Pergamon

Tetrahedron: *Asymmetry* 13 (2002) 2461–2469

TETRAHEDRON: *ASYMMETRY*

Optical activity of *vic*-amino alcohols in the presence of dimolybdenum tetracetate

Jadwiga Frelek,* Agata Klimek and Patrycja Ruśkowska

Institute of Organic Chemistry of the Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland

Received 20 September 2002; accepted 7 October 2002

Abstract—A straightforward and versatile method for the determination of the absolute configuration of *vic*-amino alcohols is proposed. The proposed method involves the in situ formation of chiral complexes of optically active ephedrine- or adrenaline-type *vic*-amino alcohols with the achiral dimolybdenum tetraacetate [$Mo_2(OAc)_4$] acting as an auxiliary chromophore. The resulting CD spectra are suitable for the assignment of absolute configuration, since the observed sign of Cotton effects arising within the *d–d* absorption bands for the metal cluster depends solely upon the chirality of the amino alcohol ligand. An empirically based rule correlating a positive/negative helicity expressed by the O–C–C–N torsional angle with the sign of Cotton effects occurring in the 400–260 nm spectral range has been formulated.

1. Introduction

Determination of the absolute configuration of bioactive compounds continues to be one of the most challenging problems in organic and pharmacological chemistry. This is due the fact that the enantiomers of a particular bio-active compound may demonstrate differences of up to several orders of magnitude in their pharmaceutical effects and potency at the same receptor. They may also have significantly different ADME (absorption, distribution, metabolism, excretion) profiles. Chiroptical methods, and in particular, circular dichroism spectroscopy (CD), appear to be convenient, sensitive and rapid techniques for the stereochemical assignments in solution. In the case of circular dichroism studies, the approach requires only that the compounds under study are non-racemic and exhibit measurable absorption(s) in an accessible frequency range. To measure the CD spectra of compounds transparent in the UV–vis region, e.g. alcohols, amines, diols, aminols etc., a suitable chromophoric system should be introduced into the molecule prior to recording the spectra. One available procedure for this is the in situ generation of so-called 'cottonogenic' derivatives by mixing the solutions of the chiral (but non-absorbing) ligand with an achiral transition metal complex acting as an auxiliary chromophore. Among various transition metal complexes employed for this purpose,[1] dimolybdenum tetraacetate has demonstrated considerable ability to form chiral complexes especially convenient for the chiroptical studies. As was shown before,[2] $Mo_2(OAc)_4$ can exchange in situ one or more of its acetate units to form chiral complexes, mostly of a bridging structure. The CD arising within the *d–d* absorption bands of such complexes depends solely upon the chirality of the ligand(s).[2] This is due to the fact that transition metal ions, when complexed with an optically active ligand, become involved in the symmetry of the ligand. Thus, Cotton effects related to the electronic transitions of the metal atom are obtained and they are strongly dependent upon the absolute configuration of the compound acting as a ligand.

The in situ dimolybdenum method was successfully used by us for the determination of the absolute configuration of different classes of biologically important compounds such as amino acids[2b,3] and 1,2- and 1,3-diols.[2c,2d,2g,2h,4] For *vic*-diols, no exception has been found to the proposed empirical helicity rule connecting the sign of the O–C–C–O torsional angle with the sign of the Cotton effect (CE) occurring at around 310 nm. Recently, this observation was further corroborated by Italian authors[5] who confirmed the dimolybdenum method to be 'a very reliable, versatile, and elastic procedure for the assignment of the absolute configuration of that fundamental class of molecules'. It was also found that, due to its low acceptor strength in the axial position,[6] $Mo_2(OAc)_4$ forms optically active complexes with various bidentate ligands by ligand exchange reactions only.[2c] The great advantage of such bidentate

* Corresponding author. E-mail: frelek@icho.edu.pl

0957-4166/02/$ - see front matter
PII: S0957-4166(02)00647-X

bonding is that in most cases, flexible molecules, such as for example, aliphatic ones, become substantially more restricted in their conformational flexibility upon complexation and, as a result, appear to exist only as a single conformer when complexed with the Mo_2-core. This reduced conformational flexibility induces particularly intense CEs and facilitates interpretation of the CD spectra.

Based on the above discussion, we decided to study the possibility of an extension of the dimolybdenum method to another class of biologically important compounds, namely *vic*-amino alcohols. Our preliminary results[2d,2h,7] indicate the ability of the Mo_2-core to form chiral complexes with amino alcohols. To date, however, no general rule that is valid for the numerous different types of amino alcohols has been established. Thus, we decided to systematically study the chiroptical properties of amino alcohols in the presence of the Mo_2-dimer to develop and validate a convenient method for the determination of the absolute configuration of the chiral ligand. This goal will be achieved based on the experimental results of CD measurements of a variety of acyclic amino alcohols of both ephedrine and adrenaline types, complexed with the stock solution of Mo_2-dimer (Fig. 1). The dependence of the recorded CD spectra on the ligand-to-metal ratio, time factors and the sensitivity of the method, will be also examined.

