Tableau 1. *Paramètres géométriques (Å, °)*

Cu1—O2	1,930 (3)	N1—C1	1,496 (6)
Cu1—O1	1,937 (3)	N2—C13	1,479 (6)
Cu1—N2	2.027 (3)	N2—C11	1,491 (6)
Cu1—N1	2,028 (4)	N2—C6	1,513 (6)
Cu1—O3	2,279 (4)	C1—C2	1,527 (7)
O1—C8	1,271 (7)	C1—C6	1,542 (7)
O2—C12	1,275 (5)	C2—C3	1,514 (8)
O3—C10	1,220 (6)	C3—C4	1,513 (9)
O4—C10	1,294 (7)	C4—C5	1,539 (9)
O5—C8	1,235 (7)	C5—C6	1,516 (7)
O6—C12	1,229 (5)	C7—C8	1,543 (7)
O7—C14	1,318 (7)	C9—C10	1,511 (9)
O8—C14	1,209 (6)	C11—C12	1,531 (6)
N1—C9	1,462 (7)	C13—C14	1,498 (7)
N1—C7	1,481 (7)		
O2—Cu1—O1	93,0 (1)	N1—C1—C6	110,0 (4)
O2—Cu1—N2	87.7 (1)	C2—C1—C6	111,5 (4)
O1—Cu1—N2	160,0 (2)	C3—C2—C1	111.7 (5)
O2—Cu1—N1	161,3 (2)	C4—C3—C2	110,6 (5)
O1—Cu1—N1	84,3 (2)	C3—C4—C5	109,8 (5)
N2—Cu1—N1	88,6 (1)	C6—C5—C4	110,8 (5)
O2—Cu1—O3	119,0 (2)	N2—C6—C5	114,6 (4)
O1—Cu1—O3	97,5 (2)	N2—C6—C1	108,9 (4)
N2—Cu1—O3	99,6 (1)	C5—C6—C1	111,4 (4)
N1—Cu1—O3	79.7 (1)	N1—C7—C8	109,7 (4)
C8—O1—Cu1	112,0 (3)	O5—C8—O1	124,7 (5)
C12—O2—Cu1	113,3 (3)	O5—C8—C7	119,4 (5)
C10—O3—Cu1	107,3 (3)	O1—C8—C7	115,8 (5)
C9—N1—C7	110,7 (4)	N1—C9—C10	112,9 (4)
C9—N1—C1	111,6 (4)	O3—C10—O4	125,1 (5)
C7—N1—C1	115.2 (4)	O3—C10—C9	123.2 (5)
C9—N1—Cu1	112,0 (3)	O4—C10—C9	111,7 (4)
C7—N1—Cu1	99,9 (3)	N2—C11—C12	112.1 (4)
C1—N1—Cu1	106,7 (3)	O6—C12—O2	122,8 (4)
C13—N2—C11	111,3 (4)	O6—C12—C11	119,0 (4)
C13—N2—C6	111,9 (3)	O2—C12—C11	117,9 (4)
C11—N2—C6	111,4 (4)	N2—C13—C14	113,6 (4)
C13—N2—Cu1	117.2 (3)	O8—C14—O7	123,8 (5)
C11—N2—Cu1	104.1 (3)	O8—C14—C13	124,8 (5)
C6—N2—Cu1	100.3 (3)	O7—C14—C13	111,4 (4)
N1—C1—C2	114,4 (4)		

La collecte a été effectuée avec la largeur de balayage $(0,87 + 1,5\mathrm{tg}\theta)^\circ$. Les intensités ont été corrigées des facteurs de Lorentz–polarisation. La structure a été résolue par les méthodes directes (*SHELXS*86; Sheldrick, 1990) puis affinée par la méthode des moindres carrés (*SHELXL*93; Sheldrick, 1993). Un atome d'oxygène de l'eau *OW*2 a été affiné en isotrope.

