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Synthesis and structures of copper(II) and nickel(II) complexes of 1,8-diaza-4-thiaoctane. Characterization of a novel polymeric trigonal bipyramidal copper(II) complex containing both bridging and meridionally coordinated ligands

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Summary

The synthesis, x-ray structure determination, and spectroscopic properties of nickel(II) and copper(II) complexes of 1,8-diaza-4-thiaoctane (aeaps) are described. $[Ni(aeaps)_2](ClO_4)_2$ crystallizes in the orthorhombic space group Pbcn with $a = 10.943(2)$, $b = 13.209(2)$, $c = 14.798(2)$ Å, and Z = 4. The complex crystallizes as the unsymmetrical facial isomer, with the sulfur atoms in *cis* positions. The copper(II) complex crystallizes in the monoclinic space group Cc, with $a = 16.041(2)$, $b = 9.223(1)$, $c = 16.048(3)$ Å, $a = 118.65(2)°$, and Z = 4. The copper(II) ion has a trigonal bipyramidal coordination geometry, with one ligand coordinated meridionally, and two bridging ligands in which the thioether is not bound to a metal ion. The structures of these complexes are discussed in terms of the known solution chemistry of this ligand with copper(II) and nickel(II).

Introduction

Metal complexes of ligands such as 1,7-diaza-4-thiaheptane (daes)(1–5), 1-thia-4,7-diazacyclononane (tasn)(1,3,6–9) and 1,8-diaza-4-thiaoctane (aeaps)(10) have been the subjects of recent investigations. The ligands are analogues of the triamines 1,4,7-triazaheptane (dien), 1,4,7-triazacyclononane (1,4,7-tacn), and 1,4,8-triazaoctane (dpt), respectively, and as such they offer opportunities to study the influences of the incorporation of a thioether on the complexation and spectroscopic properties of N_3 and N_2S ligand types. Crystallographic and spectroscopic investigations of transition metal complexes of $[M(daes)_2]^{n+}$ [M = nickel(II)(2), copper(II)(1), and cobalt(III)(5)], $[M(tasn)_2]^{n+}$ [M = copper(II)(1), nickel(II)(3), and cobalt(III)(8)] and $[M(aeaps)_2]^{n+}$ [M = cobalt(III)(10)] have revealed the presence of unsymmetrical facial [M = nickel(II)(2), cobalt(III)(5), L = daes; M = cobalt(III), L = tasn(11), aeaps(10)] and symmetrical facial [M = nickel(II)(3), copper(II)(1), cobalt(III)(8), L = tasn; M = cobalt(III), L = aeaps(10); and M = copper(II), L = daes(1)] isomers. Meridional coordination of daes and aeaps has not been reported although it has been observed for the copper(II) complex of the triamine dien(12). Stability constant measurements have revealed that nickel(II) forms octahedral complexes with all the ligands, whilst incomplete coordination of the second molecule of ligand has been proposed for the copper(II) complexes in a number of instances(3,13–16). We report here the crystal structures of nickel(II) and copper(II) complexes of aeaps. The nickel complex, $[Ni(aeaps)_2](ClO_4)_2$, *(1)*, has been characterized as its unsymmetrical facial isomer. The copper(II) complex, *(2)*, consists of a polymeric complex cation with one ligand coordinated meridionally and two bridging ligands, resulting in trigonal bipyramidal geometry around each copper(II) site.

Experimental

U.v./visible spectra were recorded with a Hewlett Packard 8450A u.v./vis spectrophotometer attached to a Hewlett Packard 7225B plotter and 8290M flexible disc drive. E.s.r. spectra were recorded on a Bruker ER200D X-band spectrometer as powder and frozen aqueous solution (110K). Magnetic susceptibilities were determined using the Gouy method, with $[Ni(en)_3]S_2O_3$ being employed as calibrant. The susceptibilities were corrected for the diamagnetism of the constituting atoms by the use of Pascals constants(17). 1,8-diaza-4-thiaoctane (aeaps) was prepared as reported(18).

