Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1114). Services for accessing these data are described at the back of the journal.

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Na2[(μ-N,N'-C10H12N2O8)(μ-O)(μ-S)-Mo2O2].2H2O

Edward J. Valente,[a] Jeffrey D. Zubkowski[b] and Kenneth W. Hicks[c]

[a]*Department of Chemistry, Mississippi College, Clinton, MS 39058-4036, USA,* [b]*Department of Chemistry, Jackson State University, Jackson, MS 39217, USA, and* [c]*Department of Chemistry, Norfolk State University, Norfolk, VA 23504, USA. E-mail: valente@mc.edu*

## Abstract

Analogs of bridging-oxo complexes of dimolybdenum(V) where sulfide replaces one or both bridges are known. After reduction of $[(MoO_3)_2(\mu\text{-edta})]^{4-}$ (edta is ethylenediaminetetraacetate) with dithionite at pH 6 in the absence of dioxygen, slow replacement of bridging oxide with sulfide produced *in situ* produces the title

compound, disodium μ-(ethylenediaminetetraacetato)-μ-oxo-μ-sulfido-bis[oxomolybdenum(V)] dihydrate, Na_2-$[Mo_2O_3S(C_{10}H_{12}N_2O_8)].2H_2O$. IR and NMR spectroscopic analyses are consistent with an unsymmetrical complex. In the molecular structure, the Mo centers have distorted octahedral coordination, with an average Mo—S distance of 2.320(1) Å and an average bridging Mo—O distance of 1.938(3) Å. The Mo···Mo contact distance [2.666(1) Å] is intermediate between those in comparable di-μ-oxo and di-μ-sulfido complexes. The two Na^+ ions have five and six nearest O atoms in their coordination spheres, which each include one disordered water oxygen.

Comment

Complexes of ethylenediaminetetraacetate (edta) with bridged dinuclear molybdenum(V) cores are known with a variety of bridging and coordinated group types. Chief among bridging chalcogenides are di-μ-oxo, di-μ-sulfido, and ordered μ-oxo-μ-sulfido. Spectroscopic (IR and electronic) properties are sensitive to the type of bridging group (Ott *et al.*, 1977; Shibahara *et al.*, 1982, 1983, 1987; Barber *et al.*, 1996). With coordinated edta, Mo^V forms all three chalcogenide bridge types (Ott *et al.*, 1977). $[Mo_2O_2(\mu\text{-O})_2(\mu\text{-edta})]^{2-}$ can be formed from $[MoOCl_5]^{2-}$ and $Na_2[H_2edta].2H_2O$ (Ikari *et al.*, 1989). Di-μ-oxo and di-μ-sulfido complexes can be made by reacting Mo^V in aqueous acid (pH 5–6) with water or aqueous H_2S/Na_2S, respectively, followed by treatment with edta (Ott *et al.*, 1977). A single bridging oxide in the Mo^{VI}-edta complex can be replaced stoichiometrically by H_2S or polysulfide (Spivak & Dori, 1970). Replacement of oxo with sulfido in the Mo^V-edta complex has not been verified. In the present case, (I), replacement of one bridging oxo ligand of the di-μ-oxo–edta complex of oxomolybdenum(V) is accomplished slowly with sulfur originating in the form of the relatively oxidized dithionite.

(I)
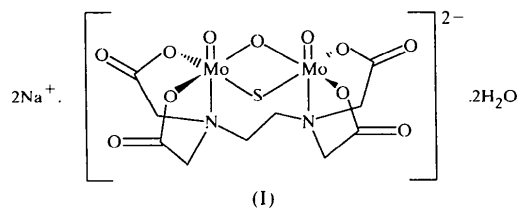
It has been established that edta stabilizes molybdenum(V) in solution below pH 7 (Pescok & Sawyer, 1956). Synthesis of the dihydrated sodium salt of the di-μ-oxo–edta complex (Ott & Schultz, 1975) was preceded by the synthesis and structure determination of the dihydrated dicaesium di-μ-sulfido–edta salt (Spivak & Dori, 1973) formed from a dimeric Mo^{VI}-edta complex, and followed by a report of the crystal structure of the hydrated barium di-μ-oxo–edta salt (Khalil & Sheldrick,

