Monoclinic
$C2/c$
$a = 24.613$ (3) Å
$b = 11.170$ (1) Å
$c = 17.211$ (3) Å
$\beta = 119.90$ (1)°
$V = 4101.9$ (9) Å$^3$
$Z = 8$
$D_x = 2.635$ Mg m$^{-3}$
$D_m$ not measured

Cell parameters from 46 reflections
$\theta = 5.018$–12.481°
$\mu = 8.96$ mm$^{-1}$
$T = 301$ K
Rod
0.20 × 0.15 × 0.10 mm
Colorless

*Data collection*

Syntex *P*4 four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: $\psi$ scan (Sheldrick, 1990) $T_{\min} = 0.168$, $T_{\max} = 0.408$
6963 measured reflections
5968 independent reflections
1929 reflections with $F > 3.5\sigma(F)$

$R_{\rm int} = 0.0347$
$\theta_{\max} = 30°$
$h = -1 \rightarrow 34$
$k = -1 \rightarrow 15$
$l = -24 \rightarrow 21$
3 standard reflections every 97 reflections intensity decay: negligible

*Refinement*

Refinement on *F*
$R = 0.058$
$wR = 0.058$
$S = 0.93$
5968 reflections
191 parameters
H atoms constrained
$w = 1/[\sigma^2(F) + 0.0008F^2]$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 1.0$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.99$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected bond distances (Å) for (III)*

| | | | |
|---|---|---|---|
| I(1)—Cu(1) | 2.650 (4) | I(3)—Cu(2) | 2.745 (4) |
| I(1)—Cu(2) | 2.633 (5) | I(3)—Cu(2$^{\rm ii}$) | 2.529 (6) |
| I(2)—Cu(1) | 2.872 (4) | Cu(1)···Cu(1$^{\rm i}$) | 2.697 (6) |
| I(2)—Cu(2) | 2.917 (4) | Cu(2)···Cu(2$^{\rm ii}$) | 2.657 (8) |
| I(2)—Cu(1$^{\rm i}$) | 2.538 (5) | Cu(1)···Cu(2) | 2.480 (7) |
| I(3)—Cu(1) | 2.747 (4) | Rb(1)···I(1) | 3.632 (3) |

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

Data were collected with a variable scan rate, using a $\theta/2\theta$ scan mode with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$. Refinement was completed using full-matrix least-squares methods.

For all compounds, data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXS*86; molecular graphics: *XP* (Siemens, 1990)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1047). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1998). C**54**, 597–600

# Tetraethylammonium Dicopper(I) Triiodide and (18-Crown-6)potassium Dicopper(I) Triiodide

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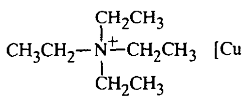
## Abstract

Tetraethylammonium triiododicopper(I), $(C_8H_{20}N)[Cu_2I_3]$, and (18-crown-6)potassium triiododicopper(I), $[K(C_{12}H_{24}O_6)][Cu_2I_3]$, crystallize with a polymeric series of edge-sharing $Cu_2I_2$ rhombs having Cu atoms bridged in pairs by an additional I atom, *i.e.* *catena*-poly-[[copper(I)-$\mu_2$-iodo-copper(I)]-di-$\mu_3$-iodo]. The pattern of projection of bridging $\mu_2$-I atoms with respect to the polymeric band is up, down, up, down.

## Comment

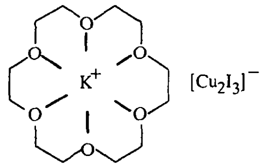
Copper(I) halide complexes have been observed to form $Cu_2I_3^-$ polymers. The polymer may be viewed as a chain of $Cu_2I_2$ rhombs which share opposite edges, with an additional I atom bridging the Cu atoms of every alternate rhomb. The additional bridging I atoms may show bridging on the same side of the polymeric sheet, bridging in the sequence two up, two down, *etc.*, or bridging on alternating sides of the polymer [see preceding paper (Nurtaeva & Holt, 1998)].

