

Determination of Absolute Configuration of Acyclic 1,2-Diols with $[\text{Mo}_2(\text{OAc})_4]$, Part 2: New Structural Evidence toward a Rationale of the Method: What Remains of $[\text{Mo}_2(\text{OAc})_4]$ in DMSO Solution?†

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Abstract: The nature of the CD-active species obtained by mixing dimolybdenum tetraacetate and a chiral 1,2-diol in DMSO has been studied by different techniques (1D and 2D ^1H NMR, CD, UV/Vis) with two substrates, (*R*)-phenyl-1,2-ethanediol (**1**) and (*R,R*)-butane-2,3-diol (**2**). The diol/dimolybdenum adducts have diagnostic CD spectra whose sign correlates with the absolute configuration of the organic substrate. It is demonstrated that, in

DMSO solution, the acetate ligands of $[\text{Mo}_2(\text{OAc})_4]$ dissociate to a large extent under the action of the dissolved water, yielding acetic acid and a polyhydrated dimolybdenum species. Addition of a 1,2-diol leads to chelation with formation of one main active spe-

cies for **2** and two for **1**, all with 1:1 stoichiometries at diol/dimolybdenum molar ratios less than 1.5. Only a small fraction (less than 20%) of the 1,2-diol is bound. The structures of the active complexes are estimated on the basis of NMR spectra, by correlating the observed chemical shifts with the quadruple bond diamagnetic anisotropy. In the predominating complexes for **1** and **2**, the 1,2-diol moiety bridges the Mo_2 core forming a six-membered ring.

Keywords: diols • circular dichroism • molybdenum • NMR spectroscopy • structure elucidation

Introduction

One of the most useful methods for rapid and effective determination of the absolute configuration of 1,2-diols is that with dimolybdenum tetraacetate.^[1,2] Approximately equimolar amounts of the nonracemic substrate and $[\text{Mo}_2(\text{OAc})_4]$ are mixed in DMSO at ambient temperature and open to the air, and the circular dichroism (CD) spectrum obtained above 250 nm (the absorption region of the dimolybdenum chromophore), which is often referred to as an induced CD (ICD),^[3] is observed. The sign of the CD band around 305 nm (“band IV”) correlates with the absolute configuration of the substrate.^[1,2a] For example, Figure 1 shows typical spectra for (*R*)-phenyl-1,2-ethanediol and (*R,R*)-butane-2,3-diol (**1** and **2**); for these substrates, the negative band IV is associated with the (*R*) absolute configuration.^[4]

This method was developed by Snatzke, Frelek, and co-workers in the 1980s and has since been applied to many substrates, including several biologically relevant ones.^[2a,f]

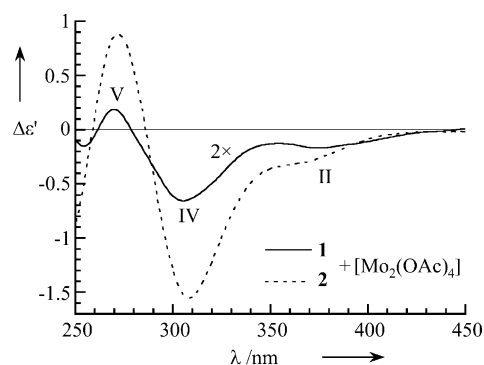
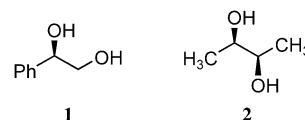


Figure 1. CD spectra in stationary conditions of (*R*)-phenylethane-1,2-diol (**1**) (3.25 mM) and (*R,R*)-butane-2,3-diol (**2**) (5.72 mM) in a solution of dimolybdenum tetraacetate (about 1:1 in DMSO); cell pathlength 0.1 cm. $\Delta\epsilon'$ is normalized on the diol concentration. Roman numerals refer to Snatzke's band nomenclature.^[2a,b]



Pursuing our interest in a rapid and reliable configurational determination of chiral 1,2-diols obtained through the asymmetric dihydroxylation of olefins^[5] we recently applied Snatzke's method^[1] to 20 chiral building blocks of known

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absolute configuration, either obtained commercially or synthesized ad hoc; our finding of no exceptions to the empirical rule further supported the previous evidence.^[2a] Because of our special interest in synthetic products, we also tested the response to some common situations such as a variable chemical and enantiomeric purity.^[1] By the same method we later determined the absolute configuration of a series of diterpenes (pimarenes) newly isolated from *Lavandula multifida* L.^[6]

Snatzke and co-workers often discussed the exact nature of the diol/dimolybdenum adduct (the Cottonogenic or CD-active species: that is, the one giving rise to the prominent CD), and suggested a comprehensive but intuitive structural picture.^[2] They assumed that the solid-state structure of the “stock complex” $[\text{Mo}_2(\text{OAc})_4]$ ^[7] remained unchanged in DMSO solution, and that one diol molecule replaced one or two acetate groups ligating the Mo^{2+} core.^[2] They envisaged two different ligation modes, defined as “parallel” and “perpendicular” (Figure 2), in accord with a wide literature on

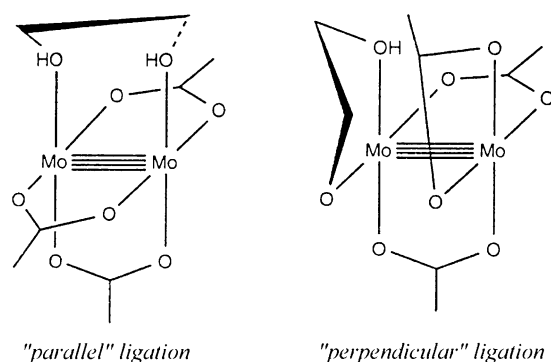


Figure 2. Snatzke's models for the “parallel” (left) and the “perpendicular” (right) complexes. (Taken from ref. [2a], with the publisher's permission).

quadruply bonded dimolybdenum(II,II) compounds with various bidentate ligands.^[8a] This picture appeared consistent with the following observations:^[2] 1) optically active mono-hydroxy alcohols do not lead to an appreciable CD, so a double ligation must occur for 1,2-diols; 2) the absorption spectrum of the “stock complex” is substantially unchanged after addition of the chiral sample, so a minimum number of acetate ligands should be displaced; 3) in some cases, the CD spectrum is apparently time-dependent, so a slow equilibrium between different Cottonogenic species is conceivable. However, no complex of dimolybdenum with 1,2-diols has ever been isolated in the crystalline form,^[2a] while the few reported examples of stable dimolybdenum compounds with alcohol, alkoxide or polyol ligands do not fit the current case.^[9,10,11,12]

We sought further experimental evidence for a solution structure of the CD-active species, to provide a more robust rationalization of the origin of the optical activity. Simple ^1H NMR evidence on the stock solution of $[\text{Mo}_2(\text{OAc})_4]$ in DMSO opened a totally different perspective, which stimulated the investigations described below.

Results

NMR and UV/Vis studies on the nature of “ $[\text{Mo}_2(\text{OAc})_4]$ ” in DMSO solution: The NMR and UV/Vis study uncovered very surprising, totally unexpected, and unreported behavior of the stock complex $\text{Mo}_2(\text{OAc})_4$ in DMSO solution.