1978). The first direct mixed μ-oxo-μ-sulfido preparations were reported by Ott *et al.* (1977). After preparation of the bridged $[MoO_2(\mu\text{-S})(\mu\text{-O})]^{2+}$ complex at low pH, edta was added at pH 6 to form the complex anion. Reactivity of hydrogen sulfide with the already formed $[MoO_2(\mu\text{-O})_2(\text{edta})]^{2-}$ complex was reported to occur 'slowly or not at all'. The product of the slow reaction of $[MoO_2(\mu\text{-O})_2(\text{edta})]^{2-}$ with a source of H_2S is shown here to be the μ-oxo-μ-sulfido analog, (I), reported by Ott *et al.* (1977). Its IR spectrum shows the characteristic splitting (two bands plus one unknown feature) of $\nu(\text{Mo=O})$ in the vicinity of $950\,cm^{-1}$. The inherent asymmetry of the complex anion is confirmed by the NMR analysis. While it is likely that the anion undergoes a fast conformational interconversion involving the ethylenic link and carboxylate arms, an inequivalence of the various methylene environments is demonstrated in that the methylene C atoms of the edta ligand and their protons show four environments, ethylenic C and H atoms show two NMR environments, and carboxyl C atoms show four environments.

Other $[MoO_2(\mu\text{-O})(\mu\text{-S})]^{2+}$ core structures have been reported with pairs of bidentate coordinating ligands [oxalato (Shibahara *et al.*, 1982), cysteinato (Shibahara *et al.*, 1987) and $S_2Fe_2(CO)_6$ (Barber *et al.*, 1996)], and with four monodentate ligands (isothiocyanato; Shibahara *et al.*, 1983) on Mo centers. The molecular structure of the anion in (I) is presented in Fig. 1. The structure of (I) exhibits a single tetradentate ligand embracing both metal atoms, which are bridged by O and S atoms. Each Mo center of the complex is in an approximate octahedral coordination with an N atom and two carboxylate O atoms of the edta, a bridging and a monodentate oxide, and a bridging sulfide. Bond distances and angles in (I) are similar to values observed in related complexes, in which Mo—S(bridging) bond distances are 2.28–2.33 Å and Mo—O(bridging) distances are 1.91–2.00 Å; Mo···Mo distances lengthen in the edta complexes on replacement of bridging oxides with sulfides, from 2.55 up to 2.77 Å (see Tables 1 and 2). In particular, relevant bond

distances and angles in (I) compare well with those in the μ-oxalato–bis(oxalato) analog (Shibahara *et al.*, 1982), in which the bridging O and S atoms are also *trans* to the carboxylate O atoms.

Na^+ ions in (I) are coordinated to the water molecules of hydration and to the (distal) edta carboxylate O atoms (Fig. 2) that are not coordinated to Mo centers. One of the water molecules, O1W, is disordered over two essentially equivalently weighted locations separated by 0.71 (1) Å. One Na^+ ion, Na1, makes contact with five O atoms, including the disordered water, at distances of 2.35 (1)–2.58 (1) Å, and two other O atoms at distances of 2.96 (1) and 3.06 (1) Å. The nearby O atoms are described by distorted square-planar coordination geometry around Na1. Considering the slight elongation of Na1 in roughly the same direction as the O1W/O1WA disorder, it is thought possible that Na1 is also slightly disordered, but by an amount below the resolution of the determination. The other Na^+ ion is six-coordinate with essentially octahedral geometry and all six Na···O distances are in the range 2.35 (1)–2.52 (1) Å. Water O atoms occupy adjacent (or *cis*) locations in the Na coordination spheres; both also serve as bridges between Na^+ ions.
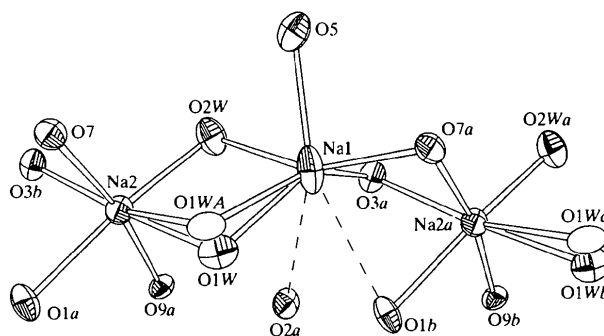

Fig. 2. Displacement ellipsoid plot (50% probability enclosure) of the cations and their coordinated O atoms, including the disordered water.

