2·177, $g_{\parallel} = 2{\cdot}065$) and remains unchanged over the temperature range 298–4·2 K. The reflectance electronic spectrum shows, in the visible region, one broad and unresolved band centred about 12000 cm^{-1}. These spectroscopic results are consistent with a geometry around the copper(II) ion near to trigonal bipyramidal (Reinen & Friebel, 1984; Hathaway & Billing, 1970), in good agreement with the crystal structure of the complex.

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Structure of Aquadibromobis(1,2,4-triazolo[1,5-*a*]pyrimidine-*N*3)copper(II), a One-Dimensional Alternating Copper(II)···Oxygen Array

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Abstract. $C_{10}H_{10}Br_2CuN_8O$, $M_r = 481{\cdot}6$, orthorhombic, *Pccn*, $a = 8{\cdot}886\,(8)$, $b = 15{\cdot}025\,(7)$, $c = 11{\cdot}928\,(5)$ Å, $V = 1592{\cdot}8$ Å^3, $Z = 4$, $D_m = 1{\cdot}98\,(5)$, $D_x = 2{\cdot}01$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·710730 Å, $\mu = 6{\cdot}313$ mm^{-1}, $F(000) = 932$, $T = 293$ K, final $R = 0{\cdot}024$ for 1111 unique observed reflections. The molecular unit contains two molecules of 1,2,4-triazolo[1,5-*a*]pyrimidine, coordinating through N3 to a copper(II) ion, two bromide ions and one water molecule completing a trigonal bipyramidal environment around copper. Both non-coordinating ligand N4 atoms of each molecule are involved in hydrogen bonding to the water ligand of the next neighboring molecule. In this way the Cu and O atoms form a one-dimensional alternating array. Cu—N 1·969 (3), Cu—Br 2·4661 (4), Cu—O 2·239 (4) Å, the N—Cu—N angle is almost linear, 177·2 (2)°. Nonbonding distances: Cu···O 3·725 (4) and N···O 2·937 (3) Å.

Introduction. Transition-metal compounds of purine analogs have been studied very often to elucidate the role of such metal ions in interaction with DNA and RNA. Most emphasis has been placed on pharmaceutically and biologically important metals, copper, platinum and zinc. Reviews have been published by Gellert & Bau (1979), Marzilli (1979), Sherman & Lippard (1987), Lippert (1988, 1989) and Berg (1989).

As has been pointed out before (Biagini-Cingi, Manotti-Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1983), the 1,2,4-triazolo[1,5-*a*]pyrimidine ring system, hereafter abbreviated by tp, can be compared with the purine system, the difference being the position of one pyrimidine N atom, which in tp is in a bridgehead position. This results in the absence of the acidic nitrogen H atom of the five-membered ring.

Because this condensed ring system has three different N atoms available for coordination, many coordination modes are possible. The N1,N3-bidentate mode was found in $[Fe(tp)_2(NCS)_2]$ (Biagini-Cingi, Manotti-Lanfredi, Tiripicchio, Cornelissen, Haasnoot & Reedijk, 1987*a*); the same coordination mode but in a very asymmetric bridge was found in $[Cu(tp)_2(NCS)_2]$ and $[Cu(tp)_2Cl_2]$ (Biagini-Cingi, Manotti-Lanfredi, Tiripicchio, Cornelissen, Haasnoot & Reedijk, 1987*b*). The N3 monodentate mode was found in $[Zn(tp)_2(NCS)_2].\frac{1}{2}H_2O$ (Bamidele Sanni, Smits, Beurskens, Haasnoot, Schild & Lenstra, 1986). The N3,N4 bridging bidentate coordination mode has so far been found only for the analogous 5,7-dimethyl-substituted ligand in $[Cu_4(dmtp)_4Cl_2][Cu_2Cl_4]$ (Haasnoot, Favre, Hinrichs & Reedijk, 1988). In the present paper, we report the structure of $[Cu(tp)_2(H_2O)Br_2]$ in which the ligand is involved in an alternating sequence of metal coordination, *via* N3, and hydrogen bonding *via* N4.

