

atoms are listed in Table 3, selected bond lengths and angles in Table 4.†

The numbering of the atoms is shown in Fig. 1 and a stereoscopic drawing of the molecule (Johnson, 1965) in Fig. 2.

**Discussion.** The preparation of the complex is described by Walther (1977, 1980). Fig. 2 shows that the central atom has the coordination number four. Benzaldehyde is  $\pi$ -coordinated. The lengthening of the C=O bond by 0.1 Å (*cf.* the C=O bond in benzophenone or CO<sub>2</sub>: 1.21 to 1.23 Å) to 1.325 (7) Å can be explained by a strong back-donation from the central metal to the  $\pi^*$  orbital of the C=O group. The atoms Ni, O, P(1), P(2) and C(43) approximately define a plane (I). The deviations from the best plane through these atoms are rather small [0.056 (1), 0.054 (4), -0.040 (2), 0.001 (2), -0.071 (6) Å, respectively]. The distances Ni-P(1), 2.244 (2), and Ni-P(2), 2.171 (2) Å, are significantly different. This may reflect the unsymmetrical binding arrangement of the Ni-carbonyl group. The plane of the phenyl group forms an angle of 21.5 (1)° with plane (I). The structure of the complex benzaldehydebis(tricyclohexylphosphine)nickel(0) resembles the structures of Ni complexes containing ketones like (CF<sub>3</sub>)<sub>2</sub>CO (Countryman & Penfold, 1972) and Ph<sub>2</sub>CO (Tsuu, Huffmann & Kochi, 1979). The structure may be described as containing an oxa-nickela-cyclopropane ring. Spectroscopic and chemical properties of the compound are in agreement with this description. For example, a decrease in the stretching frequency of the C=O group from the normal value 1718 cm<sup>-1</sup> to less than 1500 cm<sup>-1</sup> is observed and the <sup>1</sup>H NMR spectrum

demonstrates an increase of the shielding of the aldehyde proton ( $\delta = 5.58$  p.p.m. in C<sub>6</sub>D<sub>6</sub>, compared to free benzaldehyde,  $\delta = 9.61$  p.p.m. in C<sub>6</sub>D<sub>6</sub>). Typical reactions of the complex coordinated aldehyde with nucleophiles (*e.g.* amines) have not been observed, but reactions with some electrophiles occur (Walther, 1977, 1980).

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36623 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## [Biuretato(2-)-N<sup>1</sup>,N<sup>5</sup>](ethylenediamine)copper(II)

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**Abstract.** [Cu(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)(C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>O<sub>2</sub>)], C<sub>4</sub>H<sub>11</sub>CuN<sub>5</sub>O<sub>2</sub>, triclinic. *P*1, *a* = 7.541 (2), *b* = 9.032 (6), *c* = 12.078 (5) Å,  $\alpha$  = 99.29 (4),  $\beta$  = 101.32 (3),  $\gamma$  = 86.98 (4)°, *V* = 795.91 Å<sup>3</sup>, *Z* = 4, *d*<sub>m</sub> = 1.88 (8), *d*<sub>c</sub> =

1.875 Mg m<sup>-3</sup>,  $\mu$ (Mo *K* $\alpha$ ) = 2.82 mm<sup>-1</sup>. The structure was refined to *R* = 0.032 for 3150 observed reflections. There are two crystallographically independent complex molecules in the structure. In one of these, two

diamine N atoms and two N atoms of the biuret ligand coordinate to Cu in a tetrahedrally distorted square-planar arrangement, with a dihedral angle of 25.6 (2)° between the planes N(1),Cu(1),N(2) and N(3),Cu(1),N(5). Tetrahedral distortion in the other molecule is smaller, with a dihedral angle of 12.6 (3)° between the N(11),Cu(2),N(12) and N(13),Cu(2),N(15) planes.

**Introduction.** From the system Cu<sup>2+</sup>, biuret (H<sub>2</sub>biu) and ethylenediamine (en) in alkaline solution, Traube (1922) prepared and described the complexes [Cu(biu)<sub>2</sub>][Cu(en)<sub>2</sub>].H<sub>2</sub>O and [Cu(biu)<sub>2</sub>][Cu(en)<sub>2</sub>].7H<sub>2</sub>O. Kato (1960) suggested that a mixed-ligand complex [Cu(biu)(en)] is also formed in the solution. In our attempt to prepare the complexes reported by Traube (1922) we obtained crystals of composition Cu<sup>2+</sup>:en:biu<sup>2-</sup> = 1:1:1, which by X-ray analysis turned out to be the mixed-ligand complex [Cu(biu)(en)].

