metal-organic compounds

Poly[μ_2-L-alanine-μ_3-nitrato-sodium(I)]

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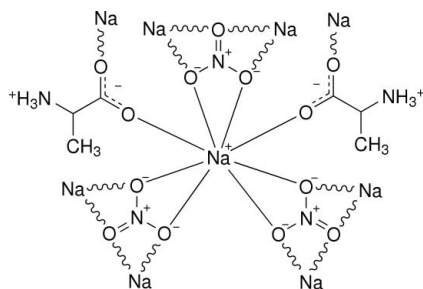Correspondence e-mail: luc.vanmeervelt@chem.kuleuven.be

The title compound, $[Na(NO_3)(C_3H_7NO_2)]_n$, was obtained unintentionally as the product of an attempted reaction of sodium molybdate in aqueous solution and the amino acid L-alanine (ala), in order to obtain a γ-type octamolybdate, $Na_4[Mo_8O_{26}(ala)_2].18H_2O$, coordinated by L-alanine. The coordination geometry around the Na atom can be considered as trigonal–bipyramidal, with three bidentate nitrate anions coordinating through their O atoms and two L-alanine molecules each coordinating through one carboxylate O atom.

Related literature

For related literature, see: Allen (2002); Cindrić *et al.* (2006); Fujita *et al.* (1992); Pope (1983); Pope & Mueller (1994); Rajagopal *et al.* (2003); Rhule *et al.* (1998); Yamase (1993); Yamase *et al.* (1996, 1999).

Experimental

Crystal data

$[Na(NO_3)(C_3H_7NO_2)]$	V = 663.55 (7) Å^3
M_r = 174.10	Z = 4
Orthorhombic, $P2_12_12_1$	Cu $K\alpha$ radiation
a = 5.3477 (3) Å	μ = 1.98 mm^{-1}
b = 9.1719 (6) Å	T = 100 (2) K
c = 13.5284 (8) Å	$0.5 \times 0.3 \times 0.2$ mm

Data collection

Bruker SMART 6000 diffractometer	6562 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)	1241 independent reflections
T_{min} = 0.431, T_{max} = 0.673	1170 reflections with $I > 2\sigma(I)$
	R_{int} = 0.048

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037	$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$wR(F^2)$ = 0.092	$\Delta\rho_{min}$ = -0.47 e Å^{-3}
S = 1.10	Absolute structure: Flack (1983), 480 Friedel pairs
1241 reflections	Flack parameter: 0.10 (12)
122 parameters	
Only H-atom coordinates refined	

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Comment

Polyoxometalates (POMs) can be considered as oligomeric aggregates of metal cations, bridged by oxide anions that form by self-assembly processes (Rhule *et al.*, 1998). There are two generic families of POMs, the isopolyoxometalates, that contain only d^0 metal cations and oxide anions and the heteropolyoxometalates, that contain one or more *p*-, d-, or f-block heteroatoms in addition to the other ions (Pope, 1983; Rhule *et al.*, 1998).

The medicinal features of these compounds cover a variety of important biological activities, such as the inhibition of specific enzymes or antiviral and antitumor activity (Pope and Mueller, 1994; Rhule *et al.*, 1998). When used in combination with β-lactam antibiotics, polyoxotungstates enhance the antibiotic effectiveness against otherwise resistant strains of bacteria (Yamase *et al.*, 1996). The heptamolybdate, $[NH_3Pr^i]_6[Mo_7O_{24}]\cdot3H_2O$ had shown a potent *in vivo* antitumor activity (Fujita, *et al.*, 1992), which has been explained by repeated redox cycles of $[Mo_7O_{24}]^{6-}$ in the tumor cells (Yamase, 1993).

The biomedical investigations of polyoxomolybdates containing amino acids or even peptides (Yamase *et al.*, 1999) have been focused upon finding polyoxomolybdates with both improved activity against cancer and clinical safety profiles.

The reported structure $Na(NO_3)C_3H_7NO_2$ was obtained unintentionally as the product of an attempted reaction of sodium molybdate in aqueous solution and the amino acid *L*-alanine, in order to obtain a γ type octamolybdate, coordinated by *L*-alanine $Na_4[Mo_8O_{26}(ala)_2].18H_2O$ (Cindrić *et al.*, 2006). In contrast to Cindrić *et al.*, *L*-alanine was used instead of *D,L*-alanine.

The asymmetric unit consists of one sodium and one nitrate ion and one *L*-alanine molecule.

The coordination geometry around the sodium atom can be considered as trigonal bipyramidal, with three bidentate nitrate anions coordinating through their oxygen atoms and two *L*-alanine molecules, each coordinating through one carboxyl oxygen atom (Figure 1,2).

Three nitrate anions are bidentate coordinating to the sodium atom (2.612 (2)–2.771 (2) Å), forming one plane, parallel with the (110) plane. The third nitrate oxygen atoms are coordinating to other symmetry equivalent sodium atoms, extending the plane formed. Almost perpendicular to this plane, two *L*-alanine molecules are coordinating to the sodium atom, each through one carboxyl oxygen atom (2.3651 (16) and 2.3891 (17) Å). The other carboxyl oxygen atoms are coordinated to sodium atoms in the planes above and beneath, respectively. Hence, infinite planes parallel with (110) are formed by the nitrate anions and the sodium atoms and these are perpendicularly linked to each other by *L*-alanine molecules (Figure 3).

