Dioxomolybdenum(VI) Complexes of Quadridentate Chiral Schiff Bases and the Crystal and Molecular Structure of Dioxo[(2*R*)-propane-1,2-diylbis(salicylideneiminato)]molybdenum(VI)

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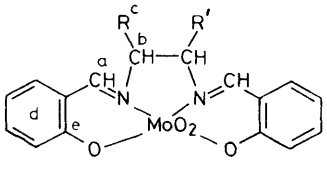
Dioxomolybdenum(VI) complexes with chiral Schiff bases have been synthesized. The structure of the title compound has been determined by *X*-ray analysis. The crystals are orthorhombic, space group $P2_12_12_1$, with $a = 10.382(3)$, $b = 12.127(4)$, $c = 13.298(4)$ Å, and $Z = 4$. The structure was determined by the heavy-atom method and refined by least squares to R 0.028 for 2 851 observed reflections. The molecule contains a *cis*-dioxomolybdenum group and the co-ordinated Schiff-base ligand is bent to form a *cis*-β structure. The conformations of the compounds in solution are discussed on the basis of ^1H and ^{13}C n.m.r. and circular-dichroism spectra.

THE conformation of the quadridentate ligands derived from the condensation of 2 mol of salicylaldehyde with chiral 1,2-diamines has been studied extensively for pseudo-planar arrangements,[1-4] and it was concluded that the conformation is strongly dependent on the substituents at the carbon atoms of the diamine and on the overall geometry of the complex.[4]

Little is known of the stereochemistry of these ligands in complexes in which they occur as non-planar arrangements. Only a few structures of complexes with the achiral derivatives of ethylenediamine and of *o*-phenylenediamine such as [Co(salen)(chelate)] and [Co(salphen)-(chelate)], in which the quadridentate Schiff base has a non-planar configuration, have been published [salen = *NN'*-ethylenebis(salicylideneiminate), salphen = *o*-phenylenebis(salicylideneiminate)].[5-9] These structures have also been discussed in relation to some stereoselective effects observed in the resolution of amino-acids with [Co{(*S*,*S*)-salchxn}{(±)-amino-acidate}] [salchxn = 1,2-cyclohexylenebis(salicylideneiminate)].[10]

Dioxomolybdenum(VI) complexes are known to invariably display a *cis* configuration of the dioxo-group,[11] even in [MoO_2(porphyrinate)].[12] In complexes of a flexible quadridentate ligand, the latter must adopt a *cis* bent configuration, as confirmed by *X*-ray analysis of



L	R	R'
salen	H	H
salpn	Me	H
salbn	Me	Me
saldpen	Ph	Ph

also L = salchxn

SCHEME 1

dioxo[propane-1,3-diylbis(salicylideneiminato)]molybdenum(VI).[13] An analogous configuration has been inferred, through n.m.r. spectroscopy, for the analogous compound [MoO_2(salen)].[14,15] despite the presence of a more rigid five-membered chelate ring.

Since the bending of the otherwise planar ligand occurs at the diamine moiety,[5-9,13] it is of interest to investigate the role of substituents at the carbon atoms of the diamine and of the conformation of the diamine chelate ring in a bent ligand. We have therefore synthesized and studied a series of complexes of general formula [MoO_2L] where L is a quadridentate Schiff base derived from the condensation of salicylaldehyde with chiral (*R*)- or (*R*,*R*)-diamines[4,16] (see Scheme 1). We also report the complete results of the *X*-ray analysis of [MoO_2\{(*R*)-salpn\}].

EXPERIMENTAL

Analyses (see Table 1) were by the microanalytical laboratory of the University of Milan. Proton n.m.r. spectra were recorded on a Varian NV 14 instrument, natural-abundance ^{13}C n.m.r. on a Varian XL-100 A instrument at 25.2 MHz in pulsed Fourier-transform, proton-noise-decoupled, and single-frequency off-resonance decoupled modes. Infrared spectra were obtained on a

TABLE 1

Analyses (calculated values in parentheses) and MoO_2^{2+} vibration bands (Nujol mulls) for [MoO_2L]

L	Analysis (%) C	H	N	ν(Mo=O)/cm^{-1}
salen	48.5	3.3	7.0	915,
	(48.7)	(3.6)	(7.3)	885
(*R*)-salpn	49.9	3.9	6.8	910,
	(50.0)	(3.9)	(6.9)	881
(*R*,*R*)-salbn	51.4	4.5	6.6	898,
	(51.2)	(4.3)	(6.6)	877
(*R*,*R*)-salchxn	53.6	4.5	6.1	911,
	(53.5)	(4.5)	(6.2)	884
(*R*,*R*)-saldpen	62.0	4.0	5.2	919,
	(61.5)	(4.0)	(5.1)	880

Perkin-Elmer 621 instrument. Circular-dichroism curves were recorded on a Roussell-Jouan Mark III spectrometer, and a Beckmann DK-2A was used to obtain electronic spectra.

The preparation of the Schiff bases of chiral diamines is reported elsewhere.[17] The complexes were obtained[14] as

yellow to orange powders by refluxing, in anhydrous ethanol, dioxobis(pentane-2,4-dionato)molybdenum(VI) [18,19] with an equimolar amount of the appropriate Schiff base. For L = (*R*)-salpn and (*R*,*R*)-saldpen, the reaction was carried out at room temperature for 24 h under an oxygen atmosphere, since, under refluxing, red ill characterized compounds were obtained, probably polymeric derivatives of Mo^{V}. Orange crystals suitable for *X*-ray analysis were obtained by carrying out the reaction at 0 °C for 4 d.

