

**Structure of the Dinuclear Copper(II) Compound of *N,N,N',N'*-Tetrakis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]-1,2-ethylenediamine (tped),  $[\text{Cu}_2(\text{tped})(\text{H}_2\text{O})_2(\text{NO}_3)_2](\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH}$**

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**Abstract.**  $\mu$ -{*N,N,N',N'*-Tetrakis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]-1,2-ethylenediamine}-bis[aquanitratocopper(II)] dinitrate dimethanol solvate, asymmetric unit  $[\text{Cu}(\text{C}_{30}\text{H}_{48}\text{N}_{10})_{0.5}(\text{H}_2\text{O})(\text{NO}_3)]\text{NO}_3 \cdot \text{CH}_3\text{OH}$ ,  $M_r = 512.0$ , monoclinic,  $P2_1/n$ ,  $a = 12.683$  (4),  $b = 10.374$  (2),  $c = 19.229$  (4) Å,  $\beta = 111.92$  (2)°,  $V = 2347.0$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.44$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.710730$  Å,  $\mu = 9.77$  cm<sup>-1</sup>,  $F(000) = 1072$ ,  $T = 298$  K; the structure was solved by the heavy-atom method and refined by least squares to a residual  $R$  of 0.036 ( $wR = 0.052$ ) for 2361 significant [ $I > 2\sigma(I)$ ] reflections. The Cu<sup>II</sup> ion is surrounded by two pyrazole N atoms at 1.993 (4) and 2.013 (3) Å, one amine N atom of tped at 2.303 (3) Å, an O atom of one of the nitrate anions at 2.063 (3) Å, and a water O atom at 1.947 (3) Å in a distorted square pyramid. The ligand accommodates two Cu<sup>II</sup> ions at a distance of 6.563 (1) Å. A hydrogen-bond network connects the methanol molecule to the coordinated nitrate ion, and the coordinated water molecule to the methanol molecule and to the non-coordinated nitrate ion. In this way the asymmetric units are linked together in zigzag chains in a plane perpendicular to the  $b$  axis.

**Introduction.** In the course of our program to design and develop model compounds for the active site of type III copper enzymes, several amine substituted pyrazole ligands were synthesized (Driessen, 1982; Hulsbergen, Driessen, Reedijk & Verschoor, 1984; Haanstra, Driessen, de Graaff, Sebregts, Suriano, Reedijk, Turpeinen, Hämäläinen & Wood, 1991). With the hexadentate N-donor ligand *N,N,N',N'*-tetrakis(1-pyrazolylmethyl)-1,2-diaminoethane several mononuclear coordination compounds of divalent transition-metal ions were obtained (Hulsbergen *et al.*, 1984). In these compounds the N(pyrazole)–metal ion–N(amine) bond angles are substantially smaller than 90° owing to the restricted ligand bite. Enlargement of this three-bond bite to a four-bond bite should result in coordination angles

which are closer to regular octahedral bond angles. This enlargement has been realized in the ligand *N,N,N',N'*-tetrakis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]-1,2-ethylenediamine (tped), which rendered with copper(II) nitrate, single crystals of  $[\text{Cu}_2(\text{tped})(\text{H}_2\text{O})_2(\text{NO}_3)_2](\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH}$  suitable for X-ray diffraction. Since it was not clear if, perhaps, a bridging ligand, such as water or nitrate (Hendriks, Birker, van Rijn, Verschoor & Reedijk, 1982) was present, a structure determination was undertaken.

