species must await the results of work now in progress on their electronic absorption spectra.

From the species described above, it would appear that perfluoropinacol is a valuable addition to the range of bidentate oxygen-containing ligands and may be expected to form a variety of complexes with many metal ions.

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An Anomalous Sign Reversal in the Circular Dichroism Spectra of Tetradentate Schiff Base Complexes of Nickel(II) and Copper(II)

Sir:

In the course of an investigation of the circular dichroism (CD) spectra of a series of square-planar metal complexes with tetradentate Schiff base ligands, we have found a correlation between the sign of the Cotton effects in the d–d transition region and the presence of substituents at the azomethine carbon atoms. This observation suggests that the chelate ring conformation, rather than the absolute configuration of the amine, is of primary importance in the induction of optical activity in the metal ion chromophore by these asymmetric ligands. These results may be rationalized by assuming a corresponding inversion in the conformation of the central chelate ring, similar to that employed to detect apical coordination in tridentate amino acid chelates.[1]

The d–d band in the visible absorption spectrum of N,N′-bis(salicylidene)-*R*-(−)-propane-1,2-diamino-nickel(II) (Ni(sal)$_2$(−)pn)[2] occurs as a shoulder at 18,500 cm^{-1} ($\epsilon_{\max}$ 150) on the more intense charge-transfer band. The spectra of the corresponding complexes derived from *o*-hydroxyacetophenone (Ni(7-CH$_3$sal)$_2$(−)pn) and 2,4-pentanedione (Ni(acac)$_2$(−)pn) also exhibit single d–d bands[3] at 18,080 cm^{-1} ($\epsilon_{\max}$ 170) and 17,730 cm^{-1} ($\epsilon_{\max}$ 65), respectively. The CD spectra of these chelates in the d–d region are presented in Table I. For the latter two complexes, which have methyl groups on their azomethine carbons, the pattern of the CD bands in the d–d region is reversed, compared to Ni(sal)$_2$(−)pn. In addition, the magnitude of the CD bands is greater for the methyl-substituted compounds. Such sign reversals may be observed in previously reported ORD spectra.[3] The reversal in the CD spectra is more definitive, however, since in these closely related complexes it is reasonably certain that the low-energy CD bands correspond to the same transitions.

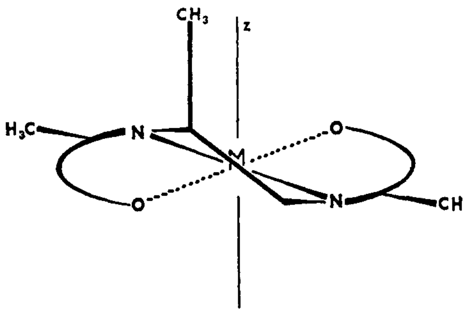
Table I. Circular Dichroism Spectra of Nickel(II) Chelates

	ν, cm^{-1}	$\Delta\epsilon_{\max}$
Ni(sal)$_2$(−)pn[2]	17,570	+0.6
	20,700	−0.4
Ni(7-CH$_3$sal)$_2$(−)pn	17,670	−5.3
	20,410 (sh)	+1.0
Ni(acac)$_2$(−)pn	17,360	−2.1
	20,200	+0.6
	22,420[a]	−2.0

[a] This band obscured by charge-transfer bands in the other compounds.

A number of crystallographic investigations have shown the central ring of these tetradentate Schiff base chelates to be nonplanar.[4] The CD results given above may be interpreted by assuming that the sign of the Cotton effect of a given d–d transition is determined by the preferred conformation of the central chelate ring. If, by analogy with coordinated 1,2-diaminopropane[5] (pn), it is assumed that in Ni(sal)$_2$(−)pn the λ conformation,[6] with the methyl group pseudo-equatorial, is favored, then the sign reversal in the CD is explained by a preference for the δ (methyl-axial) conformation in Ni(7-CH$_3$sal)$_2$(−)pn and Ni(acac)$_2$(−)pn. This methyl-axial preference in these compounds is reasonable, owing to the severe interaction between the methine methyl and an equatorial pn methyl group. The increase in magnitude of the CD is a consequence of the stronger conformational preference in the case of the methyl-substituted complexes.

The assumption of a λ conformation for the central ring in Ni(sal)$_2$(−)pn may be questioned, however, since those interactions which favor an equatorial orientation for the methyl group in chelated pn are absent in these Schiff base chelates. The crystal structure[7] of Cu(sal)$_2$(−)pn·H$_2$O in fact shows the pn methyl to be pseudo-axial, although this may be due to interaction with the coordinated water molecule. Inspection of a model of Ni(sal)$_2$(−)pn suggests that the only appreciable steric interaction is that between the methine hydrogen and pn methyl, and should tend to favor the methyl-axial, δ conformation. Similar conformational reasoning can also be used to explain the fact that the complexes Cu(gly)$_2$S(+)pn and Cu(gly)$_2$RR(−)chxn (gly = glycyl, chxn = 1,2-diaminocyclohexane) have low-energy CD bands with the same sign.[8] In-plane methyl–oxygen interaction may favor the axial position for the pn methyl, so that Cu(gly)$_2$(+)pn will have a central ring



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[8] M. Parris and A. E. Hodges, *J. Amer. Chem. Soc.*, **90**, 1909 (1968).

with predominantly the same λ conformation as that in the rigid Cu(gly)$_2$(−)chxn, and hence a Cotton effect of the same sign, but smaller magnitude.