The ^1H NMR spectrum of $\text{Mo}_2(\text{OAc})_4$ in $[\text{D}_6]\text{DMSO}$ had been described as consisting of a single peak at $\delta = 2.6$,^[13] but three distinct peaks appeared as singlets at $\delta = 1.90$, 2.60 and 11.94 ppm in all our spectra (Figure 3).^[14] Similarly,

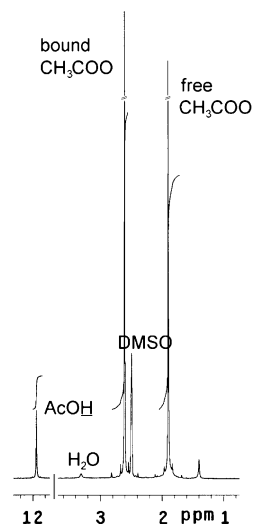


Figure 3. ^1H NMR spectrum (300 MHz) of $\text{Mo}_2(\text{OAc})_4$ (21.3 mM) in commercial $[\text{D}_6]\text{DMSO}$.

the proton-decoupled ^{13}C NMR spectrum consists of two major peaks at $\delta = 21.1$ and 23.6 ppm, and two smaller ones at $\delta = 172.1$ and 180.6 ppm. Following the previous reasoning, the resonance of ^1H at $\delta = 2.60$ ppm,^[13] and of ^{13}C at $\delta = 23.6$ and 180.6 ppm, can be assigned to the methyls of acetate groups in $[\text{Mo}_2(\text{OAc})_4]$ (“bound” acetate). The ^1H signals at $\delta = 1.90$ and 11.94 ppm (always in an integral ratio of about 3:1), and the ^{13}C ones at $\delta = 21.1$ and 172.1 ppm, coincide instead with the resonances of acetic acid in DMSO solution (“free” acetate). The ^1H shift $\Delta\sigma = \sigma_{\text{free}} - \sigma_{\text{bound}} = -0.70$ ppm for the methyl groups of the bound acetate with respect to the free one is due to the large diamagnetic anisotropy exerted by the Mo–Mo quadruple bond,^[8b,13,15] which brings about a strong deshielding effect on the protons lying along a direction perpendicular to the bond itself. From Equation (1) (valid for a nucleus at distance r along the direction forming the angle ψ with the Mo–Mo bond, both measured from its center; see Figure 4), a value of $-3000 \times 10^{-6} \text{ \AA}^3$ can be estimated for the anisotropy $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ ^[16] (using the solid-state geometry of $\text{Mo}_2(\text{OAc})_4$).^[7]

$$\Delta\sigma = \frac{1}{4\pi} \frac{(1-3\cos^2\psi)}{3r^3} \Delta\chi \quad (1)$$

From saturation transfer experiments, it appears that free and bound acetate do not exchange at room temperature

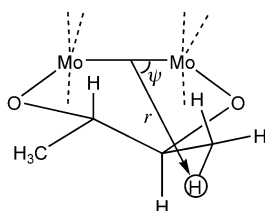


Figure 4. Structural parameters for Equation (1).

(exchange rates below 0.5 s^{-1}). Thus, under the present experimental conditions, the NMR spectra reveal two main species: the stock complex itself, $[\text{Mo}_2(\text{OAc})_4]$, and free, undissociated^[17,18] acetic acid. The absence of evidence of intermediate species with one to three bound acetate ligands demonstrates that the dissociation is strongly cooperative.^[19]

We realized that the nonnegligible amount of water present in DMSO could play a role in the dissociation of the stock complex,^[20] and we easily demonstrated that the quantity of free, nondissociated acetic acid is proportional to the water content of the solvent: the proportion of signals at $\delta = 2.60$ and 1.90 ppm is a) about 1:1 in commercial $[\text{D}_6]\text{DMSO}$ (Fluka, puriss. grade) with an untreated tube, and b) about 9:1, on average, in more anhydrous conditions (see the Experimental and Computational Section). Starting from a sample from the latter group, the ratio changes progressively in favor of the peak at $\delta = 1.90$ ppm as water is added; the acetate dissociation is immediate. The sum of integrals for the two acetate signals at $\delta = 1.90$ and 2.60 ppm is constant and, when checked against an internal standard (benzene), it accounts for the whole weight of $[\text{Mo}_2(\text{OAc})_4]$ present. After addition of 10–20 equivalents of H_2O with respect to $[\text{Mo}_2(\text{OAc})_4]$, the signal of the bound acetate disappears. We conclude that water promotes the dissociation from $[\text{Mo}_2(\text{OAc})_4]$ in DMSO of acetate ligands, which thereafter form undissociated acetic acid.

Exactly the same behavior could be followed by UV/Vis spectroscopy. Figures 5 and 6 show the UV/Vis spectra and the relative plot of $\epsilon(303 \text{ nm})$ of $[\text{Mo}_2(\text{OAc})_4]$ (2.62 mM in DMSO) as a function of the addition of H_2O (the spectrum is normalized using the total $[\text{Mo}_2(\text{OAc})_4]$ concentration); the solvent had been thoroughly dried and contained ap-

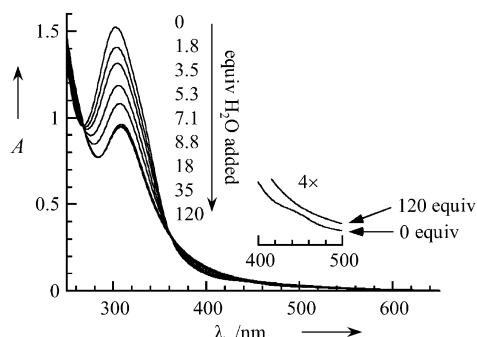


Figure 5. UV/Vis spectra of $[\text{Mo}_2(\text{OAc})_4]$ (2.62 mM in DMSO) as a function of addition of water. The total amount of water added is listed for each sample; the initial quantity was about 1.6 equiv H_2O . Insert: magnification of the spectra between 400 and 500 nm for 0 and 120 equiv H_2O added.

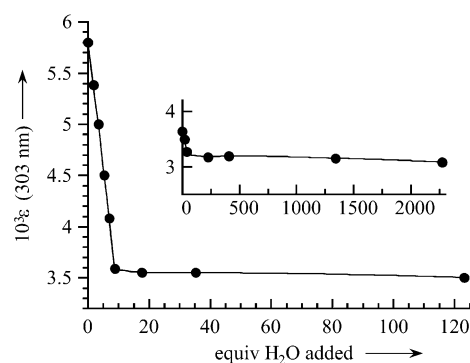


Figure 6. $\epsilon(303 \text{ nm})$ vs. water added (equiv), for UV/Vis spectra of $[\text{Mo}_2(\text{OAc})_4]$ (2.62 mM (main graph) and 2.42 mM (insert)) in DMSO; the initial samples contained about 1.6 equiv H_2O . Cell pathlength 0.1 cm.

proximately 70 ppm of H_2O (Karl Fischer method), corresponding to about 1.6 equivalents with respect to $[\text{Mo}_2(\text{OAc})_4]$. After an initial rapid decrease in ϵ , a stationary plateau is reached starting from about 10 equivalents of water added (Figure 6). The first spectrum recorded (Figure 5, 0 equiv H_2O), in close analogy to the one reported,^[2a] has its maximum at 303 nm (band C, $\epsilon = 5800$), a shoulder at 334 nm (band B), and a small band at 446 nm ($\epsilon = 180$, band A) which is superimposed on the tail of the strongest one. In contrast, in the spectra for the stationary region (Figure 5, from 10 equiv water added, upward) band A has disappeared, and band C is reduced and red-shifted (308 nm, $\epsilon \approx 3500$); the extent of the shift is partially masked by the coalescence with the strong absorption at shorter wavelengths: the second derivative has its extremum at 312 nm. Notably, Frelek et al.^[2a] described the same effect as a consequence of the aging of the solution after 24 h; we may now interpret it as due to the absorbed water (possibly slowly released by the glassware also). Intermediate spectra (up to 10 equiv of added water) show intermediate features, with band C progressively reduced and red-shifted; none of these spectra evolves with time. Two neat isosbestic points appear at 268 and 361 nm (Figure 5), supporting the presence of two distinct species.