Experimental

The Mo^{VI}–edta complex was prepared *in situ* according to the method of Chaudhury (1983) by combining two molar equivalents of $Na_2MoO_4.2H_2O$ with one equivalent of $Na_2[H_2\text{edta}]$ in water. After deoxygenating the solution with gaseous N_2, the solution of $[(MoO_3)_2(\text{edta})]^{4-}$ was cooled to 278 K and the pH was adjusted to 6 with $1\,M$ NaOH or $HClO_4$ as needed. An equivalent of $Na_2S_2O_4$ was added and the mixture stirred under N_2 for 12 h. The deep-orange–red solution was filtered and an equal volume of 2-propanol mixed with the aqueous phase and the solution cooled to 263 K. After several days, the alcohol supernatant was removed. The volume was replaced by adding an equal volume of water and 2-propanol, and mixing. The mixture was cooled again to 263 K for several days. The supernatant was again removed and the solution allowed to warm to room temperature. Red–orange crystals of (I), with composition
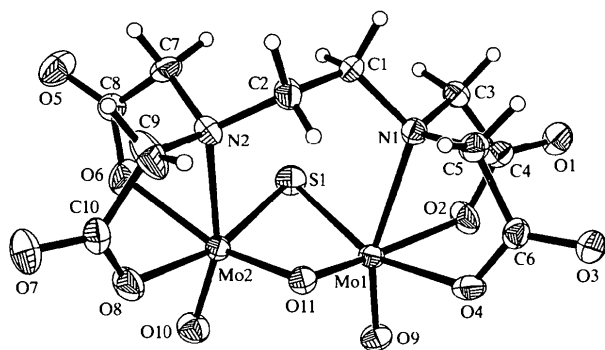

Fig. 1. Displacement ellipsoid plot (50% probability enclosure) of the complex anion of (I).

$Na_2[Mo_2O_3S(C_{10}H_{12}N_2O_8)].2H_2O$, formed over an extended period from which single-crystal diffraction-quality specimens were retrieved. IR spectrum in KBr pellet (cm^{-1}): 951 (s, Mo=O), 935 (m, Mo=O), 917 (s, unknown band), 752 (m, Mo—μ-O), 478 (m, Mo—μ-O), 455 (m, Mo—μ-S); ^{1}H NMR spectrum of the salt (D_2O, 300 K, in p.p.m., downfield from internal reference DSS): 2.55 (broad singlet, 4H, CH_2N), 3.03, 3.20, 3.48, 3.65 (broad singlets, 2H each, CH_2CO); ^{13}C NMR spectrum: 57.6, 58.5 (CH_2N), 64.2, 65.1, 68.8, 69.2 (CH_2CO), 179.98, 180.29, 180.38, 180.40 (CO_2).

Crystal data

$Na_2[Mo_2O_3S(C_{10}H_{12}N_2O_8)].2H_2O$

$M_r = 642.17$

Monoclinic

Cc

$a = 11.059\,(3)$ Å

$b = 7.862\,(2)$ Å

$c = 21.828\,(4)$ Å

$\beta = 97.17\,(2)°$

$V = 1883.0\,(8)$ Å^3

$Z = 4$

$D_x = 2.265$ Mg m^{-3}

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 40 reflections

$\theta = 18-30°$

$\mu = 1.559$ mm^{-1}

$T = 295\,(2)$ K

Prism

$0.40 \times 0.15 \times 0.10$ mm

Red–orange

Data collection

Siemens $P3$ diffractometer

ω scans

Absorption correction: refined from ΔF (Blessing, 1995)

$T_{min} = 0.57$, $T_{max} = 0.86$

7149 measured reflections

6973 independent reflections

3893 reflections with $I > 2\sigma(I)$

$R_{int} = 0.036$

$\theta_{max} = 42.48°$

$h = 0 \rightarrow 20$

$k = 0 \rightarrow 14$

$l = -41 \rightarrow 41$

3 standard reflections every 97 reflections intensity decay: $-0.01\,(2)\%$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.115$

