Endres, H., Keller, H. J., Moroni, W. & Noethe, D. (1979). *Acta Cryst.* B**35**, 353–357.
James, D. W. & Nolan, M. J. (1973). *Aust. J. Chem.* **26**, 1433–1441.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kuppusamy, P., Ramakrishna, B. L. & Manoharan, P. T. (1984). *Inorg. Chem.* **23**, 3886–3892.
Matsubayashi, G. E., Akiba, K. & Tanaka, T. (1988). *Inorg. Chem.* **27**, 4744–4749.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Soos, Z. G. & Keller, H. J. (1977). In *Chemistry and Physics of One-Dimensional Metals*, edited by H. J. Keller. NATO ASI Series No. 25. New York: NATO.
Vivian, D. L. (1956). *J. Org. Chem.* **21**, 822–824.

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*Acta Cryst.* (1998). C**54**, 614–616

# Bis(1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol-$\kappa^3N$)copper(II) Dichloride Tetrahydrate†

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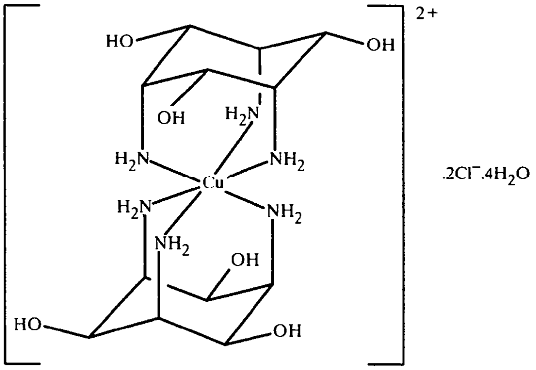
## Abstract

Crystals of the title compound, $[Cu(C_6H_{15}N_3O_3)_2]Cl_2.4H_2O$, are isotypic with those of the analogous $Cu^{II}$ bromide and the corresponding $Ni^{II}$ and $Zn^{II}$ bromides [Hegetschweiler *et al.* (1992). *Inorg. Chem.* **31**, 2341–2346]. The coordination polyhedron of the Cu atom shows a strong Jahn–Teller distortion from octahedral symmetry. The location of all H-atom positions gives a more detailed understanding of the three-dimensional hydrogen-bonding framework in (I) and its related compounds.

## Comment

A remarkable property of the ligand 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) is its rigidity. Its large number of OH and $NH_2$ groups gives rise to a variety of different coordination modes and to extended inter- and intramolecular hydrogen bonding. In particular, it has been found for some metal complexes of taci that these substituents are arranged so as to form characteristic cavities that accommodate the counteranions (Hegetschweiler *et al.*, 1992).

Crystals of the title compound, (I), are composed of the cationic 2:1 complex of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol with a copper(II) ion (Fig. 1), two chloride anions and four water molecules, all connected by hydrogen bonds. The coordination polyhedron of the Cu atom (Cu1, site symmetry $2/m$) shows a strong Jahn–Teller distortion from octahedral symmetry. The N atoms of four crystallographically equivalent $NH_2$ groups (N2) form a square [N—Cu—N 88.91 (5)–91.09 (5)°], with short N—Cu distances [2.0712 (9) Å]. Two more weakly bonded $NH_2$ groups, with their N atoms on the mirror plane $0yz$ [N4—Cu1 2.3472 (15) Å], occupy the axial positions, additionally displaced by 4.54 (4)° from the normal of the equatorial square plane, reducing the point-group symmetry to $C_{2h}(2/m)$ (Fig. 1).



(I)

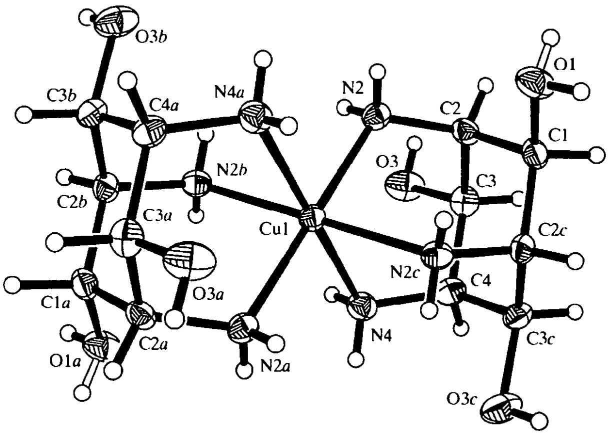


Fig. 1. Diagram of the bis(1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol)-copper(II) cation. Displacement ellipsoids are drawn at the 50% probability level. The two H atoms at O1 represent the two possible positions of this disordered H atom. Symmetry codes: (*a*) $-x, 1-y, -z$; (*b*) $x, 1-y, -z$; (*c*) $-x, y, z$.