Thus, NMR and UV/Vis results concur in suggesting that a new species is formed in DMSO solution of $[\text{Mo}_2(\text{OAc})_4]$ owing to the presence of water, with the acetate ligands cooperatively dissociating in the form of acetic acid; this species is characterized by a UV spectrum with a transition at 312 nm, and a complete absence of a band above 400 nm, allied to a $\delta \rightarrow \delta^*$ transition, which is typical of quadruply bonded dimolybdenum complexes with bridging carboxylate ligands.^[8c]

Investigation of active species: NMR spectra of mixtures of 1,2-diols and $[\text{Mo}_2(\text{OAc})_4]$: In the ^1H NMR spectrum of a mixture of $[\text{Mo}_2(\text{OAc})_4]$ and (*R*)-phenyl-1,2-ethanediol (**1**) in anhydrous $[\text{D}_6]\text{DMSO}$ (Figure 7), two new sets of signals appear compared with the component spectra. They have quite low intensity and an integral ratio of 1.5–2:1, and may be completely resolved by TOCSY. The bound diol moieties in the two species have aromatic *ortho* protons at $\delta = 7.90$

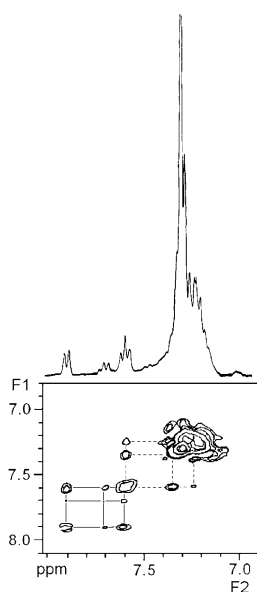


Figure 7. ^1H NMR TOCSY spectrum (300 MHz, $\tau_{\text{mix}} = 30$ ms) of (*R*)-phenylethane-1,2-diol (**1**) (46.6 mM) in a solution of dimolybdenum tetraacetate (48.5 mM) in dehydrated $[\text{D}_6]\text{DMSO}$.

(major species) and 7.60 ppm (minor species), more deshielded than the free diol: the diamagnetic anisotropy shifts are $\Delta\sigma_{\text{r,exp}} \approx -0.6$ and $\Delta\sigma_{\text{r',exp}} \approx -0.3$ respectively.^[21] The two sets of new signals do not give rise to an observable saturation transfer with the free diol, and the exchange between the two complexes could not be measured due to signal overlap. The intensity of the prominent peaks at $\delta = 7.60\text{--}7.90$ ppm increases slightly with time, and reaches a maximum stationary value (integral around 10% with respect to all the aromatic protons of the free diol, indicating 15–20% overall complexation) about 40–60 min after mixing, corresponding to the stationary conditions observed for the CD too.^[1,2a] The sum of peak integrals for the free and the two bound diol species is constant over the time, and accounts for all the substrate added, when checked against benzene as internal standard. Notably, the signals relative to the methine CH and methylene CH_2 protons are so broad that they can be detected (at $\delta = 5.7\text{--}6.2$ and 4.6 ppm, respectively) only by resorting to TOCSY experiments. No signals corresponding to the acetate groups of any diol/dimolybdenum complex, distinct from that of bound acetate at $\delta = 2.60$ ppm, could be detected.^[22]

It is clear from Figure 8 that the formation and dissociation of the two dimolybdenum/diol complexes (both with a ^1H resonance at $\delta = 7.60$ ppm), as a function of progressive addition of water to anhydrous DMSO, parallels the observed CD intensity for band IV (Figure 8, insert; Figure S1 in the Supporting Information).^[23] From an initial overall complexation of about 10%, the proportion of the complex and the measured CD intensity increase slightly until the bound acetate is just detectable, and then they both decrease upon further addition of water.

The NMR spectra of mixtures of $[\text{Mo}_2(\text{AcO})_4]$ and (*R,R*)-butane-2,3-diol (**2**) reveal the presence of one major complex and two minor species (Figure S2, Supporting Informa-

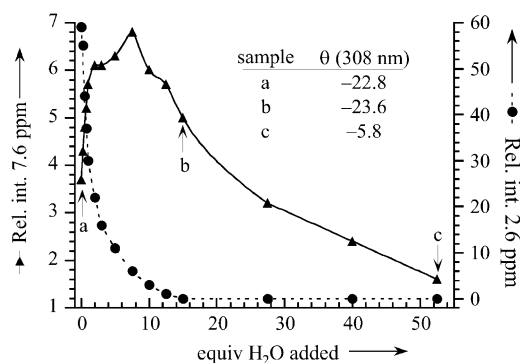


Figure 8. Variation of the relative intensity of the signal at $\delta = 7.60$ ppm with respect to the one at $\delta = 7.1\text{--}7.4$ ppm, and of the signal at 2.60 ppm with respect to the one at $\delta = 1.90$ ppm, versus equivalents of water added, for the ^1H NMR spectrum (300 MHz) of (*R*)-phenylethane-1,2-diol (**1**) (45.8 mM) in a solution of dimolybdenum tetraacetate (44.4 mM) in dehydrated $[\text{D}_6]\text{DMSO}$. Insert: CD intensity (θ , mdeg) at 308 nm for three samples; cell pathlength 0.01 cm.

tion). The prominent new signal appears as a doublet at $\delta = 1.44$ ppm and can be assigned to the methyls of bound butane-2,3-diol for the diol/dimolybdenum complex predominating in solution; its proportion relative to the free diol is usually around 10%.^[24] The estimated shift due to diamagnetic anisotropy is $\Delta\sigma_{2,\text{exp}} = -0.50$. Once again, the signals due to the bound and free diol do not give rise to observable saturation transfer, and the peaks relative to the methine CH protons are not apparent but can be identified by TOCSY at $\delta = 3.5\text{--}3.9$ ppm.

In the Discussion section below we show how a semi-quantitative analysis of the above NMR data, with particular reference to the anisotropy shifts $\Delta\sigma$, enabled us to draw the most likely structures of the diol/dimolybdenum complexes present in solution.

Complex stoichiometry and formation constant: CD titration studies: Given the achirality of the stock complex $[\text{Mo}_2(\text{OAc})_4]$ and the absence of absorptions above 250 nm for most 1,2-diols (when not further substituted with chromophoric residues), circular dichroism represents the ideal technique for monitoring the formation of the active complex in solution.

