A new dinuclear molybdenum(V)-sulfur complex containing citrate ligand: synthesis and characterization of K_{2.5}Na₂NH₄[Mo₂O₂S₂(cit)₂].5H₂O

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ABSTRACT. The complex, $K_{2,s}Na_2NH_4[Mo_2O_2S_2(cit)_2]\cdot 5H_2O$ (1), was obtained by crystallization from a solution of $(NH_4)_2MoS_4$, potassium citrate (K_3cit) and hydroxyl sodium in methanol and water under an atmosphere of pure nitrogen at ambient temperature. The crystals are triclinic, space group PI, a = 7.376 (3)Å, b = 14.620 (2) Å, c = 14.661 (1) Å, α = 71.10 (1)°, β = 81.77 (1)°, γ = 78.27(2)°, R = 0.0584 for 2545 observed (I > 2 σ (I)) reflections. Single crystal structure analysis reveals that citrate ligand coordinated to molybdenum atom through two carboxylato oxygens and one deprotonated hydroxyl oxygen together with two bridging sulfur atoms and a terminal oxygen atom completes distorted coordination octahedron around each molybdenum atom. Principal dimensions are: Mo = O₁, 1.707 Å (av); Mo-S_b, 2.341 Å (av); Mo-O_(hydroxyl), 2.021 Å (av); Mo-O_(a-carb.-yl), 2.1290 Å (av) and Mo-O_(β-carbexyl), 2.268(av) Å. IR spectrum is in agreement with the structure.

INTRODUCTION

Recent studies on single crystal structure of MoFe protein of nitrogenase reveal that its active center, FeMo-Co, consists of a MoFe₇S₉ cluster with homocitrate ligand, in which octahedral coordination sphere of Mo atom is completed through three sulfides, a

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nitrogen atom from the imidazol group of a histidine residue and two oxygen atoms from the hydroxyl group and α - carboxyl moiety of homocitrate ligand[1,2]. It has been shown that, as for coordination environment of Mo atom, a hydroxyl group and a minimum of two carboxyl groups are required for activity of nitrogenase[3]. Although the synthesized FeMo-Co in vitro using such alternative hydroxyl polycarboxyl acids (e.g. citric, malic and citramalic etc.) for replacing homocitric acid only display N₂ reduction activity much lower than that found with homocitrate[4], it is still of interest to synthesize model compounds containing hydroxy polycarboxyl acid mentioned above (much cheaper than homocitric acid) for better understanding the role of ligands around Mo atom having an insight into the mechanism of substrates reduction of nitrogenase.

Citric acid is an important compound in biological processes. Its complexes with oxo molybdenum have been studied in the solid and in solution[5-16]. Crystal structures of some the compounds have been determined, for instance, $K_2[MoO(O_2)_2(H_2cit)]$. $1/2H_2O_2\cdot 3H_2O[13]$ (2) $[Me_3N(CH_2)_6NMe_3]_2[(MoO_2)_4O_3(Hcit)_2]\cdot 12H_2O[14]$ (3), K_4 - $[(MoO_2)_4O_3(Hcit)_2]\cdot 6H_2O[9]$ (4), $K_6[(MoO_2)_2O(cit)_2]\cdot 5H_2O[15]$ (5) and K_2Na_4 $[(MoO_2)_2-O(cit)_2]\cdot 5H_2O[16]$ (6) etc. Although study on Mo-Fe-S cluster compound with citrate ligand was carried out by elemental analysis and spectroscopy, no crystal data was provided [17]. To date, to our knowledge, no Mo-S-citrate complex determined crystal structure has been reported. Now we just report the synthesis and structure of one such compound, $K_{2.3}Na_2NH_4[Mo_2O_2S_2(cit)_2]\cdot 5H_2O(1)$

EXPERIMENTAL

All solvents and chemicals were commercial reagent grade or better and were used without further purification; and the reactions were carried out under an atmosphere of purified nitrogen. $(NH_4)_2MOS_4$ was prepared as described in the literature[18]. Analyses for C, H and N were carried out with a Perkin-Elmer Analyzer model 240C; Mo, K and Na contents were determined by atomic absorption spectrophotometer Varian AA-475; IR Spectra were recorded with Perkin-Elmer 783 Spectrophotometer, using KBr pellets. EPR spectra were recorded with ER200D spectrometer.

