Acta Cryst. (1992). C**48**, 14–16

Structure of [1-(3,5-Dimethyl-1-pyrazolyl)-3-thiapentane-*N*,*S*]-bis(nitrato-*O*,*O*)copper(II)

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(*Received* 27 *June* 1991; *accepted* 26 *July* 1991)

Abstract. [Cu($C_9H_{16}N_2S$)(NO_3)$_2$], $M_r = 371.9$, orthorhombic, $Pca2_1$, $a = 11.55$ (1), $b = 7.877$ (2), $c = 16.866$ (5) Å, $V = 1534$ Å^3, $Z = 4$, $D_x = 1.6$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 16$ cm^{-1}, $F(000) = 764$, $T = 298$ K, $R = 0.026$ and $wR = 0.040$ for 1507 observed reflections [$I > 2\sigma(I)$]. The structure of this compound consists of a copper(II) ion coordinated by one pyrazole nitrogen [1.943 (4) Å], one thioether sulfur [2.332 (1) Å] and two monodentate nitrate anions [1.979 (4) and 2.021 (3) Å]. The basic coordination geometry is square planar with the nitrates in *cis* positions. The orientation of the nitrates results in semi coordination of two additional nitrate oxygen atoms at 2.411 (4) and 2.479 (4) Å. The so-defined coordination geometry is a severely distorted octahedron.

Introduction. In the course of our programme (Haanstra, Driessen, Reedijk, Turpeinen & Hämäläinen, 1989; Haanstra, van der Donk, Driessen, Reedijk & Wood, 1990) towards the design and development of model compounds for the blue copper active site (Karlin & Zubieta, 1984; Bouwman, Driessen & Reedijk, 1990) several pyrazole containing N_2S_2 ligands were synthesized. The results obtained showed that these pyrazole ligands exhibit interesting coordination behaviour, *e.g.* non-coordinating thioethers (Haanstra *et al.*, 1989, 1990) and remarkable stable copper(I) compounds (Stoffels, Haanstra, Driessen & Reedijk, 1990). In order to investigate these features the study of the coordination behaviour of the ligand 1-(3,5-dimethyl-1-pyrazolyl)-3-thiapentane (abbreviated as mdtp) towards copper(II) salts was undertaken. This ligand is an NS donor ligand which can be interpreted as being a half N_2S_2 ligand, described in previous publications (Haanstra *et al.*, 1989, 1990). Only a few well defined compounds could be isolated with this ligand, among which is Cu(mdtp)(NO_3)$_2$. To ascertain the coordination geometry, and especially to establish whether or not the thioether sulfur was coordinated, a crystal structure determination was undertaken.

Experimental. The ligand mdtp was synthesized analogously to the N_2S_2 ligand bddo as described before (Haanstra *et al.*, 1989). Synthesis of Cu(mdtp)(NO_3)$_2$ was performed by mixing hot ethanolic solutions of 2 mmol hydrated copper(II) nitrate and 2 mmol of mdtp. On cooling to room temperature a crystalline solid was obtained with the composition Cu(mdtp)(NO_3)$_2$. A rod-like crystal (0.5 × 0.4 × 0.3 mm) suitable for X-ray structure determination was isolated from this batch.

The crystal was mounted in a glass capillary and diffraction data were collected on a CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The unit-cell parameters were refined from 25 reflections with $8.9 < \theta < 11°$. 4914 reflections were collected ($2.6 < \theta < 29.7°$, $-16 < h < 16$, $0 < k < 11$ and $0 < l < 23$) in the ω–2θ scan mode, yielding 2568 unique and 1507 observed reflections [$I > 2\sigma(I)$]. $R_{\rm int}$ was 8.6% and the transmission factors were between 86 and 109%. Three standard reflections were used with a 5% variation in intensity. Absorption correction was performed using the program *DIFABS* (Walker & Stuart, 1983). The anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The structure was solved in the space group $Pca2_1$. The fractional coordinates of the copper and sulfur atoms were determined using the Patterson function. The remaining non-hydrogen atoms were located by difference Fourier maps. The positions of the hydrogen atoms were calculated at 0.95 Å from the parent atom and during refinement coupled to that parent atom. The non-H atoms were refined anisotropically and the hydrogen atoms were refined isotropically with a coupled thermal parameter. The function minimized was $\sum(w|F_o| - |F_c|)^2$ with $w = 1/\sigma(F)$ using a locally developed set of programs (Kinneging & de Graaff, 1984). The final refinement resulted in the R values of 0.026 (R) and 0.040 (wR), $S = 0.53$ and maximum Δ/σ less than 0.03. Minimum and maximum electron densities in the final difference Fourier map were 0.39 and -0.55 e Å^{-3}. The fractional coordinates of the non-hydrogen atoms with isotropic thermal parameters are given in