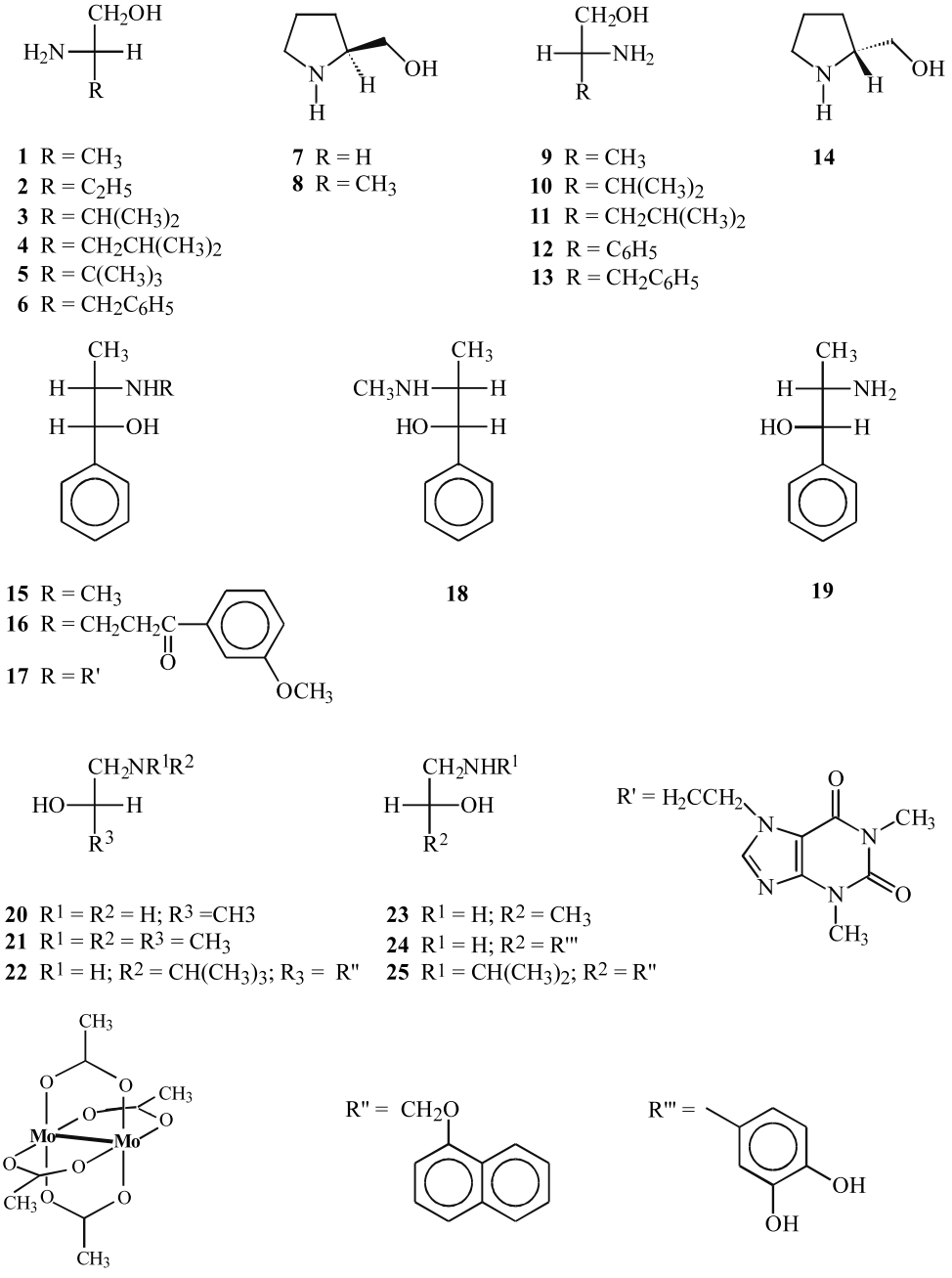

Figure 1. Investigated amino alcohols **1**–**25** and dimolybdenum tetraacetate.

2. Results and discussion

CD data for the in situ formed Mo-complexes of amino alcohols **1**–**25** are summarized in Table 1. As can be seen from this table, the molybdenum complexes formed in situ with *vic*-amino alcohols show several CEs between 650 and 250 nm. In common with *vic*-diols, the most intense (and therefore the most suitable bands for the determination of the absolute configuration of the analyte) appear in the spectral range between 400 and 260 nm. Two bands with the same sign appear near 260 nm (E) and 330 nm (C), and a third one (D), of sign opposite to the first two, occurs at ca. 290 nm.

In the spectra of compounds **7**, **20**, **23** and **24**, the band D (at ca. 300 nm) is present as a negative minimum (compounds **7** and **20**) or a positive minimum (compounds **23** and **24**) located between two distinct maxima or minima, respectively. In the spectra of (*R*)- and (*S*)-propranolols **22** and **25**, respectively, bands D and E cannot be seen at all as they are obscured by their own electronic absorptions in the same spectral range. Similarly, in the spectrum of L-cafedrine **17** with the Mo_2-core, the band E is obscured by its own absorption. CD spectra of some representative amino alcohols are presented in Fig. 2.

Interestingly, $Mo_2(OAc)_4$ forms optically active complexes with the salts of *vic*-amino alcohols very slowly and with poor efficiency. However, the addition of a trace of alkali (a drop of aqueous NaOH) usually results in rapid development of several intense Cotton effects. In our study, compounds **5**, **15**–**19**, **21**, **22** and **25** were investigated in the form of respective hydrochlorides. In general, no CEs were present prior to the addition of aqueous NaOH. However, following addition of a drop of aqueous NaOH to the complex solution several intense CEs appeared, as shown in Fig. 3 for compound **5**.

In order to establish whether the shape of CD curves depends on the concentration ratio, the CD spectra of L-leucinol **4** with the Mo-cluster in 0.5:1, 1:1, 1.5:1, 3:1, 5:1 and 10:1 ligand-to-metal ratio were recorded (Fig. 4). In experiments where the ligand-to-metal ratio was

Table 1. CD data of in situ formed Mo-complexes of compounds **1**–**25** recorded in DMSO 0.5 h after dissolving in the 1.5:1 ligand–metal mixture