Preparation of the title compound

2.45 g (8 mmol) potassium citrate was dissolved in water (20 cm³) and MeOH (50 cm³), the pH of solution was adjusted to 7.5 with 1 M NaOH. Then 1.03 g (4 mmol) $(NH_4)_2MoS_4$ was added to the solution, after stirring for 48h at room temperature, the reaction mixture was filtered to remove precipitate, the solution was placed at room temperature for several months. Dark red prismatic crystals grew up. The crystals was not stable in air, it decompose gradually by loosing lattice water. Therefore, it would be preserved at an atmosphere of nitrogen. Anal. calcd. For Mo₂K₃Na₂-C₁₂H₂₂NO₂₁S₂: C, 15.72; H, 2.40; N, 1.53; Na. 5.02; K, 10.64; Mo, 20.95. Found: C, 15.50; H, 2.39; N, 1.60; Na, 5.90; K, 11.1; Mo, 20.80. IR (cm⁻¹): C = O (1620, 1550), Mo = O (930, 900, 850), Mo-S_b (450).

Crystallographic structure determination

A selected single crystal of title compound with dimensions $0.40 \times 0.24 \times 0.12$ mm was mounted and the cell dimensions were obtained by a least squares fit of setting angles for 25 reflections. Diffraction data were collected on a Siemens P4 Four-Circle diffractionmeter using graphite-monochromated MoK α ($\lambda = 0.71073$ Å) radiation. The scan mode was $\omega - 2\theta$. A total of independent reflections were collected in the range $1.75^{\circ} < \theta < 25^{\circ}$ and 2901 observed reflections with I > 2σ (I) were used for further computation. All calculation was performed on a COMPAQ 486 computer with SHELXTL-PLUS program package and the hydrogen atoms were not included in the calculations. Intensity data were corrected for Lorentz and polarization effects and empirical absorption based on φ - scan. The coordinates of the metal atoms were determined by direct methods and all the remaining non-hydrogen atoms were located from successive difference Fourier syntheses. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. The crystal and refinement data for the complex are shown in TABLE I, together with some experimental details. Atomic coordinates, and the selected bond lengths and bond angles for the complex are given in TABLE II and III, respectively. Fig.1 is a perspective view of the anion of the title complex.

TABLE I: Crystal data for K2.5Na2NH4[Mo2O2S2(C6H4O7)2]·5H2O

Chemical formula Formula Weight Colour Crystal system	K _{2.5} Na ₂ NH ₄ [Mo ₂ O ₂ S ₂ (C ₆ H ₄ O ₇) ₂] [.] 5H ₂ O 916.04 Dark-red Triclinic
Space group	PĪ
a (Å)	7.376(3)
b (Å)	14.620(2)
c (Å)	14.661(1)
α (°)	71.10(1)
β (°)	81.77(1)
γ (°)	78.27(2)
$V(A^3)$	1459.4(6)
Z	2
μ (cm ⁻¹)	14.77
F(OOO)	928
GOF	1.033
Dcalc (g cm ⁻³)	2.085
Temp (K)	293(2)
No. of refl. collected	4335
No. of refl. observed	2901
Rª	0.0584
WR ₂ ^b	0.1602
Largest different peak (e Å ³)	2.488 and -0.933

a: $R=\sum ||Fo| - |Fc|| / \sum |Fo||$ b: $wR_2 = (\sum w(Fo^2 - Fc^2)^2 / \sum w(Fo^2)^2)^{1/2}$ w=1 / $(\sigma^2(Fo)^2 + (0.1025P) + 15.62P)$, P = $(Max.(Fo^2, 0) + 2 \times Fc)^2 / 3$

