Tetrahedron Vol 37, pp 349 to 361
Pergamon Press Ltd 1981 Printed in Great Britain

0040-4020/81/0115-0349 $02.00/0

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COTTONOGENIC DERIVATIVES OF CHIRAL BIDENTATE LIGANDS WITH THE COMPLEX $[Mo_2(O_2CCH_3)_4]$

G. Snatzke*, U. Wagner and H. P. Wolff
Lehrstuhl fur Strukturchemie, Ruhruniversität Bochum, D-4630 Bochum 1, Postfach 10 21 48, Germany

(*Received in Germany 25 January 1980*)

Abstract $[Mo_2(O_2CCH_3)_4]$ forms optically active complexes in DMSO after addition of chiral ligands. Bidentate ligands (carboxylic acids, diols, and amino alcohols) but also a primary amine (α-phenylethylamine) were shown to form these complexes. For molar ratios of less that appr. 1 5:1 (ligand to complex) up to 5 Cotton effects (A to E, from 600 to 270 nm) can be observed. The signs of those between 300 and 400 nm can be used for empirical determination of absolute configuration of complexing ligands. Bands A–D are assigned to the following transitions: A: mainly $\pi_{Mo-Mo} \rightarrow \delta^*$ $(A_{1g} \rightarrow E_g)$; B: $\delta \rightarrow \sigma^*_{Mo-O}$ $(A_{1g} \rightarrow A_{2g})$; C: mainly $\delta \rightarrow \pi^*_{Mo-Mo}$ $(A_{1g} \rightarrow E_g)$; D: $\delta \rightarrow \delta^*$ $(A_{1g} \rightarrow A_{2u})$. Sector rules for the pair of CD-bands A/C (hexadecant rule) and for CD-band B (hexadecant rule with two additional nodal planes through the MoO_4-planes) are derived from qualitative MO theory

$[Mo_2(O_2CCH_3)_4]$ is an easily available[2-4] and stable complex with D_{4h}-symmetry,[5] which is kinetically labile in solution as its acetate ligands can be exchanged rapidly by other acylate moieties. Complexation proceeds exclusively via the CO_2^- group even if other groups are present in the ligand which are very prone to form bonds with the metal, e.g. the primary NH_2-group of glycine, as has been proved for the crystal by X-ray diffraction.[6]

The experimental CD-curves of complexes $[Mo_2(O_2CCH_3)_{(4-k)}(O_2CR^*)_k]$

We have found that in DMSO solution immediate exchange of the acetate(s) with the anions of chiral acids takes place leading up to 7 Cotton effects in the wavelengths range between 270 and 750 nm. Most other usual solvents for CD-spectroscopy did not dissolve sufficiently the complex, alcohols decompose it quickly. Figure 1 shows three typical CD-curves of the mixture between *S*-(+)-mandelic acid with the "stock complex" $[Mo_2(O_2CCH_3)_4]$ for the molar ratios 40:1, 3.5:1 and 0.13:1 Tests with the corresponding benzoate or trifluoroacetate complex showed no advantage. With a large excess of the chiral ligand the appearance of the CD-spectrum differs from that with equivalent or less amounts (Fig. 1). The same holds for the complexes with *S*-(+)-lactic acid (Fig. 2), but not with acids which do not contain other donor groups, as, e.g. *R*-(−)-hydratropic acid (Fig. 3). It may be that at higher concentrations of the ligand also the OH-group binds to the Mo_2-cluster, eventually to the axial positions, which weakly bind in crystals to donor atoms of the solvent of crystallization or to an oxygen atom of the neighbour complex molecule.[4,7-9]

This complex can be used for the empirical determination of the absolute configuration of related acids. For this it is important to measure the CD always at similar concentration ratios. E.g. homochirally analogous acids like mandelic acid, its O-methyl ether, hydratropic acid, and α-phenyl butyric acid all give the same signs for the more pronounced Cotton effects between 300 and 400 nm. The same is due for lactic acid, its O-methyl ether and its O-acetate. The CD-spectra of the chiral complexes obtained *in situ* from the stock complex and amino acids differ scarcely from those mentioned hitherto; the signs of the Cotton effects between 300 and 450 nm are the same for such acids of the same absolute configuration as alanine, its N-acetate, phenyl alanine or arginine.

This method is very sensitive. E.g. the pen deflection on the dichrograph for a sensitivity setting of 5×10^{-6} ΔA-units/mm and 1 cm path length at 405 nm of a solution of 0.2 mg lactic acid in 10 ccm DMSO is still 43 mm.

It is obvious that the shape of the CD-curves must depend on the concentration ratio (ligand:Mo), as besides the achiral stock complex (k = 0) 5 other chiral complexes of type $[Mo_2(O_2CCH_3)_{(4-k)}(O_2CR^*)_k]$ may be present in solution (k = 1–4; for k = 2 a cis- and a trans-complex is possible; R* is a chiral group). If the contributions of the individual ligands to the CD were (approximately) additive one would expect that Δε tends towards an upper limit for each band with rising concentration of the chiral ligand $R^*CO_2^-$. Surprisingly the contrary holds: the differential absorbance $\Delta A \equiv A_L - A_R$ increases considerably for diminishing ratios ligand: Mo. The complex with k = 1 has obviously the largest rotational strength. For a rough estimation of the Δε-values we can assume that all ligands (they are very similar) are statistically distributed over all positions in the complex and the solution; if the dissociation of the complexes were negligibly small we obtain thus, e.g. for the complex with *S*-(+)-mandelic acid at 425, 360 and 310 nm Δε-values of +0.9, −3.4 and +5.5, resp. These values, which are lower limits, remain appr. constant over a broader concentration range provided that primarily only the complex with k = 1 is present.

As also Mo_2-clusters with other organic ligands than acids are known (see Refs. 4, 7, 10) we tested also some of these. Addition of monoalcohols like menthol to the stock complex do not induce CD, several Cotton effects are, however, obtained with diols and polyols as,

