benzene was refluxed with stirring under nitrogen for 24 hr. After cooling, the orange-yellow solution was filtered and the residue washed with a small amount of ether. The combined filtrate was evaporated on a rotary evaporator; the residue was dissolved in benzene and chromatographed on Florisil with benzene as eluent to give 240 mg (89%) of yellow crystals of $C_5Me_5Ir(CO)_2$, mp 145–148° dec. This compound is very soluble in organic solvents and could also be sublimed at 50° (10^{-2} mm). It is air stable for a few days. The infrared spectrum shows strong ν_{CO} at 1925 and 2000 cm^{-1}.

It could also be prepared from $[C_5Me_5IrCl_2]_2$ and $Fe_2(CO)_9$, and as follows. Carbon monoxide was bubbled into the suspension of $[C_5Me_5IrCl_2]_2$ (100 mg) and anhydrous sodium carbonate (50 mg) in 30 ml of ethanol with stirring at 70° for 3 hr. The orange-yellow solution was filtered and the solvent was evaporated under reduced pressure. The residue was extracted with benzene, the solvent removed, and the residue purified by sublimation at 50° (10^{-2} mm); yield 65 mg (62%) of $C_5Me_5Ir(CO)_2$.

Attempts to prepare $C_5Me_5Rh(CO)_2$ by any of these routes led only to very unstable materials which showed complex absorptions in the carbonyl stretching region of the infrared but were not otherwise characterized.

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The Circular Dichroism of Square-Planar, Tetradentate Schiff Base Chelates of Copper(II)[1]

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Abstract: The circular dichroism (CD) and electronic absorption spectra of a series of nine copper(II) complexes with tetradentate Schiff bases derived from (*R*)-(−)-propane-1,2-diamine and (*RR*)-(−)-cyclohexane-1,2-diamine have been measured in chloroform and in pyridine. The signs of the Cotton effects of d–d and ligand transitions for this series of complexes can be correlated with the absolute configuration of a proposed flattened tetrahedral array of donor atoms about the copper ion. This configuration is produced stereospecifically by the conformational preference of the central (*gauche*) chelate ring which results from the steric requirements of the ligands. The circular dichroism spectra of these complexes reveal more detailed band splittings in the d–d transition region than do the corresponding electronic spectra. By comparison of these CD bands with published polarized crystal spectra, tentative assignments of the metal ion transitions are proposed. Solvent effects, when they are not precluded by steric interactions, assist in the assignment of the metal ion transitions.

The circular dichroism (CD) spectra of transition metal complexes have been extensively studied in recent years, as their interpretation can yield valuable information concerning the origin of absorption bands in the electronic spectra of the complexes.[2] In addition, the sensitivity of circular dichroism to molecular structure makes the technique valuable for investigating the conformations and configurations of chelate molecules.[3]

The majority of previous investigations of optically active complexes have dealt with the inert, dihedral chelates of d^3 and d^6 metal ions.[2] The study of complexes in which the optical activity is induced by means of active ligands, however, is also of great interest.[3] Several important studies of this type have appeared,[4–7] but no extensive study of a series of related compounds has been carried out to provide generalizations regarding the effect of the extra-chromophoric portion of the molecule on the optical activity of the metal ion transitions. Such correlations, involving the 3000-Å absorption of the carbonyl chromophore, are very familiar.[8] Since the n → π* transition of the carbonyl chromophore, like metal ion d–d transitions, is an example of a magnetic-dipole-allowed transition which is formally parity forbidden but acquires electric-dipole intensity by means of a noncentrosymmetric perturbation,[9] it is of interest to compare structure–activity relationships in the two systems. For the copper(II) ion, attempts have been made to see to what extent the optical activity of the d–d transitions is governed by symmetry rules,[10–12] similar to the octant rule[8] for the carbonyl group.

Since the initial study[13] of the optical rotatory dispersion (ORD) of chelates of the type described here,

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[1] Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract INOR-76.