Red-violet crystals of [Cu(biu)(en)] were formed by slow evaporation in a desiccator of a solution containing 0.01 mol of freshly precipitated Cu(OH)<sub>2</sub>, 0.01 mol of ethylenediamine and 0.01 mol of biuret in water. The needle-shaped crystals were triclinic. The cell parameters (297 K) were obtained from a least-squares refinement of angular settings of 22 reflections with a Nicolet P3 single-crystal diffractometer. Three-dimensional intensity data were collected on the same diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) by the  $\omega$ -scan method. A total of 3873 reflections with  $3^\circ < 2\theta < 55^\circ$  were measured and those 3150 with  $I > 2\sigma(I)$  were considered significant. The net intensities were corrected for Lorentz and polarization effects and for absorption using the  $\varphi$ -scan data. The transmission factors varied between 0.594 and 1.00.

The Cu positions were determined by Patterson methods and electron density maps gave the positions of all non-H atoms. These atoms were refined anisotropically. H atoms were found from a difference map and were included in the refinement with a fixed isotropic temperature factor of  $U = 0.06 \text{ \AA}^2$ . The full-matrix least-squares refinement converged at  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.032$ . The function minimized was  $\sum w(|F_o| - |F_c|)^2$  and the weighting scheme used was  $w = (a + |F_o| + b|F_o|^2 + c|F_o|^3)^{-1}$ . The values of  $a$ ,  $b$  and  $c$  in the final refinement were 10.0, 0.020 and 0.00050. The final difference map was featureless. The atomic coordinates, interatomic distances and bond angles are given in Tables 1 and 2.\*

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36624 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and  $U_{eq}$  ( $\times 10^2$ ) for the nonhydrogen atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$ ( $\text{\AA}^2$ )
Cu(1)	5620.3 (4)	2730.3 (4)	5463.6 (3)	2.55 (4)
Cu(2)	7638.8 (5)	36.3 (4)	517.1 (3)	2.56 (4)
O(1)	1419 (4)	601 (4)	6217 (2)	5.3 (2)
O(2)	2431 (3)	313 (3)	2676 (2)	4.0 (1)
O(11)	5667 (4)	3654 (3)	-1056 (2)	4.5 (1)
O(12)	6944 (4)	3876 (3)	2751 (2)	4.2 (1)
N(1)	6456 (4)	4386 (3)	6781 (2)	3.6 (1)
N(2)	8034 (4)	2999 (3)	5036 (2)	3.6 (1)
N(3)	3789 (4)	2083 (4)	6156 (2)	3.9 (2)
N(4)	2107 (3)	721 (3)	4506 (2)	3.1 (1)
N(5)	4556 (4)	1726 (3)	3984 (2)	3.3 (1)
N(11)	7434 (3)	-1760 (3)	-743 (2)	2.9 (1)
N(12)	9123 (3)	-1381 (3)	1474 (2)	2.8 (1)
N(13)	6610 (4)	1387 (3)	-526 (2)	3.5 (1)
N(14)	6328 (4)	3508 (3)	828 (2)	3.0 (1)
N(15)	7624 (5)	1573 (3)	1805 (2)	4.1 (1)
C(1)	8121 (6)	5033 (5)	6579 (4)	5.4 (2)
C(2)	9234 (5)	3808 (5)	6032 (3)	5.1 (2)
C(3)	2471 (4)	1153 (4)	5684 (2)	3.6 (2)
C(4)	3075 (4)	929 (3)	3677 (2)	2.7 (1)
C(11)	8705 (5)	-2969 (4)	-385 (3)	3.9 (2)
C(12)	8876 (5)	-2932 (3)	894 (3)	4.1 (2)
C(13)	6201 (4)	2821 (3)	-311 (2)	2.9 (1)
C(14)	7004 (4)	2971 (3)	1852 (2)	2.9 (1)

