A Classical Polarizability Treatment for Planar Bis{2-[(*R*)-1,2,2-trimethylpropyliminomethyl]naphtholato(1−)-*NO*}nickel(II)

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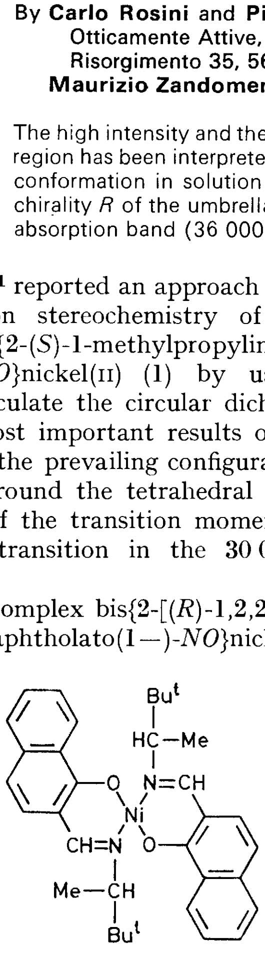
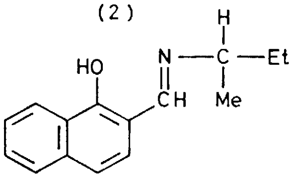
The high intensity and the shape of the circular dichroism spectrum of the title complex in the 30 000—50 000 cm^{-1} region has been interpreted on the basis of the DeVoe theory. The complex assumes preferentially a chiral umbrella conformation in solution and a maximum value (133°) is suggested for the umbrella angle ϕ. In addition, the chirality *R* of the umbrella can be deduced making reasonable assumptions about the polarization direction of the absorption band (36 000 cm^{-1}) employed in the calculations.

WE previously [1] reported an approach to the elucidation of the solution stereochemistry of the tetrahedral complex bis{2-(*S*)-1-methylpropyliminomethyl]naphtholato(1—)-*NO*}nickel(II) (1) by using the DeVoe theory [2] to calculate the circular dichroism (c.d.) spectrum. The most important results obtained were the assignment of the prevailing configuration to the chiral arrangement around the tetrahedral nickel atom, and the direction of the transition moment of the organic ligand $\pi \rightarrow \pi^*$ transition in the 30 000—40 000 cm^{-1} region.

The planar complex bis{2-[(*R*)-1,2,2-trimethylpropyliminomethyl]naphtholato(1—)-*NO*}nickel(II) (2), exhibits in the same spectral range a strong couplet [$\Delta(\Delta\varepsilon) \simeq$ 200], Figure 5(*a*), which is absent in the spectrum of the free ligand. The typical shape of the c.d. curve is consistent with the hypothesis that also in this case the optical activity is dominated by coupling between the two naphthalene-like chromophores of the ligands. Therefore, in spite of the centrosymmetric structure shown in the solid state by planar complexes of this type,[3] in solution a chiral structure must be assumed by (2), at least in part. Provided that the conditions imposed by the theory [2] are realized, the approach used for (1) can also be employed to account for the observed c.d. of (2) in the 30 000—50 000 cm^{-1} region.


(2)


(3)

Complex (2) is largely planar in solution as in indicated by the low absorption coefficient ($\varepsilon \simeq 5$ dm^{3}mol^{-1} cm^{-1}) in the 7 000 cm^{-1} region (the absorption band due to the $^3T_1 \rightarrow {}^3A_2$ transition characteristic of the tetrahedral arrangement around the nickel atom [3] has ε values of $\simeq 50$ dm^3 mol^{-1} cm^{-1}). Therefore, in the ^{1}H n.m.r. spectrum the resonances are not shifted with respect to those of the free ligand, as expected for diamagnetic planar complexes.[3] The complex can exist in two chiral ' umbrella ' and one quasi-centrosymmetric ' stepped ' conformation (Figure 1). When the naphthalene long axes are segments of a right- or left-handed helix having the screw axis coincident with C_2 [Figure 1(*c*)] the chirality of the umbrella is *R* or *S* respectively.[4,*] For an unassociated molecule in solution the stereochemistry can be represented by the equilibria in (1) whose positions

$$\text{umbrella } (R) \rightleftharpoons \text{stepped} \rightleftharpoons \text{umbrella } (S) \qquad (1)$$

depend on the asymmetric induction [6] exerted by the chiral carbon atom attached to the nitrogen of both the two Schiff-base ligands. The geometry of an umbrella conformation has been derived from the structure of the tetrahedral complex (1), by means of a 90° rotation of one half of the molecule around the bisector axis of the NNiO angle in order to obtain a planar arrangement around the nickel atom. Other umbrella conformations can be easily obtained by variation of the ' umbrella ' angle ϕ (Figure 1).