X-*Ray Analysis*.—*Crystal data*. $C_{17}H_{16}MoN_2O_4$, M = 408.3, Orthorhombic, space group $P2_12_12_1$ (no. 19), a = 10.382(3), b = 12.127(4), c = 13.298(4) Å, U = 1 674.3 Å^3, D_m = 1.60(2) (by flotation), Z = 4, D_c = 1.62 g cm^{-3}, $F(000)$ = 824, μ(Mo-K_α) = 7.97 cm^{-1}.

Intensity measurements. A small crystal was mounted on the BASIC diffractometer (see footnote to ref. 19). Diffraction intensities were collected using graphite-monochromatized Mo-K_α radiation (λ = 0.710 7 Å) within the range $3 < \theta < 25°$ by the ω-scan method. A total of 3 293 reflections was measured, corresponding to a quarter of the reciprocal lattice ($\pm h$, k, l). No decay of the sample was observed during the collection. The intensities were corrected for Lorentz and polarization effects but not for absorption. After rejection of all reflections having $\sigma(I)/I > 0.40$, a set of 2 851 significant data was used in the structure solution and refinement, 1 493 of which were independent.

Structure solution and refinement. The structure was solved by deconvolution of the three-dimensional Patterson map, which showed the Mo atom location. A difference-Fourier map revealed the position of all the non-hydrogen atoms. The refinements were carried out by blocked-matrix least squares, with the metal atom treated anisotropically. A subsequent difference-Fourier synthesis showed the locations of the hydrogen atoms. Refinement was continued by assigning an anisotropic thermal factor to all the non-hydrogen atoms, while these were treated isotropically.

At this point, in order to determine the absolute configuration of the molecule, refinements of the two enantiomorphs were performed, taking into account anomalous scattering effects.[20] Although the imaginary part of the anomalous dispersion of molybdenum is small, we found a significant difference in the values of the conventional agreement indices in the two cases, with R and R' = 0.028 and 0.031 7, and 0.031 and 0.033 2, respectively. The analysis is corroborated by the finding of the (*R*) configuration for the diamine.

TABLE 2

Positional parameters ($\times 10^5$ for Mo, $\times 10^4$ for remainder) within the molecule [MoO_2{(*R*)-salpn}]

Atom	*x*	*y*	*z*
Mo	13 096(3)	6 219(3)	9 473(2)
O(1)	3 168(2)	738(2)	1 582(2)
O(2)	1 405(2)	−931(2)	1 214(2)
O(3)	25(2)	689(2)	145(2)
O(4)	726(2)	1 200(2)	2 028(2)
N(1)	2 047(2)	2 080(2)	261(2)
N(2)	2 471(3)	140(2)	−462(2)
C(1)	2 756(3)	2 822(3)	689(3)
C(2)	1 989(3)	2 032(3)	−849(3)
C(3)	2 812(4)	1 051(3)	−1 150(3)
C(4)	4 255(4)	1 294(4)	−1 074(4)
C(5)	2 816(3)	−840(3)	−702(2)
C(6)	3 634(3)	1 629(2)	2 011(2)
C(7)	3 332(3)	2 707(3)	1 655(3)
C(8)	3 882(4)	3 631(3)	2 134(3)
C(9)	4 682(4)	3 521(4)	2 941(3)
C(10)	4 989(4)	2 457(4)	3 284(3)
C(11)	4 491(3)	1 541(3)	2 823(3)
C(12)	1 823(3)	−1 849(3)	762(3)
C(13)	2 527(3)	−1 838(3)	−145(3)
C(14)	2 949(4)	−2 838(4)	−549(3)
C(15)	2 670(4)	−3 823(4)	−103(4)
C(16)	1 961(4)	−3 833(3)	769(4)
C(17)	1 520(4)	−2 864(3)	1 197(3)
H(1)	2 952(36)	3 460(33)	369(31)
H(21)	1 168(38)	1 900(32)	−1 016(31)
H(22)	2 295(41)	2 691(36)	−1 063(37)
H(3)	2 610(38)	801(36)	−1 832(32)
H(41)	4 500(47)	1 416(44)	−263(42)
H(42)	4 697(47)	619(51)	−1 321(39)
H(43)	4 469(48)	1 880(50)	−1 416(44)
H(5)	3 246(38)	−986(35)	−1 283(31)
H(8)	3 670(37)	4 305(33)	1 860(27)
H(9)	5 023(37)	4 169(35)	3 262(31)
H(10)	5 498(42)	2 409(40)	3 873(38)
H(11)	4 691(32)	811(32)	3 069(28)
H(14)	3 413(32)	−2 871(30)	−1 129(27)
H(15)	2 938(41)	−4 566(39)	−384(34)
H(16)	1 766(38)	−4 508(38)	1 016(35)
H(17)	985(34)	−2 844(31)	1 849(28)