$[Ni(aeaps)_2](ClO_4)_2$ (1)

Aeaps (1.0 g) in H_2O was added to $Ni(ClO_4)_2 \cdot 6H_2O$ (1.36 g) in H_2O and, after warming, the purple solution was allowed to stand. A purple solid was collected, and purple crystals were obtained by recrystallization from aqueous solution with slow cooling (1.1 g, 55%) (Found: C,22.7; H,5.5; N,10.6; S,12.4. $Ni(C_{10}H_{28}N_4S_2)(ClO_4)_2$ calcd.: C,22.8; H,5.37; N,10.6; S,12.2%). λ_{max} (H_2O) 920 (ε 20 $dm^3 mol^{-1} cm^{-1}$) 860 (21), 556 (22), and 354 nm (36).

$[Cu(aeaps)_2](ClO_4)_2$ (2)

The copper(II) complex was prepared as described above for the nickel(II) complex, using copper(II) perchlorate. Blue single crystals suitable for x-ray diffraction were obtained after two crystallizations from aqueous solution. (Found: C,22.1; H,5.3; N,10.2; S,11.9. $Cu(C_{10}H_{28}N_4S_2)(ClO_4)_2$ calcd.: C,22.6; H,5.3; N,10.5; S,12.1%) λ_{max} 610(ε 155 $dm^3 mol^{-1} cm^{-1}$), 317 (2330), 300 (2690), and 235 nm (2960)$\cdot \mu_{eff} = 1.70\, \mu_B$.

*(**Caution!** Perchlorate salts of metal complexes can be explosive and must be handled with care. Compounds should not be heated as solids.)*

Crystal data for *(1)*: $C_{10}H_{28}Cl_2N_4NiO_8S_2$, M = 526.1, orthorhombic, $a = 10.943(3)$, $b = 13.209(2)$, $c = 14.798(2)$ Å, U = 2139.0 $Å^3$ (by least squares refinement of diffractometer setting angles for 25 automatically

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centred reflections, $\lambda = 0.71069$ Å, $Z = 4$, $D_c = 1.633\,\mathrm{g\,cm^{-3}}$. Blue prisms, crystal dimensions $0.14 \times 0.11 \times 0.10$ mm, $\mu(\mathrm{Mo{-}K\alpha}) = 13.42\,\mathrm{cm^{-1}}$. Data collection and processing.–CAD4 diffractometer, ω-$1.33\,\theta$ mode with ω scan width $(1.0 + 0.35 \tan\theta)°$, aperture width $(2.40 + 0.50 \tan\theta)$mm, graphite-monochromated Mo–Kα radiation; 2162 reflections measured ($1.0 \leqslant \theta \leqslant 25.0$, +h, +k, +l). Lorentz, polarization and absorption effects corrected for. The structure was solved by heavy atom (Patterson) methods and successive Fourier synthesis(19). Hydrogen atoms were included at sites calculated assuming tetrahedral geometry about carbon and nitrogen (C—H 0.97 Å, N—H 0.91 Å) with individual isotropic thermal parameters. Full-matrix least-squares refinement converged with $R = 0.032$, $R' = 0.034$*, and $\omega = 2.61/[\sigma^2(F_0) + 0.00006\,F_0{}^2]$ for 1367 reflections with $I > 2.5\,\sigma(I)$**. The largest peak in a final difference map was less than $0.4\,\text{Å}^{-3}$ in height. Scattering factors (neutral Ni for $\mathrm{Ni^{II}}$) and anomalous dispersion terms were taken from International Tables(20). All calculations were carried out using SHELX 76(19), ORTEP(21), and local data reduction programs implemented on a CYBER 825 computer. Bond lengths and angles are given in Table 1.

