1·45 Å). These observations are comparable to the Cu complex of 5-(trifluoromethyl)tetrazole, where the metal is again bonded at the N(2) site (Gaughan, Bowman & Dori, 1972). The monodentate mode of bonding observed in the Ni complex contrasts the chelating and bridging character of the same ligand in mercuric 5-nitrotetrazolate, where there is coordination of the NO_2 group to the Hg atom (Huang, Jin, Shao, Wang & Zhu, 1982). The short intermolecular distance $H(1w)\cdots N(4)(-\frac{1}{2}-x,\ y,\ -\frac{1}{2}-z)$ (2·19 Å) is an indication of hydrogen bonding linking the complex molecules into infinite chains.

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Structure of Aqua[*N*,*N*′-bis(β-carbamoylethyl)-*N*-methyltrimethylenediamine]copper(II) Perchlorate Monohydrate*

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Abstract. $[Cu(C_{10}H_{22}N_4O_2)(H_2O)](ClO_4)_2.H_2O$, $M_r = 528{\cdot}8$, monoclinic, $P2_1/c$, $a = 10{\cdot}195\ (2)$, $b = 14{\cdot}245\ (4)$, $c = 14{\cdot}372\ (5)$ Å, $\beta = 96{\cdot}76\ (2)°$, $V = 2072{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}695$, $D_m = 1{\cdot}687$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}7093$ Å, $\mu = 1{\cdot}38$ mm^{-1}, $F(000) = 1094{\cdot}7$, $T = 297\ (5)$ K. Final $R = 0{\cdot}064$ for 1513 significant reflections. The Cu atom is five-coordinate in a slightly distorted square-pyramidal geometry, and is displaced 0·9 Å from the best plane of the two amino N atoms and the two amide O atoms toward the apex of the pyramid, which is occupied by a water O atom with the Cu—O distance 2·38(2)Å. Two of the three six-membered rings are in chair forms and the other is in a twist form. Hydrogen bonds play an important role in the crystal structure.

Introduction. In a previous paper we have reported the crystal structure of aqua[*N*,*N*′-bis(β-carbamoylethyl)-trimethylenediamine]perchloratocopper(II) perchlorate monohydrate, $[Cu(ClO_4)(bctn)(H_2O)]ClO_4.H_2O$ (Hong, Lee, Lee, Chao & Chung, 1987). In this work, the crystal structure of aqua[*N*,*N*′-bis(β-carbamoylethyl)-*N*-methyltrimethylenediamine]copper(II) perchlorate monohydrate, $[Cu(N\text{-}CH_3bctn)(H_2O)](ClO_4)_2.H_2O$, has been determined.

Experimental. The N-CH_3bctn ligand was prepared as follows: 13·6 ml (0·2 mol) of *N*-methyltrimethylenediamine and 28·4 g (0·4 mol) of acrylamide in 80 ml acetonitrile were refluxed for 2 h. The solution was cooled and the product, N-CH_3bctn, filtered off. These crystals were washed with chloroform, m.p. 328–329 K (found: C, 51·6; H, 9·51; N, 23·8%; calculated for $C_{10}H_{22}N_4O_2$: C, 52·1; H, 9·63; N, 24·3%), recrystallized from chloroform, and dried in air. N-CH_3bctn was reacted with $Cu(ClO_4)_2.6H_2O$ in water. Blue $[Cu(N\text{-}CH_3bctn)(H_2O)](ClO_4)_2.H_2O$ was crystallized from absolute alcohol.

Density measured by flotation. CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; a crystal of about 0·2 × 0·3 × 0·2 mm was cut for data collection, unit-cell parameters from 25 reflections with $20 < 2\theta < 28°$, data collected by ω–2θ scans with scan width of $2 \times (0{\cdot}9 + 0{\cdot}35\tan\theta)°$ and scan speed of $\frac{20}{3}-\frac{20}{16}°$ min^{-1}, standard reflections 017, $0\bar{1}7$ and $01\bar{7}$ checked every 2h, varied within $2\sigma(I)$. Max. $(\sin\theta)/\lambda = 0{\cdot}66$ Å^{-1} $(-12 \le h \le 13,\ 0 \le k \le 18,\ 1 \le l \le 18)$, 4983 reflections collected, 1513 significant with $I > 2{\cdot}5\sigma(I)$. Empirical absorption correction based on azimuthal rotation from three reflections (004, $0\bar{1}7$, $\bar{1}08$) (North, Phillips & Mathews, 1968); the minimum, maximum and average correction factors are 0·8817, 0·9994 and 0·9329, respectively. Heavy atom Cu was located by using Patterson synthesis. Other atom

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* Aqua(4-methyl)-4,8-diazaundecanediamide)copper(II) diperchlorate monohydrate.