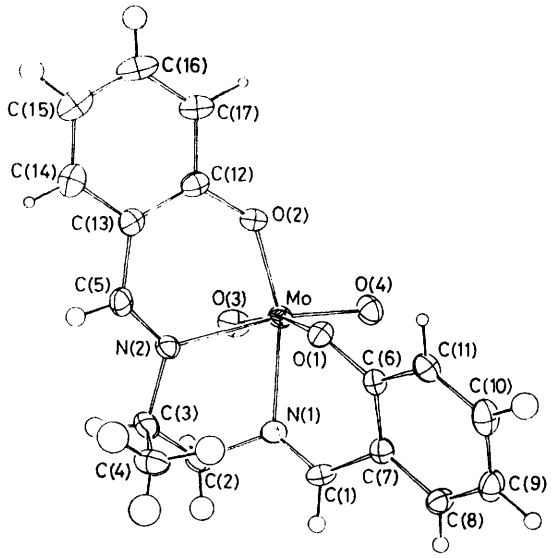


FIGURE 1 View of the molecule [MoO_2{(*R*)-salpn}] showing the atom numbering. The hydrogen atoms are numbered according to the carbon atoms to which they are attached

During the refinements weights were applied according to the formula $w = 1/(A + BF_o + CF_o^2)$; in the final cycles, A, B, and C had values 2.4, −0.07, and 9 × 10^{-4}, chosen on the basis of the analysis of $\Sigma w\Delta^2$. The atomic scattering factors were taken from ref. 21 for Mo, O, N, and C, and from ref. 22 for hydrogen.

The final difference-Fourier map was flat showing residual peaks not exceeding 0.5 e Å^{-3}. The results of the refinements are reported in Table 2. Thermal parameters and a list of the observed and computed structure factor moduli are given in Supplementary Publication No. SUP 23008 (13 pp.).* All computations were carried out on an UNIVAC 1100/80 computer using local programs.

A view of the molecule is shown in Figure 1.

RESULTS AND DISCUSSION

The compounds [MoO_2L] are easily obtained by reaction of [MoO_2(acac)$_2$] (acac = acetylacetonate) and the free Schiff base,[14] as yellow to orange solids, very

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

TABLE 3

Distances (Å) and selected bond angles (°) within the molecule $[MoO_2\{(R)\text{-salpn}\}]$

(*a*) Distances

Mo–O(1)	2.112(2)	C(12)–C(13)	1.412(6)
Mo–O(2)	1.920(2)	C(13)–C(14)	1.396(6)
Mo–O(3)	1.709(3)	C(14)–C(15)	1.365(7)
Mo–O(4)	1.710(3)	C(15)–C(16)	1.375(8)
Mo–N(1)	2.133(3)	C(16)–C(17)	1.384(7)
Mo–N(2)	2.304(3)	C(12)–C(17)	1.395(6)
O(1)–C(6)	1.314(4)	C(1)–H(1)	0.91(4)
O(2)–C(12)	1.337(5)	C(2)–H(21)	0.89(4)
N(1)–C(1)	1.294(5)	C(2)–H(22)	0.90(4)
N(1)–C(2)	1.479(5)	C(3)–H(3)	0.98(4)
N(2)–C(3)	1.478(5)	C(4)–H(41)	1.12(6)
N(2)–C(5)	1.284(5)	C(4)–H(42)	0.99(6)
C(2)–C(3)	1.519(6)	C(4)–H(43)	0.87(6)
C(3)–C(4)	1.530(6)	C(5)–H(5)	0.91(4)
C(1)–C(7)	1.424(6)	C(8)–H(8)	0.92(4)
C(5)–C(13)	1.450(6)	C(9)–H(9)	0.96(4)
C(6)–C(7)	1.424(5)	C(10)–H(10)	0.95(5)
C(7)–C(8)	1.410(6)	C(11)–H(11)	0.97(4)
C(8)–C(9)	1.364(6)	C(14)–H(14)	0.91(4)
C(9)–C(10)	1.405(7)	C(15)–H(15)	1.01(5)
C(10)–C(11)	1.370(7)	C(16)–H(16)	0.90(5)
C(6)–C(11)	1.403(5)	C(17)–H(17)	1.03(4)

(*b*) Angles

O(1)–Mo–O(2)	86.8(1)	Mo–N(1)–C(1)	126.3(3)
O(1)–Mo–O(4)	87.7(1)	Mo–N(1)–C(2)	112.3(2)
O(1)–Mo–N(1)	77.7(1)	Mo–N(2)–C(3)	116.1(2)
O(1)–Mo–N(2)	82.2(1)	Mo–N(2)–C(5)	125.7(3)
O(2)–Mo–O(3)	101.7(1)	N(1)–C(2)–C(3)	105.7(3)
O(2)–Mo–O(4)	105.4(1)	N(2)–C(3)–C(2)	106.7(3)
O(2)–Mo–N(2)	82.8(1)	N(2)–C(3)–C(4)	109.7(4)
O(3)–Mo–O(4)	103.2(1)	C(2)–C(3)–C(4)	112.5(4)
O(3)–Mo–N(1)	88.5(1)	O(1)–C(6)–C(7)	121.9(3)
O(3)–Mo–N(2)	85.0(1)	C(1)–C(7)–C(6)	118.9(3)
O(4)–Mo–N(1)	98.4(1)	N(1)–C(1)–C(7)	124.6(4)
N(1)–Mo–N(2)	71.0(1)	C(1)–N(1)–C(2)	119.3(3)
O(1)–Mo–O(3)	163.6(1)	O(2)–C(12)–C(13)	123.0(4)
O(2)–Mo–N(1)	151.0(1)	C(5)–C(13)–C(12)	123.5(4)
O(4)–Mo–N(2)	166.6(1)	N(2)–C(5)–C(13)	126.1(3)
Mo–O(1)–C(6)	124.4(2)		
Mo–O(2)–C(12)	138.6(2)	C–C–C (phenyl)	117.8(3)—121.8(4)

soluble in donor solvents. The i.r. spectra (Nujol mulls, Table 1) show two bands at *ca.* 880 and 920 cm^{-1} which can be attributed to the symmetric and antisymmetric stretchings of the *cis*-MoO_2 moiety,[23-25] an arrangement typical of dioxomolybdenum species.[11] The compounds are usually stable in solution although, on refluxing, they give ill characterized orange to red species which do not show the two i.r. bands of the *cis*-MoO_2 group; they are probably polymeric species containing Mo^V–O–Mo^V chains. This trend is particularly marked for the salpn and saldpen derivatives which must be prepared at low temperature and under oxygen.

