Crystal Structures of *cis*-Dibromodioxobis(triphenylphosphine oxide)-molybdenum(VI), *cis*-Dichlorodioxobis(triphenylphosphine oxide)molybdenum(VI), and *cis*-Bis(butane-2,3-diolato)dioxomolybdenum(VI)–Butane-2,3-diol (1/2): A Comparison of Co-ordination Spheres and the General Stereochemistry of Molybdenum(VI) Oxo-complexes

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The crystal and molecular structures of the title complexes *cis*-$[\mathrm{MoO_2Br_2(PPh_3O)_2}]$ (1), *cis*-$[\mathrm{MoO_2Cl_2(PPh_3O)_2}]$ (2), and the i.r. spectra of these complexes and of a third complex, *cis*-$[\mathrm{MoO_2F_2(PPh_3O)_2}]$ (3), have been determined. Crystal data: (1), space group $P2_1/c$, $Z = 4$, $a = 19.081(1)$, $b = 9.964(1)$, $c = 19.202(1)$ Å, $\beta = 111.52(2)°$, $R = 0.068$ for 5 023 reflections; (2), space group $P2_1/c$, $Z = 4$, $a = 18.95(3)$, $b = 10.003(1)$, $c = 19.278(2)$ Å, $\beta = 112.06(4)°$, R 0.052 for 6 520 reflections. Complexes (1) and (2) have distorted octahedral symmetry with *cis* $\mathrm{PPh_3O}$ ligands. Apart from those bonds involving halogens, there are no significant differences in bond lengths in the two complexes. Assignments of the i.r. spectra of (1)—(3) have been correlated with their structural features. General aspects of the stereochemistry of molybdenum(VI) complexes are highlighted, and it is shown how these can be successfully applied to predict the gross stereochemistry of a molybdenum(VI) complex with butane-2,3-diol (HL), *cis*-$[\mathrm{MoO_2L_2}]\cdot 2\mathrm{HL}$, whose structure was previously unknown. Crystal data for (4): space group $C2/c$, $Z = 4$, $a = 16.269(5)$, $b = 9.848(5)$, $c = 14.313(5)$ Å, $\beta = 91.31(5)°$, R 0.076 for 1 368 reflections. The crystal contains isolated $\mathrm{MoO_2L_2}$ molecules connected by hydrogen bonds to two HL molecules. The complex also has distorted octahedral symmetry with two short, two medium, and two long Mo–O bonds. A general principle is established that in mixed-ligand complexes the weaker π-bonding donors are found to be *trans* to the terminal oxygen where they are not directly competing for the available empty metal 4*d* orbitals.

IN recent years there has been considerable interest in the co-ordination chemistry of molybdenum-(V) and -(VI) in view of its role in a number of important enzymatic systems,[1-3] in which molybdenum is believed to be associated with flavins and amino-acid residues. The exact nature of these interactions is not understood, and a number of model studies have been carried out to characterize further the co-ordination chemistry of molybdenum.[3-7] These have involved both i.r. spectroscopic and structural investigations.

One system on which model studies can readily be carried out is provided by $\mathrm{MoO_2X_2L_2}$ (X = halide, L = unidentate ligand). In a previous study[4] the effect of varying L was studied. In this work the effect of changing X on both the stereochemistry and i.r. vibrations of the $\mathrm{MoO_2X_2L_2}$ core is reported. The systems chosen were the triphenylphosphine oxide adducts of $\mathrm{MoO_2Cl_2}$ and $\mathrm{MoO_2Br_2}$. Here the changes in the vibrational modes of both the metal–oxide, –halide, and –phosphine oxide bonds can be correlated with the structural data.

It can be demonstrated that general aspects of molybdenum(VI) stereochemistry can be used to predict the structure of previously unknown molybdenum compounds, and these generalizations are applied to the previously uncharacterized complex of $\mathrm{Mo^{VI}}$ with butane-2,3-diol. This complex was prepared as part of a systematic study of the co-ordination chemistry of $\mathrm{Mo^{V}}$ and $\mathrm{Mo^{VI}}$ with ligands of biological interest.[5]

EXPERIMENTAL

Preparation of the Complexes.—The complexes *cis*-$[\mathrm{MoO_2Br_2(PPh_3O)_2}]$ (1), *cis*-$[\mathrm{MoO_2Cl_2(PPh_3O)_2}]$ (2), and *cis*-$[\mathrm{MoO_2F_2(PPh_3O)_2}]$ (3) were prepared by the general methods outlined in ref. 4. Molybdic acid (2 g) was dissolved in concentrated hydrohalic acid (15 cm³) and triphenylphosphine oxide was added dissolved in the minimum amount of ethanol. The resulting precipitate was recrystallized from dichloromethane. Crystals were obtained by slow evaporation of dichloromethane solutions of the respective complexes. The complex *cis*-$[\mathrm{MoO_2L_2}]\cdot 2\mathrm{HL}$ (4; HL = butane-2,3-diol) was prepared by heating $\mathrm{MoO_3}$ in butane-2,3-diol to the boiling point, filtering, and cooling the resulting solution slowly to room temperature. Clear crystals with well defined faces were obtained by recrystallizing the complex from acetonitrile.

Infrared Spectra.—Infrared spectra were recorded from 400—4 000 cm⁻¹ on a Perkin-Elmer 337 or Shimadzu IR-27G spectrophotometer calibrated with polystyrene. Either Nujol mulls with KBr plates or KBr discs were used. Spectra were obtained in the range 40—400 cm⁻¹ by the use of a R.I.I.C. Fourier FS-720 spectrophotometer producing an interferogram which yielded the absorption spectrum after application of a Fourier-transform program (R.I.I.C.) *via* an IBM 360/44 computer (accuracy ± 2 cm⁻¹).

Crystal Data.—(1), $\mathrm{C_{36}H_{30}Br_2MoO_4P_2}$, $M = 844.3$, Monoclinic, $a = 19.081(1)$, $b = 9.964(1)$, $c = 19.202(1)$ Å, $\beta = 111.25(2)°$, $U = 3\,402.7(9)$ Å³, $D_m = 1.651(5)$ g cm⁻³, $Z = 4$, $D_c = 1.648$ g cm⁻³, $F(000) = 1\,680$, $\mu(\text{Mo-}K_\alpha) = 30.04$ cm⁻¹.