Intermolecular hydrogen bonds are observed between N1(H1A)···O(1)[1/2 + *x*,-1/2 − *y*,2 − *z*] (1.92 (4) Å), N1(H1B)···O(5)[1/2 + *x*,1/2 − *y*,2 − *z*] (2.10 (3) Å) and N1(H1C)···O(2)[1 + *x*,*y*,*z*] (1.87 (4) Å) and an intramolecular hydrogen bond is found for N1(H1B)···O(2) (2.44 (3) Å).

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Only four structures of alanine coordination complexes are found in the CSD (Version 5.28) (Allen, 2002). Only in one of them (Rajagopal *et al.*, 2003), two alanine molecules are coordinated to the same cobalt ion. Concerning the nitrate ions, the reported structure is the first structure where three nitrate ions are coordinated to a sodium atom.

Experimental

L-Alanine (0.18 g, 2 mmol) was added to an aqueous solution of Na_2MoO_4 (0.484 g, 2 mmol) and the solution was acidified by addition of HNO_3 to pH 3.4. Colourless crystals of the title compound were obtained after standing for 5 days at room temperature 0.02 g, 10%). *L*-Alanine and Na_2MoO_4 were purchased from Acros Organics (Geel, Belgium).

Refinement

All hydrogen atoms could be located in a difference Fourier map, and were further refined unrestrained with isotropic temperature factors fixed at 1.5 times U_{eq} of the parent atoms for the methyl and ammonia groups and 1.2 times U_{eq} of the parent atom for the H2(C2) atom.

Figures
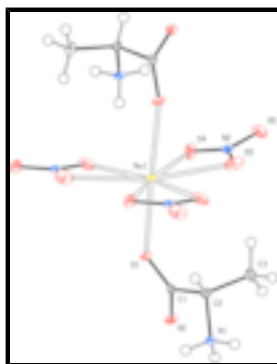

Fig. 1. Coordination geometry of the title compound, showing atom-labelling scheme and 50% probability displacement ellipsoids. Hydrogen atoms are drawn at arbitrary size.
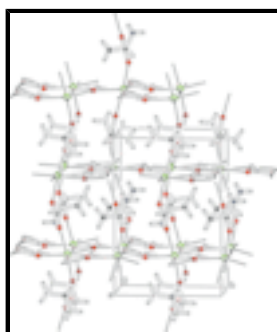

Fig. 2. Packing diagram of the title compound.

Poly[μ₂-*L*-alanine-μ₃-nitrato-sodium(I)]

Crystal data

$[Na(NO_3)(C_3H_7NO_2)]$	$F_{000} = 360$
$M_r = 174.10$	$D_x = 1.743$ Mg m^{-3}

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 5.3477 (3)$ Å

$b = 9.1719 (6)$ Å

$c = 13.5284 (8)$ Å

$V = 663.55 (7)$ Å^3

$Z = 4$

Cu $K\alpha$ radiation

$\lambda = 1.54178$ Å

Cell parameters from 2690 reflections

$\theta = 5.8–70.3°$

$\mu = 1.98$ mm^{-1}

$T = 100 (2)$ K

Rod, colourless

$0.5 \times 0.3 \times 0.2$ mm

Data collection

Bruker SMART 6000
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: crossed Göbel mirrors

$T = 100(2)$ K

ω and φ scans

Absorption correction: multi-scan
(SADABS; Bruker, 1997)

$T_{min} = 0.431$, $T_{max} = 0.673$

6562 measured reflections

1241 independent reflections

1170 reflections with $I > 2\sigma(I)$

$R_{int} = 0.048$

$\theta_{max} = 70.3°$

$\theta_{min} = 5.8°$

$h = -6 \rightarrow 6$

$k = 0 \rightarrow 11$

$l = 0 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.092$

$S = 1.10$

1241 reflections

122 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

Only H-atom coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.32$ e Å^{-3}

$\Delta\rho_{min} = -0.47$ e Å^{-3}

Extinction correction: SHELXL97,
Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$

Extinction coefficient: 0.046 (3)

