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Acta Cryst. (1991). C**47**, 1202–1204

Structure of Dinitrato(2-thia-5,8-diazaoctane)copper(II)

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(*Received* 6 *February* 1990; *accepted* 17 *December* 1990)

Abstract. $[Cu(NO_3)_2(C_5H_{14}N_2S)]$, $M_r = 321{\cdot}79$, orthorhombic, $P2_12_12_1$, $a = 14{\cdot}883\ (4)$, $b = 8{\cdot}936\ (3)$, $c = 8{\cdot}917\ (3)$ Å, $V = 1185{\cdot}9\ (6)$ Å^3, $Z = 4$, $D_m = 1{\cdot}79$, $D_x = 1{\cdot}802$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 20{\cdot}362$ cm^{-1}, $F(000) = 660$, room temperature, $R = 0{\cdot}036$, $wR = 0{\cdot}038$ for 2201 reflections with $I \geq 3\sigma(I)$. The structure consists of monomeric molecules $[Cu\{2,2\text{-}NNS(Me)\}(NO_3)_2]$, where 2,2-NNS(Me) = 2-thia-5,8-diazaoctane. The coordination polyhedron of Cu^{II} is a tetragonal bipyramid: the tridentate, meridionally coordinated 2,2-NNS(Me) ligand, one bidentate and one monodentate nitrate ligand form a $[CuN_2O_3S]$ chromophore.

Introduction. The complexation properties of α,β- and α,ω-thiadiamines as potential tridentate ligands have been extensively studied with various transition metal ions in solution (Herman & Goeminne, 1977; Herman, Goeminne & Eeckhaut, 1978, 1979). A preference for 1/1 complex formation with Cu^{II} was noted for most of these ligands (Huys, Herman & Goeminne, 1982; Huys, Schaubroeck, Herman & Goeminne, 1982). A difference in complexation activity between the S atoms of α,β- and α,ω-thiadiamines has been observed (Huys, Herman & Goeminne, 1982; Huys, Hoste, Goeminne & Van der Kelen, 1983). As part of a structural study of copper complexes with sulfur–nitrogen chelating ligands the crystal and molecular structure of dinitrato(2-thia-5,8-diazaoctane)copper(II) is presented here.

Experimental. The preparation of 2,2-NNS(Me) and $[Cu\{2,2\text{-}NNS(Me)\}(NO_3)_2]$ has been described elsewhere (Herman & Goeminne, 1977; Herman, Goeminne & Eeckhaut, 1978, 1979). Blue prism-shaped crystals, $0{\cdot}33 \times 0{\cdot}16 \times 0{\cdot}20$ mm; density measured by flotation. Cell parameters refined on Siemens diffractometer (Mo $K\alpha$ radiation) by least squares from 20 reflections with $7{\cdot}00 \leq \theta \leq 8{\cdot}85°$. Absorption and extinction ignored. Intensity measurements from θ–2θ scans carried out for $0 \leq \theta \leq 28°$. h,k,l range h −17 to 17, k 0 to 10, l 0 to 10. Two standard reflections every 98 measurements decreased in intensity by 15% during the course of the experiment. 2201 independent reflections with $I \geq 3\sigma(I)$ (291 unobserved reflections). Average Friedel pairs were used. Cu-atom position from Patterson function, other non-H atoms from Fourier syntheses. H atoms from difference syntheses. Anisotropic full-matrix refinement for non-H atoms based

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Table 1. *Final positional parameters and equivalent isotropic thermal parameters* (Å^2 × 10^4) *for the non-*H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
Cu	0·42172 (3)	0·14261 (5)	−0·04478 (6)	223 (2)
S	0·4448 (1)	0·1736 (2)	0·2133 (1)	403 (3)
N(1)	0·3453 (2)	0·3243 (4)	−0·0325 (5)	338 (10)
N(2)	0·3957 (3)	0·1496 (5)	−0·2662 (5)	439 (13)
C(1)	0·3780 (4)	0·0326 (7)	0·3036 (8)	571 (19)
C(2)	0·3724 (4)	0·3376 (6)	0·2354 (6)	446 (16)
C(3)	0·3708 (4)	0·4238 (6)	0·0912 (5)	384 (14)
C(4)	0·3445 (3)	0·3922 (6)	−0·1839 (6)	419 (16)
C(5)	0·3299 (4)	0·2695 (7)	−0·2949 (7)	497 (18)
N(3)	0·4081 (3)	−0·1553 (4)	−0·0517 (5)	461 (14)
O(1)	0·4738 (2)	−0·0613 (4)	−0·0512 (5)	451 (10)
O(2)	0·3314 (3)	−0·1062 (6)	−0·0336 (6)	654 (16)
O(3)	0·4248 (4)	−0·2868 (4)	−0·0706 (6)	772 (19)
N(4)	0·6247 (2)	0·2645 (5)	−0·0674 (5)	364 (12)
O(4)	0·5452 (2)	0·3045 (5)	−0·0906 (4)	477 (11)
O(5)	0·6868 (2)	0·3503 (4)	−0·0990 (5)	511 (12)
O(6)	0·6410 (3)	0·1411 (5)	−0·0130 (7)	729 (19)