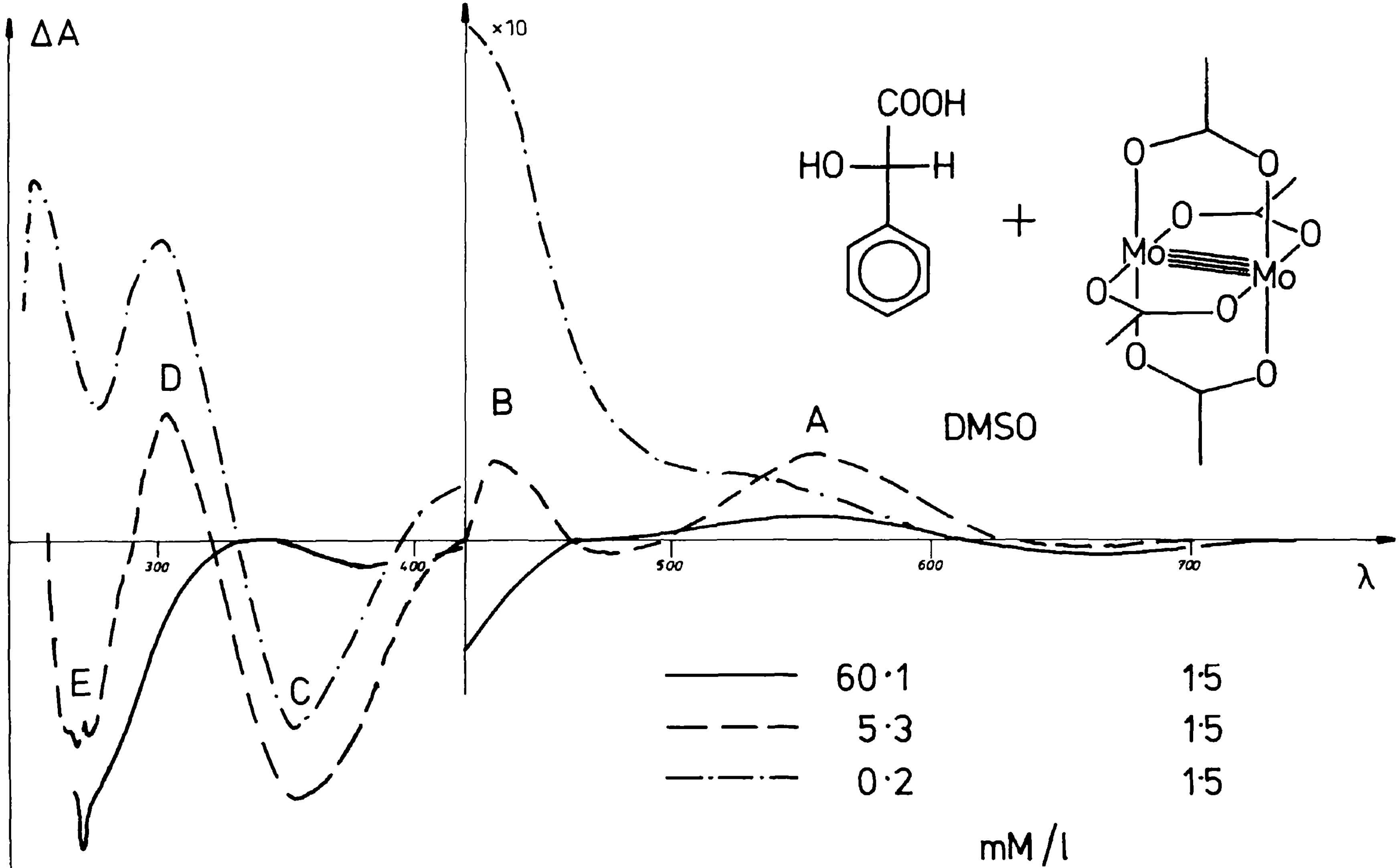

Fig. 1. CD (shown as differential absorbance ΔA) of the complex prepared *in situ* from $[Mo_2(O_2CCH_3)_4]$ and *S*-(+)-mandelic acid at 3 different concentration ratios in DMSO. The ordinate is not scaled in Figs. 1–4 as no exact concentrations of the active species present are known. In the right part of the Figure, the curves are enlarged by a factor of 10.

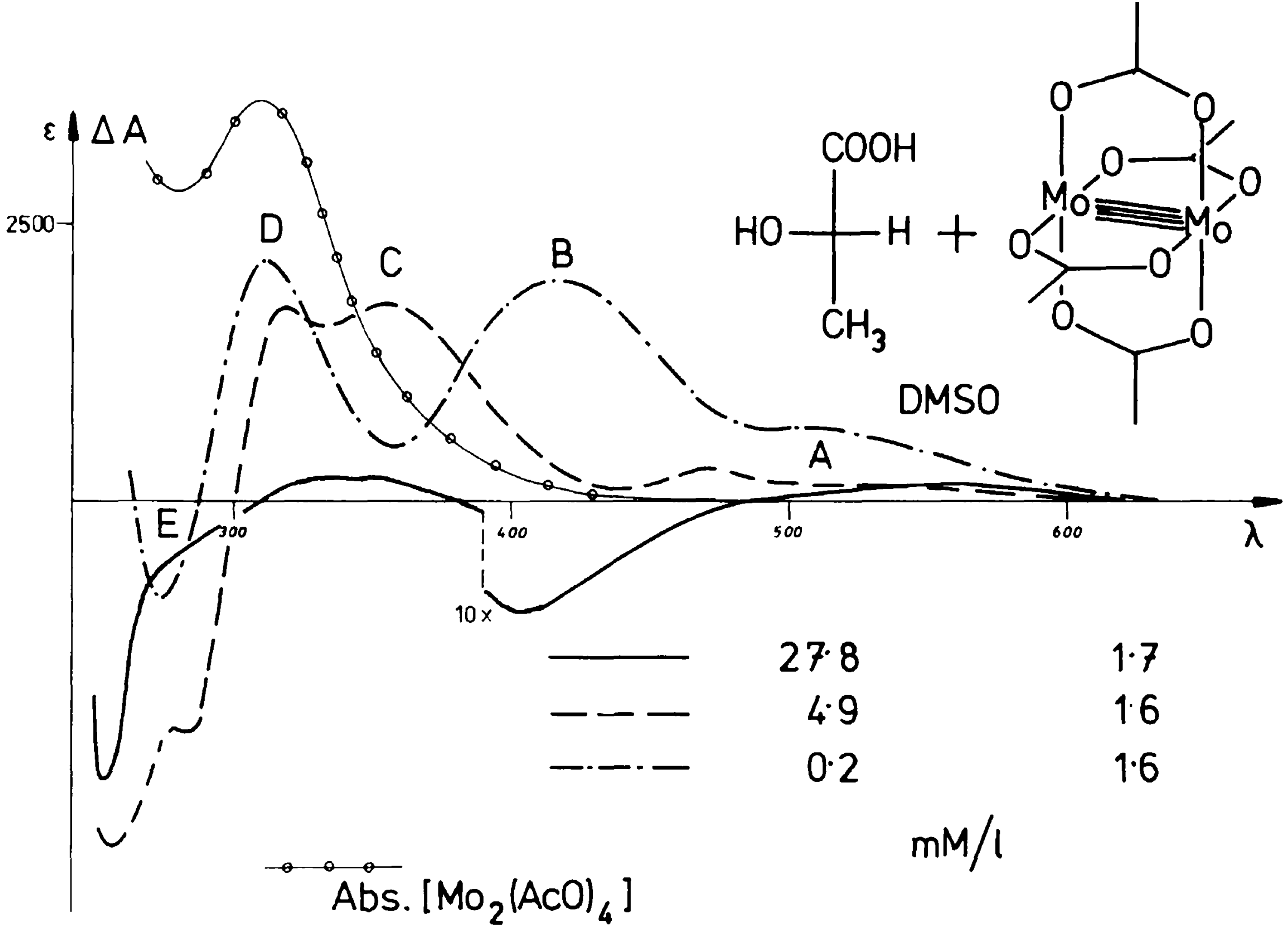

Fig. 2. CD (shown as differential absorbance ΔA) of the complex prepared *in situ* from $[Mo_2(O_2CCH_3)_4]$ and *S*-(+)-lactic acid at 3 different concentration ratios in DMSO. The solid curve is enlarged by a factor of 10 on the right side. —⊖ ⊖—⊖—⊖ - is the isotropic absorption curve of the stock complex in DMSO.