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

Cu(1)-N(1)	2.026 (3)	Cu(2)-N(11)	2.027 (3)
Cu(1)-N(2)	2.024 (3)	Cu(2)-N(12)	2.012 (3)
Cu(1)-N(3)	1.909 (3)	Cu(2)-N(13)	1.921 (3)
Cu(1)-N(5)	1.911 (2)	Cu(2)-N(15)	1.912 (3)
N(1)-C(1)	1.490 (6)	N(11)-C(11)	1.476 (4)
C(1)-C(2)	1.500 (6)	C(11)-C(12)	1.520 (5)
C(2)-N(2)	1.469 (4)	C(12)-N(12)	1.465 (4)
N(3)-C(3)	1.315 (4)	N(13)-C(13)	1.312 (4)
C(3)-N(4)	1.390 (3)	C(13)-N(14)	1.402 (3)
N(4)-C(4)	1.390 (4)	N(14)-C(14)	1.395 (4)
C(4)-N(5)	1.319 (4)	C(14)-N(15)	1.320 (4)
C(3)-O(1)	1.280 (5)	C(13)-O(11)	1.258 (4)
C(4)-O(2)	1.260 (3)	C(14)-O(12)	1.256 (3)
N(1)-Cu(1)-N(2)	84.4 (1)	N(11)-Cu(2)-N(12)	84.1 (1)
N(1)-Cu(1)-N(3)	93.9 (1)	N(11)-Cu(2)-N(13)	92.7 (1)
N(1)-Cu(1)-N(5)	161.2 (1)	N(11)-Cu(2)-N(15)	171.8 (1)
N(2)-Cu(1)-N(3)	162.4 (1)	N(12)-Cu(2)-N(13)	169.3 (1)
N(2)-Cu(1)-N(5)	94.5 (1)	N(12)-Cu(2)-N(15)	92.8 (1)
N(3)-Cu(1)-N(5)	92.6 (1)	N(13)-Cu(2)-N(15)	91.6 (1)
Cu(1)-N(1)-C(1)	108.2 (2)	Cu(2)-N(11)-C(11)	110.3 (2)
N(1)-C(1)-C(2)	109.4 (3)	N(11)-C(11)-C(12)	108.7 (3)
C(1)-C(2)-N(2)	107.2 (3)	C(11)-C(12)-N(12)	109.3 (3)
C(2)-N(2)-Cu(1)	108.9 (2)	C(12)-N(12)-Cu(2)	110.2 (2)
Cu(1)-N(3)-C(3)	128.0 (2)	Cu(2)-N(13)-C(13)	129.3 (2)
N(3)-C(3)-N(4)	119.8 (3)	N(13)-C(13)-N(14)	119.0 (3)
C(3)-N(4)-C(4)	130.8 (2)	C(13)-N(14)-C(14)	131.1 (3)
N(4)-C(4)-N(5)	119.0 (2)	N(14)-C(14)-N(15)	118.4 (2)
C(4)-N(5)-Cu(1)	128.9 (2)	C(14)-N(15)-Cu(2)	130.1 (2)
N(3)-C(3)-O(1)	125.6 (2)	N(13)-C(13)-O(11)	125.1 (2)
N(4)-C(3)-O(1)	114.6 (3)	N(14)-C(13)-O(11)	115.9 (3)
N(4)-C(4)-O(2)	115.3 (3)	N(14)-C(14)-O(12)	116.1 (3)
N(5)-C(4)-O(2)	125.6 (3)	N(15)-C(14)-O(12)	125.5 (3)

**Discussion.** There are two crystallographically independent [Cu(biu)(en)] units in the asymmetric unit (one is shown in Fig. 1). Most of the bond lengths and angles

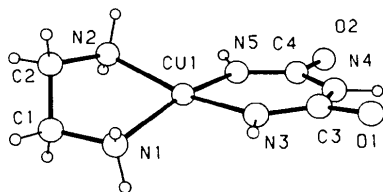


Fig. 1. Perspective view of one of the two crystallographically independent complex molecules.

are very similar in the two molecules. Both Cu atoms have a tetrahedrally distorted planar coordination but the degree of distortion differs in the two molecules. The N atoms of ethylenediamine and the N atoms of the amide groups of the biuret ligand coordinate to Cu(1) in a pseudotetrahedral manner, with a dihedral angle of 25.6 (2)° between the N(1),Cu(1),N(2) and N(3),Cu(1),N(5) planes. The geometry around Cu(2) is much closer to planar, the dihedral angle between the N(11),Cu(2),N(12) and N(13),Cu(2),N(15) planes being only 12.6 (3)°.