**Experimental.** The ligand *N,N,N',N'*-tetrakis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]-1,2-ethylenediamine (tped) was synthesized by a published procedure (Haanstra *et al.*, 1991). Crystals of  $[\text{Cu}_2(\text{tped})(\text{H}_2\text{O})_2(\text{NO}_3)_2](\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH}$  were grown by cooling a hot methanol solution of 0.010 mol  $\text{Cu}(\text{H}_2\text{O})_6(\text{NO}_3)_2$ , 0.06 mol trimethylorthoformate, and 0.005 mol tped. A blue–green needle (0.5 × 0.2 × 0.2 mm) mounted in a glass capillary, was subjected to graphite-monochromated Mo  $K\alpha$  radiation on a four-circle Enraf–Nonius CAD-4 diffractometer, operated in the  $\omega/\theta$  mode. The asymmetric unit contains half of the molecule. Cell dimensions were determined from the setting angles of 24 reflections ( $10 < \theta < 12^\circ$ ). Intensities were corrected for Lorentz and polarization effects; absorption corrections were not applied. The scanning rate was adjusted to the required precision of  $\sigma(I)/I = 0.01$  with a maximum scan time of 60 s per reflection. The instrument and crystal stability were checked every 5400 s of radiation time by measuring three reference reflections ( $\bar{6}23, 45\bar{3}, 15\bar{2}$ ); no significant changes in the intensities were observed. Ranges:  $2.0 < \theta < 25^\circ$ ,  $-15 < h < 15$ ,  $0 < k < 12$ ,  $0 < l < 22$ . A total of 4512 unique reflections were measured of which 2361 with  $I > 2\sigma(I)$  were used for the structure solution and refinement.

The position of the Cu atom was determined from a Patterson map. The positions of the other non-H atoms were obtained using the program *AUTOFOUR* (Kinneging & de Graaff, 1984). The atomic scat-

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Table 1. Fractional coordinates [Cu(1) × 10<sup>5</sup>, others × 10<sup>4</sup>] and equivalent isotropic thermal parameters [Cu(1) Å<sup>2</sup> × 10<sup>3</sup>, others Å<sup>2</sup> × 10<sup>2</sup>] of the non-H atoms of [Cu(tped)<sub>0.5</sub>(H<sub>2</sub>O)(NO<sub>3</sub>)](NO<sub>3</sub>).CH<sub>3</sub>OH

	$B_{eq} = (8\pi^2/3)(\text{trace } U)$			
	x	y	z	$B_{eq}$
Cu(1)	17248 (8)	11449	92343 (5)	2452 (15)
N(2)	-82 (2)	1252 (3)	9246 (2)	221 (8)
C(3)	-145 (3)	711 (4)	9952 (2)	241 (10)
O(4)	2409 (2)	1146 (3)	10325 (2)	338 (8)
O(5)	5642 (3)	22 (5)	8942 (3)	627 (15)
C(6)	5274 (6)	-174 (10)	8183 (4)	106 (4)
N(11)	1061 (3)	3905 (3)	8940 (2)	275 (9)
N(12)	1944 (3)	3065 (3)	9217 (2)	288 (10)
C(13)	2882 (4)	3779 (5)	9486 (3)	349 (13)
C(14)	2601 (4)	5067 (5)	9378 (3)	373 (14)
C(15)	1444 (4)	5139 (4)	9041 (3)	325 (13)
C(16)	4035 (4)	3182 (5)	9867 (4)	52 (2)
C(17)	698 (5)	6278 (5)	8806 (4)	46 (2)
C(18)	-112 (3)	3437 (4)	8652 (3)	279 (11)
C(19)	-376 (3)	2645 (4)	9239 (3)	274 (11)
N(21)	191 (3)	95 (4)	7804 (2)	312 (10)
N(22)	1074 (3)	918 (4)	8125 (2)	304 (10)
C(23)	1457 (5)	1245 (5)	7589 (3)	411 (14)
C(24)	814 (6)	629 (7)	6940 (3)	58 (2)
C(25)	19 (6)	-86 (6)	7073 (3)	49 (2)
C(26)	2432 (5)	2135 (6)	7731 (4)	60 (2)
C(27)	-899 (6)	-995 (8)	6580 (4)	73 (2)
C(28)	-439 (4)	-428 (5)	8237 (3)	313 (12)
C(29)	-936 (3)	615 (4)	8575 (3)	271 (11)
N(80)	2274 (4)	3304 (5)	11613 (3)	451 (14)
O(81)	2792 (5)	2362 (5)	11950 (3)	94 (2)
O(82)	1918 (4)	3295 (5)	10927 (3)	71 (2)
O(83)	2115 (3)	4224 (5)	11956 (3)	702 (14)
N(90)	3124 (3)	-878 (4)	9255 (2)	346 (12)
O(91)	2159 (2)	-781 (3)	9314 (2)	365 (10)
O(92)	3533 (3)	-1914 (3)	9237 (3)	631 (14)
O(93)	3622 (3)	144 (3)	9222 (2)	478 (12)