Crystal data for *(2)*: $\mathrm{C_{10}H_{28}Cl_2CuN_4O_8S_2}$, $M = 530.9$, monoclinic, $a = 16.041(2)$, $b = 9.223(1)$, $c = 16.048(3)$ Å, $\beta = 118.65(2)°$, $U = 2083.6\,\text{Å}^3$ [as for *(1)*], space group Cc, $Z = 4$, $D_c = 1.692\,\mathrm{g\,cm^{-3}}$. Blue air sensitive plates, crystal dimensions $0.22 \times 0.10 \times 0.22$ mm, $\mu(\mathrm{Mo{-}K\alpha}) = 14.93\,\mathrm{cm^{-1}}$. Data collection and processing. –CAD4 diffractometer, ω-$1.33\,\theta$ mode with ω scan width $(1.0 + 0.35 \tan\theta)°$, aperture width $(2.40 + 0.50 \tan\theta)$mm, graphite-monochromated Mo–Kα radiation; 2023 reflections measured ($1.0 \leqslant \theta \leqslant 25.0°$, +h, +k, ± l). Lorentz, polarization and absorption effects corrected for. Solution and refinement as for *(1)*. Final $R = 0.037$, $R' = 0.042$*, $\omega = 2.72/[\sigma^2(F_0) + 0.00019\,F_0{}^2]$ for 1742 reflections with $I > 2.5\,\sigma(I)$**. The largest peak in a final difference map was less than $0.5\,\text{Å}^{-3}$ in height. Scattering factors (neutral Cu for $\mathrm{Cu^{II}}$) and anomalous dispersion terms were taken from International Tables(20). Programs as for *(1)*. Bond lengths and angles are given in Table 2.

Table 1. Bond lengths (Å) and bond angles (°) for *(1)*.

Bond lengths (Å)

S(1)–Ni(1)	2.473(1)	N(1)–Ni(1)	2.129(3)
N(2)–Ni(1)	2.101(3)	C(2)–S(1)	1.794(4)
C(3)–S(1)	1.813(4)	C(1)–N(1)	1.482(4)
C(5)–N(2)	1.493(5)	C(2)–C(1)	1.488(5)
C(4)–C(3)	1.506(5)	C(5)–C(4)	1.502(5)

Bond angles (°)

N(1)–Ni(1)–S(1)	83.4(1)	N(2)–Ni(1)–S(1)	93.3(1)
N(2)–Ni(1)–N(1)	92.3(1)	C(2)–S(1)–Ni(1)	95.3(1)
C(3)–S(1)–Ni(1)	112.8(1)	C(3)–S(1)–C(2)	103.7(2)
S(1)–Ni(1)–S(1)	81.8(0)	C(1)–N(1)–Ni(1)	115.4(2)
C(5)–N(2)–Ni(1)	119.4(2)	N(2)–Ni(1)–N(2)$^{\mathrm{i}}$	92.4(2)
C(2)–C(1)–N(1)	111.5(3)	C(1)–C(2)–S(1)	113.2(3)
C(4)–C(3)–S(1)	118.2(3)	C(5)–C(4)–C(3)	115.7(4)
C(4)–C(5)–N(2)	113.8(4)		

Table 2. Bond lengths (Å) and bond angles (°) for *(2)*.

Bond lengths (Å)

S(1)–Cu(1)	2.449(2)	N(1)–Cu(1)	2.044(7)
N(2)–Cu(1)	1.975(8)	N(3)–Cu(1)	2.131(6)
N(4)–Cu(1)	2.042(6)	C(2)–S(1)	2.08(2)
C(3)–S(1)	1.72(2)	C(3′)–S(1)	1.60(3)
C(4)–S(1)	2.47(1)	C(8)–S(2)	1.82(1)
C(7)–S(2)	1.78(1)	C(1)–N(1)	1.53(2)
C(5)–N(2)	1.46(2)	C(6)–N(3)	1.48(2)
C(10)–N(4)	1.47(2)	C(2)–C(1)	1.39(2)
C(3′)–C(2)	1.59(4)	C(4)–C(3)	1.57(2)
C(5)–C(4)	1.41(2)	C(7)–C(6)	1.52(1)
C(9)–C(8)	1.55(1)	C(10)–C(9)	1.52(1)

Bond angles (°)