Experimental. Crystals of the title compound were grown from a filtered solution of 2 mmol of anhydrous $CuBr_2$ and 4 mmol of tp in 20 ml of water by standing at room temperature. The crystals were collected by filtration and dried in air. A green, bar-shaped single crystal, dimensions $0{\cdot}55 \times 0{\cdot}13 \times 0{\cdot}17$ mm, was selected and mounted in a glass capillary. Density was determined by flotation using chloroform and dibromomethane. Intensity data were collected at room temperature on an Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Cell constants from setting angles of 24 reflections, $10 < \theta < 12°$. Data were collected with $4 < 2\theta < 55°$ (by using the ω-scan method). The range for h was 0 to 11, k 0 to 19 and l 0 to 15. The intensity variation of the standard reflections was 12% from the mean value. Corrections were applied for Lorentz and polarization effects. Absorption correction necessary, and a Monte Carlo numerical integration method (de Graaff, 1973) was used; the transmission factors range from 0·12 to 0·38. 2118 reflections were measured, 2114 independent, 1111 of these are unique observed reflections $[I > 2\sigma(I)]$. Scattering factors, including anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The copper position, located in a three-dimensional Patterson synthesis, was used as input data for *AUTOFOUR* (Kinneging & de Graaff, 1984). The position of the water H atom H(1) was found in a difference Fourier map; the carbon H atoms were placed at 0·97 Å from the parent atoms and refined riding on their parent atom with one isotropic B value for all atoms. All non-H atoms were refined with anisotropic thermal parameters. The function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$, with 109 parameters refined. The refinement converged to $R = 0{\cdot}0240$, $wR = 0{\cdot}0268$ and $S = 1{\cdot}5134$; $\Delta/\sigma < 0{\cdot}30$. The max. and min. heights in final $\Delta\rho$ map were 0·5 and $-0{\cdot}4$ e Å^{-3}. The calculations were carried out on the Leiden University Computer (Amdahl V7B); all computer programs used were part of a locally written or modified program system.

Discussion. Positional parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms and atom H(1) are listed in Table 1.* Atomic distances and intramolecular bond angles for all relevant atoms are listed in Table 2. An *ORTEP* (Johnson, 1965) projection of the molecule and the atomic labelling are given in Fig. 1.

The Cu atom, like the O atom situated on a crystallographic twofold axis, is surrounded by two N3 atoms of the tp ligands, two Br atoms and the O atom of the water molecule, the N—Cu—N angle being almost linear [177·2 (2)°]. For such systems Addison, Rao, Reedijk, Van Rijn & Verschoor (1984) introduced the structural index τ to show the relative amount of trigonality (square pyramid $\tau = 0{\cdot}0$, trigonal bipyramid $\tau = 1{\cdot}0$). In this case the value of τ is 0·64, which implies that the geometry may be termed distorted trigonal bipyramidal. Five-coordinate CuN_2Br_2O chromophores reported in the literature are distorted-tetragonal: even trigonal CuN_2Cl_2O chromophores are scarce. A related trigonal compound is aquadichloro-3,3′-dimethylene-2,2′-bis(1,8-naphthyridine)copper(II) (Draux, Bernal, Lefoulon & Thummel, 1985), in which the axial donor N and O atoms are at distances of 2·005 (7) and 2·019 (6) Å, respectively, and the equatorial donors are two Cl atoms at 2·287 (2) and 2·291 (2), and an N atom at 2·243 (7) Å.

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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 53684 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* [$(8\pi^2/3)$trU] *for* [$Cu(tp)_2(H_2O)Br_2$]: *atom numbering between parentheses refers to Fig.* 1 *and other tables and is compared with the IUPAC numbering for the ligand used in the text*

E.s.d.'s are given in parentheses.

