Circular Dichroism of Square-Planar, Tetradentate Schiff-Base Chelates of Nickel(II)

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Abstract: The circular dichroism (CD) and electronic absorption spectra of a series of ten nickel(II) complexes with tetradentate Schiff bases derived from (*R*)-(−)-propane-1,2-diamine and (*R*,*R*)-(−)-cyclohexane-1,2-diamine have been measured in chloroform solution. The signs of the Cotton effects of the electronic transitions can be correlated with the preferred conformation of the central (*gauche*) chelate ring, which is produced by the stereochemical requirements of the ligands. The CD spectra of these compounds, in general, reveal more band multiplicity than do the corresponding absorption spectra. By appeal to molecular orbital treatments and comparison with published spectral data for related compounds, transition assignments for the ligand-field bands in the CD spectra can be proposed. Optically active, tetradentate Schiff-base chelates are useful compounds for the study of the electronic structures of transition metal ions in square-planar geometries, using the optical rotatory dispersion (ORD) or, preferably, the circular dichroism (CD) technique. In addition, it is of interest to ascertain to which stereochemical features of the molecules the signs and magnitudes of the Cotton effects are most sensitive, since such information is prerequisite for the investigation of conformation and chirality in metal chelates.

The early ORD studies[1] by Pfeiffer on complexes of the present type were extended[2] by Terent'ev. While the present work was in progress, Bosnich reported[3] on an intensive study of a single member of the series N,N′-bis(salicylidene)-(*R*)-(−)-propane-1,2-diaminonickel(II), Ni(sal)$_2$(−)pn. Recent papers from this laboratory have dealt with the CD of copper(II) complexes[4] of the same series of ligands, and have described some preliminary results in the nickel series.[5] The series of complexes to be discussed consists of N,N′-bis(salicylidene)-(*R*)-(−)-propane-1,2-diaminonickel(II),(Ni(sal)$_2$(−)pn), and chelates derived from *o*-hydroxyacetophenone (H-7-Mesal); 2,4-pentanedione (Hacac); *o*-aminobenzaldehyde (Haba); pyrrole-2-carboxaldehyde (Hpca); and methyl pyrrol-2-yl ketone (Hmpk); with (*R*)-(−)-propane-1,2-diamine ((−)pn), and (R,R)-(−)cyclohexane-1,2-diamine ((−)chxn). In these compounds, the optical activity of the metal ion chromophore is induced by the chiral ligands. The limited amount of distortion from planarity permitted by these ligands, and the fact that the chelates are soluble in nondonor solvents, enables the square-coordinated, d^8 nickel(II) ion to be studied in the absence of complications due to the presence of significant proportions of pseudotetrahedral or pseudotetragonal species, with triplet ground states.

Experimental Section

For the sources of the materials employed, the methods of preparation of the Schiff-base ligands, and details of most of the physical measurements, a previous paper[4] may be consulted.

Nickel(II) Chelates. The chelates were prepared by literature methods, *cf.* Table I, except for Ni(7-Mesal)$_2$(−)chxn and Ni(mpk)$_2$(−)pn. The former compound was prepared by adding to an absolute methanol solution, containing the ligand (H-7-Mesal)$_2$-(−)chxn (0.002 mol) and triethylamine (0.004 mol), an absolute methanol solution of nickel sulfate hexahydrate. After stirring at room temperature for a 0.5 hr, the orange needles that precipitated were suction filtered off, recrystallized from toluene, and dried at 80° *in vacuo*. To prepare Ni(mpk)$_2$(−)pn, tetraethylammonium tetrachloronickelate(II)[6] (0.002 mol) and sodium methoxide (0.004 mol), as solutions in absolute methanol, were added successively to an absolute methanol solution containing (−)pn (0.002 mol) and methyl pyrrol-2-yl ketone (0.004 mol), prepared by the method of Dorofeenko.[7] The solution was refluxed for 1 hr, cooled, filtered, and evaporated to dryness, and the orange product recrystallized from benzene.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Gaussian analyses of some of the CD spectra were carried out with the aid of a Du Pont Model 310 curve resolver.

