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Structural Comparison of Octahedral MoO_2^{2+} Complexes of Bidentate and Linear Tetradentate N,S-donor Ligands

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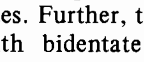
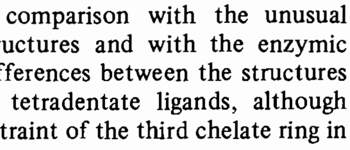
The structures of $MoO_2[NH_2C(CH_3)_2CH_2S]_2$ *and* $MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$ *have been determined using X-ray diffraction intensity data collected by counter techniques.* $MoO_2[NH_2C(CH_3)_2CH_2S]_2$ *crystallizes in space group Pbca with* $a = 11.234(3)$, $b = 11.822(3)$ *and* $c = 20.179(5)$ Å, $V = 2680(2)$ Å^3 *and* $Z = 8$. *Its structure is derived from octahedral coordination with* cis *oxo groups* [$Mo–O = 1.705(3)$ *and* $1.705(3)$], trans *thiolate donors* cis *to the oxo groups* [$Mo–S = 2.416(1)$ *and* $2.402(1)$] *and N donors* trans *to oxo* [$Mo–N = 2.325(3)$ *and* $2.385(4)$ Å]. $MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$ *crystallizes in the space group* $P2_1/c$ *with* $a = 10.798(5)$, $b = 6.911(2)$, $c = 20.333(9)$ Å, $\beta = 95.20°$, $V = 1511(2)$ Å^3 *and* $Z = 4$. *Its structure is very similar to that of* $MoO_2[NH_2C(CH_3)_2CH_2S]_2$ *with* $Mo–O = 1.714(2)$ *and* $1.710(2)$, $Mo–S = 2.415(1)$ *and* $2.404(1)$ *and* $Mo–N = 2.316(3)$ *and* $2.362(3)$. *The small differences in the geometries of the two compounds are attributed to the constraints of the extra chelate ring in the complex with the tetradentate ligand. The structures in this paper stand in contrast to those reported for complexes of similar ligands wherein steric hindrance produces complexes with a skew trapezoidal bipyramidal structure.*

Introduction

Recent work [2–10] has focussed on Mo(VI) complexes of N,S donor ligands as potential model complexes for biological molybdenum centers. These complexes display Mo–O and Mo–S distances [2] which are very similar to distances found in sulfite oxidase by EXAFS studies [11, 12]. Although it is tempting to assign a near octahedral structure to the enzyme site based upon this comparison, it should be borne in mind that angular information cannot be directly obtained from the present EXAFS experiments. Furthermore, recent structural results [4, 13] show that non-octahedral Mo(VI) complexes are possible which contain Mo–O and Mo–S distances similar to those found in octahedral complexes. Complexes of the form MoO_2L_2 where L is an N-substituted cysteaminato ligand such as $^-SC(CH_3)_2CH_2N(CH_3)_2$ possess a skew trapezoidal bipyramidal structure [4, 13]. To compare fully this new structural type with conventional structures we require near octahedral complexes which contain ligands that are as similar as possible. This paper reports the structures of MoO_2L_2 and MoO_2L' where L is the bidentate cysteaminato ligand **I** and L′ is the tetradentate ligand **II**. Details of the coordination spheres reported here are similar to those of other octahedral structures containing N,S-donor ligands [3, 6, 7] and allow detailed comparison with the unusual skew trapezoidal structures and with the enzymic sites. Further, the differences between the structures with bidentate and tetradentate ligands, although small, reveal the constraint of the third chelate ring in the latter case.



I = L



II = L′

Experimental

The complexes were synthesized from the reaction of $MoO_2(acac)_2$ with the appropriate ligand in methanol [14]. Crystals were grown from the reaction media at ~4 °C.

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Data Collection and Reduction

All X-ray diffraction experiments were performed on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochrometer using Mo-K_α radiation. The crystals were mounted on thin glass fibers with epoxy cement. The crystallographic data are summarized in Table I.

The intensity data were collected and processed as described previously including analytical absorption corrections [15]. Crystals of MoO_2L_2 belong to the orthorhombic crystal system with $a = 11.234(3)$, $b = 11.822(3)$, and $c = 20.179(5)$ Å. The systematic absences 0kl, $k \neq 2n$; h0l, $l \neq 2n$; and hk0, $h \neq 2n$ are consistent only with the space group Pbca. There is one molecule per asymmetric unit. All reflections of the form +h, ±k, +l were collected for $3° < 2\theta < 60°$.

