Table 2. *Distances* (Å) *and angles* (°) *in the* Li—O *polyhedra*

| | | | |
|---|---|---|---|
| Li(1)—O(12$^{i}$) | 1·865 (7) | Li(3)—O*W*(3$^{iv}$) | 1·892 (8) |
| Li(1)—O(13) | 1·964 (7) | Li(3)—O*W*(2$^{v}$) | 1·914 (8) |
| Li(1)—O(1) | 1·969 (7) | Li(3)—O(14$^{ii}$) | 1·956 (6) |
| Li(1)—O(4) | 2·004 (6) | Li(3)—O*W*(1) | 2·040 (8) |
| All others | > 3·11 | All others | > 3·24 |
| | | | |
| Li(2)—O*W*(1) | 2·044 (8) | Li(4)—O(14$^{iii}$) | 1·936 (7) |
| Li(2)—O(4) | 2·061 (7) | Li(4)—O(3) | 1·983 (7) |
| Li(2)—O(13) | 2·069 (6) | Li(4)—O(1) | 2·062 (6) |
| Li(2)—O(2$^{ii}$) | 2·122 (6) | Li(4)—O(1$^{iii}$) | 2·170 (7) |
| Li(2)—O(2$^{iii}$) | 2·189 (7) | Li(4)—O(2$^{iii}$) | 2·243 (7) |
| All others | > 3·11 | All others | > 3·13 |
| | | | |
| O(12$^{i}$)—Li(1)—O(13) | 124·4 (3) | O*W*(3$^{iv}$)—Li(3)—O*W*(2$^{v}$) | 118·0 (4) |
| O(12$^{i}$)—Li(1)—O(1) | 110·5 (3) | O*W*(3$^{iv}$)—Li(3)—O(14$^{ii}$) | 119·1 (4) |
| O(12$^{i}$)—Li(1)—O(4) | 107·3 (3) | O*W*(3$^{iv}$)—Li(3)—O*W*(1) | 107·5 (3) |
| O(13)—Li(1)—O(1) | 110·3 (3) | O*W*(2$^{v}$)—Li(3)—O(14$^{ii}$) | 102·7 (3) |
| O(13)—Li(1)—O(4) | 91·1 (3) | O*W*(2$^{v}$)—Li(3)—O*W*(1) | 108·7 (4) |
| O(1)—Li(1)—O(4) | 111·3 (3) | O(14$^{ii}$)—Li(3)—O*W*(1) | 99·0 (3) |
| O*W*(1)—Li(2)—O(4) | 106·1 (3) | O(14$^{iii}$)—Li(4)—O(3) | 97·1 (3) |
| O*W*(1)—Li(2)—O(13) | 93·5 (3) | O(14$^{iii}$)—Li(4)—O(1) | 112·4 (3) |
| O*W*(1)—Li(2)—O(2$^{ii}$) | 94·0 (3) | O(14$^{iii}$)—Li(4)—O(1$^{iii}$) | 102·4 (3) |
| O*W*(1)—Li(2)—O(2$^{iii}$) | 155·3 (4) | O(14$^{iii}$)—Li(4)—O(2$^{iii}$) | 133·3 (3) |
| O(4)—Li(2)—O(13) | 86·6 (2) | O(3)—Li(4)—O(1) | 106·1 (3) |
| O(4)—Li(2)—O(2$^{ii}$) | 88·6 (2) | O(3)—Li(4)—O(1$^{iii}$) | 151·4 (3) |
| O(4)—Li(2)—O(2$^{iii}$) | 98·2 (3) | O(3)—Li(4)—O(2$^{iii}$) | 90·8 (3) |
| O(13)—Li(2)—O(2$^{ii}$) | 172·0 (4) | O(1)—Li(4)—O(1$^{iii}$) | 85·7 (2) |
| O(13)—Li(2)—O(2$^{iii}$) | 92·2 (3) | O(1)—Li(4)—O(2$^{iii}$) | 109·3 (3) |
| O(2$^{ii}$)—Li(2)—O(2$^{iii}$) | 82·1 (2) | O(1$^{iii}$)—Li(4)—O(2$^{iii}$) | 60·5 (2) |
| | | O(14$^{iii}$)—Li(4)—C(8$^{iii}$) | 120·4 (4) |
| | | O(3)—Li(4)—C(8$^{iii}$) | 120·9 (3) |
| | | O(1$^{iii}$)—Li(4)—C(8$^{iii}$) | 99·7 (2) |