(2), $\mathrm{C_{36}H_{30}Cl_2MoO_4P_2}$, $M = 755.4$, Monoclinic, $a = 18.95(3)$, $b = 10.003(8)$, $c = 19.278(2)$ Å, $\beta = 112.04(4)°$, $U = 3\,387(7)$ Å³, $D_m = 1.498(5)$ g cm⁻³, $Z = 4$, $D_c = 1.492$ g cm⁻³, $F(000) = 1\,536$, $\mu(\text{Mo-}K_\alpha) = 6.77$ cm⁻¹.

(3), $\mathrm{C_{36}H_{30}F_2MoO_4P_2}$, $M = 722.5$, Monoclinic, $a = 10.130(2)$, $b = 18.782(3)$, $c = 17.658(2)$ Å, $\beta = 106.52(4)°$, $U = 3\,218(2)$ Å³, $D_m = 1.487(5)$ g cm⁻³, $Z = 4$, $D_c = 1.491$ g cm⁻³, $F(000) = 1\,472$, $\mu(\text{Mo-}K_\alpha) = 5.55$ cm⁻¹.

(4), $\mathrm{C_{16}H_{38}MoO_{10}}$, $M = 486$, Monoclinic, $a = 16.269(5)$, $b = 9.848(5)$, $c = 14.313(5)$ Å, $\beta = 91.31(5)°$, $U = 2\,293(3)$ Å³, $D_m = 1.410(5)$ g cm⁻³, $Z = 4$, $D_c = 1.408$ g cm⁻³, $F(000) = 1\,024$, $\mu(\text{Mo-}K_\alpha) = 6.11$ cm⁻¹.

For complexes (1), (2), and (4), cell dimensions were obtained and refined and intensity data collected as described elsewhere,[8] by use of an Enraf–Nonius four-circle

CAD-4 diffractometer controlled by a PDP8/M computer. For complex (4) similar data were obtained by use of a Hilger and Watts four-circle diffractometer controlled by a PDP8/I computer, as described elsewhere.[6,7]

The θ—2θ scan technique was used to record the intensities of all reflections having $0 < 2\theta < 54°$ for crystals (1) and (2). The symmetric scans were centred on the calculated peak positions [λ(Mo-K_α) 0.710 7 Å]. Reflection data were considered unobserved if intensities registered less than 10 counts above background on a rapid prescan, and were rejected automatically by the computer. For each crystal the intensities of four standard reflections, monitored at 100 reflection intervals, were relatively constant throughout the data collection. The raw intensity data were corrected for Lorentz and polarization effects but not for absorption. Of 5 023 (1) and 6 520 (2) independent intensities, 4 515 (1) and 5 908 (2) had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics as determined in ref. 9. These data were used in the final refinement of the structural parameters.

For crystal (4) the θ—2θ scan technique was used to record the intensities of all reflections having $0 < 2\theta < 43.6°$ as previously outlined.[6,7] The intensities of three strong reflections, well separated in reciprocal space, were used as standards and monitored at regular intervals throughout the data collection and showed no significant variation. The raw intensity data were corrected for Lorentz and polarization effects and absorption corrections were applied before the final refinement. Transmission factors ranged from 0.83 to 0.93 for the 0, 6, $\overline{12}$ and 0, 2, 1 reflections respectively. In all, 1 750 reflections were collected and after editing and averaging equivalent forms there were 1 368 independent reflections of which 245 were unobserved with intensities less than $\sigma(I)$.

Solution and Refinement of the Structures.—Full-matrix least-squares refinement was based on F, and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where weights, w, were taken as $[2F_o/\sigma(F_o^2)]^2$. Atomic scattering factors for non-hydrogen atoms were taken from ref. 10, and for hydrogen atoms from ref. 11. The effects of anomalous dispersion were included in F_c ($\Delta f'$,$\Delta f''$).[12] The weighted agreement factor is defined as $R' = [|\Sigma w(|F_o| - |F_c|)|^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

For (1) the position of the molybdenum atom was determined from the Patterson function and refined, and the remaining non-hydrogen atoms were located by successive difference-Fourier maps, with further refinement. The remaining diffraction data were added to the calculations, anisotropic temperature factors were introduced, and hydrogen atoms inserted as fixed atoms in trigonal positions attached to phenyl carbon atoms with isotropic temperature factors of 5.0, assuming C–H 0.98 Å. After convergence, new positions were calculated for the hydrogen atoms. For (2) the positions of all the non-hydrogen atoms were taken from the refined values of (1) and isotropic temperature factors of 4.0 were assumed. After convergence, hydrogen atoms were inserted and handled as in (1). For (3) a full structure determination did not prove possible.

For (4) the position of the molybdenum atom on the two-fold axis was determined from the Patterson function but subsequent difference-Fourier maps were complicated by the presence of two images of the structure resulting from the fact that the y co-ordinate of the molybdenum atom was very close to zero (y 0.009). The structure was finally solved from an F_o Fourier map, from which the positions for the atoms in the chelate ring could be determined. Subsequent difference-Fourier maps revealed the remaining non-hydrogen atoms. Hydrogen atoms could not be located at their calculated positions in difference-Fourier maps and so were not included in the refinement process.

The models converged with $R = 0.068$, $R' = 0.072$ (1), 0.052, 0.071 (2), and 0.076, 0.068 (4). The error in an observation of unit weight is 2.87 (1), 7.53 (2), and 5.47 (4). A structure-factor calculation with all observed and unobserved reflections included (no refinement) gave R values of 0.074 (1), 0.071 (2), and 0.091 (4). On this basis, it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. A final difference-Fourier map was featureless. Observed and calculated structure factors, thermal parameters, and some calculations on the mean planes are available as Supplementary Publication No. SUP 22423 (52 pp.).*

RESULTS AND DISCUSSION

Structures of $[MoO_2Br_2(PPh_3O)_2]$ *and* $[MoO_2Cl_2(PPh_3O)_2]$.—Final positional parameters for the atoms are given in Table 1, and non-phenyl bond lengths and angles in Tables 2 and 3. The estimated standard deviations were derived from the inverse matrix in the course of least-squares refinement. The labelling system of the atoms is as indicated for (1) in Figure 1. Figures 1 and 2 are stereoscopic pairs for the molecular structure of (1) and for the molecular packing in the unit cell. As is evident from the packing diagram, the crystal structures consist of well separated molecules of the metal complex.