Results and Discussion

Characterization data for the series of nickel(II) complexes are presented in Table I. Chelates **3**, **5**, **7**, **8**, and **9** are described for the first time; **4** and **10** have not previously been reported in their optically active forms. The elemental analyses, osmometric molecular weights, and infrared and visible absorption spectra are consistent with their formulation as anhydrous, monomeric, square-planar, Schiff-base chelates. As was also found[4] in the copper series, it proved impossible to prepare the chelates of (Hacac)$_2$(−)chxn, and the similarly crowded compound Ni(7-Mesal)$_2$(−)chxn could not be obtained from aqueous solvents.

Electronic Spectra in Chloroform. Ultraviolet and visible solution spectra have been reported[8–11] for a number of nickel(II) complexes of the present type. Substitution of propane-1,2-diamine or cyclohexane-1,2-diamine for ethylenediamine in these complexes produces little change in the electronic spectra. The electronic spectral data for the present series of nickel(II) chelates are presented in Table II and representative spectra are shown in Figures 1 and 2.

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(1) P. Pfeiffer, W. Christeleit, Th. Hesse, H. Pfitzner, and H. Thielert, *J. Prakt. Chem.*, 150, 261 (1938).

(2) (a) A. P. Terent'ev, G. V. Panova, and E. G. Rukhadze, *J. Gen. Chem. USSR*, **34**, 3049 (1964); (b) A. P. Terent'ev, G. V. Panova, E. G. Rukhadze, and N. M. Viktorova, *ibid.*, **34**, 3060 (1964); (c) *ibid.*, **35**, 1109 (1965).

(3) B. Bosnich, *J. Amer. Chem. Soc.*, 90, 627 (1968).

(4) R. S. Downing and F. L. Urbach, *ibid.*, **91**, 5977 (1969).

(5) R. S. Downing and F. L. Urbach, *ibid.*, 90, 5344 (1968).

(6) N. S. Gill and F. B. Taylor, *Inorg. Syn.*, **9**, 140 (1967).

(7) G. N. Dorofeenko, A. P. Kucherenko, and N. V. Prokov'eva, *J. Gen. Chem. USSR*, **33**, 580 (1963).

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(9) S. Crawford, *Spectrochim. Acta*, **19**, 255 (1963).

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(11) G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).

Table I. Characterization Data for the Nickel(II) Chelates

	Compound	Prepn method ref	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	$\bar{\nu}_{str}$(C=N), cm^{-1}
1	Ni(sal)$_2$(−)pn	1	60.23	60.18	4.76	4.76	8.27	8.42	1615
2	Ni(7-Mesal)$_2$(−)pn	2b	62.17	61.89	5.49	5.38	7.64	7.42	1605
3	Ni(aba)$_2$(−)pn	12	60.58	60.37	5.38	5.64	16.62	16.67	1610
4	Ni(pca)$_2$(−)pn	13	54.79	54.73	4.95	4.93	19.65	19.81	1580[a]
5	Ni(mpk)$_2$(−)pn	This work	*b*		*b*		*b*		1575[a]
6	Ni(acac)$_2$(−)pn	2c	52.93	53.22	6.83	6.81	9.50	9.40	1500
7	Ni(sal)$_2$(−)chxn	2c	63.37	63.37	5.32	5.23	7.39	7.28	1620
8	Ni(7-Mesal)$_2$(−)chxn	This work	64.90	65.47	5.94	6.04	6.88	6.42	1600
9	Ni(aba)$_2$(−)chxn	12	63.69	63.59	5.88	5.89	14.86	14.70	1590
10	Ni(pca)$_2$(−)chxn	13	59.12	59.44	5.58	5.67	17.24	17.44	1575[a]

[a] Doublet. [b] No analytical data found owing to small sample of complex.