		x	y	z	B_{eq}(Å^2)
Cu*		0·25000	0·25000	−0·00024 (5)	2·29 (1)
Br		0·41956 (4)	0·36976 (3)	−0·06366 (3)	3·271 (9)
N(11)	N3	0·4237 (3)	0·1688 (2)	0·0039 (2)	2·42 (7)
C(12)	C2	0·5046 (5)	0·1422 (2)	0·0944 (3)	3·10 (10)
N(13)	N1	0·6228 (4)	0·0914 (2)	0·0724 (3)	3·66 (9)
N(14)	N8	0·6152 (3)	0·0845 (2)	−0·0419 (2)	2·53 (8)
C(15)	C7	0·7099 (4)	0·0382 (3)	−0·1082 (3)	3·16 (10)
C(16)	C6	0·6798 (4)	0·0407 (2)	−0·2197 (3)	3·24 (10)
C(17)	C5	0·5587 (4)	0·0910 (3)	−0·2574 (3)	3·39 (10)
N(18)	N4	0·4656 (3)	0·1366 (2)	−0·1923 (3)	2·81 (8)
C(19)	C3*a*	0·4958 (4)	0·1317 (2)	−0·0826 (3)	2·42 (9)
O*		0·25000	0·25000	0·1875 (3)	2·87 (9)
H(1)		0·202 (4)	0·216 (2)	0·228 (3)	4·5 (4)

* Special positions.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *of the relevant atoms in* [$Cu(tp)_2(H_2O)Br_2$], *including the hydrogen bond geometry*

E.s.d.'s are given in parentheses.

Cu—Br	2·4661 (4)	N(14)—C(19)	1·365 (4)
Cu—N(11)	1·969 (3)	C(15)—C(16)	1·356 (5)
Cu—O	2·239 (4)	C(16)—C(17)	1·390 (5)
N(11)—C(12)	1·357 (4)	C(17)—N(18)	1·325 (5)
N(11)—C(19)	1·335 (4)	N(18)—C(19)	1·337 (4)
C(12)—N(13)	1·324 (5)	O—H(1)	0·81 (3)
N(13)—N(14)	1·369 (4)	O—N(18)*	2·937 (3)
N(14)—C(15)	1·348 (4)	H(1)···N(18)*	2·13 (3)

N(11)—Cu—N(11)†	177·2 (2)	C(15)—N(14)—C(19)	123·0 (3)
Br—Cu—N(11)	88·9 (8)	N(13)—N(14)—C(19)	110·6 (3)
N(11)—Cu—Br†	91·9 (8)	N(14)—C(15)—C(16)	115·9 (3)
Br—Cu—O	107·8 (2)	C(15)—C(16)—C(17)	118·9 (4)
Br—Cu—Br†	144·2 (3)	C(16)—C(17)—N(18)	125·0 (3)
N(11)—Cu—O	88·5 (8)	C(17)—N(18)—C(19)	114·8 (3)
Cu—N(11)—C(12)	128·1 (3)	N(11)—C(19)—N(14)	108·3 (3)
C(12)—N(11)—C(19)	103·8 (3)	N(14)—C(19)—N(18)	122·1 (3)
N(11)—C(12)—N(13)	115·5 (3)	O—H(1)···N(18)*	166·5 (4)
C(12)—N(13)—N(14)	101·6 (3)		

Atoms marked * are related to the original by symmetry operation $\frac{1}{2}-x, y, \frac{1}{2}+z$ and those marked † by symmetry operation $\frac{1}{2}-x, \frac{1}{2}-y, z$.

The Cu—N distance of 1·969 (3) Å in the present compound is somewhat smaller than found in [$Cu(tp)_2(NCS)_2$] [2·035 (5) Å] and [$Cu(tp)_2Cl_2$] [2·021 (4) Å] (Biagini-Cingi, Manotti-Lanfredi, Tiripicchio, Cornelissen, Haasnoot & Reedijk, 1987*b*), but is in agreement with distances found earlier with the dimethyl substituted ligand dmtp for five-coordinated copper(II) (Biagini-Cingi, Manotti-Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1983; Haasnoot, Driessen & Reedijk, 1984). The Cu—Br distance of 2·4661 (4) Å is also normal and has been found earlier for five-coordinated compounds (Elder & McKenzie, 1978; Veldhuis, Driessen & Reedijk, 1986). The Cu—O distance of 2·239 (4) Å is shorter than is found generally for axial Cu—O bonds in six-coordinated systems (Favre, Haasnoot & Reedijk, 1986; Vreugdenhil, Birker, Ten Hoedt, Verschoor & Reedijk, 1984), but appears to be normal for slightly compressed trigonal bipyramidal coordinations around copper (Addison *et al.*, 1984; Bouwman, 1990). From these distances it was concluded, therefore, that in this compound the axial bonds are of the short type and the equatorial ones are of the long type (Gillespie, 1963), *i.e.* with a d_{z^2} groundstate for Cu^{2+}. The fact that the water molecule coordinates equatorially, however, is not in accordance with the theoretical predictions of Rossi & Hoffmann (1975) for the coordination site of highly electronegative atoms and in this respect it differs from the CuN_2Cl_2O chromophore mentioned above (Draux, Bernal, Lefoulon & Thummel, 1985). However, because our ligand is monodentate there is no steric reason to force the two N atoms into a *cis* orientation, and the most important origin is likely to be the intermolecular hydrogen bonding system.

