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X-Ray Structures of Di-μ-oxo, μ-Oxo-μ-thio-, and Di-μ-thio-μ-[(*R*)-propylenediaminetetraacetato]-bis[oxomolybdate(V)] Ions

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The crystal structures of $Na_2[Mo_2O_4(R\text{-pdta})]\cdot 3H_2O$ (**1**), $Na_2[Mo_2O_3S(R\text{-pdta})]\cdot 4H_2O$ (**2**), and $Na_2[Mo_2O_2S_2(R\text{-pdta})]\cdot 4H_2O$ (**3**) have been determined from diffractometer data collected by the use of Mo $K\alpha$ radiation. The structures of **1**, **2**, and **3** were refined by the least-squares method to *R* 0.064, 0.040, and 0.058 for 1370, 2794, and 2141 nonzero reflections respectively. Each Mo^V ion has a distorted octahedral coordination, and the two coordination octahedra share a common edge to form a binuclear complex. Two terminal oxo ligands are *cis* to the bridging oxide or sulfide. The *R*-pdta^{4-} ligand bridges two Mo^V ions, yielding a Mo–N–CH_2–CH(CH_3)–N–Mo ring with an equatorial methyl group, the N and carboxyl O atoms occupying the axial (*trans* to the terminal O) and equatorial positions respectively. A specific distortion of the donor-atom disposition is observed, which is represented as the twist (Δ) of the terminal O–O edges in the O, L_b, Mo, Mo, O, L_b, O portion about the axis passing through the mid-points of the O–O edges (Δ denotes the absolute disposition of two skew edges or bonds), and as the twist (Δ) of Mo–N bonds about the Mo–Mo axis. The O=Mo bonds of the O=Mo–Mo=O segment in **1** twist in Δ, but those in **2** and **3** are virtually parallel. The distortion of donor-atom disposition is discussed on the basis of the strain due to chelate-ring formation.

Few studies have been reported on the structure-circular dichroism (CD) correlation for molybdenum complexes, despite the rapid and extensive development of molybdenum chemistry.[1] Four of the present authors (K. Z. S., Y. S., S. O., and K. S.) have previously measured the CD spectra of a number of the binuclear Mo(V) complexes in solution and in crystalline state and have found, from a comparison of the spectral features with the X-ray structure, that the signs of the CD bands in the 26000—33000 cm^{-1} region are related to the distortion of the two coordination polyhedra about the Mo–Mo axis.[2] The present work has been conducted to provide structural data for this investigation. The structural details of $Na_2[Mo_2O_4(R\text{-pdta})]\cdot 3H_2O$ (**1**), $Na_2[Mo_2O_3S(R\text{-pdta})]\cdot 4H_2O$ (**2**), and $Na_2[Mo_2O_2S_2(R\text{-pdta})]\cdot 4H_2O$ (**3**) (*R*-pdta^{4-}, (*R*)-propylenediaminetetraacetate) will now be reported, thus providing the first example of the crystal structure of a complete series of binuclear Mo(V) complexes with three kinds of bridging structures and a common ligand.

Experimental

The preparation of the compounds was described elsewhere.[2] All three compounds are red-brown in color. The crystal data are shown in Table 1, where the experimental details are also given. The Laue symmetries and approximate unit-cell dimensions were determined from Weissenberg photographs. The cell dimensions were refined by the least-squares analyses of 15, 31, and 24θ values, as measured on a Philips four-circle diffractometer, for **1**, **2**, and **3** respectively.

The intensities were measured on the diffractometer using graphite-monochromated Mo $K\alpha$ radiation, and corrected for the Lp factor, but not for absorption. The backgrounds were measured on each side of the scan range. The intensities of three standard reflections were monitored every 4 h for each of the three compounds, but they showed no appreciable decay.

The crystal structure was solved by the heavy-atom technique. The positional and thermal parameters were refined by the least-squares method. The minimized function was $\sum w(F_o-|F_c|)^2$. Weights were assigned as $w=p$ for $F_o<F_{min}$, $w=1.0$ for $F_{min}\leq F_o\leq F_{max}$, and $w=(F_{max}/F_o)^2$ for $F_o>F_{max}$. The p, F_{max}, and F_{max} for each compound are as follows:

	p	F_{min}	F_{max}
1	0.1	16.9	42.3
2	0.6	7.8	31.2
3	0.7	9.5	35.6

No attempt was made to locate the H atoms. The atomic scattering factors, with corrections for anomalous dispersions of Mo^0 and S, were taken from Ref. 3. The absolute crystal structure was determined on the basis of the configuration of the asymmetric carbon atom. The atomic coordinate are given in Table 2. The F_o-F_c table and the anisotropic thermal parameters for heavy atoms are preserved by the Chemical Society of Japan (Document No. 8136). All computations were performed by means of a FACOM 230-60 computer at Osaka City University using programs in the UNICS.[4]

Results and Discussion

Crystal Structure. Figures 1 and 2 show the crystal structures of **1** and **2**. Compound **3** is isostructural with **2**. In **2** and **3** the complex anion is surrounded by 6 Na^+ ions, which are in contact with the O(O=C) atoms of the COO portions at distances of 2.30—2.55 Å. Although the cation disposition around the complex anion in **1** is somewhat different from those in **2** and **3**, the 6 Na^+ ions also lie in the vicinities of the O(O=C) atoms.

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TABLE 1. CRYSTAL DATA AND INTENSITY DATA COLLECTION

	1	2	3
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1$	P1	P1
a/Å	23.215(6)	11.438(3)	11.450(5)
b/Å	7.105(2)	7.401(2)	7.416(2)
c/Å	6.714(2)	6.563(2)	6.675(2)
α/°		89.54(2)	89.26(6)
β/°	99.66(3)	97.04(2)	95.90(3)
γ/°		90.82(2)	90.74(5)
U/Å^3	1091.8(5)	551.4(3)	563.7(3)
D_m/g cm^{-3}	1.98	2.08	2.06
D_c/g cm^{-3}	2.00	2.09	2.09
Z	2	1	1
μ(Mo $K\alpha$)/cm^{-1}	12.5	13.3	13.9
Crystal size/mm^3	0.1×0.1×0.1	0.24×0.12×0.19	0.11×0.08×0.15
Scan type	$\omega-2\theta$	ω	$\omega-2\theta$
Scan speed (ω/°s^{-1})	0.017	0.024	0.008
Scan range (ω/°)	(0.8+0.2 tan θ)	(1.7+0.2 tan θ)	(1.5+0.2 tan θ)
Background count/s^{-1}	20	20	20
$2\theta_{max}$/°	55.0	60.0	55.0
Reflections measured	$\pm h, +k, +l$	$\pm h, \pm k +l$	$\pm h, \pm k, +l$
No. of unique data ($F_o^2 > 2\sigma(F_o^2)$)	1370	2974	2141
R	0.064	0.040	0.058
R′(=$[\sum w\Delta^2/\sum wF_o^2]^{1/2}$	0.081	0.047	0.072