CALCULATIONS

In order to obtain the chromophore polarizability data for the c.d. computations, we have taken into account the u.v.

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[*] In reality the chelate rings are distorted, defining a chirality λ or δ.[5] We have disregarded this distortion in order to reduce the treatment to its essentials. The *R* chirality is allied to a $\lambda\lambda$ chirality of the chelate rings.

[1] M. Zandomeneghi, C. Rosini, and P. Salvadori, *Chem. Phys. Letters*, 1976, **44**, 533.

[2] M. DeVoe, *J. Chem. Phys.* 1964, **41**, 393; 1965, **43**, 3199.

[3] R. M. Holm, G. W. Everett, jun., and A. Chakravorty, *Progr. Inorg. Chem.*, 1966, **7**, 83; R. H. Holm and M. J. O'Connor, *ibid.*, 1969, **10**, 241.

[4] R. Grinter and S. F. Mason, *Trans. Faraday Soc.*, 1964, **60**, 274.

[5] Proposed I.U.P.A.C. nomenclature, *Inorg. Chem.*, 1970, **9**, 1.

[6] J. D. Morrison and H. S. Mosher, 'Asymmetric Organic Reactions,' Prentice-Hall, Englewood Cliffs, New Jersey, 1971, p. 1.

spectrum of complex (2) and that of the Schiff base 2-[(*S*)-1-methylpropyliminomethyl]naphthol (3) which can be assumed as a model of the free ligand. Quite close to the energies of the two c.d. couplets observed at *ca.* 37 400 and 47 400 cm^{-1}, the u.v. spectra of both (2) and (3) exhibit two relatively strong absorption bands. In n-heptane complex (2) shows two maxima at 35 800 ($\varepsilon_{\text{max.}}$ 78 000) and 46 000 cm^{-1} ($\varepsilon_{\text{max.}}$ 69 000 dm^3 mol^{-1} cm^{-1}) and compound (3) exhibits bands at 37 400 ($\varepsilon_{\text{max.}}$ 40 000) and 45 000 cm^{-1} ($\varepsilon_{\text{max.}}$ 26 000 dm^3 mol^{-1} cm^{-1}) respectively. The high intensity and position of the bands strongly suggest that they are $\pi\rightarrow\pi^*$ transitions of the naphthalene moiety and hence are plane polarized. On resolving the spectrum into components of gaussian type (Figure 2), it can be seen that the dipolar strength (single chromophore) of the two bands corresponding to the above maxima of (2) (8.1 × 10^{-35} c.g.s. units) and of (3) (7.4 × 10^{-35} c.g.s. units) is similar to that shown by naphthalene (6.8 × 10^{-35} c.g.s. units). As recently reported [7] the u.v. spectra of monosubstituted naphthalenes show energy shifts (1 000—2 000 cm^{-1}) and splittings (5 000—6 000 cm^{-1}) of the bands with respect to the parent compound, depending on the position and nature of the substituents.*

