Monoclinic
$P2_1/c$
$a = 12.504\,(3)$ Å
$b = 5.5750\,(10)$ Å
$c = 14.450\,(2)$ Å
$\beta = 102.300\,(10)°$
$V = 984.2\,(3)$ Å^3
$Z = 2$
$D_x = 1.620$ Mg m^{-3}
D_m not measured

Cell parameters from 136 reflections
$\theta = 1.75$–$27.50°$
$\mu = 1.351$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.32 × 0.22 × 0.16 mm
Dark blue

Data collection

Rigaku RAXIS IIC imaging-plate diffractometer
Oscillation IP photos
Absorption correction: *ABSCOR* (Higashi, 1995)
$T_{\min} = 0.65$, $T_{\max} = 0.88$
2362 measured reflections
2260 independent reflections

1777 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\max} = 27.50°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 7$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.132$
$S = 1.068$
2260 reflections
133 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 0.13P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.390$ e Å^{-3}
$\Delta\rho_{\min} = -0.446$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—N1$^{\rm i}$	1.922 (2)	N1—C2	1.290 (4)
Cu1—N1	1.922 (2)	N1—N2	1.400 (3)
Cu1—S1	2.1842 (7)	N2—C1	1.307 (3)
Cu1—S1$^{\rm i}$	2.1842 (7)	N3—C1	1.340 (4)
S1—C1	1.740 (3)		
N1$^{\rm i}$—Cu1—N1	180.0	N1$^{\rm i}$—Cu1—S1$^{\rm i}$	84.86 (7)
N1$^{\rm i}$—Cu1—S1	95.14 (7)	S1—Cu1—S1$^{\rm i}$	180.0

Symmetry code: (i) $-x, -y, -z$.

Data were collected on a Rigaku RAXIS IIC imaging-plate diffractometer using Mo $K\alpha$ radiation from a rotating-anode generator operating at 50 KV and 90 mA ($2\theta_{\max} = 55.2°$, 60 oscillation frames in the range of 0–180°), exposure 8 min per frame. Absorption corrections were made using the *ABSCOR* (Higashi, 1995) program based on Fourier-coefficient fitting to the intensities of symmetry-equivalent reflections (Tanner & Krause, 1990*a*,*b*; Kraus & Phillips, 1992; Higashi, 1995). All the non-H atoms were refined anisotropically. All H atoms were placed in calculated positions (C—H 0.96 Å), assigned fixed isotropic displacement parameters 1.2 times the equivalent isotropic U value of the attached atom and allowed to ride on their respective parent atoms.

Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1119). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 33–36

Aqua(dicyanonitrosomethanido-*O*)bis(1,10-phenanthroline-*N*,*N*′)copper(II) Dicyanonitrosomethanide

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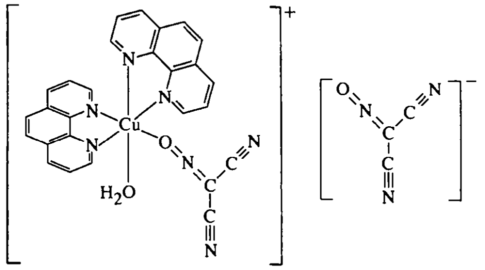
Abstract

The crystal structure of the title complex, $[\mathrm{Cu}\{\mathrm{ONC(CN)_2}\}(\mathrm{C_{12}H_8N_2})_2(\mathrm{H_2O})][\mathrm{ONC(CN)_2}]$, is composed of discrete $[\mathrm{Cu(dcnm)(H_2O)(phen)_2}]^+$ cations and dcnm anions [phen is 1,10-phenanthroline and dcnm is dicyanonitrosomethanide, $\mathrm{ONC(CN)_2^-}$]. The coordination polyhedron of the Cu$^{\rm II}$ atom is a distorted elongated tetragonal bipyramid with a $\mathrm{CuN_4O_2}$ chromophore. The water molecule occupies an axial position, while the dcnm anion occupies an equatorial position.