TABLE II: Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters $(Å^2 \times 10^3)$ for K₃Na₂NH₄[Mo₂O₂S₂(C₆H₄O₇)₂]·5H₂O. U(eq) is defined as one third of the trace of the orthogonalize U_{ii} tensor

	X	Y	Z	Um	
Mo(1)	3379(2)	9784(1)	-1865(1)	20(1)	

Mo(2)	5755(2)	8013(1)	-2034(1)	19(1)
S(1)	6315(7)	9646(2)	-2678(2)	22(2)
S(2)	2577(7)	8235(2)	-1603(2)	26(2)
O(11)	525(18)	10271(6)	-1487(6)	30(4)
O(12)	3089(18)	11264(6)	-2424(6)	19(4)
O(13)	2125(17)	10086(5)	-3281(5)	25(4)
O(14)	-1848(24)	11484(8)	-1927(7)	29(6)
O(15)	1081(19)	10835(6)	-4701(6)	40(4)
O(16)	683(23)	12271(8)	-822(7)	59(6)
O(17)	2808(26)	13179(10)	-1547(9)	60(6)
O(18)	3939(19)	9644(6)	-729(5)	33(4)
O(21)	5668(17)	6664(5)	-2088(5)	16(4)
O(22)	8449(17)	7583(6)	-2652(6)	25(4)
O(23)	5149(17)	8282(5)	-3581(5)	25(4)
O(24)	4355(19)	8040(6)	-4843(6)	38(4)
O(25)	10068(20)	6565(7)	-3413(7)	37(5)
O(26)	7012(25)	4253(8)	-765(8)	75(6)
O(27)	9126(31)	5233(8)	-1145(11)	104(9)
O(28)	6585(17)	7724(5)	-932(5)	33(4)
C(11)	-182(41)	11159(11)	-1971(8)	33(10)
C(12)	1242(28)	11750(8)	-2643(8)	18(6)
C(13)	990(27)	11829(9)	-3694(8)	32(6)
C(14)	1427(26)	10845(9)	-3909(8)	26(6)
C(15)	962(26)	12783(8)	-2541(9)	21(6)
C(16)	1483(37)	12738(10)	-1547(11)	36(9)
C(21)	5123(26)	7715(8)	-4078(8)	21(7)
C(22)	6943(27)	6341(8)	-2781(8)	47(6)
C(23)	8636(30)	6834(9)	-2961(9)	21(7)
C(24)	6016(28)	6649(8)	-3744(8)	29(7)
C(25)	7452(27)	5226(8)	-2407(9)	24(6)
C(26)	7938(36)	4876(10)	-1375(11)	52(9)
K(1)	893(6)	-1321(2)	6200(2)	31(2)
K(2)	5000	0	5000	34(2)
K(3)	-2205(7)	9289(2)	-524(2)	43(2)
Na(1)	6365(12)	2459(4)	-673(3)	43(3)
Na(2)	267(12)	3444(4)	388(4)	52(3)
N	4173(20)	-2201(6)	3406(6)	47(2)
OW(1)	2761(28)	5584(11)	-1148(12)	100(5)
OW(2)	2157(17)	4151(5)	-322(5)	24(2)
OW(3)	12971(28)	4911(11)	-2845(12)	145(5)
OW(4)	15181(30)	4251(13)	-3994(13)	188(6)
UW(5)	11232(41)	5509(18)	-4822(19)	187(10)

TABLE II (continued)