However, two factors greatly affect the significance of any quantitative measurement in the present case. First, the time dependence of the signal (due to the slow complexation kinetics) and the aging of the stock solutions make the CD spectra poorly reproducible.^[25] Nonetheless, we found that the following conditions ensure at least satisfactory reproducibility of the titration:^[1] a) the same stock solution is used and b) spectra are recorded as rapidly as possible in succession, making it possible to c) reach the stationary conditions (usually obtained 40–60 min after the mixing) carefully. With these measures the standard deviation of the CD spectra decreases below 3% (relative to different samples from the same chiral diol at similar millimolar concentrations). Second, since in principle several distinct species may form in solution, the analysis of experimental data is seriously complicated by the presence of multiple equilibria. The sit-

uation will become especially complicated by the presence of possible complexes with non-1:1 stoichiometry, whose presence is likely to affect the CD spectra substantially, and even to hamper the configurational assignment.^[2] This has been avoided by employing, for all the substrates analyzed so far, a limited range of values of both the concentration (of the order of millimolar) and the ligand/metal (namely, diol/dimolybdenum) ratio $\rho = C_L/C_M$ (around 0.5–1:1).^[1,2a]

Despite these inherent difficulties, the analysis of CD spectra by the molar ratio method^[26] affords at least an approximate assessment of the complexation parameters. For any single 1:1 species i , the formation constant may be written as Equation (2), where M represents all unbound dimolybdenum species, L the free diol, ML the 1:1 complex, and C_L and C_M the initial dimolybdenum and diol concentrations.

$$K_i = \frac{[\text{ML}]_i}{[\text{M}][\text{L}]} = \frac{[\text{ML}]_i}{(C_M - \sum_i [\text{ML}]_i)(C_L - \sum_i [\text{ML}]_i)} \quad (2)$$

In stationary conditions, the various diol/dimolybdenum complexes will also reach the equilibria described through exchange constants $K_{ij} = [\text{ML}]_j/[\text{ML}]_i$. The observed ellipticity θ (in mdeg, related to the overall circular dichroism $\Delta\epsilon$) in general will be the summation of the contributions due to all the CD-active species present [Eq. (3)], where $\Delta\epsilon_i$ is the molar CD of the i th species, and b the cell pathlength in cm.

$$\Delta A = \frac{\theta}{33\,000b} = \sum_i [\text{ML}]_i \cdot \Delta\epsilon_i \quad (3)$$

Figure 9 shows the CD at 308 nm for (*R*)-phenyl-1,2-ethanediol (**1**) as a function of $\rho = C_L/C_M$, at a constant concentration of the metal ($C_M = 3.25$ mM). Both the positions and

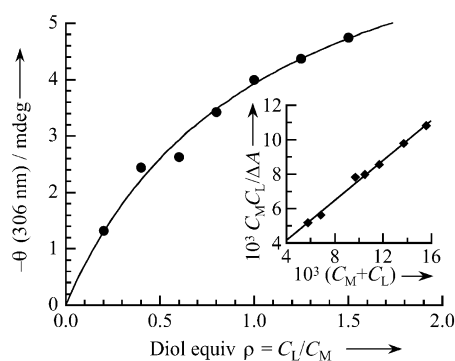


Figure 9. Variation of $-\theta$ (mdeg) at 306 nm versus diol/metal molar ratio ρ , for CD spectra in stationary conditions of (*R*)-phenylethane-1,2-diol (**1**) in a solution of dimolybdenum tetraacetate (3.25 mM) in DMSO; cell pathlength 0.1 cm. Insert: Equation (4) plot for the same points.

the relative intensities of spectral bands remain substantially unchanged as the proportion of the chiral ligand is varied up to $\rho = 1.5$ equiv.^[1] The $\theta(\rho)$ function obtained describes a weak complexation phenomenon with 1:1 stoichiometry that can be fitted by a hyperbolic curve of the type $\theta(\rho) \propto \rho/(a +$

$\rho)$. This may be better appreciated through linearization [Eq. (4)], obtained by rearranging Equations (2) and (3) with the approximation $[\text{ML}] \ll C_L, C_M$ expected for a weak complexation, after putting $\Sigma = \sum_j K_{ij}$ and $\Delta = \sum_j \Delta\epsilon_j K_{ij}$ (the sums extend over the total number of diol/dimolybdenum complexes).

$$\frac{1}{K_i \Delta} + \frac{C_M + C_L}{\Delta/\Sigma} = \frac{C_M C_L}{\Delta A} \quad (4)$$

By plotting the last term as a function of $C_M + C_L$ (Figure 9, insert), a very good linear fit is obtained ($R = 0.996$), which safely confirms that only 1:1 species contribute to the CD at 308 nm. Moreover, the quantities $K_i \Delta = 320 \pm 50 \text{ M}^{-1}$ and $\Delta/\Sigma = 1.7 \pm 0.1 \text{ M}^{-1} \text{ cm}^{-1}$ are extracted from the fitting. Provided that the data obtained through NMR experiments may be extrapolated to these lower concentrations,^[27] two $\mathbf{1}[\text{Mo}_2(\text{OAc})_4]$ complexes are present with $K_{1,1'} \approx 2$, and hence $K_1 \approx 100$ and $K_{1'} \approx 50 \text{ M}^{-1}$. This corresponds to relative proportions of about 20% for the major and 10% for the minor species at approximately millimolar concentrations, which is in fair agreement with the NMR results.

We applied the same reasoning to (*R,R*)-butane-2,3-diol (**2**), for which the CD intensity at 308 nm is linear up to $\rho = 1$, with $C_M = 5.72$ mM (Figure 10). Owing to weaker complexation (and despite the stronger CD; Figure 1), the second term in Equation (4) is negligible, so it rearranges to Equation (5), which precludes the separation of Δ and K_i .

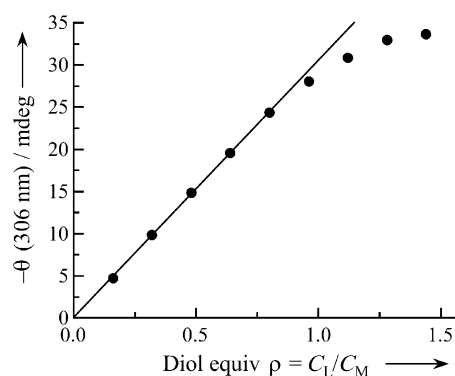


Figure 10. Variation of $-\theta$ (mdeg) at 306 nm versus diol/metal molar ratio ρ , for CD spectra in stationary conditions of (*R,R*)-butane-2,3-diol (**2**) in a solution of dimolybdenum tetraacetate (5.72 mM) in DMSO; cell pathlength 0.1 cm.

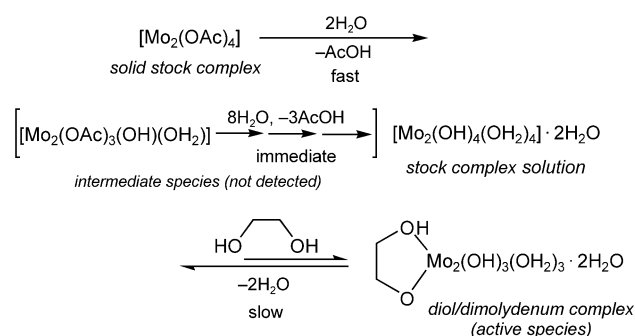
$$\Delta A \approx C_M^2 \rho K_i \Delta \quad (5)$$

However, the perfect fitting of the first points of $\theta(\rho)$ by Equation (5) ($R > 0.999$) is once again in keeping with the prevalence of 1:1 species (diol/ $\text{Mo}_2 = 2:1$ and higher stoichiometries may be excluded). The calculated value of $K_i \Delta$ from two independent measurements ($C_M = 5.72$ and 10.0 mM) is $150 \pm 50 \text{ M}^{-2} \text{ cm}^{-1}$ for **2**. By extrapolation of the NMR results,^[27] one CD-active species is found to predominate, a few percent being present at the current concentrations ($K_2 \approx 2.5 \text{ M}^{-1} \text{ cm}^{-1}$, which is probably an underesti-

mate). This leads to evaluation of the molar circular dichroism for the CD band IV of compound **2** as $\Delta\epsilon \approx 60 \text{ M}^{-1} \text{ cm}^{-1}$.