Collection des données: *CAD*-4 *EXPRESS* (Duisenberg, 1992; Macicek & Yordanov, 1992; Enraf–Nonius, 1994). Affinement des paramètres de la maille: *CAD*-4 *EXPRESS*. Réduction des données: *MolEN* (Fair, 1990). Graphisme moléculaire: *ZORTEP* (Zsolnai, 1994). Logiciel utilisé pour préparer le matériel pour publication: *SHELXL*93.

Les auteurs remercient Dr A. Driss pour la collecte des données.

Des documents complémentaires concernant cette structure peuvent être obtenus à partir des archives électroniques de l'UICr (Référence: GS1006). Les processus d'accès à ces archives sont donné au dos de la couverture.

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Tris(ethylenediamine-*N*,*N*′)nickel(II) tetrathiomolybdate

Jan Ellermeier, Christian Näther and Wolfgang Bensch

Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Olshausenstraße 4, D-24089 Kiel, Germany. E-mail: wbensch@ac.uni-kiel.de

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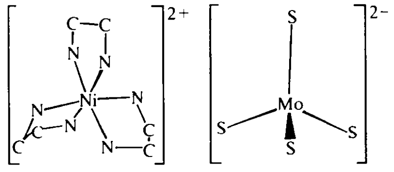
Abstract

The reaction of $(NH_4)_2[MoS_4]$, $NiBr_2$ and sulfur in 1,2-ethanediamine (en, $C_2H_8N_2$) under hydrothermal conditions yields red crystals of $[Ni(en)_3][MoS_4]$. The structure contains tetrahedral $[MoS_4]^{2-}$ anions and octahedral $[Ni(en)_3]^{2+}$ cations.

Comment

The structure determination of the title compound, (I), was undertaken as part of a project on the synthesis of new thiomolybdates under mild solvothermal conditions.



(I)

Due to the structural variety of thiomolybdate anions, ranging from the tetrahedral $[MoS_4]^{2-}$ anion to the more complex $[Mo_3S_{13}]^{2-}$ anion, synthetic investigations of the Mo–S system have been intensified in recent years. The chemical flexibility of the $[MoS_4]^{2-}$ anion is also demonstrated by the formation of complexes with elements of the Ni, Cu and Zn subgroups (Müller *et al.*, 1971; Callahan & Piliero, 1980).

The title compound was mentioned in an earlier communication, but no structural data were given (Spacu & Pop, 1938/39). The structure consists of isolated $[Ni(en)_3]^{2+}$ cations and $[MoS_4]^{2-}$ anions (Fig. 1). Each Ni^{2+} cation is sixfold coordinated by the six N atoms of the chelating en ligands within a distorted octahedron. The Ni—N distances are between 2.099 (3) and 2.135 (2) Å, and the *trans*-N—Ni—N angles range from 170.0 (2) to 173.2 (2)°. There are short intermolecular contacts between the amino H atoms of the en ligand and the S atoms of the $[MoS_4]^{2-}$ anion of 2.653 (3) (H4N· · ·S1), 2.655 (3) (H1N· · ·S2) and 2.680 (3) Å (H6N· · ·S3). The N—H· · ·S angles of 144.94 (8), 171.03 (7) and 146.02 (7)° indicate weak hydrogen bonding. In the $[MoS_4]^{2-}$ anion, the Mo—S distances are between 2.1766 (9) and 2.187 (2) Å. The MoS_4 tetrahedron is only slightly distorted; the S—Mo—S angles vary from 107.25 (4) to 110.52 (4)°. All structural parameters are in good agreement with those found in other compounds containing $[MoS_4]^{2-}$ anions, such as $Cs_2[MoS_4]$ (Raymond *et al.*, 1995) and $(NH_4)_2[MoS_4]$ (Schaefer *et al.*, 1964). Recently, we demonstrated that under solvothermal conditions the reaction of $(NH_4)_2[MoS_4]$ with different amines in aqueous ammonia solution can lead to the $[Mo_3S_{13}]^{2-}$ anion (Bensch & Schur, 1997). Further studies are in progress in order to obtain more information about the processes involved in the formation of thiomolybdates under mild solvothermal conditions and their consequences on product formation.

