15 min in boiling ethanol (50 ml). Ethylenediamine (0.3 ml) was then added and heating continued for 2 h. The black precipitate was filtered off, dissolved in CH_2Cl_2 and covered with a layer of hexane. Upon exposure to air at 293 K, brownish crystals of $[Fe(EBTA)]_2O$ were obtained.

Crystal data

$[Fe_2O(C_{18}H_{18}N_2S_2)_2]$
$M_r = 780.63$
Monoclinic
$P2_1/n$
$a = 11.663\,(4)$ Å
$b = 25.704\,(5)$ Å
$c = 12.070\,(4)$ Å
$\beta = 103.856\,(14)°$
$V = 3513.2\,(17)$ Å^3
$Z = 4$
$D_x = 1.476$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 18.5–25.2°$
$\mu = 9.124$ mm^{-1}
$T = 223\,(2)$ K
Plate
0.30 × 0.15 × 0.07 mm
Brown

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (Enraf–Nonius, 1985)
$T_{min} = 0.443$, $T_{max} = 0.528$
8821 measured reflections
5950 independent reflections
4395 reflections with $F > 2\sigma(F)$

$R_{int} = 0.067$
$\theta_{max} = 65°$
$h = -3 \rightarrow 13$
$k = 0 \rightarrow 30$
$l = -14 \rightarrow 14$
3 standard reflections every 100 reflections frequency: 60 min intensity decay: 2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.151$
$S = 0.854$
5948 reflections
424 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1131P)^2 + 13.2629P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.508$ e Å^{-3}
$\Delta\rho_{min} = -0.845$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Fe1—S1	2.350 (2)	N1—C1	1.474 (7)
Fe1—S2	2.341 (2)	C1—C2	1.508 (8)
Fe1—N1	2.161 (4)	N2—C2	1.466 (7)
Fe1—N2	2.129 (5)	N1—C10	1.295 (7)
Fe1—O1	1.773 (4)	N2—C20	1.294 (7)
Fe2—S3	2.307 (2)	N3—C3	1.478 (7)
Fe2—S4	2.357 (2)	C3—C4	1.520 (8)
Fe2—N3	2.215 (5)	N4—C4	1.477 (7)
Fe2—N4	2.112 (5)	N3—C30	1.289 (7)
Fe2—O1	1.763 (4)	N4—C40	1.283 (7)
S1—Fe1—S2	88.47 (6)	S3—Fe2—N3	88.20 (13)
S1—Fe1—N1	87.32 (13)	S3—Fe2—N4	129.06 (13)
S2—Fe1—N2	84.64 (12)	N3—Fe2—N4	75.7 (2)
N1—Fe1—N2	79.4 (2)	S3—Fe2—O1	117.74 (14)
S1—Fe1—O1	106.63 (14)	S4—Fe2—O1	105.94 (13)
S2—Fe1—O1	113.40 (13)	N3—Fe2—O1	93.3 (2)
N1—Fe1—O1	116.5 (2)	N4—Fe2—O1	111.3 (2)
N2—Fe1—O1	97.1 (2)	Fe2—O1—Fe1	160.6 (2)
S3—Fe2—S4	93.08 (7)		

Methyl H atoms were located from difference syntheses, idealized and refined as rigid groups allowed to rotate but not to tip; other H atoms were calculated at ideal positions and refined using a riding model. Computations were performed on a DEC VAX Station 3100, a CONVEX C3860 and a PC Pentium 120.

Data collection: *SDP* (Enraf–Nonius, 1985). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984) in *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1316). Services for accessing these data are described at the back of the journal.

References

Ashmawy, F. M., Ujaimi, A. R., McAuliffe, C. A., Parish, R. V. & Pritchard, R. G. (1991). *Inorg. Chim. Acta*, **187**, 155–158.
Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* A**40**, C-410.
Coggon, P., McPhail, A. T., Mabbs, F. E. & McLachlan, V. N. J. (1971). *J. Chem. Soc. A*, pp. 1014–1019.
Coombes, R. C. & Fenton, D. E. (1983). *Phosphorus Sulfur*, **14**, 139–142.
Enraf–Nonius (1985). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
Gerloch, M., McKenzie, E. D. & Towl, A. D. C. (1969). *J. Chem. Soc. A*, pp. 2850–2858.
Marini, P. J., Murray, K. S. & West, B. O. (1983). *J. Chem. Soc. Dalton Trans.* pp. 143–151.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Zsolnai, L. (1994). *ZORTEP. Program for the Presentation of Thermal Ellipsoids.* University of Heidelberg, Germany.

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Bis(μ-3,7-diethyl-3,7-diazanonane-1,9-dithiolato)dimanganese(II)

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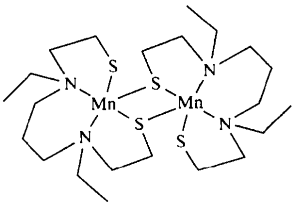
Abstract

The electroneutral title complex, bis(μ-3,7-diethyl-3,7-diazanonane-1,9-dithiolato-$S,N,N',S'{:}S'$)dimanganese(II), $[Mn_2(C_{11}H_{24}N_2S_2)_2]$, is a dimercapto-bridged dimer

with an Mn···Mn distance of 3.550 (1) Å. Each Mn atom is surrounded by an N_2S_3 donor set in a trigonal-bipyramidal arrangement.