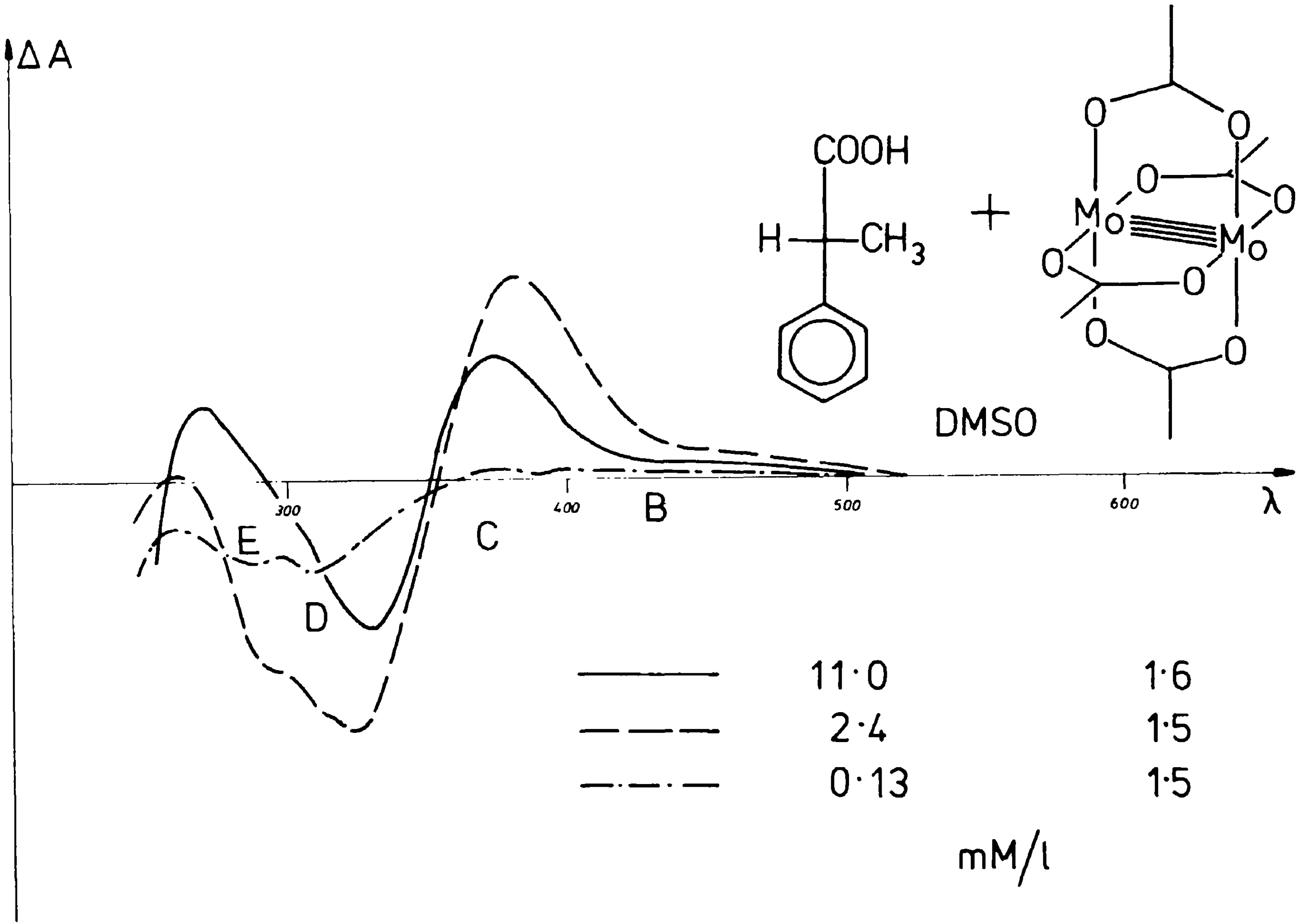

Fig. 3. CD (shown as differential absorbance ΔA) of the complex prepared *in situ* from [$Mo_2(O_2CCH_3)_4$] and *R*-(−)-hydratropic acid at 3 different concentration ratios in DMSO.

e.g. 2-deoxy-D-ribose (Fig. 4), glucose, 5α-cholestane-diol-2β,3β (Fig. 4), and some 1,3-diols which are derived from 1,2-diphenylethane.[11] Ether groups are not sufficient for complexing: permethylated glucose or O-methyl methyl mandelate do not give CD in presence of the stock complex.

Similarly 1,2-amino alcohols like ephedrine and its analogues,[12] or 1,3-amino alcohols derived from 1,2-diphenyl ethane[11] give several CD-bands with the stock complex, which can be used for the empirical determination of the absolute configuration of such compounds. We have also tested several other unidentate ligands: hitherto only with *S*-(−)-α-phenyl ethyl amine we obtained Cotton effects (Fig. 4). Its N,N-dimethyl derivative no longer complexes, as expected.

Assignment of CD- and absorption bands

The absorption spectra of $[Mo_2(O_2CR)_4]$ complexes have been described several times (see Refs. 6, 9, 13, 14); e.g. the formate complex gave[14] (alcohol matrix, 80 K) at longest wavelengths a very weak band (I) with pronounced fine structure between 420 and 480 nm. The strongest absorption band (III, $\varepsilon = 7200$) appears at 299 nm, another absorption is visible as a shoulder on this around 325 nm (band II, $\varepsilon \simeq 6000$), and a fourth band (IV, $\varepsilon = 2000$) can be seen at 225 nm. In the CD-spectra we found (see Figs. 1-3) for concentrations which give rise to mainly $[Mo_2(O_2CCH_3)_3(O_2CR^*)]$ as only chiral complex a very weak CD-band between 500 to 600 nm (band A), another one (B) between 400 to 450 nm coincides with I. A third Cotton effect (band C) of opposite sign to the first two ones appears around 360 nm. A comparison of the spectra in Figs. 1 and 2 suggests that the positive minimum found for the *S*-(+)-lactic acid complex is actually a negative maximum, whose $\Delta\varepsilon$-values are, however, shifted towards positive values because of overlap with CD-bands B and D. Band D around 310 nm coincides with the maximum of the isotropic absorption of the complex in DMSO ($\varepsilon = 3600$, Fig. 2), the last Cotton effect which can be detected in DMSO-solution (band E) apears around 270–300 nm. Bands D and E may correspond to the bands II and III of the isotropic absorption spectrum.[14]

The energies of the orbitals for the $[Mo_2(O_2CH)_4]$ complex have been calculated;[14] those for the filled ones agree quite well with data obtained from PE-spectra, band positions in the absorption spectra and thus energies of the virtual MOs are less satisfactorily predicted. The following MOs (the five highest filled and six lowest virtual) will be the most relevant for the spectra according to these calculations:[14]