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $1+x, y, z$; (iii) $-x, 1-y, 1-z$; (iv) $1-x, -y, 1-z$; (v) $1-x, 1-y, 1-z$.

82 and 94°. In the polyhedron around Li(4) the two farthest O atoms [O(1) and O(2)] belong to the same carboxylic group. Since the relatively short distance between O(1) and O(2) is restrained by the covalent forces within the carboxylic group the angle O(1)—Li(4)—O(2) is only 60·5°. The remaining O atoms of this polyhedron are arranged such that if the closely spaced O(1) and O(2) are regarded as a 'single' anion, then using the bisector of O(1)—Li(4)—O(2) [*i.e.* approximately the line Li(4)—C(8)] the polyhedron has roughly the appearance of a distorted tetrahedron. The angles between the appropriate bonds emanating from Li(4) range between 97·1 and 120·9°.

O*W*(1) is the only water oxygen atom exhibiting two well defined hydrogen bonds [O*W*(1)—O(11) = 2·747 (5) and O*W*(1)—O(11)′ = 2·806 (4) Å] and the appropriate H atoms could be resolved clearly in the course of the structure determination. In contrast, both O*W*(2) and O*W*(3) form only one distinct hydrogen bond [O*W*(2)—O(3) = 2·650 (5) and O*W*(3)—O(12)′ = 2·827 (5) Å, respectively] and only the corresponding H atoms could be clearly located. The other two H atoms seem to be distributed irregularly and show unrealistic temperature factors.

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# The Structure of {*N*,*N*-Bis[(3,5-dimethyl-1-pyrazolyl)methyl]aminoethane}iodocopper(I)

By Yvon C. M. Pennings, Willem L. Driessen* and Jan Reedijk

*Department of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box* 9502, 2300 *RA Leiden, The Netherlands*

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**Abstract.** [Cu($C_{14}H_{23}N_5$)I], $M_r = 451{\cdot}82$, monoclinic, $C2/c$, $a = 24{\cdot}324$ (6), $b = 8{\cdot}875$ (2), $c = 17{\cdot}020$ (5) Å, $\beta = 95{\cdot}89$ (2)°, $V = 3654{\cdot}6$ Å$^3$, $Z = 8$, $D_x = 1{\cdot}64$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 28{\cdot}71$ cm$^{-1}$, $F(000) = 891$, $T = 293$ K, final $R = 0{\cdot}036$ for 2570 significant reflections. The copper(I) ion is coordinated to three ligand N atoms and to the I$^-$ ion. The I$^-$ ion is non-bridging. The geometry of the Cu environment can be described as a distorted trigonal pyramid, in which the amine N atom forms the top of

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* Author to whom correspondence should be addressed.

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the pyramid. The Cu—I distance is 2·5231 (7) Å. The Cu—N distances are 2·031 (4) and 2·040 (4) Å for the pyrazole N atoms and 2·445 (4) Å for the amine N atom. Although the Cu—N(amine) distance is extremely long for a copper(I) compound, it is regarded as bonding.

