Absorption correction:
ψ scan (*SHELXTL-Plus*; Sheldrick, 1990*b*)
$T_{\min} = 0.77$, $T_{\max} = 0.88$
4108 measured reflections
4108 independent reflections

$\theta_{\max} = 25.01°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 24$
3 standard reflections
every 150 reflections
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.102$
$S = 1.02$
3674 reflections
307 parameters
H atoms riding (C—H 0.96 Å)

$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 1.35P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Fe—C31	2.062 (3)	C14—C15	1.377 (4)
Fe—C32	2.038 (3)	C15—O15	1.380 (4)
Fe—C33	2.042 (3)	C15—C16	1.398 (4)
Fe—C34	2.034 (3)	O12—C17	1.424 (4)
Fe—C35	2.045 (3)	O15—C18	1.429 (4)
Fe—C36	2.041 (4)	C21—C22	1.403 (4)
Fe—C37	2.034 (4)	C21—C26	1.408 (4)
Fe—C38	2.052 (3)	C22—O22	1.379 (4)
Fe—C39	2.051 (3)	C22—C23	1.388 (4)
Fe—C40	2.043 (4)	C23—C24	1.385 (4)
C1—C31	1.516 (4)	C24—C25	1.379 (4)
C1—C21	1.523 (4)	C25—O25	1.365 (4)
C1—C11	1.535 (4)	C25—C26	1.406 (4)
C11—C16	1.391 (4)	C26—C29	1.437 (4)
C11—C12	1.409 (4)	O22—C27	1.428 (4)
C12—O12	1.376 (4)	O25—C28	1.436 (4)
C12—C13	1.388 (4)	C29—N30	1.151 (4)
C13—C14	1.389 (5)		
C31—C1—C21	113.4 (2)	C22—C21—C26	116.7 (3)
C31—C1—C11	113.2 (2)	C22—C21—C1	123.0 (3)
C21—C1—C11	112.3 (2)	C26—C21—C1	120.2 (3)
C16—C11—C12	118.1 (3)	O22—C22—C23	123.3 (3)
C16—C11—C1	123.0 (3)	O22—C22—C21	116.1 (3)
C12—C11—C1	118.9 (3)	C23—C22—C21	120.6 (3)
O12—C12—C13	124.0 (3)	C24—C23—C22	121.3 (3)
O12—C12—C11	115.7 (3)	C25—C24—C23	120.3 (3)
C13—C12—C11	120.2 (3)	O25—C25—C24	126.0 (3)
C12—C13—C14	120.7 (3)	O25—C25—C26	115.8 (3)
C15—C14—C13	119.8 (3)	C24—C25—C26	118.2 (3)
C14—C15—O15	124.9 (3)	C25—C26—C21	122.8 (3)
C14—C15—C16	119.9 (3)	C25—C26—C29	117.1 (3)
O15—C15—C16	115.2 (3)	C21—C26—C29	120.0 (3)
C11—C16—C15	121.3 (3)	C22—O22—C27	117.6 (3)
C12—O12—C17	117.8 (3)	C25—O25—C28	116.9 (3)
C15—O15—C18	116.8 (3)	N30—C29—C26	178.1 (3)

Data were corrected for Lorentz, polarization and absorption effects. All non-H atoms were refined anisotropically; all H atoms were included using a riding model.

Data collection: *R*3*m*/*V* diffractometer software. Cell refinement: *R*3*m*/*V* diffractometer software. Data reduction: *R*3*m*/*V* diffractometer software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*). 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: BK1350). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 464–468

Bis(1,10-phenanthroline-N,N')copper(II) Tetrathionate and Tris(1,10-phenanthroline-N,N')copper(II) Tetrathionate Pentahydrate

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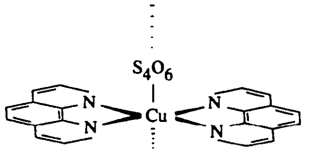
Abstract