$7e_u$ (π^-_{COO})
$3b_{2g}$ (π_{COO})
$4b_{2u}$ (σ^*_{Mo-O}; $d_{x^2-y^2}$)
$5b_{1g}$ (σ^*_{Mo-O}; $d_{x^2-y^2}$)
$5e_g$ (π^*_{Mo-Mo}; $d_{xz,yz}$)
$2b_{1u}$ (δ^*_{Mo-Mo}; d_{xy}, LUMO)
$2b_{2g}$ (δ_{Mo-Mo}, d_{xy}, HOMO)
$6e_u$ (π_{Mo-Mo} and π_{Mo-O}; $d_{xz,yz}$)
$4e_g$ (n_O)
$1a_{1u}$ (n_O)
$5e_u$ (π_{Mo-O} and π_{Mo-Mo}; $p_{x,y}$ and $d_{xz,yz}$)

The following assignments for the excited states corresponding to bands I–IV have been proposed:[14] I: $E_g(2b_{2g} \to 5e_g)$; II: $A_{2u}(2b_{2g} \to 2b_{1u})$; III: $E_u(2b_{2g} \to 7e_u)$; and IV: $A_{2u}(6e_u \to 5e_g)$. Besides the first one these are only electrically allowed transitions. In the CD-spectra one recognizes, however, also those excitations which are associated with a magnetic transition moment ($m_{x,y}$: $A_{1g} \to E_g$; m_z: $A_{1g} \to A_{2g}$).

If one orders the transitions between these above mentioned MOs and introduces electron configurational interaction then the excited state with lowest energy should correspond mainly to the transition $2b_{2g} \to 5e_g$ ($A_{1g} \to E_g$) to which the other one of same symmetry, $6e_u \to 2b_{1u}$ is admixed in such a way that the two magnetic transition moment vectors (partially) compensate each other. The corresponding second combination, for which the two moments have to be added (mainly $6e_u \to 2b_{1u}$, with some $2b_{2g} \to 5e_g$-character) appears then at somewhat higher energy. The rotational strength of that latter Cotton effect must be larger than of the first one, because firstly its **m** is larger, and secondly it lies closer to the first E_u-state from which the necessary electric transition moment has to be stolen. As is shown later both Cotton effects have to have opposite signs. If thus band C is assigned the second $A_{1g} \to E_g$ transition either A or B may be the first $A_{1g} \to E_g$ band. Because of the small **m** which is expected it is rather A which corresponds then to this first E_g-state. A splitting of the doubly degenerate $A_{1g} \to E_g$ band for the complex $[Mo_2(O_2CCH_3)_3(O_2CR^*)]$ is improbable because the chromophore still retains its D_{4h}-symmetry.

At a higher concentration of the ligand R^*CO_2 other species will be present on which several chiral ligands complex to the same Mo_2-cluster. Here several conformations will be possible and this may then lead to reduction even of the local D_{4h}-symmetry. For higher ligand concentrations we indeed occasionally found a splitting of the CD-band A (appearance of another very weak band between 600 and 700 nm). This again supports the assignment for band A

Band B must then correspond either to another E_g state or to one with A_{2g}-symmetry. The first could come from the $5e_u \to 2b_{1u}$-transition, whose **m** is, however, expected to be rather small, as there is a stronger participation of the $p_{x,y}$-orbitals on Mo. **B** may thus better be assigned the $2b_{2g} \to 5b_{1g}$-transition, which is associated with a reasonably strong m_z (see Fig. 5).

Band D is the first strong absorption band at longest wavelengths and is thus assigned in agreement with other authors[14] the $2b_{2g} \to 2b_{1u}$ ($A_{1g} \to A_{2u}$)-transition. Too many possibilities exist then for band E, which on the basis of our CD- and UV-spectra cannot any more be assigned unequivocally. Following the literature[14] it corresponds most probably to the $2b_{2g} \to 7e_u$-transition with x,y-polarization.

CD-sector rules

For the first three CD-bands A, B, and C sector rules may be obtained with the help of Qualitative MO Theory.[15,16] All three transitions are magnetically allowed, the necessary electric transition moment has to be stolen from an electrically allowed transition, which must then be at higher energy. After mixing by the chiral environment for these first three states we