TABLE 2a. POSITIONAL AND THERMAL PARAMETERS FOR **1**

	x	y	z	U/Å^2
Mo(1)	0.2019(1)	−0.0130(4)	−0.0674(2)	0.0230[a]
Mo(2)	0.3094(1)	0.0 (5)	0.0841(2)	0.0253[a]
O(1)	0.1936(6)	0.184(3)	−0.208(2)	0.033(3)
O(2)	0.1454(6)	−0.153(2)	−0.300(2)	0.031(3)
O(3)	0.1211(6)	0.045(2)	0.030(2)	0.030(3)
O(4)	0.0693(6)	−0.338(2)	−0.378(2)	0.031(3)
O(5)	0.0519(6)	−0.034(3)	0.201(2)	0.041(4)
O(6)	0.3283(7)	0.190(3)	−0.040(3)	0.043(4)
O(7)	0.3643(7)	0.091(3)	0.350(2)	0.041(4)
O(8)	0.3831(7)	−0.157(3)	0.048(2)	0.039(4)
O(9)	0.4243(6)	0.023(3)	0.631(2)	0.046(4)
O(10)	0.4434(8)	−0.397(3)	0.116(3)	0.058(5)
O(11)	0.2409(5)	0.060(2)	0.199(2)	0.024(3)
O(12)	0.2670(6)	−0.164(2)	−0.117(2)	0.026(3)
N(1)	0.1714(7)	−0.301(3)	0.088(2)	0.021(3)
N(2)	0.3154(7)	−0.269(3)	0.323(3)	0.023(4)
C(1)	0.1123(8)	−0.291(3)	−0.270(3)	0.020(4)
C(2)	0.1374(9)	−0.408(3)	−0.082(3)	0.030(5)
C(3)	0.0992(9)	−0.067(3)	0.146(3)	0.031(5)
C(4)	0.1326(9)	−0.233(3)	0.226(3)	0.026(5)
C(5)	0.3823(7)	−0.014(5)	0.503(2)	0.024(4)
C(6)	0.3482(10)	−0.200(4)	0.523(4)	0.039(6)
C(7)	0.3973(9)	−0.314(4)	0.124(3)	0.027(4)
C(8)	0.3535(9)	−0.412(4)	0.240(3)	0.035(5)
C(9)	0.2194(8)	−0.434(3)	0.187(3)	0.024(4)
C(10)	0.2596(8)	−0.358(3)	0.370(3)	0.026(4)
C(11)	0.2710(9)	−0.520(6)	0.518(3)	0.044(5)
Na(1)	−0.0029(4)	0.424(1)	0.517(1)	0.034(2)
Na(2)	0.4782(4)	−0.082(2)	−0.066(2)	0.044(2)
O_w(1)	0.0607(7)	0.181(3)	−0.349(3)	0.043(4)
O_w(2)	0.4768(9)	0.170(4)	0.208(4)	0.075(7)
O_w(3)	0.0294(8)	0.378(3)	0.185(3)	0.054(5)

a) Equivalent isotropic mean-square amplitude (W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959)).

TABLE 2b. POSITIONAL AND THERMAL PARAMETERS FOR **2**

	x	y	z	U/Å^2
Mo(1)	−0.2276(1)	0.0788(1)	−0.0390(1)	0.0214[a]
Mo(2)	0.0 (1)	0.0 (1)	0.0 (1)	0.0200[a]
S	−0.1323(2)	−0.0498(2)	−0.2934(3)	0.0281[a]
O_X	−0.0905(5)	0.1753(7)	0.1322(8)	0.029(1)
O(1)	−0.2809(5)	−0.0961(8)	0.0912(9)	0.034(1)
O(2)	−0.3370(6)	0.2525(9)	0.1117(10)	0.038(1)
O(3)	−0.3747(5)	0.0963(8)	−0.2689(9)	0.031(1)
O(4)	−0.4539(6)	0.4929(9)	0.0813(11)	0.041(1)
O(5)	−0.4860(5)	0.2499(8)	−0.5042(10)	0.035(1)
O(6)	−0.0017(5)	−0.1911(8)	0.1388(9)	0.032(1)
O(7)	0.1394(5)	−0.1104(7)	−0.1467(8)	0.027(1)
O(8)	0.1459(5)	0.1169(8)	0.1720(9)	0.031(1)
O(9)	0.2795(6)	−0.0813(9)	−0.3506(10)	0.040(1)
O(10)	0.2824(6)	0.3261(9)	0.2473(10)	0.039(1)
N(1)	−0.2187(5)	0.3751(8)	−0.2033(9)	0.023(1)
N(2)	0.0750(5)	0.2519(8)	−0.2075(9)	0.022(1)
C(1)	−0.3655(7)	0.4107(11)	0.0452(12)	0.030(2)
C(2)	−0.2784(8)	0.5041(13)	−0.0783(15)	0.038(2)
C(3)	−0.3923(7)	0.2298(10)	−0.3934(12)	0.028(1)
C(4)	−0.2877(7)	0.3555(11)	−0.4087(13)	0.032(2)
C(5)	0.1937(7)	−0.0199(10)	−0.2761(12)	0.028(1)
C(6)	0.1459(8)	0.1595(12)	−0.3514(13)	0.033(2)
C(7)	0.1992(6)	0.2643(10)	0.1334(11)	0.026(1)
C(8)	0.1528(7)	0.3663(12)	−0.0617(13)	0.034(2)
C(9)	−0.0992(7)	0.4615(10)	−0.2182(12)	0.029(1)
C(10)	−0.0152(8)	0.3645(9)	−0.3424(10)	0.022(1)
C(11)	0.0428(8)	0.5090(13)	−0.4676(15)	0.038(2)
Na(1)	0.4306(3)	0.5291(4)	0.3544(5)	0.029(1)
Na(2)	0.3751(3)	0.0254(5)	0.3636(6)	0.037(1)
O_w(1)	−0.4399(7)	−0.1963(10)	0.4154(11)	0.047(2)
O_w(2)	0.4313(9)	0.0642(14)	0.0293(16)	0.075(3)
O_w(3)	0.3865(7)	−0.4174(11)	−0.3001(13)	0.055(2)
O_w(4)	0.2810(6)	−0.2527(10)	0.2214(11)	0.046(2)

a) Equivalent isotropic mean-square amplitude.