The ^1H n.m.r. spectra show rather unexpected patterns (see Table 4 and Figure 2). For instance, for the salpn derivative, four doublets having different intensities, but of total intensity corresponding to three protons (evaluated with respect to the intensity of the two

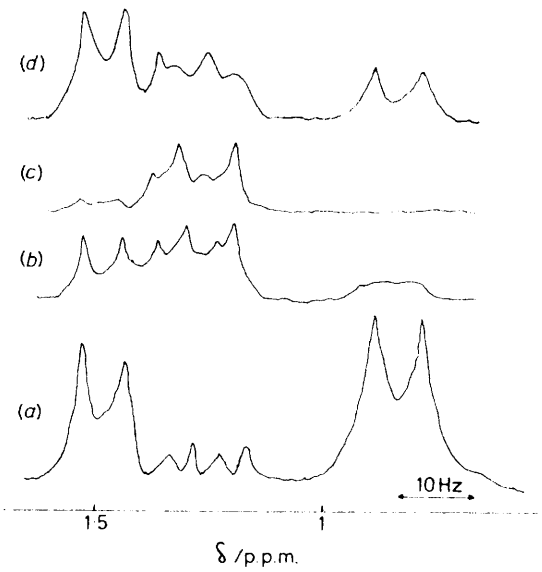


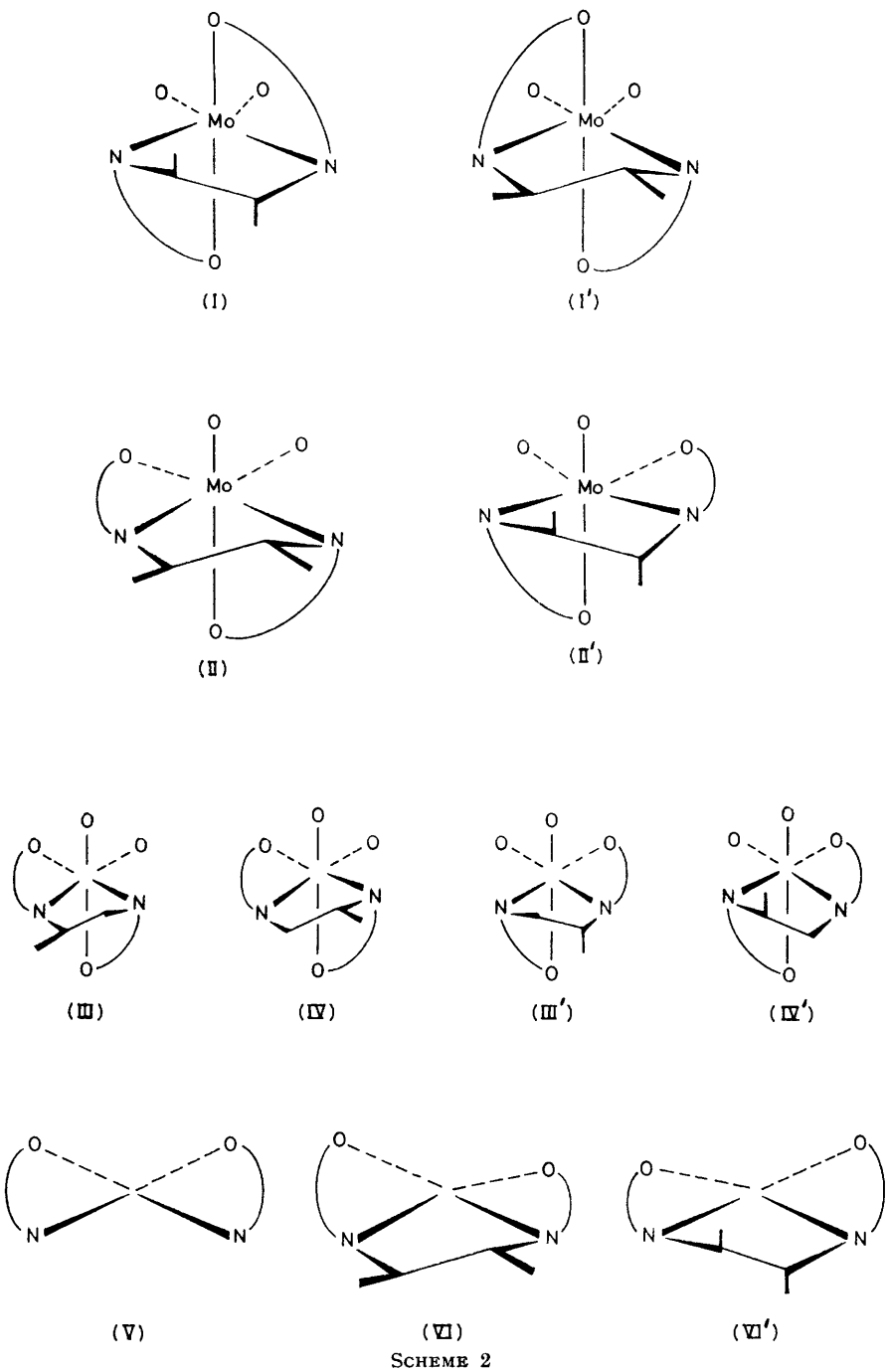
FIGURE 2 Proton n.m.r. spectra of $[MoO_2\{(R)\text{-salpn}\}]$ in dimethyl sulphoxide at various temperatures: (*a*) 26, (*b*) 120, (*c*) 150, and (*d*) 26 °C immediately after cooling. Spectrum (*d*) became identical to (*a*) if the solution was left at 26 °C for 24 h