The bond lengths and angles of the biuret ligand are essentially the same as those found for dipotassium bis[biuretato(2-)-N<sup>1</sup>,N<sup>5</sup>]cuprate(II) tetrahydrate (Freeman, Smith & Taylor, 1961) and dipotassium di- $\mu$ -hydroxo-bis{[biuretato(2-)-N<sup>1</sup>,N<sup>5</sup>]copper(II)} tetrahydrate (Birker & Beurskens, 1974). The biuret residues are not planar. Each residue is slightly bent about the line joining Cu to the terminal N atom of the six-membered ring; and the two halves of each ligand are twisted in opposite directions around the bonds N(4)–C(3) [N(14)–C(13)] and N(4)–C(4) [N(14)–C(14)]. As a result of this twisting the angles between the N(3),C(3),O(1),N(4) and N(5),C(4),O(2),N(4) planes and between the N(13),C(13),O(11),N(14)

Table 3. Hydrogen-bond distances (Å) and angles (°)

D–H...A	D...A	H...A	D–H...A
N(1)–H(N1)...O(12 <sup>b</sup> )	3.036 (4)	2.22 (5)	156 (5)
N(1)–H'(N1)...O(11 <sup>ii</sup> )	2.971 (4)	2.21 (5)	146 (4)
N(2)–H(N2)...O(12)	2.944 (4)	2.06 (5)	174 (4)
N(4)–H(N4)...O(1 <sup>iii</sup> )	2.889 (4)	2.07 (4)	175 (4)
N(11)–H'(N11)...O(2 <sup>iv</sup> )	2.874 (4)	2.08 (5)	159 (4)
N(12)–H(N12)...O(1 <sup>v</sup> )	2.868 (4)	2.03 (5)	155 (4)
N(12)–H'(N12)...O(2 <sup>vi</sup> )	2.989 (3)	2.23 (4)	151 (4)
N(13)–H(N13)...O(2 <sup>v</sup> )	2.993 (4)	2.26 (5)	139 (4)
N(14)–H(N14)...O(11 <sup>vii</sup> )	2.905 (4)	2.19 (4)	165 (4)

#### Symmetry code

(i)	1 - x, 1 - y, 1 - z	(ii)	x, y, 1 + z
(iii)	-x, -y, 1 - z	(iv)	1 - x, -y, -z
(v)	1 - x, -y, 1 - z	(vi)	1 + x, y, z
(vii)	1 - x, 1 - y, -z		

and N(15),C(14),O(12),N(14) planes are 7.7 (7) and 5.9 (6)°, respectively.

The diamine ligands are in a *gauche* conformation. The packing is mainly determined by intermolecular N–H...O hydrogen bonds involving the diamine N atoms and the O atoms of the biuret ligand. The parameters of the hydrogen bonds are listed in Table 3.

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## Tris(ethylenediamine)cobalt(III) Dihydrogen Tetrahydrofuran tetracarboxylate Trihydrogen Tetrahydrofuran tetracarboxylate Hydrate (1:1:1:2½)

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**Abstract.** (C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>Co<sup>3+</sup>·C<sub>8</sub>H<sub>7</sub>O<sub>9</sub><sup>-</sup>·C<sub>8</sub>H<sub>6</sub>O<sub>9</sub><sup>2-</sup>·2½H<sub>2</sub>O, triclinic, *P*1̄, *a* = 11.822 (2), *b* = 13.100 (2), *c* = 11.461 (2) Å,  $\alpha$  = 68.81 (4),  $\beta$  = 79.72 (3),  $\gamma$  = 77.30 (3)°, *V* = 1605 Å<sup>3</sup>, *D*<sub>c</sub> = 1.58 Mg m<sup>-3</sup>, *Z* = 2. Final *R* = 0.070 for 2460 observed reflexions. Both

anions are of the *trans.cis.trans* isomer with very similar geometry. The anions are linked to the N protons of the cation and to the water molecules by an extensive three-dimensional network of hydrogen bonds.