Discussion

On the basis of our results, a coherent and reasonable picture has been derived (as outlined in Scheme 1) by which the experimental information can be interpreted.



Scheme 1.

The Mo₂ species in “wet“ DMSO solution: The UV/Vis, conductometric,^[17] IR,^[19] and NMR data of [Mo₂(AcO)₄] reported above show unequivocally that, unless the solvent and the flasks are dehydrated thoroughly, for the conditions commonly employed^[20] most of the acetate ligands are dissociated immediately in DMSO solution, forming acetic acid under the action of water. Although the lability of the carboxylate ligands in quadruply bonded dimolybdenum complexes is well recognized,^[8a] the behavior described above is not exemplified in the literature.^[28] The effect of water on [Mo₂(AcO)₄] in DMSO solution has been, to our knowledge, completely overlooked. The formation of the aquo ion Mo₂(aq)₈⁴⁺, which can be more fully represented as [Mo₂(H₂O)₈]⁴⁺·2H₂O,^[29] requires the action of strong acids on sulfate salts of dimolybdenum.^[30] The UV/Vis spectrum of such species in water is characterized by a band at 504 nm ($\epsilon = 337$) assigned to a $\delta \rightarrow \delta^*$ transition, which disappears as a consequence of oxidation processes.^[31] Similar behavior has been envisaged also for acetate-containing complexes, and the disappearance of the $\delta \rightarrow \delta^*$ band, caused by exposure to air, has been attributed to oxidation and Mo–Mo bond breaking,^[32] but we obtained analogous spectral effects merely by adding water. The formation of complexes with unpaired electrons cannot be appreciated from the NMR spectra, and any significant formation of NMR-invisible species (caused by extensive paramagnetic shift and/or line-broadening) containing acetate or diol ligands may be ruled out by use of an internal standard; however, some decomposition of the dimolybdenum core of [Mo₂(AcO)₄] into ligand-free Mo species cannot be excluded. Oxidation of the Mo₂ core is certainly observed after storing the DMSO solution for one to two days at room temperature and open to the air; this is apparent through a color change from yellow to green,^[2a] and makes the NMR peaks for the bound ligands disappear. However, at the

short times after the mixing when the CD spectra are recorded, the total amounts of ligands (acetate and diol) remain observable by NMR spectroscopy, and they are therefore either free or associated into diamagnetic species; moreover, the signals for diol/dimolybdenum complexes confirm the existence of a group responsible for a strong diamagnetic anisotropy, that is, a quadruply bonded dimolybdenum core.

Our results suggest the formation of a hydrated species, containing as many hydroxy anions (OH⁻) as the displaced acetate ligands (Scheme 1). A structure similar to that reported^[9b] for alkoxide/alcohol complexes [Mo₂(OR)₄(HOR)₄] seems the most plausible, with bridging H–O···H···O–H ligands. In this view, the value (10 equiv) of water necessary to obtain a stationary UV spectrum (see Figures 5 and 6) is especially significant, because it coincides with the number (eight) of water molecules required to displace the four acetates, plus two molecules ligating the dimolybdenum axially,^[8d,29] thus leading to the stoichiometry [Mo₂(OH)₄(OH₂)₄]·2H₂O (Scheme 1). No NMR signals are detected for the protons of such species: as noted above, however, all protons in the immediate vicinity of the dimolybdenum core feature exceptionally broad resonances. The absence of any NMR signal corresponding to intermediate species with one to three acetate ligands, along with the results of the UV titration, suggest that the ligation of water and the consequent acetate displacement are strongly cooperative processes.

Some questions remain open: for example, in the UV/Vis spectrum of the hydrated complex [Mo₂(OH)₄(OH₂)₄]·2H₂O (Scheme 1), the transition observed at 312 nm (Figure 5) may be ascribed to a ligand-to-metal charge transfer transition ($p_\pi(\text{O}) \rightarrow \delta^*(\text{Mo})$ or else $p_\pi(\text{O}) \rightarrow \pi^*(\text{Mo})$), which in alcohol-containing quadruply bonded complexes appears at similar energies.^[9b,12b] In contrast, we have noticed the absence of the band above 500 nm that is detectable in the alcohol-containing complexes and in the aquo ion^[9b,30] and has been assigned to a $\delta \rightarrow \delta^*$ transition. Remarkably, upon addition of H₂SO₄ (final concentration $\approx 1 \text{ M}$) to the DMSO solution of the hydrated dimolybdenum complex, to reproduce the strongly acidic conditions needed for generating the aquo ion,^[30] a clear-cut color change from yellow to dark orange is observed; it follows from the appearance of a broad band with $\lambda_{\text{max}} = 455 \text{ nm}$, $\epsilon_{\text{max}} = 900$, which we interpret as a $\delta \rightarrow \delta^*$ transition. The absence of transitions around 370 nm, typical of oxidation products of Mo₂⁴⁺ aquo ions,^[31] demonstrates that the Mo–Mo quadruple bond is preserved in the newly generated species. It may be concluded that the acidification of [Mo₂(OH)₄(OH₂)₄] in DMSO yields spectral features close to those of the aquo ion [Mo₂(H₂O)₈]⁴⁺.^[30,33] In particular, the $\delta \rightarrow \delta^*$ transition of the hydrated dimolybdenum complex is seemingly sensitive to the degree of protonation of the water ligands, possibly through the overall charge distribution around the dimolybdenum core; further work on this topic is in progress.

Nature of the active species, and the effect of water on their formation: Whatever may be the dimolybdenum species in solution, there is no doubt that a chelation must occur after

the addition of the 1,2-diol, as previously suggested;^[2] however, both the CD and the NMR results indicate that the complexation is far from being complete (which may be partly responsible for the difficulties encountered in crystallization of the complex from DMSO).^[2a] Provided that one diol moiety HO~OH replaces one OH⁻/H₂O ligand, a 1:1 species with stoichiometry [Mo₂(HO~O)(OH)₃(OH₂)₃]-2-H₂O will be obtained (Scheme 1). NMR measurements give evidence for the formation of one (for diol **2**) or two (for diol **1**) main active species; no exchange phenomena are apparent between the complexes and the free diol, proving they are kinetically inert on the NMR timescale.

NMR and CD studies paint the same picture for the role played by water. At low water concentrations, the 1,2-diol competes with the acetate and the OH/H₂O ligands already formed for the formation of the Cottonogenic derivative. When water is added, the UV band at 303 nm and the ¹H NMR signal at $\delta = 2.60$ ppm first decrease in intensity, while the CD spectrum remains almost constant. At this stage, water is displacing acetate from the complex, thus favoring diol association (as witnessed by the intensity increase of the ¹H peaks at $\delta = 7.60$ ppm for **1**, and by slower complexation kinetics).^[23] After the addition of about 10 equivalents of water, acetate is completely displaced (the ¹H peak at $\delta = 2.60$ ppm vanishes), and the UV spectrum becomes stationary. Instead, the CD spectrum (as well the NMR peaks of the bound diol) decreases in intensity, and it eventually disappears: clearly, water is now competing strongly with the 1,2-diol.

Proposed structures of the active species: A comprehensive and reasonable structural picture is afforded by interpretation of the ¹H NMR chemical shifts. The prominent deshielding effects allied to the detectable proton signals for the diol/dimolybdenum adducts (one species for diol **2** and two for diol **1**) lend themselves to semi-quantitative structural analysis. By means of several MM and ZINDO-optimized molecular models (see the Experimental and Computational Section), we calculated the diamagnetic anisotropy deshieldings through Equation (1) for those diol/dimolybdenum adduct structures we envisaged as the most likely, and compared them with the experimental values.