TABLE 4

N.m.r. data for $[MoO_2L]$ in dimethyl sulphoxide

L	a	b	c	d	e
(*i*) ^1H [a]					
(*R*)-salpn	8.7—9.0 [b]	3.5—4.5 [c]	0.83 (d), 1.26 (d) 1.31 (d), 1.51 (d) [d]	6.6—7.8 [c]	
(*R,R*)-salbn	8.8—9.1 [b]	3.5—4.5 [c]	0.63 (d), 1.23 (d) 1.43 (d), 1.55 (d) [e]	6.6—7.8 [c]	
(*R,R*)-salchxn	8.8 [b]	3.9—4.2 [c]	1.8—2.2 [c]	6.6—7.8 [c]	
(*R,R*)-saldpen	8.58 (s)	5.12 (s)	7.35	6.7—7.7 [c]	
(*ii*) ^{13}C [a,f]					
(*R*)-salpn	157.6, 158.5 159.1, 160.1 162.1, 162.4 162.5, 162.6	61.6, 64.0 66.9, 68.5	17.7, 18.1 19.2, 19.6	115.7—138	163.5, 164.7 165.7, 166.6 167.0, 167.3 167.7, 167.8
(*R,R*)-salchxn	156.3 160.3 161.0	70.4 71.1 73.3	23.5, 23.6 23.9, 24.9 27.7, 30.2 32.4	116—136	162.7, 164.3 165.5
(*R,R*)-saldpen	159.9	77.5	127.5, 127.9	116—140	166.0

[a] δ in p.p.m. *vs.* $SiMe_4$; d = doublet; s = singlet. Integrations are consistent with the assignments. For lettering see Scheme 1. [b] Various unresolved peaks, total intensity corresponding to two protons. [c] Complex pattern. [d] The total intensity of these four doublets corresponds to three protons. [e] The total intensity of the four doublets corresponds to six protons. [f] δ in p.p.m. *vs.* $SiMe_4$. Assignments are consistent with single-frequency off-resonance experiments. The spectrum of the salbn derivative could not be measured because of the low solubility of the compound.



SCHEME 2

salicylaldehyde groups), can be observed in the methyl region (between $\delta = 0.8$ and 1.5 p.p.m. relative to $SiMe_4$), whereas the azomethine region is very complicated (Table 4). Carbon-13 n.m.r. spectroscopy confirms the existence of four different methyl groups, and eight resonances can be attributed to magnetically different azomethine carbon atoms.

The presence, in solution, of different isomers has already been discussed in the case of $[MoO_2(salen)]$.[14,15] It was concluded that structure (I) (*cis*-α) (Scheme 2) which possesses a two-fold axis should give rise to only one azomethine resonance in the ^1H n.m.r. spectrum, whereas for (II) (*cis*-β) two signals are expected {as has been found for $[MoO_2(salen)]$ [14,15]}. The presence of one methyl group in the ethylenediamine chelate ring increases the number of possible isomers which for (*R*)-salpn are (III), (IV) and their diastereoisomers (III'), (IV').

To try to understand the behaviour of these complexes we have undertaken a crystal-structure determination

of [MoO_2{(*R*)-salpn}]. The sample was obtained by reaction at 0 °C in ethanol which gives only one kind of crystals.

Crystal Structure of [MoO_2{(*R*)-salpn}].—A view of the species characterized by *X*-ray analysis is shown in Figure 1, and bond distances and angles are reported in Table 3. The crystal structure consists of discrete molecules separated by normal van der Waals contacts. The co-ordination around the metal atom is distorted octahedral, two *cis* positions being occupied by the two oxygen atoms of the MoO_2^{2+} group, in agreement with the i.r. data. The quadridentate Schiff base co-ordinates to the metal ion forming three condensed rings with six, five, and six members; to fulfil the requirements of the *cis*-MoO_2^{2+} moiety the Schiff base is bent. The overall structure has a *cis*-β configuration, with the analogous donor atoms [O(1) and O(2), N(1) and N(2)] mutually *cis*. The two M–O(oxide) bond distances are very similar (mean 1.71 Å, corresponding [26] to a bond order of *ca.* 2), and these distances and the subtended O–Mo–O angle [103.2(1)°] are comparable with those found in analogous compounds.[13,27] The distances between molybdenum and the ligand atoms *trans* to the oxide atoms are lengthened by a strong *trans* influence: [28] Mo–O(2) 1.920(2) and Mo–O(1) 2.112(2); Mo–N(1) 2.133(3) and Mo–N(2) 2.304(3) Å. The previously mentioned distortion of the octahedral co-ordination is evidenced by the values of the co-ordination angles around molybdenum: the *cis* ones range from 71.0(1)° for N(1)–Mo–N(2) to 105.4(1)° for O(2)–Mo–O(4), and the *trans* ones from 151.0(1)° for O(2)–Mo–N(1) to 166.6(1)° for O(4)–Mo–N(2). Such distortion arises from both the steric requirements of the MoO_2^{2+} group and the strains induced by the presence of a five-membered ring in the folded quadridentate ligand.[13]

Bond distances in the ligand are as expected: C(1)–N(1) and C(5)–N(2) (average 1.289 Å) are normal for double bonds; C(1)–C(7) and C(5)–C(13) (average 1.437 Å) are a little shorter than those of a single bond, indicating partial delocalization of the π-electron system. The mean C–C distance of the two phenyl rings is 1.392 Å.