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† Dedicated to Professor C. G. Kreiter on the occasion of his 60th birthday.

The OH group, the O atom of which also lies on the mirror plane $0yz$, shows a 1:1 disorder of its H atom with crystallographically equivalent hydrogen-bonding environments for the two split positions (Fig. 1). Besides the O1 and N4 atoms, C1, C4 and O1*W* are situated on the mirror plane $0yz$, while O2*W* lies on the mirror plane $xy\frac{1}{4}$.

The packing of (I) is best described as a sequence of two different types of regions parallel to the *ab* plane (Fig. 2). The broader region 1, intersecting the *c* axis at 0 and $\frac{1}{2}$, is built up by metal-organic copper complexes connected to one another by N—H···O hydrogen bonds, with cavities filled with the Cl2 anions (site symmetry $2/m$) (Table 3). The narrower region 2, at $c = \frac{1}{4}$ and $\frac{3}{4}$, consists of the water molecules and the Cl1 anions (site symmetry $m2m$). The two crystallographically independent Cl anions have completely different environments, also expressed by significant differences in their $U_{eq}$ values [0.0585 (2) Å$^2$ for Cl1 and 0.02875 (11) Å$^2$ for Cl2]. The Cl1 anion is coordinated by four water molecules, while Cl2 is located in a cavity formed by six $NH_2$ groups of two neighbouring copper complexes, and two water molecules. The cationic complex forms strong hydrogen bonds *via* its OH groups; the $NH_2$ groups are only weakly connected (Table 3).

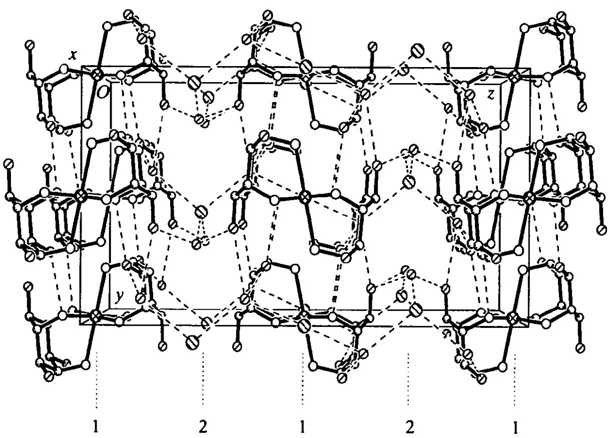

Fig. 2. Diagram showing the packing of (I) perpendicular to [001].

It could be shown that smaller counterions do not effect significant changes in the crystal structure or the coordination of the Cu atom in this case; compound (I) crystallizes isotypically with its bromide analogue (Hegetschweiler *et al.*, 1992).

## Experimental

The title complex was prepared by dissolving 0.5 mmol of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol dihydrate and 0.5 mmol of $CuCl_2.H_2O$ in 10 ml of water. The solution was adjusted to pH 5.3 by adding dilute acetic acid and concentrated *in vacuo*. Single crystals were grown by slow diffusion of ethanol into the aqueous solution.

*Crystal data*

$[Cu(C_6H_{15}N_3O_3)_2]Cl_2.4H_2O$
$M_r = 560.92$
Orthorhombic
*Cmcm*
$a = 9.2753\ (6)$ Å
$b = 11.3756\ (8)$ Å
$c = 21.720\ (2)$ Å
$V = 2291.7\ (3)$ Å$^3$
$Z = 4$
$D_x = 1.626$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 5.45$–$12.46°$
$\mu = 1.246$ mm$^{-1}$
$T = 293\ (2)$ K
Plate
0.65 × 0.33 × 0.07 mm
Clear intense blue

