

Disodium Bis{*cis*-[nitrilotriacetato(2-)-O¹,N,O²]- μ -oxo-dioxomolybdate(VI)]-Water (1/8), Na₂[Mo₂(C₆H₇NO₆)₂O₅].8H₂O

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Abstract. 2Na⁺.C₁₂H₁₄Mo₂N₂O₁₇.8H₂O, $M_r = 840.2$, triclinic, $P\bar{1}$, $a = 8.753$ (2), $b = 12.806$ (3), $c = 6.644$ (2) Å, $\alpha = 94.98$ (2), $\beta = 103.82$ (2), $\gamma = 101.03$ (2)°, $V = 702.89$ Å³, $Z = 1$, $D_m = 1.96$ (2), $D_x = 1.98$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.912$ mm⁻¹, $F(000) = 412$, $R = 0.074$, $wR = 0.080$, for 2075 reflections. The complex anion contains an O₂MoOMoO₂ core with the core-bridging O atom lying on a crystallographic centre of symmetry. The ligand is tridentate with coordination through the N atom and two carboxylate groups. The cation grouping contains a pair of Na⁺ ions bridged by two water molecules.

Introduction. At pH 6–7 nitrilotriacetic acid, N(CH₂CO₂H)₃ (trianion nta), and uramildiacetic acid, CO–NH–CO–NH–CO–CH–N(CH₂CO₂H)₂ (trianion uda), form Mo^{VI} complexes of composition [MoO₃(nta)]³⁻ and [MoO₃(uda)]³⁻ (Butcher, Powell, Wilkins & Yong, 1976). It has been established that the nta complex comprises a *cis*-trioxo core, with the ligand coordinated through the N atom and two carboxylate groups (Butcher & Penfold, 1976*a*). At pH 2, different anions are found; that from uda is of composition [MoO₂(uda)]⁻ with the tetradentate enolic form of the ligand (Butcher & Penfold, 1976*b*), but the complex formed by nta is of a different type (Knobler, Penfold, Robinson, Wilkins & Yong, 1980). Salts containing this nitrilotriacetato complex anion show a strong infrared band at 775–790 cm⁻¹ indicative of core-oxygen bridging. We now report the crystal structure of the sodium salt, which shows it to have the formulation Na₂[Mo₂O₅(Hnta)]₂.8H₂O with the core O₂MoOMoO₂.

Experimental. 0.5 × 0.6 × 0.8 mm, sealed in glass capillary, D_m by flotation (CCl₄+CHBr₃), no symmetry elements observed on X-ray photographs, space group $P\bar{1}$, seven reflections for measuring lattice parameters, Hilger & Watts four-circle diffractometer, Zr-filtered Mo $K\alpha$, θ - 2θ scans, $2\theta_{\max} = 48^\circ$, $-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $0 \leq l \leq 7$, standard reflections 060, 300, 322 – no change; 2181 reflections measured, 2075 with $I > 3\sigma(I)$ used in refinement on F (Countryman & Penfold, 1972), absorption corrections 1.58–1.86 applied, coordinates of Mo readily obtained from Patterson calculations, 21 non-hydrogen atoms

from difference Fourier, full-matrix least squares; Mo, Na, N, and the nine O atoms from the core and the carboxylate groups anisotropic, no H atoms located, those of methylene groups introduced at calculated positions (C–H = 1.0 Å) and refined with a common temperature factor, $R = 0.074$, $wR = 0.080$, $w = [\sigma^2(F) + 0.0245F^2]^{-1}$, ratio of maximum LS shift to error 1.900 [O(7) x], heights in difference Fourier (max.) 0.9, (min.) –3.3 e Å⁻³, scattering factors for Na, Mo, C, O from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965), anomalous-dispersion corrections from Cromer & Liberman (1970); *SHELX* (Sheldrick, 1976) for structure determination and refinement, *HILGOUT* (based on *DRED* by J. F. Blount and *PICKOUT* by R. J. Doedens), *ABSORB* (revision of *AGNOST* by L. K. Templeton & D. Templeton) for processing intensity data.

