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A pentanuclear complex exhibiting two short Ni–Cu distances

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Racemic crystals of the title species, (1*S*/*R*,2*S*′/*R*)-bis[(1*S*,2*S*)-*trans*-3,3′-(1,2-cyclohexanediyldinitrilo)bis(2-methylpropane-2-thiolato)]-1$\kappa^4N^1,N^{1'},S^1,S^{1'}$;2$\kappa^4N^2,N^{2'},S^2,S^{2'}$;3$\kappa^2S^1,S^{2'}$;4$\kappa^2S^{1'},S^2$;5$\kappa^2S^{1'},S^{2'}$-trichloro-3$\kappa Cl$,4$\kappa Cl$,5$\kappa Cl$-tricopper(I)dinickel(II) bis(dimethylformamide) solvate, contain *C*-centered columns of chiral pentanuclear $[Ni_2(C_{14}H_{28}N_2S_2)_2\{Cu^ICl\}_3]$ complexes (*R*,*R* and *S*,*S*) hydrogen bonded to dimethylformamide (C_3H_7NO) solvent molecules. Intercluster $C-H\cdots Cl$ hydrogen bonds link the complexes to form layers parallel to the *ab* plane. In each complex, three Cu^ICl groups bridge four S(thiolate) atoms of two $Ni(C_{14}H_{28}N_2S_2)$ units, forming an $Ni_2Cu_3S_4$ core with the connectivity of the C atoms in bicyclo[3.3.1]nonane. Two of the Cu^I ions exhibit short contacts with Ni, suggesting weak Ni—Cu bonding. The complex molecule exhibits twofold site symmetry (site 4*e* in space group *C*2/*c*).

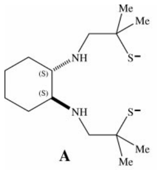
Key indicators

Single-crystal X-ray study
T = 223 K
Mean σ(C–C) = 0.005 Å
R factor = 0.035
wR factor = 0.092
Data-to-parameter ratio = 16.5

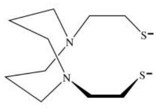
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Tetradentate $NiN(amine)_2S(thiolate)_2$ complexes of ligands such as *A* and *B* can serve as building blocks for multinuclear metal complexes. Thiolate bridging with metals such as Fe^{II} (Mills *et al.*, 1991), Ni^I (Fox *et al.*, 2001), Ni^{II} (Farmer *et al.*, 1992; Turner *et al.*, 1990), Cu^I (Fox *et al.*, 1996), or Zn^{II} (Tuntulani *et al.*, 1992) leads to tri- (Ni^I, Ni^{II}), tetra- (Fe^{II}), and pentanuclear (Cu^I, Zn^{II}) species. Part of the interest of these species has been in their use as models for the active sites of certain metalloenzymes.



A



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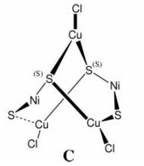
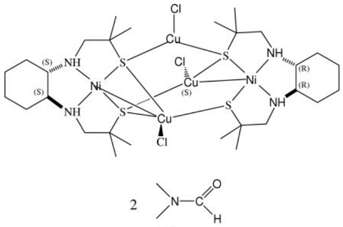


C



(I)

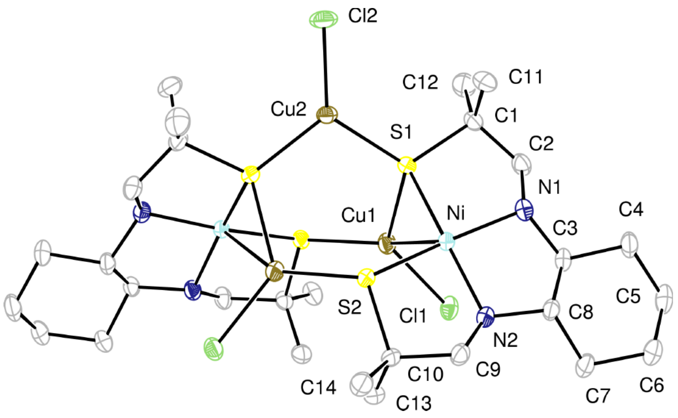


Figure 1
The molecular structure of the title complex showing 25% probability displacement ellipsiods and the atom-numbering scheme for the contents of the asymmetric unit. Atom Cu1*A*, H atoms and dimethylformamide molecules have been omitted for clarity.