Co	Band E	Band D	Band C	Band B	Band A
1	–2.36 (261.0)	**+0.68 (289.5)**	**–1.46 (322.5)**	a (368.0)	–0.04 (530.0)
2	–2.11 (261.5)	**+0.53 (290.0)**	**–1.30 (323.0)**	a (374.5)#	–0.03 (524.0)
3	–2.30 (261.5)	**+0.45 (290.5)**	**–1.48 (322.5)**	a (375.0)#	–0.02 (525.5)
4	–2.27 (261.5)	**+0.54 (287.5)**	**–1.51 (320.5)**	–0.36 (398.5)°	–0.03 (527.5)
5	–0.55(264.0)	**+0.36 (291.0)**	**–0.95 (335.0)**	+0.26 (440.5)	–0.04 (513.0)
6	–1.44 (260.0)	**+0.56 (289.0)**	**–1.00 (323.5)**	–0.38 (394.0)°	–0.01 (519.0)
7	–2.33 (260.5)	**a (289.0)**	**–1.00 (317.0)**	–0.64 (408.5)°	+0.02 (555.0)
4	–1.13 (259.0)	**+0.31 (288.5)**	**–0.77 (324.0)**	–0.08 (415.0)°	+0.12 (461.5)
9	+2.11 (260.5)	**–0.61 (288.5)**	**+1.33 (320.0)**	+0.22 (402.5)′	+0.03 (527.5)
10	+1.67 (261.0)	**–0.36 (290.0)**	**+1.24 (321.0)**	+0.51 (387.5)’	+0.02 (531.5)
11	+2.44 (261.0)	**–0.23 (289.0)**	**+1.53 (320.0)**	+0.28 (395.0)′	+0.06 (509.0)
12	+1.68 (261.5)	**–0.59 (289.0)**	**+1.49 (327.5)**	+0.56 (392.5)′	+0.03 (526.5)
13	+1.39 (260.5)	**–0.57 (288.0)**	**+0.95 (324.0)**	+0.30 (395.5)′	+0.03 (513.5)
14	+3.01 (258.0)	**–0.01 (289.5)**	**+1.08 (315.5)**	+0.71 (412.5)′	
15	+0.99 (263.0)	**–0.79 (297.0)**	**+1.66 (350.0)**	–0.25 (434.0)	+0.07 (521.5)
16	+0.67 (269.0)	**–0.34 (296.5)**	**+0.92 (351.5)**	–0.16 (425.5)	
17	c	**–0.32 (295.0)**	**+1.14 (344.5)**	–0.21 (421.5)	+0.05 (514.5)
18	–0.48 (263.0)	**+0.73 (293.5)**	**–1.50 (350.0)**	+0.11 (440.5)	
19	–0.41 (270.0)	**+0.16 (296.5)**	**–0.63 (344.5)**	+0.33 (425.5)	
20	–0.84 (269.5)	**a (298.5)**	**–0.28 (318.5)**	+0.40 (410.0)	
21	–0.28 (259.0)	**+0.17 (293.5)**	**–0.37 (330.5)**	+0.29 (426.5)	
22	c	**c**	**–0.36 (325.5)**	+0.32 (418.5)	
23	+0.66 (268.5)	**b (298.0)**	**+0.23 (310.0)**	–0.56 (418.5)	
24	+1.66 (256.5)	**b (292.0)**	**+0.64 (316.0)**	–0.32 (387.5)	+0.02 (523.5)
25	c	**c**	**+0.38 (324.0)**	–0.23 (425.5)	

a – negative minimum; b – positive minimum; c – own electronic absorption: * for explanation of term $\Delta\varepsilon'$ see text; # an additional positive CD around 460 nm; ° an additional negative minimum at ca. 360 nm; ′ an additional positive minimum at 364 nm.

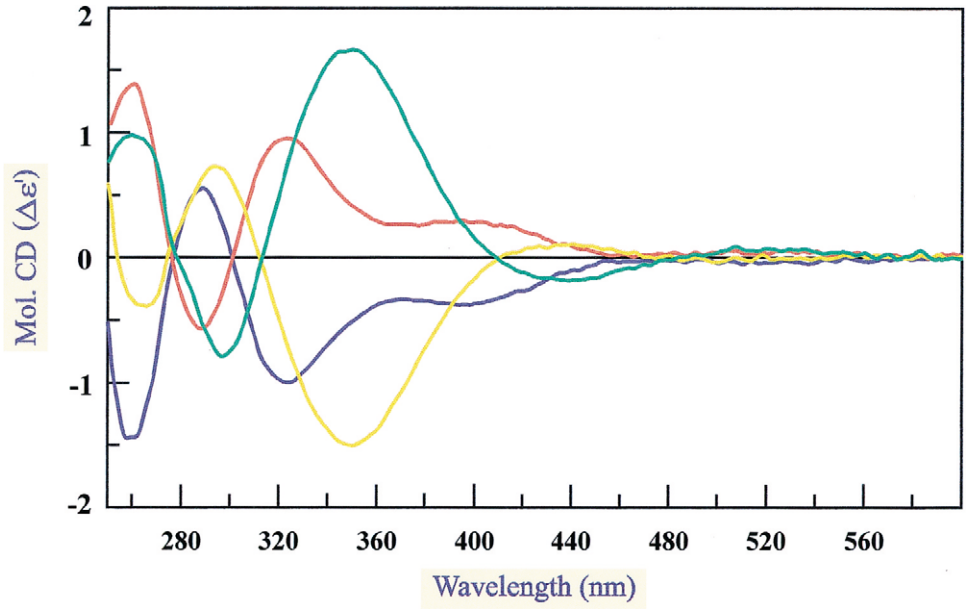

Figure 2. CD spectra of in situ formed Mo-complexes of amino alcohols **6** (blue line), **13** (red line), **15** (green line) and **18** (yellow line) recorded in DMSO after 0.5 h from dissolving in the 1.5:1 ligand–metal mixture.

