

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KH1133). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## (Diethylenetriamine)(imidazole)(thiocyanato)copper(II) Perchlorate

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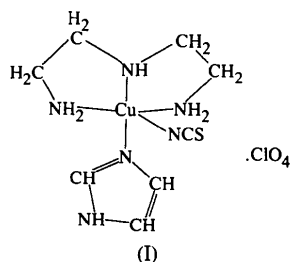
## Abstract

The Cu atom in the title complex, [*N*-(2-aminoethyl)-1,2-ethylenediamine-*N,N'*](imidazole-*N*<sup>3</sup>)(thiocyanato-*N*)copper(II) perchlorate, [Cu(NCS)(C<sub>4</sub>H<sub>13</sub>N<sub>3</sub>)(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)]ClO<sub>4</sub>, is coordinated in a trigonal bipyramidal arrangement by two primary N atoms of *N*-(2-aminoethyl)-1,2-ethylenediamine (diethylenetriamine) and one N atom of thiocyanate in equatorial positions, and by

the 'pyridine' N atom of imidazole and one secondary N atom of diethylenetriamine in axial positions. The Cu—N(imidazole) and Cu—N(thiocyanate) bond lengths are 1.978 (3) and 2.245 (4) Å, respectively.

## Comment

Imidazolate-bridged dinuclear complexes have been synthesized and studied extensively (O'Young, Dewan, Lilienthal & Lippard, 1978; Kolks, Frihart, Coughlin & Lippard, 1981; Coughlin & Lippard, 1984). Polynuclear imidazolate-bridged structures with additional imidazole neutral ligands in the solid state have been reported (Ivarsson, Lundberg & Ingri, 1972; Lundberg, 1972; Sato, Nagae, Uehara & Nakaya, 1984; Sato *et al.*, 1986). Although dinuclear and polynuclear imidazolate-bridged copper(II) complexes have been reported, the known structures and properties of mononuclear complexes with mixed ligands are few. In this paper, we describe the preparation and crystal structure of the monocopper(II) complex, [Cu(dien)(imH)(NCS)]ClO<sub>4</sub>, (I), where dien is diethylenetriamine and imH is imidazole.



The geometry around the Cu atom is trigonal bipyramidal, comprising the tridentate diethylenetriamine, the imidazole and the thiocyanate ligands (Fig. 1). The two primary N atoms of dien and the N atom of thiocyanate are coordinated in the trigonal plane, and the 'pyridine' N atom of imidazole and the secondary N atom of dien occupy the apical sites. The Cu and imidazole-ring atoms are coplanar, with a maximum

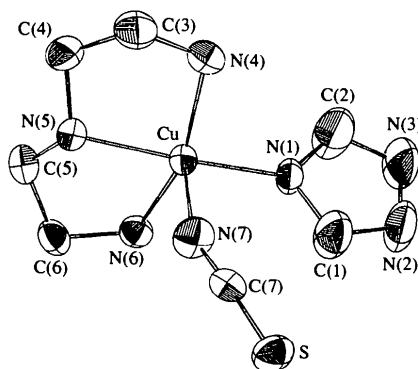


Fig. 1. The cation structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. Atoms N(2) and N(3) are both disordered (50:50% N:C).

deviation of 0.024 (7) Å. The imidazole-ring plane is approximately perpendicular to the trigonal coordination plane, the dihedral angle between these planes being 89.7 (2)°. The Cu—N bond lengths to dien fall in the range 2.012 (3)–2.022 (4) Å. Among these, the copper to secondary nitrogen bond is marginally the shortest, as found also by Sato *et al.* (1986). The copper–imidazole bond length [Cu—N(1) 1.978 (3) Å] is essentially the same as those of similar complexes, *e.g.* 1.970 (6) in [Cu(imH)(dien)](ClO<sub>4</sub>)<sub>2</sub> (Hu *et al.*, 1989) and 1.969 (6) Å in [Cu(imH)<sub>2</sub>(nma)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (where nma is *N*-methylacetamide; Su, Tsai, Ko, Wang & Cheng, 1991).