N(1)–Cu(1)–S(1)	83.2(3)	N(2)–Cu(1)–S(1)	87.9(3)
N(2)–Cu(1)–N(1)	171.1(4)	N(3)–Cu(1)–S(1)	106.3(2)
N(3)–Cu(1)–N(1)	91.4(3)	N(3)–Cu(1)–N(2)	91.2(3)
N(4)–Cu(1)–S(1)	126.9(2)	N(4)–Cu(1)–N(1)	91.9(3)
N(4)–Cu(1)–N(2)	93.3(3)	N(4)–Cu(1)–N(3)	126.7(3)
C(2)–S(1)–Cu(1)	93.2(4)	C(3)–S(1)–Cu(1)	97.7(6)
C(3)–S(1)–C(2)	96.3(7)	C(3′)–S(1)–Cu(1)	101(1)
C(8)–S(2)–C(7)	101.4(3)	C(1)–N(1)–Cu(1)	110.7(6)
C(5)–N(2)–Cu(1)	115.8(6)	C(6)–N(3)–Cu(1)	116.2(5)
C(10)–N(4)–Cu(1)	114.9(5)	C(2)–C(1)–N(1)	114(1)
C(1)–C(2)–S(1)	111.1(8)	C(4)–C(3)–S(1)	97(1)
C(2)–C(3′)–S(1)	81(2)	C(5)–C(4)–C(3)	116(1)
C(4)–C(5)–N(2)	116(1)	C(7)–C(6)–N(3)	112.8(7)
S(2)–C(7)–C(6)	114.3(5)	C(9)–C(8)–S(2)	110.9(5)
C(10)–C(9)–C(8)	113.8(7)	C(9)–C(10)–N(4)	113.2(7)

Results and discussion

The structure of the bis open chain complex *(1)* consists of the complex cation lying on a two fold rotation axis and a disordered perchlorate anion. There are numerous close contacts between the amine hydrogen atoms and the perchlorate oxygen atoms.

The coordination geometry about the nickel atom is unsymmetrical facial with the sulfur atoms in *cis* positions (Figure 1). A similar geometry was observed for $[\mathrm{Ni(daes)_2}]^{2+(2)}$. The two six-membered rings lie in the same coordination plane. The five membered chelate rings adopt relatively normal skew conformations while the six-membered rings adopt neither chair nor boat geometries but rather a distorted skew-boat conformation. Atoms Ni(1), S(1), N(2) and C(3) are coplanar [deviations < 0.02 Å) and C(4) and C(5) lie 0.28 and 0.54 Å above and below the plane respectively]. The Ni—S bond length [2.473 (1) Å] is longer than those observed in the $[\mathrm{Ni(daes)_2}]^{2+}$ complex [2.455 (5), 2.463 (6) Å](2) consistent with the increased strain introduced by the six membered chelate ring. A number of bond angles within this ring also indicate considerable strain; in particular the Ni(1)–S(1)–C(3) angle which at 112.8(1)° is at least 12° larger than normal. The Ni—N bond lengths are normal for high-spin six coordinate nickel(II) complexes.

The structure of the copper complex *(2)* consists of a polymeric complex cation of infinite length and two disordered perchlorate anions. There are numerous close

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* $R = \Sigma(\|F_0| - |F_c\|)/\Sigma|F_0|$,
$R' = [\Sigma(\|F_0| - |F_c\|)\omega^{\frac{1}{2}}/\Sigma(|F_0|\omega^{\frac{1}{2}})]$.

**Supplementary data available: Tables of atomic fractional coordinates, observed and calculated structural factors, hydrogen atom coordinates and thermal parameters, close intermolecular contacts and details of least squares planes calculations. Atomic coordinates have also been degrated with the Cambridge Crystallographic Data Centre.