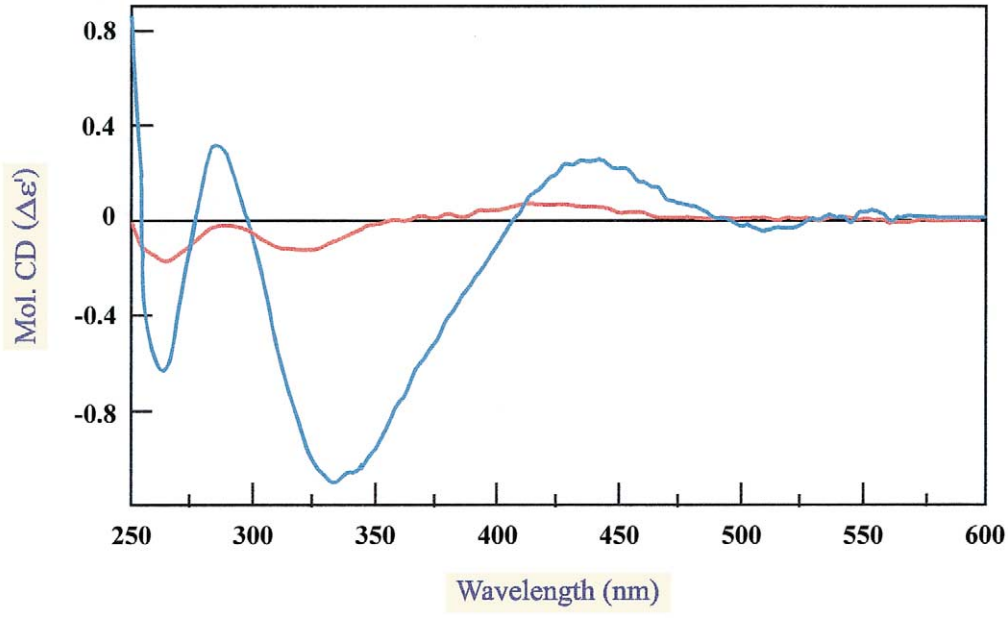

Figure 3. CD spectra of in situ formed Mo-complexes of amino alcohol **5** without (red line) and with (blue line) a trace of alkali recorded in DMSO 0.5 h after dissolving in the 1.5:1 ligand–metal mixture.

0.5:1, 1:1 and 1.5:1, the general shape of the CD curves was unchanged. We observed that the intensity of the bands increased with the concentration of the chiral ligand to reach a maximum at the 1.5:1 ligand-to-metal ratio. Generally, the shape of the curve for the ligand-to-metal ratio 3:1 (green line in Fig. 4) remains unchanged even though the band at ca. 288 nm appears as a negative minimum. The shape of the CD curve, however, changes for the ligand-to-metal ratio of 5:1 and 10:1 (yellow and red lines in Fig. 4, respectively). In either case, both the positive band D (around 280 nm) and the negative band C (around 320 nm) disappear and a new positive band (around 317 nm) is observed instead. Thus, to avoid a possibility of misinterpretation, it is recommended to work with concentrations in the range of 0.5:1 to 3:1 for ligand-to-metal ratio. Based on these results, we decided to measure the CD spectra of amino alcohols **1**–**25** with the Mo_2-core in DMSO solution with a ligand-to-metal ratio of 1.5:1.

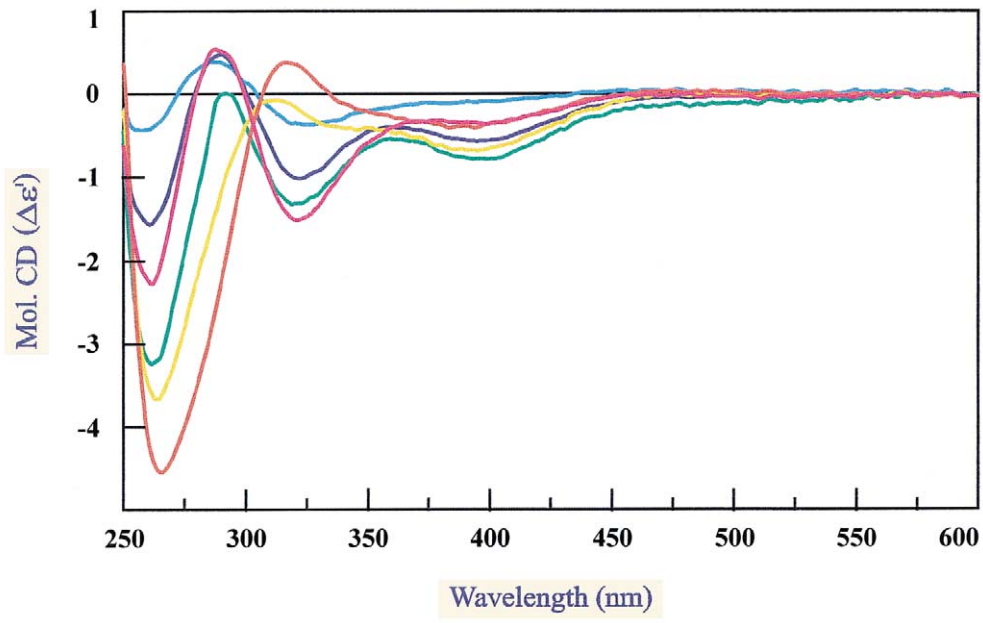

Figure 4. CD spectra of in situ formed Mo-complexes of L-leucinol **4** at ligand-to metal ratios: 0.5:1 (blue line); 1:1 (navy blue line); 1.5:1 (purplish-red line); 3:1 (green line); 5:1 (yellow line) and 10:1 (red line).

To establish the limits of applicability of the proposed method, the CD spectra at very low concentrations of the ligand and with the ligand-to-metal ratio of 1.5:1 were measured. In general, to obtain well developed CEs, about 1 mg of the ligand is sufficient. In some cases, however, as little as 0.2 mg ($\sim 3\times10^{-4}$ M/L) of the ligand is sufficient to record the CD spectrum with good S/N-ratio. In one extreme case it was possible to obtain a barely adequate spectrum of L-alaninol at a concentration of approx. $\sim 8\times10^{-5}$ M/L. However, in that case only band C was well developed.

The time dependence of the spectra was also investigated. In general, the signs of CEs and the relative intensities of the bands are not time dependent. However, as is evident from Fig. 5, the intensity of certain CD bands does change somewhat with time. In the case of D-phenylalaninol **13**, the intensity of band D increased two-fold within 24 h. The remaining bands remain unchanged within the same timeframe. The observed intensity of certain bands can also decrease with time: For example, in the case of L-valinol **3** there is a significant decrease in the intensity of all bands