Comment

The title compound was prepared and its crystal structure solved as part of our study on the synthesis, crystal chemistry and properties of copper compounds with pseudo-halide anions. In our previous papers, we described several structures of Cu^{II} complexes containing $ONC(CN)_2^-$ and similar $C(CN)_3^-$ anions. We have shown that the complexes were five-coordinated with smaller anions [CN^-, NCS^- or $N(CN)_2^-$] coordinated to the Cu^{II} atom, and $ONC(CN)_2^-$ and $C(CN)_3^-$ out of the copper coordination sphere (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 1996*a*,*b*,*c*; Potočňák, Dunaj-Jurčo, Mikloš, Kabešová & Jäger, 1995*b*). Both the $ONC(CN)_2^-$ and $C(CN)_3^-$ anions are known to have quite good coordination ability (Golub, Köhler & Skopenko, 1986) and we decided, therefore, to prepare a compound using only one kind of anionic ligand (dcnm) in a reaction mixture. The aim was to find whether this relatively bulky ligand would be able to coordinate the Cu atom in the presence of two molecules of another bulky ligand (phen) in the coordination sphere to form a five-coordinated compound. The other expected possibility would be that the four-coordinated $[Cu(phen)_2]^{2+}$ species would be formed, as in the case of $[Cu(phen)_2](PF_6)_2$ (Amournjarusiri & Hathaway, 1991). The preparation resulted in the title compound, (I), with, surprisingly, a six-coordinated Cu atom.



(I)

The labeling scheme of one formula unit of (I) is shown in Fig. 1. The Cu atom is six-coordinated by two phen molecules, one dcnm ligand (in the equatorial plane) through the O atom, and by one water molecule (in an axial position). The coordination polyhedron is a distorted elongated tetragonal bipyramid with a CuN_4O_2 chromophore. The second dcnm anion does not enter the inner coordination sphere. Six-coordinated bis(phenanthroline)copper(II) compounds are mostly in a 4+1+1* arrangement. The fifth and the sixth coordination positions are occupied by two O atoms from anionic ligands, such as $RCOO^-$ and ONO^- groups, in the equatorial plane, with one Cu—O distance substantially longer than the second (Fitzgerald & Hathaway, 1984). A *cis* arrangement of ligands in the equatorial plane was also observed in the structures of $[Cu(NCX)_2(phen)_2]$ compounds (X = S, Se) (Sedov, Kabešová, Dunaj-Jurčo, Gažo & Garaj, 1982). The ligands in (I) (H_2O and dcnm) are also in a *cis* arrangement, but the water molecule occupies an axial position. As a consequence, one phen molecule occupies both the axial and the equatorial positions but the second molecule lies only in the equatorial plane. A similar arrangement was observed in the structures of $[Cu(N(CN)_2)_2(phen)_2]$ (Potočňák, Dunaj-Jurčo, Mikloš, Kabešová & Jäger, 1995*a*) and *cis*-$[CuCl(NCS)(phen)_2]$ (Parker & Breneman, 1995).

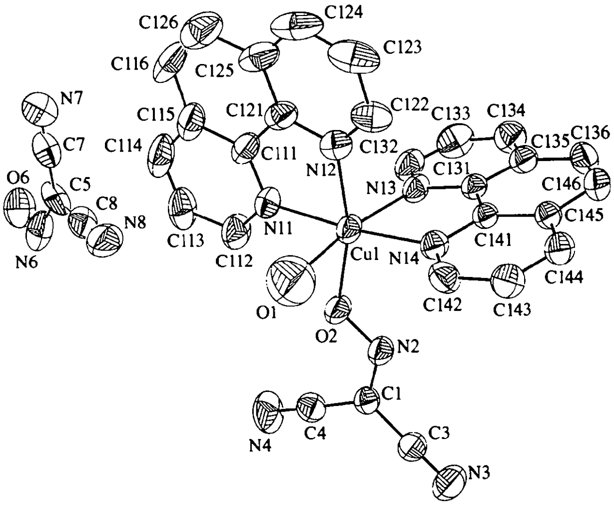


Fig. 1. *ORTEP* drawing (Johnson, 1965) of the formula unit and labeling of atoms in (I). Displacement ellipsoids are plotted at the 40% probability level.

Three N atoms of the two phen molecules in (I) lie in the equatorial plane at distances of 1.991 (3)–2.049 (3) Å from the Cu1 atom, and the distance of the fourth N atom (Cu1—N13, axial position) is 2.275 (3) Å. The other two positions in the coordination polyhedron are occupied by O atoms at distances of 1.933 (2) (Cu1—O2, equatorial plane) and 2.394 (4) Å (Cu1—O1, axial position). The bond distances and angles in the phen molecules are normal and range from 1.324 (6) to 1.453 (7) Å, and from 116.2 (4) to 126.1 (5)°, respectively (for C—C distances and C—C—C angles, respectively). Both phen molecules are nearly planar; the largest deviation of atoms from their mean planes is 0.090 (6) Å. The mean planes of the two phen molecules are perpendicular with respect to one another [89.80 (6)°].