**Introduction.** Several copper(I) compounds with *N,N*-bis(1-pyrazolylmethyl)aminoethane (aebp) and *N,N*-bis(3,5-dimethyl-1-pyrazolylmethyl)aminoethane (aebd) have been described recently (Pennings, Driessen & Reedijk, 1988), including the crystal structures of [Cu(aebp)Cl]$_2$ and [Cu(aebp)$_2$](CF$_3$SO$_3$). The binding mode of aebp in these copper(I) compounds is bidentate; only the pyrazole N atoms are coordinated. This is also the case with the copper(I) tetrafluoroborate compound of *N,N,N′,N′*-tetrakis(1-pyrazolylmethyl)-1,2-diaminoethane (edtp) (Driessen, Hulsbergen, Reedijk & Verschoor, 1985). With copper(II) and other divalent transition metals, however, the ligands aebp and aebd are tridentate (Schoonhoven, Driessen, Reedijk & Verschoor, 1984; Veldhuis, Driessen & Reedijk, 1986) and the ligand edtp is hexadentate (Hulsbergen, Driessen, Reedijk & Verschoor, 1984): all pyrazole N atoms as well as the amine N atom(s) coordinate.

The infrared spectra and the X-ray powder diagrams of [Cu(aebp)Cl]$_2$, [Cu(aebp)Br]$_2$ and [Cu(aebp)I]$_2$ are identical, indicating an identical bonding mode of the ligand. The infrared spectrum and the X-ray powder diagram of [Cu(aebd)I], however, are quite different from those of [Cu(aebd)Cl]$_2$ and [Cu(aebd)Br]$_2$, indicating a different coordination mode of the ligand aebd. To elucidate this phenomenon an X-ray crystal structure determination of [Cu(aebd)I] was carried out.

**Experimental.** White plates grown from acetonitrile at room temperature with approximate dimensions 0·36 × 0·26 × 0·06 mm. Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromatized Mo *Kα*. $\omega$–$2\theta$ scans. Cell constants from setting angles of 24 reflections, $9 \leq \theta \leq 12°$. Corrections for Lorentz and polarization effects. Absorption correction, Monte Carlo method (de Graaff, 1973) applied because $\mu = 28{\cdot}71$ cm$^{-1}$ and transmission coefficients from 63·30 to 116·19. $\theta_{\max} = 27{\cdot}5°$, $h$ −31 to 31, $k$ 0 to 11, $l$ 0 to 22. Standard reflections $\bar{6}80$, $\overline{12},0,4$ and $12,\bar{2},2$, intensity variation 4·3%. 4695 measured reflections, 4458 independent, $R_{\rm int} = 0{\cdot}021$, 1888 unobserved with $I < 2\sigma(I)$. Heavy atoms located from a Patterson map. Structure solved with the computer program *AUTOFOUR* (Kinneging & de Graaff, 1984). *F* used in LS refinement. All but one H atom found in difference Fourier syntheses; the only one (H162) not thus found was placed at 0·98 Å from its parent atom. Least-squares refinement of non-H-atom positional and anisotropic thermal parameters; positional parameters

Table 1. *Atomic coordinates* (I *and* Cu ×10$^5$, *others* ×10$^4$) *and equivalent isotropic thermal parameters* (I *and* Cu Å$^2$ ×10$^2$, *others* Å$^2$ ×10) *of the non*-H *atoms with e.s.d.'s in parentheses*

$B_{\rm eq} = \frac{8}{3}\pi^2$ trace **U**.

| | $x$ | $y$ | $z$ | $B_{\rm eq}$ |
|---|---|---|---|---|
| I(01) | 90553 (1) | 21923 (4) | 4738 (2) | 512 (1) |
| Cu(02) | 87111 (2) | 47866 (7) | 650 (4) | 420 (2) |
| N(03) | 9045 (1) | 7336 (4) | 379 (2) | 41 (1) |
| C(04) | 9375 (2) | 7580 (7) | 1140 (3) | 56 (2) |
| C(05) | 9835 (2) | 6487 (8) | 1281 (4) | 79 (2) |
| C(10) | 8516 (2) | 8119 (6) | 324 (3) | 48 (2) |
| N(11) | 8134 (1) | 7229 (4) | 750 (2) | 40 (1) |
| N(12) | 8092 (1) | 5736 (4) | 621 (2) | 41 (1) |
| C(13) | 7685 (2) | 5269 (6) | 1034 (3) | 45 (1) |
| C(14) | 7470 (2) | 6480 (7) | 1409 (3) | 48 (2) |
| C(15) | 7757 (2) | 7739 (6) | 1223 (3) | 43 (1) |
| C(16) | 7534 (2) | 3659 (7) | 1055 (4) | 64 (2) |
| C(17) | 7710 (2) | 9346 (7) | 1453 (4) | 64 (2) |
| C(20) | 9350 (2) | 7750 (6) | −283 (3) | 49 (1) |
| N(21) | 9092 (2) | 7048 (5) | −1006 (2) | 45 (1) |
| N(22) | 8910 (2) | 5611 (5) | −983 (2) | 42 (1) |
| C(23) | 8799 (2) | 5190 (7) | −1725 (3) | 47 (2) |
| C(24) | 8916 (2) | 6360 (9) | −2226 (4) | 61 (2) |
| C(25) | 9103 (2) | 7522 (7) | −1759 (4) | 56 (2) |
| C(26) | 8628 (2) | 3610 (10) | −1895 (4) | 73 (2) |
| C(27) | 9318 (5) | 9095 (12) | −1915 (5) | 105 (3) |