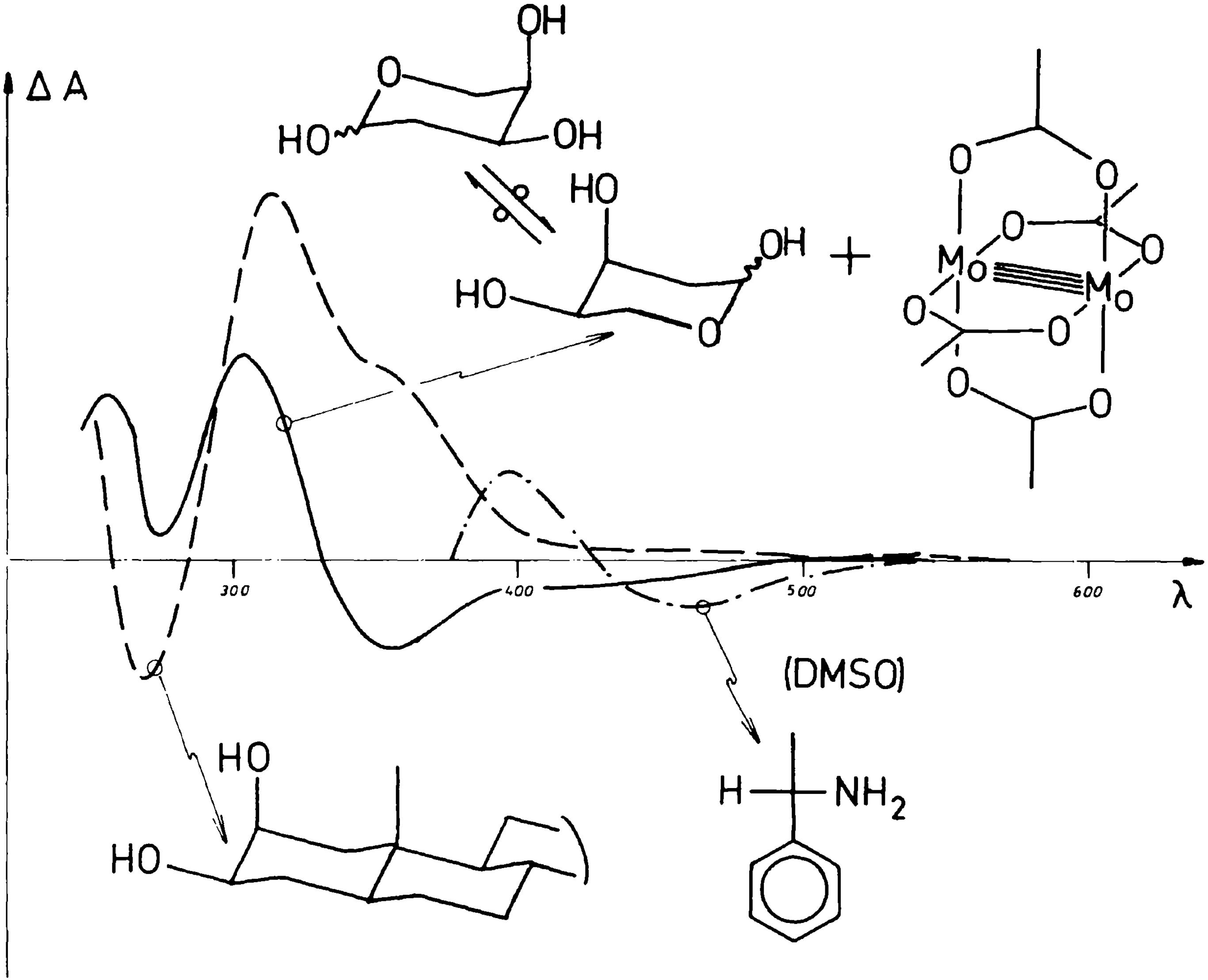

Fig. 4. CD (shown as differential absorbance ΔA) of the complexes prepared *in situ* from $[Mo_2(O_2CCH_3)_4]$ and 2-deoxy-D-ribose (—— -), 5α-cholestane-2β,3β-diol (– – – -), and S-(–)-α-phenyl ethyl amine (- · - · · · -) in DMSO.

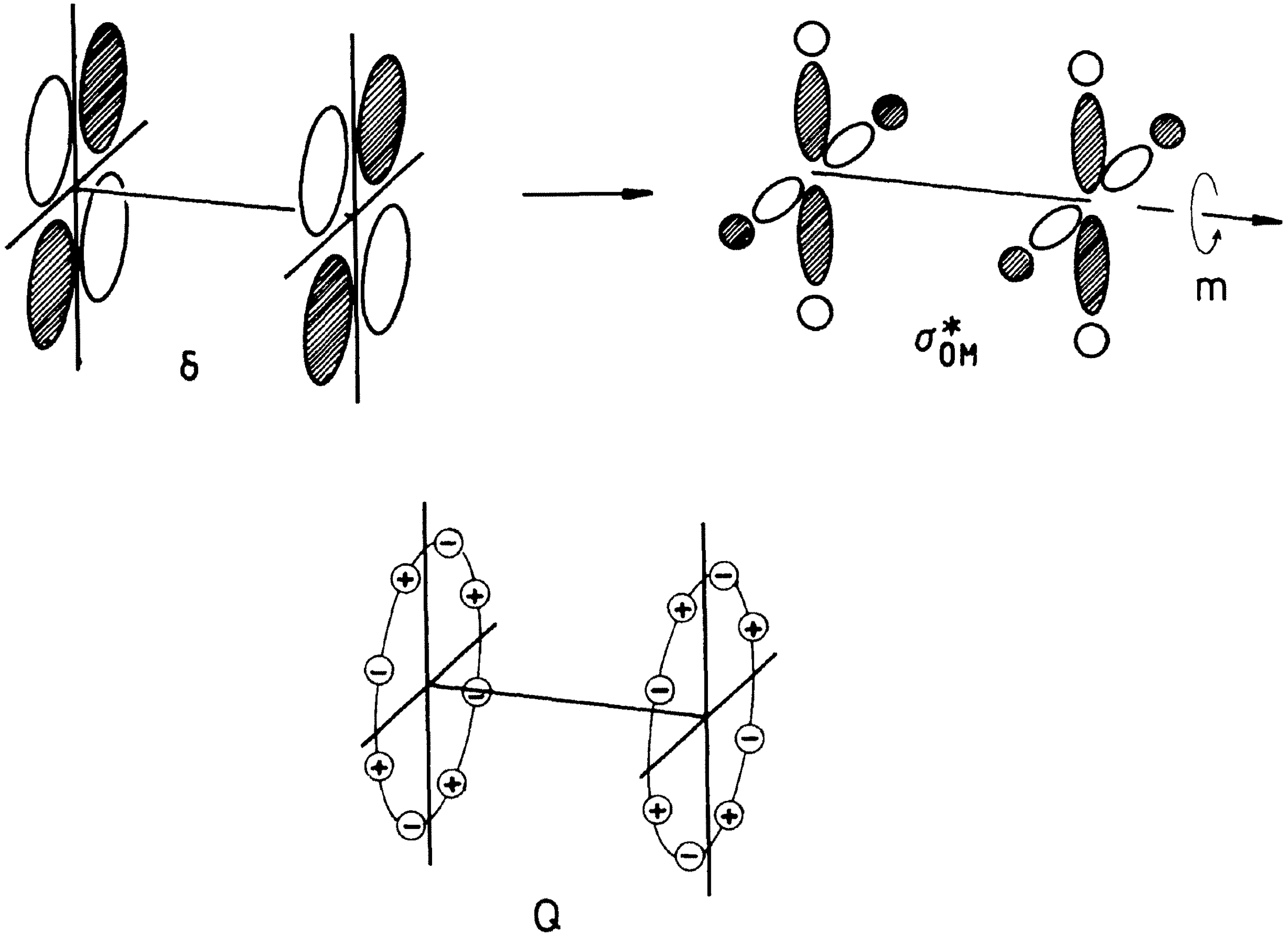

Fig. 5. $2b_{2g} \to 5b_{1g}$ ($\delta_{Mo-Mo} \to \sigma^*_{Mo-O}$) transition: Formal orbital multiplication according to the "recipe"[15,16] and correlation of the obtained transition multipole with the direction of the magnetic transition moment m, describing the charge rotation during the excitation.