In the benzenoid complexes, the $\pi \rightarrow \pi^*$ transition associated with the benzene ring occurs[3] at a frequency (39,000 cm^{-1}) close to that in the free ligands. At about 30,000 cm^{-1} occurs another intense band, presumed[3] to be due to the ligand $\pi \rightarrow \pi^*$ transition which is associated chiefly with the azomethine chromophore. This also is shifted only slightly from its position in the ligands, but the band shows structure—up to three components in, *e.g.*, Ni(7-Mesal)$_2$(−)pn (see Table II)—which is not seen in the ligands.

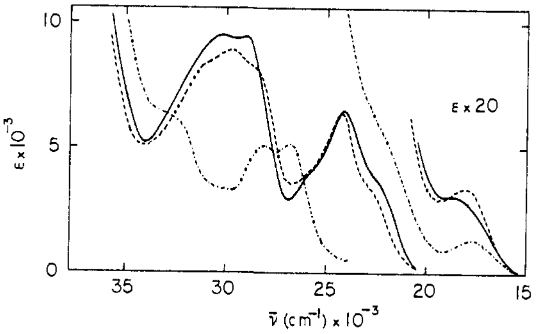

Figure 1. Electronic absorption spectra, in chloroform, of Ni(sal)$_2$(−)pn (——), Ni(7-Mesal)$_2$(−)pn (- - - -), and Ni(acac)$_2$(−)pn (-·-·-·).

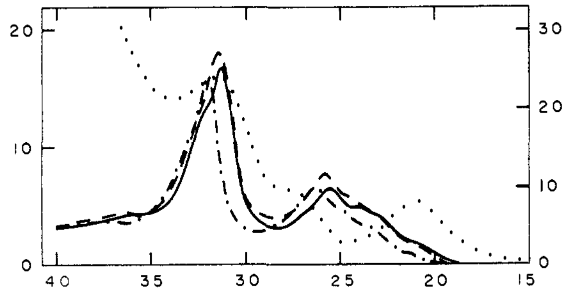

Figure 2. Electronic absorption spectra, in chloroform, of Ni(pca)$_2$(−)pn (——), Ni(pca)$_2$(−)chxn (- - - -), Ni(mpk)$_2$(−)pn (-·-·-·), and Ni(aba)$_2$(−)pn (. . . . .) (right-hand coordinates).

Dominating the visible spectra of these chelates is a band occurring at 21,000–27,000 cm^{-1}, with ϵ_{max} 5000–10,000, and showing considerable structure. This is considered to originate in charge-transfer transitions, and detailed assignments for the chelate Ni(sal)$_2$(−)pn have been proposed by Bosnich.[3] For the complexes containing the NiN$_2$O$_2$ chromophore only, there is a shoulder with ϵ ranging from 65 to 400 (see Table II) on the low-energy side of this charge-transfer band. It is generally agreed that this feature encompasses the several possible d–d transitions. For the chelates which contain the NiN$_4$ chromophore, no weak low-energy shoulder is observed. This may be attributed to the fact that in the NiN$_4$ chelates the charge-transfer bands appear at lower energies, presumably obscuring the d–d transitions.