Table 2. *Bond lengths* (Å) *and selected valence angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| I(01)—Cu(02) | 2·5231 (7) | C(13)—C(14) | 1·379 (7) |
| Cu(02)—N(03) | 2·445 (4) | C(13)—C(16) | 1·476 (8) |
| Cu(02)—N(12) | 2·040 (4) | C(14)—C(15) | 1·371 (7) |
| Cu(02)—N(22) | 2·031 (4) | C(15)—C(17) | 1·486 (7) |
| N(03)—C(04) | 1·467 (6) | C(20)—N(21) | 1·462 (7) |
| N(03)—C(10) | 1·458 (6) | N(21)—N(22) | 1·352 (5) |
| N(03)—C(20) | 1·459 (6) | N(21)—C(25) | 1·352 (7) |
| C(04)—C(05) | 1·481 (8) | N(22)—C(23) | 1·319 (6) |
| C(10)—N(11) | 1·466 (6) | C(23)—C(24) | 1·391 (8) |
| N(11)—N(12) | 1·346 (5) | C(23)—C(26) | 1·48 (1) |
| N(11)—C(15) | 1·395 (6) | C(24)—C(25) | 1·352 (8) |
| N(12)—C(13) | 1·339 (6) | C(25)—C(27) | 1·52 (1) |

| | | | |
|---|---|---|---|
| I(01)—Cu(02)—N(03) | 133·69 (9) | Cu(02)—N(03)—C(04) | 117·9 (3) |
| I(01)—Cu(02)—N(12) | 119·2 (1) | Cu(02)—N(03)—C(10) | 98·9 (3) |
| I(01)—Cu(02)—N(22) | 118·0 (1) | Cu(02)—N(03)—C(20) | 104·3 (3) |
| N(03)—Cu(02)—N(12) | 76·2 (1) | C(04)—N(03)—C(10) | 112·7 (4) |
| N(03)—Cu(02)—N(22) | 75·8 (1) | C(04)—N(03)—C(20) | 111·7 (4) |
| N(12)—Cu(02)—N(22) | 120·8 (2) | C(10)—N(03)—C(20) | 110·3 (4) |

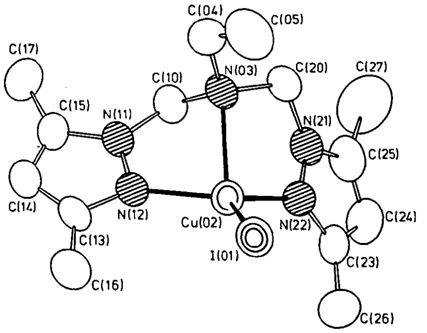

Fig. 1. *ORTEP* projection (Johnson, 1965) and atomic labelling of [Cu(aebd)I]. For clarity the H atoms are omitted.

of H atoms coupled to parent atoms; fixed isotropic thermal factor of 8·0 Å$^2$ for the H atoms. $S = 2{\cdot}33$, $w = 1/\sigma^2(F)$, $R = 0{\cdot}036$, $wR = 0{\cdot}041$. $(\Delta/\sigma)_{\max} < 0{\cdot}20$. Max., min. $\Delta\rho$ values in final difference synthesis 0·47, −0·43 e Å$^{-3}$. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Leiden University Computer (Amdahl 5860); programs written or modified by Mrs E. W. Rutten-Keulemans and R. A. G. de Graaff.