[2] R. D. Gillard in "Physical Methods in Advanced Inorganic Chemistry," H. A. O. Hill and P. Day, Ed., Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1968, Chapter 5, and references therein.

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[10] K. M. Wellman, W. Mungall, T. G. Mecca, and C. R. Hare, *J. Amer. Chem. Soc.*, **89**, 3647 (1967).

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other workers have extended the ORD studies to similar systems,[14] and the CD spectra of nickel(II),[4,15] zinc(II),[4] and oxovanadium(IV)[16] chelates have been reported. This paper reports on the electronic and CD spectra of a series of nine square-planar copper(II) complexes; *viz.*, N,N′-bis(salicylidene)-(*R*)-(−)-propane-1,2-diaminocopper(II) (Cu(sal)$_2$(−)pn), and chelates derived from *o*-hydroxyacetophenone (H-7-Mesal), 2,4-pentanedione (Hacac), *o*-aminobenzaldehyde (Haba), and pyrrole-2-carboxaldehyde (Hpca); with (*R*)-(−)-propane-1,2-diamine ((−)pn) and (*RR*)-(−)-cyclohexane-1,2-diamine ((−)chxn). In these compounds the optical activity of the metal ion chromophore is induced by the optically active tetradentate Schiff base ligands. These Schiff base ligands, with their extensive possibilities for structural variation, provide a useful series of complexes for investigating structure–activity relationships. In addition, the complexes obtained give rise to only one well-defined species in nondonor solvents, in contrast to the extensively studied aqueous copper(II)–amino acid systems which are defined by competing equilibria.[3]

In the electronic spectra of square-planar copper(II) chelates, theory predicts[17–20] that three or four transitions, depending on the symmetry of the complex, should occur within the 3d manifold of the metal ion. The lack of detail observed in the solution spectra of these chelates has, in general, precluded assignments of these d–d transitions.[21] Polarized crystal spectra have provided information about the electronic structure;[22,23] however, distortions caused by lattice requirements and the increase of coordination number by intermolecular bonding often limit the application of these results to the interpretation of solution spectra.

Owing to the narrower band widths observed in circular dichroism, compared to absorption spectroscopy, and the fact that CD bands are signed, CD spectra often reveal more detailed band splittings[2] than the corresponding solution absorption spectra. The application of CD to the interpretation of electronic transitions is complicated, however, by the fact that, as the spectra consist of overlapping bands of opposite sign,[2,24] band magnitudes and positions may not be reliable. It should be possible, however, by studying a series of closely related complexes, to differentiate between actual CD bands and manifestations of overlapping bands.

Experimental Section

Materials. (a) Diamines. Propane-1,2-diamine (Aldrich Chemical Co.) was resolved by the method of Dwyer, *et al.*:[25] $[\alpha]^{21}\text{D}$ for *R*(−)pn, −34.0° (benzene), lit.[25] −34.2°. Technical grade cyclohexane-1,2-diamine (Aldrich) was separated into *cis* and *trans* forms by fractional crystallization of the isomeric hexahydro-2,3-diphenylquinoxalines.[26] The *trans* isomer was resolved by the method of Asperger;[27] $[\alpha]^{21}\text{D}$ for *RR*(−)chxn, −42.6° (benzene); lit.[28] −36°; mp 41–44°, lit.[28] 42.7°.

(b) Aldehydes and Ketones. All aldehydes and ketones were obtained commercially with the exception of *o*-aminobenzaldehyde, which was prepared by the method of Smith and Opie.[29]

(c) Schiff Bases. The Schiff base ligands were prepared by the method of Terent'ev, *et al.*,[14] except for (Hacac)$_2$(−)pn and (Hpca)$_2$(−)pn, which were prepared by methods described by McCarthy, *et al.*,[30] and Weber,[31] respectively.