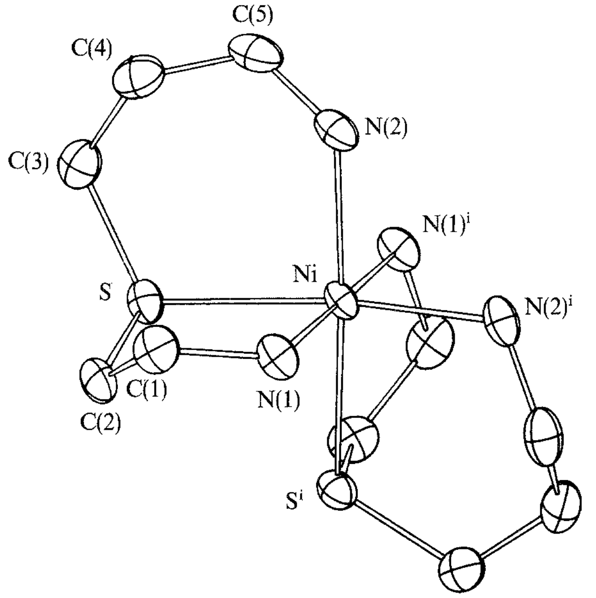

Figure 1. ORTEP drawing of *(1)* showing the atom labeling scheme for the molecule.

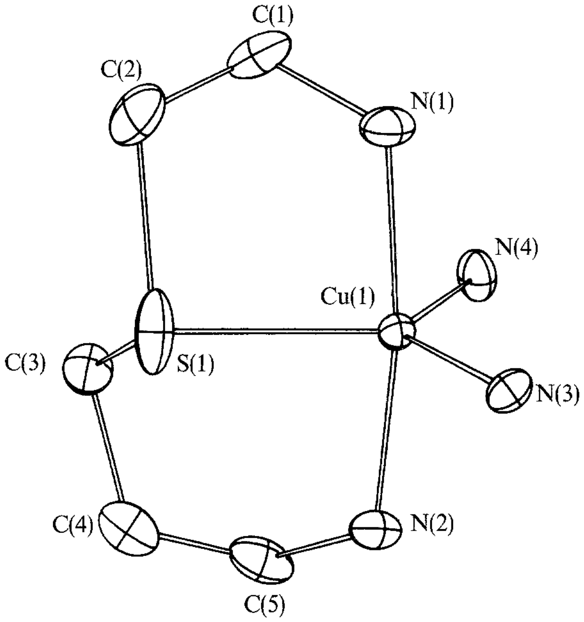

Figure 2. ORTEP drawing of *(2)* showing the atom labeling scheme for the molecule.

contacts between amine hydrogen atoms and perchlorate oxygen atoms.

The copper atom is five-coordinate; one ligand is coordinated to a single atom providing two nitrogen and one sulfur donor atoms and the other ligand is coordinated to two copper atoms, through the nitrogen donor atoms only, giving rise to an infinite polymeric chain (Figures 2 and 3). The tridentate ligand is coordinated in an approximately meridional fashion, [N(1) – Cu(1) – N(2) 171.1(4)°]. Meridional coordination has not previously been reported for open chain tridentate ligands with a sulfur hinge atom. The C—S—C angle, which is generally in the 95–105° range, confers a strong preference for facial coordination on such ligands. Presumably the greater flexibility and/or size of the six-membered chelate ring facilitates the meridional binding in the present case. The tridentate ligand is disordered with the five membered and six-membered rings swapping positions. Most of the resultant carbon sites are too close together to resolve but major and minor sites were refined for C(3) [occupancy 58(2): 42(2)]. As a result of the disorder bond lengths and angles within the ligand are unreliable. The geometry about the copper atom approximates a trigonal bipyramid with the two nitrogen atoms of the tridentate ligand occupying the axial sites. Metal centred bond angles within the trigonal plane (106.3–126.9°) sum to 359.9°. Bond angles between the axial and equatorial atoms range from 83.2 to 93.3° with the low angle being that associated with the five membered chelate ring. The copper to sulfur bond length [2.449(2) Å] is shorter than that observed for the six-coordinate complex $[Cu(daes)_2]^{2+}$ [2.745(1), 2.772(1) Å]$^{(1)}$, but is in the range of those observed in $[Cu(1,4,7\text{-ttcn})]^{2+}$ (1,4,7-ttcn = 1,4,7-trithiacyclononane) [2.419(3)–2.459(3) Å]$^{(22)}$. Other five-coordinate copper(II) complexes have revealed Cu—S (thioether) bond lengths in the 2.310(5)–2.461(2) Å range$^{(23,24)}$, encompassing the value observed in this work. The copper to nitrogen bond lengths cover a wide range [1.975(8)–2.131(6) Å] with shorter bond lengths being to the axially coordinated atoms. This has been observed previously for other trigonal bipyramidal copper(II) complexes–[Cu(NCS) (tren)] (SCN) (Cu—N 2.04, 1.95 axial; 2.07, 2.16 equatorial), [Cu(NCS) (tetramine)] (SCN) (Cu—N 1.97, 2.00 axial; 2.05, 2.03 equatorial)$^{(25)}$.