The molybdenum atom exhibits distorted octahedral co-ordination in both complexes. Both the terminal oxygen atoms (O_t) and the triphenylphosphine oxide ligands (O_L) are *cis* to one another and mutually *trans* while the halogen ligands (X) are *trans* to one another. It has been established that in mixed-ligand complexes of Mo^V and Mo^{VI} the π bonding is concentrated in bonds to terminal oxygen atoms at the expense of bonds to other atoms.[13-15] This is shown up most clearly in significant lengthening of bonds involving atoms *trans* to the terminal oxygen atoms in complexes containing otherwise identical ligand atoms.[13] The literature data, taken with the present results, establish a general principle that in mixed-ligand complexes the weaker π-bonding donors are found to be *trans* to the terminal oxygen atom where they are not directly competing for the available empty metal 4*d* orbitals.[6,7] This is illustrated in the present study by the fact that the neutral oxygen-donor atoms (O_L) are *trans* to the O_t atoms while the X^- donors are *cis* to the O_t atoms and mutually *trans*. The greatest distortion from octahedral symmetry involves the displacement of the molybdenum atom towards the terminal oxygen atoms. The values of 1.673—1.73 Å for Mo–O_t found in (1) and (2) indicate a double bond between the molybdenum and these oxygen atoms.[16] The O_t–Mo–O_t angles of 103.2(5) and 103.17(7)° for (1) and (2) are in the range found for oxymolybdenum(VI) complexes (not containing co-ordinated fluorine[17]), while the Mo–O_L bond distances at 2.17(1) and 2.19(1) Å for (1) and

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 1

Positional parameters and their estimated standard deviations

Atom	x	y	z
(a) Complex (1)			
Mo	0.255 7(1)	0.230 8(2)	0.071 6(1)
Br(1)	0.112 6(1)	0.250 7(3)	0.026 5(2)
Br(2)	0.396 4(1)	0.269 4(3)	0.111 9(2)
P(1)	0.221 2(3)	0.464 5(6)	−0.081 9(3)
P(2)	0.280 3(3)	0.538 1(6)	0.180 5(3)
O(1)	0.259 4(7)	0.117(1)	0.007 9(7)
O(2)	0.256 8(7)	0.132(2)	0.146 3(7)
O(3)	0.260 5(8)	0.412(1)	0.136 0(8)
O(4)	0.244 9(7)	0.390(1)	−0.009 7(7)
C(111)	0.298(1)	0.495(2)	−0.109(1)
C(112)	0.367(1)	0.545(2)	—0.054(1)
C(113)	0.426(1)	0.573(2)	−0.075(1)
C(114)	0.424(1)	0.558(2)	−0.147(1)
C(115)	0.357(1)	0.509(2)	−0.201(1)
C(116)	0.297(1)	0.482(2)	−0.179(1)
C(121)	0.181(1)	0.627(2)	−0.076(1)
C(122)	0.132(1)	0.631(2)	−0.038(1)
C(123)	0.101(1)	0.750(3)	−0.030(1)
C(124)	0.122(1)	0.865(2)	−0.057(1)
C(125)	0.174(1)	0.857(3)	−0.090(1)
C(126)	0.206(1)	0.740(2)	−0.104(1)
C(131)	0.153(1)	0.372(2)	−0.158(1)
C(132)	0.091(1)	0.440(2)	−0.211(1)
C(133)	0.043(1)	0.365(2)	−0.271(1)
C(134)	0.053(1)	0.231(2)	−0.274(1)
C(135)	0.114(2)	0.166(2)	−0.223(1)
C(136)	0.161(1)	0.238(2)	−0.166(1)
C(211)	0.325(1)	0.501(2)	0.281(1)
H(214)	0.414(1)	0.414(2)	0.484(1)
H(215)	0.397(2)	0.636(3)	0.448(1)
H(216)	0.351(2)	0.694(2)	0.320(1)
H(222)	0.244(1)	0.817(3)	0.196(1)
H(223)	0.133(1)	0.939(3)	0.170(1)
H(224)	0.021(1)	0.871(3)	0.146(1)
H(225)	0.013(1)	0.589(3)	0.124(2)
H(226)	0.125(1)	0.463(3)	0.135(1)
H(232)	0.262(1)	0.752(3)	0.073(1)
H(233)	0.343(1)	0.905(3)	0.047(2)
H(234)	0.473(2)	0.883(3)	0.105(1)
H(235)	0.519(1)	0.736(3)	0.207(1)
H(236)	0.440(1)	0.575(3)	0.234(2)
(b) Complex (2)			
Mo	0.258 54(2)	0.230 48(4)	0.072 48(2)
Cl(1)	0.122 75(8)	0.253 2(2)	0.026 45(9)
Cl(2)	0.392 20(8)	0.271 1(2)	0.113 20(9)
P(1)	0.222 45(7)	0.467 2(1)	−0.079 82(6)
P(2)	0.280 49(7)	0.534 2(1)	0.183 50(6)
O(1)	0.259 3(2)	0.116 5(3)	0.007 7(2)
O(2)	0.262 6(3)	0.135 7(4)	0.145 4(2)
O(3)	0.260 5(2)	0.406 6(3)	0.138 8(2)
O(4)	0.249 3(2)	0.393 4(3)	−0.007 2(2)
C(111)	0.301 1(3)	0.504 1(4)	−0.107 2(2)
C(112)	0.368 7(3)	0.551 5(5)	−0.052 7(3)
C(113)	0.430 4(3)	0.580 3(6)	−0.072 5(3)
C(114)	0.424 9(3)	0.563 6(6)	−0.145 5(3)
C(115)	0.359 5(3)	0.516 7(5)	−0.198 4(3)
C(116)	0.297 8(3)	0.487 2(5)	−0.181 6(2)
H(116)	0.249 4(2)	0.454 8(5)	−0.219 8(3)
H(122)	0.113 4(3)	0.542 0(6)	−0.019 0(3)
H(123)	0.054 6(3)	0.750 0(6)	−0.007 4(3)
H(124)	0.099 0(3)	0.952 8(6)	−0.042 0(4)
H(125)	0.184 9(3)	0.948 1(6)	−0.102 3(4)
H(126)	0.239 4(4)	0.744 3(8)	−0.118 8(5)
H(132)	0.084 9(4)	0.539 4(9)	−0.205 8(4)
H(133)	0.000 9(4)	0.416(1)	−0.307 9(5)
H(134)	0.015 8(4)	0.185 8(9)	−0.316 9(4)
H(135)	0.118 6(4)	0.075(1)	−0.225 6(5)
H(136)	0.203 4(4)	0.193 9(8)	−0.124 1(4)
H(212)	0.321 2(4)	0.292 5(8)	−0.267 8(4)
H(213)	0.378 8(4)	0.239 4(9)	0.396 4(5)
H(214)	0.414 6(4)	0.412 9(9)	0.487 5(4)
H(215)	0.399 7(5)	0.637(1)	0.447 2(5)
H(216)	0.343 6(4)	0.688 8(9)	0.320 9(4)
H(222)	0.241 7(4)	0.813 8(9)	0.200 6(5)
H(223)	0.123 6(4)	0.922(1)	0.173 6(5)
H(224)	0.011 5(5)	0.808(1)	0.141 6(6)
H(225)	0.008 3(4)	0.574(1)	0.112 4(5)
H(226)	0.124 1(4)	0.459(1)	0.133 1(4)
H(232)	0.260 0(4)	0.745 3(9)	0.078 6(4)
H(233)	0.340 9(4)	0.902 3(9)	0.053 4(5)
H(234)	0.473 2(4)	0.896(1)	0.123 2(5)
H(235)	0.525 7(4)	0.725(1)	0.213 5(6)
H(236)	0.442 5(4)	0.571 7(9)	0.239 6(5)
(c) Complex (4)			
Mo	0.0	0.009 0(1)	0.250 0
O(1)	−0.055 7(5)	−0.093 6(8)	0.315 6(6)
O(2)	0.088 5(4)	0.067 5(6)	0.333 2(5)
O(3)	−0.049 3(4)	0.188 4(8)	0.332 9(6)
O(4)	0.251 3(4)	0.025 9(7)	0.288 3(6)
O(5)	0.201 4(4)	0.270 9(6)	0.179 6(5)
C(1)	0.075 2(8)	0.150(1)	0.414(1)
C(2)	0.002 7(6)	0.234(1)	0.406 9(8)
C(3)	0.148 5(7)	0.188(1)	0.467 1(9)
C(4)	−0.034 0(8)	0.310(1)	0.482(1)
C(5)	0.303 6(6)	0.138(1)	0.262 7(9)
C(6)	0.275 6(6)	0.194(1)	0.166 7(9)
C(7)	0.392 7(6)	0.081(1)	0.258(1)
C(8)	0.257 8(8)	0.082(1)	0.089(1)

