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Di-μ-aqua-bis[(trimethanol-*O*)sodium] *anti*-bis(μ-2-propanethiolato-*S*:*S*)bis[bis(2-propanethiolato-*S*)iron(II)] and bis(benzyltrimethylammonium) *anti*-bis(μ-2-propaneselenolato-*Se*:*Se*)bis[bis(2-propaneselenolato-*Se*)iron(II)]

Ralf Hauptmann,[a] Jörg Lackmann,[a] Changneng Chen[b] and Gerald Henkel[a]

[a] *Gerhard-Mercator-Universität Duisburg, Institut für Synthesechemie, Lotharstraße 1, 47048 Duisburg, Germany, and* [b] *Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China. E-mail: biohenkel@uni-duisburg.de*

(*Received 18 September 1998; accepted 4 March 1999*)

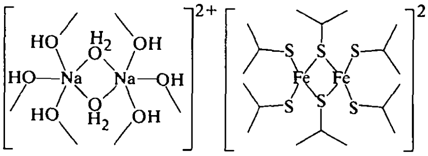
Abstract

In the $[Fe_2(S^iC_3H_7)_6]^{2-}$ and $[Fe_2(Se^iC_3H_7)_6]^{2-}$ complex anions of the title compounds, $[Na_2(CH_4O)_6(H_2O)_2][Fe_2(C_3H_7S)_6]$ and $(C_{10}H_{16}N)_2[Fe_2(C_3H_7Se)_6]$, the Fe atoms are coordinated by four chalcogen atoms in a distorted tetrahedral fashion. The FeE_4 tetrahedra of the Fe_2E_6 frameworks (E = S or Se) share a common edge. The central Fe_2E_2 unit is an exactly planar rhomb with acute $M—E—M$ angles. The oxidation state of iron is +2. The $[Fe_2(S^iC_3H_7)_6]^{2-}$ anion was crystallized with the novel counter-cation $[(MeOH)_3Na(H_2O)_2Na(MeOH)_3]^{2+}$.

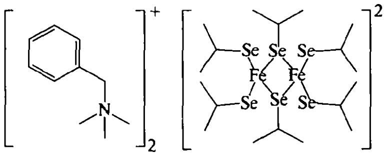
Comment

Iron–chalcogenolate and mixed iron–chalcogenide–chalcogenolate complexes have been studied extensively due to their importance as model compounds for enzyme centres (Holm *et al.*, 1990; Krebs & Henkel, 1991). The homoleptic iron(II)–chalcogenolate complexes with sterically unencumbered monofunctional chalcogenolate ligands contain iron in a tetrahedral chalcogen environment. Within this class of complexes, mononuclear (Millar *et al.*, 1982, 1984), dinuclear (Hagen & Holm, 1984) and tetranuclear species (Hagen *et al.*, 1982) are known. Recently, a novel type of a dinuclear iron–thiolate complex was described (Henkel & Chen, 1993). This complex consists of two approximately tetrahedral $[Fe(SR)_4]$ units which share a common face. The nucleophilicity of the ligands are expected to be of importance for stabilizing this unusual degree of condensation. Transition metal complexes with bitetrahedral M_2S_5 units have been described with secondary (Henkel & Weißgräber, 1992) and tertiary alkane chalcogenolate ligands (Weißgräber, 1994; Henkel & Weißgräber, 1999). Related complexes containing substituted thiophenolate groups are also known (Ruhlandt-Senge & Power, 1993; Silver & Millar, 1992).

During our investigations of the reaction behaviour of iron(II) towards secondary alkane chalcogenolate ligands, we were able to isolate the compounds $[(MeOH)_3Na(H_2O)_2Na(MeOH)_3][Fe_2(S^iC_3H_7)_6]$, (1), and $[BzMe_3N]_2[Fe_2(Se^iC_3H_7)_6]$, (2). Compound (1) is the product of the reaction of iron(II) chloride with sodium 2-propanethiolate in methanol, whereas (2) was obtained by reaction of iron(II) chloride with sodium 2-propaneselenolate and benzyltrimethylammonium bromide in acetonitrile.