The structures of [Cu(C$_{12}$H$_8$N$_2$)$_2$(S$_4$O$_6$)], (I), and [Cu(C$_{12}$H$_8$N$_2$)$_3$](S$_4$O$_6$).5H$_2$O, (II), are reported. Compound (I) consists of infinite polymeric chains where copper displays a typical (4+2) coordination and S$_4$O$_6$ connects Cu(phen)$_2$ (phen is phenanthroline) units through rather long Cu$\cdots$O contacts. Compound

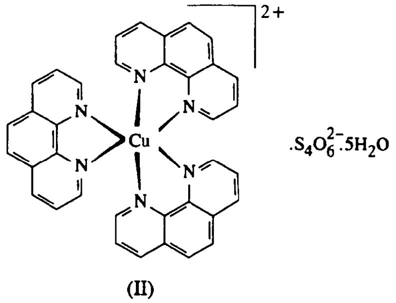
(II), instead, has a purely ionic character displaying $[Cu(phen)_3]^{2+}$ and $S_4O_6^{2-}$ monomeric units. Equatorial and apical bonds in the copper coordination spheres have mean values of 2.003 (5)/2.467 (12) and 2.056 (3)/2.311 (13) Å for (I) and (II), respectively. Some short O···*OW* contacts in (II) suggest the existence of hydrogen bonding involving some of the water molecules of hydration.

Comment

We have been interested in the coordination properties of some sulfur oxyanions. In this context, we have found the reaction between Cu^{2+} and $S_2O_3^{2-}$ in the presence of phenanthroline to be a very prolific one, with several compounds of quite different characteristics being generated depending on the diverse conditions of reaction. In particular, when these conditions favour the redox reaction between thiosulfate and the metal ion, compounds containing the $S_4O_6^{2-}$ anion were isolated. In the present paper, we report the crystal structures of two such compounds, namely, $[Cu(phen)_2(S_4O_6)]$, (I) and $[Cu(phen)_3](S_4O_6).5H_2O$, (II).



(I)



(II)

The structure of (I) consists of infinite chains parallel to the shortest crystallographic axis, which are built up through the connection of $[Cu(phen)_2]$ and S_4O_6 units. Both groups lie on special positions, each being bisected by a twofold axis. The presence of disorder in the terminal SO_3 group (see *Experimental* section) led to a fuzzy description of the apical bonding scheme of the Cu atom due to the existence of two different atom sites sharing the role (O1 and O1′). However, the very similar distances of both atoms from copper [2.455 (7) and 2.455 (6) Å] were considered to be convincing evidence of the presence of semi-coordination, resulting in a typical (4+2) arrangement around the metal centre. This situation is not unusual in the chemistry of copper, and a number of structures with comparably long Cu—O_{apical} distances can be found in the literature, *e.g. catena*-[diaqua(ethylenediamine)-(μ^2-sulfato)-copper(II)] 2.494 (5) Å (Manriquez *et al.*, 1996), (μ^2-sulfato-*O*,*O*′)-diaqua(1,10-phenanthroline-*N*,*N*′)copper(II) 2.468 (8) Å (Healy *et al.*, 1984), bis(ethylenediamine)bis(dodecylsulfato)copper(II) 2.518 (6) Å (Birker *et al.*, 1977) and aqua(2,2′:6′,2″-terpyridyl)bis(trifluoromethanesulfonato)-copper(II) 2.486 (9) Å (Castro *et al.*, 1992).

A view of the copper coordination polyhedron in (I) is shown in Fig. 1(*a*): the Cu^{2+} ion lies on a twofold symmetry axis, the basal CuN_4 group being a flattened tetrahedron with an angle of 40.7 (3)° between the two planar phenanthroline molecules. The two independent C—N bond lengths are 2.002 (5) and 2.004 (5) Å, respectively. These values are almost equal to those reported in the isomorphous compound $[Cu(bpy)_2(S_4O_6)]$ (bpy is bipyridine) (Harrison & Hathaway, 1978).