As to the conformation of the quadridentate ligand, three features are relevant. (*i*) The C(12)–C(17) phenyl ring and the N(2),C(5),C(13),C(12),O(2),Mo six-membered chelate ring are nearly coplanar (dihedral angle *ca.* 3°), and this planarity extends also to C(3). (*ii*) The O(1) atom lies on the C(6)–C(11) phenyl-ring plane, whereas the C(1) atom is displaced by 0.33 Å out of this plane. The plane of hybridization of C(1), *i.e.* C(7),C(1),N(1), is twisted by 24.3° with respect to the phenyl plane by 27.5° with respect to the plane of hybridization of N(1), namely C(1),N(1),C(2). (*iii*) The six-membered chelate ring Mo,O(1),C(6),C(7),C(1),N(1) is in a twisted δ conformation; [29] the diamine chelate ring is also in a δ conformation.

Finally, the overall chirality of the complex, determined by anomalous scattering, and specified by considering the chelate rings of the two salicylaldehyde moieties whose relative positions are analogous to that in a *cis*-bis(bidentate ligand) complex, is Λ.[29]

Distribution of Isomers in Solution.—[MoO_2{(*R*)-salpn}]. Only one of the possible isomers has been found in the solid state, *i.e.* (III′) of Scheme 2. If this configuration is retained in solution it should give rise to a methyl-proton resonance at high field, since these protons are shielded by the phenyl ring of the salicylaldehyde moiety bent towards them. The doublet at $\delta = 0.83$ (dimethyl sulphoxide solution, Table 4) is readily attributed to the methyl group of (III′), but the presence of three other doublets (Figure 2) and of eight azomethine resonances indicates that, in solution, four isomers of the type *cis*-β are present, *i.e.* (III), (III′), (IV), and (IV′). The isomeric distribution which gives rise to the spectrum in Figure 2(*a*) has also been found in solutions of samples prepared under different conditions, including the crystals used for the *X*-ray analysis, indicating that, in solution, isomerization occurs. It varies with temperature, as shown by high-temperature ^1H n.m.r. spectra (Figure 2), but the interconversion of the different isomers is not fast; when the temperature is rapidly decreased from 150 °C to room temperature a large amount of the isomer predominant at the higher temperature is still present and only decreases slowly [Figure 2(*d*)].

In Figure 3 the circular dichroism (c.d.) spectra (dimethyl sulphoxide solution and in the solid state) of all the compounds are reported. These essentially consist of a Cotton effect at *ca.* 430 nm, below an absorption band probably of charge-transfer (c.t.) character, and a positive negative doublet centred at *ca.* 330 nm which is likely to be the exciton splitting of the $\pi \rightarrow \pi^*$ transition of the azomethine groups.[1] This transition appears in the absorption spectrum as an ill defined shoulder (Figure 3). The spectra are not solvent dependent, and are similar also in the solid state.

Inspection of Figure 3 shows that the chirality of the chromophores is the same for the derivatives of (*R*,*R*)-salchxn, -salbn, and -saldpen, but opposite for the compound with (*R*)-salpn. For the latter, following a previous argument,[1,4] the two chromophores should be arranged to form a right-handed helix, because the higher energy component of the exciton doublet is negative. However, since ^1H n.m.r. evidence suggests the presence of different isomers, the observed c.d. spectra are those of an equilibrium mixture, and the observed chirality must be that of the most abundant isomer(s).

For [MoO_2{(*R*)-salpn}] only in the isomers (III′) and (IV′) are the two azomethine chromophores arranged in a right-handed helix, which corresponds to a δ conformation of the diamine chelate ring and a Λ configuration of the molecule,[2,4] as demonstrated by the *X*-ray data for (III′), in agreement with the solid-state spectra of this compound and models in the case of (IV′). On the basis of previous studies on the conformation of these ligands,[1,4,30,31] (III′) and (IV′) should be the most probable isomers for [MoO_2{(*R*)-salpn}]. In fact they

can be described as resulting from the tetrahedral distortion usually observed with this class of ligands. For the derivatives of (*R*)-salpn the sign of the tetrahedral distortion is dictated by the preferred δ-axial conformation of the diamine[2,4] and the sequence of increasing dis-