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Table 1. *Fractional coordinates and isotropic thermal parameters* (Å^2) *for the non-hydrogen atoms of* Cu(mdtp)(NO$_3$)$_2$ *with e.s.d.'s in parentheses*

$B_{iso} = (8/3)\mathrm{trace}\,\mathbf{U}$.

	x	y	z	B_{iso}
Cu(1)	0.38161 (4)	0.12355 (6)	0.5	3.095 (11)
S(20)	0.34737 (9)	−0.11684 (13)	0.57725 (6)	3.40 (3)
N(11)	0.4070 (3)	−0.1512 (5)	0.3845 (2)	3.22 (9)
N(12)	0.3574 (3)	0.0027 (5)	0.4009 (2)	3.04 (9)
C(13)	0.3022 (4)	0.0511 (8)	0.3349 (3)	3.85 (12)
C(14)	0.3162 (4)	−0.0699 (9)	0.2774 (3)	4.70 (14)
C(15)	0.3819 (4)	−0.1980 (8)	0.3095 (3)	4.16 (13)
C(16)	0.2365 (5)	0.2132 (9)	0.3324 (4)	5.4 (2)
C(17)	0.4241 (8)	−0.3638 (9)	0.2751 (4)	5.9 (2)
C(18)	0.4674 (4)	−0.2439 (6)	0.4462 (3)	3.48 (10)
C(19)	0.3864 (3)	−0.2939 (5)	0.5141 (3)	3.58 (12)
C(21)	0.4704 (5)	−0.1069 (8)	0.6437 (4)	4.55 (14)
C(22)	0.4703 (7)	−0.2519 (10)	0.7028 (5)	6.0 (2)
N(31)	0.2754 (4)	0.3303 (5)	0.5942 (3)	4.11 (11)
O(32)	0.3758 (3)	0.2621 (6)	0.5978 (3)	4.87 (11)
O(33)	0.2484 (5)	0.4304 (6)	0.6456 (4)	6.93 (15)
O(34)	0.2157 (3)	0.2912 (6)	0.5375 (3)	5.39 (13)
N(41)	0.5640 (3)	0.2851 (6)	0.4430 (3)	4.35 (11)
O(42)	0.4550 (3)	0.3221 (4)	0.4432 (3)	4.13 (9)
O(43)	0.6313 (3)	0.3794 (5)	0.4092 (5)	6.4 (2)
O(44)	0.5930 (3)	0.1539 (5)	0.4789 (4)	5.50 (15)

Table 1 and interatomic distances and angles in Table 2.*

Discussion. The structure of Cu(mdtp)(NO$_3$)$_2$ is depicted in Fig. 1. The copper(II) atom is coordinated by one pyrazole nitrogen at 1.943 (4) Å, one thioether sulfur at 2.332 (1) Å and two apparently monodentate nitrate anions at 1.979 (4) and 2.021 (3) Å. The coordination geometry is square planar with the nitrates in *cis* positions. The angles between the several donors at Cu(1) are listed in Table 2 and show that there is a small distortion from planarity. The orientation of the nitrates in fact results in semi coordination of two additional nitrate oxygen atoms at 2.411 (4) and 2.479 (4) Å. The so-defined coordination geometry is a highly distorted octahedron, which is illustrated by the small angles O(44)—Cu—O(42) 56.2 (1)° and O(34)—Cu—O(32) 56.8 (2)° as well as the angle O(34)—Cu—O(44) 140.1 (1)°. Inspection of the crystal packing only shows normal van der Waals interactions.

Table 2. *Complete list of bond distances* (Å) *and bond angles* (°) *of* Cu(mdtp)(NO$_3$)$_2$ *with e.s.d.'s in parentheses*