tering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Standard least-squares refinement was based on  $F$ . The non-H atoms were refined anisotropically. The function minimized was  $\sum w|F_o - F_c|^2$  with  $w = 1/\sigma^2(F)$ . Some H-atom positions were found from difference Fourier maps. The other H atoms were placed at 0.95 Å from their parent atom. The positional parameters of the H atoms were coupled to their parent atoms during the refinement stages. The temperature factors of the H atoms were coupled to each other and refined isotropically with a final  $B_{eq}$  value of 6.34 Å<sup>2</sup>. At the final stage the conventional discrepancy index  $R$  had been reduced to 0.036 and the weighted factor  $wR$  to 0.052, and  $\Delta_{max}/\sigma < 0.1$ . Maximum positive and negative densities in the final difference Fourier map were 0.42 and  $-0.34 \text{ e } \text{Å}^{-3}$ , respectively. E.s.d.'s were calculated with the use of a correlation matrix. The fractional coordinates of the non-H atoms of [Cu(tped)<sub>0.5</sub>(H<sub>2</sub>O)(NO<sub>3</sub>)](NO<sub>3</sub>).CH<sub>3</sub>OH are listed in Table 1. Bond distances and bond angles of the non-H atoms are given in Table 2.\*

\* 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 55087 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: L10124]

Table 2. Complete lists of bond distances (Å) and bond angles (°) of the non-H atoms of [Cu(tped)<sub>0.5</sub>(H<sub>2</sub>O)(NO<sub>3</sub>)](NO<sub>3</sub>).CH<sub>3</sub>OH with e.s.d.'s in parentheses