Two $Cu_2I_3^-$ polymers with alternating up, down, up, down projections of bridging I atoms have been reported: $[Et_4N][Cu_2I_3]$ and $[(CH_3)_2—N{=}CH—N{=}CH—N(CH_3)_2][Cu_2I_3]$ were mentioned by Hartl & Mahdjour-Hassan-Abadi (1981) without full crystallographic details (only ranges and mean values of distances were reported). In connection with a study of the emission properties of these materials, we have prepared crystalline $[Et_4N][Cu_2I_3]$, (I) (Fig. 1*a*), according to published procedures and report here full structural details. We have also prepared the up, down, up, down polymer (18-crown-6)potassium dicopper(I) triiodide, (II) (Fig. 1*b*), which was unknown in the literature. $[(CH_3)_4N][Cu_2I_3]$ (Andersson & Jagner, 1985) displays a similar pattern of alternation of direction of projection of the bridging I atoms as bis[aqua(15-crown-5)sodium] bis[(15-crown-5)sodium] hexaiodotetracopper(I) tetraiododicopper(I) (Hu & Holt, 1994), which contains also an isolated $Cu_4I_6^{2-}$ cluster in the asymmetric unit.



$CH_3CH_2-\overset{CH_2CH_3}{\underset{CH_2CH_3}{N^{+}}}-CH_2CH_3\ [Cu_2I_3]^-$

(I)



(II)

Both title compounds show close Cu···Cu contacts across bridged rhombs and greater Cu···Cu separations in the non-bridged rhombs. Cu···Cu separations across bridged rhombs range from 2.470 (5) to 2.467 (3) Å and those across non-bridged rhombs are in the range 2.639 (5)–2.661 (4) Å for the title structures (I) and (II). The corresponding distances in [2,4,6-triphenylthiopyrylium]$[Cu_2I_3]$ (Batsanov *et al.*, 1982) are 2.479 and 2.634 Å, respectively.

The Cu—I distances involving the $\mu_2$-bridging I atoms are in the range 2.588 (4)–2.657 (3) Å in the two title structures, which is similar to the range 2.642–2.651 Å reported in the all-up variant [2,4,6-triphenylthiopyrylium]$[Cu_2I_3]$. All known $Cu_2I_3$ polymers display alternation of long and short Cu—I distances along the edge of the polymeric sheet with the shorter distances forming the edges of unbridged rhombs. Sequential Cu—I distances of 2.505 (4) and 2.785 (4) Å were found along one edge of the polymeric sheet of (I), and sequential Cu—I distances of 2.510 (4) and 2.720 (4) Å were found along the opposite edge; sequential distances of 2.523 (3) and 2.831 (3) Å, and 2.528 (3) and 2.773 (3) Å were found for (II). Batsanov *et al.* (1982) reported similar long–short sequences of 2.522 and 2.779 Å, and 2.541 and 2.847 Å. Thus, details of bonding are similar and independent of the tertiary structure of the polymer.

The $Cu_2I_3$ polymers crystallize with the same internal symmetry elements. Successive repetitions of the polymeric sequences are linked by glide planes: in (I), the mirror is at $y = \frac{1}{4}$ and the translation is along the *a* axis, and in (II), the mirror is at $y = \frac{3}{4}$ and the translation is along the *c* axis.

In (I), the cation is totally isolated from the polymeric chain (Fig. 1*a*), whereas in (II), $K^+$ is in the plane of the O atoms of the crown ether ring and shows a single ionic interaction [3.414 (3) Å] with a bridging I atom.