Crystals of MoO_2L' belong to the monoclinic system with $a = 10.798(5)$, $b = 6.911(2)$, $c = 20.333(9)$ Å, and $\beta = 95.20(4)$. The systematic absences h0l, $l \neq 2n$ and 0k0, $k \neq 2n$ reveal the space group $P2_1/c$. The asymmetric unit contains one complete molecule. All reflections of the form +h, +k, ±l for $3° < 2\theta < 60°$ were collected.

Structure Solution and Refinement

The structures were solved using standard heavy atom methods. All non-hydrogen atoms were refined anisotropically using full matrix least-squares. Hydrogen atom positions were calculated assuming tetrahedral geometries and C–H distances of 0.98 Å with the orientations of the methyl groups determined from difference Fourier maps. These atoms were included as fixed contributions in the final least-squares cycles. Final difference Fourier maps showed no peaks higher than 25% of the height of a carbon atom peak. The final agreement factors are given in Table I. The positional and thermal parameters for the non-hydrogen atoms are given in Table II. Calculated hydrogen atom positions and structure factor tables are included as supplementary material.

Results and Discussion

The structures of MoO_2L_2 and MoO_2L' consist of well separated mononuclear complexes. Although N–H protons are present in both complexes there is no intermolecular H-bonding of the types found in the structures of $MoO_2[SC(CH_3)_2CH_2NHCH_3]_2$ and $MoO_2[SC(CH_3)_2C(CH_3)_2NHCH_3]_2$ [4, 13].

Figures 1 and 2 present ORTEP drawings of the two complexes. Bond distances and angles are found in Tables III and IV, respectively. The structures are extremely similar. Each is based on octahedral coordination of Mo by two O-, two N- and two S-donor atoms. Each structure has an approximate two-fold axis which bisects the O1–Mo–O2, N1–Mo–N2 and S1–Mo–S2 angles. The Mo–O, Mo–N and Mo–S distances are in the range found for other near octahedral Mo complexes containing this set of donor atoms [3, 4, 6, 7]. The oxo ligands are in *cis* positions while the thiolate donors are *trans* to each other and *cis* to both oxo groups. This placement is probably due largely to electronic effects with the oxo groups maintaining their *cis* arrangement to most effectively utilize the Mo d-orbital set [16]. *Trans* placement of the two oxo groups would require these two powerful ligands to share the same σ- and π-acceptor orbitals. Similarly, placement of the S ligands *trans* to

TABLE I. Crystallographic Data.

		$MoO_2[NH_2C(CH_3)_2CH_2S]_2$	$MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$
Formula		$C_8H_{20}MoN_2O_2S_2$	$C_{10}H_{22}MoN_2O_2S_2$
a, Å		11.234(3)	10.798(5)
b, Å		11.822(3)	6.911(2)
c, Å		20.179(5)	20.333(9)
β, deg			95.20(8)
V, Å^3		2680(2)	1511(2)
Z		8	4
Space group		Pbca	$P2_1/c$
d_{calc} g/cm^3		1.667	1.593
Transmission factors	max	85.8	83.1
	min	77.3	70.8
Absorption coefficient cm^{-1}		12.5	11.1
Number of observations		1682	2025
Number of variables		136	154
Error in obs of unit wt.		1.367	1.298
R		0.038	0.032
R_w		0.047	0.043

TABLE II. Positional and Thermal Parameters[a].