(d) Copper(II) Chelates. The chelates were prepared by literature methods (*cf.* Table I) except for the following: Cu(pca)$_2$-(−)pn and Cu(pca)$_2$(−)chxn were prepared by adding to an absolute methanol solution, containing 0.002 mol of ligand and 0.004 mol of sodium methoxide, an absolute methanol solution of anhydrous copper(II) chloride (0.002 mol), freshly prepared from CuCl$_2$·2H$_2$O and an excess of 2,2-dimethoxypropane. After stirring at room temperature for 1 hr, the brown crystals were filtered off and recrystallized from absolute methanol and benzene, respectively. Cu(7-Mesal)$_2$(−)chxn was prepared in a similar manner, except that triethylamine was employed as the base, and the solution was stirred for 16 hr at room temperature. The fine green needles, obtained upon volume reduction and cooling, were washed with cold absolute methanol and were not recrystallized.

Physical Measurements. Circular dichroism spectra were measured with a Cary Model 60 recording spectropolarimeter equipped with a Cary Model 6001 circular dichroism accessory. Electronic absorption spectra were obtained with a Cary Model 14 recording spectrophotometer. All spectra were obtained at room temperature (27°) in Spectroquality solvents (Matheson Coleman and Bell). Room-temperature magnetic moments of the solid complexes were measured by the Faraday method, using mercury(II) tetrathiocyanatocobaltate(II) as a calibrant.[32] Diamagnetic corrections for the ligands were calculated from tables of Pascal's constants.[33] Molecular weights of the complexes, as 10^{-2} *M* solutions in chloroform, were determined using a Mechrolab Model 301 vapor phase osmometer, calibrated with benzil. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

Characterization data for the series of copper(II) complexes are presented in Table I. Complexes **4** and **6–8** are described for the first time; **5** and **9** have not previously been reported in their optically active forms. The elemental analyses, infrared spectra, μ'_{eff}, and visible absorption spectra of the complexes are consistent with their formulation as anhydrous, square-planar, Schiff base chelates. The osmometric molecular weights of the chelates are all within 5% of the calculated monomeric values. Most of the chelates in this study were prepared by literature methods. The preparation of Cu(7-Mesal)$_2$(−)chxn, however, required anhydrous conditions, aqueous solvents presumably causing hydrolysis of the ligand. A previous

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(14) (a) A. P. Terent'ev, G. V. Panova, and E. G. Rukhadze, *Russ. J. Gen. Chem.*, **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).

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(20) R. L. Belford and J. W. Carmichael, Jr., *J. Chem. Phys.*, **46**, 4514 (1967).

(21) In a few cases, however, solution spectra have revealed evidence for low-symmetry components of the d–d envelope: *cf.* A. Chakravorty and S. Basu, *Nature*, **184**, 50 (1959).

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Table I. Characterization of the Copper(II) Chelates

	Complex	Method of prepn (ref)	μ_{eff}, BM	ν_{str}(C=N), cm^{-1}	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
1	Cu(sal)$_2$(−)pn	13	1.87[a]	1630	59.38	59.17	4.69	4.58	8.15	8.40
2	Cu(7-Mesal)$_2$(−)pn	14b	1.85	1600	61.36	61.29	5.41	5.51	7.54	7.39
3	Cu(acac)$_2$(−)pn	14c	1.87	1510[b]	52.07	52.25	6.70	6.75	9.35	9.39
4	Cu(aba)$_2$(−)pn	34	1.80	1610	59.72	59.92	5.30	5.34	16.38	16.23
5	Cu(pca)$_2$(−)pn	This work	1.85[c]	1600	53.87	53.82	4.83	4.85	19.33	19.10
6	Cu(sal)$_2$(−)chxn	14c	1.83	1630	62.57	62.46	5.21	5.18	7.29	7.10
7	Cu(7-Mesal)$_2$(−)chxn	This work	1.86	1590	64.14	64.21	5.87	6.05	6.79	6.59
8	Cu(aba)$_2$(−)chxn	34	1.81	1610, 1600[d]	62.89	63.10	5.80	5.82	14.67	14.61
9	Cu(pca)$_2$(−)chxn	This work	1.84[e]	1605	58.26	58.54	5.50	5.54	17.01	17.05