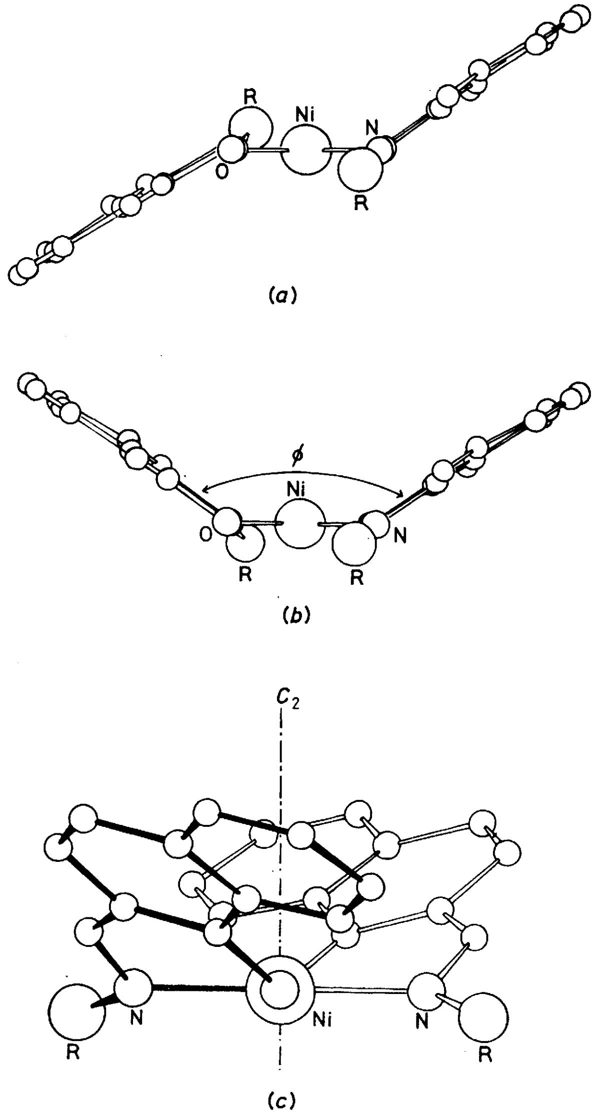

FIGURE 1 ORTEP diagrams of complex (2) showing (*a*) a stepped conformation, (*b*) an umbrella conformation and its ϕ angle, and (*c*) a view along the O–Ni–O axis of an umbrella conformation, defining the *R* chirality of the molecule. Hydrogen atoms are not shown, and carbon atoms appear as unlabelled circles

In similar computations [1,2,8,9] the imaginary part of the polarizability is usually obtained from the u.v. spectrum of a model compound. In our case, the u.v. spectrum of (3) is highly solvent-dependent, because of the keto-enol tautomerism.[10] Indeed the spectra in different solvents are similar in shape and in the overall dipolar strength (7.4 × 10^{-35} and 6.9 × 10^{-35} c.g.s. units in n-heptane and methanol respectively) but differ in the maximum intensities (*i.e.* 30% from n-heptane to methanol) making the choice of the 'monomer' polarizability quite arbitrary. Since the calculated c.d. depends on the input polarizabilities, the equation [1] $\delta(\Delta\varepsilon)/\Delta\varepsilon = 2\,\delta\varepsilon/\varepsilon$ is approximately valid for two equal interacting chromophores, an uncertainty of *ca.* 60% being expected. Therefore we tried to obtain the monomer polarizability from the u.v. spectrum of (2) itself by means of a decoupling procedure. This may be achieved if the absorption bands due to the chromophore considered can be singled out to a good approximation.

A polarizability centre is subject to an 'external' electromagnetic field and an 'internal' electromagnetic field arising from the polarizabilities of the surroundings. The all-order treatment of DeVoe leads to equations which have to be solved at each frequency. Explicit frequency-dependent solutions are easily obtained in the simplest case of two equal interacting chromophores. For *N* interacting polarizabilities one can again obtain analytical solutions by using first-order perturbation schemes. In this case, the

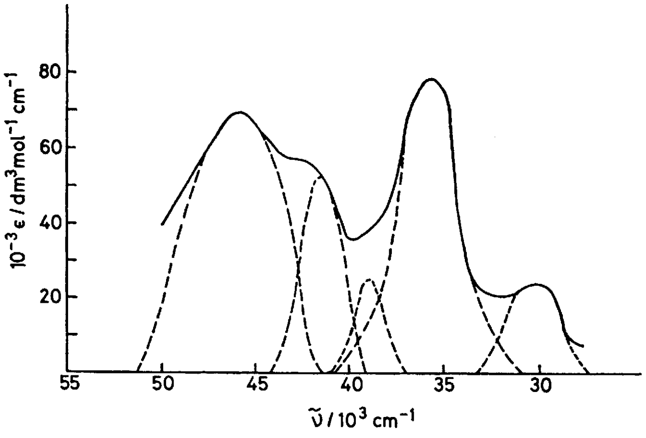

FIGURE 2 Experimental u.v. spectrum (n-heptane) of (2) (——) and its resolution into gaussian-type components (– – –)

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* Semiempirical CI calculations show that excited charge-transfer configurations of relatively small weight (1—5%) play an important role in mixing excited states of different symmetry in naphthalene and give rise to several new absorptions.[7]

[7] S. Suzuki, T. Fujii, and T. Ishikawa, *J. Mol. Spectroscopy*, 1975, **57**, 490.