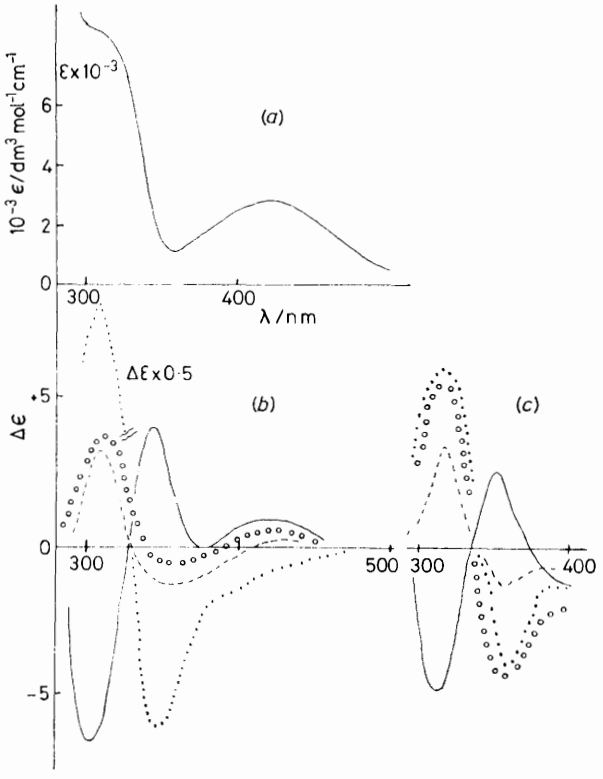


FIGURE 3 Electronic absorption spectrum of [MoO_2{(*R*)-salpn}] in dimethyl sulphoxide (*a*) and c.d. spectra of [MoO_2L] in the same solvent (*b*) and in the solid state (*c*, KBr pellets, arbitrary units). L = (*R*)-salpn (——), (*R,R*)-salbn (– – –), (*R,R*)-salchxn (· · ·), or (*R,R*)-saldpen (○)

tortion is (V) (planar) ⟶ (VI) (as in [Cu{(*R*)-salpn}][2,4]) ⟶ (III′) (present case) (Scheme 2). This accounts for the fact that the sign of the exciton splitting at *ca.* 370 nm is the same in a vast series of complexes such as [Cu{(*R*)-salpn}],[2,4] [VO{(*R*)-salpn}],[32] and [MoO_2{(*R*)-salpn}] [in refs. 4 and 32 the spectra of the derivatives of (*S*)-salpn are reported, which are obviously enantiomeric to those of the compounds with (*R*)-salpn].

It must be noted, however, that the observation, in solution, of other diastereoisomers (which correspond to the λ-equatorial conformation of the diamine) is not surprising since a λ ⇌ δ equilibrium is likely to be operative in solution. However, to our knowledge, this is only the second case in which the various isomers have been observed, since the separation of the four possible isomers of [VO{(±)-salpn}] was reported.[33] In the present case, any attempt to separate the four isomers by chromatography failed, indicating that the isomerization, although slow on the n.m.r. scale, is quite fast.

[MoO_2{(*R,R*)-salchxn}]. The ^{13}C n.m.r. spectrum of this compound shows the presence of three azomethine resonances and three signals for the two CH groups of the diamine (Table 4). This is consistent with the presence, in solution, of two isomers, one having no element of symmetry and one with a two-fold axis. Circular-dichroism evidence (Figure 3) supports an arrangement of the two azomethine chromophores of opposite chirality to that of the (*R*)-salpn derivative, because of the opposite patterns of the spectra. Since in the case of (*R,R*)-salchxn complexes the diamine chelate ring must be λ-equatorial,[2] the configuration of the complex must be Δ as in (II). A further increase of the tetrahedral distortion leads to (I′) which must be termed Λ according to the I.U.P.A.C. nomenclature, but which has the same (λ) conformation of the diamine chelate ring as (II) and the same mutual disposition of the azomethine groups, and will give rise to a c.d. spectrum having the same sign as (II). This compound is therefore a mixture, in solution, of (II) and (I′).

[MoO_2{(*R,R*)-salbn}]. The two methyl groups of this compound give rise to four doublets in the ^1H n.m.r. spectrum (see Table 4), suggesting the presence of two isomers, each with non-equivalent methyl groups, *i.e.* (II) and (II′). Circular-dichroism spectra (Figure 3) suggest that the most abundant isomer has the same configuration as the (*R,R*)-salchxn derivative and it is therefore (II) which possesses the λ-equatorial conformation of the butanediamine chelate ring. N.m.r. evidence is also in agreement with these points; the doublet at δ *ca.* 0.6, attributable to that methyl group of (II′) (axial conformation) which is shielded by one benzene ring, is of low intensity An estimate of the isomer ratio (II) : (II′), from the intensity of the four doublets, is 5 : 1.

[MoO_2{(*R,R*)-saldpen}]. This compound shows only one resonance of the azomethine group (see Table 4). Its structure, in solution, is likely to be (I′) since its c.d. spectrum is similar to that of the (*R,R*)-salchxn derivative. For saldpen derivatives, it has already been found that the two phenyl groups can easily be accommodated in a diequatorial conformation.[4,32]

Conclusions.—The quadridentate ligands described in this paper appear to be more flexible than previously supposed, giving rise to a wide variety of isomers. The relative stability of the isomers is dictated by the substituents at the carbon atoms of the diamine moiety, thus salchxn and saldpen readily give rise to symmetrical structures as (I) or (I′), whereas in the presence of methyl groups structure (II) or (II′) is more stable.

An interesting feature is the preference of the diamine chelate ring for the equatorial conformation, displayed by all the compounds except the salpn derivative. Such a conformation has seldom been observed in complexes of the quadridentate Schiff bases described here, especially in the case of butanediamine derivatives.[4] Preference for an axial conformation has been attributed to the steric repulsion between the azomethine hydrogen atom and the substituents in the equatorial positions,[2,4] and this seems to be typical of complexes of polydentate Schiff bases.[34] In the present case it is likely that the

bending of the ligand will minimize such repulsion, although more subtle, and at present unknown, factors must also influence the conformation since we cannot rationalize the opposite behaviours of the (*R*)-salpn and (*R*,*R*)-salbn derivatives.