Discussion. Atomic coordinates and isotropic thermal parameters are listed in Table 1,* and interatomic distances and bond angles in Table 2. O(1) is the core-bridging atom (of type O_b) lying at the centre of symmetry of the anion. O(2) and O(3) are the terminal (or O_t) atoms of the core, O(4)–O(9) belong to carboxylate groups, and O(10)–O(13) refer to water molecules.

Both the complex anion and the cationic grouping contain crystallographic centres of symmetry. The interrelationship of the ions in the crystal is shown in Fig. 1. The anion is shown separately in Fig. 2. The cationic group contains a pair of equivalent ions Na⁺(1) and Na⁺(1') bridged by O(11) and O(11') from water molecules. The ions are in octahedral coordination involving [in the case of Na⁺(1)] O(6) and O(9) from carboxylate groups, O(10) and O(12) from non-bridging water molecules, along with the bridging atoms O(11) and O(11').

The O_b and O_t atoms of the anion occupy mutually *cis* positions around Mo in a geometry (Knobler *et al.*,

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38290 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^3$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

E.s.d.'s for atomic coordinate values are 0.001 in all cases except for O(1) which lies on the inversion centre at (0,0, $\frac{1}{2}$). Superscript *a* denotes U_{eq} values [$= \frac{1}{3}(U_{11} + U_{22} + U_{33})$].

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{iso}
Mo	-1.5	111.0	332.7	16 (1) ^a
Na	-474	395	825	24 (2) ^a
N	-131	197	560	14 (2) ^a
O(1)	0	0	500	24 (3) ^a
O(2)	133	91	191	36 (2) ^a
O(3)	-185	71	165	33 (2) ^a
O(4)	186	199	595	25 (2) ^a
O(5)	17	268	274	34 (2) ^a
O(6)	273	311	899	29 (2) ^a
O(7)	-72	419	271	34 (2) ^a
O(8)	-465	80	767	35 (2) ^a
O(9)	-342	252	806	36 (2) ^a
C(1)	-193	283	441	25 (2)
C(2)	-76	330	325	20 (2)
C(3)	-13	244	760	30 (2)
C(4)	160	254	749	16 (2)
C(5)	-263	120	593	19 (2)
C(6)	-362	158	732	17 (2)
O(10)	421	350	456	34 (2)
O(11)	394	548	807	25 (1)
O(12)	242	472	187	34 (2)
O(13)	432	147	85	39 (2)

Table 2. Interatomic distances (\AA)

Bond lengths within anion			
Mo—N	2.410 (6)	C(2)—O(7)	1.22 (1)
Mo—O(1)	1.880 (1)	C(3)—C(4)	1.51 (1)
Mo—O(2)	1.710 (6)	C(3)—N	1.47 (1)
Mo—O(3)	1.680 (6)	C(4)—O(4)	1.29 (1)
Mo—O(4)	2.134 (5)	C(4)—O(6)	1.28 (1)
Mo—O(5)	2.069 (5)	C(5)—C(6)	1.52 (1)
C(1)—C(2)	1.50 (1)	C(5)—N	1.45 (1)
C(1)—N	1.51 (1)	C(6)—O(8)	1.29 (1)
C(2)—O(5)	1.31 (1)	C(6)—O(9)	1.23 (1)

Na⁺ coordination distances

E.s.d.'s are 0.01 \AA . The coordination sphere comprises: O(6), O(9) from carboxylate; O(10), O(12), non-bridging H₂O; O(11), bridging H₂O. O(13), included for comparison, lies beyond the coordination sphere, but is strongly H-bonded to carboxylate O(8).

Na—O(6 ⁱ)	2.45	Na—O(11 ^h)	2.45
Na—O(9)	2.36	Na—O(12 ^{hh})	2.42
Na—O(10 ^l)	2.38	Na—O(13 ^{lv})	3.79
Na—O(11 ^h)	2.38		

Oxygen—oxygen distances

E.s.d.'s are 0.01 \AA .