TABLE 2

Non-phenyl bond lengths (Å) for $[MoO_2X_2(PPh_3O)_2]$ [X = Br (*a*) or Cl (*b*)] and for complex (4) (*c*)

	(*a*)	(*b*)
Mo–X(1)	2.556(3)	2.397(1)
Mo–X(2)	2.540(3)	2.388(1)
Mo–O(1)	1.69(1)	1.695(1)
Mo–O(2)	1.73(1)	1.673(1)
Mo–O(3)	2.17(1)	2.169(1)
Mo–O(4)	2.19(1)	2.201(1)
O(3)–P(2)	1.49(1)	1.507(1)
O(4)–P(1)	1.49(1)	1.492(1)
P(1)–C(111)	1.75(2)	1.796(2)
P(1)–C(121)	1.81(2)	1.796(2)
P(1)–C(131)	1.81(2)	1.803(2)
P(2)–C(211)	1.85(2)	1.812(2)
P(2)–C(222)	1.79(2)	1.804(2)
P(2)–C(231)	1.78(2)	1.793(2)

(*c*)

Mo–O(1)	1.662(7)	C(2)–C(4)	1.46(1)
Mo–O(2)	1.935(7)	C(4)–C(5)	1.44(1)
Mo–O(3)	2.284(7)	O(5)–C(6)	1.44(1)
O(2)–C(1)	1.44(1)	C(5)–C(6)	1.54(2)
O(3)–C(2)	1.41(1)	C(5)–C(7)	1.55(1)
C(1)–C(2)	1.44(1)	C(6)–C(8)	1.59(2)
C(1)–C(3)	1.44(2)		

2.169(1) and 2.201(1) Å for (2) are in the range expected for a unidentate oxygen donor.[18,19] The expansion of the O_t–Mo–O_t angle to *ca.* 103° means that the O_L–Mo–O_L angle is compressed to 77.0(4) and 77.81(5)° for (1) and (2) while the X–Mo–X angle is 166.72(9) and 164.92(2)°, giving a very distorted $MoO_2X_2L_2$ octahedron of approximately C_{2v} symmetry.

The bond distances and angles found in the PPh_3O molecules are similar to those found in other metal complexes of this ligand [19,20] and also in the free ligand itself [21,22] with the exception of those parameters involving the P–O$_L$ bonds. In the free ligand the P–O distance is 1.46(1),[21] 1.483(2) Å,[22] while in (1) it is found to be 1.49(1) and 1.49(1) Å and in (2) 1.507(1) and 1.492(1) Å, reflecting some degree of weakening of this bond on co-ordination. The Mo–O$_L$–P angles at 168.0(8) and 160.8(6) in (1) and 165.97(9) and 159.20(8)° in (2) are considerably greater than those normally found in PPh_3O metal complexes [20,23] and reflect the much greater steric crowding found in these complexes with their *cis* arrangement of PPh_3O ligands (O$_L$–Mo–O$_L$ at *ca.* 77°).

TABLE 3

Non-phenyl bond angles (°) for [$MoO_2X_2(PPh_3O)_2$] [X = Br (*a*) or Cl (*b*)] and for complex (4) (*c*)

	(*a*)	(*b*)
X(1)–Mo–X(2)	166.72(9)	164.62(2)
X(1)–Mo–O(1)	97.3(4)	95.51(5)
X(1)–Mo–O(2)	90.9(4)	93.94(6)
X(1)–Mo–O(3)	87.0(3)	85.37(4)
X(1)–Mo–O(4)	83.7(3)	83.01(4)
X(2)–Mo–O(1)	90.3(4)	93.15(5)
X(2)–Mo–O(2)	98.0(4)	96.43(6)
X(2)–Mo–O(3)	83.0(3)	83.52(4)
X(2)–Mo–O(4)	85.6(3)	84.27(4)
O(1)–Mo–O(2)	103.2(5)	103.17(7)
O(1)–Mo–O(3)	165.1(5)	167.83(6)
O(1)–Mo–O(4)	89.3(5)	90.23(6)
O(2)–Mo–O(3)	90.9(5)	88.86(6)
O(2)–Mo–O(4)	167.0(5)	166.50(6)
O(3)–Mo–O(4)	77.0(4)	77.81(5)
Mo–O(3)–P(2)	168.0(8)	165.97(9)
Mo–O(4)–P(1)	160.8(6)	159.20(8)
O(4)–P(1)–C(111)	110.8(8)	110.44(8)
O(4)–P(1)–C(121)	112.3(9)	110.96(8)
O(4)–P(1)–C(131)	112.5(7)	113.39(7)
C(111)–P(1)–C(121)	106.6(9)	106.58(9)
C(111)–P(1)–C(131)	106.6(9)	107.51(8)
C(121)–P(1)–C(131)	107.8(8)	107.66(8)
O(3)–P(2)–C(211)	110.0(8)	109.67(8)
O(3)–P(2)–C(221)	109.1(8)	108.98(8)
O(3)–P(2)–C(231)	115.2(9)	116.56(8)
C(211)–P(2)–C(221)	106.7(9)	107.39(8)
C(211)–P(2)–C(231)	106.4(8)	106.72(8)
C(221)–P(2)–C(231)	108.1(9)	107.13(9)
P(1)–C(111)–C(112)	119(2)	118.5(2)
P(1)–C(111)–C(116)	125(1)	123.0(1)
P(1)–C(121)–C(122)	116(2)	118.4(1)
P(1)–C(121)–C(126)	119(2)	122.3(2)
P(1)–C(131)–C(132)	120(1)	120.7(1)
P(1)–C(131)–C(136)	121(1)	118.8(1)
P(2)–C(211)–C(212)	120(1)	119.7(1)
P(2)–C(211)–C(216)	121(2)	121.1(1)
P(2)–C(221)–C(222)	122(2)	122.7(2)
P(2)–C(221)–C(226)	120(2)	118.1(2)
P(2)–C(231)–C(232)	121(1)	120.3(1)
P(2)–C(231)–C(236)	124(1)	120.9(1)