Table II. Electronic Spectra of the Nickel(II) Chelates in Chloroform

Compound	$\bar{\nu}$, cm^{-1} (ϵ_{max})
Ni(sal)$_2$(−)pn	18,600[a] (150); 22,800[b] (4000); 24,200 (7500); 25,500[b] (4300); 29,100[a] (9400); 30,200 (9500); 38,800 (59,000)
Ni(7-Mesal)$_2$(−)pn	18,200[a] (170); 22,800[b] (3300); 24,400 (6500); 25,800[b] (4100); 28,900[b] (8400); 29,800 (8900); 31,000[b] (8400); 39,100 (56,000)
Ni(aba)$_2$(−)pn	20,800 (5200); 27,800[a] (6200); 30,300 (11,400); 38,600 (25,000)
Ni(pca)$_2$(−)pn	20,700[b] (2500); 22,700[b] (5900); 23,900[a] (7400); 25,500 (9700); 26,800[b] (6800); 31,300 (25,000); 31,900[b] (21,000); 35,600[a] (6600)
Ni(mpk)$_2$(−)pn	21,700[a] (1870); 23,600[a] (4880); 25,100[a] (7350); 26,300 (10,000); 27,600[a] (6800); 32,000 (23,800); 37,000 (5360)
Ni(acac)$_2$(−)pn	17,700 (65); 22,500[b] (300); 26,800 (5200); 28,100 (5100); 33,200[b] (5800); 36,800 (16,000)
Ni(sal)$_2$(−)chxn	18,700[a] (140); 22,800[b] (4000); 24,200 (7200); 25,600[b] (4200); 29,000 (8500); 31,200 (8600); 38,900 (59,000)
Ni(7-Mesal)$_2$(−)chxn	19,400[b] (450); 22,500[b] (1800); 24,900 (6500); 29,700[a] (6200); 38,500 (36,000)
Ni(aba)$_2$(−)chxn	11,800[b] (11); 20,800 (5100); 27,600[b] (6100); 31,600 (14,000); 40,300 (37,000)
Ni(pca)$_2$(−)chxn	21,200[b] (2800); 23,000[b] (6500); 24,500[b] (8600); 25,800 (12,000); 31,500 (27,000); 32,300[b] (20,000); 36,000 (6700)

[a] Shoulder. [b] Inflection.

Circular Dichroism Spectra in Chloroform. The CD spectral data for the nickel(II) complexes are presented in Table III, and representative spectra are illustrated in Figures 3–6. These spectra are considerably more complex than those[4] of the copper(II) series, owing to the

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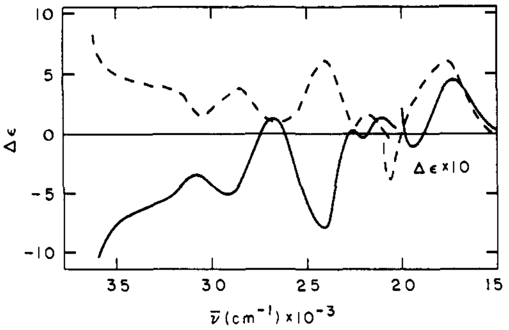

Figure 3. Circular dichroism spectra, in chloroform, of $Ni(sal)_2(-)chxn$ (——) and $Ni(sal)_2(-)pn$ (- - - -).

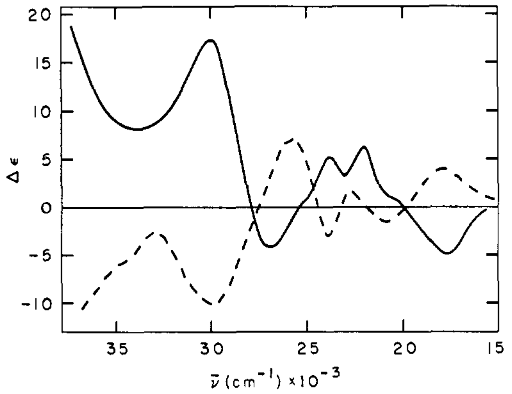

Figure 4. Circular dichroism spectra, in chloroform, of $Ni(7\text{-}Mesal)_2(-)pn$ (——), and $Ni(7\text{-}Mesal)_2(-)chxn$ (- - - -).

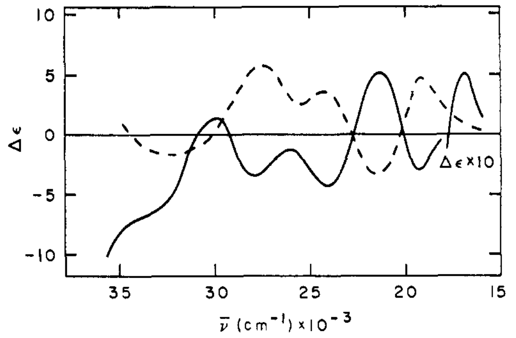

Figure 5. Circular dichroism spectra, in chloroform, of $Ni(aba)_2(-)chxn$ (——) and $Ni(aba)_2(-)pn$ (- - - -).