An alternative explanation of the CD results, which does not depend on a conformational inversion, may be that in Ni(7-CH$_3$sal)$_2$(−)pn and Ni(acac)$_2$(−)pn the methyl–methyl interaction can only be relieved by distortion of the donor atom symmetry from planarity, as shown in **1**.

In Ni(sal)$_2$(−)pn the optical activity of the d–d transitions results from perturbation of the nondissymmetric, planar NiO$_2$N$_2$ (C$_{2v}$) chromophore by the central ring helicity. The NiO$_2$N$_2$ chromophore is itself dissymmetric (C$_2$) in the other two complexes, the side rings conferring helicity which is right-handed (with respect to the vertical axis), and opposite to that of the central ring.

The copper(II) complexes of the same three ligands show similar sign reversals.[9] This study is being extended to other compounds of the series, in order to make band assignments and provide further tests of the ideas introduced above.

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Book Reviews

Spectroscopic Techniques for Far Infra-red, Submillimetre and Millimetre Waves. Edited by D. H. MARTIN, Queen Mary College, University of London. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1967. vii + 389 pp. 16 × 23 cm. $18.00.

To chemists the far-infrared region, defined by the Triple Commission on Spectroscopy as the range in wavelengths of 50–1000 μm or in wave numbers of 200–10 cm^{-1}, has been of limited usefulness because of the difficulties of working in the region. These have slowly yielded to improvements in instrumentation. Double-beam spectrometers and small interferometers for the far-infrared can now be purchased commercially, though they are still expensive and rather temperamental. The present volume is a collection of seven authoritative articles written by physicists on the instrumentation and methods of spectrometry in the region and the adjacent millimeter wavelength range.

The article titles are Spectrometry between 3 cm^{-1} and 200 cm^{-1}, Fourier Transform Spectroscopy, Grating Spectroscopy, Detectors, Harmonic Generators and Semiconductor Detectors, Coherent Sources Using Electron Beams, and Techniques of Propagation at Millimeter and Submillimeter Wavelengths. The first article, by the editor, D. H. Martin, compares the merits of interferometry and grating spectrometry and concludes strongly in favor of the former. The second, by P. L. Richards, gives the details on which one can base such a conclusion. The third, by G. R. Wilkinson and the editor, is the one likely to be of most interest and usefulness to chemists. In it attention is devoted to small grating instruments for the far-infrared, sample handling techniques, assessment of instrumental performance, and wave-number calibration. The content of the remainder of the articles, as indicated by their titles, is of less general interest to chemists. In short, this is a book in which the chemist can find expert knowledge of the techniques of far-infrared and millimeter-wave spectroscopy but will obtain little indication of the kind of chemical problems for which the techniques are useful.

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Rotational Spectra and Molecular Structure. By JAMES E. WOLLRAB. Research Division, McDonnell Douglas Corporation, St. Louis, Mo. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1967. xiii + 468 pp. 16 × 23.5 cm. $20.00.

Microwave spectroscopy of gases has steadily grown in the number of its practitioners and in the range of its applications, especially to chemistry. This book will be welcomed by those who are working in this field because it is a very complete and quite thorough summary of the principal theoretical treatments needed to extract useful information from this branch of spectroscopy. Much of the contents will be relevant also to other branches of spectroscopy where rotational fine structure is resolved. There is also a chapter outlining the basic kinds of microwave spectrometers and their components. An extensive, organized bibliography and a number of useful tables add to the value of the book.

The casual reader seeking a quick idea of what the subject is about and what its main applications are may wish to turn elsewhere; this is a book with a considerable coverage of the mathematical formulas useful in interpreting spectra. On the other hand, limitations of space prevented the complete derivation of many of the equations, although the references are given.

The topics covered include the theory of the energy levels and transitions of the rigid rotor, effects of centrifugal distortion, coriolis coupling and Fermi resonance, methods of determining molecular structure from rotational spectra, theory of nuclear quadruple coupling, effect of internal rotation, inversion, and electric and magnetic fields. There are a number of appendices containing derivations of some of the formulas, an up-to-date table of barriers to internal rotation, as well as the extensive bibliography.

This book should be especially useful as a quite thorough guide to the literature and especially to the considerable literature of quantum-mechanical derivations carried out to provide the equations needed to extract molecular structures, dipole moments, force constants, nuclear field gradients, barriers to internal rotation, inversion barriers, conformations, and magnetic moments from observed microwave spectra.

The basic book of Townes and Schawlow carries an authority that is not likely to be challenged, but there has been considerable progress in the field since it was published in 1954. Therefore it is very gratifying to have an up-to-date, well-organized, and quite thorough new book made available.

Any work with as many equations as this one is bound to contain some misprints and errors and this reviewer found a few, but the number seems very acceptable.

The book is well indexed and well printed in a pleasant and readable type and format. It will surely be important to all workers in the field; the only serious regret this reviewer has is the price, which seems somewhat high.

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1,2-Cycloaddition Reactions. The Formation of Three- and Four-Membered Heterocycles. By LINDA LEE MULLER and JAN HAMER, Department of Chemistry, Tulane University, New Orleans, La. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1967. x + 362 pp. 16 × 23.5 cm. $15.00.

This Interscience monograph presents the first exhaustive survey of 1,2-cycloaddition reactions, which give rise to three- and four-