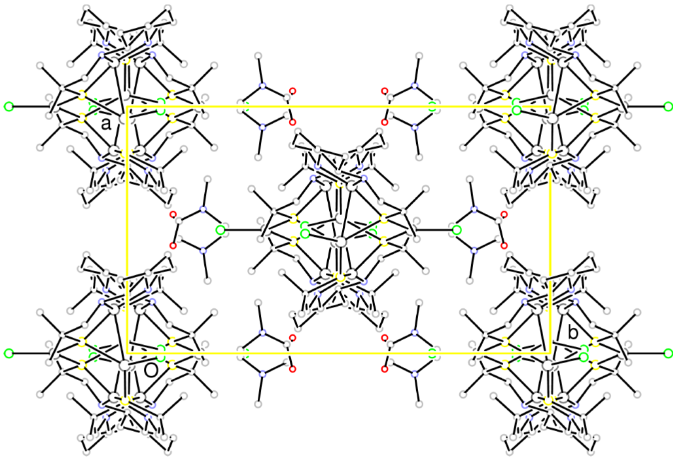


Figure 2
Projection of the structure along the *c* axis. H atoms have been omitted for clarity.

The title compound, (Ni*A*)$_2$(CuCl)$_3$, (I), contains two Ni^{II}N$_2$S$_2$ units bridged by three Cu^{I}Cl groups (Fig. 1). Each molecule exhibits twofold site symmetry (site 4e in space group *C*2/*c*) with the twofold axis passing through atoms Cu2 and Cl2. Doubly bridging atom S1 ligates one Ni and two Cu atoms, while singly bridging S2 ligates one Ni and one Cu atom. From this perspective, the complex can be viewed as an Ni$_2$Cu$_3$S$_4$ core with the connectivity of the C atoms in bicyclo[3.3.1]nonane (*C*) augmented by weak Cu1—Ni bonds. In this core, the six-membered Cu$_2$S$_3$Ni rings adopt the twist-boat conformation. Decoration of the core by the Cl atoms and the remainder of ligands *A* complete the coordination of the metals. Because 1,2-disubstituted cyclohexyl groups contain stereogenic centers, the resulting pentanuclear complexes are chiral. Owing to the site symmetry, individual molecules are either *R,R* or *S,S*, while the crystallographic centers of symmetry ensure that the crystals are racemic.

The Ni—Cu1 and Ni—Cu1*A* distances [2.6973 (8) and 2.604 (5) Å, respectively, for the major and minor sites] are relatively short and are consistent with weak Ni—Cu bonding interactions similar to that reported for (Cu*A*)$_2$(CuCl)$_3$, the all-Cu analog of the title compound (Stibrany *et al.*, 2002). In contrast, the iodide analog, (Ni*A*)$_2$(CuI)$_3$, exhibits somewhat longer Ni—Cu distances (2.765 and 2.875 Å; Fox *et al.*, 1996). Taken together, these data suggest somewhat shallow potential surfaces with possible multiple minima for the bridging species in polynuclear complexes of this sort.

If weak Cu—Ni bonding is ignored, the several coordination geometries are typical: distorted square-planar (Ni), distorted trigonal-planar (Cu1, Cu2), distorted tetrahedral (S1), and distorted pyramidal (S2). Cu1—Ni bonding affects only the coordination geometries of these metals, changing them to distorted square-pyramidal and distorted trigonal-pyramidal for Ni and Cu1, respectively. Metric parameters for the Ni*A* units are not unusual and compare favorably with those reported for (Ni*A*)$_2$(CuI)$_3$ (Fox *et al.*, 1996).

When viewed along *c* (Fig. 2), the structure appears as a *C*-centered pattern of columns consisting of individual complexes linked to dimethylformamide solvent molecules *via* N—H···O hydrogen bonds (Table 2). Intercluster C—H···Cl hydrogen bonds link the complexes to form layers parallel to the *ab* plane. Intracluster N—H···Cl hydrogen bonds also help to stabilize the structure.

Experimental

The title compound was prepared by the reaction of a 3:2 mixture of Cu^{I}Cl with rac-Ni*A* (Fox *et al.*, 2000) in acetontrile under an inert atmosphere. The detailed procedure was similar to that used to prepare the analogous iodo complex (Fox *et al.*, 1996). Suitable crystals were obtained by slow evaporation of a solution of the product in a mixture of ethanol and dimethylformamide.