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu—S	2·343 (2)	N(4)—O(5)	1·233 (5)
Cu—N(1)	1·985 (4)	N(4)—O(6)	1·229 (6)
Cu—N(2)	2·013 (4)	S—C(1)	1·796 (7)
Cu—O(1)	1·981 (4)	S—C(2)	1·830 (6)
Cu—O(2)	2·600 (5)	C(2)—C(3)	1·499 (7)
Cu—O(4)	2·374 (4)	N(2)—C(3)	1·467 (6)
N(3)—O(1)	1·289 (6)	N(2)—C(4)	1·480 (7)
N(3)—O(2)	1·234 (6)	C(4)—C(5)	1·493 (8)
N(3)—O(3)	1·213 (5)	N(1)—C(5)	1·475 (7)
N(4)—O(4)	1·254 (5)		
S—Cu—N(1)	86·2 (1)	N(2)—Cu—O(4)	87·8 (2)
S—Cu—N(2)	171·1 (1)	O(1)—Cu—O(2)	54·3 (2)
S—Cu—O(1)	94·6 (1)	O(1)—Cu—O(4)	104·6 (1)
S—Cu—O(2)	98·0 (1)	O(2)—Cu—O(4)	158·1 (1)
S—Cu—O(4)	89·1 (1)	O(1)—N(3)—O(2)	118·1 (4)
N(1)—Cu—N(2)	85·3 (2)	O(1)—N(3)—O(3)	118·4 (5)
N(1)—Cu—O(1)	168·0 (2)	O(2)—N(3)—O(3)	123·5 (5)
N(1)—Cu—O(2)	113·6 (1)	O(4)—N(4)—O(5)	119·5 (4)
N(1)—Cu—O(4)	87·4 (2)	O(4)—N(4)—O(6)	120·4 (4)
N(2)—Cu—O(1)	94·3 (2)	O(5)—N(4)—O(6)	120·0 (4)
N(2)—Cu—O(2)	88·0 (2)		

on F (isotropic refinement for H atoms). $R = 0·036$, $wR = 0·038$, $w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$ ($k = 1·0754$, $g = 0·001161$); $(\Delta/\sigma)_{max} = 0·65$ in final least-squares cycle; $|\Delta\rho| \leq 0·9$ e Å^{-3}. Calculations performed with *SHELX76* (Sheldrick, 1976); scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. The final coordinates for the non-H atoms are listed in Table 1.* Selected interatomic distances and angles are presented in Table 2. The molecular structure of dinitrato(2-thia-5,8-diazaoctane)copper(II) and the atomic numbering are shown in Fig. 1.

Each molecule of the title complex consists of one Cu^{II} atom, one 2-thia-5,8-diazaoctane and two nitrate ligands. The Cu^{II} atom shows sixfold coordination in the form of a distorted and elongated tetragonal bipyramid. The 2,2-NNS(Me) ligand is meridionally disposed, thus occupying three equatorial coordination sites of the tetragonal bipyramid, as was proposed on the basis of the spectral (Huys, Schaubroeck, Herman & Goeminne, 1982) and the ESCA studies (Hoste, Huys, Schaubroeck & Van der Kelen, 1982; Huys, Hoste, Goeminne & Van der Kelen, 1983). The remaining three coordination sites are occupied by the O atoms of bidentate and monodentate nitrate ligands, thus completing the [CuN_2O_3S] chromophore.

The Cu—S distance of 2·343 (2) Å is only slightly greater than the sum of the covalent radii (Ball & Norbury, 1974) of Cu (1·176 Å) and S (1·04 Å).

The Cu—N(1), Cu—N(2) and Cu—O(1) distances [1·985 (4), 2·013 (4) and 1·981 (4) Å, respectively] are typical for equatorially bound atoms found for Cu^{II} complexes with N or O donor atoms (Gažo, Bersuker, Garaj, Kabešová, Kohout, Langfelderová, Melník, Serátor & Valach, 1976). The slight lengthening of Cu—N(2) relative to Cu—N(1) corresponds to the lower basicity of primary compared with secondary amine N(1) atoms.

The Cu—O(2) bond length [2·600 (5) Å] and the O(1)—Cu—O(2) bond angle [54·3 (2)°] clearly confirm the previous (Huys, Schaubroeck, Herman & Goeminne, 1982) suggestion that one of the two nitrate groups is asymmetrically bonded to the Cu^{II} atom as a bidentate ligand. The other nitrate group

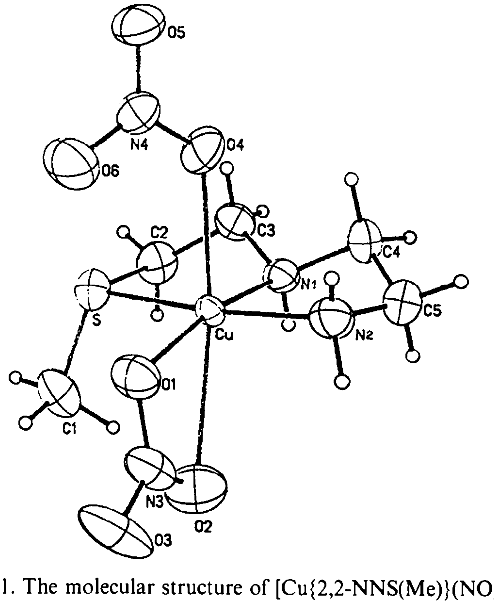

Fig. 1. The molecular structure of [Cu{2,2-NNS(Me)}(NO_3)$_2$].