[a] 1.81 BM: S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968). [b] K. Ueno and A. E. Martell, *J. Phys. Chem.*, **59**, 998 (1955). [c] 1.86 ± 0.01 BM.[36] [d] Doublet. [e] 1.86 ± 0.02 BM.[36]

observation[35] that (Hacac)$_2$(*trans*-chxn) failed to form metal complexes in aqueous solution has been attributed to severe interaction between the methyl substituent at the azomethine carbon and the bridging cyclohexylene group. In this work even rigorously anhydrous techniques[36] failed to yield Cu(acac)$_2$(−)chxn.

Electronic Spectra in Chloroform

The electronic spectra of complexes of the type described here have been reported[17, 23, 37, 38] previously. In particular, the spectra of Cu(sal)$_2$en and Cu(acac)$_2$en have been investigated extensively.[17,23] Substitution of propane-1,2-diamine or cyclohexane-1,2-diamine for ethylenediamine (en) in these complexes produces little change in the spectra. The electronic absorption spectra for the present series of copper(II) chelates are summarized in Table II.

Table II. Absorption Spectra of the Copper(II) Chelates in Chloroform

Complex	$\tilde{\nu}$, cm^{-1} (ϵ_{max})
Cu(sal)$_2$(−)pn	17,760 (400); 25,970 sh[a] (9000); 27,250 (11,600); 36,100 sh (18,000)
Cu(7-Mesal)$_2$(−)pn	18,180 (330); 26,300 sh (8700); 27,470 (11,200); 36,200 sh (24,000)
Cu(acac)$_2$(−)pn	15,600 sh (60); 18,420 (200); 30,000 sh (8000); 32,360 (24,000); 36,400 (11,000)
Cu(aba)$_2$(−)pn	14,710 (190); 18,870 sh (360); 21,200 sh (4300); 23,980 (11,300); 33,400 sh (11,000); 39,500 (57,000)
Cu(pca)$_2$(−)pn	18,760 (325); 20,000 sh (330); 27,470 (16,300); 33,330 sh (11,900); 34,250 (12,000)
Cu(sal)$_2$(−)chxn	17,760 (360); 22,220 sh (190); 25,640 sh (7600); 27,250 (11,800); 36,100 sh (25,000)
Cu(7-Mesal)$_2$(−)chxn	14,620 (245); 18,280 (260); 23,810 sh (3400); 26,670 (7800); 36,400 sh (16,000)
Cu(aba)$_2$(−)chxn	14,810 (270); 18,870 sh (480); 22,220 sh (5050); 24,040 (10,100); 33,300 sh (6700)
Cu(pca)$_2$(−)chxn	18,590 (290); 27,700 (17,400); 33,330 sh (12,300); 34,840 (12,800)

[a] Shoulder.