Table 2c. Positional and thermal parameters for **3**

	x	*y*	*z*	*U*/Å²
Mo(1)	−0.6204(1)	0.5399(2)	−0.5274(2)	0.0186[a]
Mo(2)	−0.3800(1)	0.4600(2)	−0.4720(2)	0.0151[a]
S(1)	−0.4807(3)	0.6558(5)	−0.2896(5)	0.0246[a]
S(2)	−0.5087(3)	0.4183(5)	−0.7621(5)	0.0196[a]
O(1)	−0.6777(10)	0.3585(15)	−0.4140(17)	0.029(2)
O(2)	−0.7455(9)	0.7083(14)	−0.4121(16)	0.029(2)
O(3)	−0.7518(10)	0.5533(16)	−0.7709(17)	0.025(2)
O(4)	−0.8505(10)	0.9583(15)	−0.4233(17)	0.041(2)
O(5)	−0.8605(12)	0.7198(19)	−0.9956(21)	0.028(3)
O(6)	−0.3851(10)	0.2586(15)	−0.3458(17)	0.027(2)
O(7)	−0.2423(9)	0.3572(14)	−0.6304(16)	0.024(2)
O(8)	−0.2312(9)	0.5681(14)	−0.3092(16)	0.022(2)
O(9)	−0.1014(11)	0.3904(18)	−0.8292(19)	0.037(3)
O(10)	−0.1002(10)	0.7834(16)	−0.2256(18)	0.032(3)
N(1)	−0.6020(11)	0.8424(17)	−0.6786(19)	0.022(2)
N(2)	−0.3067(10)	0.7188(15)	−0.6741(17)	0.017(2)
C(1)	−0.7654(12)	0.8753(19)	−0.4611(21)	0.024(3)
C(2)	−0.6688(14)	0.9673(22)	−0.5615(24)	0.031(3)
C(3)	−0.7681(13)	0.6936(21)	−0.8864(23)	0.020(3)
C(4)	−0.6680(15)	0.8285(23)	−0.8883(26)	0.027(3)
C(5)	−0.1858(13)	0.4505(20)	−0.7496(22)	0.023(3)
C(6)	−0.2309(13)	0.6349(21)	−0.8122(23)	0.024(3)
C(7)	−0.1825(13)	0.7239(21)	−0.3398(23)	0.024(3)
C(8)	−0.2310(13)	0.8320(21)	−0.5233(23)	0.024(3)
C(9)	−0.4844(14)	0.9300(21)	−0.6889(24)	0.026(3)
C(10)	−0.3944(12)	0.8334(19)	−0.8041(21)	0.019(3)
C(11)	−0.3305(14)	0.9815(22)	−0.9255(24)	0.027(3)
Na(1)	−0.9546(6)	0.9898(8)	−0.1335(10)	0.027(1)
Na(2)	−0.0045(6)	0.4902(10)	−0.1132(11)	0.035(2)
$O_w(1)$	−0.8227(13)	0.2649(20)	−0.0774(22)	0.044(3)
$O_w(2)$	−0.9560(16)	0.5063(26)	−0.4462(29)	0.067(5)
$O_w(3)$	−0.0055(14)	0.0447(23)	−0.7906(25)	0.054(4)
$O_w(4)$	−0.1026(13)	0.2052(19)	−0.2493(22)	0.043(3)

a) Equivalent isotropic mean-square amplitude.

Although no H atoms were located in the structure analyses, some possible hydrogen bonds, inferred from the interatomic distances and angles, are listed in Table 3. All the H atoms of $O_w(1)$, $O_w(2)$, and $O_w(3)$ in **2** and **3**, and those of $O_w(2)$ and $O_w(3)$ in **1**, seem to participate in O–H···O(carboxylate) hydrogen bonding, while one of the H atoms of $O_w(4)$ in **2** and **3** and that of $O_w(1)$ in **1** do not seem to be involved in the hydrogen bonding.

The O atom of Mo=O is generally distant from the Na^+ ions. The $O_w(1)$ atoms in **2** and **3** are located at distances of 3.04(1) and 3.00(2) Å respectively from O(1)(O=Mo), and one of the H atoms of $O_w(1)$ seems to be in contact with the O(1). The O(1) in **2** and **3** also has a short contact with the $C(2)H_2$ group of the adjacent anion at $(x, 1+y, z)$, the O(1)···C(2) distances being 3.17(2) and 3.08(3) Å respectively. However, the O(1)···H(CH_2) distances, calculated on the assumption of C–H=1.05 Å, are 2.57 and 2.70 Å even in **3**. No such contacts are found in **1**.

In **1**—**3**, however, there are no remarkable short distances indicative of a strong interaction; accordingly, the interatomic interaction seems to produce no significant deformation of the complex anion.

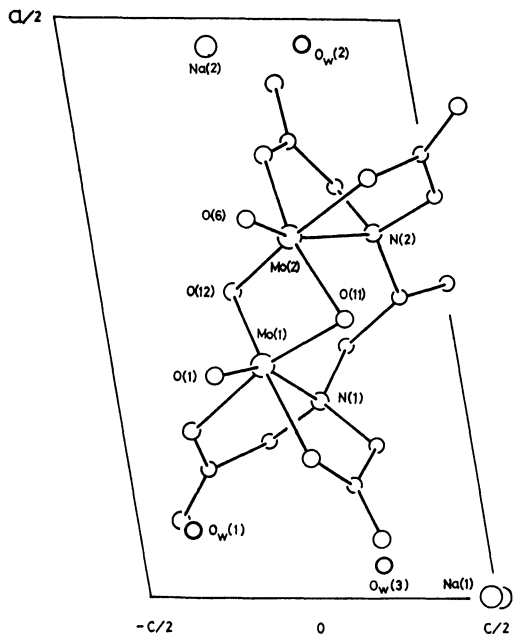

Fig. 1. The crystal structure of $Na_2[Mo_2O_4(R\text{-pdta})]\cdot 3H_2O$ viewed down the b axis.

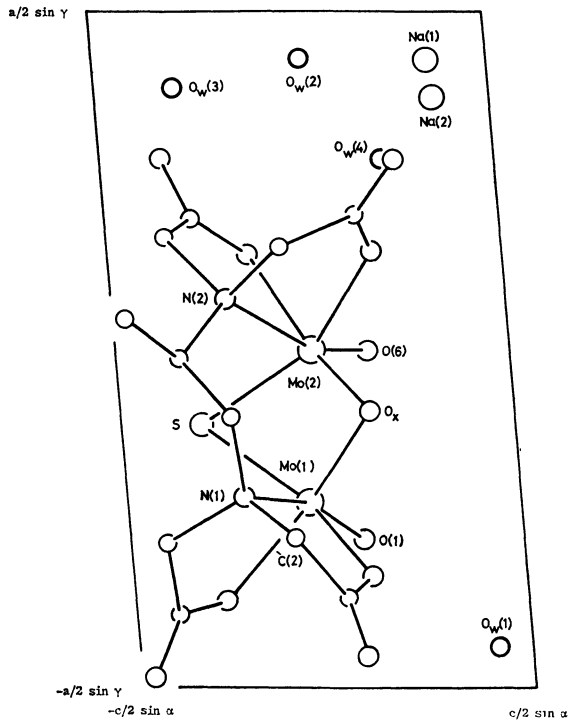

Fig. 2. The crystal structure of $Na_2[Mo_2O_3S(R\text{-pdta})]\cdot 4H_2O$ viewed down the b axis.