Mo(1)-O(18)	1.712(8)	Mo(1)-O(12)	2.028(8)
Mo(1)-O(11)	2.135(12)	Mo(1)-O(13)	2.270(9)
Mo(1)-S(1)	2.322(5)	Mo(1)-S(2)	2.354(4)
Mo(1)-Mo(2)	2.877(2)	Mo(2)-O(28)	1.701(9)
Mo(2)-O(21)	2.014(7)	Mo(2)-O(22)	2.123(11)
Mo(2)-O(23)	2.266(8)	Mo(2)-S(2)	2.324(5)
Mo(2)-S(1)	2.364(3)	O(11)-C(11)	1.30(2)
O(12) - C(12)	1.43(2)	O(13)-C(14)	1.26(12)
0(14)-C(11)	1.23(2)	O(15)-C(14)	1.23(2)
O(16)-C(16)	1.21(2)	O(17)-C(16)	1.28(2)
O(21)-C(22)	1.41(2)	O(22)-C(23)	1.29(2)
O(23)-C(21)	1.273(14)	O(24)-C(21)	1.24(2)
O(25)-C(23)	1.23(2)	O(26)-C(26)	1.28(2)
O(27)-C(26)	1.24(3)	C(11)-C(12)	1.54(3)
C(12)-C(15)	1.54(2)	C(12-C(13)	1.54(2)
C(13)-C(14)	1.522(15)	C(15)-C(16)	1.54(2)
C(21)-C(24)	1.51(2)	C(22)-C(23)	1.52(2)
O(w1)-Na(2) ⁱ	2.70(2)	K(1)-O(28)''	2 879(10)
$Na(2)-O(26)^{ii}$	2.95(2)	$Na(1) - O(14)^{iii}$	2 719(12)
C(22)-C(25)	1.53(2)	C(22)-C(24)	1.55(2)
$O(18)-M_0(1)-O(12)$	99 7(4)	$O(18) - M_0(1) - O(11)$	91.0(5)
O(12)-Mo(1)-O(11)	76 5(4)	O(18) - Mo(1) - O(13)	169.8(5)
O(12)-Mo(1)-O(13)	77.1(3)	$O(11)-M_0(1)-O(13)$	78 8(4)
O(18)-Mo(1)-S(1)	100.8(4)	O(12)-Mo(1)-S(1)	89 5(3)
O(11)-Mo(1)-S(1)	163.1(2)	$O(13)-M_0(1)-S(1)$	89.0(3)
$O(18)-M_0(1)-S(2)$	99.6(3)	O(12)-Mo(1)-S(2)	154 8(4)
O(11)-Mo(1)-S(2)	87.2(3)	O(13)-Mo(1)-S(2)	81 1(2)
S(1)-Mo(1)-S(2)	102.54(14)	O(18)-Mo(1)-Mo(2)	95 0(3)
O(12)-Mo(1)-Mo(2)	141.6(3)	O(11)-Mo(1)-Mo(2)	138 8(2)
O(13)-Mo(1)-Mo(2)	93.5(2)	S(1)-Mo(1)-Mo(2)	52 75(7)
Mo(1)-S(1)-Mo(2)	75.76(17)	$O(28)-M_0(2)-O(21)$	100 4(3)
O(28-Mo(2-O(22	91.0(4)	$O(21)-M_0(2)-O(22)$	76 8(4)
O(28)-Mo(2)-O(23)	170.2(5)	$O(21)-M_0(2)-O(23)$	76.5(3)
O(22)-Mo(2)-O(23)	79.3(4)	O(28)-Mo(2)-S(2)	100 3(4)
O(21)-Mo(2)-S(2)	89.9(3)	O(22)-Mo(2)-S(2)	164.0(3)
O(23)-Mo(2)-S(2)	89.1(3)	O(28)-Mo(2)-S(1)	99 1(3)
O(21)-Mo(2)-S(1)	154.9(2)	O(22)-MO(2)-S(1)	87 1(2)
O(23)-Mo(2)-S(1)	81.7(2)	S(2)-Mo(2)-S(1)	102 17(14)
O(28)-Mo(2)-Mo(1)	94.2(3)	O(21)-Mo(2)-Mo(1)	1417(3)
O(22)-Mo(2)-Mo(1)	138.5(2)	O(23)-Mo(2)-Mo(1)	03 0(2)
S(2)-Mo(2)-Mo(1)	52.46(8)	S(1)-Mo(2)-Mo(1)	51.42(10)
O(12)-C(12)-C(15)	110.0(13)	$M_0(2)-S(2)-M_0(1)$	75 9(2)
C(11)-O(11)-Mo(1)	116.5(12)	$C(12)-O(12)-M_0(1)$	114 9(0)
C(14)-O(13)-Mo(1)	134.9(7)	C(22) - O(21) - Mo(2)	117.7(2)
C(23)-O(22)-Mo(2)	115.2(11)	C(21)-O(23)-Mo(2)	133 3(7)
O(14)-C(11)-O(11)	123.4(18)	O(14)-C(11)-C(12)	122 8(13)
			124.0(13)