**Discussion.** Positional parameters and isotropic thermal parameters for the non-H atoms are listed in Table 1.* Bond distances and selected valence angles are given in Table 2. An *ORTEP* projection (Johnson, 1965) of [Cu(aebd)I] and the atomic labelling are given in Fig. 1.

The Cu$^{\rm I}$ ion is coordinated to three ligand N atoms and to the I$^-$ ion. The I$^-$ is non-bridging, which is unusual; only one Cu$^{\rm I}$ compound has so far been described with a terminally coordinated I$^-$ ion (Healy, Pakawatchai & White, 1983). The geometry of the Cu environment can be described as intermediate between a tetrahedron and (but closer to) a trigonal pyramid, with the N(pz)—Cu—N(pz) and the two N(pz)—Cu—I bond angles of about 120°, the two N(pz)—Cu—N(am) angles of approximately 76°, and the I—Cu—N(am) angle of about 134° (with pz = pyrazole and am = amine). N(am) forms the top of the pyramid. The Cu—N(pz) distances are 2·031 (4) and 2·040 (4) Å, the Cu—N(am) distance is 2·445 (4) Å and the Cu—I distance is 2·5231 (7) Å. The Cu—N(am) distance is unusually long. To our knowledge the longest Cu$^{\rm I}$—N distance reported so far amounts to 2·30 Å (Gagné, Kreh, Dodge, Marsh & McCool, 1982). Therefore, the question arises whether the long Cu—N(am) distance found here is to be regarded as bonding or as non-bonding. The almost regular trigonal planar Cu-[N(pz)]$_2$I geometry could be an argument in favour of the non-bonding of the amine N atom. However, in that case another conformation of the ligand, with a longer Cu···N(am) distance, would have been more appropriate in analogy to the behaviour of the ligand bis-(3,5-dimethyl-1-pyrazolylmethyl)aminobenzene (Blonk, Driessen & Reedijk, 1985). Moreover, reported *M*—N distances of up to 2·50 Å in coordination compounds with first-row divalent transition-metal ions are regarded as bonding (Hulsbergen, Driessen, Reedijk & Verschoor, 1984; Blonk, Driessen & Reedijk, 1985).

The deviation from the expected tetrahedral coordination of Cu$^{\rm I}$ is invoked by the ligand bite: the bridge between the amine N atom and the pyrazole N atom is too short for a tridentate tetrahedral geometry. In fact, the shape of the ligand seems to be the origin of the bidentate binding mode of the ligands aebp and aebd towards Cu$^{\rm I}$ (Schoonhoven *et al.*, 1984, Veldhuis *et al.*, 1986). A pyrazole ligand with a longer bridge to the amine N atom (Sorrell & Borovik, 1984) forms a Cu$^{\rm I}$ compound with the pyrazole N atoms as well as the amine N atom taking part in the tetrahedral Cu$^{\rm I}$ coordination. In the present case of [Cu(aebd)I] the tridentate bonding mode of the aebd ligand is invoked by the size of the I$^-$ ion and by its polarizability. In the aebd compound there is not enough space for two I$^-$ anions to form a bridge between two Cu ions. In contrast, in [Cu(aebp)I]$_2$ such a bridge is formed because there is no steric hindrance of methyl groups as in the aebd ligand. This also means that there is no need to utilize the amine N atom of the ligand aebp for coordination (Pennings *et al.*, 1988). Also, the larger polarizability of I$^-$ makes bridging of I$^-$ between two Cu$^{\rm I}$ ions less necessary than with Cl$^-$ and Br$^-$.

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* Lists of H-atom coordinates, anisotropic thermal parameters, valence angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51244 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.