Both dcnm anions are nearly planar; the largest deviations of atoms from the mean planes are 0.038 (4) and 0.011 (5) Å for the coordinated and the free anion, respectively. The anions have similar bond distances and angles except for the nitroso part. The C—C bond distances range from 1.400 (7) to 1.419 (7) Å, the C≡N bond distances from 1.099 (7) to 1.151 (6) Å, and the values of the C—C≡N angles lie in the interval from

176.8 (6) to 179.2 (4)°. All these values are comparable with corresponding values found for the dcnm anion in $[Cu(NCS)(phen)_2][ONC(CN)_2]$, (II) (Potočňák, Dunaj-Jurčo, Mikloš, Kabešová & Jäger, 1995*b*). The O—N and C—N bond lengths in (I) are 1.280 (3) and 1.296 (4) Å for the coordinated anion, and 1.139 (5) and 1.455 (6) Å for the free anion. The O—N and C—N bond distances in (II) lie between the two corresponding values in (I).

Apart from coulombic forces, two cations and two anions in (I) are held together by a system of hydrogen bonds indicated by the O···O distances $O1\cdots O6^{i}$ 2.699 (7) and $O1\cdots O6^{ii}$ 2.886 (6) Å [symmetry codes: (i) $x-1$, $y+1$, $z-1$; (ii) $-x$, $-y-1$, $-z$].

Experimental

Crystals of (I) were prepared by mixing 10 ml of a 0.1 *M* water solution of $Cu(NO_3)_2$ with 20 ml of a 0.1 *M* ethanol solution of phen and 20 ml of a 0.1 *M* ethanol solution of $NaONC(CN)_2$. After several days, green prismatic crystals of (I) appeared.

Crystal data

$[Cu(C_3N_3O)(C_{12}H_8N_2)_2$-
$(H_2O)](C_3N_3O)$
$M_r = 630.08$
Triclinic
$P\overline{1}$
$a = 9.291$ (5) Å
$b = 11.773$ (5) Å
$c = 13.079$ (9) Å
$\alpha = 108.10$ (5)°
$\beta = 92.96$ (5)°
$\gamma = 96.01$ (4)°
$V = 1347.0$ (13) $Å^3$
$Z = 2$
$D_x = 1.554$ Mg m^{-3}
$D_m = 1.50$ (1) Mg m^{-3}
D_m measured by flotation in $CCl_4/CHBr_3$/benzene

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 3.86$–10.69°
$\mu = 0.866$ mm^{-1}
$T = 293$ (2) K
Prism
0.65 × 0.40 × 0.20 mm
Dark green

Data collection

Syntex $P2_1$ diffractometer
θ–2θ scans
Absorption correction: empirical *via* ψ scans of 17 reflections (North, Phillips & Mathews, 1968)
$T_{min} = 0.710$, $T_{max} = 0.841$
5906 measured reflections
5906 independent reflections

2553 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.56°$
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = 0 \rightarrow 16$
2 standard reflections every 100 reflections intensity decay: 4.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.099$
$S = 0.784$

$(\Delta/\sigma)_{max} = 0.013$
$\Delta\rho_{max} = 0.417$ e $Å^{-3}$
$\Delta\rho_{min} = -0.326$ e $Å^{-3}$
Extinction correction: none

5906 reflections
461 parameters
All phen H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—O2	1.933 (2)	C1—C4	1.419 (4)
Cu1—N14	1.991 (3)	C3—N3	1.123 (4)
Cu1—N11	1.993 (3)	C4—N4	1.122 (4)
Cu1—N12	2.049 (3)	O6—N6	1.139 (5)
Cu1—N13	2.275 (3)	N6—C5	1.455 (6)
Cu1—O1	2.394 (4)	C5—C8	1.400 (7)
O2—N2	1.280 (3)	C5—C7	1.419 (7)
N2—C1	1.296 (4)	C7—N7	1.151 (6)
C1—C3	1.415 (5)	C8—N8	1.099 (7)
O2—Cu1—N14	98.65 (10)	N13—Cu1—O1	169.47 (11)
O2—Cu1—N11	88.50 (11)	N2—O2—Cu1	120.2 (2)
N14—Cu1—N11	172.82 (12)	O2—N2—C1	114.0 (3)
O2—Cu1—N12	164.00 (10)	N2—C1—C3	117.6 (3)
N14—Cu1—N12	91.42 (12)	N2—C1—C4	122.9 (3)
N11—Cu1—N12	81.74 (12)	C3—C1—C4	119.3 (3)
O2—Cu1—N13	98.46 (11)	N3—C3—C1	178.8 (4)
N14—Cu1—N13	77.46 (12)	N4—C4—C1	179.2 (4)
N11—Cu1—N13	100.95 (11)	O6—N6—C5	103.1 (6)
N12—Cu1—N13	95.84 (11)	C8—C5—C7	124.0 (4)
O2—Cu1—O1	82.43 (13)	C8—C5—N6	109.7 (5)
N14—Cu1—O1	92.03 (13)	C7—C5—N6	126.2 (6)
N11—Cu1—O1	89.55 (13)	N7—C7—C5	176.8 (6)
N12—Cu1—O1	84.83 (13)	N8—C8—C5	178.1 (6)