TABLE III: Selected bond lengths (Å) and angles (°) for $K_{2.5}Na_2NH_4[Mo_2O_2S_2(C_6H_4O_7)_2] \cdot 5H_2O$

TABLE III (continued)

O(11)-C(11)-C(12)	113.8(19)	O(12)-C(12)-C(11)	110.5(11)

Symmetry codes: i -x, -y+1, -z; ii x-1, y, z; iii x+1, y-1, z.

RESULTS AND DISCUSSION

The title compound was prepared in near neutral methanol-water reaction medium. We found that the pH value of the reaction solution has substantial effect on the synthesis reaction. Appropriate pH value range is 6.5-8.0. When pH < 6.5 starting material $MOS_4^{2^2}$ obviously decomposes, but pH > 8 coordination of citrate to Mo atom does not occur easily. It was found to form elemental sulfur (being confirmed by element analysis) and escape small amount of H₂S gas during the course of the reaction. Hence it may be concluded that intramolecular redox reaction (Mo(VI) – Mo(V)) of $MOS_4^{2^2}$ occurred in the formation process of the compound:

 $2MoS_4^{2-} + 2cit^{3-} + 2H_2O \rightarrow [Mo_2O_2S_2(cit)_2]^{6-} + S + 3H_2S + 2S^{2-}$

The crystal structure is consists of Packing of K⁺ Na⁺ and NH⁴⁺ cations and $[Mo_2O_2S_2(cit)_2]^{-6}$ anion and lattice water. Each molybdenum atom is coordinated to a terminal oxygen and two bridging sulfur atoms. The remaining coordination positions are occupied by a full deprotonated citrate acting as a terdentate ligand with an uncoordinated carboxylate "arm" through oxygen atom of hydroxyl group, and one of α -carboxyl group and a β -carboxyl group, resulting in a distorted octahedral coordination geometry of molybdenum atom. Terminal oxygen and two bridging sulfur adopt a facstereochemistry. Two terminal oxygen groups are in a cis-configuration, and the two citrate ligands are basically located at trans positions.

Compound 1 possess a four-membered ring MoS_2Mo with $Mo-S_b$ distance of 2.341 Å (av), Mo-Mo distance of 2.877(2) Å , and bond angles Mo-S-Mo of 75.83°(av) and

Sb-Mo-Sb of 102.35° (av). It can be seen from Table IV that related bond distances and angles in four-membered MoS₂Mo ring are close to each other for binuclear molybdenum(V) compounds with core $[Mo_2O_2(\mu-S)_2]^{2+}$. Thus, the size of the fourmembered MoS₂Mo ring in the compounds are similar. This implies that the electronic structural features of the molybdenum atoms in compounds 1, 7, 8, 9, 10 and 11 are comparable, although the molybdenum atoms are coordinated to different ligands (citrate for 1, cys for 7 and 8, edta for 9, dtc for 10 and S₂²⁻ for 11, respectively) with different electrophilic abilities. It was notice that Mo-S_b bond distances (2.294 Å (av)) in compound 9 are comparatively small. This is probably due to that in Cs₂[Mo₂O₂S₂(edta)]·2H₂O (9) two molybdenum atoms are coordinated to one edta chelating ligand resulting in two molybdenum atoms to draw close together, whereas each molybdenum atom in 1,7, 8, 10 and 11 individually links a chelating ligand.

compounds	Mo-Mo	Mo-S _b (av)	S_b-Mo-S_b	Mo-S _b -Mo	Ref.
1	2.877(2)	2.341	102.17(14) 102.54(14)	75.76(13) 75.9(2)	This work
7	2.82	2.33	104 103	75 75	19
8	2.8329(13)	2.328	102.12(11) 102.36(11)	75.03(9) 74.89(9)	21
9	2.799(1)	2.294	102.1(1)	75.4(1) 75.0(1)	20
10	2.82091)	2.3245	101.1	74.7 74.7	22
11	2.825(2)	2.324	101.8(2) 101.7(2)	74.8(1) 74.9(1)	23

TABLE IV: Comparison for related bond distances(Å) and angles (°) in fourmembered MoS₂Mo ring of some compounds^a

SYNTHESIS AND CHARACTERIZATION OF K2.5Na2NH4[Mo2O2S2(cit)2].5H2O 753

a) 1: $K_3Na_2NH_4[Mo_2O_2S_2(cit)_2] \cdot 5H_2O$, 7: $Na_2[Mo_2S_2(cys)_2] \cdot 2H_2O$ 8: $K_2[Mo_2O_2S_2(cys)_2] \cdot CH_3OH \cdot 4H_2O$, 9: $Cs_2[Mo_2O_2S_2(edta)] \cdot 2H_2O$ 10: $[Mo_2O_2S_2(dtc)_2] \cdot 2CH_3CN$, 11: $[N(CH_3)_4]_2[Mo_2O_2S_2(S_2)_2]$



Fig.1 A perspective view of the anion of the title complex

The terminal Mo=O distance of 1.707 Å (av) and Mo-O (β -carboxyl) distance of 2.268Å (av) in 1 are very close to that (1.707(av) and 2.264 Å (av), respectively) found in K₂Na₄[(MoO₂)₂O(cit)₂].5H₂O (6) [16]. The Mo-O (α -carboxyl)distance of 2.130(av) of 1 is shorter than the one of 2.208Å in 6, whereas the Mo-O(hydroxyl) bond length of 2.201 Å in 5 is longer than that of 1.944 Å (av) in 6. The situation mentioned above is probably related to trans influence of a coordination atom. In coordination octahedra of Mo atoms in 1 and 6, Mo-O₁ bonds are all trans to O(carboxylate) atoms, and Mo-O(β -carboxylate) bonds all trans to O₁ atoms, leading to these two kinds of corresponding bond lengths in 1 and 2 are very similar, respectively. The trans atom of Mo-O(α -carboxylate) bond is a bridging sulfur atom S_b in 1, whereas a O_t atom in 6, and the Mo-O(hydroxyl) bond is trans to a S_b atom in 1, but a bridging oxygen atom O_b in 6. The different trans atoms have different trans ability and lead to different corresponding bond lengths in 1 and 2.

In the IR spectrum of 1 the main characteristic absorption: v_{ssym} (C=O), 1620cm⁻¹, 1550cm⁻¹; v_{sym} (C=O), 1380cm⁻¹; v(Mo=O), 930 cm⁻¹, 900cm⁻¹, 850cm⁻¹. The absorption band at 1720cm⁻¹ showing presence of uncoordinated and protonated -COOH group was not observed[9,17]. The band at 450cm⁻¹ is assigned to Mo-S_b vibration absorption. These structural features have been confirmed by X-ray structural analysis.

No signal of monomeric molybdenum(V) species in the EPR spectrum of 1 was exhibit at room or low temperature(75K), indicating the title compound is diamagnetic. This is probably because of existing of marked spin-spin coupling between two molybdenum atoms. It accord with that there is strong metal-metal interaction in reduced clusters of the4d and 5d metals[24].

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SYNTHESIS AND CHARACTERIZATION OF K2.5Na2NH4[Mo2O2S2(cit)2].5H2O 755

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