Cu(1)—S(20)	2.332 (1)	Cu(1)—N(12)	1.943 (4)
Cu(1)—O(32)	1.979 (4)	Cu(1)—O(34)	2.411 (4)
Cu(1)—O(42)	2.021 (3)	Cu(1)—O(44)	2.479 (4)
S(20)—C(19)	1.811 (4)	S(20)—C(21)	1.811 (6)
N(11)—N(12)	1.370 (5)	N(11)—C(15)	1.348 (6)
N(11)—C(18)	1.450 (6)	N(12)—C(13)	1.338 (6)
C(13)—C(14)	1.369 (8)	C(13)—C(16)	1.486 (8)
C(14)—C(15)	1.374 (8)	C(15)—C(17)	1.510 (9)
C(18)—C(19)	1.531 (6)	C(21)—C(22)	1.515 (9)
N(31)—O(32)	1.280 (6)	N(31)—O(33)	1.213 (7)
N(31)—O(34)	1.219 (6)	N(41)—O(42)	1.292 (5)
N(41)—O(43)	1.217 (7)	N(41)—O(44)	1.243 (6)
S(20)—Cu(1)—N(12)	93.3 (1)	S(20)—Cu(1)—O(32)	88.6 (1)
S(20)—Cu(1)—O(42)	164.7 (1)	N(12)—Cu(1)—O(32)	169.1 (1)
N(12)—Cu(1)—O(42)	91.8 (2)	O(32)—Cu(1)—O(42)	89.0 (2)
O(34)—Cu(1)—S(20)	99.4 (1)	O(34)—Cu(1)—N(12)	112.3 (1)
O(34)—Cu(1)—O(32)	56.8 (2)	O(34)—Cu(1)—O(42)	91.9 (1)
O(34)—Cu(1)—O(44)	140.1 (1)	O(44)—Cu(1)—S(20)	109.0 (1)
O(44)—Cu(1)—N(12)	93.7 (1)	O(44)—Cu(1)—O(32)	95.7 (2)
O(44)—Cu(1)—O(42)	56.2 (1)	Cu(1)—S(20)—C(19)	104.8 (1)
Cu(1)—S(20)—C(21)	100.2 (2)	C(19)—S(20)—C(21)	101.7 (2)
N(12)—N(11)—C(15)	110.0 (4)	N(12)—N(11)—C(18)	120.1 (4)
C(15)—N(11)—C(18)	129.7 (4)	Cu(1)—N(12)—N(11)	123.2 (3)
Cu(1)—N(12)—C(13)	130.1 (3)	N(11)—N(12)—C(13)	106.4 (4)
N(12)—C(13)—C(14)	109.6 (4)	N(12)—C(13)—C(16)	120.8 (4)
C(14)—C(13)—C(16)	129.6 (5)	C(13)—C(14)—C(15)	107.3 (4)
N(11)—C(15)—C(14)	106.7 (4)	N(11)—C(15)—C(17)	121.8 (5)
C(14)—C(15)—C(17)	131.4 (5)	N(11)—C(18)—C(19)	111.9 (4)
S(20)—C(19)—C(18)	113.2 (3)	S(20)—C(21)—C(22)	112.0 (4)
O(32)—N(31)—O(33)	118.1 (5)	O(32)—N(31)—O(34)	116.3 (4)
O(33)—N(31)—O(34)	125.5 (5)	Cu(1)—O(32)—N(31)	102.8 (3)
O(42)—N(41)—O(43)	119.0 (4)	O(42)—N(41)—O(44)	116.7 (4)
O(43)—N(41)—O(44)	124.3 (4)	Cu(1)—O(42)—N(41)	103.6 (3)

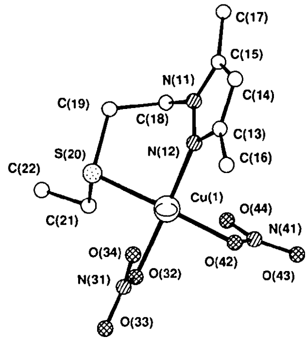

Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing of Cu(mdtp)(NO$_3$)$_2$. Hydrogen atoms are omitted for clarity.

The ligand field spectrum of Cu(mdtp)(NO$_3$)$_2$ shows one broad absorption at 15.6 × 10^3 cm^{-1}, in good agreement with other square-planar copper(II) coordination compounds (Lever, 1984). The infrared spectrum, as a Nujol mull, shows in the $\nu_1 + \nu_4$ overtone region of the N—O stretch vibration two sharp vibrations at 1710 and 1750 cm^{-1}. The splitting between these vibrations, 40 cm^{-1}, can be related to the coordination mode of the nitrate anion (Lever, Mantovani & Ramaswamy, 1971). A splitting of 40 cm^{-1} can be interpreted as being intermediate between that of a monodentate nitrate anion (16–26 cm^{-1}) and that of a didentate nitrate anion (38–56 cm^{-1}). This agrees well with the short O—Cu distances [1.979 (4) and 2.021 (3) Å] and the long O—Cu distances [2.411 (4) and 2.479 (4) Å], observed in the present crystal structure. Combining

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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 54477 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI0094]

the spectroscopic and structural results, the coordination mode of the nitrates can best be described as asymmetric didentate.