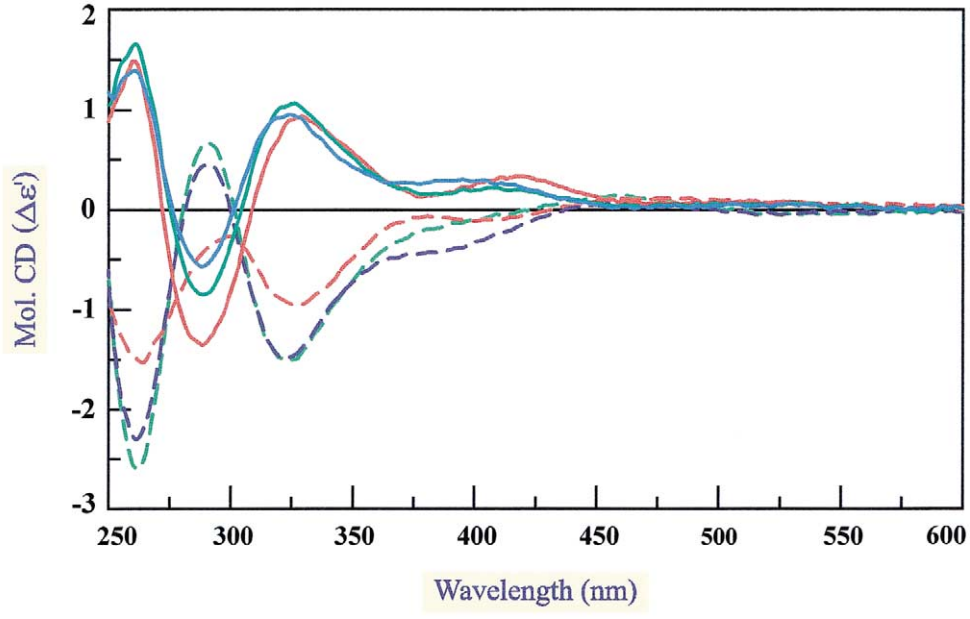

Figure 5. CD spectra of in situ formed Mo-complexes of D-phenylalaninol (**13**, continuous lines) and L-valinol (**3**, dashed lines) recorded in DMSO in the 1.5:1 metal-to-ligand ratio after: 0.5 h (blue line), 3 h (green line) and 24 h (red line).

after 24 h, while no intensity change is evident within the first 3 h. Therefore, we decided to record the CD spectra of the Mo-complexes of compounds **1**–**25** not more than 0.5 h from the moment of complex formation, to avoid the complications related to the intensity changes.

A similar time-dependence of the spectra can be observed in the respective UV–vis spectra. The electronic absorption spectrum of the stock complex in DMSO shows a lowest energy band at ca. 440 nm with an absorption coefficient ε of 163 M^{-1} cm^{-1}. This band (A) of low intensity is assigned to the $\delta \rightarrow \delta^*$ transition and it is polarized parallel to the Mo–Mo axis (z-polarization).[6b] There are higher energy absorptions in the UV–vis region with a much larger molar extinction coefficient, namely band C with ε of 5740 M^{-1} cm^{-1}, appearing at 304 nm and overlapping with another absorption band which is visible only as a shoulder at longer wavelengths (band B, around 325 nm). Regrettably, there is a significantly lower certainty about the assignments of these bands, based on the available literature. For our purpose, however, it may not be necessary to assign the individual transitions, because only the net CD is important for the establishment of the chiroptical rules.

After storage for 24 h, the Mo-complex solution remains yellow, however its UV–vis spectrum shows a disappearance of the band A whereas band C is slightly red-shifted and becomes weaker (307 nm, $\varepsilon = 3600$ M^{-1} cm^{-1}). After 48 h storage, the solution of the stock complex turns green and in the respective UV–vis spectrum in the range 250–550 nm there is only one well-developed band (band C, 312 nm, $\varepsilon = 3170$ M^{-1} cm^{-1}).

As with 1,2-diols,[4a] the replacement of acetate ligand(s) of the Mo_2 complex with the chiral 1,2-amino alcohol ligand does not result in any significant changes in the absorption spectrum (Fig. 6). This suggests that ligand exchange within the Mo_2O_8 chromophoric system is not accompanied by any other significant changes and may also indicate that only one acetate group of the Mo-cluster is replaced by an amino alcohol ligand.

As can be seen in Table 1 and Fig. 2, the CD spectra of Mo-complexes of enantiomeric amino alcohols are of mirror image type (compounds **1**, **9**; **3**, **10**; **4**, **11**; **6**, **13**; **15**, **18**; **20**, **23** and **22**, **25**). The small differences observed in the magnitude of particular CEs can be attributed to the fact that the precise concentration of the chiral complex in each of the studied solutions is not known. Therefore, the CD data are presented as artificial $\Delta\varepsilon'$ values. These $\Delta\varepsilon'$ values are calculated in the usual way as $\Delta\varepsilon' = \Delta A/c \times d$, where c is the molar concentration of the amino alcohol, assuming 100% complexation.

On the basis of the data presented in Table 1, the investigated compounds **1**–**25** may be divided into two groups that differ in the sign of the 260 nm (E), 280 nm (D) and 330 nm (C) bands. In the first group, consisting of amino alcohols **1**–**8** and **18**–**22**, the CE around 280 nm is positive with two strong negative CEs at ca. 260 and 330 nm. In the second group, represented by amino alcohols **9**–**17** and **23**–**25**, the opposite relation of CE sign pattern is observed, i.e. both CD bands E and C are positive and the one near 280 nm is negative.

Since the shape of the CD spectra of *vic*-diols and corresponding *vic*-amino alcohols is very similar (Fig. 7), it seems reasonable to assume that the mode of complexation of amino alcohols to dimolybdenum tetraacetate is the same as that for the respective glycols.[8] This means that the probable structure of the chiral Mo-complex with an amino alcohol ligand is the one with a 'parallel' or 'perpendicular' arrangement of the amino alcohol unit(s) to the dimolybdenum core, as shown in Fig. 8. According to the reported data,[2a,2e] however, the bridging ligation (β-form) of a 1,2-amino alcohol molecule to the Mo-core appears to be more probable, because the α-dimolybdenum complexes with, e.g. chelating diphosphines and diamines show no measurable CD. Independently of the actual complexation