O(2)—O(13)	2.86	O(7)—O(12)	2.89
O(4)—O(10)	2.92	O(8)—O(13 ^{lv})	2.63
O(6)—O(12 ^v)	2.78	O(10)—O(11 ^h)	2.88
O(6)—O(13 ^v)	2.94	O(10)—O(12)	2.86
O(7)—O(11 ^{hh})	2.86		

Symmetry code

(i) $-1 + x, y, z$	(iv) $-1 + x, y, 1 + z$
(ii) $-x, 1 - y, 2 - z$	(v) $x, y, 1 + z$
(iii) $-x, 1 - y, 1 - z$	(vi) $1 - x, 1 - y, 1 - z$

Bond angles in the complex anion

Mo—O(1)—Mo	180.0	C(1)—N—C(3)	112.1 (6)
O(1)—Mo—O(2)	103.6 (2)	C(1)—N—C(5)	110.8 (6)
O(1)—Mo—O(3)	101.4 (2)	C(1)—N—Mo	103.9 (4)
O(1)—Mo—O(4)	83.5 (2)	C(2)—C(1)—N	110.1 (6)
O(1)—Mo—O(5)	155.6 (2)	C(2)—O(5)—Mo	123.6 (5)
O(1)—Mo—N	88.0 (1)	C(3)—C(4)—O(4)	117.9 (7)
O(2)—Mo—O(3)	105.8 (3)	C(3)—C(4)—O(6)	118.8 (7)
O(2)—Mo—O(4)	92.4 (3)	C(3)—N—C(5)	111.0 (6)
O(2)—Mo—O(5)	91.6 (2)	C(3)—N—Mo	109.3 (5)
O(2)—Mo—N	160.8 (3)	C(4)—C(3)—N	113.3 (7)
O(3)—Mo—O(4)	159.2 (3)	C(4)—O(4)—Mo	123.6 (5)
O(3)—Mo—O(5)	92.5 (3)	C(5)—C(6)—O(8)	112.1 (6)
O(3)—Mo—N	86.4 (3)	C(5)—C(6)—O(9)	123.3 (7)
O(4)—Mo—O(5)	76.7 (2)	C(5)—N—Mo	109.4 (4)
O(4)—Mo—N	73.4 (2)	C(6)—C(5)—N	117.8 (6)
O(5)—Mo—N	72.9 (2)	O(4)—C(4)—O(6)	123.2 (7)
C(1)—C(2)—O(5)	116.3 (6)	O(5)—C(2)—O(7)	121.9 (7)
C(1)—C(2)—O(7)	121.6 (7)	O(8)—C(6)—O(9)	124.6 (7)

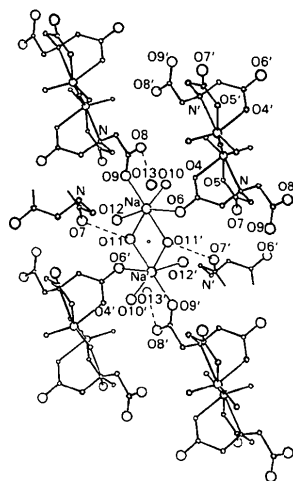


Fig. 1. The structure of Na₂[Mo₂(Hnta)₂].8H₂O, showing coordination around the Na⁺ ions. O atoms from H₂O, and those from carboxylate participating in Na⁺ coordination, are shown as large open circles (ORTEP II; Johnson, 1965).

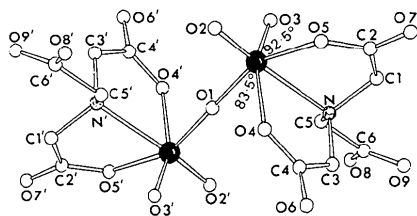


Fig. 2. Perspective view of the [Mo₂O₅(Hnta)₂]²⁻ anion, showing the coordination around Mo (ORTEP II; Johnson, 1965).

1980) corresponding closely with that found in [Mo₂(C₂O₄)₂O₅(OH)₂]²⁻ (Cotton, Morehouse & Wood, 1964). The ligand is linked through the N atom and through O(4) and O(5) of two of the carboxylate groups, as in the [MoO₃(nta)]³⁻ complex which is formed at higher pH (see above). One of the O atoms, O(9), of the third carboxylate group, which is not involved in the Mo coordination, enters the Na⁺ coordination sphere.