(*c*)

O(1)–Mo–O(1′)	105.2(5)	O(3)–C(2)–C(3)	110(1)
O(1)–Mo–O(2)	103.9(3)	O(3)–C(2)–C(4)	118.1(9)
O(1)–Mo–O(3)	96.9(3)	C(1)–C(2)–C(4)	125(1)
O(2)–Mo–O(2′)	145.4(4)	C(2)–C(1)–C(3)	124(1)
O(2)–Mo–O(3)	73.4(3)	O(4)–C(1)–C(6)	109.6(9)
O(3)–Mo–O(3′)	78.6(4)	O(4)–C(5)–C(7)	107.1(8)
Mo–O(2)–C(1)	122.8(5)	O(5)–C(5)–C(5)	107.9(9)
Mo–O(3)–C(2)	115.0(6)	O(5)–C(6)–C(8)	108.3(9)
O(2)–C(1)–C(2)	114(1)	C(5)–C(6)–C(8)	114.8(8)
O(2)–C(1)–C(3)	115(1)	C(6)–C(5)–C(7)	110(1)

Primed atoms are symmetry-related to the unprimed atoms *via* the two-fold axis.

The i.r. spectra of these complexes have been assigned from 4 000 to 140 cm^{-1} (Tables 4 and 5). Of the ligand vibrational modes only those involving the P–O bonds are of interest. The decrease in ν(P–O) from 1 193 cm^{-1} in the free ligand [24] to 1 152 and 1 141 cm^{-1} for (1) and (2) reflects the weakening of this bond on co-ordination to the metal as shown by the increase in P–O bond length from 1.46(1) to *ca.* 1.50(1) Å. The assignment of the vibrational modes associated with the $MoO_2X_2L_2$ skeleton was carried out by the method outlined in ref. 4, involving computer-assisted assignments of bending modes. For a molecule of C_{2v} symmetry 15 vibrational modes are expected of which 13 are i.r. active. The values for ν(Mo–O$_L$) indicate that the Mo–O$_L$ bond

TABLE 4

Infrared assignments of [$MoO_2X_2(PPh_3O)_2$] complexes (X = F, Cl, or Br) from 4 000 to 500 cm^{-1}

PPh_3O	F, PPh_3O	Cl, PPh_3O	Br, PPh_3O	Assignment
3 065	3 075	3 040	3 040	ν(C–H)
1 594	1 590	1 592	1 590	ν(C–C)
1 578	1 575			ν(C–C)
1 487	1 489	1 489	1 489	ν(C–C)
1 444	1 435	1 423	1 435	ν(C–C)
1 335	1 312	1 315	1 315	ν(C–C)
1 314w				combination
1 281				β(C–H)
1 193	1 138	1 141	1 152	β(P–O)
1 188	1 185	1 170 (sh)	1 180 (sh)	β(C–H)
1 168	1 165	1 155 (sh)	1 160 (sh)	β(C–H)
1 122	1 116	1 119	1 121	X-sensitive
1 097	1 095	1 086	1 091	overtone
1 074	1 071	1 071	1 074	β(C–H)
1 028	1 028	1 028	1 030	β(C–H)
997	996	997	998	ϕ ring
973	979		961 (sh)	γ ring
	947	947	944	ν_{sym} (Mo–O$_t$)
	918	905	903	ν_{asym}(Mo–O$_t$)
860	856			
		848	850	γ(C–H)
843	844			
755	761	755	758	γ(C–H)
750(sh)	750	749	752	
	726	721		
721			724	X-sensitive
	718	715		
698	692	690	690	ϕ(C–C)
619	615	619	619	α(C–C)
	588			ν(Mo–F)
	575			ν(Mo–F)
542	536	537	539	X-sensitive
	509	522	521	

TABLE 5

Infrared absorptions and their assignments for the $MoO_2X_2L_2$ core (X = F, Cl, or Br; L = PPh_3O) from 1 000 to 140 cm^{-1}

F, PPh_3O	Cl, PPh_3O	Br, PPh_3O	Assignment
947	947	944	ν_{sym} (Mo–O$_t$)
918	905	903	ν_{asym} (Mo–O$_t$)
588			ν_{asym} (Mo–F)
575			ν_{sym} (Mo–F)
410	415	417	ν_{sym} (Mo–O$_L$)
389	390	391	ν_{asym} (Mo–O$_L$)
380	378	379	δ [Mo(O$_t$)$_2$] in-plane
	320		ν_{asym} (Mo–Cl)
	295		ν_{sym} (Mo–Cl)
261	260	259	δ_{asym} [Mo(O$_t$)$_2$]
219	218	210	
203			δ[Mo(O$_L$)$_2$]
	202	202	
		180	ν(Mo–Br)

strength in these complexes is comparable to that found in the dimethylformamide (dmf) complexes [4] and this is reflected in the similar Mo–O_L bond lengths in the dmf [18] and PPh_3O structures. Values for ν(Mo–X) at 180 cm^{-1} for (1) and 320, 295 cm^{-1} for (2) are similar to those found in other $MoO_2X_2L_2$ complexes.