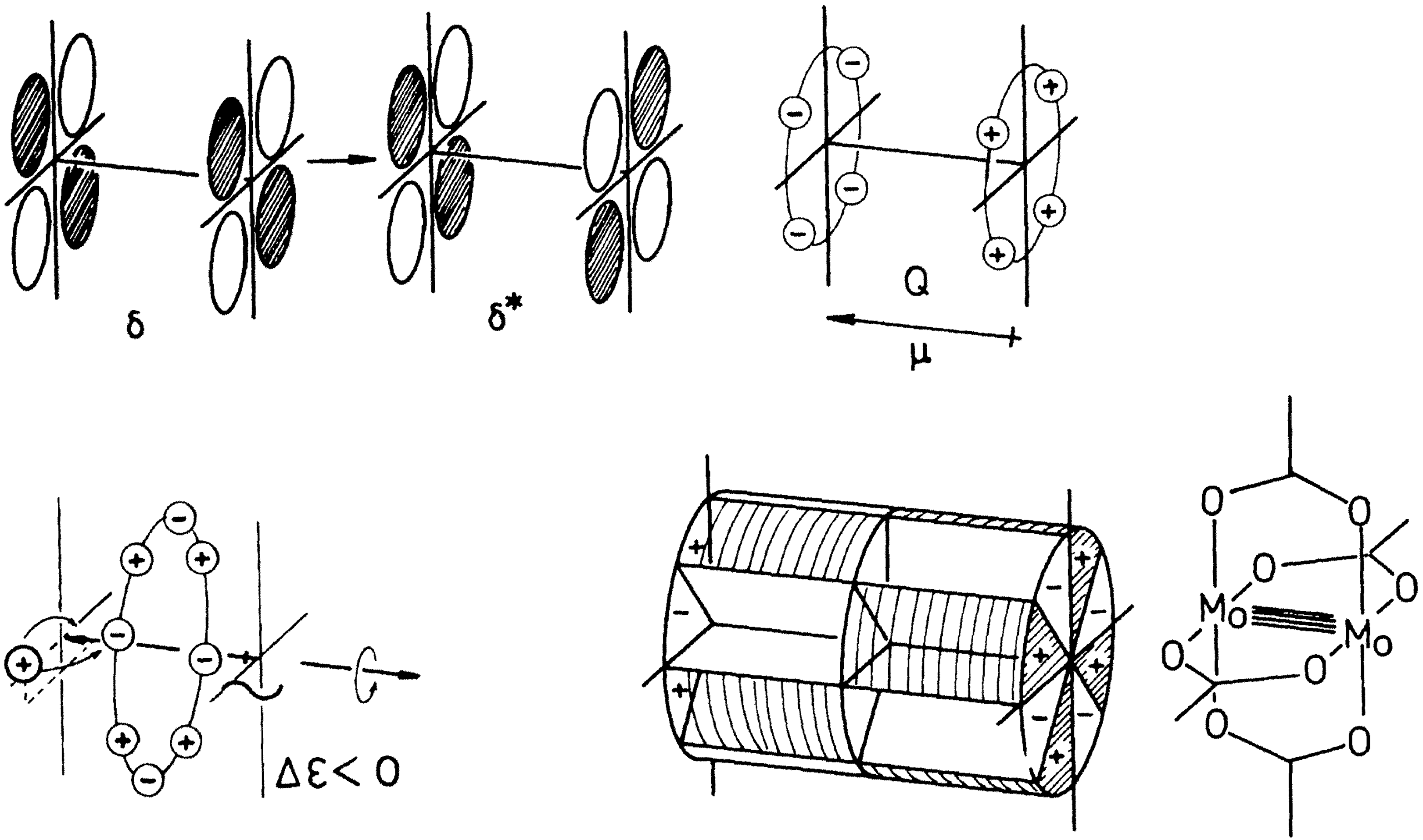

Fig. 6 $2b_{2g} \rightarrow 2b_{1u}$ ($\delta_{Mo-Mo} - \delta^*_{Mo-Mo}$) transition: Top: determination of the direction of the transition dipole. Bottom left: Induction of the sign patterns within dipole and multipole by a chirally arranged perturbing charge. Comparison with Fig. 5 shows that this multipole corresponds to m, directed to the right, i.e. opposite to the direction of the dipole. The CD is thus negative. Bottom right: Hexadecant rule which follows from this "recipe".[15,16]

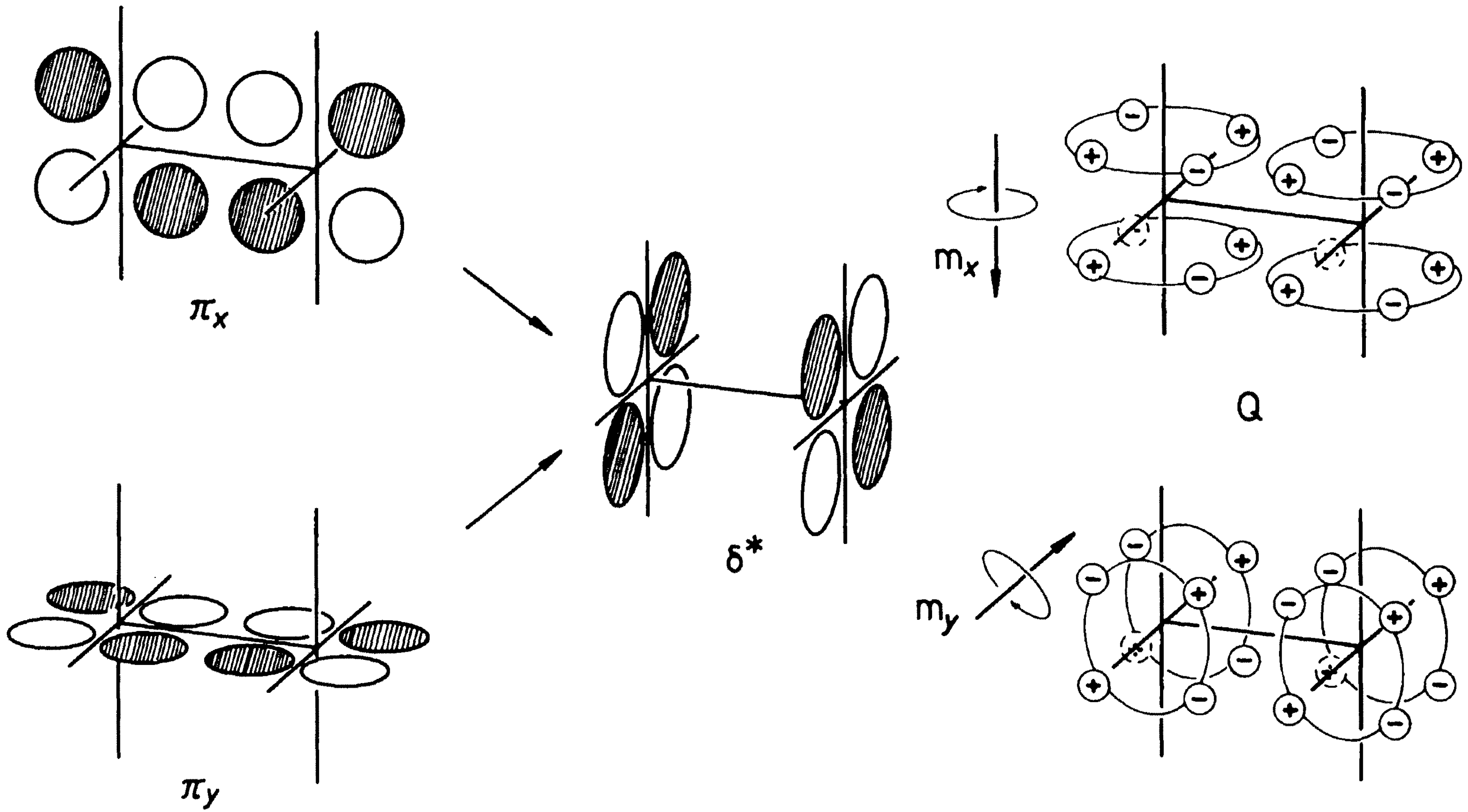

Fig 7. $6e_u \rightarrow 2b_{1u}$ ($\pi_{Mo-Mo} \rightarrow \delta^*_{Mo-Mo}$) transition: correlation between the sign patterns within the transition multipoles and the directions of m_x and m_y according to the "recipe".[15,16]