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53834 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

is bonded to the Cu^{II} atom only through O(4), with the Cu—O(4) bond length [2·374 (4) Å] significantly shorter than that of Cu—O(2).

The molecules of the complex are held together by a system of intermolecular hydrogen bonds formed between O atoms O(3), O(5) and O(6), respectively, and the secondary [H(8)] and primary [H(13) and H(14)] amine H atoms of neighboring molecules [2·15 (6), 2·25 (6), 2·19 (7) and 2·35 (7) Å for O(5)···H(8), O(6)···H(8), O(5)···H(13) and O(3)···H(14), respectively].

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Acta Cryst. (1991). C**47**, 1204–1206

Structure of *trans*-Bis(1,4-butanedione dioximato)bis(triphenylarsine)copper(II), $[Cu(Hdmg)_2(Ph_3As)_2]$

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(*Received* 15 *February* 1990; *accepted* 19 *December* 1990)

Abstract. $C_{44}H_{44}As_2CuN_4O_4$, $M_r = 906{\cdot}24$, monoclinic, $P2_1/c$, $a = 8{\cdot}972\ (2)$, $b = 15{\cdot}730\ (3)$, $c = 15{\cdot}074\ (3)$ Å, $\beta = 105{\cdot}95\ (2)^\circ$, $Z = 2$, $V = 2045{\cdot}6\ (9)$ Å^3, $D_m = 1{\cdot}471$, $D_x = 1{\cdot}471$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 29{\cdot}163$ cm^{-1}, $F(000) = 926$, room temperature, $R = 0{\cdot}053$, $wR = 0{\cdot}062$ for 1869 reflections with $I \geq 3\sigma(I)$. The structure consists of isolated centrosymmetric $[Cu(Hdmg)_2(Ph_3As)_2]$ molecules (Hdmg = $C_4H_7N_2O_2$). Copper is hexacoordinated with dioximate ligands in the equatorial plane and the axial Ph_3As ligands [Cu—As = 3·044 (1) Å].

Introduction. In the course of our study of the stabilization of Cu^{II} complexes with reducing ligands, $[Cu(Hdmg)_2(Ph_3P)]$ has been prepared (Ondrejovič, Máriássy & Koman, 1989). The related complexes with copper/phosphine or copper/arsine ratios of 1/2 are unusual; addition of a second Ph_3P or Ph_3As ligand to pentacoordinate β-diketonate copper(II) complexes (Zelonka & Baird, 1972) invariably leads to the reduction of Cu^{II} to Cu^{I}. The title complex is therefore a copper dioximate arsine of novel type (Ondrejovič, Máriássy & Koman, 1989). Because of this and also since there is a paucity of known structures of copper(II)–R_3E (E = P,As,Sb) complexes [only dimeric copper carboxylates with Ph_3P were structurally characterized (McCrindle, Ferguson, McAlees & Roberts, 1981; Koman, Valigura & Ondrejovič, 1988)] a structure determination of the title complex was undertaken.

Experimental. Dark-brown prism-shaped crystals (Máriássy, 1988), 0·30 × 0·15 × 0·20 mm; density measured by flotation. Syntex $P2_1$ diffractometer, 15 reflections with $8{\cdot}14 \leq \theta \leq 15{\cdot}10^\circ$ for determining lattice parameters; absorption and extinction ignored. Intensity measurements from θ–2θ scans carried out for $0 \leq 2\theta \leq 100^\circ$. h 0–9, k 0–16, l −15–15. Two reflections every 98 measurements decreased in intensity by 15% during the course of the experiment, 1869 independent reflections with $I \geq 3\sigma(I)$, 237 unobserved reflections. Cu- and As-atom positions from Patterson function, other non-H atoms from Fourier syntheses. Position of H(1) from difference synthesis; those of other H atoms were calculated. Anisotropic full-matrix refinement for non H-atoms based on F. $R = 0{\cdot}053$, $wR = 0{\cdot}062$, $w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$ ($k = 1{\cdot}0000$, $g = 0{\cdot}01633$); $(\Delta/\sigma)_{\max} = 0{\cdot}8$ in final least-squares cycle; $|\Delta\rho| \leq 0{\cdot}9$ e Å^{-3}. Calculations performed with *SHELX76*

0108-2701/91/061204-03$03.00