Absolute structure: Flack, 1983

Flack parameter: 0.10 (12)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-

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factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6356 (4)	1.05721 (19)	−0.00853 (15)	0.0078 (4)
C2	0.3525 (4)	1.0453 (2)	0.00305 (15)	0.0090 (4)
C3	0.2757 (4)	0.8870 (2)	0.02082 (14)	0.0136 (4)
H2	0.300 (5)	1.109 (3)	0.0538 (19)	0.016*
H1A	0.247 (7)	1.201 (3)	−0.0929 (19)	0.020*
H3A	0.322 (5)	0.825 (3)	−0.033 (2)	0.020*
H1B	0.287 (6)	1.064 (3)	−0.140 (2)	0.020*
H3B	0.095 (6)	0.881 (3)	0.028 (2)	0.020*
H1C	0.062 (6)	1.080 (3)	−0.087 (2)	0.020*
H3C	0.348 (6)	0.841 (3)	0.082 (2)	0.020*
N1	0.2284 (4)	1.10123 (18)	−0.08786 (11)	0.0082 (3)
N2	0.7554 (4)	0.71413 (16)	0.24472 (10)	0.0087 (3)
Na1	0.75451 (17)	1.04449 (8)	0.23836 (5)	0.0127 (3)
O1	0.7615 (3)	1.09249 (14)	0.06664 (8)	0.0097 (3)
O2	0.7253 (3)	1.02859 (15)	−0.09235 (10)	0.0122 (3)
O3	0.5568 (3)	0.7841 (2)	0.24054 (13)	0.0209 (4)
O4	0.9608 (3)	0.7753 (2)	0.23456 (13)	0.0201 (4)
O5	0.7487 (4)	0.57822 (15)	0.26006 (9)	0.0211 (4)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0083 (9)	0.0061 (9)	0.0090 (9)	0.0009 (7)	−0.0015 (8)	0.0025 (7)
C2	0.0072 (9)	0.0125 (9)	0.0072 (9)	−0.0007 (8)	0.0004 (7)	−0.0005 (8)
C3	0.0106 (10)	0.0135 (9)	0.0166 (10)	−0.0021 (10)	0.0000 (9)	0.0047 (7)
N1	0.0056 (8)	0.0122 (8)	0.0067 (7)	0.0012 (8)	0.0001 (7)	−0.0007 (5)
N2	0.0103 (8)	0.0103 (7)	0.0056 (7)	−0.0002 (8)	−0.0003 (8)	−0.0019 (5)
Na1	0.0135 (4)	0.0164 (4)	0.0084 (4)	−0.0005 (4)	−0.0010 (4)	0.0027 (2)
O1	0.0089 (6)	0.0119 (6)	0.0082 (6)	0.0011 (7)	−0.0022 (7)	−0.0005 (4)
O2	0.0086 (7)	0.0214 (8)	0.0067 (6)	0.0002 (7)	0.0014 (6)	−0.0014 (5)
O3	0.0142 (8)	0.0329 (9)	0.0157 (8)	0.0120 (7)	−0.0030 (7)	−0.0045 (9)
O4	0.0142 (8)	0.0264 (8)	0.0197 (9)	−0.0095 (7)	0.0053 (7)	−0.0051 (7)
O5	0.0418 (10)	0.0106 (7)	0.0108 (6)	−0.0020 (9)	0.0036 (9)	−0.0012 (5)

Geometric parameters (Å, °)

C1—O2	1.259 (3)	N1—H1B	0.84 (3)
C1—O1	1.262 (2)	N1—H1C	0.91 (3)
C1—C2	1.526 (3)	N2—O4	1.241 (3)
C2—N1	1.489 (2)	N2—O3	1.242 (3)
C2—C3	1.528 (3)	N2—O5	1.264 (2)
C2—H2	0.94 (3)	N2—Na1	3.0312 (17)

C3—H3A	0.96 (3)	Na1—O1	2.3647 (13)
C3—H3B	0.97 (3)	Na1—O3	2.612 (2)
C3—H3C	1.00 (3)	Na1—O4	2.705 (2)
N1—H1A	0.92 (3)		
O2—C1—O1	125.16 (19)	C2—N1—H1C	110.9 (19)
O2—C1—C2	117.11 (17)	H1A—N1—H1C	108 (3)
O1—C1—C2	117.72 (17)	H1B—N1—H1C	106 (3)
N1—C2—C1	109.44 (16)	O4—N2—O3	121.22 (17)
N1—C2—C3	109.74 (16)	O4—N2—O5	119.3 (2)
C1—C2—C3	110.54 (17)	O3—N2—O5	119.5 (2)
N1—C2—H2	104.8 (17)	O4—N2—Na1	63.02 (11)
C1—C2—H2	109.2 (17)	O3—N2—Na1	58.74 (12)
C3—C2—H2	112.9 (17)	O5—N2—Na1	171.99 (11)
C2—C3—H3A	111.7 (17)	O1—Na1—O3	100.82 (6)
C2—C3—H3B	109.6 (18)	O1—Na1—O4	98.33 (6)
H3A—C3—H3B	108 (2)	O3—Na1—O4	47.99 (5)
C2—C3—H3C	115.1 (16)	O1—Na1—N2	102.35 (5)
H3A—C3—H3C	106 (2)	O3—Na1—N2	23.98 (6)
H3B—C3—H3C	106 (2)	O4—Na1—N2	24.14 (6)
C2—N1—H1A	110.8 (18)	C1—O1—Na1	137.35 (13)
C2—N1—H1B	112.4 (19)	N2—O3—Na1	97.28 (13)
H1A—N1—H1B	108 (3)	N2—O4—Na1	92.84 (13)

Fig. 1

Fig. 2