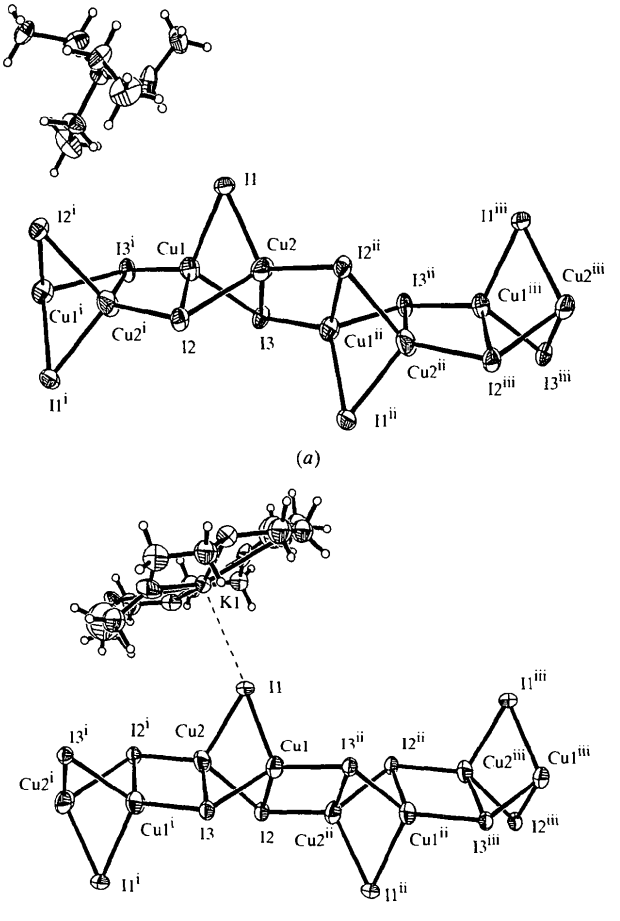


Fig. 1. Projection views of (*a*) tetraethylammonium dicopper triiodide, (I) [symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (iii) $x-1, y, z$], and (*b*) (18-crown-6)potassium dicopper(I) triiodide, (II) [symmetry codes: (i) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (iii) $x, y, 1+z$], with ellipsoids shown at 50% probability.

Neither of the two title structures emits in the visible region when excited with ultraviolet radiation. Other polymeric copper(I) halide species have been found to display solid-state emission and thus further work is aimed at examination of the molecular orbital distributions of the $Cu_2I_3$ polymer.

## Experimental

For the preparation of (I), a mixture of $[(C_2H_5)_4N]I$ (1.26 g, 5 mmol), Cu powder (1.27 g, 20 mmol) and $I_2$ (1.28 g, 5 mmol) in 100 ml acetone was heated under reflux until the solution turned yellow. On cooling and following filtration, colorless needle-like crystals appeared. For the preparation of (II), a mixture of CuI (0.382 g, 2 mmol), 18-crown-6 (0.528 g, 2 mmol) and KI (0.498 g, 3 mmol) dissolved in 3 ml water, was heated under reflux in 15 ml acetone for 11 h. Ascorbic acid (0.213 g) was added to prevent copper(I) oxidation. The resulting hot yellow solution was filtered. On cooling and standing for 3 d, colorless rod-like crystals appeared.

### Compound (I)

*Crystal data*

$(C_8H_{20}N)[Cu_2I_3]$
$M_r = 638.0$
Orthorhombic
$Pna2_1$
$a = 8.313\ (5)$ Å
$b = 17.486\ (7)$ Å
$c = 10.566\ (5)$ Å
$V = 1536.8\ (13)$ Å$^3$
$Z = 4$
$D_x = 2.758$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 4.625–12.364°$
$\mu = 8.765$ mm$^{-1}$
$T = 301$ K
Needle
$0.20 \times 0.15 \times 0.10$ mm
Colorless

*Data collection*

Syntex $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: $\psi$ scan (Sheldrick, 1990)
$T_{min} = 0.207$, $T_{max} = 0.416$
3055 measured reflections
2577 independent reflections
1302 reflections with $F > 4.5\sigma(F)$

$R_{int} = 0.055$
$\theta_{max} = 30°$
$h = -1 \rightarrow 11$
$k = -24 \rightarrow 1$
$l = -1 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: negligible