[8] W. Hugh, F. Ciardelli, and I. Tinoco, *J. Amer. Chem. Soc.*, 1974, **96**, 3407.

[9] C. L. Cech, W. Hug, and I. Tinoco, *Biopolymers*, 1976, **15**, 131.

[10] G. O. Dudek and E. P. Dudek, *J. Chem. Soc.* (*B*), 1971, 1356.

effective field acting on a polarizability centre is the ' external ' one plus that coming from the other centres polarized only by the ' external ' field. Considering the solvent as the vacuum * and assuming the usual approximations [2] one obtains equation (2) where ε and $\Delta\varepsilon$ are in dm^3 mol^{-1} cm^{-1}, c.g.s. units are used throughout,

$$\varepsilon(\bar{\nu}) = 6.887 \times 10^{21}\bar{\nu} \sum_{i=1}^{N} \mathrm{Im}\alpha_i(\bar{\nu}) - 1.377 \times 10^{22}\bar{\nu} \sum_{\substack{i,j=1 \\ i>j}}^{N} G_{ij}\boldsymbol{e}_i\cdot\boldsymbol{e}_j[\mathrm{Im}\alpha_i(\bar{\nu})\mathrm{Re}\alpha_j(\bar{\nu}) + \mathrm{Im}\alpha_j(\nu)\mathrm{Re}\alpha_i(\bar{\nu})] \quad (2)$$

$\alpha_i(\bar{\nu})$ is the ith polarizability, $\boldsymbol{e}_i$ its polarization direction, and G_{ij} is the dipole–dipole interaction term between i and j transition-unit dipoles ($G_{ij} = 0$ if the dipole locations are the same). Equation (2) gives a perfect addition of ' monomeric ' absorptions (the first sum) if interaction terms (second sum) are zero as the result of averaging in the case of uncorrelated molecules. However, if the perturbation effects are small (a condition for the validity of the overall treatment) it is reasonable to expect that the first summation is the dominant one. When the N monomers are equal, a zero-order approximation for $\mathrm{Im}\alpha(\bar{\nu})$ is then obtained from equation (2): $\mathrm{Im}\alpha^0(\bar{\nu}) = 1.452 \times 10^{-22}\varepsilon(\bar{\nu})/N\bar{\nu}$. From this approximation, $\mathrm{Re}\alpha^0(\bar{\nu})$ can be calculated by Kronig–Kramers transform. If the $G_{ij}\boldsymbol{e}_i\cdot\boldsymbol{e}_j$ values for the aggregate are known the second sum of equation (2) can be computed at the same order of approximation. By an iterative procedure, values of $\mathrm{Im}\alpha(\bar{\nu})$ and $\mathrm{Re}\alpha(\bar{\nu})$ can be obtained which satisfy equation (2). Owing to its perturbation origin, this equation can be expected to be less satisfactory around the maximum polarizability frequencies, where higher-order effects cannot be neglected.

In practice the following procedure was used. The two most intense bands of the resolved u.v. spectrum (Figure 2) corresponding to the two c.d. couplets, as discussed above, were used to give zero-order polarizabilities and hence to perform c.d. calculations. Owing to the naphthalene-like nature of both the absorption bands, the corresponding polarizabilities were assumed to be located at the centre of each naphthalene ring and plane polarized. As far as the direction of the transition dipole moment and the solution geometry of the molecule are concerned, there is no reason to consider a preferential situation. Therefore, they are used as parameters in our calculations, which were carried out by assuming an umbrella with R chirality as the conformation of the whole molecule.

RESULTS AND DISCUSSION

Assuming that the two aforementioned bands independently contribute to the computed c.d., the best doublet (θ_1 and θ_2) of the polarization angles θ (defined in Figure 3) for the absorption bands at 36 000 and 46 000 cm^{-1} respectively can be found simply by considering one polarizability at a time. In this case,[1] a c.d. couplet is given by the frequency-dependent function $\bar{\nu}^2\mathrm{Im}\alpha(\bar{\nu})\mathrm{Re}\alpha(\bar{\nu})$ and the polarization direction of the transition affects the overall curve by a constant geometry-dependent factor. In other words, by use of this treatment one obtains a couplet whose amplitude is dependent on θ. A plot of $\Delta\varepsilon_{\mathrm{max.}}$ against θ for the lower-energy component of the couplet at 36 000 cm^{-1} is reported for several ϕ angles in the ' homochromophoric diagram ' in Figure 3.