(1)



(2)

Crystals of (1) and (2) consist of discrete $[Fe_2(E^iC_3H_7)_6]^{2-}$ (E = S or Se) complex anions and isolated counter-cations, namely $[(MeOH)_3Na(H_2O)_2Na(MeOH)_3]^{2+}$ in the case of (1) and $[BzMe_3N]^+$ in the case of (2). The $[Fe_2(S^iC_3H_7)_6]^{2-}$ and $[Fe_2(Se^iC_3H_7)_6]^{2-}$ anions have crystallographically imposed

Acta Crystallographica Section C
ISSN 0108-2701 © 1999

centres of inversion. In both cases, the iron centres (oxidation state +2) are surrounded by four chalcogen atoms in a distorted tetrahedral manner. The FeE_4 tetrahedra share a common edge. In (1), the S—Fe—S angles range from 101.49 (6) to 117.85 (6)°, giving an average of 109.26°. The average of the Se—Fe—Se angles in (2), which range from 105.25 (3) to 117.76 (2)°, is 109.35°. The bridge angles at the chalcogen atoms are somewhat larger than the value of 70.5° for an edge-shared perfect tetrahedral dimer. Consequently, the (μ-E)—Fe—(μ-E) angles are smaller than 109.5°. These values are comparable with those found in the corresponding tetramethylammonium salt of $[Fe_2(S^iC_3H_7)_6]^{2-}$ [80.8 (1) and 99.2 (1)°; Henkel & Chen, 1993] and in the analogous complex anion $[Fe_2(SEt)_6]^{2-}$ in its $[Et_4N]^+$ salt [77.7 (1) and 102.3 (1)°; Hagen & Holm, 1984]. The central Fe_2E_2 units are rhombs with longer $E\cdots E$ [3.676 (2) (E = S) and 3.962 (1) Å (E = Se)] and shorter Fe···Fe distances [3.003 (1) (E = S) and 3.026 (1) Å (E = Se)]. The $Fe_2(\mu$-$E)_2$ units are exactly planar. The alkyl groups adopt an *anti* configuration with respect to the central heterocyclic Fe_2E_2 ring system. As expected, the Fe—E bonds within these rings are longer than the terminal ones, and they are comparable to the values given in the literature (Henkel & Chen, 1993; Hagen & Holm, 1984). In both complexes, the isopropyl groups assume expected geometries.

The novel counter-cation of (1) consists of two Na atoms each coordinated by five O atoms (three from methanol, two from water) in a distorted trigonal–bipyramidal manner (average bond angle 106.9°). The NaO_5 polyhedra share a common edge. The bridging positions are occupied by water molecules. The sodium–oxygen bond lengths range from 2.274 (3) to 2.426 (3) Å, giving an average of 2.329 Å. These values are comparable to those observed in the (15-crown-5)–sodium cation (Ruhlandt-Senge & Müller, 1990). As expected, the Na—O bonds of the bridging water molecules are longer than those of the terminally bonded methanol ligands. The Na···Na distance within the binuclear cation is as long as 3.558 (4) Å.

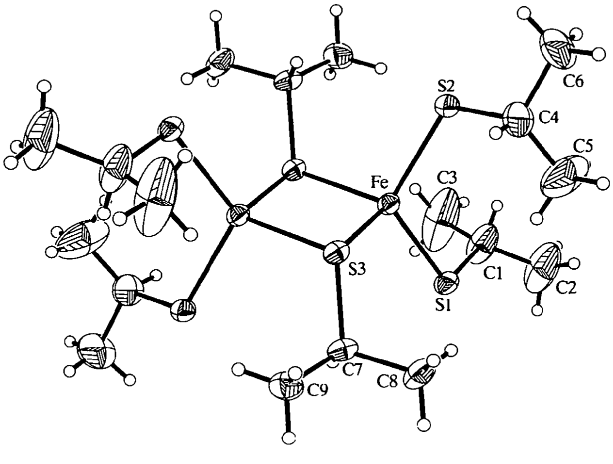


Fig. 1. The structure of the $[Fe_2(S^iC_3H_7)_6]^{2-}$ anion at the 35% probability level. H atoms are drawn as spheres of arbitrary radii.

The $[BzMe_3N]^+$ cations of (2) have their expected geometries. The N—C distances range from 1.485 (5) to 1.525 (5) Å, giving an average of 1.502 Å.