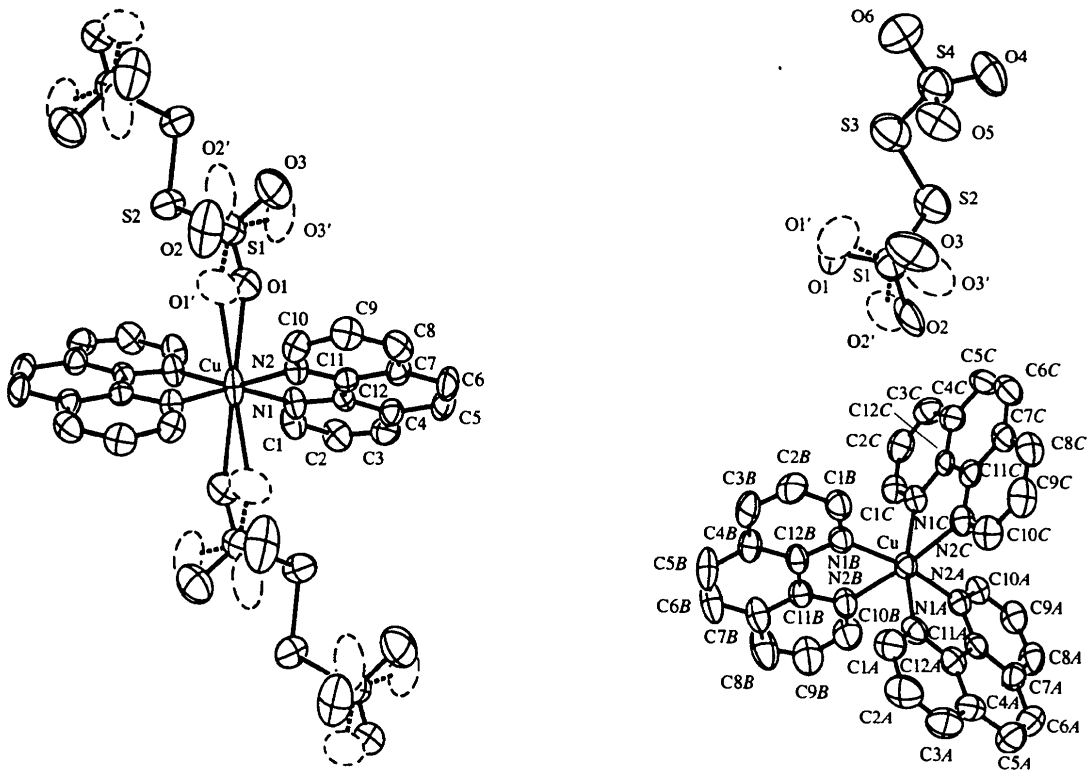
Due to the disordered nature of the oxyanion, the observation of any effect the semi-coordination of O1 (O1′) might have had on the corresponding S—O (S—O′) distances was obviously precluded.

The structure of (II) consists of $[Cu(phen)_3]^{2+}$ cations and $S_4O_6^{2-}$ anions, with no evidence of any direct interaction of the tetrathionate ions with the Cu^{2+} cations. The latter contain a six-coordinated CuN_6 chromophore with the metal attached to three different phenanthroline groups. The result is a Jahn–Teller-distorted octahedral coordination, with four Cu—N bond distances being quite similar [mean 2.056 (3) Å] and defining the distorted equatorial plane, with the remaining two occupying the apical sites at a significantly larger distance [mean 2.311 (13) Å]. Fig. 1(*b*) shows the two ionic units making up the structure.

A search in the Cambridge Structural Database (*CSD*; Allen *et al.*, 1983) provided only two other structures containing $[Cu(phen)_3]^{2+}$ groups, *i.e.* tris(1,10-phenanthroline-*N*,*N*′)copper(II) bis(tetracyanoquinodimethanide) methanol solvate (Bencini *et al.*, 1989) displaying the same two clear types of bonds as in (II), with a similar narrow spread [2.04 (3) and 2.33 (1) Å], and tris(1,10-phenanthroline)copper(II) diperchlorate (Anderson, 1973), where Cu—N distances scatter almost uniformly between the limiting ones, giving rise to larger e.s.d.'s for the mean values [2.09 (4) and 2.23 (6) Å].