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positions were solved successively by alternate difference Fourier synthesis and least-squares fit. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, $\sigma(F_o)$ from counting statistics. 262 parameters with anisotropic temperature factors for non-H atoms. $R = 0{\cdot}064$, $wR = 0{\cdot}051$, $S = 2{\cdot}14$, $(\Delta/\sigma)_{max} = 0{\cdot}4$ in the final cycle. $\Delta\rho_{max} = 0{\cdot}8$ e Å^{-3} [around $Cl(2)O_4$]. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 1. *Atomic coordinates and* B_{iso} *values*

E.s.d.'s refer to the last digit printed.

	x	*y*	*z*	B_{iso}*(Å^2)
Cu	0·29208 (16)	0·05505 (12)	0·28749 (10)	2·63 (6)
Cl(1)	0·3335 (5)	0·3320 (3)	0·3098 (3)	5·10 (23)
Cl(2)	0·8052 (7)	0·2367 (4)	0·5074 (4)	6·4 (3)
O(11)	0·4473 (16)	0·3213 (12)	0·2714 (13)	13·6 (13)
O(12)	0·2856 (15)	0·2491 (9)	0·3291 (10)	11·2 (10)
O(13)	0·2460 (15)	0·3736 (10)	0·2419 (10)	11·6 (10)
O(14)	0·350 (3)	0·3855 (14)	0·3824 (11)	21·4 (22)
O(21)	0·7443 (19)	0·3071 (14)	0·5387 (13)	16·3 (15)
O(22)	0·8889 (20)	0·1923 (12)	0·5717 (13)	15·0 (14)
O(23)	0·737 (3)	0·1731 (15)	0·4693 (24)	31·7 (27)
O(24)	0·871 (3)	0·2685 (16)	0·4517 (19)	34·6 (32)
O(1)	0·4806 (8)	0·0733 (7)	0·2781 (6)	3·7 (5)
O(2)	0·3597 (8)	0·0366 (7)	0·4204 (5)	3·6 (4)
O(*W*1)	0·6889 (12)	0·3888 (6)	0·2178 (7)	4·8 (6)
O(*W*2)	0·9455 (16)	0·2328 (10)	0·2705 (11)	12·0 (11)
N(1)	0·2450 (10)	0·0651 (8)	0·1454 (6)	3·1 (5)
N(2)	0·1067 (10)	0·0680 (8)	0·3157 (7)	3·2 (5)
N(3)	0·3772 (13)	0·0555 (9)	0·5750 (7)	4·6 (6)
N(4)	0·6544 (12)	0·1422 (9)	0·2317 (9)	4·6 (6)
C(1)	0·5374 (14)	0·1025 (9)	0·2144 (10)	3·4 (7)
C(2)	0·4781 (16)	0·0960 (12)	0·1136 (9)	4·8 (8)
C(3)	0·3578 (15)	0·0347 (10)	0·0988 (9)	4·0 (8)
C(4)	0·2072 (22)	0·1580 (13)	0·1153 (11)	6·6 (11)
C(5)	0·1336 (15)	−0·0010 (12)	0·1150 (9)	4·7 (8)
C(6)	0·0042 (14)	0·0183 (11)	0·1558 (10)	5·0 (8)
C(7)	0·0110 (15)	0·0032 (11)	0·2589 (10)	4·5 (8)
C(8)	0·0825 (12)	0·0562 (11)	0·4138 (8)	3·3 (6)
C(9)	0·1785 (14)	0·1132 (10)	0·4819 (10)	3·6 (7)
C(10)	0·3118 (12)	0·0682 (9)	0·4888 (8)	2·9 (6)

* B_{iso} is the mean of the principal axes of the thermal ellipsoid.

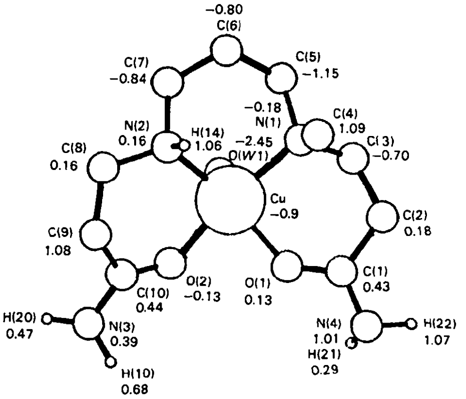

Fig. 1. Molecular structure excluding the perchlorate ions, showing the displacements of atoms from the N_2O_2 plane (Å) (the atom positions below the plane are indicated by negative signs).