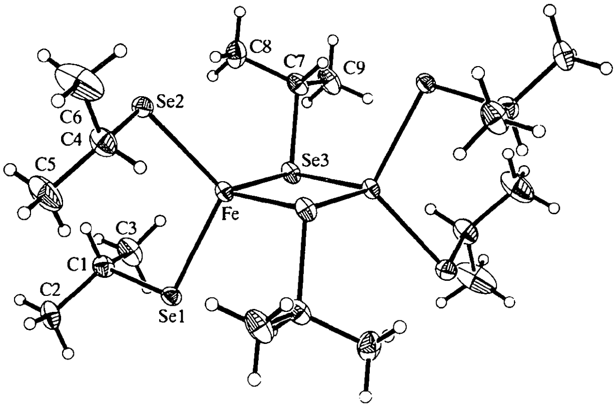


Fig. 2. The structure of the $[Fe_2(Se^iC_3H_7)_6]^{2-}$ anion at the 35% probability level. H atoms are drawn as spheres of arbitrary radii.

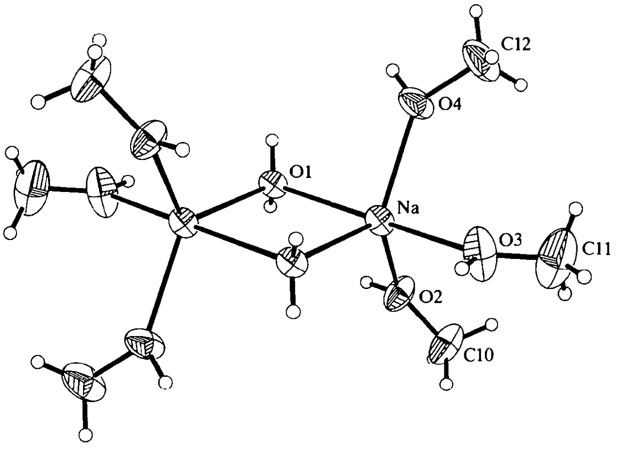


Fig. 3. The structure of the $[(MeOH)_3Na(H_2O)_2Na(MeOH)_3]^{2+}$ cation at the 35% probability level. H atoms are drawn as spheres of arbitrary radii.

Experimental

All operations were performed under a dinitrogen atmosphere in a glove box. Sodium 2-propanethiolate and sodium 2-propaneselenolate were prepared by reaction of sodium with the corresponding alkane chalcogenol in tetrahydrofuran. The white solid was collected by filtration, washed with ether, and dried *in vacuo*. For the preparation of $[Na_2(MeOH)_6$-

$(H_2O)_2][Fe_2(S^iC_3H_7)_6]$, (1), sodium 2-propanethiolate (2.45 g, 25 mmol) was dissolved in methanol (15 ml) and treated dropwise with a solution of iron(II) chloride tetrahydrate (1.00 g, 5 mmol) in methanol (10 ml). The reaction mixture was stirred for 4 h and filtered. Brown crystals of (1) were obtained by keeping the filtrate at 275 K. For the preparation of $[BzMe_3N]_2[Fe_2(Se^iC_3H_7)_6]$, (2), a suspension of iron(II) chloride (0.63 g, 5 mmol) in acetonitrile (50 ml) was treated with sodium 2-propaneselenolate (2.17 g, 15 mmol). The brown slurry was stirred for 1 h and benzyltrimethylammonium bromide (1.15 g, 5 mmol) was added. After stirring for a further 24 h, the brown slurry was filtered. Cooling the filtrate to 248 K afforded (2) as brown crystals.

Compound (1)

Crystal data

$[Na_2(CH_4O)_6(H_2O)_2]$-$[Fe_2(C_3H_7S)_6]$
$M_r = 836.84$
Triclinic
$P\bar{1}$
$a = 10.516\ (7)$ Å
$b = 11.484\ (6)$ Å
$c = 11.705\ (7)$ Å
$\alpha = 113.89\ (4)°$
$\beta = 112.11\ (4)°$
$\gamma = 95.83\ (4)°$
$V = 1142.3\ (14)$ Å^3
$Z = 1$
$D_x = 1.216$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 18 reflections
$\theta = 10$–$20°$
$\mu = 0.962$ mm^{-1}
$T = 150$ K
Column
0.65 × 0.23 × 0.21 mm
Brown