In general, these chelates possess a low-energy absorption band, ϵ_{max} 200–400, between 15,000 and 18,000 cm^{-1}. This is generally agreed to encompass the d–d transitions, and Gaussian analysis of this band in the solution spectrum of Cu(acac)$_2$en has in fact yielded three components.[21] In the polarized crystal spectrum[23] of Cu(sal)$_2$en, two bands are found in this region. At higher energies (24,000–28,000 cm^{-1}) the sal, 7-Mesal, and aba Schiff base chelates exhibit an intense band (ϵ_{max} 8000–24,000), which may, by analogy with the chelate Zn(sal)$_2$(−)pn, be attributed to a $\pi \rightarrow \pi^*$ transition originating in the azomethine chromophore. Compared to its position in the free ligands, this band has undergone a bathochromic shift of 3500–5000 cm^{-1}. Such shifts are expected when coordination to a metal ion increases the extent of conjugation in a molecule.[39] An alternative assignment attributing the intense band to a d $\rightarrow \pi^*$ charge-transfer transition is rejected because no additional bands appear when the ligands are coordinated to copper(II) ion, except for the weak d–d band, in sharp contrast to the situation with the nickel(II) complexes,[4] where additional strong bands appear upon complexation, interposed between the d–d band envelope and the $\pi \rightarrow \pi^*$ transition. Furthermore, except for the weak d–d band, the absorption and CD spectra of Cu(sal)$_2$(−)pn are very similar to those of the corresponding zinc(II) chelate.[4] At still higher energies, intense bands attributed to benzene ring $\pi \rightarrow \pi^*$ transitions occur.[4] For Cu(acac)$_2$(−)pn and the pyrrole-2-carboxaldehyde complexes, the first intense ligand $\pi \rightarrow \pi^*$ band (32,000–35,000 cm^{-1}) is not shifted significantly from its position in the ligand spectrum, although changes in intensity occur.[36,40]

Circular Dichroism Spectra

The circular dichroism spectra for the series of copper(II) complexes in chloroform solution are summarized in Table III, and representative spectra are given in Figures 1–4. In all cases, the CD spectra of the complexes reveal more detail than the corresponding absorption spectra. The spectra of the complexes derived from pyrrole-2-carboxaldehyde are significantly different from the remaining complexes and will be discussed separately.

Comparing the CD spectra of the complexes derived from (−)pn with their appropriate counterparts in the (−)chxn series, it can be seen that the spectra of these two series bear a mirror-image relationship, despite the fact that *R*(−)pn and *RR*(−)chxn, and hence the ligands derived from them, have the same absolute configuration.[41] This result may be explained by assuming that

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(34) P. Pfeiffer, Th. Hesse, H. Pfitzner, W. Scholl, and H. Thielert, *J. Prakt. Chem.*, 149, 217 (1937).

(35) M. Honda and G. Schwarzenbach, *Helv. Chim. Acta*, 40, 27 (1957).

(36) R. E. Clarke and J. H. Weber, *J. Inorg. Nucl. Chem.*, 30, 1837 (1968).

(37) T. N. Waters and D. Hall, *J. Chem. Soc.*, 1200, 1203 (1959).

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(39) S. J. Perry, R. S. Quinn, and E. P. Dudek, *Inorg. Chem.*, 7, 814 (1968).

(40) K. Ueno and A. E. Martell, *J. Phys. Chem.*, 61, 257 (1957).

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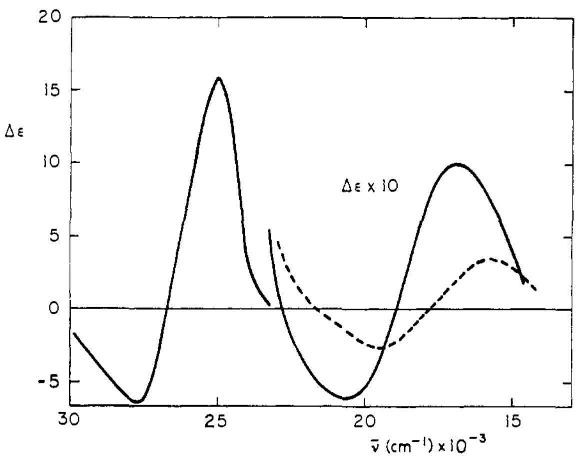


Figure 1. CD spectrum of Cu(sal)$_2$(−)pn in chloroform (——) and in pyridine (------).

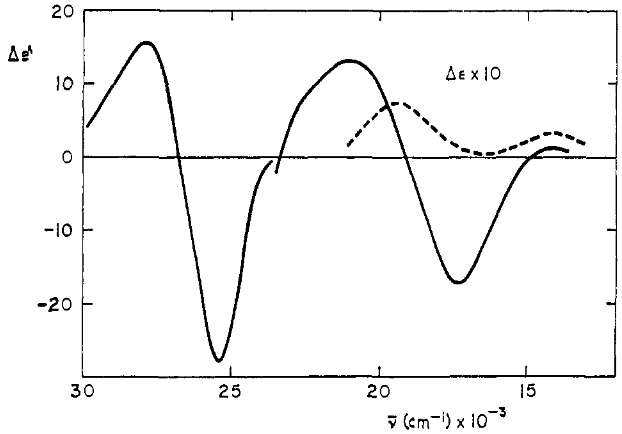


Figure 2. CD spectrum of Cu(sal)$_2$(−)chxn in chloroform (——) and in pyridine (------).

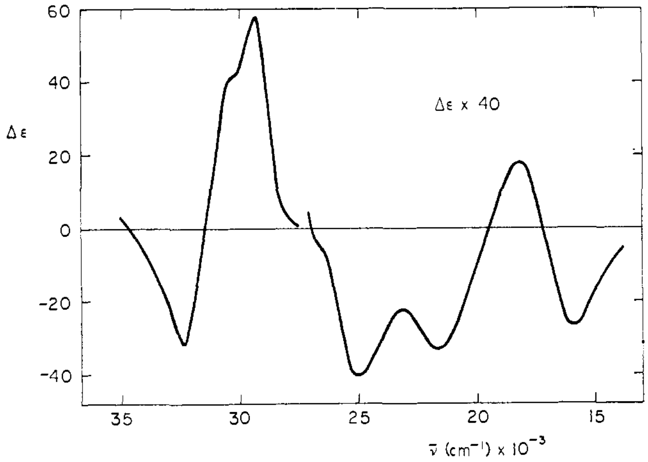


Figure 3. CD spectrum of Cu(acac)$_2$(−)pn in chloroform.

the sign of the Cotton effect of a given transition reflects the conformation of the central chelate ring, known to be *gauche* from X-ray crystallographic studies.[42]

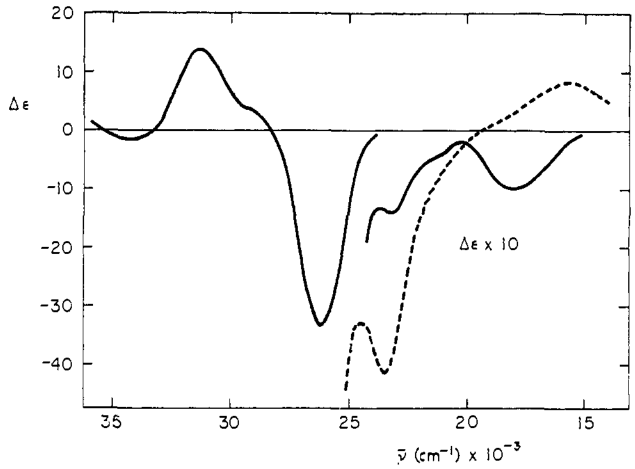
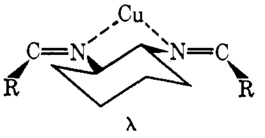


Figure 4. CD spectrum of Cu(pca)$_2$(−)chxn in chloroform (——) and in pyridine (------).

In the (*RR*)-(−)-cyclohexane-1,2-diamine Schiff base chelates, the cyclohexane ring is *trans*-fused to the central chelate ring, forming a rigid structure in which the chelate ring is locked stereospecifically in the λ conformation (**10**). In the propane-1,2-diamine complexes,



10, R=H or CH$_3$

however, a conformational inversion is possible wherein the pn methyl group is pseudo-axial when the central ring is in the δ conformation (**12**), and pseudo-equatorial when the ring conformation is λ (**11**). The relation-

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

Complex	$\tilde{\nu}$, cm^{-1} ($\Delta\epsilon$)
Cu(sal)$_2$(−)pn	16,950 (0.95) (II);[a] 20,700 (−0.57) (III); 25,060 (14.9); 27,700 (−6.12); 36,200 (17)
Cu(7-Mesal)$_2$(−)pn	16,030 (−1.47) (I); 18,350 (0.18) (II); 20,580 (−0.14) (III); 21,980 sh (0.25); 25,320 (26.6); 28,010 (−12.8); 36,400 (24)
Cu(acac)$_2$(−)pn	15,950 (−0.67) (I); 18,150 (0.45) (II); 21,690 (−0.83); (III); 25,060 (−1.01); 26,670 sh (−0.12); 29,330 (59.8); 30,300 sh (43.0); 32,360 (−32.2); 36,600 (10)
Cu(aba)$_2$(−)pn	13,890[b] (0.95) (II); 18,380 (−0.07) (III); 21,410 (17.3); 22,470 sh (11.3); 25,130 (−7.39)
Cu(pca)$_2$(−)pn	18,180 (−0.15) (II); 21,460 sh (−0.25); 23,420 (−0.55) 25,770 (−4.51); 28,740 (1.8)
Cu(sal)$_2$(−)chxn	13,890[b] (0.11) (I); 17,360 (−1.49) (II); 20,920 (1.07) (III); 25,320 (−24.6); 27,860 (14.5); 36,200 (−27)
Cu(7-Mesal)$_2$(−)chxn	14,490 (2.93) (I); 18,180 (−1.16) (II); 21,410 (2.54) (III); 24,570 (−9.39); 26,810 (6.84); 33,900 (−13)
Cu(aba)$_2$(−)chxn	13,890[b] (−1.27) (II); 21,600 (−21.3); 22,570 sh (−13.1); 25,380 (12.7); 30,900 (−1); 38,900 (−16)
Cu(pca)$_2$(−)chxn	18,180 (−0.94) (II); 21,740 sh (−0.54); 23,200 (−1.33); 26,110 (−31.4); 29,240 sh (2.31); 31,450 (13.3); 34,720 (−1.30)

[a] See text for band designations. [b] Band lies too close to long wavelength limit of instrument to be fully resolved.

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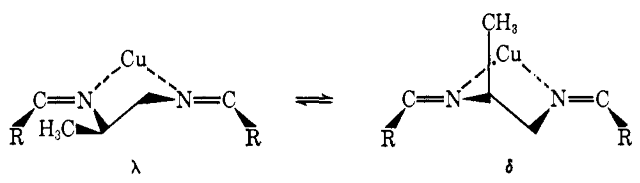
(42) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, 7, 83 (1966), and references therein.

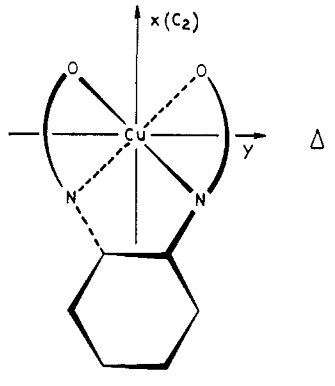


11 R=H or CH_3 12

ship between these two possibilities is diastereomeric, and one should predominate in solution. Although in $[Co(pn)_3]^{3+}$ it is well known[3] that the methyl-equatorial conformation is preferred, in the present complexes the intra- and interligand, 1,3 interactions which favor this conformation are absent. Instead, inspection of a model shows a significant "in-plane, 1,3-interaction" between the pn methyl group and the substituent at the azomethine carbon atom. The interaction is severe when the azomethine substituent is a methyl group, as in the *o*-hydroxyacetophenone and 2,4-pentanedione derivatives, less so when the substituent is hydrogen. In each case, however, this interaction leads to the prediction that the pn methyl-axial conformation, in which this steric strain is partially relieved, will predominate in solution. From steric grounds, therefore, the predicted predominant conformation for the (−)pn complexes is opposite to that which is stereospecifically fixed in the (−)chxn compounds, in agreement with the CD results.