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
$MoO_2(SCH_2C(CH_3)_2NH_2)_2$									
Mo	0.19368(4)	0.22241(4)	0.10665(2)	2.42(2)	2.06(2)	2.98(2)	0.11(2)	0.35(2)	0.10(2)
S1	0.0597(1)	0.3514(1)	0.05130(7)	2.18(5)	3.11(5)	4.53(6)	0.61(4)	−0.11(5)	−0.11(5)
S2	0.3776(1)	0.1638(1)	0.15670(8)	3.80(6)	2.49(5)	4.78(6)	0.90(5)	−0.78(6)	0.44(6)
O1	0.0966(3)	0.2106(3)	0.1713(2)	3.8(2)	3.8(2)	4.1(2)	−0.1(2)	1.2(1)	−0.2(2)
O2	0.1860(3)	0.0986(3)	0.0635(2)	4.1(2)	2.2(1)	3.9(2)	0.1(1)	−0.1(2)	−0.1(1)
N1	0.3108(3)	0.3027(4)	0.0241(2)	2.4(2)	2.8(2)	2.8(2)	0.1(1)	0.0(1)	0.3(1)
N2	0.2591(4)	0.3888(3)	0.1627(2)	3.4(2)	2.4(2)	2.7(2)	0.3(2)	0.2(2)	0.0(2)
C1	0.1453(5)	0.4128(4)	−0.0153(3)	2.7(2)	2.3(2)	4.6(3)	0.4(2)	−0.7(2)	0.5(2)
C2	0.2487(5)	0.3395(4)	−0.0381(2)	3.1(2)	2.5(2)	2.8(2)	0.3(2)	−0.4(2)	0.3(2)
C3	0.2065(5)	0.2362(5)	−0.0751(3)	4.9(3)	3.6(2)	3.4(2)	0.0(2)	−0.8(2)	−0.4(2)
C4	0.3335(5)	0.4094(5)	−0.0802(3)	4.7(2)	3.7(3)	3.5(2)	0.3(2)	0.6(2)	1.1(2)
C5	0.3703(6)	0.2564(5)	0.2287(3)	5.4(3)	4.4(3)	4.3(3)	0.3(3)	−0.7(3)	0.9(2)
C6	0.3612(4)	0.3792(4)	0.2098(3)	2.4(2)	2.9(2)	3.4(2)	−0.3(2)	−0.4(2)	0.1(2)
C7	0.4696(5)	0.4205(6)	0.1755(3)	3.5(3)	5.5(3)	6.0(3)	−0.4(3)	0.0(3)	0.7(3)
C8	0.3382(7)	0.4530(6)	0.2698(3)	6.6(3)	5.6(4)	4.1(3)	−0.3(3)	−0.5(3)	−0.6(3)
$MoO_2(SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S)$									
Mo	0.25754(3)	0.24910(4)	0.24714(1)	1.56(1)	1.55(1)	3.09(1)	−0.15(1)	0.48(1)	−0.01(1)
S1	0.21203(9)	0.2754(2)	0.36091(5)	2.30(3)	3.07(4)	3.44(4)	0.73(4)	0.69(3)	−0.32(4)
S2	0.30826(9)	0.1007(2)	0.14606(5)	2.37(4)	4.25(5)	3.58(4)	−0.94(4)	1.05(3)	−0.89(4)
O1	0.1226(2)	0.3739(4)	0.2260(1)	2.3(1)	2.4(1)	4.4(1)	0.5(1)	0.1(1)	0.4(1)
O2	0.3822(2)	0.4008(4)	0.2447(1)	2.7(1)	2.7(1)	4.8(1)	−1.1(1)	1.2(1)	−0.5(1)
N1	0.3860(3)	0.0215(5)	0.3022(2)	1.5(1)	2.3(1)	3.4(1)	0.2(1)	0.1(1)	−0.3(1)
N2	0.1438(3)	−0.0432(5)	0.2437(2)	1.7(1)	1.9(1)	3.7(1)	−0.1(1)	0.3(1)	0.1(1)
C1	0.3476(4)	0.1772(7)	0.4111(2)	2.7(2)	3.6(2)	3.4(2)	0.1(2)	0.1(1)	−0.2(2)
C2	0.4415(3)	0.0997(6)	0.3653(2)	2.0(1)	3.2(2)	3.7(2)	0.5(1)	−0.1(1)	−0.1(2)
C3	0.3314(4)	−0.1738(6)	0.3041(2)	3.0(2)	1.7(2)	5.3(2)	0.3(2)	−0.3(2)	0.1(2)
C4	0.1900(4)	−0.1667(6)	0.3003(2)	2.9(2)	2.3(2)	4.4(2)	−0.6(2)	−0.2(2)	0.8(2)
C5	0.1380(4)	−0.1563(6)	0.1815(2)	2.7(2)	2.7(2)	4.2(2)	−0.8(2)	−0.1(1)	−0.8(2)
C6	0.1665(3)	−0.0386(7)	0.1217(2)	2.4(2)	3.5(2)	3.6(2)	−0.8(2)	0.2(1)	−1.1(2)
C7	0.4107(4)	0.3437(8)	0.4513(2)	4.3(2)	4.9(2)	4.1(2)	0.0(2)	−0.8(2)	−1.4(2)
C8	0.3057(5)	0.0270(8)	0.4589(2)	4.8(2)	5.6(3)	3.7(2)	0.1(2)	0.8(2)	1.1(2)
C9	0.0601(4)	0.0940(8)	0.0966(2)	3.5(2)	5.5(3)	4.2(2)	−1.1(2)	−0.3(2)	0.3(2)
C10	0.1947(5)	−0.1783(9)	0.0675(2)	5.1(2)	6.1(3)	4.8(2)	−1.1(2)	0.6(2)	−2.5(2)

[a] The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

each other avoids their placement *trans* to oxo. The strong donor properties of the oxo ligands dominate the coordination spheres. The avoidance of the position *trans* to oxo, firstly by the other oxo ligand and secondly by the thiolate ligands specifies the remaining atomic positions in the octahedral coordination sphere. This result is typically found in other complexes containing the MoO_2^{+2} core [3, 4, 6, 7, 16–22].