Structure of the Binuclear Complex Anion. Figure 3 shows a perspective view of the binuclear complex anion in **1**. As the three complex anions have configurations similar to one another, a common atom numbering was used for all three, as is shown in figure, except for the bridging atoms. The projections and elevations of the anions are given in Fig. 4. Table 3 lists the interatomic distances and bond angles. The corresponding bond lengths agree well within the experimental

TABLE 3. INTERATOMIC DISTANCES AND ANGLES[a)]

Bond length (l)

	1 l/Å	2 l/Å	3 l/Å
Mo(1)–O(1)	1.68(2)	1.691(6)	1.70(1)
O(2)	2.11(1)	2.135(7)	2.12(1)
O(3)	2.13(1)	2.124(5)	2.10(1)
N(1)	2.45(2)	2.440(6)	2.47(1)
L_b(1)	1.94(1)	2.318(2)	2.318(4)
L_b(2)	1.93(2)	1.946(5)	2.301(4)
Mo(2)–O(6)	1.68(2)	1.676(6)	1.71(1)
O(7)	2.11(2)	2.134(6)	2.14(1)
O(8)	2.09(2)	2.080(5)	2.08(1)
N(2)	2.49(2)	2.501(6)	2.52(1)
L_b(1)	1.93(1)	2.329(2)	2.331(3)
L_b(2)	1.92(1)	1.943(6)	2.299(4)
Mo(1)–Mo(2)	2.533(2)	2.656(1)	2.808(2)
O(1)···O(6)	3.14(2)	3.255(8)	3.42(2)
N(1)···N(2)	3.46(3)	3.495(9)	3.51(2)
L_b(1)···L_b(2)	2.79(2)	3.246(6)	3.613(5)
O(2)–C(1)	1.28(3)	1.277(10)	1.29(2)
O(4)–C(1)	1.18(2)	1.234(11)	1.21(2)
N(1)–C(2)	1.48(3)	1.488(12)	1.49(2)
C(1)–C(2)	1.54(3)	1.514(13)	1.51(2)
O(3)–C(3)	1.28(3)	1.279(9)	1.29(2)
O(5)–C(3)	1.24(3)	1.231(9)	1.24(2)
N(1)–C(4)	1.48(3)	1.484(10)	1.53(2)
C(3)–C(4)	1.46(3)	1.516(11)	1.51(2)
O(7)–C(5)	1.28(3)	1.288(10)	1.27(2)
O(9)–C(5)	1.22(2)	1.240(11)	1.24(2)
N(2)–C(6)	1.51(3)	1.492(11)	1.48(2)
C(5)–C(6)	1.56(4)	1.498(11)	1.51(2)
O(8)–C(7)	1.25(3)	1.280(9)	1.30(2)
O(10)–C(7)	1.23(3)	1.223(9)	1.23(2)
N(2)–C(8)	1.51(3)	1.487(10)	1.51(2)
C(7)–C(8)	1.55(3)	1.523(11)	1.52(2)
N(1)–C(9)	1.53(3)	1.514(10)	1.50(2)
N(2)–C(10)	1.52(3)	1.527(9)	1.52(2)
C(9)–C(10)	1.51(3)	1.522(11)	1.54(2)
C(10)–C(11)	1.54(4)	1.534(12)	1.58(2)
C(6)···C(11)	2.89(4)	2.914(13)	2.89(2)
C(8)···C(11)	2.99(3)	2.996(12)	3.01(2)

Short contact

A	B	1 l/Å	2 l/Å	3 l/Å
Na(1)···	O_w(1)	2.35(2)^{III}	2.503(8)^{IV}	2.53(2)^{II}
		2.43(2)^{XII}		
	O_w(3)	2.49(2)	2.418(9)^{VI}	2.46(2)^{IX}
	O_w(4)		2.446(8)^{II}	2.40(2)^{VIII}
	O(4)	2.40(2)^{VI}	2.370(8)^{I}	2.39(2)
		2.49(2)^{XII}		
	O(5)	2.39(2)^{XIV}	2.416(7)^{V}	2.41(2)^{III}
	O(10)		2.297(7)	2.29(1)^{X}
Na(2)···	O_w(1)		2.681(9)^{I}	2.67(2)^{I}
	O_w(2)	2.57(3)	2.372(12)	2.35(2)^{I}
		2.34(3)^{XV}		
	O_w(4)		2.446(8)	2.51(2)
	O(5)		2.377(8)^{V}	2.43(2)^{V}
	O(8)	2.51(2)		
	O(9)	2.32(2)^{XI}	2.404(8)^{III}	2.39(2)^{III}
	O(10)	2.31(3)^{XIII}	2.548(7)	2.52(1)
		2.74(3)		

A	B	1 l/Å	2 l/Å	3 l/Å
O_w(1)···	O(3)	2.86(2)	3.031(10)^{III}	3.02(2)^{III}
	O(1)		3.041(10)	3.00(2)
O_w(2)···	O(2)		2.969(13)	2.81(2)
	O(7)	2.98(3)		
	O(9)		3.056(12)	3.03(2)^{X}
	O(10)	3.12(3)^{XIII}		
O_w(3)···	O(4)		2.990(11)^{VII}	2.95(2)^{VII}
	O(5)	2.97(3)		
		3.00(3)^{XII}		
	O(9)		2.785(11)	2.80(2)
O_w(4)···	O(7)		2.937(9)	3.07(2)

Roman numeral superscripts refer to the position of the B atom in the respective A···B contacts: I $1+x, y, z$; II $x, 1+y, z$; III $x, y, 1+z$; IV $1+x, 1+y, z$; V $1+x, y, 1+z$; VI $x, 1+y, 1+z$; VII $1+x, y-1, z$; VIII $x-1, 1+y, z$; IX $x-1, 1+y, 1+z$; X $x-1, y, z$; XI $x, y, z-1$; XII $-x, (1/2)+y, -z$; XIII $1-x, (1/2)+y, -z$; XIV $-x, (1/2)+y, 1-z$; XV $1-x, -(1/2)+y, -z$.

Bond angle (ϕ)