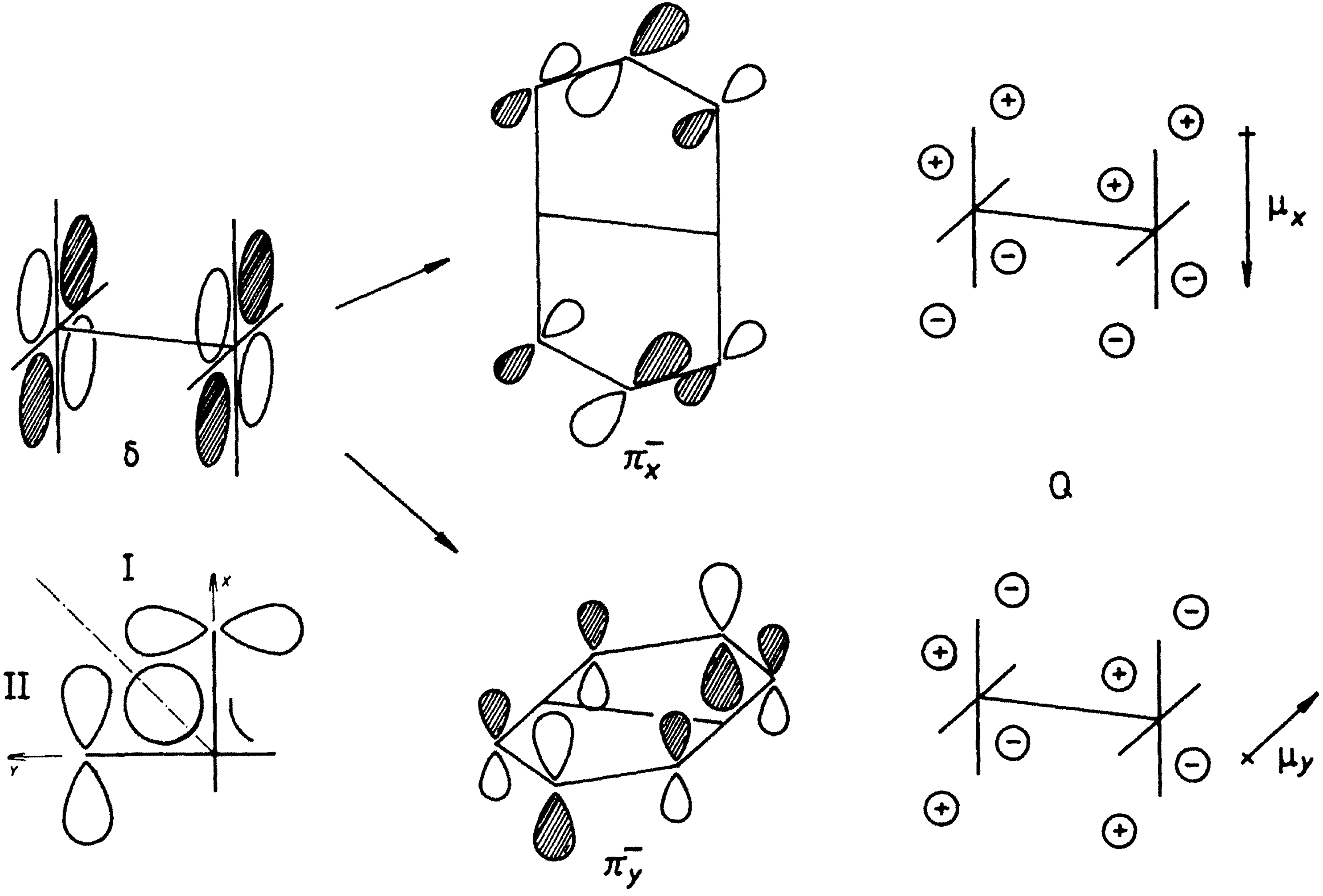

Fig. 8. $2b_{2g} \rightarrow 7e_u$ ($\delta_{Mo-Mo} \rightarrow \pi_{COO}$) transition: orbitals and the corresponding transition dipoles. Bottom left: partition of each octant into two sectors I and II by the bisecting plane.

