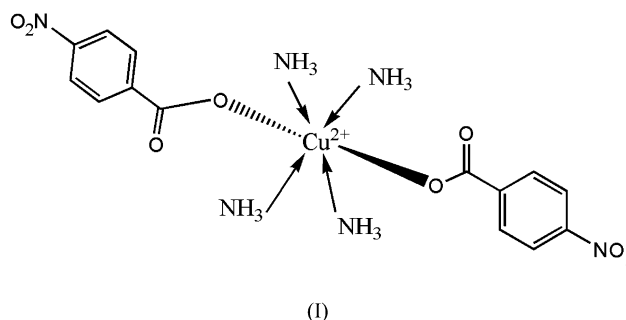
Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.042
 wR factor = 0.107
Data-to-parameter ratio = 12.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Tetraamminebis(4-nitrobenzoato- κO)copper(II)Received 1 March 2006
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In the title compound, $[\text{Cu}(\text{C}_7\text{H}_4\text{NO}_4)_2(\text{NH}_3)_4]$, the Cu atom is six-coordinated by four ammine N and two 4-nitrobenzoate O atoms. Of the two nitrobenzoate ligands, one gives weaker coordination than the other. These Cu complexes are connected through a complex pattern of hydrogen-bonding interactions, resulting in a three-dimensional network.

Comment

As a part of our study of copper(II) carboxylate complexes with molecular ligands showing biologically interesting properties, the title compound, (I) has been prepared and its structure determined. We report here this new structure of a Cu^{II} -carboxylate coordination complex.



The asymmetric unit of (I) contains a Cu complex coordinated by four ammine N and two 4-nitrobenzoate O atoms (Fig. 1). Although the two Cu—O distances, 2.389 (2) Å and 2.8744 (2) Å, are different, the longer one may be regarded as a normal bond in a complex with Jahn–Teller distortion where distances in the range 2.6–3.0 Å are frequently reported (Harding, 2000).

The four coordinating ammine N atoms around the central Cu are coplanar, constituting the equatorial square plane. The Cu atom lies -0.0798 (12) Å from this N_4 plane, whereas atoms O1 and O7 atoms are, respectively, -2.431 (2) and 2.736 (3) Å from it. The Cu1—N distances range from 2.013 (3) to 2.032 (3) Å, values comparable to those observed in diamminediaquabis(4-pyridylthioacetato)copper(II) (Huang *et al.*, 2004).

The shortest Cu—O(4-nitrobenzoate) bond length, 2.388 (3) Å, is longer than the corresponding bond distances reported for related Cu–nitrobenzoate coordination complexes: 1.962 (5) Å in $[\text{Cu}(\text{C}_7\text{H}_4\text{NO}_4)_2(\text{C}_6\text{H}_{12}\text{N}_2)(\text{H}_2\text{O})]_n$, (Lin & Lu, 2004) and 1.971 (1) Å in $[\text{Cu}(2\text{-NO}_2\text{bz})_2(3\text{-pyme})_2(\text{H}_2\text{O})_2]$ (Stachova *et al.*, 2006).

The ammine ligands and O atoms of 4-nitrobenzoate are engaged in extensive hydrogen bonding (Table 1), leading to the formation of a three-dimensional network (Fig. 2).

Experimental

All reagents and solvents were used as obtained without further purification. CuO (1 mmol, 80 mg) and 4-nitrobenzoic acid (2 mmol, 332 mg) were dissolved in an aqueous ammonia solution (10 ml, 30%), and the mixture was stirred for about 20 min at room temperature and then poured into a Teflon vessel till 30% of its volume was filled. The vessel was then placed in a stainless steel tank for hydrothermal treatment. The crystallization reaction was performed at 423 K under autogenous pressure for 24 h. After the autoclave was cooled and depressurized, large deep-blue crystals were found at the bottom of the vessel. The crystals were isolated, washed three times with water and dried in a vacuum desiccator using anhydrous CaCl₂ (yield 66%). Elemental analysis found: C 36.04, H 4.64, N 18.35%; calculated for C₁₄H₂₀CuN₆O₈: C 36.25, H 4.34, N 18.11%.