From an inspection of the curves in Figure 3 a negative couplet at 135° (36 000 cm^{-1} band) and a positive one at 0° (46 000 cm^{-1} band), both of amplitude comparable to the experimental one, are deducible, starting from $\phi = 133°$. DeVoe computations [1,2] were then carried out using values around these approximate θ values and considering the two bands simultaneously. The zero-order polarizabilities of the bands at 36 000 and 46 000 cm^{-1} were used in the calculations. The best values (θ_1 135, θ_2 5°) obtained were successively used for the evaluation of the interaction terms (3) in equation (2).

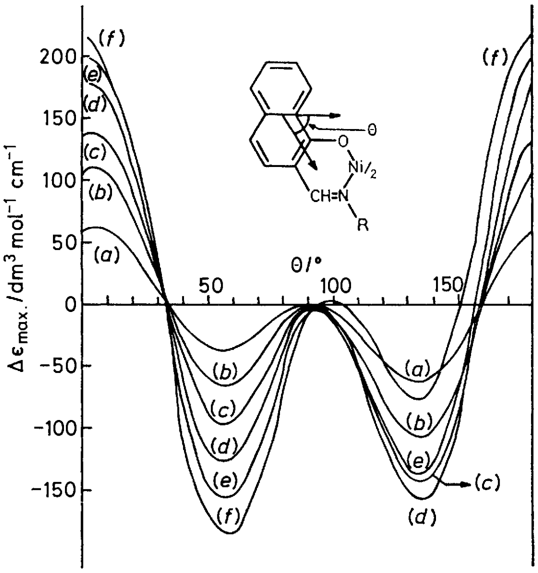

FIGURE 3 Homochromophoric diagram: a plot of $\Delta\varepsilon_{\mathrm{max.}}$ for the lower-energy component of the couplet at *ca.* 36 000 cm^{-1} against the angle of polarization. ϕ = 153 (*a*), 133 (*b*), 114 (*c*), 96 (*d*), 78 (*e*), and 61° (*f*)

$$\sum_{i,j} G_{ij}\boldsymbol{e}_i\cdot\boldsymbol{e}_j(\mathrm{Im}\alpha_i\mathrm{Re}\alpha_j + \mathrm{Re}\alpha_i\mathrm{Im}\alpha_j) \quad (3)$$

A correction was made which disregarded the crossed terms in (3) corresponding to different polarizabilities. Finally, the ' effective chromophore ' polarizabilities obtained were employed in calculating $\varepsilon(\bar{\nu})$ and $\Delta\varepsilon(\bar{\nu})$. The u.v. and c.d. spectra obtained for θ_1 = 135 and θ_2 = 5° are shown in Figure 4(*c*) and 5(*c*) respectively. The following features have to be considered.

(*a*) The information about the θ angles obtained from

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* We have omitted any solvent correction because: (*i*) the traditional Lorentz factor $(n^2 + 2)^2/9n$ disregards the electromagnetic field coming from the solvent molecules which are not included in the ' continuum ' spherically arranged around the complex [11] (*i.e.* it disregards the nearest molecules of solvent); (*ii*) Schuyer treatment [12] leads to smaller corrections; (*iii*) our interaction term (G_{12}) represents an *in vacuo* interaction between the chromophores even if this vacuum is, in reality, filled with the non-chromophoric part of the complex; (*iv*) u.v. and c.d. spectra of the complex in n-neptane, methylcyclohexane, and chloroform are practically coincident.

[11] H. A. Lorentz, ' The Theory of Electron,' Teubner, Leipzig, 1916.

[12] J. Schuyer, *Rec. Trav. chim.*, 1953, **72**, 933.

Figure 3 is semiquantitative. However, the validity of our procedure can be verified by taking into account the ' crossed-interaction ' terms, for c.d., between different transition dipoles. These are expressed, to first order, by equation (4) where $\boldsymbol{R}$ is the interchromophoric distance.

$$0.864\,7 \times 10^{23}\cdot\boldsymbol{R}\cdot\boldsymbol{e}_1 \times \boldsymbol{e}_2\cdot G_{12}\tilde{\nu}^2 \left[\mathrm{Re}\alpha_1(\tilde{\nu})\mathrm{Im}\alpha_2(\tilde{\nu}) + \mathrm{Im}\alpha_1(\tilde{\nu})\mathrm{Re}\alpha_2(\tilde{\nu})\right] \quad (4)$$

In our case $\mathrm{Im}\alpha_1(\tilde{\nu})$ and $\mathrm{Im}\alpha_2(\tilde{\nu})$ cannot be simultaneously different from zero since the absorption bands do not overlap and only one term in (4) contributes alternately to the calculated c.d. The sign of the contribution to the dichroism of the lower-energy band is determined by the positive sign of the real part of the polarizability of the band at higher energies. The opposite is true for the higher-energy band. This constitutes an effective mechanism of transfer of rotational strength between the bands.