Comment

During our investigations of transition metal complexes with mixed S/N ligand spheres (Schneider *et al.*, 1999; Hauptmann *et al.*, 1998), we were able to synthesize bis[μ-(3,7-diethyl-3,7-diazanonane-1,9-dithiolato)]-dimanganese(II), (I), by reaction of (*N*,*N*′-diethyl-3,7-diazanonane-1,9-dithiolato)nickel(II) with dimanganese decacarbonyl in acetonitrile. We present here the crystal structure of (I).



(I)

The structure of (I) (Fig. 1) consists of discrete molecules which display crystallographic inversion symmetry. There is no evidence for intermolecular S···H interactions (shortest intermolecular S···H distance: 3.038 Å). The atoms of the central four-membered heterocyclic Mn_2S_2 unit are constrained to be coplanar by symmetry and the bridging Mn—S2—Mn^i angle is 88.06 (1)° [symmetry code: (i) $1-x$, $-y$, $1-z$]. The two Mn atoms are surrounded by two N and three S atoms in a distorted trigonal-bipyramidal arrangement (average bond angle: 107.0°). Atoms N2, S1 and S2^i form the equatorial plane, whereas the axial positions are occupied by atoms N1 and S1. The L_{ax}—Mn—L_{eq} bond angles range from 81.16 (4) to 97.02 (2)°. The axial Mn—*L* bonds are longer than the equatorial ones; Mn—S2 [2.613 (1) Å] is greater than Mn—S2^i [2.493 (1) Å], and Mn—S1 [2.409 (1) Å] and Mn—N1 [2.370 (1) Å] are greater than Mn—N2 [2.251 (1) Å]. The Mn···Mn distance of 3.550 (1) Å is considered to be too long for a direct metal–metal interaction. The two coordination polyhedra share a common edge defined by both the equatorially and axially bonded S atoms. As expected, the Mn—(μ-S) bonds [2.493 (1) and 2.613 (1) Å] are longer than the terminal Mn—S bonds [2.409 (1) Å].

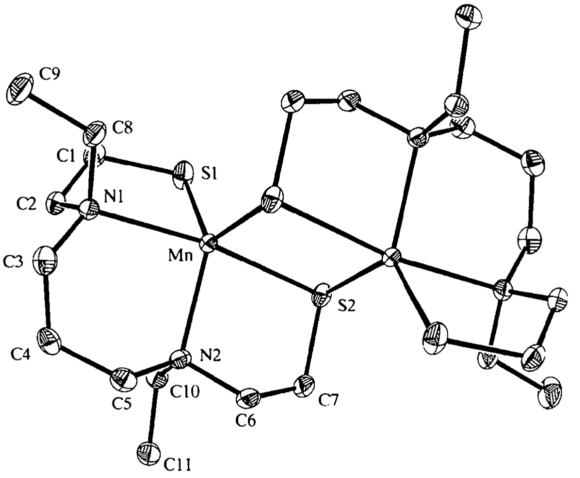


Fig. 1. The molecular structure of the title compound, showing atom labels and 50% displacement ellipsoids. H atoms have been omitted for clarity.

The metal–ligand arrangement is a polycyclic system with five- and six-membered chelate subunits. The six-membered chelate ring is formed by coordination of the propylene-bridged N-donor functions to the Mn centre and adopts the chair conformation. The basal plane of the chair is defined by atoms N1, N2, C3 and C5, which are coplanar within 0.030 (3) Å. The C4 and Mn atoms are displaced in opposite directions from this plane by 0.722 (2) and 0.783 (2) Å, respectively. The ethyl groups are on opposite sides of the plane, resulting in the following configurations of the N atoms: N1(*R*), N2(*R*), N1^i(*S*) and N2^i(*S*). Therefore, the dinuclear title compound appears in the *meso* form. The two five-membered chelate rings containing the S-donor functions adopt envelope-like arrangements with C2 and C6 in the flap positions. In comparison with square-planar-coordinated metal centres, *e.g.* in the monomeric complex (*N*,*N*′-diethyl-3,7-diazanonane-1,9-dithiolato)-nickel(II) (Schneider *et al.*, 1999), the distorted trigonal-bipyramidal coordination of the Mn atoms of the title compound results in more distorted chelate rings. Moreover, both ethyl groups in the monomeric nickel complex reside on the same side of the six-membered chelate ring in contrast to the situation observed here. The related iron complex, bis{μ-[*N*,*N*′-dimethyl-*N*,*N*′-bis(β-mercaptoethyl)-1,3-propanediamine]}diiron(II), is also known (Hu & Lippard, 1974).