Intensities were corrected for Lorentz and polarization factors using *XP*21 (Pavelčík, 1993). The structure was solved by the heavy-atom method with *XFPS* (Pavelčík, Rizzoli & Andreetti, 1990) and subsequent Fourier syntheses using *SHELXL*93 (Sheldrick, 1993). Anisotropic displacement parameters were refined for all non-H atoms. All H atoms (except water H atoms, the positions of which were neither found nor calculated) were located from the difference Fourier map and refined with free isotropic displacement parameters. Geometrical analysis was performed using *PARST* (Nardelli, 1983) and *SHELXL*93.

Data collection: Syntex $P2_1$ software. Cell refinement: Syntex $P2_1$ software. Data reduction: *XP*21. Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1234). Services for accessing these data are described at the back of the journal.

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An Additional Isomer of the Neutral Dicarbollide Analogue of Ferrocene [Fe{C$_2$B$_9$H$_{10}$(SMe$_2$)}$_2$]

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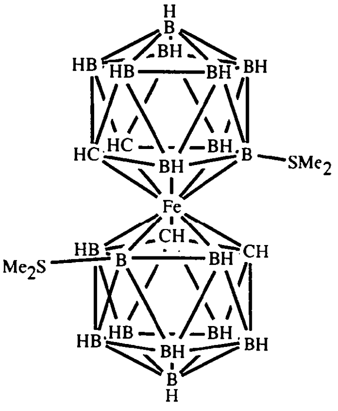
Abstract

The title compound, 8,8′-bis(dimethyl sulfido)-3,3′-ferra-*commo*-bis[3,1,2-ferradicarba-*closo*-dodecaborane(11)], has the expected overall geometry in which two {FeC$_2$B$_9$} icosahedra are linked *via* a common Fe atom; additionally, the whole cluster has crystallographically imposed C_2 symmetry. The structure is compared with those of its geometric isomers and of some related compounds.

Comment

There is, at present, considerable interest in the structural behaviour of metallacarbaborane sandwich complexes and their derivatives, and in particular their possible application as novel molecular materials (see for example, Yan & Mingos, 1995). Prompted by the recent structural accounts of one such compound, *commo*-[3,3′-Fe{4-(Me$_2$S)-1,2-C$_2$B$_9$H$_{10}$}$_2$], as its *DD/LL*- (Yan *et al.*, 1994) and *meso*- (Yan, Mingos & Williams, 1995) isomers, hereinafter (I) and (II), respectively, and its varied structural behaviour, we report our own determination of the molecular geometry of the title compound, (III), a structural isomer of the ferracarbaboranes (I) and (II).



(III)

A perspective view of a whole molecule of (III), showing the atomic numbering scheme, is presented in Fig. 1. The molecule is chiral and has crystallographically imposed twofold symmetry, with Fe3 lying on a C_2 axis, which coincides with the crystallographic c axis. Thus, the two η^5-{C$_2$B$_3$} faces binding to the Fe atom have a staggered conformation and the cage C atoms are not fully *cisoid*; the C1—C2 and C1$^{\rm i}$—C2$^{\rm i}$ vectors, and likewise the pendant dimethyl sulfide

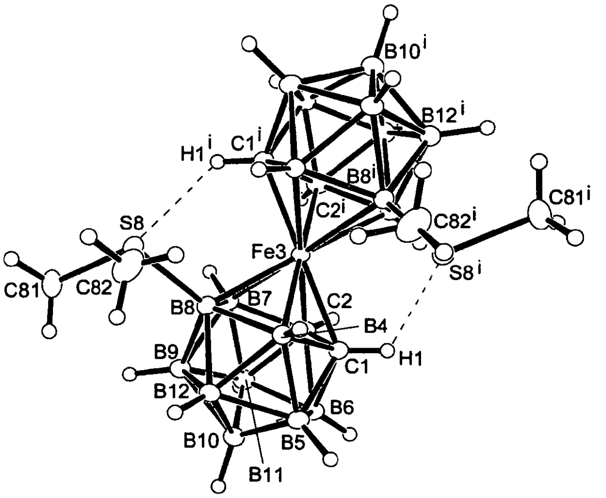


Fig. 1. Perspective view of a single molecule of (III) drawn with 40% probability ellipsoids and with H atoms shown as small circles of artificial radii for clarity. [Symmetry code: (i) $2 - x$, $2 - y$, z.]