*Data collection*

Siemens *P*4 four-circle diffractometer
$\omega$ scans
Absorption correction: numerical
$T_{min} = 0.511$, $T_{max} = 0.923$
3405 measured reflections
2683 independent reflections
1817 reflections with $I > 2\sigma(I)$

$R_{int} = 0.009$
$\theta_{max} = 34.99°$
$h = -1 \rightarrow 14$
$k = -1 \rightarrow 18$
$l = -1 \rightarrow 35$
3 standard reflections every 100 reflections intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.059$
$S = 1.045$
2683 reflections
125 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0195P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.018$

$\Delta\rho_{max} = 0.448$ e Å$^{-3}$
$\Delta\rho_{min} = -0.371$ e Å$^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00247 (15)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 0 | 1/2 | 0 | 0.01561 (6) |
| Cl1 | 0 | 0.06448 (9) | 1/4 | 0.0585 (2) |
| Cl2 | 0 | 0 | 0 | 0.02875 (11) |
| C1 | 0 | 0.49631 (15) | 0.15759 (6) | 0.0194 (3) |
| C2 | 0.13742 (11) | 0.45373 (9) | 0.12666 (5) | 0.01812 (19) |
| C3 | 0.13392 (13) | 0.31926 (9) | 0.12045 (5) | 0.0211 (2) |
| C4 | 0 | 0.27107 (13) | 0.08876 (7) | 0.0201 (3) |
| N2 | 0.15939 (10) | 0.51241 (9) | 0.06647 (4) | 0.01839 (18) |
| N4 | 0 | 0.29823 (13) | 0.02261 (7) | 0.0216 (3) |
| O1 | 0 | 0.62151 (11) | 0.16047 (6) | 0.0265 (3) |
| O3 | 0.25725 (9) | 0.27560 (8) | 0.08857 (5) | 0.0295 (2) |
| O1*W* | 0 | 0.89454 (13) | 0.13354 (7) | 0.0400 (3) |
| O2*W* | −0.19743 (18) | 0.68953 (18) | 1/4 | 0.0516 (4) |

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cu1—N2 | 2.0712 (9) | C2—C3 | 1.5360 (15) |
| Cu1—N4 | 2.3472 (15) | C3—O3 | 1.4264 (14) |
| C1—O1 | 1.426 (2) | C3—C4 | 1.5222 (14) |

| | | | |
|---|---|---|---|
| C1—C2 | 1.5201 (13) | C4—N4 | 1.470 (2) |
| C2—N2 | 1.4819 (13) | | |
| N2—Cu1—N2$^{i}$ | 91.09 (5) | O3—C3—C4 | 108.03 (9) |
| N2—Cu1—N4 | 85.46 (4) | O3—C3—C2 | 111.87 (9) |
| O1—C1—C2 | 109.74 (9) | C4—C3—C2 | 114.56 (10) |
| C2—C1—C2$^{i}$ | 113.97 (12) | N4—C4—C3 | 111.49 (8) |
| N2—C2—C1 | 111.20 (9) | C3—C4—C3$^{i}$ | 109.38 (13) |
| N2—C2—C3 | 111.96 (9) | C2—N2—Cu1 | 119.08 (7) |
| C1—C2—C3 | 109.78 (10) | C4—N4—Cu1 | 114.21 (10) |

Symmetry code: (i) $-x, y, z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H21N···O3$^{i}$ | 0.785 (13) | 2.347 (14) | 3.1292 (13) | 173.7 (14) |
| N2—H22N···Cl2$^{ii}$ | 0.864 (13) | 2.668 (13) | 3.4763 (9) | 156.3 (12) |
| N4—H41N···O3$^{iii}$ | 0.796 (15) | 2.673 (14) | 3.4068 (15) | 154.1 (13) |
| O1—H1O···O2$W$ | 0.755 (9) | 2.029 (10) | 2.7808 (15) | 174 (3) |
| O3—H3O···O1$W^{iv}$ | 0.759 (8) | 2.057 (9) | 2.8026 (12) | 167.2 (16) |
| O1$W$—H11$W$···Cl1$^{v}$ | 0.785 (12) | 2.409 (12) | 3.1836 (16) | 169 (2) |
| O1$W$—H12$W$···Cl2$^{v}$ | 0.795 (12) | 2.403 (15) | 3.1389 (16) | 154 (2) |
| O2$W$—H21$W$···Cl1$^{vi}$ | 0.791 (12) | 2.360 (12) | 3.146 (2) | 173 (3) |
| O2$W$—H22$W$···O1 | 0.782 (12) | 2.010 (14) | 2.7808 (15) | 169 (3) |