One of the S_2O_3 ends in the tetrathionate ion presents rotational disorder around the S—S bond, a fact which seems to be distinctive for this terminal group. The restrained refinement performed led to bond lengths and angles comparable to those reported for the free anion (Foss & Hendrik, 1958).

The phenanthroline moieties do not display any unusual features with regard to bond lengths and angles in either of the two compounds studied, compared with the free molecule (Nishigaki *et al.*, 1978). However,



(a) (b)

Fig. 1. (a) View of the copper coordination polyhedron in (I). (b) The two ionic units making up the structure in (II). In both figures, the numbering scheme used is shown and the displacement ellipsoids are drawn at the 40% probability level. H atoms and hydration water molecules are not shown for clarity.

they do exhibit meaningful deviations from planarity, as measured by the dihedral angle between opposite pyridine groups [3.4 (2)° in (I), and 3.3 (2), 3.3 (2) and 2.0 (2)° in (II)].

Inspection of a packing view of the structure along the *a* axis reveals a spatial distribution of the $[Cu(phen)_3]^{2+}$ cations in the form of broad sheets parallel to $(01\bar{1})$. The space between sheets is in turn occupied by the $S_4O_6^{2-}$ anions, as well as by the water molecules of hydration. The latter seems to participate in hydrogen-bonding interactions, as suggested by some short intermolecular O···O distances present in the structure [O1*W*···O3*W* 2.80 (1), O1*W*···O2*W* 2.82 (1), O4···O3*W* 2.85 (1), O6···O3*W*($-x+1$, $-y-1$, $-z$) 2.70 (2), O1*W*···O2*W*($-x$, $-y-1$, $-z$) 2.79 (2) Å]. However, failure in finding the corresponding H atoms prevented any detailed analysis of the subject.

Experimental

$[Cu(phen)_2(S_4O_6)]$, (I), was prepared by the slow mixing of 15 ml of an aqueous solution of 2 mmol of copper sulfate and 2 mmol of sodium thiosulfate, with 10 ml of a methanolic solution of 2 mmol of phenanthroline. The resulting solution became dark red. On standing, blue crystals appeared while the solution turned orange. $[Cu(phen)_3][S_4O_6].5H_2O$, (II), was prepared in a similar way to (I) but using only 1 mmol of copper sulfate. When the resulting blue solution was allowed to stand, a crop of blue crystals suitable for X-ray diffraction work was obtained.

Compound (I)

Crystal data

$[Cu(C_{12}H_8N_2)_2(S_4O_6)]$
$M_r = 648.18$
Orthorhombic
Pbcn
$a = 11.253\ (1)$ Å
$b = 13.033\ (1)$ Å
$c = 17.563\ (2)$ Å
$V = 2575.8\ (4)$ Å^3
$Z = 4$
$D_x = 1.671$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5–12.5°$
$\mu = 1.22$ mm^{-1}
$T = 293\ (2)$ K
Block
0.38 × 0.26 × 0.10 mm
Blue

Data collection

Siemens *R*3*m* diffractometer
$\omega/2\theta$ scans

$R_{int} = 0.041$
$\theta_{max} = 25.04°$

Absorption correction:
ψ scan (*SHELXTL/PC*; Sheldrick, 1990*b*)
$T_{\min} = 0.62$, $T_{\max} = 0.90$
2603 measured reflections
2279 independent reflections
1470 reflections with $I > 2\sigma(I)$

$h = -1 \rightarrow 13$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 20$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.180$
$S = 0.951$
2279 reflections
209 parameters
H atoms not refined, but riding on host atom

$w = 1/[\sigma^2(F_o^2) + (0.104P)^2 + 10.389P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.63$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu—N1	2.004 (5)	Cu—O1	2.478 (7)
Cu—N2	2.002 (5)	Cu—O1′	2.455 (6)

Compound (II)