Data collection

Siemens *P4/RA* diffractometer
ω scans
Absorption correction: ψ scan (*SHELXTL-Plus*; Sheldrick, 1990)
$T_{min} = 0.682$, $T_{max} = 0.818$
8099 measured reflections
4982 independent reflections

3914 reflections with $F > 4\sigma(F)$
$R_{int} = 0.030$
$\theta_{max} = 27.00°$
$h = -13 \rightarrow 6$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 14$
1 standard reflection every 99 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.045$
$wR(F^2) = 0.120$
$S = 1.040$
4982 reflections
197 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0580P)^2 + 0.6249P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.713$ e Å^{-3}
$\Delta\rho_{min} = -0.426$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. *C*)

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

Fe—S1	2.295 (2)	Na—O2	2.284 (3)
Fe—S2	2.297 (2)	Na—O3	2.310 (4)
Fe—S3	2.368 (2)	Na—O1^{ii}	2.349 (3)
Fe—S3^{i}	2.378 (2)	Na—O1	2.426 (3)
Na—O4	2.274 (3)	Na—Na^{ii}	3.558 (4)
S1—Fe—S2	117.85 (6)	O4—Na—O2	116.27 (12)
S1—Fe—S3	109.12 (7)	O4—Na—O3	95.45 (13)
S2—Fe—S3	108.89 (6)	O2—Na—O3	101.38 (13)
S1—Fe—S3^{i}	112.34 (5)	O4—Na—O1^{ii}	124.26 (12)
S2—Fe—S3^{i}	105.86 (7)	O2—Na—O1^{ii}	117.35 (11)
S3—Fe—S3^{i}	101.49 (6)	O3—Na—O1^{ii}	88.19 (11)
C1—S1—Fe	107.7 (2)	O4—Na—O1	85.11 (10)
C4—S2—Fe	111.06 (15)	O2—Na—O1	86.84 (10)
C7—S3—Fe	110.37 (12)	O3—Na—O1	170.44 (11)
C7—S3—Fe^{i}	109.98 (11)	O1^{ii}—Na—O1	83.66 (10)
Fe—S3—Fe^{i}	78.51 (6)		

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $1 - x, -y, 1 - z$.

Compound (2)

Crystal data

$(C_{10}H_{16}N)_2[Fe_2(C_3H_7Se)_6]$
$M_r = 1144.45$
Triclinic
$P\bar{1}$
$a = 10.322\ (8)$ Å
$b = 10.482\ (7)$ Å
$c = 13.259\ (8)$ Å
$\alpha = 97.640\ (5)°$
$\beta = 103.98\ (5)°$
$\gamma = 115.430\ (5)°$
$V = 1210.5\ (15)$ Å^3
$Z = 1$
$D_x = 1.570$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 18 reflections
$\theta = 10$–$20°$
$\mu = 5.135$ mm^{-1}
$T = 150$ K
Column
0.63 × 0.24 × 0.14 mm
Brown

Data collection

Siemens *P4/RA* diffractometer
ω scans
Absorption correction: ψ scan (*SHELXTL-Plus*; Sheldrick, 1990)
$T_{min} = 0.294$, $T_{max} = 0.487$
5578 measured reflections
5260 independent reflections

4258 reflections with $F > 4\sigma(F)$
$R_{int} = 0.031$
$\theta_{max} = 27.03°$
$h = 0 \rightarrow 13$
$k = -13 \rightarrow 12$
$l = -16 \rightarrow 16$
1 standard reflection every 99 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.034$
$wR(F^2) = 0.083$
$S = 1.016$
5260 reflections
223 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 1.5412P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.928$ e Å^{-3}
$\Delta\rho_{min} = -0.590$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0017 (4)
Scattering factors from *International Tables for Crystallography* (Vol. *C*)

Table 2. *Selected geometric parameters (Å, °) for (2)*

Fe—Se1	2.4359 (13)	Fe—Se3	2.4957 (15)
Fe—Se2	2.429 (2)	Fe—Se3^{i}	2.4895 (15)
Se2—Fe—Se1	110.58 (3)	C1—Se1—Fe	100.04 (11)
Se2—Fe—Se3^{i}	110.13 (6)	C4—Se2—Fe	99.11 (14)
Se1—Fe—Se3^{i}	105.85 (5)	C7—Se3—Fe^{i}	103.53 (12)