The H atoms of the water molecule were located between the O atom and N4 of the neighboring ligand indicating that this water molecule forms two hydrogen bonds to the tp ligands, with the distances

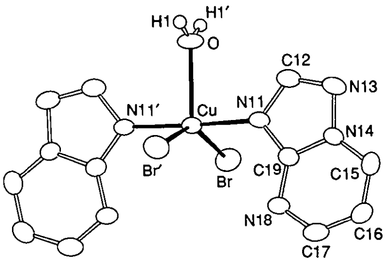

Fig. 1. *ORTEP* (Johnson, 1965) projection with 50% probability contours (non-H atoms) and atomic labelling. The primed atoms are generated by symmetry operation $\frac{1}{2}-x, \frac{1}{2}-y, z$.

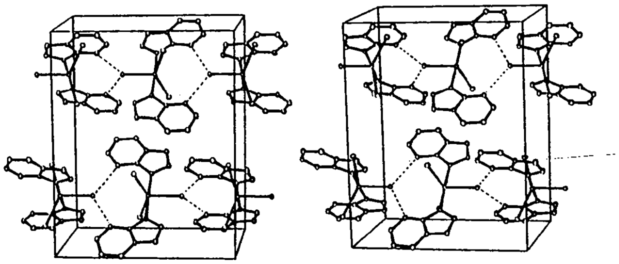

Fig. 2. Stereoscopic projection of the unit cell showing the hydrogen bonds. *a* is vertical, *c* is horizontal and *b* is into the plane of the paper.

O···N being 2·937 (3) Å and the angle O—H···N 166·5 (4)°. These bonds are depicted in Fig. 2 as dashed lines. In this way the Cu and O atoms form alternating chains in the cell parallel to the *c* axis. The Cu—Cu distance in this chain is 5·964 (5) Å, Cu—O 2·239 (4) and Cu···O 3·725 (4) Å.

There is no intermolecular stacking of the aromatic rings; closest distances between the tp rings are larger than 4·6 Å. The packing of the molecules is dictated by normal van der Waals contacts between the cationic chains and the bromide ions and the hydrogen bonds.

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Structure of Ethylenediammonium Orthofluoroberyllate

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Abstract. $[C_2H_{10}N_2][BeF_4]$, $M_r = 147{\cdot}12$, tetragonal, $P4_12_12$, $a = 5{\cdot}904\,(1)$, $c = 17{\cdot}841\,(4)$ Å, $V = 621{\cdot}9\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}571$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 3{\cdot}033$ mm^{-1}, $F(000) = 304$, room temperature, final $R = 0{\cdot}038$ for 449 independent observed reflections. BeF_4 tetrahedra and $[(CH_2)_2(NH_3)_2]^{2+}$ groups alternate in planes perpendicular to the *c* axis. Hydrogen bonds link together all the organic groups and BeF_4 tetrahedra to form a three-dimensional network.

Introduction. Up to now, only two types of ethylenediammonium fluoroberyllates have been synthetized and characterized: a metafluoroberyllate $(CH_2)_2(NH_3)_2(BeF_3)_2$, under study, and an orthofluoroberyllate $(CH_2)_2(NH_3)_2BeF_4$, the title compound.

Experimental. Crystals are prepared by slowly adding ethylenediammonium chloride, in a stoichiometric ratio, to a water solution of silver orthofluoroberyllate obtained by the reaction

$$Ag_2CO_3 + BeCO_3 + 4HF \rightarrow Ag_2BeF_4 + 2CO_2 + 2H_2O,$$

$$Ag_2BeF_4 + 2(CH_2)NH_3Cl \rightarrow 2AgCl + (CH_2)_2(NH_3)_2BeF_4.$$

0108-2701/91/050949-03$03.00