	1 ϕ/°	2 ϕ/°	3 ϕ/°
O(1)–Mo(1)–O(2)	88.9(7)	87.9(3)	90.1(5)
O(1)–Mo(1)–O(3)	89.3(7)	96.1(3)	95.9(5)
O(1)–Mo(1)–L_b(1)	106.7(7)	105.9(2)	104.6(4)
O(1)–Mo(1)–L_b(2)	112.6(7)	107.1(3)	105.0(4)
O(1)–Mo(1)–N(1)	156.8(6)	159.3(3)	161.0(5)
N(1)–Mo(1)–O(2)	74.4(6)	73.4(2)	72.2(4)
N(1)–Mo(1)–O(3)	72.5(6)	72.5(2)	74.1(4)
N(1)–Mo(1)–L_b(1)	87.5(6)	90.7(2)	90.7(3)
N(1)–Mo(1)–L_b(2)	84.3(6)	81.9(2)	82.1(3)
O(2)–Mo(1)–O(3)	81.3(6)	80.3(2)	78.2(4)
L_b(1)–Mo(1)–L_b(2)	92.8(6)	98.8(2)	102.9(1)
Mo(2)–Mo(1)–O(1)	101.9(5)	100.6(2)	100.8(4)
Mo(2)–Mo(1)–N(1)	101.3(4)	99.1(1)	97.4(3)
O(6)–Mo(2)–O(7)	90.1(7)	88.3(3)	89.2(5)
O(6)–Mo(2)–O(8)	94.8(8)	96.3(2)	98.1(5)
O(6)–Mo(2)–L_b(1)	108.8(8)	105.6(2)	104.0(4)
O(6)–Mo(2)–L_b(2)	106.4(7)	106.5(3)	104.6(4)
O(6)–Mo(2)–N(2)	161.1(6)	160.0(2)	161.2(5)
N(2)–Mo(2)–O(7)	74.4(6)	73.9(2)	73.2(4)
N(2)–Mo(2)–O(8)	72.9(6)	71.9(2)	72.1(4)
N(2)–Mo(2)–L_b(1)	82.7(6)	84.0(1)	82.7(3)
N(2)–Mo(2)–L_b(2)	87.4(6)	88.9(2)	90.7(3)
O(7)–Mo(2)–O(8)	82.8(6)	79.3(2)	78.1(4)
L_b(1)–Mo(2)–L_b(2)	93.1(6)	98.5(2)	102.6(1)
Mo(1)–Mo(2)–O(6)	98.7(5)	99.9(2)	100.0(4)
Mo(1)–Mo(2)–N(2)	100.1(4)	100.0(1)	98.0(3)
Mo(1)–L_b(1)–Mo(2)	82.0(5)	69.7(1)	74.3(1)
Mo(1)–L_b(2)–Mo(2)	82.4(6)	86.1(2)	75.3(1)
Mo(1)–O(2)–C(1)	124(1)	123.0(6)	126(1)
Mo(1)–N(1)–C(2)	105(1)	107.0(5)	107(1)
O(2)–C(1)–O(4)	126(2)	125.4(8)	125(1)
O(2)–C(1)–C(2)	113(2)	115.5(7)	115(1)
O(4)–C(1)–C(2)	121(2)	119.0(8)	121(1)
N(1)–C(2)–C(1)	115(2)	112.4(7)	113(1)
Mo(1)–O(3)–C(3)	122(1)	123.7(5)	123(1)
Mo(1)–N(1)–C(4)	104(1)	105.5(4)	105(1)
O(3)–C(3)–O(5)	122(2)	122.3(7)	123(2)
O(3)–C(3)–C(4)	119(2)	116.1(6)	118(1)

	1	2	3
	ϕ/°	ϕ/°	ϕ/°
O(5)-C(3)-C(4)	119(2)	121.4(7)	120(1)
N(1)-C(4)-C(3)	112(2)	109.6(6)	110(1)
C(2)-N(1)-C(4)	110(2)	109.6(6)	107(1)
Mo(2)-O(7)-C(5)	124(2)	122.8(5)	124(1)
Mo(2)-N(2)-C(6)	107(1)	104.2(4)	105(1)
O(7)-C(5)-O(9)	124(3)	122.2(7)	123(1)
O(7)-C(5)-C(6)	118(2)	118.8(7)	118(1)
O(9)-C(5)-C(6)	119(2)	118.8(7)	119(1)
N(2)-C(6)-C(5)	113(2)	114.4(7)	115(1)
Mo(2)-O(8)-C(7)	126(2)	127.4(5)	127(1)
Mo(2)-N(2)-C(8)	105(1)	106.5(4)	105(1)
O(8)-C(7)-O(10)	125(2)	122.9(7)	122(1)
O(8)-C(7)-C(8)	117(2)	117.2(6)	118(1)
O(10)-C(7)-C(8)	117(2)	119.9(7)	121(1)
N(2)-C(8)-C(7)	111(2)	112.5(6)	113(1)
C(6)-N(2)-C(8)	108(2)	110.2(6)	109(1)
Mo(1)-N(1)-C(9)	117(1)	118.7(4)	121(1)
Mo(2)-N(2)-C(10)	120(1)	117.9(4)	119(1)
N(1)-C(9)-C(10)	116(2)	118.0(6)	118(1)
N(2)-C(10)-C(9)	114(2)	112.4(6)	115(1)
C(9)-C(10)-C(11)	106(2)	107.2(6)	107(1)
N(2)-C(10)-C(11)	113(2)	112.5(6)	111(1)

a) $L_b(1)$ and $L_b(2)$stand for O(11) and O(12) in **1**, S and O_x in **2**, and for S(2) and S(1) in **3**.

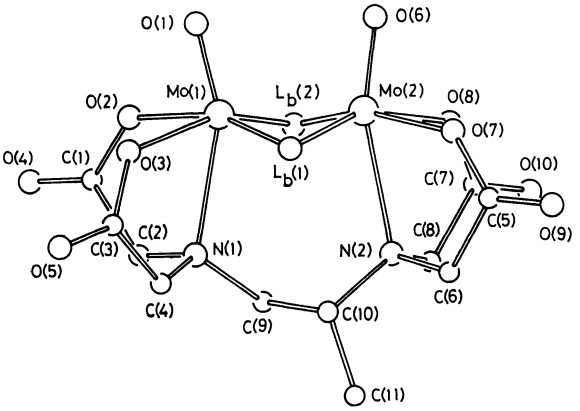

Fig. 3. A perspective view of $[Mo_2O_4(R\text{-pdta})]^{2-}$ anion with atom numbering. The same numbering is used for $[Mo_2O_3S(R\text{-pdta})]^{2-}$ and $[Mo_2O_2S_2(R\text{-pdta})]^{2-}$ anions. The $L_b(1)$ and $L_b(2)$ stand for O(11) and O(12) in $[Mo_2O_4(R\text{-pdta})]^{2-}$, S and O_x in $[Mo_2O_3S(R\text{-pdta})]^{2-}$, and S(2) and S(1) in $[Mo_2O_2S_2(R\text{-pdta})]^{2-}$.

error in the three complexes, except for those in which L_b atoms are concerned (L_b, bridging ligand).

Structure of the $Mo_2O_2L_{b2}$ Core: The geometry and dimensions of $Mo_2O_2L_{b2}$ core are not much different from those of the corresponding core in the other binuclear Mo(V) complexes.[5,6] Each Mo atom has a very distorted octahedral coordination. The deviation of the Mo atom from the mean plane defined by two O(carboxylate) and two L_b atoms is in the range of 0.35—0.37 Å, irrespective of the kind of bridging ligand (Table 4).

The Mo–Mo distance increases in the order of **1**, **2**, and **3**. The distance in **1** is slightly shorter than those so far found in Mo_2O_4 cores (2.541—2.580 Å),[5] while that in **2** is comparable to that in $[Mo_2O_3S(S_2CNPr_2)_2]$ (2.673(3) Å).[7] The Mo–Mo bond in **3** is comparable in length to that in $Cs_2[Mo_2O_2S_2(edta)]\cdot 2H_2O$ (2.799 (1) Å),[8] but shorter than those in the other complexes with a $Mo_2O_2S_2$ core.[6] Although the Mo–Mo=O(1) and Mo–Mo=O(6) bond angles in **2** and **3** are nearly equal, they are significantly different from each other in **1**.

The Mo–S bond length in **3** ranges from 2.299 to 2.331(3) Å. The Mo–S(1) distances are longer than the Mo–S(2) distances; concomitantly, the Mo–S(2)–Mo angle is 1.0° larger than the Mo–S(1)–Mo angle. However, the average value of the Mo–S bond length (2.312 Å) is comparable to that of the edta complex (2.294(1) Å).[8] The Mo–S–Mo angle in **2** is smaller by *ca.* 5° than any of the corresponding angles in the $Mo_2O_2S_2$ cores of other complexes.[6] The Mo–O–Mo angles in **1** are normal and close to those in $[Mo_2O_4(H_2PO_2)_2(bpy)_2]$ (82.5°, 82.9(5)°),[9] but the Mo–O–Mo angle in **2** is greater by 4° than those in **1**. The two L_b–Mo–L_b angles in each complex agree well with each other, and increase in the order of **1**, **2**, and **3**.