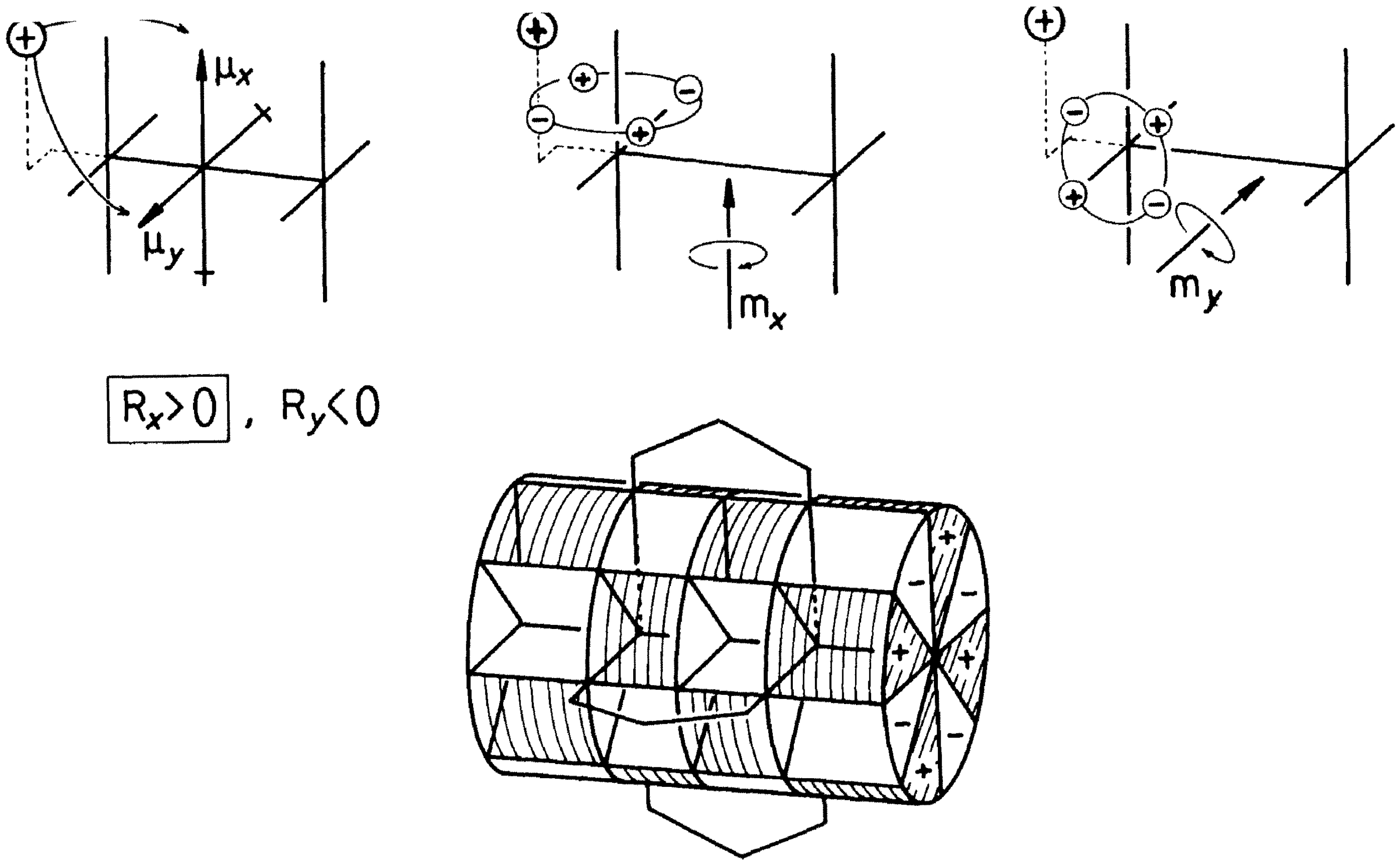

Fig. 9. Sector rule for CD-band A. A chirally arranged perturbing charge induces according to the "recipe"[15,16] the given sign patterns for the dipoles, and the multipoles associated with the magnetic transition moments. Only one quarter of the latter is drawn. The direction of m_x and m_y follows from comparison with Fig. 7. As the perturbing group was located in sector I (see Fig. 8) the interaction potential for the x-component of μ is larger than for the y-component, thus $R_x = \mu_x.m_x$, which is positive for the chosen arrangement, is larger than the negative $R_y = \mu_y.m_y$. No such discrimination is obtained for m_x and m_y. In the given sector the CD is then positive, and this leads to the sector rule shown on Bottom of the Figure: a hexadecant rule with the two MoO_4-planes as additional MO-determined nodal planes (32 sectors). The oxygen atoms are not shown in the schematic rule.

The sector rule for band C is obtained from this one by sign inversion for all contributions (see text).

have thus to use the energetically favoured combinations, i.e. both times attraction (or both times repulsion).[15,16] Figure 5 shows the correlation between the charge pattern in the transition multipole and the direction of the magnetic transition moment vector for the $2b_{2g} \rightarrow 5b_{1g}$-transition which we assigned to band B. That z-polarized transition which is energetically nearest to it is the $2b_{2g} \rightarrow 2b_{1u}$-transition (Fig. 6). Figure 6 shows also the induction of the signs of the charges within the dipole and that transition multipole which is associated with m_z by a chirally arranged perturbing charge, using the "recipe".[15,16] Comparison with Fig. 5 indicates that for the chosen position of the perturbing group both transition moments are antiparallel to each other, the rotational strength is therefore negative. The whole sector rule which follows from this is also drawn in Fig. 6. As the multipole which is associated with **m** consists of 8 charges we obtain 8 "left" and 8 "right" sectors, a *hexadecant rule* results thus. This is in agreement with theory, as according to Schellman[17] the symmetry planes of the chromophore become nodal planes of the corresponding sector rule ("symmetry-determined" nodal planes).

If we apply it to the complex with *R*-(−)-hydratropic acid we have to make assumptions about the preferred conformation of the ligand. If it were the same as found for carboxylic acids in general, i.e. a synperiplanar arrangement of the methyl group with one of the C———O-bonds, then all atoms of the benzene ring are positioned in a positive sector, in agreement with the positive Cotton effect within band B of that complex (see Fig. 3).

For the hydroxy acids of the enantiomeric series the CD within band B is also positive. No simple prediction of the conformation in the complex of such ligands seems, however, possible because of the dipole interactions. Here we have to rely on empirical correlations.

For the $A_{1g} \rightarrow E_g$-transition at longer wavelengths (band A) we have discussed mainly $2b_{2g} \rightarrow 5e_g$ parentage. Figure 7 shows the relevant orbitals, the transition multipoles built up during the excitation, and their correlation with the magnetic transition moments m_x and m_y. For the rotational strength we need to borrow again $\mu_{x,y}$, and the transition which seems to be closest in energy and is formally x,y-polarized would be of $4e_g \rightarrow 2b_{1u}$-type. As the overlap between the lone pairs on the oxygen atoms and the δ^*-MO is, however, very small no large $\mu_{x,y}$ can be associated with this transition. The same holds for the next, $1a_{1u} \rightarrow 5e_g$. The missing μ comes thus most probably from the $2b_{2g} \rightarrow 7e_u$-transition (band III of Ref. 14), and Fig. 8 shows how its components are built up. Testing the influence of a perturbing charge upon **m** and μ (Fig. 9) leads to the result that the x- and y-components to the rotational strength are of opposite sign. One should note, however, that only a charge lying on the plane bisecting each octant has exactly the same interaction with both dipoles. Is the perturbing group located in sector I (see Fig. 8, bottom left) then the interaction potential with μ_x is larger, in sector II however, with μ_y. For the position chosen in Fig. 9 (in sector I) the magnitude of $R_x = \mu_x.m_x$ is then larger than that of $R_y = \mu_y.m_y$, the contribution in this sector is thus positive. From this follows then the sector rule shown in Fig. 9, which contains besides the 5 symmetry-determined nodal planes also two others, the "orbital-determined" ones, which are the two planes of the MoO_4-units. These planes are the nodal planes of the $\pi^*_{x,y}$-orbitals.

The determinaton of the correlation between the sign pattern within the transition multipoles and the direction of the magnetic transition moments for the $6e_u \rightarrow 2b_{1u}$-transition follows exactly the same lines (see Fig. 7), and the result is opposite to that obtained for the $2b_{2g} \rightarrow 5e_g$-transition. The corresponding sector rule must then also be the mirror image of that given in Fig. 9. In the CD-spectrum of the complex with *R*-(−)-hydratropic acid band A cannot be recognized, band C (Fig. 3) is, however, easily detected and positive. The enantiomorphous sector rule to that of Fig. 9 is valid for band C, and if we assume the same conformation as before for the chiral ligand most of the atoms of the benzene ring are positioned in an "inner" positive sector, in agreement with the measurement (Fig. 3).

From the general treatment of the Cotton effects it follows that the corresponding transition at higher energy which provided the electric transition moment should have a CD-sign which is opposite to that of the transition at lower energy. This is, however, only the case if no other transitions are possible at still higher energy, which provide also magnetic transition moments, which could then instead be used to produce rotational strength. Such a situation is obviously present in the case of our chiral complexes and the determination of absolute configuration from the Cotton effects below 400 nm should thus better rely on empirical comparisons.

EXPERIMENTAL

The measurements were obtained on a Dichrograph Mark III of Jobin-Yvon-ISA at room temperature. The concentration of the stock solution was *ca.* 1.5 mmole/l in pure DMSO. The solution is stable at room temperature for a few hours, but can be kept in the refrigerator for a long time. For the *in situ* preparation of the complexes the chiral ligand is added to the stock solution and the CD is measured from 800 to 270 nm in cells of 1.0 and 0.2 cm pathlength. In general a ligand concentration of 0.5–1.0 mmole/l is sufficient. The CD remains constant over several hours.

Acknowledgements –G.S. thanks the Deutschen Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.

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