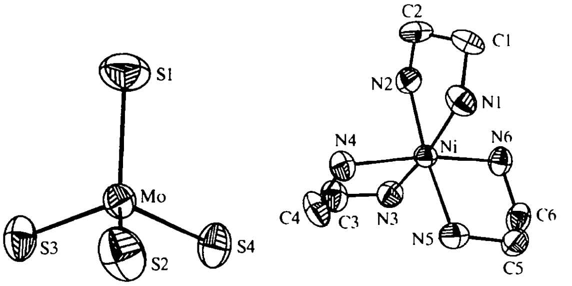


Fig. 1. The crystal structure of the title anion and cation, with displacement ellipsoids drawn at the 50% probability level (disordered C and H atoms have been omitted for clarity).

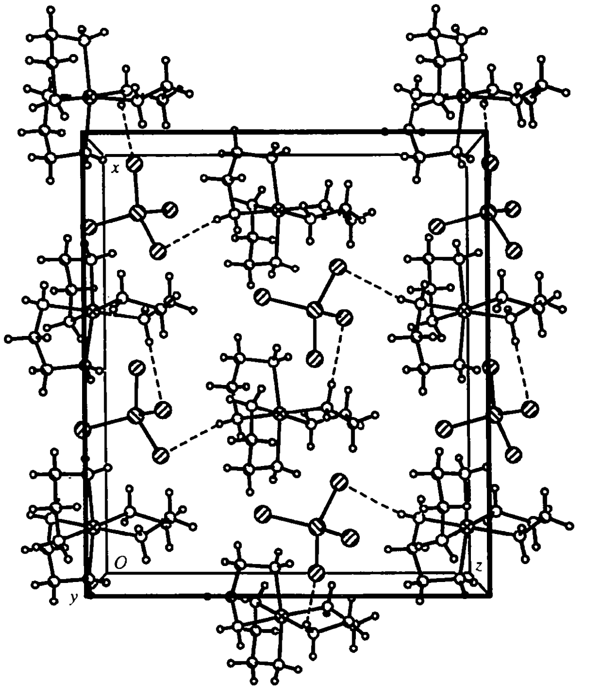


Fig. 2. A packing diagram, viewed along the *y* axis, with short intermolecular S· · ·H distances indicated by dotted lines.

Experimental

$(NH_4)_2[MoS_4]$, $NiBr_2$ and sulfur (0.50 mmol, molar ratio 1:2:3) were reacted in 1,2-ethanediamine (3 ml) in a Teflon-lined steel autoclave at 403 K for 7 d. The product was filtered off and washed with water. The yield of phase-pure product is about 70%.

Crystal data

$[Ni(C_2H_8N_2)_3][MoS_4]$
$M_r = 463.20$
Orthorhombic
$Pna2_1$
$a = 16.169\ (2)$ Å
$b = 7.6796\ (9)$ Å
$c = 14.153\ (2)$ Å
$V = 1757.4\ (4)$ Å^3
$Z = 4$
$D_x = 1.751$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 114 reflections
$\theta = 15–21°$
$\mu = 2.253$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.20 × 0.05 × 0.05 mm
Red

Data collection

Stoe AEDII four-circle diffractometer
ω/θ scans
Absorption correction: empirical *via* ψ scans (Siemens, 1990)
$T_{min} = 0.793$, $T_{max} = 0.893$
5093 measured reflections
2854 independent reflections
2301 reflections with $I > 2\sigma(I)$

$R_{int} = 0.024$
$\theta_{max} = 30.01°$
$h = -22 \rightarrow 17$
$k = -10 \rightarrow 0$
$l = -19 \rightarrow 1$
4 standard reflections
frequency: 120 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.050$
$S = 1.010$
2854 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0260P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.371$ e Å^{-3}
$\Delta\rho_{\min} = -0.328$ e Å^{-3}