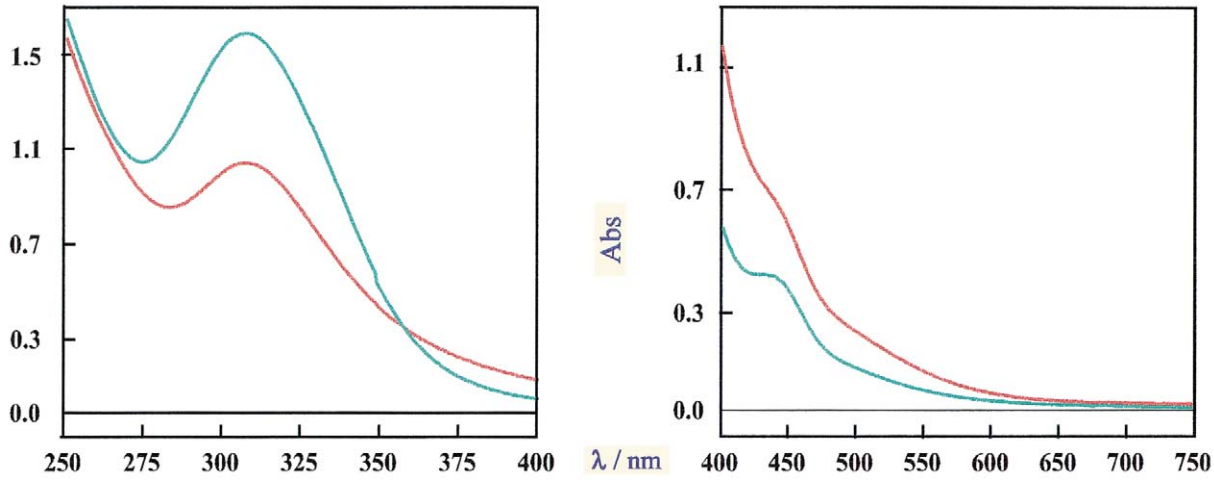

Figure 6. UV–vis spectra of $[Mo_2(OAc)_4]$ (red line) and in situ formed Mo-complex of L-leucinol **4** (green line) recorded in DMSO 0.5 h after dissolving.

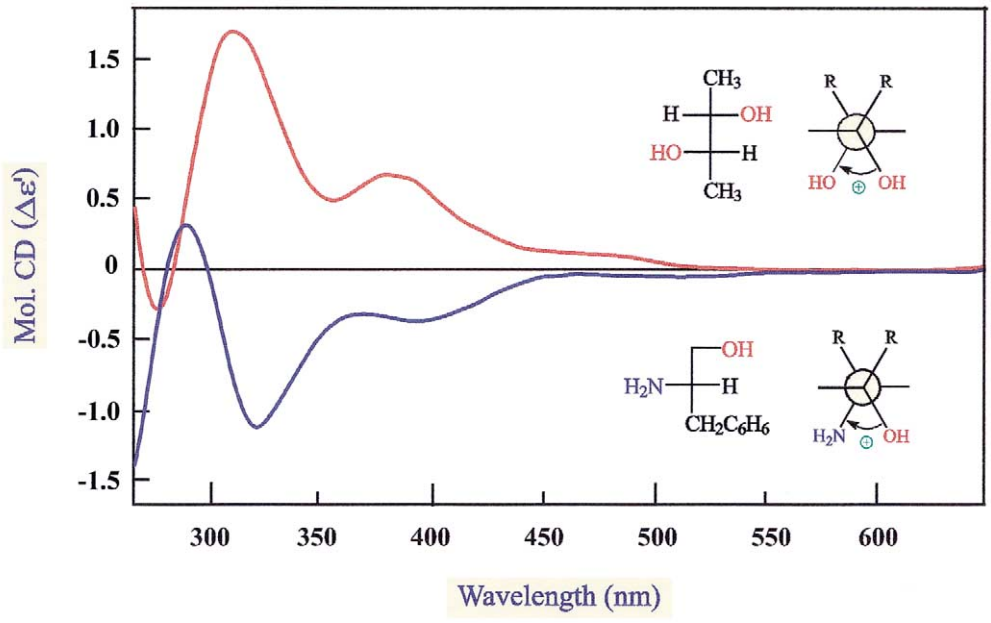

Figure 7. CD spectra of in situ formed Mo-complexes of L-phenylalaninol (blue line) and L-butane-2,3-diol (red line).

mode (either 'parallel' or 'perpendicular'), an amino alcohol, analogously to the glycols, can be accommodated preferentially in such a conformation in which both N–C–C–R and O–C–C–R units, for steric reasons, adopt an antiperiplanar conformation. Thus, the acyclic amino alcohol ligand is considerably restricted in its conformational mobility. This fixed conformation results in much more intense CEs compared to those of conformationally flexible molecules. In addition, the conformational preferences of the resulting Mo_2-containing rings impose a twist about the Mo–Mo bond so that the core is no longer in an eclipsed form. Thus, the achiral chromophore is incorporated into a chiral ring ('chiral second sphere' according to Snatzke[9]) which implies that the CD is mainly governed by a 'helicity rule', which means that the sign of the torsional angle determines the signs of particular CEs, and also, to a great extent, their observed magnitudes.

On the basis of the above argument it seems reasonable to assume that a helicity rule, similar to that established for *vic*-diols,[2c,g] should correlate the helicity of the amino alcohol moiety with the sign of the Cotton effects in the 400–300 nm spectral range. As can be seen from Fig. 7, however, the CD spectra of the amino alcohol and of the glycol with the same sign of the torsional angle N–C–C–O and O–C–C–O, respectively, are of mirror image type with some red or blue shifts of certain CEs. Since it is not known if the parentage of the individual transitions is the same when the oxygen is replaced by nitrogen, the empirical correlation between the signs of particular CEs and the torsional angle N–C–C–O can be formulated in one of two ways:

1. the correlation between the torsional angle and the sign of the CEs occurring between 400 and 300 nm is opposite for *vic*-amino alcohols compared to that for *vic*-diols, or
2. the correlation is the same, but because of the very strong CE around 330 nm the 300 nm CD band is blue shifted to ca. 280 nm.

Whichever point of view one prefers to adopt, the results collected in Table 1 demonstrate that amino alcohols with the same absolute configuration have the same sign of their CEs in the presence of the Mo-cluster. This statement appears to be valid for both ephedrine- and adrenaline-type amino alcohols.