One of the interests in these structures was to see how the change in X affects the molybdenum co-ordination environment and also to what extent these changes are reflected in the $MoO_2X_2L_2$ vibrational modes in the i.r. spectra. It can be seen from both the spectral assignments and also the structural data that changing X from chlorine to bromine has only a minimal effect. This is to be expected since these atoms are mutually *cis* to both the terminal oxygen atoms and also the ligand oxygen atoms, and are thus not directly competing with them for the available empty 4*d* orbitals. However, changing X to fluorine would be expected to cause a greater change in the $MoO_2X_2L_2$ core in view of the close similarities in electronegativity between oxygen and fluorine. In particular, this would be reflected in an increase in both the Mo–O_t bond length and a decrease in the O_t–Mo–O_t bond angle.

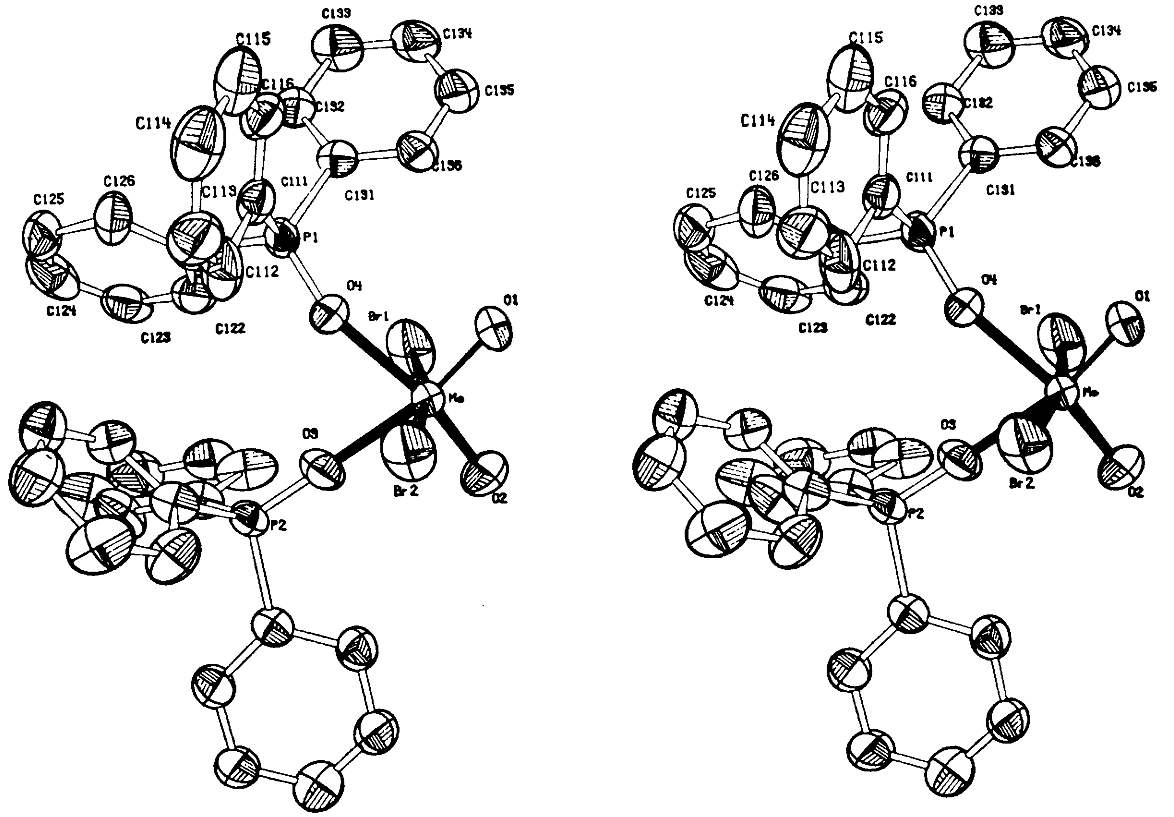

FIGURE 1 Stereoscopic pair view of $[MoO_2Br_2(PPh_3O)_2]$

Stereochemistry of Molybdenum(VI) *Complexes*.—The stereochemistry of oxomolybdenum(VI) complexes is now sufficiently well documented that the gross arrangement of donor atoms can be predicted, based on a number of generalizations.

(1) The complexes are almost invariably six-co-ordinate distorted octahedral complexes (only one documented exception).[14]

(2) There are one to three short bonds (1.64—1.74 Å) to *cis* terminal oxygen atoms with the molybdenum at the centre of the distorted octahedron being significantly displaced towards these terminal oxygen atoms.[6,7,15]

(3) There is significant lengthening of bonds *trans* to terminal oxygen atoms.[6,7,15]

(4) There is also significant lengthening of bonds *trans* to bridging oxygen atoms [but less than in (3)].[13,25]

(5) In a mixed-ligand complex the weaker π-bonding donor atoms will be *trans* to the terminal oxygen atoms: conversely, the strongest π-bonding donor atoms will be *cis* to the terminal oxygen atoms where they will not be competing with them for the available *d* orbitals.[6,7,21]

The only documented exceptions in the literature to these generalizations are in the complexes $[Mo(O_2)_2(tptp)]$ [26] [tptp = tetra(*p*-tolyl)porphyrinate] and $[MoOX_2(dtc)_2]$ [14] (dtc = disubstituted dithiocarbamate; X = F, Cl, or Br). In the former case the very rigid planar nature of the ligand forces the two peroxide groups to take up a *trans* configuration {*cf*. $[Mo_2O_3(tpp)_2]$, where there is an unprecedented *linear* O=Mo–O–Mo=O group for the same reason [27]}. The diperoxo-complex is also formally eight-co-ordinate if one regards a side-on co-ordinated peroxide group as occupying two donor positions. The complex $[MoOX_2(dtc)_2]$ has a sevenco-ordinate distorted pentagonal-bipyramidal structure with two halide atoms replacing one terminal oxygen.