(*b*) The measured absorption of complex (2) [Figure 4(*a*)] is almost perfectly reproduced by the ' effective-chromophore ' treatment [Figure 4(*c*)] with respect to the zero-order approximation [Figure 4(*b*)]. As expected (for a first-order treatment), higher-order effects can be important around the polarizability maxima and discrepancies are observable at these frequencies.

(*c*) From the homochromophoric diagram [Figure 3(*b*)] (ϕ 133°) another doublet of polarization angles, $\theta_1 = 55°$ and $\theta_2 = 0°$, could be considered. Corresponding to the best doublet of angles obtainable by means of the DeVoe treatment (θ_1 58 and θ_2 175°), we have a c.d. curve very similar to the observed one, within a scale factor of 0.74.

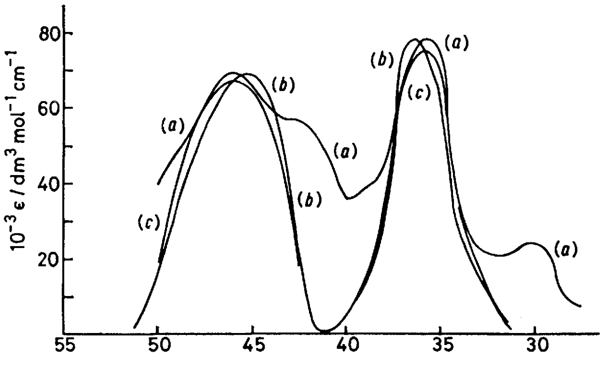

FIGURE 4 (*a*) Experimental u.v. spectrum of (2). (*b*) Calculated spectrum using zero-order polarizabilities. (*c*) As (*b*) but using first-order polarizabilities. The polarization angles $\theta_1 = 135$ and $\theta_2 = 5°$, and the umbrella angle $\phi = 133°$

$\Delta\varepsilon$ is a ϕ-dependent function and, as shown in Figure 3, there are no solutions in agreement with experimental values for $\phi > 133°$. It is interesting to note that this is approximately the angle ($\approx$ 129°) deducible from the stepped conformation of the similar complex bis{1-[(*S*)-1-methylpropyliminomethyl]-2-naphtholato(1—)-*NO*}-nickel(II) in the solid state.[13] The c.d. expected for a single umbrella conformation would be greater than that experimentally observed. In fact, on decreasing the temperature an increase in c.d. is observed and a very preliminary evaluation indicates that the contribution of the dominant chiral conformation is of the order of 80%. Thus smaller ϕ angles can be suitably considered and yield two series of couples of polarization angles about the values $\theta_1 = 135$ and $\theta_2 = 5$ and $\theta_1 = 55$ and $\theta_2 = 5°$. However, solutions are not obtainable with $\phi < 70°$ for the former doublet while a limit is not deducible for the latter. As far as the chirality of the system is concerned, the inversion of the chirality of the umbrella involves, in practice, the exchange of the values of the θ_1 and θ_2 angles, and hence the couples $\theta_1 = 5$ and $\theta_2 = 135°$ and $\theta_1 = 5$ and $\theta_2 = 55°$ should be taken into account for the *S* chirality.