A common feature of the amino alcohols from the first group (compounds **1**–**8** and **18**–**22**) is their P-helicity expressed by a positive N–C–C–O torsional angle whereas amino alcohols from the second group, (amino alcohols **9**–**17** and **23**–**25**), follow the M-helicity manifested by a negative torsional angle of the same unit. In the case of *threo*-compounds, the amino alcohol unit adopts such a conformation where both O–C–C–R and N–C–C–R moieties exist in antiperiplanar conformations (Fig. 9, left). Only in such a conformation the larger R group does avoid the steric interaction with other acetate ligands still present in the complex and

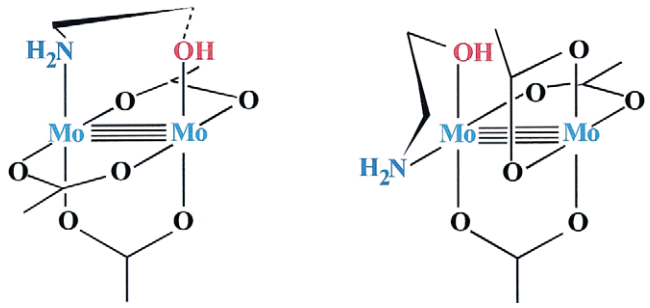

Figure 8. Possible bidentate ligations of an *vic*-amino alcohol in the 'parallel' (left) and 'perpendicular' mode (right).

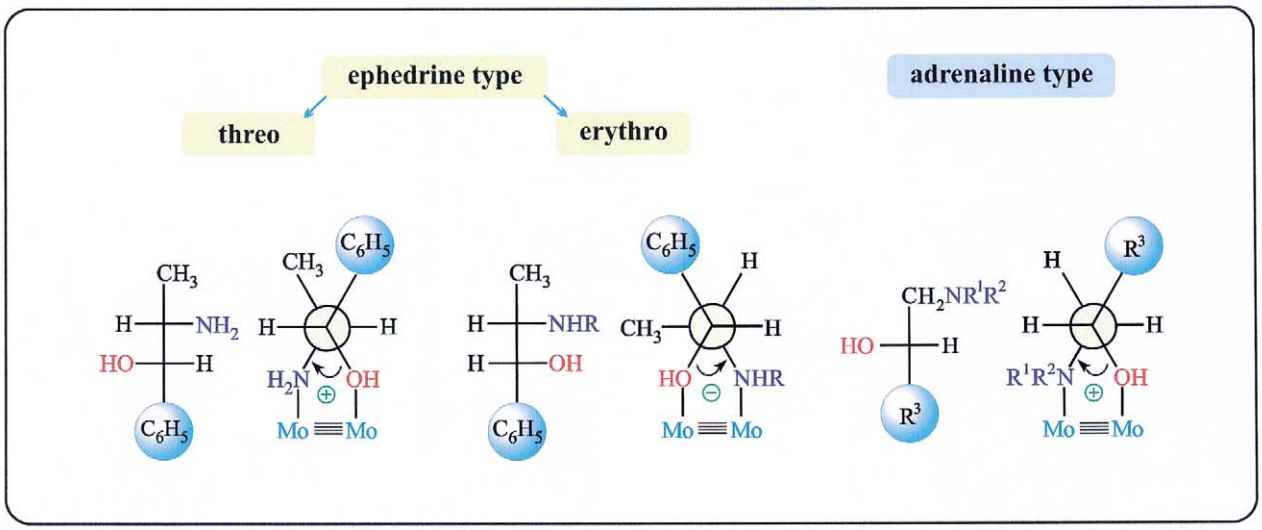

Figure 9. Preferred antiperiplanar conformation of an aliphatic 1,2-amino alcohol from ephedrine type-(1*S*,2*S*)-*threo* (left) and (1*R*,2*S*)-*erythro* (middle) as well as from adrenaline type (right) when complexed to Mo-dimer.

points away from the rest of the complex. It is, therefore, safe to assume that in Mo-complexes such a conformation is the preferred one. A more complicated situation is observed in the case of *erythro* aminopropanols **15**–**18**, where two R groups are not able to adopt an antiperiplanar conformation at the same time. In the case of compounds **15**–**17** with 1*R*,2*S* configuration, left handed helicity is expected to dominate, in accordance with the relative dimensions of phenyl and methyl groups. Therefore, for these compounds the preferred conformation in their Mo-complexes is the one with a phenyl group in an antiperiplanar arrangement relative to the nitrogen atom and with a methyl group in a *gauche* arrangement relative to a hydroxy group, as shown in the middle of Fig. 9. On the contrary, compound **18** with 1*S*,2*R* configuration follows P-helicity, again adopting a conformation with an arrangement with the phenyl group antiperiplanar relative to the nitrogen atom and with a methyl group in a *gauche* arrangement relative to the hydroxy group.

Thus, a general rule connecting the sign of particular CEs with the helicity of an amino alcohol complexed to the Mo_2-core can be formulated as follows: a positive (negative) torsional angle of the N–C–C–O amino alcohol subunit correlates with a positive (negative) sign of the CE around 280 nm or a positive (negative) torsional angle of the N–C–C–O amino alcohol subunit correlates with a negative (positive) sign of the CE observed at around 330 nm.

3. Conclusions

The present study demonstrates that the dimolybdenum method can be successfully extended to *vic*-amino alcohols thus allowing the assignment of their absolute configuration based on their CD spectra with dimolybdenum tetraacetate acting as an auxiliary chromophore. The absolute configuration can be determined by means of the proposed empirical rule relating the sign of the CEs around 280 and 330 nm with the helicity of the N–C–C–O subunit. The proposed helicity rule is based on the CD spectra of 25 acyclic *vic*-amino alcohols of both ephedrine and adrenaline types, complexed with $Mo_2(OAc)_4$. Dimolybdenum tetraacetate acts not only as an auxiliary chromophoric system but also, due to its steric requirements, reduces or totally restricts the conformational mobility of amino alcohol molecules bound to the metal core. Thus, in the dimolybdenum method the determination of the absolute configuration becomes possible from the chiroptical data alone.