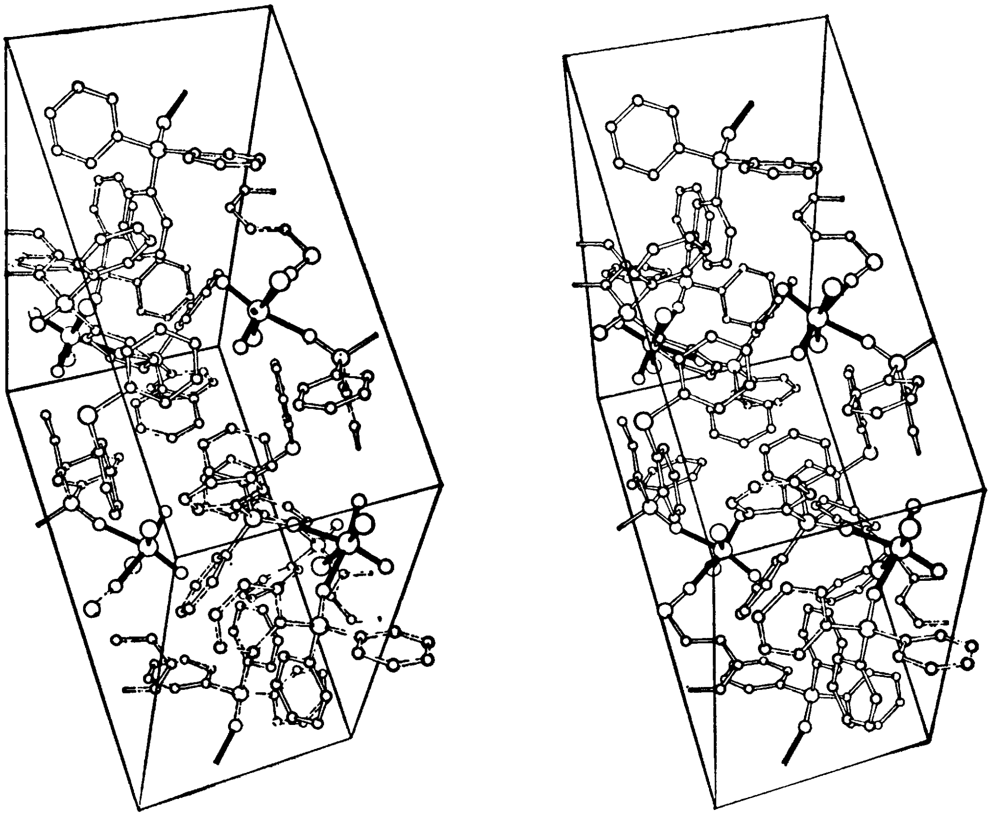

FIGURE 2 Molecular packing in the unit cell of [$MoO_2Br_2(PPh_3O)_2$]

Prediction and Confirmation of the Structure of cis-*Bis(butane-2,3-diolato)dioxo-molybdenum*(VI).—As a consequence of these generalizations, the gross stereochemistry of a *structurally unknown* complex can be predicted. Consider the complex formed between Mo^{VI} and the ligand butane-2,3-diol (HL) which analyses as $MoO_2L_2{\cdot}2HL$.[28] For this complex the arrangement of donor atoms can now be predicted. Since molybdenum(VI) complexes are invariably six-co-ordinate, the butane-2,3-diolate ligand will be bidentate. There will be two *cis* terminal oxygen atoms with bond lengths in the range 1.64—1.74 Å. The OH donor groups will be *trans* and the O^- donor atoms will be *cis* to the terminal oxygen atoms, the former having a significantly longer Mo–O bond length (2.2—2.4 Å) compared to the latter (1.9—2.1 Å). The structure of this complex has now been determined and these predictions have been confirmed.

Structure of [MoO_2L_2]$\cdot$2HL.—Positional parameters and their estimated standard deviations for (4) are listed in Table 1. Tables 2 and 3 give the intramolecular bond lengths and angles, Table 6 gives the hydrogen-bond lengths and angles. The crystal structure consists of molecules of MoO_2L_2 each surrounded by two molecules of HL which are attached by hydrogen bonds to the molybdenum complex and also linked by hydrogen bonds to neighbouring HL molecules. Figure 3 shows the MoO_2L_2 unit while Figure 4 shows how the molecules are packed in the unit cell. As can be seen from Figure 4, the extensive hydrogen bonding results in a layered structure.

Although the co-ordination number for the molybdenum atom is six there is considerable distortion from an ideal octahedral geometry due to the large O–Mo–O angle [105.2(5)°] for the MoO_2 group. This distorting effect of molybdenum–terminal oxygen bonds is encountered in all molybdenum-(V) and -(VI) structures.[29] The angle subtended by the donor atoms of the chelating ligand has been compressed to 73.4(3)°. A comparison of the lengths and angles of the *cis*-dioxide group in this structure with those found in other structures [6,7] shows that these values fall within the range expected, *i.e.* Mo=O (1.63—1.83 Å), and O=Mo=O (102.2—106°).

TABLE 6

Hydrogen bond lengths (Å) and angles (°) in complex (4)

Atom 1	Length	Atom 1	Atom 2	Atom 3	Angle
Intramolecular					
O(4)–H · · · O(2)	2.770(8)	C(1)	O(2)	O(4)	127.4(5)
O(4′)–H · · · O(2′)	2.770(8)	C(5)	O(4)	O(2)	121.3(5)
O(3)–H · · · O(5′)	2.606(9)	C(2)	O(3)	O(5)	122.3(5)
O(3′)–H · · · O(5)	2.606(9)	C(6)	O(5)	O(3)	128.6(6)
Intermolecular					
O(5)–H · · · O(4)	2.664(9)	C(5)	O(4)	O(5)	126.3(5)
O(5′) · · · O(4)	2.664(9)	C(6)	O(5)	O(4)	106.2(5)

{The value for MoO_2F_4,[30] 95(1)°, is anomalous and can perhaps be explained by the presence of the very electronegative fluorine atoms and their consequent withdrawal of electrons from the $[MoO_2]^{2+}$ moiety.}

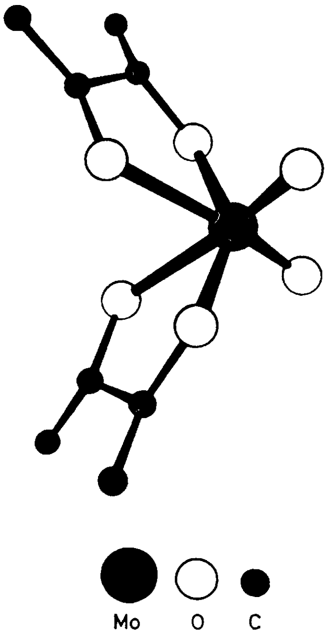

FIGURE 3 The MoO_2L_2 unit

An interesting feature of this structure is the presence of both ' free ' and co-ordinated ligand molecules giving an internal comparison on intraligand bond lengths and angles in both the free and complexed states. From chemical evidence (analyses and i.r. spectra) it is known that the ligand molecule loses a proton on co-ordination. Thus, it would be expected that there would be two quite distinct Mo–O(ligand) bond lengths corresponding to the protonated and deprotonated donor oxygen atoms. However, the fact that one Mo–O(ligand) bond is *trans* to a terminal oxygen atom means that the Mo–O(ligand) bond will be longer than an exactly equivalent bond which was not *trans* to a terminal oxygen atom. Thus it is impossible to distinguish between the ligand oxygen atoms solely on the grounds of their bond lengths to molybdenum. However, it is of interest to examine the difference between the lengths and angles about the two oxygen atoms [see Tables 2(*c*) and 3(*c*)].