The e.s.r. spectrum of a frozen microcrystalline powder of the copper(II) complex of aeaps was analyzed according to a previously described procedure for polycrystalline complexes of the copper(II) ion in this environment$^{(26,27)}$. The expected pattern for trigonal bipyramidal copper(II) compounds ($g_\perp > g_\parallel$)$^{(28-31)}$ is observed, with the lower g value nearer to 2.00 ($g_\parallel = 2.01$, $g_\perp = 2.15$) as expected for this environment$^{(26)}$.

The nature of the copper(II) complex in solution is uncertain. The absence of splitting of the d–d band, commonly observed in the visible spectra of trigonal bipyramidal copper(II) complexes$^{(31-36)}$, suggests that the solid state structure is not retained in solution. The visible spectrum of the $[Ni(aeaps)_2]^{2+}$ is however, analogous to those reported for nickel(II) complexes of daes and tasn$^{(3)}$.

The complexation behaviour of copper(II) and nickel(II) with aeaps and daes in solution has been investigated previously. For $[ML]^{2+}$ complexes [M = copper(II), nickel(II)] the ligand stability order is aeaps > daes (Cu) and daes > aeaps (Ni)$^{(13)}$. For the nickel complexes of the triamines the sequence of 5 and 6 membered connected chelate rings is more stable than two 5 membered rings (dpt > dien)$^{(14)}$. Formation constants for the complexes $[NiL_2]^{2+}$ (L = daes or aeaps) indicate that the nickel(II) is octahedrally coordinated in solution$^{(13)}$, and the crystal structures for both complexes reveal unsymmetrical facial configuration$^{(2)}$. The solution behaviour of the complexes $[CuL_2]^{2+}$ is more complicated and again parallels the behaviour of this metal ion with the analogous triamine ligands. Thus, the stepwise stability constants were found to decrease with increasing bulk of the ligand (daes $\log K_2$ 5.08, aeaps $\log K_2$ 2.86; dien $\log K_2$ 5.21, dpt $\log K_2$ 3.28)$^{(3,13,14)}$ and incomplete coordination of the second molecule of ligand