Crystal data

[Cu(C ₇ H ₄ NO ₄) ₂ (NH ₃) ₄]	Z = 2
<i>M_r</i> = 463.90	<i>D_x</i> = 1.665 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 7.2429 (6) Å	Cell parameters from 2000 reflections
<i>b</i> = 10.6794 (9) Å	θ = 2.0–24.5°
<i>c</i> = 12.6156 (11) Å	μ = 1.24 mm ⁻¹
α = 83.864 (1)°	<i>T</i> = 298 (2) K
β = 74.835 (1)°	Block, dark blue
γ = 79.867 (1)°	0.28 × 0.23 × 0.19 mm
<i>V</i> = 925.24 (14) Å ³	

Data collection

Siemens SMART CCD area-detector diffractometer	3204 independent reflections
φ and ω scans	2668 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R</i> _{int} = 0.024
<i>T</i> _{min} = 0.701, <i>T</i> _{max} = 0.790	θ _{max} = 25.0°
5762 measured reflections	<i>h</i> = -8 → 8
	<i>k</i> = -12 → 12
	<i>l</i> = -14 → 14

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.042	$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2]$
<i>wR</i> (<i>F</i> ²) = 0.107	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 1.03	(Δ/σ) _{max} = 0.001
3204 reflections	$\Delta\rho$ _{max} = 0.55 e Å ⁻³
266 parameters	$\Delta\rho$ _{min} = -0.33 e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H3A...O4 ⁱ	0.89	2.46	3.313 (4)	160
N3—H3B...O5 ⁱⁱ	0.89	2.13	3.017 (4)	173
N3—H3C...O5 ⁱⁱⁱ	0.89	2.51	3.357 (4)	160
N4—H4A...O2 ^{iv}	0.89	2.14	3.012 (4)	165
N4—H4B...O2	0.89	2.32	2.959 (3)	128
N4—H4C...O6 ⁱⁱⁱ	0.89	2.16	3.049 (3)	177
N5—H5A...O2 ^{iv}	0.89	2.10	2.958 (3)	161
N5—H5B...O6 ^v	0.89	2.19	3.073 (4)	170
N5—H5C...O3 ^{vi}	0.89	2.32	3.205 (3)	175
N6—H6A...O5 ⁱⁱ	0.89	2.12	3.007 (4)	172
N6—H6B...O4 ^{vi}	0.89	2.53	3.374 (4)	159
N6—H6C...O5 ^v	0.89	2.15	3.036 (4)	170

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

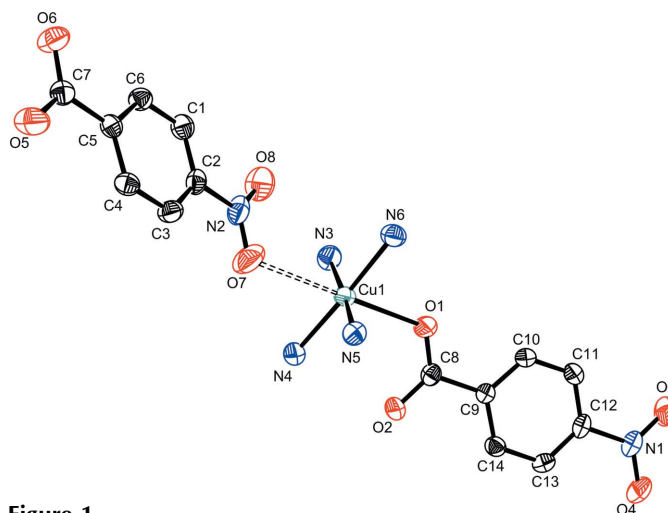


Figure 1

Molecular structure of the title compound, (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

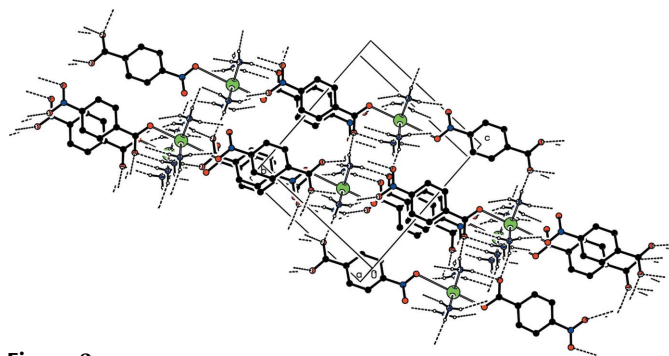


Figure 2

Crystal packing of (I), showing the three-dimensional hydrogen-bonding network. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonds have been omitted.

H atoms were placed in calculated positions, with C—H and N—H distances of 0.93 and 0.89 Å, respectively, and with *U*_{iso}(H) = 1.2*U*_{eq}(C) and 1.5*U*_{eq}(N).

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97.

References

- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Harding, M. M. (2000). *Acta Cryst.* **D56**, 857–867.
 Huang, Y. Q., Zhang, H. & Chen, J. G. (2004). *Acta Cryst.* **E60**, m133–m134.
 Lin, Z. D. & Lu, J. Y. (2004). *Acta Cryst.* **E60**, m1798–m1800.
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Systems Inc., Madison, Wisconsin, USA.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
 Stachova, P., Korabik, M., Koman, M. & Valigura, D. (2006). *Inorg. Chim. Acta*, **359**, 1257–1281.