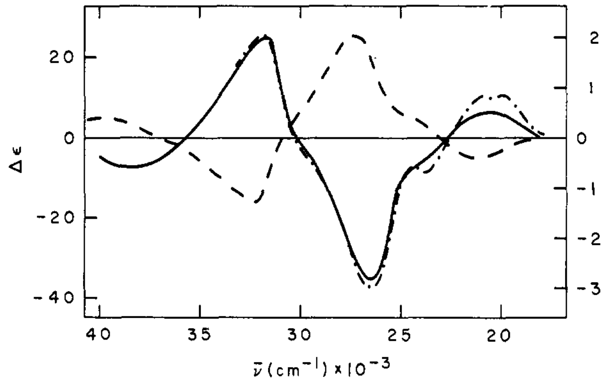

Figure 6. Circular dichroism spectra, in chloroform, of $Ni(pca)_2(-)chxn$ (——) (left-hand coordinates), $Ni(mpk)_2(-)pn$ (- - - -) (left-hand coordinates), and Ni $(pca)_2(-)pn$ (-·-·-·) (right-hand coordinates).

strong charge-transfer bands interposed between the d–d and ligand bands. However, careful comparison of the spectra of the entire series reveals that, for the benzenoid compounds, the spectra of the complexes derived from *R*(−)pn bear a mirror image relationship to those of their counterparts in the *RR*(−)chxn series, although the parent diamines have the same absolute configuration.[14] This was also found[4] for the copper(II) complexes, and is contrary to the situation in the free ligands, where corresponding bands have the same sign. The mirror image relationships between the *R*(−)pn nickel(II) complexes and their *RR*(−)chxn counterparts are not as readily apparent as was observed for the copper(II) series.[4] The slight discrepancies in this relationship in the nickel(II) series are attributed to the increased complexity of the nickel(II) CD spectra. Overlapping, oppositely signed CD bands tend to cancel and obscure the overall mirror image relationship. This relationship is most clearly seen in a comparison of $Ni(7\text{-}Mesal)_2(-)pn$ and $Ni(7\text{-}Mesal)_2(-)chxn$ (Figure 4) and in Figure 5, $Ni(aba)_2(-)pn$ *vis-à-vis* $Ni(aba)_2(-)$-chxn. It is therefore proposed that in the nickel(II) series also, the sign of the Cotton effect associated with a given transition reflects the conformation of the central (*gauche*)[15] chelate ring. In the (−)chxn Schiff-

Table III. Circular Dichroism Spectra of the Nickel(II) Chelates in Chloroform

Compound	$\bar{\nu}$, cm^{-1} ($\Delta\epsilon$)
$Ni(sal)_2(-)pn$	17,600 (0.58) (II);[a] 20,700 (−0.39) (III); 21,800 (1.8) (IV); 24,000 (6.1) (VI); 28,700 (3.5); 32,800[b] (4.1); 38,200 (15)
$Ni(7\text{-}Mesal)_2(-)pn$	17,700 (−5.0) (I); 20,400[b] (0.75); 22,000 (6.1) (IV); 23,800 (5.1) (VI); 25,200[b] (0.75); 26,700 (−3.5); 29,900 (16); 38,200 (25)
$Ni(aba)_2(-)pn$	19,200 (4.3) (IV); 21,400 (−3.5) (V); 24,100 (3.4) (VI); 27,500 (5.6); 31,900 (−1.1)
$Ni(pca)_2(-)pn$	20,000 (0.92) (I); 20,800 (0.95); 23,800 (−0.73); 26,500 (−3.3); 31,800 (2.1)
$Ni(mpk)_2(-)pn$	21,000 (−5.2); 24,600 (5.8); 27,600 (28); 30,100[b] (6.0); 32,100 (−18); 39,600 (5.4)
$Ni(acac)_2(-)pn$	17,400 (−2.0) (I); 20,200 (0.053) (II); 22,400 (−1.9) (III); 24,100[b] (1.3); 26,200 (17); 27,400[b] (8.3); 29,500[c] (2.1); 33,100[c] (5.1); 35,800 (17)
$Ni(sal)_2(-)chxn$	17,300 (0.48) (I); 19,400 (−0.12) (II); 21,100 (1.4) (III); 22,000 (−0.40) (IV); 22,600 (0.35) (V); 24,200 (−8.0) (VI); 26,800 (1.4); 29,200 (−5.1); 33,900[b] (−5.9); 38,300 (−22)
$Ni(7\text{-}Mesal)_2(-)chxn$	17,800 (4.1) (I); 20,800 (−1.7); 22,500 (1.9) (V); 23,800 (−3.0) (VI); 25,600 (7.3); 29,800 (−10); 38,200 (−19)
$Ni(aba)_2(-)chxn$	16,900 (0.51) (I); 19,300 (−3.1) (IV); 21,400 (5.2) (V); 24,000 (−4.4) (VI); 27,900 (−3.5); 29,900 (1.3); 33,300[c] (−6.4); 37,500 (−19)
$Ni(pca)_2(-)chxn$	20,300 (6.5); 24,000[b] (−6.5); 26,500 (−37); ; 31,600 (25); 38,300 (−7.3)

[a] See text for band designations. [b] Inflection. [c] Shoulder.

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(14) R. D. Gillard, *Tetrahedron*, **21**, 503 (1965).

(15) G. R. Clarke, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 223 (1968), and previous papers in this series.

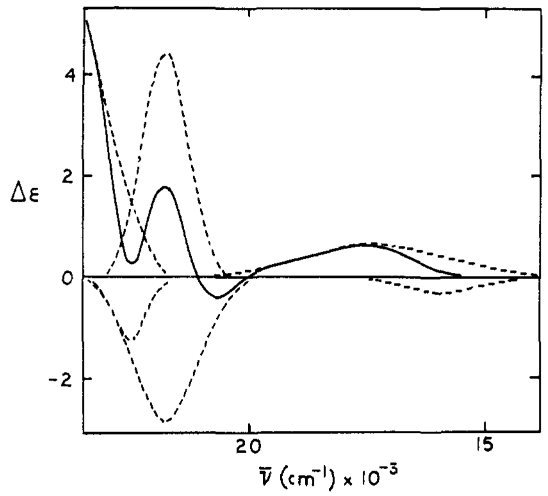
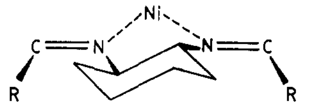


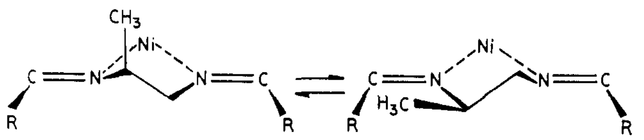
Figure 7. Gaussian components of the low-energy region of the circular dichroism spectrum of Ni(sal)$_2$(−)pn.

base chelates, the central chelate ring is locked stereospecifically in the λ[16] conformation, **1**, while in the (−)pn series, the preference for the opposite, δ[16] conformation, **2**, can be ascribed to the in-plane 1,3 interaction between the hydrogen or methyl group at the azomethine carbon, and the pn methyl group when equatorial (λ conformation, **3**). The signs of the ligand-field CD bands of Ni(acac)$_2$(−)pn are the same as those of Ni(7-Mesal)$_2$(−)pn, and it is proposed that in this complex also, the δ, methyl-axial conformation predominates.



λ

1



δ

2

λ

3

A similar correlation to the above was found[4] to apply to the copper(II) series of chelates. However, in contrast to the zinc(II)[3] and copper(II)[4] complexes, none of the benzenoid chelates of the nickel(II) series exhibits CD "couplets"[17] interpretable[3] as exciton components of the $\pi \rightarrow \pi^*$ band of the azomethine chromophore. It is not possible to ascertain whether this is because the nickel complexes are insufficiently distorted from planarity to cause such splitting,[3,18] or whether one of the exciton components is canceled by a charge-transfer band of opposite sign and similar energy.

The low-energy CD of Ni(sal)$_2$(−)pn, as analyzed[3] by Bosnich, is anomalous[5] in that band I, in contrast to all the other compounds of the series, has the same sign as band II, violating the mirror image relationship of the spectrum to that of Ni(sal)$_2$(−)chxn. The Gaussian analysis of Bosnich[3] has been found by us to be reproducible, but it is not unambiguous, and the alternative analysis, shown in Figure 7, gives band I a positive sign, bringing this spectrum into line with the remainder of the series, and removing the apparent anomaly.

In contrast to the situation existing in the benzenoid complexes, the corresponding CD bands of Ni(pca)$_2$-(−)pn and Ni(pca)$_2$(−)chxn have the same sign. This was also found[4] for the copper(II) complexes, and the tentative hypothesis was advanced that the smaller side rings (five membered, compared to six membered in the benzenoid compounds) reduced the in-plane steric interaction between the azomethine hydrogen and the pn methyl to the point where it no longer favored the δ conformation of the central chelate ring. Support for this argument in the nickel case is provided by the complex Ni(mkp)$_2$(−)pn (the corresponding copper chelate could not be made). In Ni(mpk)$_2$(−)pn the methyl–methyl interaction should be large enough to favor the δ conformation, and the signs of the CD bands are indeed opposite to those of Ni(pca)$_2$(−)chxn (stereospecifically λ) and Ni(pca)$_2$(−)pn. The rotatory strengths of the three compounds are in line with the predicted degree of stereoselectivity, *i.e.*, Ni(pca)$_2$(−)-chxn > Ni(mkp)$_2$(−)pn > Ni(pca)$_2$(−)pn.

Band Assignments. In the electronic spectra of square-planar nickel(II) complexes, theory predicts[19,20] that three or four transitions, depending on the symmetry of the complex, should occur within the d-orbital manifold of the metal ion. For the compounds of the present series which contain the NiN$_2$O$_2$ chromophore, up to three d–d bands are seen in the CD, corresponding to the single shoulder in the absorption spectra. By reference to other square-planar nickel(II) complexes,[21,22] whose electronic structures should be similar, it is proposed that bands I and II originate in the transitions $d_{x^2-y^2} \rightarrow d_{xy}$ ($^1A_1 \rightarrow {}^1B_2$) and $d_{z^2} \rightarrow d_{xy}$ ($^1A_1 \rightarrow {}^1B_2$) (in C_{2v} symmetry, and using the coordinate convention of Belford[19]). In contrast to the corresponding copper complexes,[4] donor solvents such as pyridine have little effect on the spectra, and it is not at present possible to make a more specific assignment. Band III, which is confirmed as a d–d band in the case of Ni(acac)$_2$(−)pn by the low intensity (ϵ 300) of the corresponding shoulder in the absorption spectrum (obscured by a charge-transfer band in the other members of the series), is proposed to originate in the transitions $d_{xz} \rightarrow d_{xy}$ ($^1A_1 \rightarrow {}^1A_1$) and $d_{yz} \rightarrow d_{xy}$ ($^1A_1 \rightarrow {}^1B_1$), since the d_{xz} and d_{yz} orbitals are not expected to differ much in energy in these compounds.[3]

Unlike the NiN$_2$O$_2$ complexes, those containing the NiN$_4$ chromophore do not show d–d bands in their absorption spectra. However, in the CD, a weak band (see Table III), at longer wavelength than that corresponding to the lowest energy component of the charge-transfer absorption band, is doubtless the counterpart of band I in the NiN$_2$O$_2$ chelates. As in the NiN$_2$O$_2$ chelates, its sign is negative in the (−)pn and positive in the (−)chxn complexes.