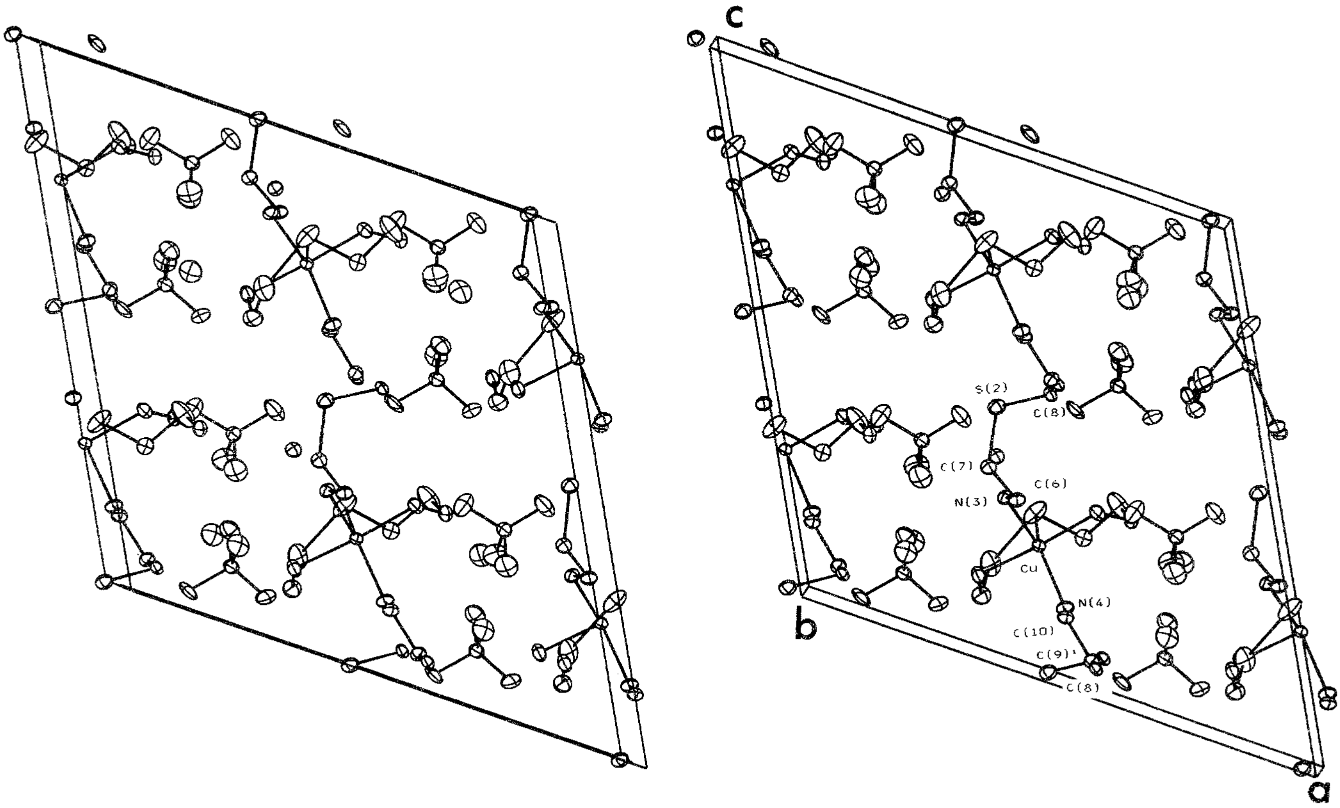

Figure 3. Stereoview down *b* of the unit cell of *(2)*. The complexes form polymeric chains in the vertical direction.

in each case was proposed. In the solid state, octahedral complexes $[CuL_2]^{2+}$ have been characterized with meridional coordination observed for L = dien⁽¹²⁾, and symmetrical facial coordination for L = daes⁽¹⁾. In this work the copper(II) complex of aeaps is found to be five coordinate with bridging ligands. The observed structure may reflect the steric requirements for the formation of $[ML_2]^{2+}$ complexes where L is a ligand possessing five and six membered condensed chelate rings and bearing a thioether donor. The structure may also reflect the nature of the anion. The structure of $[Cu(daes)_2](NO_3)_2$ consists of the symmetrical facial isomer with the two nitrate anions each intimately involved in two hydrogen bonds to protons on coordinated primary amine groups⁽¹⁾. The planar nature and small bite angle of the nitrate anion appears to permit it to effectively tie up each primary amine and link them through the hydrogen bonds. The resulting structure has the appearance of two tridentate ligands being held around the copper(II) ion, enforcing octahedral coordination. For the complex with aeaps however, the tetrahedral perchlorate anions occupy spaces between chains of copper atoms and the structure consists of alternating chains of perchlorate anions and copper(II) complex cations, linked together by hydrogen bonds. The polymeric structure appears therefore to be a consequence of the spatial requirements and packing of the perchlorate anions.

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