The interplanar angle between the two MoL_{b2} planes is 145.4° in **1**, comparable to that in the bpy complex (143°),[9] but smaller than that in $Na_2[Mo_2O_4(R\text{-cys})_2]\cdot 5H_2O$ (151°).[10] The angle increases with the elongation of the Mo–Mo bond (Table 4), and that in **3** is nearly equal to that in the edta complex (152.3°).[8] The two Mo=O bonds in **1** are twisted in a Δ configuration with an O=Mo–Mo=O torsion angle of 5.4(8)°, whereas those in **2** and **3** are virtually parallel (Δ or Λ is used to designate the chirality of two skew edges or bonds, according to the definition given in our previous paper[2]).

Structure of the Chelate Ring: The Mo(1)–N bond in

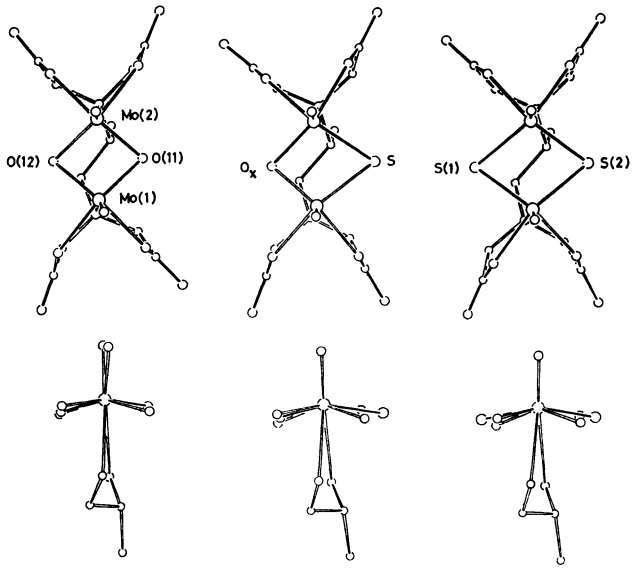

Fig. 4. The projection (top) on [O(2), O(3), O(7), O(8)] plane and the elevation (bottom) viewed along Mo(1)→Mo(2) vector, for each of the three complex anions: $[Mo_2O_4(R\text{-pdta})]^{2-}$ (left), $[Mo_2O_3S(R\text{-pdta})]^{2-}$ (middle), and $[Mo_2O_2S_2(R\text{-pdta})]^{2-}$ (right). The glycinato rings are not drawn in the elevation for clarity. The Mo–L_b bond is shown by solid line in the elevation.

Table 4. Deviations (d) of atoms from mean planes, interplanar angles (ϕ), and torsion angles (τ)[a)]

Plane	Atom	1 d/Å	2 d/Å	3 d/Å
	Mo(1)	0.353(8)	0.362(3)	0.370(4)
	O(2)	0.047(17)	0.080(7)	0.065(11)
[O(2),O(3),L_b(1),L_b(2)]	O(3)	−0.048(15)	−0.078(6)	−0.067(12)
	L_b(1)	0.048(15)	0.066(2)	0.047(4)
	L_b(2)	−0.047(16)	−0.068(6)	−0.047(4)
	Mo(2)	0.364(9)	0.365(3)	0.371(4)
	O(7)	0.055(19)	0.080(5)	0.092(11)
[O(7),O(8),L_b(1),L_b(2)]	O(8)	−0.058(19)	−0.091(6)	−0.097(10)
	L_b(1)	−0.054(15)	−0.066(2)	−0.067(4)
	L_b(2)	0.057(16)	0.077(6)	0.072(4)
	Mo(1)	0.055(3)	0.094(1)	0.114(1)
	Mo(2)	−0.054(3)	−0.093(1)	−0.112(1)
	N(1)	−0.040(18)	−0.072(6)	−0.091(13)
[Mo(1),Mo(2),N(1),N(2)]	N(2)	0.040(18)	0.070(6)	0.090(12)
	C(9)	−0.490(27)	−0.434(14)	−0.432(27)
	C(10)	0.416(28)	0.516(12)	0.508(24)
	C(11)	0.430(43)	0.627(17)	0.639(30)

Interplanar angle between [Mo(1),L_b(1),L_b(2)] and [Mo(2),L_b(1),L_b(2)] planes

	ϕ/°
1	145.4°
2	149.6°
3	153.4°

Torsion angle

Segment	1 τ/°	2 τ/°	3 τ/°
N(1)–C(9)–C(10)–N(2)	−94(2)	−98(1)	−96(2)
N(1)–Mo(1)–Mo(2)–N(2)	−5.4(6)	−9.1(2)	−10.8(4)
O(2)···O(3)···O(7)···O(8)	−8.6(7)	−11.5(2)	−10.4(5)
O(2)···O(3)···L_b(1)···L_b(2)	−4.0(6)	−5.7(2)	−4.6(4)
O(8)···O(7)···L_b(1)···L_b(2)	−4.5(7)	−5.8(2)	−6.1(3)
O(1)–Mo(1)–Mo(2)–O(6)	−5.4(8)	−0.2(3)	0.2(6)

a) The sign of the torsion angle in the A–B–C–D segment is negative if the direction of the rotation which superimposes the A–B bond on the C–D bond is counterclockwise.

every pdta complex is significantly shorter than the Mo(2)–N bond, whose N atom is nearer to the methyl group than that of the Mo(1)–N. The Mo–Mo–N bond angle decreases in the sequence of **1**, **2**, and **3**. The decrement along the sequence is 3.9° in Mo(2)–Mo(1)–N, but 2.1° in Mo(1)–Mo(2)–N; the replacement of the bridging ligands has a greater influence on the Mo–Mo–N bond angle containing an N atom more distant from the methyl group.

The propylenediamine portion of the ligand takes a λ gauche conformation. The methyl group is equatorial with respect to the 6-membered Mo(1)–N(1)–C(9)–C(10)–N(2)–Mo(2) ring. The N···N distance and N–C–C–N torsion angle are in the 3.46—3.51 Å and 94—98° range respectively, and are thus relatively insensitive to the kind of bridging ligand. The torsion angle is much larger than that in the usual 5-membered chelate ring of propylenediamine.[11] The N–Mo–Mo–N frame is not planar, but the two terminal bonds are twisted in a Δ configuration (Fig. 4) and the torsion angle ranges from 5.4° in **1** to 10.8° in **3**. The bond angles in the 6-membered ring indicate the presence of considerable strain: the Mo–N–C and N–C–C angles are considerably larger than the tetrahedral angle and rather near to the trigonal one, except for the C(9)–C(10)–N(2) angle. The methyl group is in short contact with the C(6)H_2 and C(8)H_2 groups. The mean value of the C(11)···C(6) distance is 0.1 Å shorter than that of C(11)···C(8).