First, the very large deshielding effect exerted by the dimolybdenum quadruple bond on the phenyl *ortho* protons in **1** (at $\delta = 7.90$ ppm for the major complex, $\Delta\sigma_{1,\text{exp}} \approx -0.6$) and the methyl groups in **2** (at $\delta = 1.44$ ppm, $\Delta\sigma_{2,\text{exp}} = -0.50$) can be justified only by assuming that they lie in a direction quasi-orthogonal to the Mo–Mo bond [Eq. (1) and Figure 4]; this condition is satisfied by a structure with the diol moiety bridging the Mo₂ core, like the “parallel” one proposed by Snatzke (Figure 2, left).^[2] The ZINDO models with a “parallel” structure, and with the diol carbon substituents (Ph for **1** and two Me for **2**) occupying an equatorial position in the six-membered ring [C–O–Mo–Mo–O–C] (Figure 11), give $\Delta\sigma_{1(\text{par/eq})} = -0.5$ for **1** and $\Delta\sigma_{2(\text{par/eq})} = -0.4$ for **2**, in very good agreement with the experimental values. Thus, we may confirm that the dominant complex has a “parallel”-like structure for both diols **1** and **2**, that is, with the diol moiety bridging the Mo₂ core,^[34] and the steri-

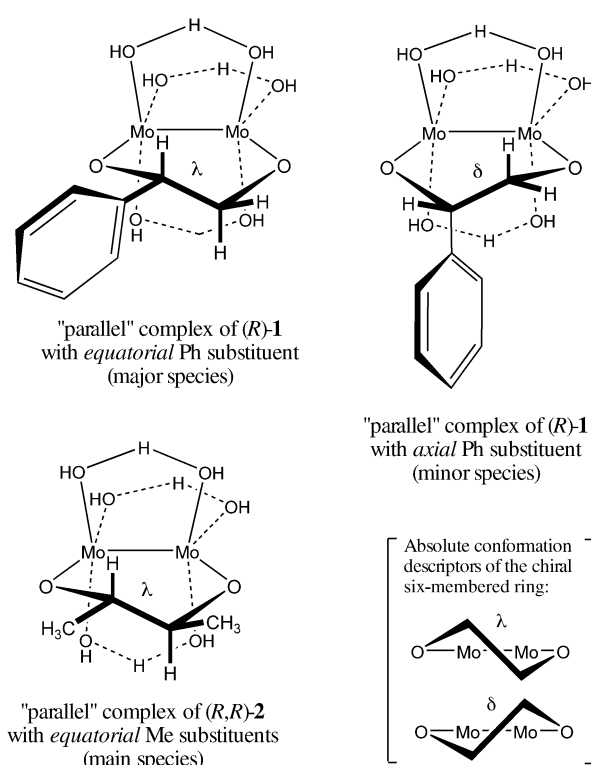


Figure 11. Model structures of (*R*)-**1** and (*R,R*)-**2**.

cally more demanding substituents occupying an equatorial position (Figure 11, left), as expected.^[1,2] Figure 12 displays the ZINDO model for this complex of (*R,R*)-**2**.

For the minor complex of diol **1** (with $\Delta\sigma_{1,\text{exp}} \approx -0.3$), we must reject a “perpendicular”-like structure (Figure 2, right), which would place the whole phenyl group in a shielding region, according to Equation (1) (see also Figure 4); the calculated shift for our ZINDO-optimized “perpendicular” complex for **1** (with an equatorial Ph group), is $\Delta\sigma_{1(\text{perp/eq})} = +1.6$, which is not supported by the NMR spectra. Instead, for a monosubstituted glycol such as **1**, structures with the carbon substituent in an axial rather than an equatorial position would also be conceivable. A ZINDO-optimized “parallel” complex with an axial Ph group (Figure 11, upper right) gives calculated $\Delta\sigma_{1(\text{par/ax})} = -0.2$, very close to the observed shift for the minor species $\Delta\sigma_{1,\text{exp}}$. Hence, we propose such a structure for the second diol/dimolybdenum adduct detected by NMR for diol **1**; unfortunately, we could not ascertain whether there is any chemical exchange between the two adducts. Our assignment would also explain why the CD spectra generally observed for monosubstituted 1,2-diols are considerably weaker than those for disubstituted ones.^[1,2a] The structure with an axial substituent has a six-membered ring with a chiral conformation (denoted by δ , for (*R*)-**1**) which is enantiotopic with the structure with an equatorial substituent (with a λ conformation for (*R*)-**1**) (Figure 11). If the observed optical activity originates from the chiral perturbation provided by the ring embracing the Mo₂ core^[2a] (but see also our Conclusions below), these two complexes are likely to give rise to similar CD spectra with opposite signs,

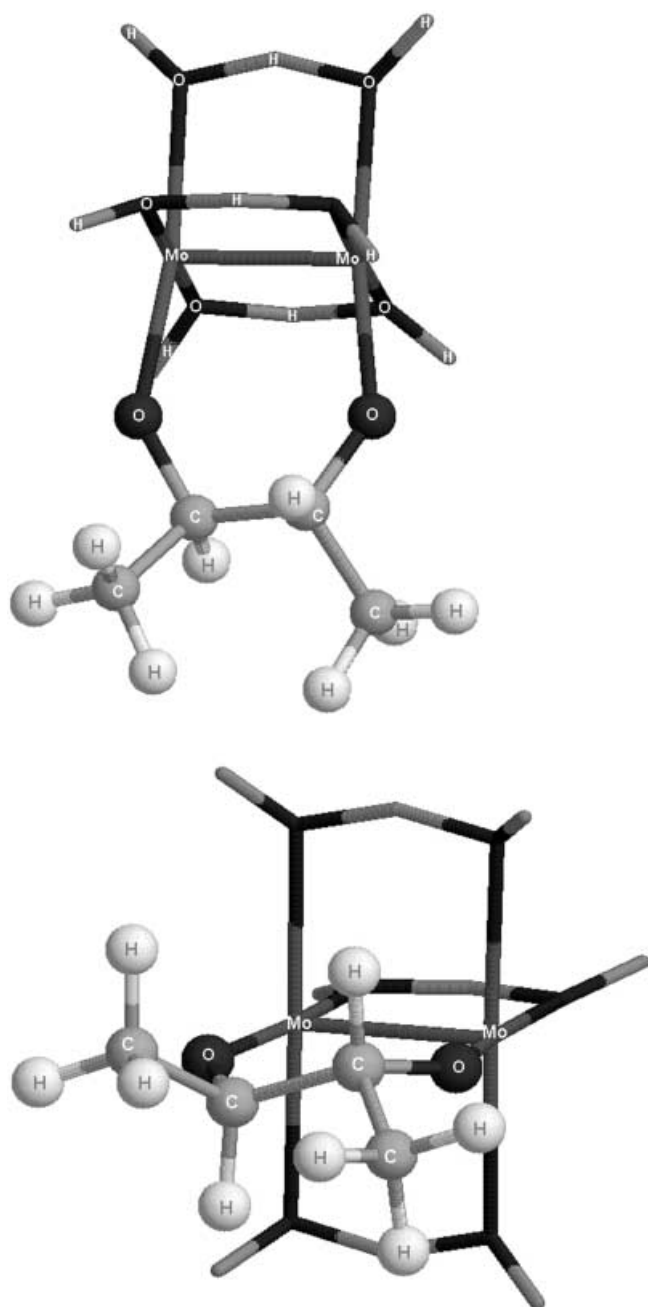


Figure 12. Two views of the ZINDO-optimized structure of the predominant complex for (*R,R*)-2,3-butanediol (**2**), with a “parallel” disposition and equatorial methyl groups.

resulting in a weak overall CD. In contrast, the CD spectrum for the complex of (*R,R*)-**2**, where the axial disposition of both methyl substituents would be less probable, is mainly attributable to only one species.