Finally, isomerization is not surprising for dioxomolybdenum(VI) species, as it has already been observed, for instance, in the case of dioxobis(pentane-2,4-dionato)molybdenum(VI).[35] Two mechanisms seem likely: dissociation of one metal–ligand bond or a twist mechanism. At the present stage no argument can be put forward in favour of either mechanism, although for these compounds a twist mechanism, involving the flexibility of the ligands, seems more likely.

[0/1031 *Received*, 2*nd July*, 1980]

REFERENCES

[1] B. Bosnich, *J. Am. Chem. Soc.*, 1968, **90**, 627.
[2] R. S. Downing and F. L. Urbach, *J. Am. Chem. Soc.*, 1968, **90**, 5344; 1969, **91**, 5977; 1970, **92**, 5861; R. L. Farmer and F. L. Urbach, *Inorg. Chem.*, 1970, **11**, 2562.
[3] M. Gullotti and A. Pasini, *Inorg. Chim. Acta*, 1975, **15**, 129.
[4] A. Pasini, M. Gullotti, and R. Ugo, *J. Chem. Soc., Dalton Trans.*, 1977, 346.
[5] M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Commun.*, 1970, 1079; M. Calligaris, G. Manzini, G. Nardin, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1972, 543.
[6] N. A. Bailey, B. M. Higson, and E. D. McKenzie, *J. Chem. Soc., Dalton Trans.*, 1972, 503.
[7] D. Cummins, B. M. Higson, and E. D. McKenzie, *J. Chem. Soc., Dalton Trans.*, 1973, 1359.
[8] D. Cummins, E. D. McKenzie, and H. Milburn, *Inorg. Chim. Acta*, 1975, **12**, L17.
[9] K. Kushi, R. Tamura, M. Kuramoto, T. Yoshizawa, and H. Yoneda, *J. Chem. Soc., Chem. Commun.*, 1978, 266.
[10] Y. Fujii, T. Isago, M. Sano, N. Yanagibashi, S. Hirasawa, and S. Takahashi, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 3509; Y. Fujii, M. Sano, and Y. Nakano, *ibid.*, 1977, **50**, 2609.
[11] E. I. Stiefel, *Prog. Inorg. Chem.*, 1977, **22**, 1.
[12] H. Ledon, M. Bonnet, and J. Y. Lallemand, *J. Chem. Soc., Chem. Commun.*, 1979, 702.
[13] A. Chiesi Villa, L. Coghi, A. Gaetani Manfredotti, and C. Guastini, *Cryst. Struct. Commun.*, 1974, **3**, 551.
[14] K. Yamanouchi and S. Yamada, *Inorg. Chim. Acta*, 1974, **9**, 161.
[15] W. E. Hill, N. Atabay, C. A. McAuliffe, F. P. McCullough, and S. M. Razzoki, *Inorg. Chim. Acta*, 1979, **35**, 35.
[16] R. D. Gillard, *Tetrahedron*, 1965, **21**, 503; R. Kuroda and S. F. Mason, *J. Chem. Soc., Dalton Trans.*, 1977, 1016.
[17] M. Gullotti, A. Pasini, P. Fantucci, R. Ugo, and R. D. Gillard, *Gazz. Chim. Ital.*, 1972, **102**, 855.
[18] H. Gehrke, jun., and J. Veal, *Inorg. Chim. Acta*, 1969, **3**, 623.
[19] G. Ciani, M. Manassero, and A. Sironi, *J. Organomet. Chem.*, 1980, **199**, 271.
[20] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3.
[21] D. J. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
[22] J. B. Forsyth and M. Wells, *Acta Crystallogr.*, 1959, **12**, 412.
[23] K. Nakamoto, ' Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1963, p. 77.
[24] W. P. Griffith and T. D. Wickins, *J. Chem. Soc. A*, 1967, 675; 1968, 400.
[25] F. W. Moore and R. E. Rice, *Inorg. Chem.*, 1968, **7**, 2510.
[26] F. A. Schoder, *Acta Crystallogr., Sect. B*, 1975, **31**, 2294.
[27] B. Spivack and Z. Dori, *Coord. Chem. Rev.*, 1975, **17**, 99.
[28] E. M. Shustorovich, M. A. Porai-Koshits, and Yu. A. Buslaev, *Coord. Chem. Rev.*, 1975, **17**, 1.
[29] *Inorg. Chem.*, 1970, **9**, 1.
[30] M. Calligaris, G. Nardin, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1973, 419; N. Bresciani, M. Calligaris, G. Nardin, and L. Randaccio, *ibid.*, 1974, 1606.
[31] N. Bresciani, M. Calligaris, G. Nardin, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1974, 498.
[32] A. Pasini and M. Gullotti, *J. Coord. Chem.*, 1974, **3**, 319.
[33] D. F. Martin and K. Ramaiah, *J. Inorg. Nucl. Chem.*, 1965, **27**, 2027.
[34] G. Ciani, M. Manassero, A. Sironi, L. Casella, M. Gullotti, and A. Pasini, *Inorg. Chim. Acta*, 1978, **26**, L1; L. Casella, M. Gulloti, A. Pasini, and A. Rockenbauer, *Inorg. Chem.*, 1979, **18**, 2825.
[35] B. M. Craven, K. C. Ramey, and W. B. Wise, *Inorg. Chem.*, 1971, **11**, 2626.