The O(carboxylate)–Mo–O(carboxylate) angle diminishes along the 1-2-3 sequence. This arises from the repulsion between the ligating carboxylate O atoms and the bridging atoms, as is indicated by the contact distances of O···O_b (2.74—2.88 Å) and O···S (2.954—3.176 Å).

The Mo–N–C–C–O glycinato rings have a highly puckered structure. The two rings, linked to a common Mo, have an enantiomeric conformation. The glycinato ring has some strain, as is indicated by the bond angle. The Mo(2)–O(8)–C(7) angles are larger than 126°, while the Mo(2)–O(7)–C(5), Mo(1)–O(2)–C(1), and Mo(1)–O(3)–C(3) angles are 122—126°. The C(2)–C(1)–O(2) angles (113—116°) are significantly smaller than 120°, though the other C–C–O(carboxylate) angles

are 116—119°. The N(1)–C(2)–C(1) and N(2)–C(6)–C(5) angles show a significant deviation from 109.5°, but N(1)–C(4)–C(3) and N(2)–C(8)–C(7) do not. All the other bond angles are normal.

As has been described above, there is a slight but significant difference between the corresponding bond lengths and angles around the two Mo's in the dimer. The difference is systematic for the three complexes, despite the difference in crystal packing. This inequivalence of the Mo's is thought to result from the methyl group disposed unsymmetrically in relation to the Mo(1) and Mo(2).

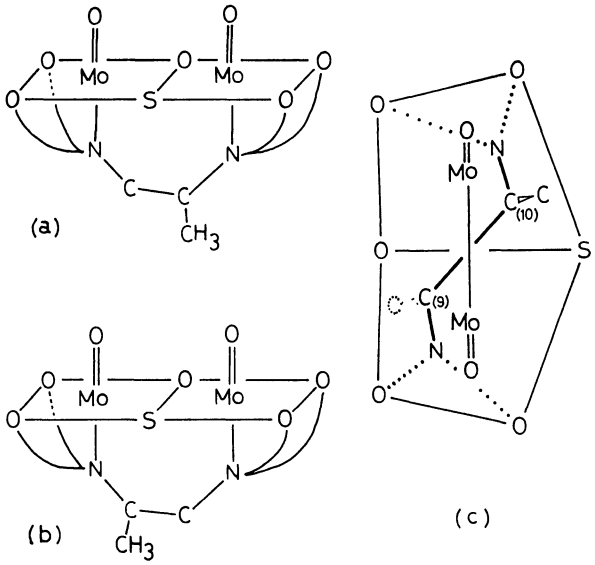

Fig. 5. The two isomers for $[Mo_2O_3S(R\text{-pdta})]^{2-}$ anion. (a) Isomer (1), (b) isomer (2), and (c) the projection of the isomer (1) showing schematically the disposition of the ethylenediamine moiety relative to the Mo_2O_3S core (the methyl carbon shown by dotted letter corresponds to that in the approximated structure of the isomer (2)).

Geometrical Isomerism of $[Mo_2O_3S(R\text{-pdta})]^{2-}$. Figures 5(a) and (b) show two geometrical isomers for this anion. The structure shown in Fig. 4 (middle) corresponds to the (1) isomer, which was selectively obtained by the method of preparation described in Ref. 2. The (1) isomer differs from (2) in the disposition of the methyl group with respect to the Mo_2O_3S core. The structure of the (2) isomer may be approximated by a structure obtained by exchanging C(10)–CH_3 for equatorial C(9)–H in the (1) isomer. Figure 5(c) shows schematically the projection of the (1) isomer. The atom arrangement is unsymmetric with respect to the Mo–Mo line because of the difference between the Mo–O_b and Mo–S distances; accordingly, the ligating $pdta^{4-}$ is bent out of the Mo–Mo line. This gives rise to a difference between the conformational energies of the (1) and (2) isomers. In the approximated structure for the (2) isomer, the $CH_3\cdots C(2)$ and $CH_3\cdots C(4)$ contact distances are estimated to be 2.72 and 2.91 Å respectively. These values are significantly smaller than those of the corresponding short contacts in the (1) isomer, although the atom overcrowding in the approximated structure may be alleviated to some extent in the actual structure of the (2) isomer. Such an unfavorable ligand structure may be responsible for low abundance of the (2) isomer in solution.

Distortion of Donor-atom Disposition. The CD signs of the binuclear Mo(V) complexes of the dissymmetric ligand in the 26000—33000 cm^{-1} region are not directly related to the configuration of asymmetric carbon in the ligand.[2] A closer investigation of the X-ray structures of the eight dissymmetric Mo(V) complexes led us to the conclusion that the asymmetric factor responsible for the sign of the crystalline CD spectra in this region is, in the first approximation, the dissymmetric distortion of the donor-atom disposition. The distortion can be represented by; i) a twist of the X–Y and X′–Y′ edges about the axis parallel to the Mo–Mo axis (Fig. 6), ii) a twist of Mo=O_t and Mo=O'_t about the Mo–Mo axis, and iii) a twist of Mo–Z and Mo–Z′ about the Mo–Mo axis. The third twist is thought to be less important for the optical activity in view of the fact that the Mo–Z(Z′) distance is longer than the other Mo–donor distances in the dimer.[2]

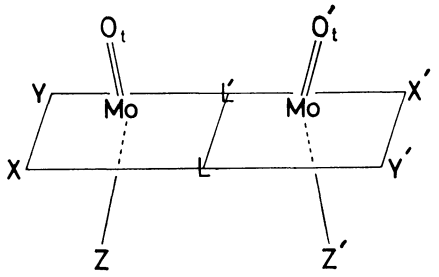

Fig. 6. The idealized corrdination framework for the binuclear Mo(V) complex.

Such a distortion should arise from the strain characteristic of the coordinating ligand. If there were no chelate rings, 2 Mo, O_t, O'_t, Z, and Z′ would lie on one plane[12] (Fig. 6). When the donor atoms of *R*-$pdta^{4-}$ occupy the X, Y, Z, X′, Y′, and Z′ coordination sites, the *R*-propylenediamine moiety takes a λ skew conformation to make C–CH_3 equatorial; accordingly the $N\langle^{C}_{C}C$ portion cannot be symmetric with respect to the [2Mo,O_t,O'_t,Z,Z′] plane of the idealized coordination framework (Fig. 6). Each NC_3 portion rotates counterclockwise about the Mo→N vector, from the symmetric position with respect to the [2Mo,O_t,O'_t,Z,Z′] plane until the N–C–C–N torsion angle becomes 94—98° as in the structures of **1**—**3**. Such a rotation brings about the upper shift of Y(Y′) and the down shift of X(X′), making the X–Y edge (X′–Y′) slant against L–L′ in the Δ configuration. The strain in the glycinato and *R*-propylenediamine rings may be alleviated by the displacement of the N atoms from the [2Mo,O_t,O'_t,Z,Z′] plane, thus twisting the N–Mo–Mo–N in the Δ configuration.