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

The assignment of the centrosymmetric space group *Cmcm* instead of the non-centrosymmetric subgroup *Cmc*$2_1$ was based on arguments summarized by Marsh (1995). The atomic coordinates of all H atoms were taken from difference Fourier syntheses. Atomic coordinates and individual $U_{iso}$ values for all H atoms belonging to the $NH_2$ groups were refined. The atomic coordinates for H atoms of OH groups were refined with the O—H distance restrained to a plausible value and the $U_{iso}$ values set to $1.3U_{eq}$(O). H atoms belonging to water molecules and the H atoms bonded to C atoms were refined with the O—H and C—H distances restrained to one common value for each type. The $U_{iso}$ values were set to $1.5U_{eq}$(O) or $1.2U_{eq}$(C).

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS* for reducing diffractometer data and *X-RED* (Stoe & Cie, 1996) for absorption correction by indexed crystal faces. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1250). Services for accessing these data are described at the back of the journal.

## References

Hegetschweiler, K., Gramlich, V., Ghisletta, M. & Samaras, H. (1992). *Inorg. Chem.* **31**, 2341–2346.

Marsh, R. E. (1995). *Acta Cryst.* B**51**, 897–907.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1992). *SHELXTL-Plus*. Release 4.22. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994). *XSCANS*. Version 2.10b. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Stoe & Cie (1996). *X-RED. Data Reduction Program.* Revision 1.07. Stoe & Cie GmbH, Darmstadt, Germany.

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# $[Ni(C_{10}H_8N_2)_3]_2[V_4O_{12}].11H_2O$

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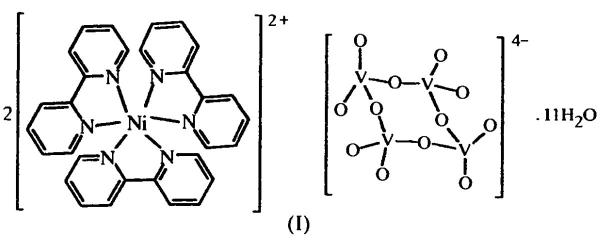
## Abstract

The crystal structure of the title compound, bis[tris(2,2′-bipyridyl-*N*,*N*′)nickel(II)] *cyclo*-tetravanadate undecahydrate, contains a centrosymmetric $[V_4O_{12}]^{4-}$ anion, which has an eight-membered ring structure formed by four $VO_4$ tetrahedra sharing vertices, and two complex cations containing octahedrally-coordinated $Ni^{II}$ ions. The anion and coordinated $Ni^{II}$ ions are isolated and make up anion and cation layers, respectively. The Ni—N distances range from 2.077 (3) to 2.112 (2) Å and the V—O distances range from 1.621 (2) to 1.803 (2) Å.

## Comment

The isopolyanions $[(\eta\text{-}C_8H_{12})Ir(V_4O_{12})]^{3-}$ and $\{[(\eta\text{-}C_8H_{12})Ir]_2(V_4O_{12})\}^{2-}$, which contain the ring anion $[V_4O_{12}]^{4-}$, were first synthesized by Day *et al.* (1990). Recently, some vanadium oxides consisting of $[V_4O_{12}]^{4-}$ clusters containing complex cations [transition metal cations coordinated by 2,2′-bipyridyl (bipy)], such as $[Cu(bipy)][V_2O_6]$ and $[Cu(bipy)_2][V_2O_6]$ (DeBord *et al.*, 1996), $[VO(VO_3)_6\{VO(bipy)_2\}_2]$ (Huan *et al.*, 1991), $[Zn(bipy)_2]_2[V_4O_{12}]$, $[Zn(phen)_2]_2[V_4O_{12}].H_2O$ and $[Zn(bipy)_3]_2[V_4O_{12}].11H_2O$ (Zhang *et al.*, 1997), have been reported. We report here the structure of a new compound, (I), built from complexed nickel cations, $[Ni(C_{10}H_8N_2)_3]^{2+}$, water molecules of crystallization and *cyclo*-tetravanadate anions, $[V_4O_{12}]^{4-}$.



(I)