Crystal data

$[Cu(C_{12}H_8N_2)_3](S_4O_6).5H_2O$
$M_r = 918.47$
Triclinic
$P\overline{1}$
$a = 11.232$ (4) Å
$b = 13.569$ (6) Å
$c = 14.654$ (6) Å
$\alpha = 99.67$ (1)°
$\beta = 99.44$ (1)°
$\gamma = 109.75$ (1)°
$V = 2012.6$ (14) Å^3
$Z = 2$
$D_x = 1.516$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–12.5°
$\mu = 0.82$ mm^{-1}
$T = 293$ (2) K
Block
0.28 × 0.20 × 0.10 mm
Blue

Data collection

Siemens *R*3*m* diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scan (*SHELXTL/PC*; Sheldrick, 1991)
$T_{\min} = 0.80$, $T_{\max} = 0.92$
7224 measured reflections
6998 independent reflections
4013 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.059$
$\theta_{\max} = 25.10°$
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 15$
$l = 0 \rightarrow 17$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.158$
$S = 0.930$
6997 reflections
552 parameters
H atoms not refined, but riding on host atom

$w = 1/[\sigma^2(F_o^2) + (0.078P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.55$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu—N1*A*	2.054 (4)	Cu—N2*A*	2.060 (4)
Cu—N1*B*	2.051 (4)	Cu—N2*B*	2.301 (4)
Cu—N1*C*	2.057 (4)	Cu—N2*C*	2.320 (4)

Two terminal (S_2O_3) groups of the tetrathionate anion (out of a total of three independent groups in both structures) exhibited rotational disorder around the S—S bond. The situation could be adequately represented by a two-site 'umbrella' model, with a slight rotation around the S—S bond. Similarity restraints were imposed to the S—O and O—O distances to ensure a regular geometry of the anion. A second problem of disorder became apparent in some of the crystallization solvent molecules: modelling two pairs of low intensity neighbouring peaks as one disordered methanol molecule failed to give reasonable results and these atoms were finally treated as disordered water molecules.

For both compounds, data collection: *P3/P4-PC* (Siemens, 1991); cell refinement: *P3/P4-PC*; data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1990*b*). Program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990*a*) for (I); *XS SHELXTL/PC* for (II). For both compounds, program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *XP* in *SHELXTL/PC*; software used to prepare material for publication: *CIFTAB* in *SHELXL*93, *PARST* (Nardelli, 1983) and *CSD* (Allen *et al.*, 1983).

Data collection was performed at the Universidad de Chile on a single-crystal diffractometer purchased by Fundación Andes.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1333). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 468–470

Bis[μ-*N*,*N*′-bis(salicylidene)-1,3-propanediaminato]bis(dimethylformamide)di(μ-nitrito)copper(II)dinickel(II)–Dimethylformamide (1/2)†

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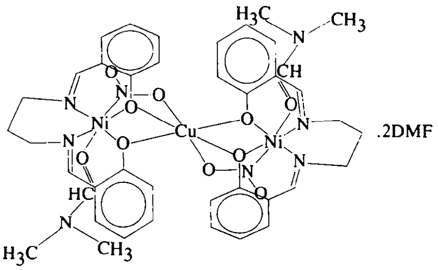
Abstract

The unit cell of the title compound, [$CuNi_2(NO_2)_2(C_{17}H_{16}N_2O_2)_2(C_3H_7NO)_2$].$2C_3H_7NO$, contains two molecules of the linear heterotrinuclear complex and four solvent molecules. The central Cu$^{\rm II}$ ion and the terminal Ni$^{\rm II}$ ions have distorted octahedral coordination spheres. The Cu–Ni pairs are each triply bridged, by the O atoms of an *N*,*N*′-bis(salicylidene)-1,3-propanediaminato (salpd^{2-}) ligand, and by an O and an N atom of a nitrite group. The central Cu$^{\rm II}$ ion, located on an inversion centre, has a total of six O atoms in its coordination sphere: two from each salpd^{2-} ligand and one from each bridging nitrite group. The Ni$^{\rm II}$ ions are related by the inversion centre and each is coordinated by the two O and two N atoms of a salpd^{2-} ligand and one N atom from a nitrite and an O atom from a dimethylformamide (dmf) ligand. The dmf and nitrite groups are mutually *trans* about the Ni$^{\rm II}$ ion. The Cu—Ni distance is 2.9967 (4) Å.