Crystal data

[Cu$_3$Ni$_2$Cl$_3$(C$_{14}$H$_{28}$N$_2$S$_2$)$_2$]·2C$_3$H$_7$NO
M_r = 1137.61
Monoclinic, *C*2/*c*
a = 11.874 (3) Å
b = 20.058 (4) Å
c = 21.348 (5) Å
β = 100.48 (1)°
V = 4999.4 (19) Å^3
Z = 4
D_x = 1.511 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 957 reflections
θ = 3.0–24.4°
μ = 2.36 mm^{-1}
T = 223 (1) K
Plate, dark orange–brown
0.40 × 0.30 × 0.06 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{\min}$ = 0.694, $T_{\max}$ = 0.868
12 812 measured reflections
4350 independent reflections
3522 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.031
$\theta_{\max}$ = 25.0°
$h = -8 \rightarrow 14$
$k = -20 \rightarrow 23$
$l = -22 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.092
S = 1.00
4350 reflections
263 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 0.1342P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.51 e Å^{-3}
$\Delta\rho_{\min}$ = −0.25 e Å^{-3}

Acta Cryst. (2003). E**59**, m630–m632 Robert T. Stibrany *et al.* • [Cu$_3$Ni$_2$Cl$_3$(C$_{14}$H$_{28}$N$_2$S$_2$)$_2$]·2C$_3$H$_7$NO **m631**

Table 1
Selected geometric parameters (Å, °).

Ni—S1	2.1710 (9)	Cu1*A*—S1	2.746 (6)
Ni—S2	2.1690 (9)	Cu1—S2^{i}	2.2202 (9)
Ni—N1	1.946 (2)	S2—Cu1*A*^{i}	2.296 (6)
Ni—N2	1.925 (3)	Ni—Cu1	2.6973 (8)
Cu1—Cl1	2.2455 (10)	Ni—Cu1*A*	2.604 (5)
Cu1*A*—Cl1	2.282 (5)	Cu2—Cl2	2.1699 (14)
Cu1—S1	2.3196 (10)	Cu2—S1	2.2134 (8)

N2—Ni—N1	86.61 (11)	S1—Ni—Cu1	55.65 (3)
N2—Ni—S2	88.94 (8)	S2^{i}—Cu1—Cl1	122.88 (3)
N1—Ni—S2	165.65 (9)	S2^{i}—Cu1—S1	111.83 (3)
N2—Ni—S1	163.11 (9)	Cl1—Cu1—S1	125.03 (3)
N1—Ni—S1	89.66 (9)	S2^{i}—Cu1—Ni	141.01 (3)
S2—Ni—S1	98.36 (3)	Cl1—Cu1—Ni	86.03 (3)
N2—Ni—Cu1	110.01 (9)	S1—Cu1—Ni	50.60 (2)
N1—Ni—Cu1	107.49 (9)	Cl2—Cu2—S1	125.31 (2)
S2—Ni—Cu1	86.86 (3)	S1^{i}—Cu2—S1	109.39 (5)

Symmetry code: (i) $-x, y, \frac{3}{2}-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O20^{ii}	0.84 (4)	2.13 (4)	2.921 (5)	157 (3)
N2—H2N···Cl1	0.92 (4)	2.57 (4)	3.359 (3)	144 (3)
C9—H9*B*···Cl2^{iii}	0.97	2.67	3.552 (4)	151

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

The structure was originally refined with the Cu1 site fully occupied. Convergence occurred with $R[F^2 > 2\sigma(F^2)] = 0.057$ and $wR(F^2) = 0.153$, but the largest residual, 3.29 e Å^{-3}, located 0.86 Å from Cu1, was well outside the range expected for normal behavior. Inclusion of this site as a second position for a disordered Cu1 atom, followed by refinement with the sum of the occupancy factors for Cu1 and Cu1*A* constrained to unity, led to much improved agreement between the observed and calculated structure factors (see *Refinement* above). We conclude that Cu1 is disordered over two sites with 0.920 (5) and 0.080 (5) site occupanies for Cu1 and Cu1*A*, respectively. The disorder is consistent with two possible pentanuclear clusters, one with two Cu1 ions and a second with one Cu1 and one Cu1*A* ion; the third possibility, two Cu1*A* ions per cluster, is unlikely because the intracluster Cu1*A*—Cu1*A* distance [2.320 (12) Å] would imply a relatively strong copper(I)–copper(I) bond, which is not expected for a relatively unconstrained complex such as (Ni*A*)$_2$(CuCl)$_3$ (Stibrany *et al.*, 2002).

H atoms attached to C atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.97 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for methyl H and 1.2$U_{\rm eq}$(C) for all others. H atoms attached to N atoms were located from a difference map and their parameters (x, y, z, $U_{\rm iso}$) were refined.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *ORTEP*32 (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

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