Cu(1)—N(2)	2.303 (3)	C(15)—C(17)	1.475 (6)
Cu(1)—O(4)	1.947 (3)	C(18)—C(19)	1.531 (6)
Cu(1)—N(12)	2.013 (3)	N(21)—N(22)	1.360 (5)
Cu(1)—N(22)	1.993 (4)	N(21)—C(25)	1.352 (6)
Cu(1)—O(91)	2.063 (3)	N(21)—C(28)	1.457 (6)
N(2)—C(3)	1.498 (5)	N(22)—C(23)	1.338 (6)
N(2)—C(19)	1.491 (5)	C(23)—C(24)	1.368 (8)
N(2)—C(29)	1.494 (5)	C(23)—C(26)	1.484 (7)
C(3)—C(3')	1.514 (8)	C(24)—C(25)	1.352 (8)
O(5)—C(6)	1.371 (8)	C(25)—C(27)	1.522 (8)
N(11)—N(12)	1.362 (5)	C(28)—C(29)	1.516 (6)
N(11)—C(15)	1.357 (5)	N(80)—O(81)	1.220 (6)
N(11)—C(18)	1.463 (5)	N(80)—O(82)	1.225 (6)
N(12)—C(13)	1.331 (5)	N(80)—O(83)	1.218 (6)
C(13)—C(14)	1.379 (6)	N(90)—O(91)	1.274 (5)
C(13)—C(16)	1.502 (6)	N(90)—O(92)	1.200 (5)
C(14)—C(15)	1.366 (6)	N(90)—O(93)	1.249 (5)
O(4)—O(82)	2.689 (5)	O(4)—O(5 <sup>H</sup> )	2.638 (5)
O(5)—O(93)	2.811 (5)		
N(2)—Cu(1)—O(4)	91.9 (1)	N(12)—C(13)—C(16)	121.7 (4)
N(2)—Cu(1)—N(12)	95.5 (1)	C(14)—C(13)—C(16)	128.5 (4)
N(2)—Cu(1)—N(22)	90.0 (1)	C(13)—C(14)—C(15)	107.2 (4)
N(2)—Cu(1)—O(91)	106.6 (1)	N(11)—C(15)—C(14)	106.3 (4)
O(4)—Cu(1)—N(12)	90.5 (1)	N(11)—C(15)—C(17)	123.8 (4)
O(4)—Cu(1)—N(22)	173.1 (1)	C(14)—C(15)—C(17)	129.9 (4)
O(4)—Cu(1)—O(91)	85.5 (1)	N(11)—C(18)—C(19)	111.8 (3)
N(12)—Cu(1)—N(22)	95.9 (1)	N(2)—C(19)—C(18)	113.8 (3)
N(12)—Cu(1)—O(91)	157.6 (1)	N(22)—N(21)—C(25)	110.1 (4)
N(22)—Cu(1)—O(91)	87.6 (1)	N(22)—N(21)—C(28)	120.6 (4)
Cu(1)—N(2)—C(3)	112.4 (2)	C(25)—N(21)—C(28)	129.2 (4)
Cu(1)—N(2)—C(19)	107.0 (2)	N(21)—N(22)—C(23)	106.5 (4)
Cu(1)—N(2)—C(29)	111.9 (2)	N(22)—C(23)—C(24)	108.7 (5)
Cu(1)—N(12)—N(11)	122.8 (3)	N(22)—C(23)—C(26)	122.2 (5)
Cu(1)—N(12)—C(13)	130.8 (3)	C(24)—C(23)—C(26)	129.1 (5)
Cu(1)—N(22)—N(21)	120.1 (3)	C(23)—C(24)—C(25)	108.4 (5)
Cu(1)—N(22)—C(23)	132.1 (3)	N(21)—C(25)—C(24)	106.2 (5)
Cu(1)—O(91)—N(90)	108.0 (3)	N(21)—C(25)—C(27)	121.4 (6)
C(3)—N(2)—C(19)	105.9 (3)	C(24)—C(25)—C(27)	132.3 (5)
C(3)—N(2)—C(29)	110.4 (3)	N(21)—C(28)—C(29)	112.6 (4)
C(19)—N(2)—C(29)	108.8 (3)	N(2)—C(29)—C(28)	113.8 (3)
N(2)—C(3)—C(3')	112.5 (4)	O(81)—N(80)—O(82)	118.3 (5)
N(12)—N(11)—C(15)	110.4 (3)	O(81)—N(80)—O(83)	120.4 (5)
N(12)—N(11)—C(18)	120.5 (3)	O(82)—N(80)—O(83)	121.3 (5)
C(15)—N(11)—C(18)	128.8 (4)	O(91)—N(90)—O(92)	120.9 (4)
N(11)—N(12)—C(13)	106.4 (3)	O(91)—N(90)—O(93)	117.3 (4)
N(12)—C(13)—C(14)	109.7 (4)	O(92)—N(90)—O(93)	121.8 (4)
Cu(1)—O(4)—H(41)	119.2	H(41)—O(4)—H(42)	100.3
Cu(1)—O(4)—H(42)	128.7	C(6)—O(5)—H(5)	102.7

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

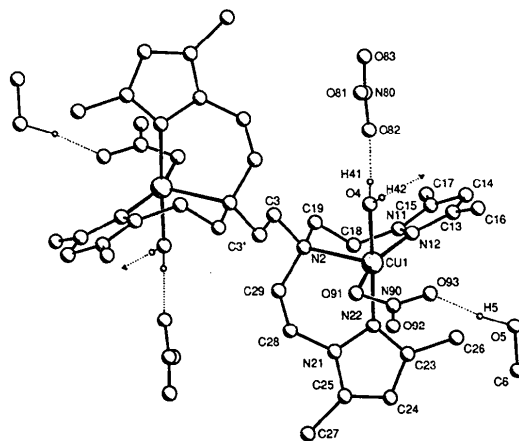


Fig. 1. A PLUTO (Motherwell & Clegg, 1978) projection of [Cu<sub>2</sub>(tped)(H<sub>2</sub>O)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2CH<sub>3</sub>OH. Most of the H atoms are omitted for clarity.