$S = 0.788$

6973 reflections

281 parameters

H atoms riding, water H atoms not found or calculated

$w = 1/[\sigma^2(F_o^2) + (0.0570P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 1.44$ e Å^{-3} (0.91 Å from Mo1)

$\Delta\rho_{min} = -1.53$ e Å^{-3} (0.58 Å from Mo1)

Extinction correction: none

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

Absolute structure: Flack (1983)

Flack parameter = $-0.04\,(5)$

Table 1. *Comparison of selected Mo—(bridging ligand) geometric parameters (Å, °) in Mo^V complex anions*

For $[(\mu\text{-edta})XMo_2O_2]^{2-}$ complexes

	$(\mu\text{-S})_2{}^a$	$(\mu\text{-O})_2{}^b$	$(\mu\text{-O})(\mu\text{-S})^c$	$(\mu\text{-S})(ox)_2{}^d$
			X	
Mo=O	1.683(6)	1.76(1)	1.687(4)	1.689(5)
		1.73(1)	1.679(4)	1.681(5)
		1.68(1)		
		1.68(1)		
Mo—μ-S	2.289(1)		2.321(2)	2.325(2)
			2.320(2)	2.326(2)

Mo—μ-O	1.89(1)	1.935(5)	1.918(5)
	1.98(1)	1.941(5)	1.934(5)
	1.92(1)		
	2.00(1)		
Mo···Mo'	2.779(1)	2.548(1)	2.666(1)	2.667(1)
		2.557(1)		
Mo—μ-O—Mo'	84.3(4)	86.9(2)	87.7(2)
	81.0(4)		
	83.6(4)		
	80.5(4)		
Mo—μ-S—Mo'	75.4(1)	70.11(5)	70.0(1)
	75.0(1)		

Notes: edta is ethylenediaminetetraacetato(4−); ox is oxalato(2−). References: (a) Spivak & Dori (1973); (b) this work; (c) Ikari *et al.* (1989); (d) Shibahara *et al.* (1982).

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

Mo1—O9	1.687 (4)	Mo2—O10	1.679 (4)
Mo1—O11	1.935 (4)	Mo2—O11	1.941 (5)
Mo1—O4	2.122 (5)	Mo2—O6	2.112 (5)
Mo1—O2	2.128 (4)	Mo2—O8	2.121 (5)
Mo1—S1	2.3207 (17)	Mo2—S1	2.3199 (17)
Mo1—N1	2.412 (5)	Mo2—N2	2.443 (5)
Mo1···Mo2	2.6655 (7)	O1*W*···O1*WA*	0.713 (12)
Mo2—S1—Mo1	70.11 (5)	Mo1—O11—Mo2	86.9 (2)

Data collection: *P3* (Siemens, 1989). Cell refinement: *P3*. Data reduction: *XDISK* in *P3*. Program(s) used to solve structure: *SHELXS93* (Sheldrick, 1993). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* in *P3*. Software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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A Linear Trinuclear Ni^{II}–Mn^{II}–Ni^{II} Complex with a μ-Acetato Bridge: Bis{(μ-acetato)[μ-bis(salicylidene)-1,3-propanediaminato](N,N-dimethylformamide)nickel(II)}manganese(II)†

FILIZ ERCAN[a] AND ORHAN ATAKOL[b]

[a]*Department of Engineering Physics, Hacettepe University, Beytepe 06532, Ankara, Turkey, and* [b]*Department of Chemistry, Ankara University, Tandoğan 06100, Ankara, Turkey. E-mail: filiz@eti.cc.hun.edu.tr*

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Abstract

The structure of the title compound, [Mn{Ni(C$_2$H$_3$O$_2$)-(C$_3$H$_7$NO)(C$_{17}$H$_{16}$N$_2$O$_2$)}$_2$], consists of a linear hetero-trinuclear unit with a central Mn^{II} ion. Both the terminal Ni^{II} ions and the central Mn^{II} ion have irregular octahedral coordinations. The central Mn^{II} ion is located on the inversion centre. Each pair of metal ions is triply bridged *via* O atoms from the N,N'-bis(salicylidene)-1,3-propanediaminato (SALPD^{2-}) ligands and from the acetate groups. The coordination around the Mn^{II} ion consists of four O atoms from two SALPD^{2-} ligands, and one O atom from each of two acetate ligands. The coordination of each terminal Ni^{II} ion is provided by the two O and two N atoms from a SALPD^{2-} ligand, and by one O atom each from a bridging acetate and a dimethylformamide (dmf) ligand. The dmf and acetate ligands are *trans* about the terminal Ni^{II} ion. The average Ni—O and Ni—N distances for the terminal ions are 2.071 (2) and 2.026 (2) Å, respectively. The Ni⋯Mn distance is 3.133 (2) Å.