## Experimental

The title complex was obtained in two steps *via* an intermediate complex, [Cu(imH)(dien)](ClO<sub>4</sub>)<sub>2</sub>. To a solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (742 mg, 2 mmol) in methanol–acetonitrile solution (5:1; 30 ml), were added diethylenetriamine (206 mg, 2 mmol) in water (3 ml) and then imidazole (136 mg, 2 mmol) in methanol (10 ml). Dark-blue crystals of [Cu(imH)(dien)](ClO<sub>4</sub>)<sub>2</sub> formed overnight, were collected by filtration, washed with ethanol and dried *in vacuo*. An aqueous solution (10 ml) of NaNCS (81 mg, 1 mmol) was added to an aqueous solution (10 ml) of [Cu(imH)(dien)](ClO<sub>4</sub>)<sub>2</sub> (1 mmol) with stirring. Blue–violet crystals were obtained on adding Na(ClO<sub>4</sub>)·H<sub>2</sub>O (500 mg) dissolved in water (5 ml) to the resulting solution. These were filtered off, washed with cold water and dried *in vacuo*. Crystals suitable for X-ray structure determination were obtained by slow evaporation of an aqueous solution at room temperature over the period of a few days. Analysis found: C 24.65, H 4.25, N 21.78%; calculated for C<sub>8</sub>H<sub>17</sub>ClCuN<sub>6</sub>O<sub>4</sub>S: C 24.49, H 4.37, N 21.42%.

### Crystal data

[Cu(NCS)(C<sub>4</sub>H<sub>13</sub>N<sub>3</sub>)-  
(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)]ClO<sub>4</sub>  
 $M_r = 392.32$   
 Orthorhombic  
*Pbc*  
 $a = 13.735 (3) \text{ \AA}$   
 $b = 16.082 (6) \text{ \AA}$   
 $c = 14.255 (4) \text{ \AA}$   
 $V = 3149 (2) \text{ \AA}^3$   
 $Z = 8$   
 $D_x = 1.65 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 25  
 reflections  
 $\theta = 13.02\text{--}13.80^\circ$   
 $\mu = 1.710 \text{ mm}^{-1}$   
 $T = 296 \text{ K}$   
 Square prism  
 $0.85 \times 0.40 \times 0.40 \text{ mm}$   
 Blue–violet

### Data collection

Enraf–Nonius CAD-4  
 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 empirical *via*  $\psi$  scans  
 (TEXSAN; Molecular  
 Structure Corporation,  
 1987)  
 $T_{\min} = 0.477$ ,  $T_{\max} = 0.505$   
 3146 measured reflections

3146 independent reflections  
 2028 reflections with  
 $I > 3\sigma(I)$   
 $\theta_{\max} = 25^\circ$   
 $h = 0 \rightarrow 16$   
 $k = 0 \rightarrow 19$   
 $l = 0 \rightarrow 16$   
 3 standard reflections  
 every 300 reflections  
 intensity decay: 0.4%

### Refinement

Refinement on  $F$   
 $R = 0.041$   
 $wR = 0.056$   
 $S = 1.77$   
 2028 reflections  
 226 parameters  
 H atoms riding  
 $w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.06$   
 $\Delta\rho_{\max} = 0.56 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.30 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

Cu—N(1)	1.978 (3)	Cu—N(6)	2.022 (4)
Cu—N(5)	2.012 (3)	Cu—N(7)	2.245 (4)
Cu—N(4)	2.019 (4)	S—C(7)	1.615 (4)
N(7)—C(7)	1.166 (5)		
N(1)—Cu—N(5)	173.7 (1)	N(5)—Cu—N(6)	84.0 (1)
C(7)—N(7)—Cu	151.9 (3)	N(5)—Cu—N(7)	91.6 (1)
N(1)—Cu—N(4)	94.7 (2)	N(4)—Cu—N(6)	156.6 (2)
N(1)—Cu—N(6)	95.3 (1)	N(7)—C(7)—S	176.8 (4)
N(1)—Cu—N(7)	94.7 (1)	N(4)—Cu—N(7)	101.0 (2)
N(5)—Cu—N(4)	83.7 (1)	N(6)—Cu—N(7)	99.2 (1)

The 3- and 4-positions of the imidazole ring are disordered and were refined with equal contributions of carbon and nitrogen at each position, corresponding to twofold disorder by rotation about the Cu—N bond. Twofold disorder was also refined for the O atoms of the perchlorate anion, with fixed occupancies of 0.7 and 0.3.

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: TEXSAN (Molecular Structure Corporation, 1987). Program(s) used to solve structure: MITHRIL (Gilmore, 1983). Program(s) used to refine structure: TEXSAN. Molecular graphics: ORTEPII (Johnson, 1976).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1139). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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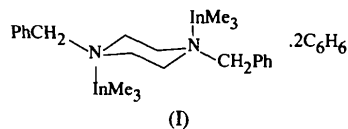
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of trimethylindium and related compounds and involves the structure determination of the dibenzene solvate of 1,4-bis(trimethylindium)-1,4-dibenzylpiperazine, (I).



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### [ $\mu$ -(1,4-Dibenzylpiperazine)-*N:N'*]bis(trimethylindium) Dibenzene Solvate

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#### Abstract

The X-ray crystal structure of the benzene solvated title compound, [In<sub>2</sub>(C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>)(CH<sub>3</sub>)<sub>6</sub>].2C<sub>6</sub>H<sub>6</sub>, shows that the In atom has a four-coordinate distorted tetrahedral geometry, with an In—N bond length of 2.504 (4) Å. The C—In—C angles lie around 115° [114.1 (3)–116.5 (3)°] and the C—In—N angles range from 96.9 (2) to 110.7 (2)°. The piperazine ring is in a chair conformation. The two trimethylindium moieties are in a *trans* configuration and an axial conformation. The complex molecule is centrosymmetric.

#### Comment

High purity trimethylindium has been used extensively in the preparation of compound semiconductor layers by metal organic chemical vapour deposition (MOCVD). The purity of trimethylindium is critical for the quality of the semiconductor material. Purification of trimethylindium by formation and then dissociation of an adduct is believed to be one of the best methods (Bradley, Chudzynska & Frigo, 1988; Bradley, Chudzynska, Factor *et al.*, 1988; Foster, Rushworth, Cole-Hamilton, Jones & Stagg, 1988). The present research is part of our efforts in search of better adducts for the purification

The X-ray structure of (I) is presented in Fig. 1. Each N atom in the ligand coordinates to one trimethylindium moiety as expected. The In atom has a four-coordinate distorted tetrahedral geometry, with an In—N bond length of 2.504 (4) Å. The In—N bond length in the title compound is longer than the corresponding bond lengths found in Me<sub>3</sub>InNHMe(CH<sub>2</sub>)<sub>2</sub>NHMeInMe<sub>3</sub> (2.369 and 2.393 Å) by about 5%, but comparable to that found in (2,2,6,6-tetramethylpiperidine)trimethylindium (2.502 Å; Bradley, Dawes, Frigo, Hursthouse & Hussain, 1987). The somewhat longer In—N bond length suggests repulsion between the methyl groups on the In atom and the methylene groups on the piperazine ring. The C(12)—In—N(1) bond angle is 110.7 (2)°, about 10% bigger than C(10)—In—N(1) [99.9 (2)°] and 14% bigger than C(11)—In—N(1) [96.9 (2)°]. These values suggest strong repulsion between the C(12) group and the methylene groups on the piperazine ring. This is in good agreement with the torsion angle C(8)—N(1)—In—C(12) of 25.7 (4)°.

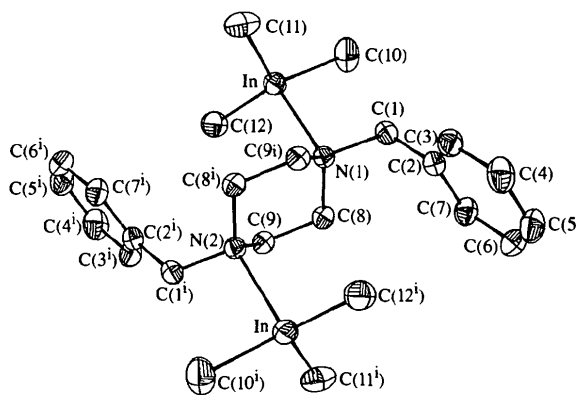


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The piperazine ring is in a chair form. The two trimethylindium moieties are in a *trans* configuration and both are in axial positions. The trimethylindium group should be sterically bulkier than the benzyl group and so would be expected to adopt an equatorial position.