Conclusions

We have reached the following conclusions by spectroscopic means, especially CD and NMR, on the structure of the CD-active complex formed in DMSO from $[\text{Mo}_2(\text{OAc})_4]$ and chiral 1,2-diols:

- Under the action of dissolved water, dimolybdenum tetracetate in DMSO loses its acetate ligands quantitatively, giving rise to a new polyhydrated species with the quadruple bond preserved, which we formulate as $[\text{Mo}_2(\text{OH})_4(\text{OH}_2)_4]\cdot 2\text{H}_2\text{O}$ (Scheme 1).
- After the addition of an equimolar amount of a chiral 1,2-diol, two diol/dimolybdenum adducts develop for diol **1** and one main adduct for diol **2**, in a modest overall proportion for each diol.
- The dominant complex has a “parallel”-like structure for both diols **1** and **2**, with the two hydroxy groups bridging the dimolybdenum core and the diol carbon substituents occupying the equatorial positions in the six-membered ring $[\text{C}-\text{O}-\text{Mo}-\text{Mo}-\text{O}-\text{C}]$ (Figure 11, left, and Figure 12). The minor species for **1** has a similar “parallel” arrangement, but with an axial Ph group (Figure 11, upper right).

Even if some details, such as the extent of dissociation of alcoholic protons after the ligation, are still unclear, the present work is a first step toward the elucidation of the molecular structure of the CD-active species, which is necessary in order to understand the origin of the optical activity. The second, crucial, step would be a complete description of the electronic properties (including excited states) of the chromophore. In the current case, this is greatly complicated by the inherent difficulties encountered in the electronic structure calculations of quadruply bonded dimolybdenum complexes, because of the molecular size, the presence of many electrons, and the dramatic impact of electron correlation.^[8d] Although several theoretical studies concerning tetracarboxylate complexes are available,^[8d,35,36] other complexes with oxygen donors have been considered only occasionally,^[12b] and none fits the current case.

We may observe qualitatively that if our structural picture is valid, the previously adopted hypothesis about the origin of the optical activity of the Cottonogenic complex has to be revised. According to Snatzke and co-workers,^[2a,b] a one-electron mechanism would account for the origin of the CD, with a symmetric $\text{Mo}_2(\text{OAc})_3$ chromophore perturbed by a second-sphere chirality^[37] provided by the five- or six-membered ring involving the diol (in a “perpendicular” and “parallel” position, respectively; Figure 2). Thus, the CD band IV at 300–310 nm would be allied to the electric dipole-allowed transition observed at 304 nm for $[\text{Mo}_2(\text{OAc})_4]$ in DMSO, and assigned to a metal-to-ligand $\delta \rightarrow \pi^*_{\text{C}=\text{O}}$ charge transfer.^[2b,8c,35] Since we demonstrated that in the conditions commonly employed^[20] no acetate ligands are present on the active complexes, it is plausible that the UV transition observed at 312 nm (to which CD band IV is allied) could involve the oxygen p_π orbitals localized on the OH/ H_2O ligands and on the diol hydroxy groups as well.^[9b,12b] As a consequence, for this transition (for which $\epsilon \approx 3500$, $\Delta\epsilon \approx 60$; dissymmetry factor $g \approx 10^{-2}$ for the complex with **2**) the one-electron simplification is not sufficient, and some character of the so-called first-sphere chirality (or inherent dissymmetry)^[37] should also be admitted. It is noteworthy that all the interpretations of the optical activity of

quadruply bonded dimolybdenum complexes available in the literature to date concern only metal $\delta_{xy} \rightarrow \delta_{xy^*}$ and $\delta_{xy} \rightarrow \delta_{x^2-y^2}$ transitions.^[8c,38,39,40]

We hope that the new evidence uncovered by this contribution will prompt further investigations into the exact nature of the dimolybdenum species present in “wet” DMSO solutions of $[\text{Mo}_2(\text{OAc})_4]$; apart from its chiroptical interest, this complex is one of the most used synthetic precursors for quadruply bonded dimolybdenum compounds.^[8a]

Experimental and Computational Section

¹H and ¹³C NMR spectra were recorded with a Varian VXR 300 spectrometer, at 300 MHz for ¹H and 75.4 MHz for ¹³C, in $[\text{D}_6]$ DMSO solutions; chemical shift values are expressed relative to tetramethylsilane. 2D TOCSY spectra were recorded, acquiring 1 K–2 K data point matrices, zero-filled to 2 K–2 K, with 30 ms isotropic mixing. Saturation transfer experiments were carried out with a 1–5 s low-power cw irradiation on the selected signal, acquiring 64 to 256 transients. UV/Vis spectra were recorded using a Varian Cary 4E spectrophotometer. CD spectra were recorded with a Jasco J600 spectropolarimeter, with a 0.1 or 0.01 cm cell in DMSO and at room temperature (speed 50 nm min⁻¹, time constant 1 s, band width 2.0 nm). IR spectra were recorded as thin films with a Perkin-Elmer FT-IR 1600 spectrometer. Conductivities were measured at room temperature (16 °C) with a Metrohm Konduktometer E882 bridge, calibrated with a KCl solution (0.01 M).

DMSO, spectroscopy or analysis grade, was purchased from Fluka, and dehydrated according to the common procedure. Sodium acetate and KCl were purchased from Carlo Erba and purified according to the common procedures. $[\text{D}_6]$ DMSO was purchased from Fluka; NMR spectra were measured in anhydrous conditions using a thoroughly dried tube, in $[\text{D}_6]$ DMSO left on strongly activated 4A molecular sieves for one day.

(*R*)-Phenylethane-1,2-diol (**1**, 99% *ee*) and (*R,R*)-butane-1,2-diol (**2**, 98% *ee*) were purchased from Aldrich. Dimolybdenum tetraacetate (purity 98%) was purchased from Fluka.

Structure optimizations were executed with the MM+ force field and the ZINDO/1 semiempirical implemented in Hyperchem 7.02.^[8b] An initial structure of $[\text{Mo}_2(\text{OH})_4(\text{OH}_2)_4]$ was obtained by adapting the solid state structure of $[\text{Mo}_2(i\text{PrO})_4(i\text{PrOH})_4]$.^[9b] The Mo–Mo and Mo–O bond lengths and Mo–Mo–O angles were set to 2.11 Å, 2.13 Å and 94.7° respectively,^[9b] with default force constants; the optimized ZINDO/1 values are 2.16 Å, 2.13 Å and 91.1° respectively. Hence, one H–O⋯H⋯O–H moiety was replaced by one diolate moiety with the O–C–C–O dihedral in a *gauche* conformation, and the whole complex was re-optimized. Several structures were generated for each diol, by keeping the same absolute configuration (*R*) while changing: a) the “parallel” or “perpendicular” orientation with respect to the Mo–Mo bond (Figure 2); b) the six- or five-membered ring conformation, that is, forcing the substituent (Ph for **1** and two Me for **2**) into an equatorial or axial disposition. The optimized structures usually have O–Mo–Mo–O twists of less than 5° and diol O–C–C–O dihedrals of ≈40° (distorted *gauche*); as an example, Figure 12 displays the complex of (*R,R*)-**2** with “parallel” disposition and equatorial methyls (the dominant species). The structural data r and ψ for the diamagnetic anisotropy shielding (Equation (1) and Figure 4) were calculated as the average of the two equivalent phenyl *ortho* protons in **1** and the three methyl protons in **2**. MM+ calculations, with the parameters for Mo–Mo and Mo–O bond lengths and Mo–Mo–O angles set as above, gave similar results for the calculated anisotropy shieldings.^[41]

[1] Part 1 of this series: L. Di Bari, G. Pescitelli, C. Pratelli, D. Pini, P. Salvadori, *J. Org. Chem.* **2001**, *66*, 4819–4825.