*Refinement*

Refinement on $F$
$R = 0.047$
$wR = 0.053$
$S = 1.11$
2577 reflections
127 parameters
H atoms constrained
$w = 1/[\sigma^2(F) + 0.0008F^2]$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.15$ e Å$^{-3}$
$\Delta\rho_{min} = -1.19$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond distances (Å) for (I)*

| | | | |
|---|---|---|---|
| I(1)—Cu(1) | 2.596 (4) | I(3)—Cu(1) | 2.720 (4) |
| I(1)—Cu(2) | 2.588 (4) | I(3)—Cu(2) | 2.831 (5) |
| I(2)—Cu(1) | 2.766 (5) | I(3)—Cu(1$^{ii}$) | 2.510 (4) |
| I(2)—Cu(2) | 2.785 (4) | Cu(1)· · ·Cu(2) | 2.470 (5) |
| I(2)—Cu(2$^{i}$) | 2.505 (4) | Cu(1)· · ·Cu(2$^{i}$) | 2.639 (5) |

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

### Compound (II)

*Crystal data*

$[K(C_{12}H_{24}O_6)][Cu_2I_3]$
$M_r = 811.9$
Monoclinic
$P2_1/c$
$a = 15.440\ (7)$ Å
$b = 17.635\ (6)$ Å
$c = 8.422\ (3)$ Å
$\beta = 97.14\ (4)°$
$V = 2275\ (2)$ Å$^3$
$Z = 4$
$D_x = 2.368$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 69 reflections
$\theta = 4.127–12.458°$
$\mu = 6.144$ mm$^{-1}$
$T = 301$ K
Rod
$0.20 \times 0.15 \times 0.10$ mm
Colorless

*Data collection*

Syntex $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: $\psi$ scan (Sheldrick, 1990)
$T_{min} = 0.294$, $T_{max} = 0.541$
8310 measured reflections
6620 independent reflections
6611 reflections with $F > 2\sigma(F)$

$R_{int} = 0.0717$
$\theta_{max} = 30°$
$h = -21 \rightarrow 21$
$k = -24 \rightarrow 1$
$l = -1 \rightarrow 11$
3 standard reflections every 97 reflections intensity decay: negligible

*Refinement*

Refinement on $F^2$
$R(F) = 0.086$
$wR(F^2) = 0.218$
$S = 0.892$
6620 reflections
363 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 2.82$ e Å$^{-3}$
$\Delta\rho_{min} = -3.23$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected bond distances (Å) for (II)*

| | | | |
|---|---|---|---|
| I(3)—Cu(1$^{i}$) | 2.528 (3) | I(1)—Cu(2) | 2.641 (3) |
| I(3)—Cu(1) | 2.773 (3) | I(1)—Cu(1) | 2.657 (3) |
| I(3)—Cu(2) | 2.824 (3) | Cu(1)· · ·Cu(2) | 2.467 (3) |
| I(2)—Cu(2$^{ii}$) | 2.523 (3) | Cu(1)· · ·Cu(2$^{ii}$) | 2.661 (4) |
| I(2)—Cu(1) | 2.789 (3) | Cu(2)· · ·Cu(1$^{i}$) | 2.661 (4) |
| I(2)—Cu(2) | 2.831 (3) | I(1)· · ·K(1) | 3.414 (3) |

Symmetry codes: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

Data were collected with a variable scan rate, using a $\theta/2\theta$ scan mode with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$. Refinement was completed using full-matrix least-squares methods. For (I), extinction was refined but was minimal. The maximum Fourier peak was 0.947 Å from Cu(1). For (II), extinction was refined but was minimal. The crown ether ring was observed to be disordered with two major conformations, each of 50% occupancy. The positions C(8) and C(17) belonged to both conformations. Whereas refinement in this manner permitted a clear observation of the two conformations, bond distances in the crown ether ring suffer from the proximity of atoms of the alternate conformation. The maximum difference Fourier peak was 0.561 Å from I(3).