We thank Mr S. Gorter for the collection and processing of the diffraction data. We are also grateful to the undergraduate students R. Fijneman and E. van Haren for the synthesis of the ligand and the coordination compounds.

References

Bouwman, E., Driessen, W. L. & Reedijk, L. (1990). *Coord. Chem. Rev.* **104**, 143–172.

Haanstra, W. G., Driessen, W. L., Reedijk, J., Turpeinen, U. & Hämäläinen, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. 2309–2314.

Haanstra, W. G., van der Donk, W. A. J. W., Driessen, W. L., Reedijk, J. & Wood, J. S. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3123–3128.

Karlin, K. D. & Zubieta, J. (1984). Editors. *Biological and Inorganic Copper Chemistry*, Vols. 1 and 2. New York: Adenine Press.

Kinneging, A. J. & de Graaff, R. A. G. (1984). *J. Appl. Cryst.* **17**, 364–365, and references therein.

Lever, A. B. P. (1984). *Inorganic Electronic Spectroscopy*. Amsterdam: Elsevier.

Lever, A. B. P., Mantovani, E. & Ramaswamy, B. S. (1971). *Can. J. Chem.* **49**, 1957–1964.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Stoffels, A. L. E., Haanstra, W. G., Driessen, W. L. & Reedijk, J. (1990). *Angew. Chem. Int. Ed. Engl.* **29**, 1419–1420.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1992). C**48**, 16–19

Structure of a Complex of 1,4,8,11-Tetraazacyclotetradecane (Cyclam) with Zinc(II) Chloride

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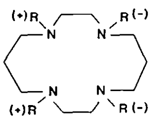
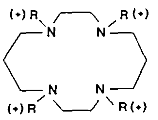
(*Received* 14 *May* 1991; *accepted* 9 *July* 1991)

Abstract. Bis[μ-chloro-(1,4,8,11-tetraazacyclotetradecane)zinc(II)] tetrachlorozincate(II) hemihydrate, $[ZnCl(C_{10}H_{24}N_4)]^+_{2n}.n[ZnCl_4]^{2-}.(n/2)H_2O$, $M_r = 818.5$ for $n = 1$, tetragonal, $I\bar{4}2d$, $a = 17.950\,(5)$, $c = 10.907\,(2)$ Å, $V = 3514\,(1)$ Å^3, $Z = 4$, $D_m = 1.52$, $D_x = 1.55$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 25.7$ cm^{-1}, $T = 290$ K, $R = 0.095$ for 750 unique observed [$I/\sigma(I) \geq 2.0$] reflections. The structure consists of infinite —Cl—[Zn(cyclam)]$^{2+}$—Cl— chains interspersed with $[ZnCl_4]^{2-}$ ions. The mean Zn—N and Zn—Cl (chain) distances are 2.13 (1) and 2.730 (4) Å, while the Zn—Cl bond length in the anion is 2.288 (5) Å.

Introduction. Complexes of the ligand 1,4,8,11-tetraazacyclotetradecane [cyclam (*A*), *R* = H] and its *N*-substituted derivatives have a number of possible conformations depending on the relative orientations of the N—*R* bonds and the metal-ion geometry (Bosnich, Poon & Tobe, 1965). The commonest conformation reported for complexes of first-row transition metals with cyclam itself is that known as *trans*-(III), in which the N—H bonds are oriented up and down as shown schematically in (*A*) [(+) and (−) represent the relative positions of the N—*R* groups above and below the macrocyclic ligand plane respectively]. The *trans*-(III) conformation was found in the octahedral $[Ni(cyclam)Cl_2]$ (Bosnich, Mason, Pauling, Robertson & Tobe, 1965), and recently in $[Zn(cyclam)(ClO_4)_2]$ (Tyson, Hodgson, Hedman & Clark, 1990). However, the factors determining the relative stability of these complexes are not always obvious, and for the related *N*-tetramethylcyclam (tmc) complexes isomerism between the *trans*-(I) and *trans*-(III) forms, and *vice versa*, has been observed in different solvents (Moore, Sachinidis & Willey, 1983). In the solid state, $[Zn(tmc)Cl](ClO_4)$ [tmc = (*B*), $R = CH_3$] shows square-pyramidal geometry with the *trans*-(I) conformation (all N—*R* groups on the same side), but in solution it is fluxional betweent two identical trigonal bipyramids (Alcock, Herron & Moore, 1978). Therefore, it is of interest to examine the structures of other related complexes, and we here report that of the complex formed between $ZnCl_2$ and cyclam, and its isomerism in aqueous solution as observed by ^{13}C NMR.



(*A*)
trans-(III)



(*B*)
trans-(I)

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