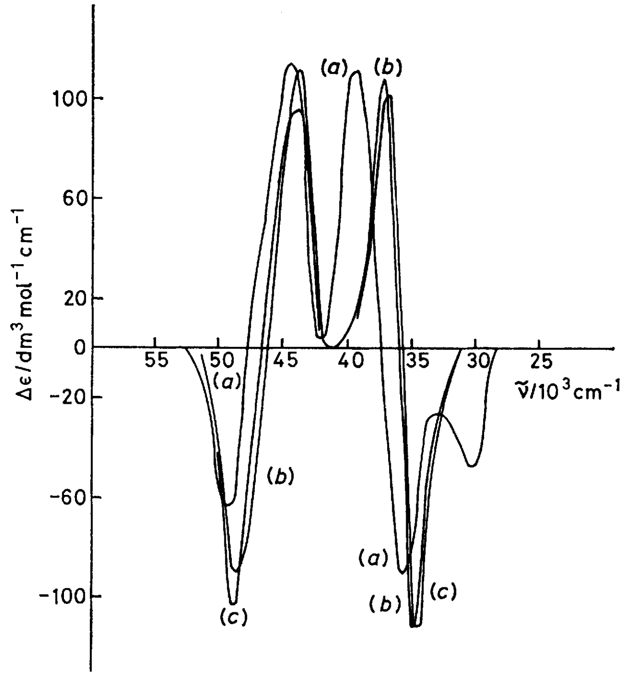

FIGURE 5 (*a*) Experimental c.d. spectrum of (2). (*b*) Calculated spectrum using zero-order polarizabilities. (*c*) As (*b*) but using first-order polarizabilities. Other details as in Figure 4

Even if the above results cannot give a definitive answer to the question of the stereochemistry of complex (2) in solution, the following conclusions can be made. (*i*) By means of the DeVoe approach it is possible to justify the high intensity as well as the shape of the c.d. spectrum in the 30 000—50 000 cm^{-1} region. The complex, therefore, must assume preferentially a chiral umbrella conformation in solution. (*ii*) The calculations allow an assignment of a maximum value (ϕ 133°) to the umbrella angle, *i.e.* the chiral umbrella conformations cannot assume an angle greater than 133° if they are to reproduce the observed c.d. spectrum. (*iii*) For each *R* or *S* chirality of the molecule there are two possible families of polarization angles around 55° or 135 and 5° which give a good fit to the experimental c.d. spectrum.

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[13] S. Merlino, personal communication.

(*iv*) The ligand chromophore is almost identical in the tetrahedral complex (1) and in the planar complex (2), only the alkyl substituent of the imine group being changed. Despite the different geometrical arrangements of the ligands around the nickel atom, it seems reasonable that the polarization angle θ_1 for the absorption band at 36 000 cm^{-1} is similar to that found [1] in the corresponding tetrahedral complex (1) ($\theta_1 \approx 68°$). Therefore the doublet $\theta_1 \approx 55$ and $\theta_2 \approx 0°$ has to be assigned to (2) and hence the dominant configuration is *R*.

EXPERIMENTAL

Some of the programs used were derived from those of Hugh *et al.*[8] Electronic-absorption and c.d. spectra were recorded on a Cary 14 spectrometer and on a Jobyn-Yvon mark III dichrograph, respectively, using dilute (10^{-4}—10^{-5} mol dm^{-3}) solutions in n-heptane.

Preparations.— 1-Hydroxynaphthalene-2-carbaldehyde, its complex with Ni^{II}, and (−)(*R*)-2-amino-3,3-dimethylbutane were prepared as previously reported.[14,15]

Bis{2-[(*R*)-1,2,2-*trimethylpropyliminomethyl*]*naphtholato*-(1−)-NO}*nickel*(II) (2). (−)(*R*)-2-amino-3,3-dimethylbutane [1.9 cm^3, 0.001 4 mol, b.p. 102—103 °C, α (298 K, 589 nm) −5.86, optical purity 91.6%] was added to the bis(1-hydroxynaphthalene-2-carbaldehydato)nickel(II) complex (1.44 g, 0.003 5 mol), suspended in anhydrous benzene (20 cm^3). The mixture was warmed and the water–benzene azeotrope eliminated. The reaction was continued for 12 h, adding anhydrous benzene to maintain the volume at *ca.* 20 cm^3. The solvent was then removed *in vacuo* and a fraction of the residue (0.50 g) was dissolved in boiling n-heptane (10 cm^3). Dark green crystals (0.15 g), m.p. 231—233 °C, were formed from the supernatant (Found: C, 71.95; H, 7.10; N, 4.95. $C_{34}H_{40}N_2NiO_2$ requires C, 72.0; H, 7.15; N, 4.95%).

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[14] M. Calvin and N. L. Mechior, *J. Amer. Chem. Soc.*, 1948, **70**, 3273.

[15] P. L. Mannella, R. Lazzaroni, and P. Salvadori, *Chimica e Industria*, 1975, **57**, 494.