Se2—Fe—Se3	117.76 (2)	C7—Se3—Fe	111.06 (12)
Se1—Fe—Se3	106.51 (5)	Fe^{i}—Se3—Fe	74.75 (1)
Se3^{i}—Fe—Se3	105.25 (3)		

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

Crystals of the title compounds were mounted on a glass capillary with silicone grease and quickly put into the cold nitrogen stream of the cooling device of the goniometer. The intensity data were corrected for Lorentz, polarization and absorption effects. After anisotropic refinement of this model, H atoms were added in idealized positions. One common isotropic displacement parameter per group was refined for the otherwise riding H atoms.

For both compounds, data collection: *P3 Software* (Siemens, 1990*a*); cell refinement: *P3 Software*; data reduction: *XDISK* (Siemens, 1990*b*); program(s) used to solve structures: *SHELXTL-Plus* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXL93*.

Financial support from the Deutsche Forschungsgemeinschaft, the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF), and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1304). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1087–1090

Diaquabis(2,2′-bipyridine-*N*,*N*′)nickel(II) diperchlorate

YOLANDA RODRÍGUEZ-MARTÍN, JAVIER GONZÁLEZ-PLATAS AND CATALINA RUIZ-PÉREZ

Grupo de Rayos X, Departamanto Física Fundamental II, Universidad de La Laguna, Avda. Astrofísico Fco. Sánchez s/n, E-38204 La Laguna, Tenerife, Spain. E-mail: caruiz@ull.es

(*Received 15 October 1998; accepted 9 March 1999*)

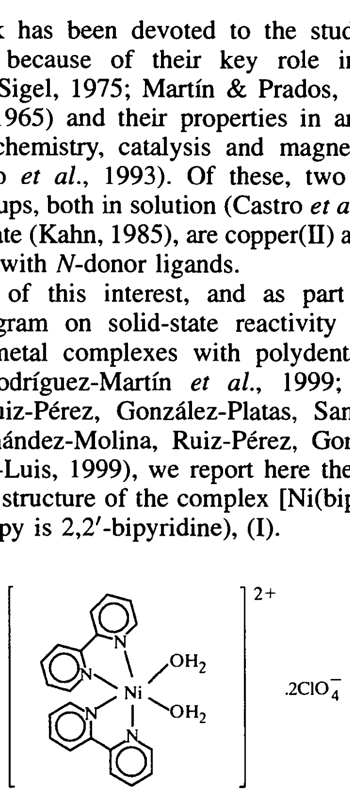
Abstract

The structure of the title compound, $[Ni(C_{10}H_8N_2)_2(H_2O)_2](ClO_4)_2$, consists of monomeric $[Ni(bipy)_2(H_2O)_2]^{2+}$ cations (bipy is 2,2′-bipyridine) and perchlorate anions. The Ni atom has octahedral coordination comprised of two water O atoms and four N atoms from two chelating bipy groups [mean values: Ni—O_{water} 2.089 (5) and Ni—N_{bipy} 2.066 (6) Å]. Hydrogen bonding plays an important role in consolidating the crystal structure.

Comment

Much work has been devoted to the study of ligand complexes because of their key role in biological processes (Sigel, 1975; Martín & Prados, 1974; Bauer & Smith, 1965) and their properties in areas such as analytical chemistry, catalysis and magneto-chemistry (De Munno *et al.*, 1993). Of these, two of the best studied groups, both in solution (Castro *et al.*, 1991) and the solid state (Kahn, 1985), are copper(II) and nickel(II) complexes with *N*-donor ligands.

In view of this interest, and as part of our research program on solid-state reactivity of first-row transition metal complexes with polydentate *N*-donor ligands (Rodríguez-Martín *et al.*, 1999; Hernández-Molina, Ruiz-Pérez, González-Platas, Sanchiz *et al.*, 1999; Hernández-Molina, Ruiz-Pérez, González-Platas & Lorenzo-Luis, 1999), we report here the preparation and crystal structure of the complex $[Ni(bipy)_2(H_2O)_2](ClO_4)_2$ (bipy is 2,2′-bipyridine), (I).



(I)