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Corresponding to the intense (ϵ 5000–12,000), structured charge-transfer band in the visible region (Table II) are found several distinct CD bands, interpreted, following Bosnich,[3] as originating in transitions from d orbitals to the azomethine π^* (a_2, b_1, in the coordinate scheme of Belford[19]) orbitals. For the benzenoid complexes, a consistent assignment of these bands can be proposed. Bands IV and V (see Table III), whose signs are positive and negative, respectively, in the complexes derived from (−)pn, and the opposite in the (−)chxn chelates, are attributed to transitions from the $d_{x^2-y^2}$ and d_{z^2} orbitals to a_2, b_1 (π^*) ($^1A_1 \rightarrow {}^1A_2$, $^1B_1$), although, as for the d–d transitions, it is not possible to say which is which. Band VI (positive in the (−)pn chelates, negative in the (−)chxn chelates) is assigned to the transitions d_{xz} and/or $d_{yz} \rightarrow a_2$, b_1 (π^*) ($^1A_1 \rightarrow {}^1B_1$, $^1A_2$, $^1B_1$, $^1A_2$). The superior resolution of the CD spectrum of $Ni(sal)_2$(−)chxn, compared to that of $Ni(sal)_2$(−)pn, has made necessary a slight modification of the assignments of Bosnich[3] for the latter compound.

At still higher energies the CD spectra reveal little more detail than the absorption spectra. It is clear however, that in the uv further new bands appear on complexation, which probably have their origin in change-transfer transitions of the ligand (σ or π) to metal type.

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Azidoruthenium(III) Complexes as Precursors for Molecular Nitrogen and Nitrene Complexes

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Abstract: The generality of the reaction whereby azidoruthenium(III) complexes are converted into nitrogen–ruthenium(II) complexes has been studied. Several new azidoruthenium(III) complexes have been prepared, and their ease of conversion into molecular nitrogen complexes has been studied, kinetically and otherwise. In the presence of acid, the reaction is more rapid; the products include ruthenium(II) nitrogen-bridged dimers and nitrogen–ruthenium(II) monomeric compounds. The products of the reaction are interpreted in terms of a reactive intermediate which is nitrene, NH, coordinated to the ruthenium ion.

Recent studies[1,2] have shown the azidopentaammineruthenium(III) species to be unstable toward decomposition to nitrogenpentaammineruthenium(II).

$$[Ru(NH_3)_5N_3]^{2+} \longrightarrow [Ru(NH_3)_5N_2]^{2+} + {}^1/_2N_2 \qquad (1)$$

This reaction was found to occur for several other azidoruthenium(III) complexes, in solution and in the solid state, and was investigated as a possible source of new nitrogen–ruthenium(II) compounds. Kinetic data for the solution reaction are reported in a variety of organic solvents. In the presence of acid, the reaction becomes more rapid and the products are more complex, yielding dimeric nitrogen-bridged complexes in addition to the monomeric nitrogenruthenium species of eq 1. Kinetic data were also collected for the acid reaction, and a qualitative interpretation of these is given.

The mechanism was investigated and is postulated to involve cleavage of a N–N bond in the azide ligand as the rate-determining step. This cleavage releases nitrogen gas and results in the formation of a metalated nitrene intermediate. While the production of nitrene species *via* the action of ultraviolet light or acid on organic azides is well established,[3,4] no similar reaction has been previously described for metal azide complexes. The stabilization of nitrenes by coordination to transition metals has been hypothesized,[5] but little evidence is available for the existence of such species. A copper–nitrene intermediate has been proposed in the copper-catalyzed decomposition of benzenesulfonylazide,[6] and recent studies indicate that nitrenes may be trapped as ligands in metal carbonyl complexes.[7,8] The ruthenium–nitrene species reported here are reactive and are attacked by a variety of Lewis bases. The reactivity of the ruthenium nitrene is dependent upon the nature of the inert ligands coordinated to the metal, the oxidation state of the ruthenium, and the initial concentration of acid used and of the azide complex.

Experimental Section

Preparation of Compounds. ***cis*-Diazidobis(ethylenediamine)ruthenium(III) Hexafluorophosphate.** *cis*-$[Ru(en)_2Cl_2]Cl \cdot H_2O$[9] (0.200

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