**Discussion.** Fig. 1 is a *PLUTO* projection (Motherwell & Clegg, 1978) of the dinuclear compound  $[\text{Cu}_2(\text{tped})(\text{H}_2\text{O})_2(\text{NO}_3)_2](\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH}$ . This compound has a centre of symmetry. In the asymmetric unit  $[\text{Cu}(\text{tped})_{0.5}(\text{H}_2\text{O})(\text{NO}_3)](\text{NO}_3) \cdot \text{CH}_3\text{OH}$  the Cu ion is in a distorted,  $\tau = 0.26$  (Addison, Rao, Reedijk, van Rijn & Verschoor, 1984), square pyramid of two pyrazole N atoms and an amine N atom of the ligand *tped*, an O atom of a water molecule and an O atom of one of the nitrate anions. The amine N atom occupies the apex of the square pyramid, and the Cu ion lies well above the N(12)—N(22)—O(91)—O(4) plane. Therefore, the coordination geometry around Cu(1) is distorted square pyramidal rather than distorted octahedral, although the Cu(1)—O(93) distance of 2.629 (3) Å could be regarded as semi-coordinating. The distances from the Cu ion to the pyrazole N atoms and to the amine N atom are 1.993 (4), 2.013 (3) and 2.303 (3) Å, respectively. Which are comparable to metal–nitrogen distances in coordination compounds of related ligands (Haanstra *et al.*, 1991; Hulsbergen *et al.*, 1984; Hendriks *et al.*, 1982; Birker, Hendriks, Reedijk & Verschoor, 1981). The distances of 1.947 (3) and 2.063 (3) Å of, respectively, the water O atom to Cu and the nitrate O atom to Cu are also comparable to such distances in related compounds (Driessen, de Graaff, Ochocki & Reedijk, 1988; Kleywegt, Wiesmeijer, van Driel, Driessen, Noordik & Reedijk, 1985). The coordination angles spanned by the pyrazole-N to amine-N bites of the ligand are 90.0 (1) and 95.5 (1)°; indeed, substantially larger than encountered with ligands with three-bond bites (Hulsbergen *et al.*, 1984; Hendriks *et al.*, 1982; Birker *et al.*, 1981).

The ligand *tped* accommodates two Cu ions at a distance of 6.563(1) Å, indicating that the  $\text{CuN}_3\text{O}_2$  chromophores are well separated. The coordinated water molecule O(4) is hydrogen bonded to the

non-coordinated nitrate O(82) anion and to the methanol molecule O(5). The methanol molecule is hydrogen bonded to O(93) of the nitrate anion which is coordinated through O(91) to Cu(1). The water–methanol–nitrate hydrogen bonds and the ligand link the asymmetric units together in a zigzag chain, which lies in a plane perpendicular to the *b* axis.

The pyrazole rings are planar with distances to the least-squares planes of less than 0.02 Å and there is no stacking between the rings; the crystal packing is thus determined by van der Waals contacts and hydrogen bonding.

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## Structure of Methylbis(salicylaldoximate-*O*<sup>1</sup>,*N*)gallium(III)

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**Abstract.**  $[\text{Ga}(\text{C}_7\text{H}_6\text{NO}_2)_2(\text{CH}_3)]$ ,  $M_r = 357.01$ , monoclinic,  $C2/c$ ,  $a = 14.760$  (1),  $b = 12.486$  (1),  $c = 8.5623$  (7) Å,  $\beta = 101.780$  (4)°,  $V = 1544.8$  (2) Å<sup>3</sup>,  $Z$

$= 4$ ,  $D_x = 1.535$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 17.91$  cm<sup>-1</sup>,  $F(000) = 728$ ,  $T = 294$  K,  $R = 0.027$ ,  $wR = 0.034$ , for 1190 reflections with  $I \geq 3\sigma(I)$ . The