Deviations of the donor atoms from the idealized octahedral geometry are substantial and attributable to repulsions between the donor atoms. The typically large O–Mo–O angle is due to O–O repulsion between the tightly bound oxo groups. Repulsions between oxo groups and S atoms are also important. The deviations from linearity of the nominally *trans* S1–Mo–S2 angles are attributed mainly to repulsions from the oxo groups although some contribution from chelate ring constraint is also possible. For each structure the S–Mo–O angles divide into two sets: S1–Mo–O1 and S2–Mo–O2 which range from 87.7 to 90.6° and S1–Mo–O2 and S2–Mo–O1 which range from 101.8 to 105.9°. In MoO_2L_2 we can compare the S1–Mo–O1 angle of 90.4° with the S1–Mo–O2 angle of 105.9°. The plane of the O1–Mo–S1 angle contains the Mo–S1–C1–C2–N2 chelate ring and thus any opening of the O1–Mo–S1 angle would require either closing of the chelate angle or movement of N1 into a position which increases repulsion from S2. By comparison, the plane determined by O2–Mo–S1 is roughly perpendicular to the Mo–S1–C1–C2–N1 plane and distortion of the O–Mo–S angle appears more facile. The smaller O–Mo–S angles are always located in the same plane

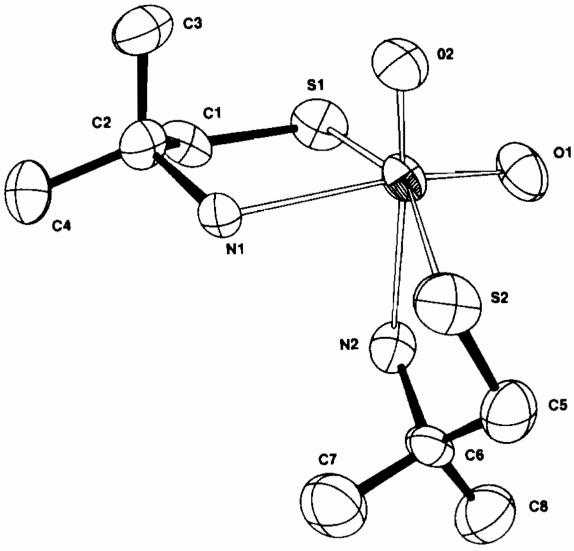

Fig. 1. ORTEP drawing of $MoO_2[NH_2C(CH_3)_2CH_2S]_2$.

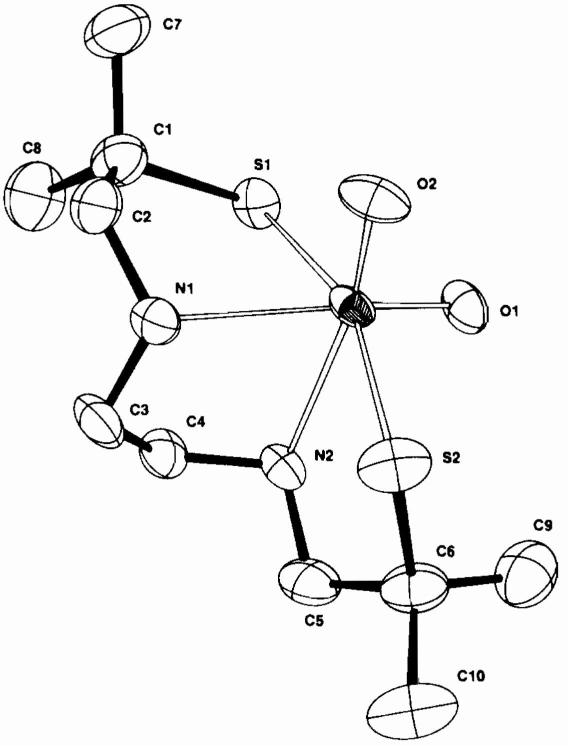

Fig. 2. ORTEP drawing of $MoO_2[SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S]$.