[2] a) J. Frelek, M. Geiger, W. Voelter, *Curr. Org. Chem.* **1999**, *3*, 117–146, and references therein. Structural details may be found especially in: b) G. Snatzke, U. Wagner, H. P. Wolff, *Tetrahedron* **1981**,

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- [3] The induced CD terminology (see, for example: K. Vickery, B. Nordén, in *Encyclopedia of Spectroscopy and Spectrometry* (Eds.: J. C. Lindon, G. E. Tranter, J. L. Holmes), Academic Press, London, **2000**, pp. 869–874) is used to emphasize the fact that the chiral diol moiety, which may be virtually transparent, induces a nonvanishing CD over the electronic transitions allied to the achiral dimolybdenum core.
- [4] In general, the empirical rule may be formulated as follows, making use of the steric descriptors “bS” and “bR”.^[1] For each alcoholic chiral carbon, the “bS”/“bR” configuration is assigned: the first priority is given to the hydroxyl, the second to the adjacent –C–OH, and the remaining two substituents are ordered according to their bulkiness (Ph/H for **1**; Me/H for **2**). In most cases “bS” corresponds to *S* and “bR” to *R*. The rule states that a “bR” or “bR,bR” 1,2-diol always gives rise to a negative CD band IV.^[12a]
- [5] a) P. Salvadori, D. Pini, A. Petri, *Synlett* **1999**, *8*, 1181–1190; b) P. Salvadori, D. Pini, A. Petri, A. Mandoli, in *Chiral Catalyst Immobilization and Recycling* (Eds.: D. E. De Vos, I. F. J. Vankelecom, P. A. Jacobs), Wiley-VCH, Weinheim, **2000**, pp. 235–259.
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- [16] The value $\Delta\chi' = -239 \times 10^{-6} \text{ \AA}^3$ reported in reference [13] must be corrected by a factor of 4π ,^[8b] giving the same value as ours. For a different quadruply bonded dimolybdenum complex, it is found $\Delta\chi = -7000 \times 10^{-6} \text{ \AA}^3$.^[15a] Equation (1) is strictly valid within the dipolar approximation for magnetic moments, and if the Mo–Mo bond is axially symmetric.
- [17] We confirmed the absence of AcO^- ions in solutions of $[\text{Mo}_2(\text{OAc})_4]$ in DMSO by a conductometric measurement (as suggested in reference [18]). The specific conductivity of a solution of

- [Mo₂(OAc)₄] (5.0 mM) in DMSO was $\Omega = 3.3 \text{ mScm}^{-1}$; a reference solution (5.0 mM) of AcONa had $\Omega = 55.8 \text{ mScm}^{-1}$.
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- [19] The possibility of the existence of ligating, nonbridging acetate moieties, envisaged for example for [Mo₂(OOCF₃)₄] in pyridine,^[18] is excluded by the NMR spectra, and also from IR of thin films of the solution: the carbonyl stretching expected at 1750 cm⁻¹ for nonbridging acetate (D. I. Arnold, F. A. Cotton, F. E. Kühn, *Inorg. Chem.* **1996**, *35*, 4733–473) is absent, and instead two bands appear at 1260 and 1713 cm⁻¹ due to AcOH (for IR, solutions must be used that are two to three orders of magnitude more concentrated than for NMR and UV/Vis/CD).
- [20] The original recipe for the preparation of Cottonogenic complexes does not stress the necessity to dehydrate the very hygroscopic solvent. Almost all 1,2-diol/[Mo₂(OAc)₄] mixtures whose spectra are reported in the literature^[2a] must be assumed to contain nonnegligible quantities of water; the solvent we used in most measurements (for example, reference [1]) was found to contain approximately 3200 ppm of water (Karl Fischer method), corresponding to a huge concentration of about 0.2 M, which is two orders of magnitude higher than concentrations commonly used for the chiral substrate and [Mo₂(OAc)₄].
- [21] The other aromatic protons for the bound diol **1** resonate at $\delta = 7.70$ and 7.61 (*para* and *meta* for the major species), and 7.35 and 7.24 ppm (minor species).
- [22] In particular, the existence of a perpendicular acetate ligand (as depicted in Figure 2, right) may be excluded, as one would expect some spectral shift with respect to the resonances of [Mo₂(OAc)₄] (where the acetates are in a “parallel” position).
- [23] The dependence of the CD spectrum of a mixture of **2** (2.7 mM) and [Mo₂(OAc)₄] ($\rho = 1$) on the amount of water (Figure S1, Supporting Information) differs from that of the UV spectrum of [Mo₂(OAc)₄] (Figures 5 and 6) and of its diol complexes, in that an excess of water makes the CD collapse. Moreover, when a tenfold more concentrated sample (28.2 mM with a 0.01 cm cell pathlength) and a thoroughly dried flask and cell (in order to minimize the relative quantity of water) are used, a twofold more intense CD is obtained, with an exceptionally slow time evolution (stationary conditions are reached two to three times more slowly).
- [24] The two minor species of the bound diol **2** have hardly detectable doublets for the methyl protons at $\delta = 1.06$ and 1.19 ppm, with integrals smaller than 10% with respect to the major species (less than 1% with respect to the free diol). These minor species are not present as regularly as the main complex, so that in some conditions (depending on the water content and the solution aging) they are not detected at all. This may explain the slight variability in the CD spectra noted before for **2** and other nonhindered 1,2-diols.^[1]
- [25] For example, using the same sample of a chiral diol and the same solvent, but various stock solutions of [Mo₂(OAc)₄] of different ages, we recorded a set of CD spectra whose normalized intensities varied, showing a dispersion above 50% and a standard variation around 30%.
- [26] F. R. Hartley, C. Burgess, R. M. Alcock, *Solution Equilibria*, Ellis Horwood, Chichester, **1980**.
- [27] Both the different order of concentration (1–5 mM for CD, ≈ 50 mM for NMR) and the different solvent used (DMSO and [D₆]DMSO) increase the effect of dissolved water, whose proportion with respect to the dimolybdenum complexes may vary considerably for the CD and NMR samples of the same diol. This cautions against a straightforward quantitative comparison between the data obtained with the two spectroscopies.
- [28] The only reported substitution of acetate ligands with alcohols requires use of a strong base for forming the alkoxide;^[12] according to one report, however, trifluoroacetate is dissociated and protonated by the action of even an amine, though one with acidic properties (M.-C. Suen, Y.-Y. Wu, J.-D. Chen, T.-C. Keng, J.-C. Wang, *Inorg. Chim. Acta* **1999**, *288*, 82–89).
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Received: February 25, 2003

Revised: October 17, 2003 [F4883]