As is usual, the Mo—ligand bonds opposite O_{*i*} are relatively long; Mo—N = 2.41, Mo—O(4) = 2.13, while

Mo—O(5) opposite O_b is somewhat shorter at 2.07 Å. There is a significant inequality of the bond angles O(3)—Mo—O(5) [92.5 (3)°] and O(1)—Mo—O(4) [83.5 (2)°] involving O_a and O_b respectively, and the O atoms of the two chemically equivalent glycinato rings. This reflects stronger repulsion from the Mo—O_a than the Mo—O_b bond (Fig. 2). In [MoO₃(nta)]³⁻, where the two corresponding core atoms are both O_a, the angles are closer (86.0, 89.4°) (Butcher & Penfold, 1976a).

In the cationic group the two Na⁺ ions, which are paired through bridging, lie 3.570 (5) Å apart. The six O atoms around each ion are all at distances 2.36–2.45 Å (Table 2). Angles (e.s.d.'s 0.4°) range from 80.8 to 103.3°, with 84.9° for O(11)—Na—O(11') between the bridging pair. As will be seen from Fig. 1, the four carboxylate atoms O(6), O(9), O(6') and O(9'), coordinated directly with the Na⁺ cations, are from four different anion complexes [and, correspondingly, the linkages through O(6), O(9), O(6') and O(9') of a particular anion complex extend to four different cation groupings]. The development of the aqua-bridged grouping is to be seen as a consequence of the total structure in which ion packing, water coordination, and hydrogen bonding all play a part. There are short O(11)—O(7) and O(11')—O(7') distances, 2.86 Å, indicative of H bonding between the bridging atoms and carboxylate O(7) and O(7') atoms. These carboxylate atoms are members of anion complexes which lie respectively above and below the four anions which are shown completely in Fig. 1. There is thus H bonding *via* the O bridges to anions which are adjacent to, but not coordinated with, a particular cation centre. At the same time the consequent H-bond charge withdrawal from O(11) and O(11') will enhance the ability of these bridging atoms to neutralize the cation field.

The requirement of charge balance means the presence of an acidic proton within the structure, perhaps formally within the ligand dianion, Hnta. In fact, the relatively long [1.29 (1) Å] C(6)—O(8) bond points to attachment of some other atom at O(8). Then, significantly, O(8) shows an unusually close approach [2.63 (1) Å] to O(13) of the only water molecule which lies outside the Na⁺ coordination sphere. It is deduced that O(8) carries the remaining carboxylate proton, but that a strong H-bonding interaction with O(13) provides, in effect, for its partial transfer to the water molecule. Other O...O distances less than 2.9 Å, probably through H bonding, which assists further spreading of charge, are O(2)...O(13), O(4)...O(10), O(6)...O(12) and O(7)...O(12) (see Table 2).

In summary, the O atoms of the three carboxylate groups within any particular Hnta ligand are used as follows. Of the O atoms of the group C(6)O(8)O(9), O(8) is protonated, and O(9) is coordinated with Na⁺. From the group C(4)O(4)O(6), O(4) is linked to Mo and O(6) is coordinated with a second cationic grouping separate from that involving O(9). Through O(5), the group C(2)O(5)O(7) also contributes to Mo coordination, but O(7) provides a H-bond cross-linkage to a H₂O bridge in a third cation grouping.

The formation of a Mo₂O₅ core with the nitrilotriacetato ligand at low pH to give the complex anion found in this crystalline compound is to be contrasted with the MoO₂ core developed by the uramildiacetato and malato ligands under corresponding conditions (Knobler *et al.*, 1983). It indicates that the type of core developed within a complex anion forming in aqueous solution can be dependent not only upon pH, but also upon the match of a ligand configuration with possible alternative core structures. A polydentate ligand and the O atoms of the core must together meet the octahedral coordination requirement of molybdenum.

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