For both compounds, data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structures: *SHELXS*86 for (I); *SHELXL*93 (Sheldrick, 1993) for (II). For both compounds, molecular graphics: *XP* (Siemens, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1046). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1998). **C54**, 600–601

# A Tetrahedral Zinc(II) Complex of Tris(2-pyridylethyl)amine

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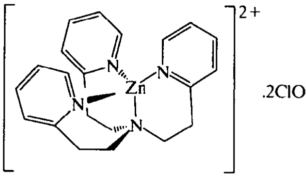
## Abstract

The zinc ion in the title complex, [*N*,*N*′-bis(2-pyridylethyl)-2-(2-pyridyl)ethylamine-$\kappa^4N$]zinc(II) diperchlorate, $[Zn(C_{21}H_{24}N_4)](ClO_4)_2$, displays a distorted tetrahedral configuration. The Zn—$N_{py}$ distances range from 1.979 (5) to 1.999 (5) Å, while the Zn—$N_{amine}$ distance is 2.028 (5) Å. The $N_{py}$—Zn—$N_{py}$ and $N_{py}$—Zn—$N_{amine}$ angles range from 111.9 (2) to 119.6 (2)° and from 102.3 (2) to 103.4 (2)°, respectively. This behavior contrasts with the five-coordinate geometry normally observed in tripodal ligands of similar structure, and can be ascribed to the presence of weakly-coordinating anions and the ligand–metal chelate-ring size.

## Comment

The title compound, (I), was isolated in the course of our studies into the design and synthesis of coordination complexes for molecular recognition (Allen *et al.*, 1995; Canary *et al.*, 1995; Chuang *et al.*, 1995). The general plan is to use coordination complexes as scaffolding to which organic functional groups can be attached for the development of synthetic receptors and enzyme mimics. Structural data on representative coordination complexes are critical for the design of such compounds. The goal of the present study was to determine coordinates that could be used for the design and modeling of supramolecular receptors.



(I)

The present structure is surprising in that previous studies of zinc(II) complexes of the closely related tripodal ligand tris(2-pyridylmethyl)amine (TPA) show them to be five-coordinate complexes, the cationic portions of which are typically very similar in structure to the analogous $Cu^{II}$ complexes. In the present case, the structure of $[Zn(tepa)]^{2+}$ [tepa is tris(2-pyridylethyl)amine] is nearly isomorphous with the $Cu^I$ complex $[Cu(tepa)]^+$ (Karlin *et al.*, 1982; Zubieta *et al.*, 1983). In the $[Cu(tepa)]^+$ complex, the Cu—$N_{py}$ distances range from 2.012 (5) to 2.022 (5) Å, with a Cu—$N_{amine}$ distance of 2.192 (6) Å. The $N_{py}$—Cu—$N_{py}$ and $N_{py}$—Cu—$N_{amine}$ angles range from 111.9 (2) to 121.2 (2)° and from 97.4 (2) to 99.8 (2)°, respectively. The three six-membered chelate rings formed in the tepa complex allow little room for anion coordination, as observed in the five-membered-chelate-ring tepa complexes.

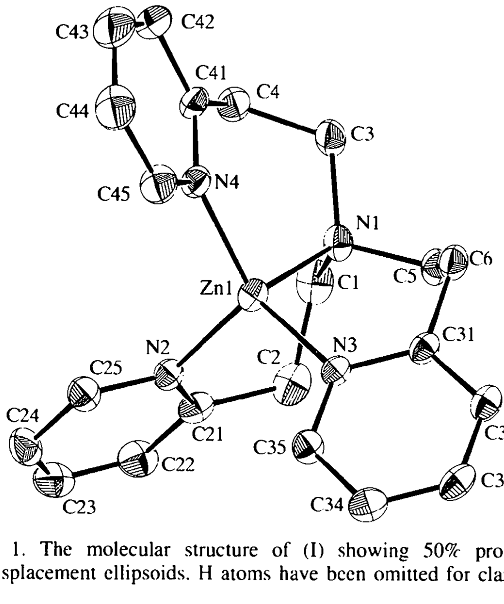


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

## Experimental

Tepa was prepared according to Karlin *et al.* (1982). Synthesis of the complexes was carried out by the slow addition of a 10 ml solution of tepa (0.69 g, 2.1 mmol) in methanol to a 10 ml solution of $Zn(ClO_4)_2.6H_2O$ (0.78 g, 2.1 mmol) dissolved in water. The resulting solution was heated for 30 min. A white precipitate formed upon cooling. The white