Comment

Binuclear and trinuclear metal complexes based on Schiff base ligands have been the subject of considerable interest in our laboratories, *e.g.* [$Cu_2(C_{11}H_{10}ClNO_2)_2$] (Tahir *et al.*, 1996), [$Cu_2(C_{14}H_{11}NO_2)_2$] (Ülkü, Ercan, Atakol, Ercan & Gencer, 1997), [$Cd(C_2H_3O_2)_2\{Ni(C_3H_7NO)(C_{17}H_{16}N_2O_2)\}_2$] (Ülkü, Tahir *et al.*, 1997) and [$Ni_3(C_{17}H_{16}N_2O_2)_2(CH_3CO_2)_2$].2[$(CH_3)_2SO$] (Ülkü, Ercan, Atakol & Dinçer, 1997). The magnetic super-exchange interactions of the paramagnetic ions over the bridges made up of diamagnetic atoms make these polynuclear complexes interesting. The structure and magnetic properties of the trinuclear complex [$Zn\{(CH_3CO_2)(salpd)Cu\}_2$] (Fukuhara *et al.*, 1990) have been reported previously. Structural details are available for similar complexes formulated as [$M_3(salpn)_2(CH_3CO_2)_2$].2dmf [*M* = Co, Fe; salpn is *N*,*N*′-bis(salicylidene)-2,2-dimethylpropylenediaminate and dmf is dimethylformamide] (Gerli *et al.*, 1991). We report here a new heterometallic trinuclear complex, (I), which, in addition to the two O-atom bridges between a pair of metal ions, has a third bridge provided by an NO_2 group. In previously studied complexes, the third bridge is usually an acetate group.



(I)

The unit cell of the title complex contains two centrosymmetric trinuclear [$Cu\{(NO_2)(salpd)Ni(dmf)\}_2$] molecules, with the central Cu$^{\rm II}$ ion located on an inversion centre. Two additional dmf solvent molecules per trinuclear complex bridge the trimers *via* hydrogen bonds C21—H21$\cdots$O4(x, y, z) and C19—H191$\cdots$O6($x-\frac{1}{2}$, $-y+\frac{1}{2}$, $z+\frac{1}{2}$). The coordination around the central Cu$^{\rm II}$ ion is distorted octahedral, consisting of four bridging O atoms from two salpd^{2-} ligands in the equatorial plane [O1, O2, O1$^{\rm i}$ and O2$^{\rm i}$; symmetry code: (i) $-x$, $-y$, $-z$] and two O atoms from two bridging NO_2 groups (Fig. 1). The Cu—O bond lengths range from 2.048 (2) to 2.103 (2) Å, the longest bond belonging to a nitrite O atom. Due to the centre of symmetry, the Cu$^{\rm II}$ ion is in the equatorial plane. The two terminal Ni$^{\rm II}$ ions, related by the inversion centre, also have distorted octahedral coordination environments, each involving two N and two O atoms from a salpd^{2-} ligand, with the apical positions of the octahedron occupied by the O and N atoms from a dmf ligand and a nitrite group, respectively. The Ni—O and Ni—N bond-length ranges are 2.003 (2)–2.152 (2) and 2.014 (3)–2.131 (3) Å, respectively. The Ni$^{\rm II}$ ion lies only 0.0377 (4) Å out of the equatorial plane defined by atoms O1, O2, N1 and N2. The equatorial plane

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† Alternative name: bis(dimethylformamide)-$1\kappa O,2\kappa O$-di-μ-nitrito-$1{:}3\kappa^2 N{:}O;2{:}3\kappa^2 N{:}O$-bis{$\mu$-2,2′-[1,3-propanediylbis(nitrilomethylidyne)diphenolato}-$1\kappa^4 N,N',O,O'{:}3\kappa^2 O,O';2\kappa^4 N,N',O,O'{:}3\kappa^2 O,O'$-copper(II)dinickel(II) bis(dimethylformamide) solvate.