TABLE III. Bond Distances.

$MoO_2(SCH_2C(CH_3)_2NH_2)_2$		$MoO_2(SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S)$	
Mo–S1	2.416(1)	Mo–S1	2.415(1)
Mo–S2	2.402(1)	Mo–S2	2.404(1)
Mo–O1	1.705(3)	Mo–O1	1.714(2)
Mo–O2	1.705(3)	Mo–O2	1.710(2)
Mo–N1	2.325(3)	Mo–N1	2.316(3)
Mo–N2	2.385(4)	Mo–N2	2.362(3)
S1–C1	1.805(5)	S1–C1	1.837(4)
C1–C2	1.521(6)	C1–C2	1.535(5)
C2–C3	1.507(7)	C1–C7	1.534(6)
C2–C4	1.520(7)	C1–C8	1.518(6)
N1–C2	1.501(5)	N1–C2	1.470(4)
S2–C5	1.821(6)	N1–C3	1.475(5)
C5–C6	1.505(7)	C3–C4	1.522(5)
C6–C7	1.484(7)	N2–C4	1.482(5)
C6–C8	1.514(7)	N2–C5	1.483(5)
N2–C6	1.495(6)	C5–C6	1.518(5)
		C6–C9	1.521(6)
		C6–C10	1.517(6)
		S2–C6	1.838(4)

TABLE IV. Bond Angles.

	$MoO_2(SCH_2C(CH_3)_2NH_2)_2$	$MoO_2(SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S)$
S1–Mo–S2	155.82(5)	158.90(4)
S1–Mo–O1	90.38(12)	87.69(9)
S1–Mo–O2	105.92(11)	102.15(9)
S1–Mo–N1	76.34(9)	75.73(7)
S1–Mo–N2	83.72(9)	86.68(7)
S2–Mo–O1	101.83(13)	104.77(9)
S2–Mo–O2	90.62(12)	89.77(9)
S2–Mo–N1	86.11(9)	87.16(7)
S2–Mo–N2	76.90(9)	76.59(7)
O1–Mo–O2	106.70(16)	109.75(13)
O1–Mo–N1	160.55(14)	157.01(11)
O1–Mo–N2	84.37(14)	89.72(10)
O2–Mo–N1	90.77(15)	89.53(11)
O2–Mo–N2	164.95(15)	158.72(11)
N1–Mo–N2	80.15(13)	73.76(10)

as an Mo–S–C–C–N chelate ring. Small interactions between the oxo groups and ligand methyl or methylene groups may also contribute to differences between the two sets of S–Mo–O angles.

Examination of Tables III and IV reveals the great similarity between the two structures. The largest angular difference lies in the N1–Mo–N2 angles. When released from the constraints of the third chelate ring the 73.8° angle in MoO_2L' opens to 80.2° in MoO_2L_2. The movement of N2 away from N1 opens the O2–Mo–N2 angle and closes the O1–Mo–N2 angle each by approximately 5°.

The conformations of the organic ligands in the two structures are revealed by the weighted least-squares planes defined by the chelate rings. The Mo–S–C–C–N chelate rings are significantly puckered. In MoO_2L_2 the deviations from the Mo–S1–C1–C2–N1 chelate plane are 0.00, –0.01, –0.13, +0.39 and –0.23 Å, respectively, whereas those from the

Mo–S2–C5–C6–N2 plane are 0.00, 0.36, –0.74, 0.02, 0.21 Å, respectively. The 0.74 Å deviation for C6 is indicative of the more severe puckering of the second ring and illustrates the departure from twofold molecular symmetry. In MoO_2L', the Mo–S1–C1–C2–N1 plane shows deviations of –0.00, 0.03, –0.32, –0.43, and 0.42 Å, respectively, while the corresponding values for Mo–S2–C5–C6–N2 are 0.00, –0.05, –0.07, 0.67, –0.23 Å, respectively.

The above considerations show that electronic and steric effects qualitatively account for the angular distortions from regular structures. In particular, these structures reinforce the idea that, after the donor atom positions are set by electronic effects, steric effects dominate details of the coordination geometry. Similar complexes of bidentate ligands with methyl substituted on nitrogen donor atoms possess unusual skew-trapezoidal bipyramidal structures [4, 14] demonstrating even more profound consequences of these effects. The structure of MoO_2L_2 presented here demonstrates that in the absence of these additional steric requirements a distorted octahedral structure is preferred.

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