Discussion. The atomic coordinates and isotropic temperature factors are listed in Table 1.* Table 2 lists bond lengths and angles, together with hydrogen-bond lengths. A perspective view of $[Cu(N\text{-}CH_3bctn)(H_2O)]^{2+}$ with the numbering scheme and the deviations of atoms from the least-squares plane through O(1)–O(2)–N(2)–N(1) are shown in Fig. 1. The equation of the least-squares plane formed by N(1), N(2), O(2) and O(1) is $-0{\cdot}1109x + 14{\cdot}15y + 1{\cdot}687z = 1{\cdot}319$.

As shown in Figs. 1 and 2, the Cu atom is five-coordinate in a slightly distorted square-pyramidal geometry with the quadridentate ligand equatorial and H_2O axial. The Cu atom is displaced from the best plane of N(1)–N(2)–O(2)–O(1) by 0·9 Å toward the apex of the pyramid, which is formed by a water O

Table 2. *Bond lengths* (Å) *and angles* (°), *together with hydrogen-bond lengths* (Å)

Cu–O(1)	1·960 (9)	Cu–O(2)	1·971 (8)
Cu–N(1)	2·048 (9)	Cu–N(2)	1·988 (10)
Cl(1)–O(11)	1·350 (16)	Cl(1)–O(12)	1·321 (13)
Cl(1)–O(13)	1·377 (13)	Cl(1)–O(14)	1·286 (14)
Cl(2)–O(21)	1·288 (5)	Cl(2)–O(22)	1·340 (6)
Cl(2)–O(23)	1·232 (6)	Cl(2)–O(24)	1·190 (6)
O(1)–C(1)	1·213 (17)	O(2)–C(10)	1·232 (14)
N(1)–C(3)	1·463 (17)	N(1)–C(4)	1·430 (21)
N(1)–C(5)	1·501 (18)	N(2)–C(7)	1·510 (18)
N(2)–C(8)	1·469 (15)	N(3)–C(10)	1·348 (15)
N(4)–C(1)	1·317 (20)	C(1)–C(2)	1·506 (19)
C(2)–C(3)	1·501 (22)	C(5)–C(6)	1·530 (21)
C(6)–C(7)	1·492 (21)	C(8)–C(9)	1·533 (20)
C(9)–C(10)	1·496 (19)	Cu–O(*W*1)	2·379 (20)
O(1)–Cu–O(2)	81·4 (3)	O(1)–Cu–N(1)	92·2 (4)
O(1)–Cu–N(2)	164·9 (4)	O(2)–Cu–N(1)	172·1 (4)
O(2)–Cu–N(2)	92·7 (4)	N(1)–Cu–N(2)	94·6 (4)
O(11)–Cl(1)–O(12)	110·0 (10)	O(11)–Cl(1)–O(13)	106·0 (10)
O(11)–Cl(1)–O(14)	111·3 (15)	O(12)–Cl(1)–O(13)	108·0 (10)
O(12)–Cl(1)–O(14)	112·0 (12)	O(13)–Cl(1)–O(14)	109·3 (13)
O(21)–Cl(2)–O(22)	114·9 (4)	O(21)–Cl(2)–O(23)	117·2 (5)
O(21)–Cl(2)–O(24)	105·6 (4)	O(22)–Cl(2)–O(23)	104·0 (4)
O(22)–Cl(2)–O(24)	106·4 (5)	O(23)–Cl(2)–O(24)	108·3 (4)
Cu–O(1)–C(1)	131·0 (9)	Cu–O(2)–C(10)	126·7 (8)
Cu–N(1)–C(3)	109·3 (8)	Cu–N(1)–C(4)	112·9 (9)
Cu–N(1)–C(5)	109·1 (8)	C(3)–N(1)–C(4)	109·5 (13)
C(3)–N(1)–C(5)	106·8 (10)	C(4)–N(1)–C(5)	109·0 (12)
Cu–N(2)–C(7)	113·8 (8)	Cu–N(2)–C(8)	117·1 (8)
C(7)–N(2)–C(8)	106·2 (10)	O(1)–C(1)–N(4)	120·4 (13)
O(1)–C(1)–C(2)	122·2 (13)	N(4)–C(1)–C(2)	117·4 (13)
C(1)–C(2)–C(3)	113·6 (12)	N(1)–C(3)–C(2)	115·8 (12)
N(1)–C(5)–C(6)	115·7 (12)	C(5)–C(6)–C(7)	114·4 (12)
N(2)–C(7)–C(6)	113·6 (12)	N(2)–C(8)–C(9)	112·7 (11)
C(8)–C(9)–C(10)	108·8 (11)	O(2)–C(10)–N(3)	119·0 (12)
O(2)–C(10)–C(9)	123·1 (11)	N(3)–C(10)–C(9)	117·7 (11)
O(*W*1)–H···O(11)	2·834	O(*W*1)–H···O(2)	2·897
O(*W*2)–H···O(22)	3·042	O(*W*2)–H···O(24)	2·845
N(2)–H···O(*W*2)	2·895	N(3)–H···O(13)	3·052
N(3)–H···O(1)	3·035	N(3)–H···O(2)	2·980