The O(1)···O(2) and O(6)···O(7) distances in the three complexes are shorter than the O(1)···O(3) and O(6)···O(8) distances (Table 5). The former distances

TABLE 5. SOME EDGE LENGTHS (l/Å) IN THE COORDINATION OCTAHEDRA OF BINUCLEAR Mo(V) COMPLEXES

	$O_t\cdots X$	$O'_t\cdots X'$	X or X'	$O_t\cdots Y$	$O'_t\cdots Y'$	Y or Y'	Ref.
$Na_2[Mo_2O_4(R\text{-pdta})]\cdot 3H_2O$	2.70(2)	2.79(3)	O	2.67(2)	2.71(2)	O	This work
$Na_2[Mo_2O_3S(R\text{-pdta})]\cdot 4H_2O$	2.852(8)	2.810(8)	O	2.674(9)	2.674(8)	O	This work
$Na_2[Mo_2O_2S_2(R\text{-pdta})]\cdot 4H_2O$	2.83(2)	2.88(2)	O	2.72(2)	2.72(2)	O	This work
$[Mo_2O_2S_2(S\text{-hist})_2]\cdot 1.5H_2O$	2.71(1)	2.85(1)	N	2.83(1)	2.83(1)	N	12
$Na_2[Mo_2O_4(R\text{-cys})_2]\cdot 5H_2O$	2.89(2)	2.88(2)	N	3.13(2)	3.12(2)	S	10
$Na_2[Mo_2O_2S_2(R\text{-cys})_2]\cdot 2H_2O$	2.86(2)	2.93(4)	N	3.08(4)	3.16(3)	S	13

are in the 2.67—2.72 Å range, and thus substantially invariable for all three complexes. This indicates that the O(1) and O(6) atoms are in short contact with the O(2) and O(7) atoms respectively; hence, the direction of the Mo=O(1) and Mo=O(6) bonds depends on the positions of the O(2) and O(7) atoms. Since the ligation of R-pdta^{4-} displaces the X and Y by 0.09—0.16 Å from the [X,Y,L,L'] plane of the idealized framework (Table 4), the O_t moves so as to keep the contact distance constant, resulting in the Δ twist of the O=Mo–Mo=O segment. The displacements of O'_t, X', and Y' from the idealized positions are similar to those of the unprimed sites and give rise to the enlargement of the O=Mo–Mo=O torsion angle.

The Mo=O bonds are virtually parallel to each other in **2** and **3**. The Mo–Mo distance and the interplanar angle between the [Mo,L_b(1),L_b(2)] planes in these complexes are significantly larger than the corresponding ones in **1**, while the N···N distance, the Mo–Mo=O bond angle, and the deviation of Mo from the equatorial plane are not different from those in **1**. On the basis of these structural features, the idealized framework for **3** can be derived from that for **1** in the following way; i) the elongation of the Mo–Mo, $O_t\cdots O'_t$, X···Y', and Y···X' distances by 0.28 Å along the Mo–Mo axis, followed by ii) the enlargement of the [Mo,L,L'] interplanar angle by 8.0°. In the derived framework, X and Y (as well as X' and Y') are calculated to lie 0.13 Å below the equatorial plane of the intermediate framework obtained by the i) operation. However, the Y(Y') shifts 0.14 Å (average) upward upon the ligation of R-pdta^{4-} (Table 4). Consequently, the atom at the Y(Y') site may be regarded as lying on the equatorial plane of the intermediate framework, in contact with $O_t(O'_t)$ without repelling it, thus making the Mo=O_t bonds nearly parallel to each other in **3**. The inherent low symmetry of the Mo_2O_3S core may have some additional influence on the donor-atom disposition in **2**.

That the twist in the O=Mo–Mo=O segment is solely found in **1**, but not in **2** and **3**, weakens the basis of the interpretation of the twist. However, the interpretation is substantiated by the following analysis of the twist of O=Mo–Mo=O in $[Mo_2O_2S_2(S\text{-hist})_2]\cdot 1.5H_2O$[13] (**4**) (hist$^-$=histidinate), $Na_2[Mo_2O_4(R\text{-cys})_2]\cdot 5H_2O$[10] (**5**), and $Na_2[Mo_2O_2S_2(R\text{-cys})_2]\cdot 2H_2O$[14] (**6**) (cys^{2-}= cysteinate), which were utilized for the investigation of the CD-structure correlation in the Mo(V) dimer.[2] These complexes have a common framework (shown in Fig. 7) and have no bridge like that of the propylenediamine moiety in **1**—**3**. The torsion angle and the

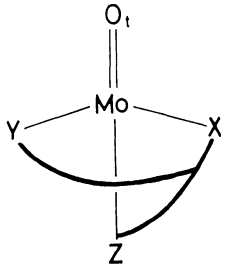

Fig. 7. A sketch of chelate ring in the half of the Mo(V) dimer with terdentate S-hist$^-$ or R-cys^{2-} ligand.

configuration of the distortion were described in Ref. 2 (torsion angle in O_t=Mo–Mo=O'_t (θ_1) and that for the X–Y and Y'–X' edges (ξ) in the respective complexes are as follows: **4** θ_1=2.5°(Δ), ξ=4.5°(Δ); **5** θ_1=4.0°(Δ), ξ=0.1°(Δ); **6** θ_1=4.7°(Δ), ξ=0.2°(Δ); the ξ values for **5** and **6** are meaningless in view of the experimental errors).

Each of the **4**—**6** complexes has an approximate two-fold axis passing the mid-point between the Mo's across the XYX'Y' plane. Figure 7 shows a sketch of this type of complex as viewed along the Mo–Mo axis. The three ligating atoms, S, N, and O of R-cys^{2-}, and N(ring), N, and O of S-hist$^-$, are located in a clockwise fashion in this order (Y, X, and Z) when the Mo atom is looked at from the asymmetric carbon of the coordinating R-cys^{2-} and S-hist$^-$. The chelate ring spanning X and Z sites is 5-membered, irrespective of the kind of ligand. Table 5 lists the distances between O_t and atoms at the X and Y sites. These distances are somewhat shorter than those to be expected from the van der Waals radii of the two atoms; therefore, the O_t atom must be in contact with atoms at the X and Y sites. The formation of a 5-membered ring between X and Z shifts X toward Z and makes O_t distant from X. In order to make the interatomic interaction optimal, O_t shifts toward X, and in turn Y approaches O_t. Such shifts lead to, as a whole, a rotation of the O_tXY triangle about its center. The rotations of the O_tXY and O'_tX'Y' triangles compatible with the symmetry of the dimer must have resulted in the twist in O_t=Mo–Mo=O'_t, as well as in that of the X–Y and Y'–X' edges. Since Mo–S(Y) is *ca.* 0.3 Å longer than Mo–N(X), the rotation of Mo–Y(S) and that of Mo–X'(N) in opposite directions about the Mo–Mo axis, giving a torsion angle of 4—5° in O_t=Mo–Mo=O'_t, seems to give the negligible twist of the X–Y and Y'–X' edges in **5** and **6**.

The distortion of the coordination framework in the binuclear Mo(V) complexes, **1**—**6**, is thus explainable

on the basis of the strain due to chelate-ring formation. The *Λ* twist in **1** and the negligible twist in **2** and **3** for the O=Mo–Mo=O segment may be taken to be intrinsic for the respective complex, and not ascribable to crystal packing.

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