It is also demonstrated that the sign of Cotton effect does not depend on the concentration of the chiral ligand or that of the achiral complex providing that the metal-to-ligand ratio is within the range of 1:0.5 to 1:3, respectively. Moreover, it has also been shown that DMSO solutions of the complexes are sufficiently stable to allow all necessary measurements to be carried out. It was found that amino alcohols in the salt form cannot be investigated by this method. However, in the form of free amine (obtained in situ after addition of a drop of aqueous base to the salt solution) CD study can be performed successfully.

The fact that no quantitative values are obtained could be regarded as a disadvantage of the proposed method. However, for the purpose of determination of the absolute configuration only the signs and relative magnitudes of the CEs are important, not their absolute values. On the other hand, this disadvantage is compensated for by the fact that there is no need to synthesize, isolate and purify any derivatives before obtaining the CD spectrum. It is additionally worth considering that, in general, less than 1 mg of the potential ligand is sufficient to obtain a very good and reproducible CD spectrum. We have demonstrated that in an extreme case the determination of absolute configuration can be

successfully carried out for ligand concentration of around 8×10^{-5} M/L.

4. Experimental

UV–vis spectra were measured on a Cary 100 spectrophotometer in DMSO. CD spectra were recorded in the 240–640 nm range, at room temperature, with a Jasco 715 spectropolarimeter using DMSO solutions in cells of 1, 10 or 20 mm path length (spectral band with 2 nm, sensitivity 10×10^{-6} or 20×10^{-6} ΔA-unit/nm). Depending on the S/N ratio the λ-scan speed was 0.2 or 0.5 nm/s.

For CD measurements the solid chiral amino alcohol (1–5 mg, ca. 0.003 M/L) was dissolved in a stock solution of dimolybdenum tetraacetate (6–7 mg, ca. 0.002 M/L) in DMSO so that the molar ratio of the stock complex to ligand was about 1:1.5, in general. In special cases, e.g. concentration-dependent CD measurements, other metal-to-ligand ratios were used (see text). Some of the $\Delta\varepsilon'$-values were very small, but nevertheless the signal-to-noise ratio in all cases was better than at least 10:1.

Source of compounds: compounds **1**–**25** were purchased from Fluka and/or Aldrich and were used without further purification. Dimolybdenum tetraacetate and DMSO (Uvasol) were purchased from Fluka and Merck, respectively, and were used without further purification.

Acknowledgements

The authors are thankful to the Polish State Committee for Scientific Research (KBN) for grant No. 7TO 9A 00421.

References

1. (a) Dillon, J.; Nakanishi, K. *J. Am. Chem. Soc.* **1974**, *96*, 4057–4059; (b) Dillon, J.; Nakanishi, K. *J. Am. Chem. Soc.* **1975**, *97*, 5417–5422; (c) Partridge, J. J.; Toome, V.; Uskokovic, M. R. *J. Am. Chem. Soc.* **1976**, *98*, 3739–3741; (d) Kerek, F.; Snatzke, G. *Angew. Chem., Int. Ed.* **1975**, *14*, 109–110; (e) Barton, D. H.; Frelek, J.; Snatzke, G. *J. Phys. Org. Chem.* **1988**, *1*, 33–38; (f) Frelek, J.; Majer-Decker, Z.; Snatzke, G. *Liebigs Ann. Chem.* **1988**, 281; (g) Ahmad, H.; Snatzke, G.; Atta-ur-Rahman *J. Am. Chem. Soc.* **1993**, *115*, 12533–12544.
2. (a) Peacock, R. D.; Fraser, I. F. *Inorg. Chem.* **1985**, *24*, 989–990; (b) Snatzke, G.; Wagner, U.; Wolff, H. P. *Tetrahedron* **1981**, *37*, 349–361; (c) Frelek, J.; Snatzke, G. *Fresenius Z. Anal. Chem.* **1983**, *316*, 261–264; (d) Frelek, J.; Perkowska, A.; Snatzke, G.; Tima, M.; Wagner, U.; Wolff, H. P. *Spectrosc. Inter. J.* **1983**, *2*, 274–295; (e) Gerards, M. *Inorg. Chim. Acta* **1995**, *229*, 101–103; (f) Acho, J. A.; Ren, T.; Yun, J. W.; Lippard, S. J. *Inorg. Chem.* **1995**, *34*, 5226–5233; (g) Frelek, J.; Ikekawa, N.; Takatsutu, S.; Snatzke, G. *Chirality* **1997**, *9*, 578–582; (h) Frelek, J.; Geiger, M.; Voelter, W. *Curr. Org. Chem.* **1999**, *3*, 145–174.
3. Frelek, J. *Pol. J. Chem.* **1999**, *73*, 229–239.
4. (a) Frelek, J.; Snatzke, G.; Szczepek, W. J. *Fresenius J. Anal. Chem.* **1993**, *345*, 683–687; (b) Frelek, J.; Szczepek, W. J.; Voelter, W. *J. Prakt. Chem.* **1997**, *339*, 135–139.
5. Di Bari, L.; Pescitelli, G.; Pratelli, C.; Pini, D.; Salvadori, P. *J. Org. Chem.* **2001**, *66*, 4819–4825.
6. (a) Cotton, F. A.; Watson, R. A. *Multiple Bonds Between Metal Atoms*; Clarenden Press: Oxford, 1993; pp. 139–243; (b) Cotton, F. A.; Watson, R. A. *Multiple Bonds Between Metal Atoms*; Clarenden Press: Oxford, 1993; pp. 682–707; (c) Wu, Y.-Y.; Chen, J.-D.; Liou, L.-S.; Wang, J.-C. *Inorg. Chim. Acta* **2002**, *336*, 71–79.
7. Frelek, J.; Majer, Z.; Perkowska, A.; Snatzke, G.; Vlahov, I.; Wagner, U. *Pure Appl. Chem.* **1985**, *57*, 441–451.
8. Liptak, A.; Frelek, J.; Snatzke, G.; Vlahov, I. *Carbohydr. Res.* **1987**, *164*, 149–159.
9. Snatzke, G. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 363.