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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 43552 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

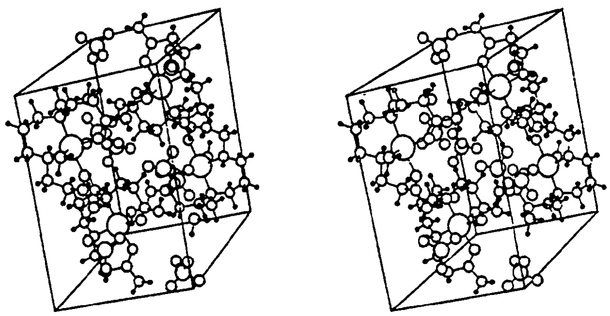

Fig. 2. Stereoview of the packing (viewed down the **b** direction).

atom with the Cu—O bond distance 2·38 (2) Å. This bond is significantly longer than the equatorial Cu—O bond distances (1·960 and 1·971 Å). The ligand molecule is coordinated in a square-planar manner with slight tetrahedral distortion. The H atom and the methyl group attached to the asymmetric atoms N(1) and N(2) are axial, and are on the same side of the N(1)–N(2)–O(2)–O(1) plane. The atoms C(3) and C(5) near the methyl group, $C(4)H_3$, are pushed out of the said best plane toward the opposite side of this methyl group. Thus the six-membered ring containing N(1) and O(1) is squeezed into an unstable twist form, the other two six-membered rings being in stable chair forms.

Both $[Cu(N\text{-}CH_3bctn)(H_2O)](ClO_4)_2.H_2O$ and $[Cu(ClO_4)(bctn)(H_2O)]ClO_4.H_2O$ contain three consecutive six-membered chelate rings. Comparing the crystal structures of these two complexes, we found the following significant results: (1) $[Cu(N\text{-}CH_3bctn)(H_2O)](ClO_4)_2.H_2O$ is monoclinic, while $[Cu(ClO_4)(bctn)(H_2O)]ClO_4.H_2O$ forms triclinic crystals. (2) For $[Cu(N\text{-}CH_3bctn)(H_2O)](ClO_4)_2.H_2O$, the Cu atom is five-coordinate in a distorted square-pyramidal geometry; for $[Cu(ClO_4)(bctn)(H_2O)]ClO_4.H_2O$, the Cu atom is six-coordinate in a tetragonally distorted octahedron. (3) For both complexes, the two chiral N centers are in the *RS* configuration.

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Bis[bis(dimethylphosphinomethyl)methylphosphine]nickel(0)*

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Abstract. $[Ni(C_7H_{19}P_3)_2]$, $M_r = 451{\cdot}01$, monoclinic, $C2/c$, $a = 17{\cdot}264\ (2)$, $b = 8{\cdot}579\ (1)$, $c = 17{\cdot}672\ (1)$ Å, $\beta = 113{\cdot}09\ (1)°$, $V = 2407{\cdot}9$ Å^3, $Z = 4$, $D_x = 1{\cdot}24$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 49{\cdot}5$ cm^{-1}, $F(000) = 960$, $T = 294$ K, $wR = 0{\cdot}051$ for 2079 unique observed structure factors. Two molecules of bis(dimethylphosphinomethyl)methylphosphine (dmmp) form a molecular complex with nickel(0) by acting as bidentate, chelating ligands to the tetrahedral metal centre. The six-membered $MeP(CH_2PMe_2)_2Ni$ rings adopt a chair conformation. The Ni—P bond lengths are 2·136 (1) and 2·140 (1) Å.

Introduction. Linear triphosphaalkanes of type (I) (R = alkyl, aryl) combine three potential phosphorus donor centres held in close spatial proximity by short, yet flexible, methylene bridges (Appel, Geisler & Schöler, 1979; Karsch, 1982; Hietkamp, Sommer & Stelzer, 1984; Brauer, Hietkamp, Sommer, Stelzer, Müller, Romão & Krüger, 1985). This gives rise to a remarkable potential for, and versatility in, forming transition-metal complexes which has not yet been

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* Part XII of the series 'Complexes with Phosphinomethanes and Phosphinomethanides as Ligands' by HHK.

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