Extinction correction: *SHELXL*93
Extinction coefficient: 0.00054 (15)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.003 (13)

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

Mo—S1	2.1766 (9)	Ni—N1	2.122 (3)
Mo—S2	2.1791 (10)	Ni—N5	2.123 (3)
Mo—S3	2.1849 (9)	Ni—N3	2.133 (3)
Mo—S4	2.1865 (11)	Ni—N6	2.133 (3)
Ni—N2	2.099 (3)	Ni—N4	2.135 (2)
S1—Mo—S2	109.67 (5)	N5—Ni—N3	94.64 (12)
S1—Mo—S3	110.29 (4)	N2—Ni—N6	93.57 (11)
S2—Mo—S3	109.09 (4)	N1—Ni—N6	91.89 (12)
S1—Mo—S4	109.96 (6)	N5—Ni—N6	82.61 (12)
S2—Mo—S4	107.25 (4)	N3—Ni—N6	91.21 (12)
S3—Mo—S4	110.52 (4)	N2—Ni—N4	93.43 (11)
N2—Ni—N1	81.71 (13)	N1—Ni—N4	96.24 (11)
N2—Ni—N5	173.21 (13)	N5—Ni—N4	91.09 (12)
N1—Ni—N5	92.77 (13)	N3—Ni—N4	81.47 (11)
N2—Ni—N3	91.04 (13)	N6—Ni—N4	169.96 (13)
N1—Ni—N3	172.28 (13)		

All N, S, C, Mo and Ni atoms were refined with anisotropic displacement parameters, except for C1′ and C2′, which are split positions of C1 and C2 and were therefore refined isotropically. The H atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters [$U_{\rm iso}$(N—H/C—H) = $1.2U_{\rm eq}$($C_{\rm methylene}/C_{\rm amine}$)] using a riding model with the parameters C—H = 0.97 and N—H = 0.90 Å. The absolute structure was determined and is in accordance with the selected setting [Flack *x* parameter = −0.003 (13)].

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1258). Services for accessing these data are described at the back of the journal.

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1,1′-Bis(3-phenylquinoxalin-2-yl)ferrocene dichloromethane solvate

S. Zaka Ahmed,[a] Christopher Glidewell[a] and George Ferguson[b]

[a]*School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, and* [b]*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1. E-mail: cg@st-andrews.ac.uk*

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Abstract

In 1,1′-bis(3-phenylquinoxalin-2-yl)ferrocene dichloromethane solvate, $[\mathrm{Fe}(\mathrm{C_{19}H_{13}N_2})_2]\cdot 0.9\mathrm{CH_2Cl_2}$, the two cyclopentadienyl rings are offset by only 21° from being completely eclipsed, so that the near parallel quinoxalinyl groups exhibit considerable overlap, with an interplanar spacing almost ideal for intramolecular π–π stacking interactions. The molecules form columns by means of intermolecular π–π stacking interactions.

Comment

The reaction of 1-ferrocenyl-2-phenylethanedione, FcCOCOPh [Fc is $(\mathrm{C_5H_5})\mathrm{Fe}(\mathrm{C_5H_4})$] with 1,2-diaminobenzene yields ferrocenyl(phenyl)quinoxaline (Zanello *et al.*, 1998). In a similar way, ferrocene-1,1′-diylbis(2-phenylethanedione), $\mathrm{Fe(C_5H_4COCOPh)_2}$, reacts with 1,2-diaminobenzene to yield 1,1′-bis(3-phenylquinoxalin-2-yl)ferrocene, $\mathrm{Fe[C_5H_4(C_8H_4N_2)C_6H_5]_2}$. This compound crystallized from diethyl ether/dichloromethane as a partial 0.9-dichloromethane solvate, (I), in which the solvent molecule is hydrogen bonded to one of the quinoxaline fragments by means of a C—H⋯N hydrogen bond (Fig. 1 and Table 2).