Comment

Trinuclear metal complexes of the first transition series are of interest because of the magnetic super-exchange interactions between their bridged metal ions. The ligand stereochemistry around the paramagnetic metal ions and the structure of the O-atom bridges influence these magnetic exchange interactions. The synthesis and magnetic properties of trinuclear complexes with the general formulae [MCu$_2$(CH$_3$CO$_2$)$_2$-(SALPD)$_2$] (M = Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+}) and [MNi$_2$(CH$_3$CO$_2$)$_2$(SALPD)$_2$] (M = Mg^{2+}, Mn^{2+}, Co^{2+} or Ni^{2+}), where H$_2$SALPD represents N,N'-bis(salicylidene)-1,3-propanediamine, have been reported previously (Fukuhara *et al.*, 1990). In these groups of compounds, only the structure of [Zn{(CH$_3$CO$_2$)-(SALPD)Cu}$_2$] has been determined by X-ray diffraction (Fukuhara *et al.*, 1990). Structural studies of the complexes formulated as [M_3(SALPN)$_2$(CH$_3$CO$_2$)$_2$].-2dmf [M = Co^{2+} or Fe^{2+}; SALPN = N,N'-bis(salicylidene)-2,2-dimethylpropylenediamine; dmf = dimethylformamide] have been reported by Gerli *et al.* (1991). [Ni$_3${(CH$_3$CO$_2$)(SALPD)(dmso)}$_2$] (dmso = dimethyl sulfoxide) (Ülkü, Ercan *et al.*, 1997) and [Cd{Ni(CH$_3$-CO$_2$)(SALPD)(dmf)}$_2$] (Ülkü, Tahir *et al.*, 1997) have also been studied in this laboratory.

We describe here the structure of a new linear heterometal trinuclear complex, [Mn{Ni(CH$_3$CO$_2$)-(SALPD)(dmf)}$_2$], (I). The structure consists of centro-symmetric trimers, with the central metal ion, Mn^{II}, occupying the inversion centre at the origin. The coordination around Mn is a distorted octahedron, involving four bridging O atoms from two SALPD^{2-} ligands in the equatorial plane and an O atom from each of the two bridging acetate groups in the axial positions. The Mn—O bond lengths range from 2.163 (1) to 2.194 (2) Å, the shortest bond being to the SALPD^{2-} O1 atom. The Ni—N1 and Ni—N2 bond lengths are 2.016 (2) and 2.036 (2) Å, respectively. The two inversion-related Ni^{II} ions also have a distorted octahedral environment. The four equatorial positions are occupied by the two N and the two O atoms from the SALPD^{2-} ligand. The axial positions of this distorted octahedron are completed by the O atom from the bridging acetate and another O atom from the dmf. The terminal Ni atom is 0.0632 (3) Å out of the equatorial plane defined by atoms N1, O1, N2 and O2.

(I)
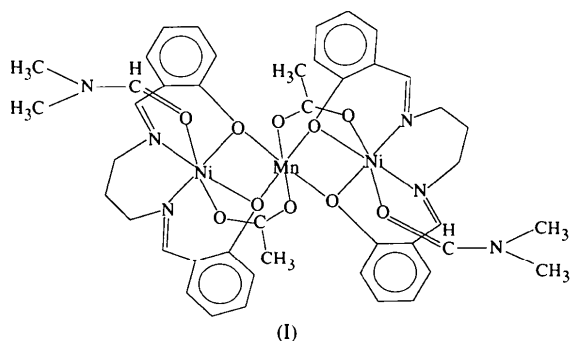
The dihedral angle between the two equatorial planes (O1, O2, O1^i, O2^i and O1, O2, N1, N2) of the neighbouring polyhedra is 23.68 (8)° [symmetry code: