Original Scientific Paper

Trans Influence of the Oxo Ligand in the Dimeric Molybdenum(V) Complexes. Crystal Structure Determinations of Caesium Di-μ-oxo-bis[aquaoxalatooxomolybdate(V)] Monohydrate (A) and Potassium Tricaesium Bis{di-μ-sulphido-bis[aquaoxalatooxomolybdate(V)]} Tetrahydrate (B), and Redetermination of the Crystal Structure of Barium Di-μ-oxo-bis[aquaoxalatooxomolybdate(V)] Trihydrate (C) and Pyridinium Di-μ-oxo-bis-[oxotris(isothiocyanato)molybdate(V)] Monohydrate (D)

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The crystal structures of the title complexes (A) and (B) have been determined and those of (C) and (D) redetermined in order to obtain new and more accurate data for explanation of the *trans* influence of the terminal oxo-oxygen atom in the di-μ-oxo and di-μ-sulphido molybdenum(V) complexes with oxalato and isothiocyanato ligands. The interatomic distances are discussed and the results compared with similar dimeric structures with molybdenum(V) in distorted octahedral coordination. Whereas a considerable lengthening of the bonds *trans* to the multiple-bonded terminal oxo-ligand was found in all structures with a double bridge of oxygen atoms and, therefore, this influence confirmed as a generally valid rule, no such *trans* influence was observed in the structures with a double bridge of sulphur atoms. In the structures of di-μ-sulphido-oxalato complexes, the Mo-L bonds *cis* to the terminal oxo ligand (*i.e. trans* to the bridging sulphur atoms) are longer than the bonds in *trans* position. These results indicate that the sulphur atom has a greater *trans* influence than the oxygen atom. This effect is not so conspicuous in the isothiocyanato complexes.

INTRODUCTION

It has been suggested that during the oxidation of xanthine to uric acid, catalyzed by the enzyme xanthine oxidase, xanthine has to be coordinated to the molybdenum atom of the enzyme. Also, such substrate coordination may occur if molybdenum in

the enzyme has a vacant coordination position or a site with a weakly bonded ligand.[1,2] Since the bonds *trans* to the oxo-groups are »almost« always lengthened and conse- quently weakened relative to the comparable bonds in *cis* geometry, it was reasonable to suppose that the position *trans* to oxo-group is a site for the interchange of the ligands and for the coordination of substrate to the enzyme-molybdenum. The *trans* repulsive influence of the terminal oxo-ligand is now generally accepted.[3,4] There are, however, a few structural examples published in the literature in which such *trans*-in- fluence of terminal oxo-ligands »was not found«. In particular, it was emphasized that the oxalato complexes of molybdenum(V) do not show any lengthening of the bonds *trans* to the oxo-ligands.[5] Such examples were the structures of barium di-μ-oxo-bis [aquaoxalatooxomolybdate(V)] trihydrate with molybdenum-to-oxalato-oxygen bond length *trans* to the oxo-ligand of 2.11 Å compared to 2.14 Å for the same bond in *cis* position,[6] and that of caesium di-μ-sulphido-bis-[aquaoxalatooxomolybdate(V)] dihy- drate where the bond *trans* to oxo-O was 2.160 Å (mean value) compared to 2.163 Å (mean value) in *cis* position.[5] In his paper W. S. McDonald suggests that »the absence of a *trans* influence on the bond lengths in the oxalato complexes indicates that the oxalato ligand has a low 'trans susceptibility' compared with the other ligands« but points out that »without bond length data of greater variety of complexes this point cannot be tested«.[5] In the structure of pyridinium di-μ-oxo-bis[oxo-tris(isothiocyanato) molybdate(V)] we have also found that one of the molybdenum-to-isothiocyanato- nitrogen bond length *trans* to Mo=O is shorter (2.11 Å) in comparison with the same Mo-N bond (2.24 Å) *cis* to the terminal oxo-group.[7] Discussing the problem of the *trans* influence of the oxo-ligand M. A. Poray-Koshits and L. O. Atovmyan conclude that there is no simple correlation between the type of the oxygen ligands (terminal and bridging) and the bond lengths with the ligand in the *trans* position.[8]

In order to contribute to the solution of this problem, we decided to redetermine the above mentioned crystal structures as well as to examine the structures of some similar oxalato complexes containing different cations.

EXPERIMENTAL

Preparation

In the attempt to prepare caesium di-μ-sulphido-bis-[aquaoxalatooxomolybdate(V)] dihydrate as described in the literature[9] we obtained two kinds of orange-coloured crystals. One was iden- tified as (A), the other as (B). Both crystals were recrystallized from water. The crystals of (C) and (D) were prepared according to the procedure given in the literature.[10,11]

Crystal Data

From Weissenberg photographs and from single crystal diffractometry:(A) $C_4H_6Cs_2Mo_2O_{15}$, $M = 751.77$, monoclinic, space group $P2/c$ (No. 13), $a = 14.758(4)$, $b = 6.031(2)$, $c = 17.069(4)$ Å, $\beta = 97.49(3)°$, $V = 1506.3(7)$ Å^3, $Z = 4$, $D_m = 3.27$ Mg m^{-3} (by flotation), $D_c = 3.31$ Mg m^{-3}, $F(000) = 1376$, $\mu(MoK\alpha) = 60.66$ cm^{-1}, $\lambda(MoK\alpha) = 0.7107$ Å, crystal of dimensions $0.34 \times 0.22 \times 0.14$ mm^3 used for the determination of unit cell parameters and data collection.

(B) $C_8H_{16}Cs_3Mo_4KS_4O_{28}$, $M = 1510.02$, tetragonal, space group $I4/m$ (No. 87), $a = 12.436(3)$, $c = 21.494(5)$ Å, $V = 3324(1)$ Å^3, $Z = 16$, $D_c = 3.02$ Mg m^{-3}, $F(000) = 2816$, $\mu(MoK\alpha) = 51.23$ cm^{-1}, $\lambda(MoK\alpha) = 0.7107$ Å, crystal dimensions $0.20 \times 0.21 \times 0.12$ mm^3.

(C) $C_4H_{10}BaMo_2O_{17}$, $M = 659.32$, trigonal, space group $P3_121$ (No. 152), $a = 10.665(2)$, $c = 11.712(2)$ Å, $V = 1153.7(4)$ Å^3, $Z = 3$, $D_m = 2.90$ Mg m^{-3} (by flotation), $D_c = 2.85$ Mg m^{-3}, $F(000) = 930$, $\mu(MoK\alpha) = 39.18$ cm^{-1}, $\lambda(MoK\alpha) = 0.7107$ Å, crystal dimensions $0.21 \times 0.11 \times 0.20$ mm^3.

(D) $C_{26}H_{26}Mo_2N_{10}O_5S_6$, M = 942.82, orthorhombic, space group $Pna2_1$ (No. 33), a = = 26.129(6), b = 9.749(4), c = 15.089(5) Å, V = 3844(2) Å^3, Z = 4, D_m = 1.64 Mg m^{-3} (by flotation), D_c = 1.63 Mg m^{-3}, $F(000)$ = 1888, $\mu(MoK\alpha)$ = 9.24 cm^{-1}, $\lambda(MoK\alpha)$ = 0.7107 Å, crystal dimensions 0.62 × 0.33 × 0.21 mm^3.

Intensity data, Structure Determination and Refinement*

For each crystal, the intensity data were collected on a fully automated diffractometer Philips PW 1100 using graphite monochromatized $MoK\alpha$ radiation within the range $4° < 2\theta < 54°$ for (A) and (B) and $4° < 2\theta < 60°$ for (C) and (D), respectively. ω - 2θ scan technique, scan widths 1.20° for (A) and (C) and 1.40° for (B) and 1.80° for (D), and scan rate 0.04°s^{-1} [for (D) 0.06°s^{-1}] were used in data collection. Reflections with $I < 5\sigma(I)$ for (A) and (B) and $I < 3\sigma(I)$ for (C) and (D), where σ is the standard deviation based on counting statistics, were not included in the calculations, which were based on the remaining 2446, 1427, 1634 and 3804 independent reflections for (A), (B), (C) and (D), respectively. The intensity data were corrected for Lorentz and polarization effects. Absorption correction was applied only to the crystal of (B)[12] since its application to (A) and (C) improved neither the interatomic distances and their e.s.d.'s nor the reliability indices R. The crystal of (D) indicated slow decomposition, so it was protected by a polystyrene coating.

All four structures were solved by the Patterson and Fourier methods. Refinement was performed using the SHELX76 programme[13] by least-squares procedure, minimizing $\Sigma w(|F_o| - |F_c|)^2$ assuming unit weights for (A) and (C), and w = 1.0000 / $\sigma^2(F)$ + 0.006677 F^2 and w = 0.6942 / / $\sigma^2(F)$ + 0.002792 F^2 for (B) and (D), respectively. Hydrogen atoms in (C) were found in a difference Fourier map, while those belonging to the pyridinium cations of (D) were generated on geometrical grounds taking C–H and N–H as 1.08 Å. They were not refined but included in the structure factor calculations. The refinements with anisotropic temperature factors for all non-hydrogen atoms [except O(9) in (C)] converged at R = 0.066, 0.039 (wR = 0.044), 0.018 and 0.050 (wR = 0.054) for (A), (B), (C) and (D), respectively.

The atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[14] Interatomic distances and angles were calculated using the CSU programme.[15] All calculations were performed either on the UNIVAC 1100/42 computer or using the IBM PC/AT compatible microcomputer (processor 80386/20MHz, coprocessor 80387).

DESCRIPTION OF THE STRUCTURES

Final atomic coordinates for all four structures are given in Tables I, II, III and IV. Structures with interatomic distances within the complex anions are, for comparison, represented in Figure 1. All selected distances and angles are given in Tables, V, VI, VII and VIII.

The structures of (A) and (C) are built up either of caesium or barium cations, $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$ anions and water molecules, the structure of (B) of potassium and caesium cations, $[Mo_2O_2S_2(C_2O_4)_2(H_2O)_2]^{2-}$ anions and water molecules and, finally, that of (D) of pyridinium cations, $[Mo_2O_4(NCS)_6]^{4-}$ anions and water molecules. The structure of (C) was already determined in 1965 from the film data (R = 0.102)[6] and the same complex anion was found also in the structure of $H(pyH)_3[Mo_2O_4(C_2O_4)_2(H_2O)_2]$ · 2H$_2$O.[17] The anion of (C) has a crystallographically imposed two-fold symmetry axis. In (A) and (C), the Mo atoms are surrounded by six oxygen atoms: one terminal oxo-O at 1.67 and 1.66 Å in (A) and 1.681 Å in (C), two bridging oxo-O at 1.93 and 1.94 Å in (A) and 1.933 and 1.930 Å in (C), one oxalato-O *cis* to the terminal-O at 2.15 Å in

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* Lists of the observed and calculated structure factors and anisotropic thermal parameters are obtainable from the authors on request.

TABLE I

*Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\mathring{A}^2 \times 10^3$, $\times 10^4$ for Cs and Mo for $Cs_2[Mo_2O_4(C_2O_4)_2(H_2O)_2] \cdot H_2O$ with estimated standard deviations (e.s.d.'s) in parentheses**

Atom	x/a	y/b	z/c	U_{eq}
Cs(1)	5000(0)	2697(4)	7500(0)	357(35)
Cs(2)	0(0)	5723(4)	2500(0)	326(5)
Cs(3)	4882(1)	7601(4)	9138(1)	513(4)
Mo(1)	1398(1)	1474(3)	1112(1)	132(4)
Mo(2)	1420(1)	3238(3)	−257(1)	132(4)
O(1)	288(9)	1439(26)	1194(8)	26(2)
O(2)	306(9)	3330(25)	−591(7)	23(3)
O(3)	1617(8)	4477(22)	801(7)	18(2)
O(4)	1604(9)	213(22)	105(7)	18(2)
O(5)	1574(9)	−1819(22)	1589(7)	20(2)
O(6)	1616(10)	6497(24)	−665(9)	29(3)
O(7)	2907(8)	1295(24)	1410(7)	21(3)
O(8)	1722(8)	2567(23)	2312(7)	17(2)
O(9)	4073(9)	2303(32)	2298(8)	36(3)
O(10)	2803(9)	2940(25)	3347(7)	23(3)
O(11)	2950(8)	3336(25)	−194(7)	23(3)
O(12)	1769(9)	2313(24)	−1395(7)	20(3)
O(13)	4115(9)	2588(32)	−860(8)	35(3)
O(14)	2846(9)	−2119(25)	2804(7)	23(3)
O(15)	3680(12)	7400(42)	695(13)	69(5)
C(1)	3257(13)	2043(33)	2082(10)	19(3)
C(2)	2534(12)	2564(31)	2636(10)	16(3)
C(3)	3305(13)	2773(35)	−807(10)	21(3)
C(4)	2601(12)	2348(33)	−1529(10)	18(3)

*Equivalent isotropic U is defined as $U_{eq} = \frac{1}{3} \sum_i \sum_j a_i^* a_j^* a_i a_j$

TABLE II

Atomic coordinates ($\times 10^4$, $\times 10^5$ for K, Cs and Mo) and equivalent isotropic thermal parameters ($\mathring{A}^2 \times 10^3$, $\times 10^4$ for K, Cs and Mo) for $KCs_3[Mo_2O_2S_2(C_2O_4)_2(H_2O)_2]_2 \cdot 4H_2O$ with e.s.d's, in parentheses

Atom	x/a	y/b	z/c	U_{eq}
K	0(0)	50000(0)	25000(0)	663(8)
Cs(1)	0(0)	0(0)	11883(5)	432(2)
Cs(2)	0(0)	0(0)	37673(6)	670(3)
Cs(3)	0(0)	50000(0)	0(0)	375(2)
Mo	24877(4)	21739(4)	6589(2)	226(1)
S(1)	3833(2)	2781(2)	0(0)	42(1)
S(2)	1025(2)	1997(2)	0(0)	32(1)
O(1)	2836(3)	899(3)	809(2)	30(1)
O(2)	3638(4)	2675(4)	1400(2)	39(1)
O(3)	2029(4)	3823(3)	866(2)	31(1)
O(4)	1366(3)	2122(3)	1447(2)	28(1)
O(5)	1191(3)	4899(3)	1543(2)	33(1)
O(6)	471(4)	3108(4)	2155(2)	34(1)
O(7)	1713(5)	1022(4)	2625(2)	51(1)
C(1)	1441(4)	4009(4)	1341(2)	22(1)
C(2)	1036(4)	3011(4)	1688(2)	25(1)

TABLE III

*Atomic coordinates ($\times 10^4$, $\times 10^5$ for Mo and Ba) and equivalent
isotropic thermal parameters ($\times 10^4$ Å^2) for
$Ba[Mo_2O_4(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$ with e.s.d.'s in parentheses*

Atom	x/a	y/b	z/c	U_{eq}
Ba	11868(3)	0(0)	33333(0)	134(1)
Mo	5538(4)	55799(4)	26688(3)	115(1)
C(1)	421(5)	3096(5)	3961(4)	153(9)
C(2)	−329(6)	3703(5)	4724(4)	188(10)
O(1)	905(4)	3791(4)	3012(3)	180(7)
O(2)	646(4)	7178(4)	2909(3)	210(7)
O(3)	2763(4)	6679(4)	3365(3)	268(8)
O(4)	1395(4)	5677(4)	1189(3)	155(7)
O(5)	−322(5)	4822(4)	4326(3)	234(9)
O(6)	−887(5)	3093(5)	5619(3)	315(10)
O(7)	506(4)	2055(4)	4288(3)	211(8)
O(8)	2408(6)	3517(7)	838(5)	614(16)
O(9)*	0(0)	966(6)	1667(0)	362(13)

*Refined isotropically
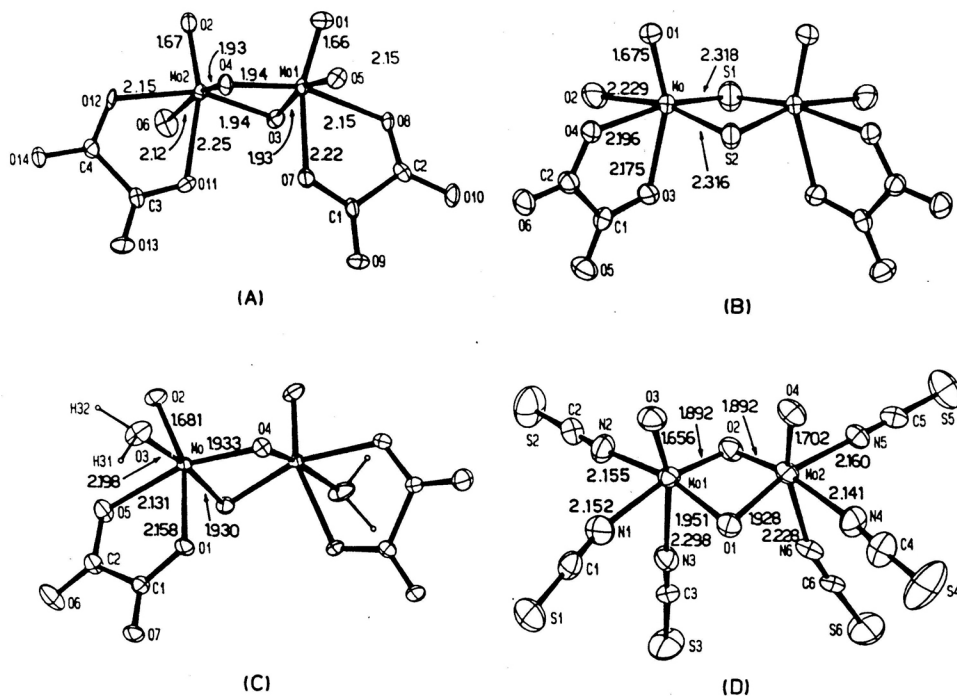

Figure 1. ORTEP drawings of the complex anions in the structures of (A), (B), (C) and (D).[16]

TABLE IV

Atomic coordinates (×10⁴, ×10⁵ for Mo) and equivalent isotropic thermal parameters (Å²×10³, ×10⁴ for Mo) for

Atomic coordinates ($\times 10^4$, $\times 10^5$ for Mo) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$, $\times 10^4$ for Mo) for
(pyH)₄[Mo₂O₄(NCS)₆] · H₂O with e.s.d's in parentheses

Atom	x/a	y/b	z/c	U_{eq}
Mo(1)	9420(3)	13604(8)	0(0)	419(2)
Mo(2)	14002(3)	14683(9)	15133(7)	434(2)
O(1)	1662(3)	1550(8)	320(5)	51(2)
O(2)	715(3)	1777(7)	1160(5)	50(2)
O(3)	827(3)	-310(7)	-17(6)	64(2)
O(4)	1375(3)	-226(8)	1781(5)	65(2)
N(1)	1190(5)	1351(11)	-1360(7)	69(3)
C(1)	1396(5)	1440(13)	-2041(8)	61(3)
S(1)	1677(2)	1607(5)	-2973(3)	97(1)
N(2)	176(4)	1814(11)	-440(7)	64(3)
C(2)	-237(6)	2068(13)	-597(8)	65(4)
S(2)	-831(2)	2440(6)	-800(4)	118(2)
N(3)	987(4)	3665(10)	-309(6)	56(2)
C(3)	966(4)	4828(11)	-373(7)	48(3)
S(3)	918(2)	6478(3)	-510(4)	103(2)
N(4)	2190(4)	1571(12)	1885(7)	68(3)
C(4)	2623(5)	1550(15)	1960(10)	79(4)
S(4)	3231(2)	1490(8)	2138(5)	164(3)
N(5)	1159(4)	1988(10)	2841(6)	53(2)
C(5)	1026(5)	2264(13)	3535(8)	62(4)
S(5)	823(2)	2664(5)	4509(3)	106(2)
N(6)	1529(4)	3727(10)	1550(7)	60(3)
C(6)	1589(4)	4905(12)	1757(7)	49(3)
S(6)	1678(2)	6469(4)	2084(3)	114(2)
C(11)	377(9)	10048(22)	-3688(11)	99(6)
N(12)	-19(8)	10494(17)	-3156(14)	132(7)
C(13)	-102(7)	10008(19)	-2358(12)	83(5)
C(14)	210(8)	9035(19)	-2089(15)	100(6)
C(15)	590(8)	8556(20)	-2551(15)	107(6)
C(16)	657(8)	8994(22)	-3350(16)	112(6)
C(21)	3058(8)	4756(20)	-1029(15)	116(7)
C(22)	3035(7)	4931(21)	-152(13)	125(7)
C(23)	2685(8)	4301(23)	308(10)	112(7)
N(24)	2337(5)	3511(17)	-140(10)	105(5)
C(25)	2361(8)	3424(19)	-1026(14)	116(6)
C(26)	2704(8)	4025(22)	-1449(11)	114(7)
C(31)	-238(8)	4577(19)	1160(11)	95(6)
C(32)	-597(6)	5419(19)	1552(17)	108(6)
C(33)	-524(8)	5794(19)	2405(14)	104(6)
C(34)	-128(9)	5427(20)	2823(13)	97(6)
C(35)	222(7)	4662(22)	2468(12)	94(6)
N(36)	160(5)	4179(10)	1636(11)	77(4)
C(41)	2855(9)	9562(21)	-714(23)	134(9)
C(42)	2844(11)	9300(28)	149(21)	143(10)
C(43)	2444(12)	8669(30)	502(14)	132(10)
N(44)	2062(9)	8309(19)	47(15)	139(7)
C(45)	2052(8)	8374(18)	-829(20)	114(8)
C(46)	2419(11)	9169(22)	-1213(10)	118(9)
O(5)	584(6)	7291(13)	1420(13)	163(6)

TABLE V

Interatomic distances (Å) and angles (°) for $Cs_2[Mo_2O_4(C_2O_4)_2(H_2O)_2] \cdot H_2O$

a) Complex anion

Mo(1)-Mo(2)	2.572(3)		
Mo(1)-O(1)	1.66(1)	Mo(2)-O(2)	1.67(1)
Mo(1)-O(3)	1.93(1)	Mo(2)-O(3)	1.94(1)
Mo(1)-O(4)	1.94(1)	Mo(2)-O(4)	1.93(1)
Mo(1)-O(5)	2.15(1)	Mo(2)-O(6)	2.12(1)
Mo(1)-O(7)	2.22(1)	Mo(2)-O(11)	2.25(1)
Mo(1)-O(8)	2.15(1)	Mo(2)-O(12)	2.15(1)
O(7)-C(1)	1.28(2)	O(11)-C(3)	1.28(2)
O(9)-C(1)	1.22(2)	O(13)-C(3)	1.22(2)
O(8)-C(2)	1.25(2)	O(12)-C(4)	1.28(2)
O(10)-C(2)	1.25(2)	O(14)-C(4)	1.25(2)
C(1)-C(2)	1.55(3)	C(3)-C(4)	1.53(2)
Mo(1)-O(3)-Mo(2)	83.4(5)	Mo(1)-O(4)-Mo(2)	83.2(5)
O(1)-Mo(1)-O(3)	103.8(6)	O(2)-Mo(2)-O(3)	109.1(6)
O(1)-Mo(1)-O(4)	109.9(6)	O(2)-Mo(2)-O(4)	103.4(6)
O(1)-Mo(1)-O(5)	91.6(6)	O(2)-Mo(2)-O(6)	91.6(6)
O(1)-Mo(1)-O(7)	161.7(6)	O(2)-Mo(2)-O(11)	162.6(6)
O(1)-Mo(1)-O(8)	91.3(6)	O(2)-Mo(2)-O(12)	92.4(6)
O(3)-Mo(1)-O(4)	94.2(5)	O(3)-Mo(2)-O(4)	93.9(5)
O(3)-Mo(1)-O(5)	163.1(5)	O(3)-Mo(2)-O(6)	86.5(5)
O(3)-Mo(1)-O(7)	84.8(5)	O(3)-Mo(2)-O(11)	85.3(5)
O(3)-Mo(1)-O(8)	87.1(5)	O(3)-Mo(2)-O(12)	156.5(5)
O(4)-Mo(1)-O(5)	87.0(5)	O(4)-Mo(2)-O(6)	164.0(6)
O(4)-Mo(1)-O(7)	85.2(5)	O(4)-Mo(2)-O(11)	84.9(5)
O(4)-Mo(1)-O(8)	157.7(5)	O(4)-Mo(2)-O(12)	90.2(5)
O(5)-Mo(1)-O(7)	78.5(5)	O(6)-Mo(2)-O(11)	79.2(5)
O(5)-Mo(1)-O(8)	85.5(5)	O(6)-Mo(2)-O(12)	83.4(5)
O(7)-Mo(1)-O(8)	72.8(5)	O(11)-Mo(2)-O(12)	72.1(5)
Mo(1)-O(7)-C(1)	118(1)	Mo(2)-O(11)-C(3)	118(1)
Mo(1)-O(8)-C(2)	120(1)	Mo(2)-O(12)-C(4)	121(1)
O(7)-C(1)-O(9)	126(2)	O(11)-C(3)-O(13)	127(2)
O(7)-C(1)-C(2)	113(2)	O(11)-C(3)-C(4)	113(2)
O(9)-C(1)-C(2)	121(2)	O(13)-C(3)-C(4)	120(2)
O(8)-C(2)-O(10)	127(2)	O(12)-C(4)-O(14)	124(2)
O(8)-C(2)-C(1)	115(2)	O(12)-C(4)-C(3)	115(2)
O(10)-C(2)-C(1)	118(2)	O(14)-C(4)-C(3)	120(2)

b) Caesium coordination

Cs(1)···O(9)	3.31(2)	Cs(2)...O(1)	3.48(2)
Cs(1)···O(9)[i]	3.31(2)	Cs(2)···O(1)[vi]	3.47(2)
Cs(1)···O(9)[ii]	3.31(2)	Cs(2)···O(2)[vii]	3.28(1)
Cs(1)···O(9)[iii]	3.31(2)	Cs(2)···O(2)[v]	3.28(1)
Cs(1)···O(13)[iv]	3.24(1)	Cs(2)···O(5)[i]	3.31(1)
Cs(1)···O(13)[v]	3.24(1)	Cs(2)···O(5)[viii]	3.31(1)
Cs(1)···O(14)[iv]	3.30(1)	Cs(2)···O(8)	3.22(1)
Cs(1)···O(14)[v]	3.30(1)	Cs(2)···O(8)[vi]	3.22(1)
Cs(1)···O(15)	3.42(2)	Cs(2)···O(12)[v]	3.24(1)
Cs(1)···O(15)[ii]	3.42(2)	Cs(2)···O(12)[vii]	3.23(1)
Cs(3)···O(7)	3.57(1)	Cs(3)···O(13)	3.12(1)
Cs(3)···O(9)	3.06(1)	Cs(3)···O(13)[iv]	3.21(2)
Cs(3)···O(9)[ii]	3.21(1)	Cs(3)···O(13)[ix]	3.23(2)
Cs(3)···O10)[ii]	3.20(1)	Cs(3)···O(15)[iv]	3.38(2)
Cs(3)···O(11)	3.51(1)		

Symmetry code:

i	= x,1+y,z	iv	= 1–x,1–y,–z	vii	= –x,1–y,–z
ii	= 1–x,y,1/2–z	v	= x,1–y,1/2+z	viii	= –x,1+y,1/2–z
iii	= 1–x,1+y,1/2–z	vi	= –x,y,1/2–z	ix	= 1–x,–y,–z

TABLE VI

Interatomic distances (Å) and angles (°) for
$KCs_3[Mo_2O_2S_2(C_2O_4)_2(H_2O)_2]_2 \cdot 4H_2O*$

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a) Complex anion

Mo-Mo'	2.832(1)	Mo-O(4)	2.196(4)
Mo-S(1)	2.318(2)	O(3)-C(1)	1.277(7)
Mo-S(2)	2.316(2)	O(4)-C(2)	1.288(6)
Mo-O(1)	1.675(4)	O(5)-C(1)	1.230(7)
Mo-O(2)	2.229(5)	O(6)-C(2)	1.231(7)
Mo-O(3)	2.175(4)	C(1)-C(2)	1.533(7)
Mo-S(1)-Mo'	75.3(1)	O(1)-Mo-O(4)	89.3(2)
Mo-S(2)-Mo'	75.4(1)	O(2)-Mo-O(3)	76.0(2)
S(1)-Mo-S(2)	103.0(1)	O(2)-Mo-O(4)	82.2(2)
S(1)-Mo-O(1)	103.8(2)	O(3)-Mo-O(4)	72.8(2)
S(1)-Mo-O(2)	83.3(1)	Mo-O(3)-C(1)	118.9(4)
S(1)-Mo-O(3)	90.4(1)	Mo-O(4)-C(2)	119.1(3)
S(1)-Mo-O(4)	160.0(1)	O(3)-C(1)-O(5)	126.2(5)
S(2)-Mo-O(1)	103.4(2)	O(3)-C(1)-C(2)	115.5(5)
S(2)-Mo-O(2)	165.3(1)	O(5)-C(1)-C(2)	118.3(5)
S(2)-Mo-O(3)	90.5(1)	O(4)-C(2)-O(6)	126.4(5)
S(2)-Mo-O(4)	88.3(1)	O(4)-C(2)-C(1)	113.3(4)
O(1)-Mo-O(2)	87.8(2)	O(6)-C(2)-C(1)	120.3(5)
O(1)-Mo-O(3)	157.1(2)		

b) Caesium and potassium coordination

K-O(5)	2.537(4)	Cs(1)-S(2)	3.783(2)
K-O(5)[i]	2.537(4)	Cs(1)-S(2)[iv]	3.783(2)
K-O(5)[ii]	2.537(4)	Cs(1)-S(2)[v]	3.783(2)
K-O(5)[iii]	2.537(4)	Cs(1)-S(2)[vi]	3.783(2)
K-O(6)	2.536(4)	Cs(1)-O(4)	3.187(4)
K-O(6)[i]	2.536(4)	Cs(1)-O(4)[iv]	3.187(4)
K-O(6)[ii]	2.536(4)	Cs(1)-O(4)[v]	3.187(4)
K-O(6)[iii]	2.536(4)	Cs(1)-O(4)[vi]	3.187(4)
Cs(2)-O(2)[vii]	3.371(4)	Cs(3)-O(1)[v]	3.393(4)
Cs(2)-O(2)[viii]	3.371(4)	Cs(3)-O(1)[x]	3.393(4)
Cs(2)-O(2)[ii]	3.371(4)	Cs(3)-O(1)[xi]	3.393(4)
Cs(2)-O(2)[ix]	3.371(4)	Cs(3)-O(1)[xii]	3.393(4)
Cs(2)-O(7)	3.491(5)	Cs(3)-O(3)	3.460(4)
Cs(2)-O(7)[iv]	3.491(5)	Cs(3)-O(3)[i]	3.460(4)
Cs(2)-O(7)[v]	3.491(5)	Cs(3)-O(3)[xiii]	3.460(4)
Cs(2)-O(7)[vi]	3.491(5)	Cs(3)-O(3)[xiv]	3.460(4)

Symmetry code:

i	= −x,1−y,z	viii	= −1/2+x,−1/2+y,1/2−z
ii	= −1/2+y, 1/2−x, 1/2−z	ix	= 1/2−y,−1/2+x,1/2−z
iii	= 1/2−y, 1/2+x, 1/2−z	x	= y, 1−x, z
iv	= −x,−y,z	xi	= y,1−x,−z
v	= −y,x,z	xii	= −y,x,−z
vi	= y,−x,z	xiii	= −x,1−y,−z
vii	= 1/2−x,1/2−y,1/2−z	xiv	= x,y,−z

* The primed atom is related to the unprimed atom by mirror plane symmetry

(A) and 2.131 Å in (C), one oxalato-O *trans* to the terminal-O at 2.22 and 2.25 Å in (A) and at 2.158 Å in (C) and one water-O at 2.12 and 2.15 Å and at 2.198 Å in (A) and (C), respectively. The octahedral coordination about the Mo atoms in both structures is significantly distorted with the angles at Mo varying from 72.1° to 109.9° in (A) and from 74.4° to 107.8° in (C). The Mo-Mo distances of 2.572 and 2.561 Å in (A)

TABLE VII

Interatomic distances (Å) and angles (°) for Ba[Mo₂O₄(C₂O₄)₂(H₂O)₂] · 3H₂O*

a) *Complex anion*

Mo-Mo'	2.561(1)	Mo-O(5)	2.131(3)
Mo-O(1)	2.158(5)	O(1)-C(1)	1.291(6)
Mo-O(2)	1.681(5)	O(5)-C(2)	1.278(8)
Mo-O(3)	2.198(4)	O(6)-C(2)	1.220(6)
Mo-O(4)	1.933(3)	O(7)-C(1)	1.220(8)
Mo-O(4)'	1.930(3)	C(1)-C(2)	1.541(9)
Mo-O(4)-Mo	83.0(2)	O(3)-Mo-O(5)	90.8(2)
O(1)-Mo-O(2)	156.5(2)	O(4)-Mo-O(4)'	93.3(2)
O(1)-Mo-O(3)	77.8(2)	O(4)-Mo-O(5)	160.4(2)
O(1)-Mo-O(4)	86.2(2)	Mo-O(1)-C(1)	118.2(3)
O(1)-Mo-O(4)'	91.5(2)	Mo-O(5)-C(2)	118.9(4)
O(1)-Mo-O(5)	74.4(2)	O(1)-C(1)-O(7)	127.1(5)
O(2)-Mo-O(3)	83.9(2)	O(1)-C(1)-C(2)	113.6(4)
O(2)-Mo-O(4)	107.8(2)	O(7)-C(1)-C(2)	119.4(5)
O(2)-Mo-O(4)'	106.1(2)	O(5)-C(2)-O(6)	125.8(5)
O(2)-Mo-O(5)	91.4(2)	O(5)-C(2)-C(1)	114.8(5)
O(3)-Mo-O(4)	87.7(2)	O(6)-C(2)-C(1)	119.4(5)
O(3)-Mo-O(4)'	169.1(2)		

b) *Barium coordination*

Ba-O(2)[i]	2.811(4)	Ba-O(2)[ii]	2.811(3)
Ba-O(6)[iii]	2.907(5)	Ba-O(6)[iv]	2.908(6)
Ba-O(7)	2.859(5)	Ba-O(7)[iii]	2.899(3)
Ba-O(7)[iv]	2.900(3)	Ba-O(7)[v]	2.859(3)
Ba-O(9)	2.788(4)	Ba-O(9)[vi]	2.788(4)

Symmetry code:

i	= x,–1+y,z	iv	= y,x,1–z
ii	= 1+x–y,1–y,2/3–z	v	= x–y,–y,2/3–z
iii	= –x+y,–x,–1/3+z	vi	= x–y, x–y,1/3+z

* Primed atoms are related to the unprimed atoms by a two-fold symmetry axis

and (C), respectively, correspond to the molybdenum-molybdenum single bond.[18,19] Out of the three crystallographically independent caesium ions in the structure of (A) two are in the special positions (2e) and (2f) while the third is in the general position of the space group P2/c. Cs(1) and Cs(2) are irregularly surrounded by ten and Cs(3) by nine oxygen atoms at distances ranging from 3.06 to 3.57 Å. Barium atom in (C) is also irregularly surrounded by ten oxygen atoms at distances ranging from 2.788 to 2.907 Å.

The analogous anion to that in the structure of (B) was already found in Cs₂ [Mo₂O₂S₂(C₂O₄)₂(H₂O)₂]·2H₂O.[5] The complex anion in (B) has a mirror plane symmetry while that in ref. 5, with an approximate non-crystallographic C_2 symmetry, is in general position of the space group P2₁/n. In the structure of (B), the Mo atom is surrounded by one terminal oxo-O atom at 1.675 Å, two bridging-S atoms at 2.318 and 2.316 Å, one oxalato-O *cis* to the terminal-O at 2.196 Å, one oxalato-O *trans* to the terminal-O at 2.175 Å, and one water-O at 2.229 Å. The octahedral coordination around the Mo atom is also distorted with the angles at Mo ranging from 72.8° to 103.8°. The Mo···Mo distance of 2.832 Å is longer than the value considered as a single Mo–Mo bond (2.6 Å).[18] All cations, potassium and caesium, are in special positions of the space group I4/m. K is in position (4d), Cs(1) and Cs(2) in position (4e) (four fold axis) and

Cs(3) in position (4*c*). The potassium ion is irregularly surrounded by eight oxygen atoms at almost the same distance of 2.537 Å, Cs(1) by four oxygen atoms at 3.187 Å and four sulphur atoms at 3.783 Å, Cs(3) by eight oxygen atoms, four at 3.393 and four at 3.460 Å, and Cs(2) by four oxygens at 3.371 Å, four oxygens at 3.491 Å and four sulphurs at 4.091 Å.

The structure of (D) was determined in 1977 and refined up to R = 0.08,[20] then again refined in 1979 up to R = 0.066.[7,*] In this structure, each Mo atom is surrounded by one terminal oxo-O atom at 1.656 and 1.702 Å, two bridging-O atoms at 1.892, and at 1.951 and 1.928 Å, two isothiocyanato-N *cis* to the terminal-O at the mean value of 2.152 Å and one isothiocyanato-N *trans* to the terminal-O at 2.298 and 2.228 Å, respectively. The angles at the Mo atoms range from 77.6° to 106.0° The Mo-Mo bond lenght is 2.582 Å. In this structure, the nitrogen atoms from the pyridinium cations (2) and (3) participate in the hydrogen bondings N–H···O (2.69 and 2.85 Å) with both

TABLE VIII

Interatomic distances (Å) and angles (°) for $(pyH)_4[Mo_2O_4(NCS)_6] \cdot H_2O$

a) Complex anion

Mo(1)-Mo(2)	2.580(1)		
Mo(1)-O(1)	1.951(8)	Mo(2)-O(1)	1.928(8)
Mo(1)-O(2)	1.892(8)	Mo(2)-O(2)	1.892(8)
Mo(1)-O(3)	1.656(7)	Mo(2)-O(4)	1.702.(8)
Mo(1)-N(1)	2.152(11)	Mo(2)-N(4)	2.141(11)
Mo(1)-N(2)	2.155(11)	Mo(2)-N(5)	2.160(9)
Mo(1)-N(3)	2.298(10)	Mo(2)-N(6)	2.228(10)
N(1)-C(1)	1.163(17)	N(4)-C(4)	1.137(17)
N(2)-C(2)	1.132(19)	N(5)-C(5)	1.136(15)
N(3)-C(3)	1.139(15)	N(6)-C(6)	1.200(15)
C(1)-S(1)	1.595(13)	C(4)-S(4)	1.612(14)
C(2)-S(2)	1.623(16)	C(5)-S(5)	1.610(13)
C(3)-S(3)	1.627(11)	C(6)-S(6)	1.619(12)
Mo(1)-O(1)-Mo(2)	83.4(3)	Mo(1)-O(2)-Mo(2)	86.0(3)
O(1)-Mo(1)-O(2)	93.0(3)	O(1)-Mo(2)-O(2)	93.8(3)
O(1)-Mo(1)-O(3)	105.8(4)	O(1)-Mo(2)-O(4)	106.0(4)
O(1)-Mo(1)-N(1)	86.9(4)	O(1)-Mo(2)-N(4)	84.3(4)
O(1)-Mo(1)-N(2)	162.3(4)	O(1)-Mo(2)-N(5)	163.7(4)
O(1)-Mo(1)-N(3)	84.7(3)	O(1)-Mo(2)-N(6)	85.9(4)
O(2)-Mo(1)-O(3)	99.7(4)	O(2)-Mo(2)-O(4)	100.6(3)
O(2)-Mo(1)-N(1)	167.8(4)	O(2)-Mo(2)-N(4)	168.1(4)
O(2)-Mo(1)-N(2)	87.1(4)	O(2)-Mo(2)-N(5)	87.0(3)
O(2)-Mo(1)-N(3)	89.7(3)	O(2)-Mo(2)-N(6)	89.6(3)
O(3)-Mo(1)-N(1)	92.0(4)	O(4)-Mo(2)-N(4)	91.2(4)
O(3)-Mo(1)-N(2)	91.6(4)	O(4)-Mo(2)-N(5)	89.8(4)
O(3)-Mo(1)-N(3)	165.4(4)	O(4)-Mo(2)-N(6)	163.6(4)
N(1)-Mo(1)-N(2)	89.2(4)	N(4)-Mo(2)-N(5)	91.6(4)
N(1)-Mo(1)-N(3)	78.2(4)	N(4)-Mo(2)-N(6)	78.6(4)
N(2)-Mo(1)-N(3)	77.6(4)	N(5)-Mo(2)-N(6)	77.8(4)
Mo(1)-N(1)-C(1)	168.9(11)	Mo(2)-N(4)-C(4)	169.8(11)
Mo(1)-N(2)-C(2)	174.1(11)	Mo(2)-N(5)-C(5)	179.1(10)
Mo(1)-N(3)-C(3)	171.1(9)	Mo(2)-N(6)-C(6)	166.3(9)
N(1)-C(1)-S(1)	178.4(12)	N(4)-C(4)-S(4)	176.0(14)
N(2)-C(2)-S(2)	178.8(13)	N(5)-C(5)-S(5)	178.5(12)
N(3)-C(3)-S(3)	177.0(10)	N(6)-C(6)-S(6)	177.2(10)

*Preparing our manuscript in 1978 we were not aware of the first determination published in Zh. neorg. Khim.

TABLE VIII, continued

b) *Pyridium cations*

C(11)-N(12)	1.38(3)	C(11)-N(12)-C(13)	123(2)
N(12)-C(13)	1.31(3)	N(12)-C(13)-C(14)	116(2)
C(13)-C(14)	1.32(3)	C(13)-C(14)-C(15)	125(2)
C(14)-C(15)	1.30(3)	C(14)-C(15)-C(16)	119(2)
C(15)-C(16)	1.29(3)	C(15)-C(16)-C(11)	122(2)
C(16)-C(11)	1.36(3)	C(16)-C(11)-N(12)	115(2)
C(21)-C(22)	1.34(3)	C(21)-C(22)-C(23)	120(2)
C(22)-C(23)	1.30(3)	C(22)-C(23)-N(24)	118(2)
C(23)-N(24)	1.37(3)	C(23)-N(24)-C(25)	120(2)
N(24)-C(25)	1.34(3)	N(24)-C(25)-C(26)	121(2)
C(25)-C(26)	1.25(3)	C(25)-C(26)-C(21)	121(2)
C(26)-C(21)	1.33(3)	C(26)-C(21)-C(22)	121(2)
C(31)-C(32)	1.38(3)	C(31)-C(32)-C(33)	118(2)
C(32)-C(33)	1.35(3)	C(32)-C(33)-C(34)	121(2)
C(33)-C(34)	1.26(3)	C(33)-C(34)-C(35)	122(2)
C(34)-C(35)	1.30(3)	C(34)-C(35)-N(36)	120(2)
C(35)-N(36)	1.35(2)	C(35)-N(36)-C(31)	120(2)
N(36)-C(31)	1.32(2)	N(36)-C(31)-C(32)	119(2)
C(41)-C(42)	1.33(5)	C(41)-C(42)-C(43)	120(3)
C(42)-C(43)	1.33(4)	C(42)-C(43)-N(44)	122(3)
C(43)-N(44)	1.26(4)	C(43)-N(44)-C(45)	123(2)
N(44)-C(45)	1.32(4)	N(44)-C(45)-C(46)	116(2)
C(45)-C(46)	1.36(3)	C(45)-C(46)-C(41)	120(2)
C(46)-C(41)	1.42(4)	C(46)-C(41)-C(42)	117(3)

bridging-O atoms similarly as the N-atoms from the pyridinium cation (1) with the water-O atom (2.69 Å).

In the structures (A), (C) and (D), the Mo_2O_2 four membered rings within the bridging systems are folded along the lines connecting two bridging oxygen atoms at angles of 154.2(5), 150.9(3) and 158.4(3)°, respectively. This angle in the Mo_2S_2 ring in (B) amounts to 157.8(9)°

DISCUSSION

The characteristic structural examples of di-μ-oxo and di-μ-sulphido-oxomolybdenum(V) complexes with octahedral coordination of Mo atoms are given in Table IX. As it can be seen from the Table, all oxalato complexes in which two octahedrally coordinated Mo atoms are doubly bridged through two oxygen atoms indicate the existence of *trans* influence of the terminal oxo-oxygen atom. This effect, however, is not equally conspicuous in all three structures, *e.g.* in the structure of (iii) the Mo-to-oxalato-oxygen bond length *trans* to the terminal oxygen amounts to only 2.158 Å (in the previous structure determination 2.11 Å),[6] which is significantly shorter than the corresponding bonds in the structures of (i) and (ii). Nevertheless, it is longer than the Mo-to-oxalato-oxygen bond length of 2.131 Å *cis* to the terminal oxo-oxygen atom. All in all, the Mo-to-oxalato-O bonds *cis* to the terminal oxo-O range from 2.13 to 2.15 Å, those *trans* to the terminal oxygen from 2.16 to 2.25 Å. However, in the analogous oxalato complexes with a double bridge of sulphurs between two Mo atoms this effect is not the same: the Mo-to-oxalato-oxygen bond lengths *cis* to the terminal oxo-O are 2.16 and

2.20 Å, as compared to such bonds of 2.16 and 2.18 Å in *trans* positions. This indicates that the sulphur atom has a larger *trans* influence than the oxygen atom. This observation is in accordance with the suggestion that the less electronegative atoms exhibit a larger *trans* influence relative to the more electronegative atoms.[22] On the other hand, although both complexes with the isothiocyanato ligand show obvious *trans* influence of the terminal oxo-oxygen, in the structure of (vii) with the double bridge of sulphur atoms the Mo-NCS bond length of 2.180 Å (*cis* to oxo-oxygen, but *trans* to the bridging sulphur) is significantly longer in comparison with the bonds *trans* to the bridging oxygen atoms in the structure of (vi). Such Mo-NCS bond lengths range from 2.141 to 2.160 Å. It is obvious that the Mo-N(6) bond length of 2.11 Å observed earlier was a result of inaccurate structure determination. In the present determination, this bond amounts to 2.228 Å and is close to 2.242 Å, the value established for such a bond in ref. 20.

The factors affecting such behaviour will have to be assessed when more and accurate structural determinations become available.

TABLE IX

Some structural parameters (in Å) in some di-μ-oxo-bis[oxomolybdenum(V)] and di-μ-sulphido-bis[oxomolybdenum(V)] complexes with six-coordinated molybdenum atoms

	COMPLEX	Mo⋯Mo	Mo-X$_{br}$*	Mo-O$_t$**	Mo-L (*cis* to O$_t$)	Mo-L (*trans* to O$_t$)	Ref.
(i)	H(pyH)$_3$[Mo$_2$O$_4$(C$_2$O$_4$)$_2$(H$_2$O)$_2$] · 2H$_2$O	2.564	1.960(O) 1.927(O)	1.677	2.144(O) 2.139(OH$_2$)	2.209(O)	17
(ii)	Cs$_2$[Mo$_2$O$_4$(C$_2$O$_4$)$_2$(H$_2$O)$_2$] ·H$_2$O	2.572	1.93 (O) 1.94 (O)	1.67	2.15 (O) 2.14 (OH$_2$)	2.22 (O) 2.25 (O)	This work[+]
(iii)	Ba[Mo$_2$O$_4$(C$_2$O$_4$)$_2$(H$_2$O)$_2$] ·3H$_2$O	2.561	1.930(O) 1.933(O)	1.681	2.131(O) 2.198(OH$_2$)	2.158(O)	This work
(iv)	Cs$_2$[Mo$_2$O$_2$S$_2$(C$_2$O$_4$)$_2$(H$_2$O)$_2$] ·2H$_2$O	2.822	2.309(S) 2.319(S)	1.697	2.163(O) 2.213(OH$_2$)	2.160(O)	5[+]
(v)	KCs$_3$[Mo$_2$O$_2$S$_2$(C$_2$O$_4$)$_2$(H$_2$O)$_2$]$_2$ ·4H$_2$O	2.832	2.317(S)	1.675	2.196(O) 2.229(OH$_2$)	2.175(O)	This work[+]
(vi)	(pyH)$_4$[Mo$_2$O$_4$(NCS)$_6$] ·H$_2$O	2.582	1.892(O) 1.951(O)	1.656 1.702	2.152(N)	2.263(N)	This work[+]
(vii)	(pyH)$_4$[Mo$_2$O$_2$S$_2$(NCS)$_6$]	2.827	2.313(S) 2.301(S)	1.683	2.180(N)	2.269(N)	21[+]

* X = O or S bridging atom; ** O$_t$ = terminal oxo-oxygen atom; [+]mean values

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SAŽETAK

Trans utjecaj okso liganda u dimernim kompleksima molibdena(V). Određivanje kristalne strukture cezij di-µ-okso-bis[akvaoksalatooksomolibdata(V)] monohidrata (A) i kalij tricezij bis{di-µ-sulfido-bis[akvaoksalatooksomolibdata(V)]} tetrahidrata (B) i ponovno određivanje kristalnih struktura barij di-µ-okso-bis[akvaoksalatooksomolibdata (V)] trihidrata (C) i piridinij di-µ-okso-bis[oksotris(izotiocijanato)molibdata(V)]-monohidrata (D)

B. Kamenar, B. Kaitner i N. Strukan

Izvedena je rendgenska strukturna analiza dvaju novih kompleksnih spojeva molibdena(V), u naslovu označena s (A) i (B), a kristalna struktura kompleksa (C) i (D) ponovno je određena i utočnjena. Međuatomski razmaci i kutevi razmotreni su i uspoređeni s onima u već poznatima sličnim strukturama. Potvrđeno je da u takvim strukturama di-µ-okso-kompleksa oksomolibdena(V) s oktaedarskom koordinacijom molibdena postojanje trans-utjecaja okso-kisika vrijedi kao opće pravilo. Međutim, strukture di-µ-sulfido kompleksa oksomolibdena(V) odstupaju od tog pravila zbog izrazitijeg trans-utjecaja atoma sumpora u dvostrukom mostu. To je u skladu s opažanjem da manje elektronegativni atomi pokazuju izrazitiji trans-utjecaj od elektronegativnih atoma.