The two Mo–O lengths are 1.935(7) and 2.284(7) Å of which the former must correspond to the deprotonated OH group. Table 7 shows a comparison of the distances and angles found in neutral diol complexes with those found in this case. Comparing values in the free and complexed butanediol moieties it can be seen that the difference in the two oxygen donors is reflected in both the C–O bond lengths and in the Mo–O–C angles. The deprotonated oxygen donor has a shorter bond to the molybdenum and a longer bond to the carbon atom, while the angle subtended about this atom by the molybdenum and carbon atoms is greater than that found for the other oxygen donor. Comparing these values with those of complexes containing neutral diol ligands,[31–34] polyether structures (which also contain a O–C–C–O group),[35–37] and also with the structure of *cis*-$[MoO_2(OCH_2CH_2OH)_2]$ [31] where some shortening of the C–C bond has been observed (to 1.48—1.52 Å), it can be seen that the magnitude of the shortening is much greater in the present instance (see Table 7).

The distortions imposed on the ligand by chelation can be readily seen from the fact that in the free ligand the distance between oxygen atoms is 2.97(1) Å while in the complexed ligand this distance is reduced to 2.53(1) Å. On the other hand, chelation has increased the distance between the two methyl groups and consequently the C(3)–C(1)–C(2) and C(4)–C(2)–C(1) angles are increased from 110(1) and 114.8(9)° in the free ligand to 124(1) and 126(1)° in the complexed ligand.

The carbon–carbon bond length [1.44(1) Å] in the chelate ring [C(1)–C(2)] is significantly shorter than that found in the free ligand [C(5)–C(6) 1.54(1) Å]. Also the angles subtended at C(1) and C(2) in the chelate ring and C(5) and C(6) in the free ligand molecule show considerable differences. A further point is the fact that the chelate rings are almost planar. The angles subtended at the carbon atoms show this change quite clearly. For C(5) and C(6) the sums of the subtended angles are 326.7 and 331.0° respectively, while at C(1) and C(2) these sums are 353 and 354° respectively. There appears to be some degree of electron delocalization about the chelate ring, making the two oxygen atoms almost equivalent instead of being anionic and neutral.

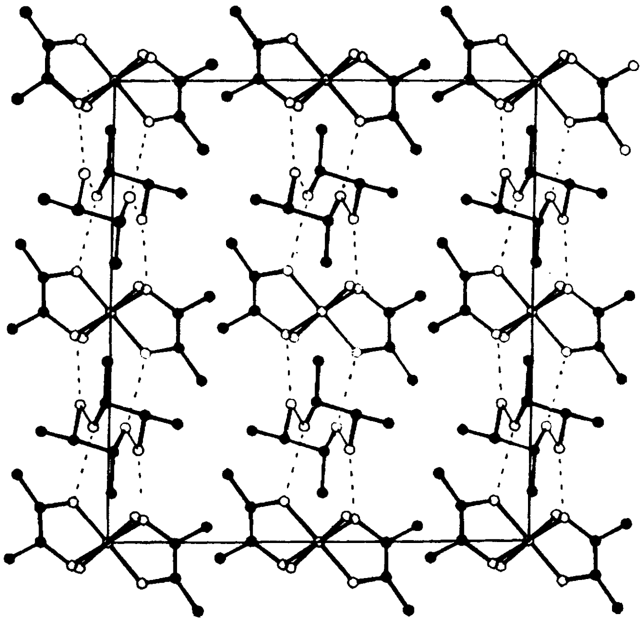

FIGURE 4 Molecular packing in the unit cell of MoO_2L_2

In this structure there is a comprehensive hydrogen-bonding system attaching the HL molecules to the complex and extending in layers throughout the structure (see Figure 4). Each central entity of MoO_2L_2 has

TABLE 7

Comparison of bond lengths (Å) and angles (°) for diol complexes [a]

Bond length/Å	$[Cu(glycol)_3][SO_4]$	$[Mn(glycol)_2Cl_2]$	' Free ' butane-2,3-diol	Complexed butane-2,3-diol	$[MoO_2(OCH_2CH_2OH)_2]$ [31]
C(1)–O(1)	1.410(14)	1.443(6)	1.44(1)	1.44(1)	1.43(2)
C(2)–O(2)	1.460(14)	1.432(6)	1.44(1)	1.41(1)	1.44(2)
C(1)–C(2)	1.520(16)	1.488(7)	1.54(1)	1.44(1)	1.50(2)
M–O(1)	1.966(8)	2.190(3)		1.935(7)	1.979(9)
M–O(2)	2.026(7)	2.240(3)		2.284(7)	2.248, 2.360(9)
M–O(3)	2.328(7) [b]				
Bond angle/°					
O(1)–C(1)–C(2)	107.8(9)	106.9(4)	109.6(9)	114(1)	109(1)
O(2)–C(2)–C(1)	108.9(9)	107.2(4)	107.9(9)	110(1)	107(1)

[a] Numbering sequence for all molecules to facilitate comparison: O(1)–C(1)–C(2)–O(2). [b] This bond length is affected by Jahn–Teller distortion.

two molecules of butane-2,3-diol attached to it in such a way that the two ligand molecules are linked by two hydrogen bonds to one HL molecule. Also there is hydrogen bonding between HL molecules so that each $[MoO_2L_2]\cdot 2HL$ unit is linked to a neighbouring unit, making a layered structure.

Conclusion.—This study has shown that changing the halide groups in $MoO_2X_2L_2$ complexes has a much smaller effect on both their i.r. spectra and their structure than changing the ligand L. This illustrates how insensitive these complexes are to the nature of the group *cis* to the terminal oxygen atoms, and further shows how these groups dominate the stereochemistry of these complexes. It has also been shown how the gross stereochemistry of molybdenum(VI) complexes can be predicted from a few simple rules. These rules have been applied to predict the gross stereochemistry of the molybdenum(VI) butane-2,3-diol complex, and the predictions confirmed by the crystal structure of this complex.

We thank the National Science Foundation for support.

[8/543 *Received*, 22*nd March*, 1978]

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