Experimental

All operations were performed under a dinitrogen atmosphere in a glove-box. (*N*,*N*′-Diethyl-3,7-diazanonane-1,9-dithiolato)nickel(II) (Osterloh, 1997) (0.06 g, 0.2 mmol) and $[Mn_2(CO)_{10}]$ (0.04 g, 0.1 mmol) were placed with CH_3CN (2 ml) in a thick-walled Pyrex-glass tube (20 cm in length, 1 cm in diameter). The tube was then cooled with liquid nitrogen and sealed under vacuum (10^{-3} mbar; 1 bar = 10^5 Pa), followed by subsequent storage of the reaction mixture for 15 h at 353 K in an oven. After cooling the mixture to room temperature and exposing it for 2–3 d to daylight, yellow crystals of the title compound were obtained.

Crystal data

$[Mn_2(C_{11}H_{24}N_2S_2)_2]$
$M_r = 606.76$

Mo *Kα* radiation
$\lambda = 0.71073$ Å

Monoclinic
*C*2/*c*
$a = 26.392\,(6)$ Å
$b = 8.041\,(1)$ Å
$c = 18.168\,(4)$ Å
$\beta = 132.39\,(1)^\circ$
$V = 2847.6\,(10)$ Å^3
$Z = 4$
$D_x = 1.415$ Mg m^{-3}
D_m not measured

Cell parameters from 18 reflections
$\theta = 10$–20°
$\mu = 1.20$ mm^{-1}
$T = 150$ K
Column
0.71 × 0.26 × 0.18 mm
Yellow

Data collection

Siemens *P*4-*RA* diffractometer
ω scans
Absorption correction: ψ scan (*SHELXTL-Plus*; Sheldrick, 1990)
$T_{\min} = 0.589$, $T_{\max} = 0.806$
3828 measured reflections
3113 independent reflections

2861 reflections with $F > 4\sigma(F)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 27.01^\circ$
$h = -33 \rightarrow 5$
$k = -10 \rightarrow 0$
$l = -19 \rightarrow 23$
1 standard reflection every 99 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0245$
$wR(F^2) = 0.0646$
$S = 1.091$
3113 reflections
148 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0298P)^2 + 0.7817P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.301$ e Å^{-3}
$\Delta\rho_{\min} = -0.165$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0029 (5)
Scattering factors from *International Tables for Crystallography* (Vol. *C*)

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

Mn—N2	2.251 (1)	Mn—S2$^{\rm i}$	2.493 (1)
Mn—N1	2.370 (1)	Mn—S2	2.613 (1)
Mn—S1	2.409 (1)		
N2—Mn—N1	91.13 (5)	N2—Mn—S2	81.16 (4)
N2—Mn—S1	124.26 (4)	N1—Mn—S2	170.38 (3)
N1—Mn—S1	82.51 (4)	S1—Mn—S2	97.02 (2)
N2—Mn—S2$^{\rm i}$	109.66 (4)	S2$^{\rm i}$—Mn—S2	91.94 (1)
N1—Mn—S2$^{\rm i}$	96.10 (3)	Mn$^{\rm i}$—S2—Mn	88.06 (1)
S1—Mn—S2$^{\rm i}$	126.06 (2)		

Symmetry code: (i) $1 - x, -y, 1 - z$.

A crystal of the title compound was mounted on a glass capillary with silicone grease and placed quickly into the cold nitrogen stream of the cooling device of the goniometer. Data were corrected for Lorentz, polarization and absorption effects. The structure was solved by direct methods and subsequent difference Fourier synthesis. After anisotropic refinement of this model, H atoms were taken from the difference Fourier synthesis and recalculated to occupy idealized positions. One common isotropic displacement parameter was refined for the otherwise riding H atoms.

Data collection: *P*3 *Diffractometer Control Program* (Siemens, 1991). Cell refinement: *P*3 *Diffractometer Control Program*. Data reduction: *XDISK* in *P*3 *Diffractometer Control Program*. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. 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: JZ1322). Services for accessing these data are described at the back of the journal.

References

Hauptmann, R., Kliss, R., Schneider, J. & Henkel, G. (1998). *Z. Anorg. Allg. Chem.* **624**, 1927–1936.

Hu, W.-J. & Lippard, S. J. (1974). *J. Am. Chem. Soc.* **96**, 2366–2372.

Osterloh, F. (1997). PhD thesis, University of Oldenburg, Germany.

Schneider, J., Hauptmann, R., Osterloh, F. & Henkel, G. (1999). *Acta Cryst.* C**55**, 328–330.

Sheldrick, G. M. (1990). *SHELXTL-Plus. Structure Determination Software Programs.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1991). *P3 Diffractometer Control Program.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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catena-Poly[[[diaqua(pyridine-2-carboxamide-*N*^{1},*O*)copper(II)]-μ-(sulfato-*O*:*O*′)] monohydrate]

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Abstract

The new title Cu$^{\rm II}$ complex of pyridine-2-carboxamide (pca, $C_6H_6N_2O$), $\{[Cu(SO_4)(pca)(H_2O)_2]\cdot H_2O\}_n$, has been synthesized and its crystal structure determined. It forms two crystallographically independent polymeric $[Cu(H_2O)_2(pca)(SO_4)]_\infty$ chains in which the sulfate ion adopts a bridging position between two Cu atoms, coordinating *via* two of its O atoms, with Cu—O bond lengths in the range 2.318 (1)–2.455 (1) Å. The pca

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