Consistent with this conformational model is the observation that the magnitude of the Cotton effects of the d–d transitions increase in going from the (−)pn complexes to their (−)chxn counterparts. This would be expected if the solutions of the (−)pn complexes contain two conformers presenting opposing chiralities to the metal ion. For CD band II, a positive sign reflects the δ ring conformation, a negative, the λ. The same has been found for other copper(II) chelates,[43,44] assuming that band II for the present series corresponds to the low-energy band in those complexes. The observation of band I at longer wavelength, in several of the tetradentate Schiff base complexes presented here, further demonstrates the importance of identifying corresponding CD bands when correlating conformations with signs of Cotton effects.

It is possible to proceed from this purely conformational model to consideration of the donor atom chirality about the copper atom. Bosnich[4] has proposed that observation of a CD "couplet"[45] with oppositely signed components, corresponding to the azomethine $\pi \rightarrow \pi^*$ absorption band, indicates that the two azomethine chromophores are noncoplanar and the donor atoms produce a flattened tetrahedral configuration. Theory predicts that when this configuration is Λ (IUPAC nomenclature[3]), the negative component of the azomethine $\pi \rightarrow \pi^*$ couplet will lie at higher energy, and at lower energy when the chirality is Δ. A molecular model shows that the *RR*(−)chxn ligands stereospecifically impose the Δ configuration on the metal, exactly as in the case of the related tetradentate ligands recently described by Holm,[46] so that these complexes should have



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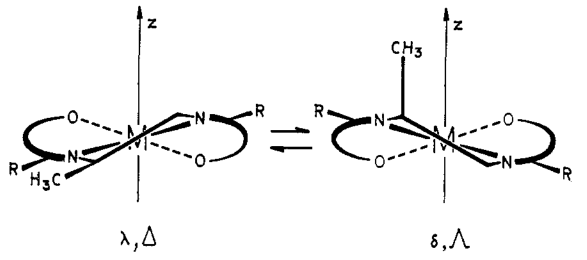
the positive and negative components of the azomethine $\pi \rightarrow \pi^*$ doublet at higher and lower energy, respectively. This is exactly what is found, and the signs of these components are reversed in the (−)pn complexes, in which the conformational inversion $\delta \rightleftharpoons \lambda$ must be accompanied by a configurational inversion $\Lambda \rightleftharpoons \Delta$, with the Λ configuration predominating. Thus the CD



M = Cu, R = H or CH_3

14 15

of the ligand bands tends to confirm the stereochemical conclusions drawn from the sign reversals in the CD of the d–d region.

Except for the case of the acetylacetone and pyrrole-2-carboxaldehyde derivatives, the CD spectra of all the free ligands are predominantly negative and do not show reversals upon substituting (−)chxn for (−)pn. The CD spectra of $(Hacac)_2(-)$pn and $(Hacac)_2(-)$chxn show couplets corresponding to the intense ligand $\pi \rightarrow \pi^*$ absorption band, with the positive component at higher energy in each. In $Cu(acac)_2(-)$pn this is reversed, and it is the negative component which is at higher energy. These observations further confirm that the differences between the CD spectra of the (−)pn and (−)chxn series are the result of conformational changes which attend complexation, the sign reversal in the ligand bands, upon complexation, no doubt being due to the fact that the conformation of the coordinated ligand is very different from that of the free Schiff base.[47]

The CD spectra of $Cu(pca)_2(-)$pn and $Cu(pca)_2(-)$chxn are almost superimposable and do not have the mirror-image relationship of the other pairs of complexes. The pyrrole-2-carboxaldehyde complexes differ from the others in having five-membered side rings, and decreased in-plane steric interaction between the azomethine hydrogen and the pn-methyl may account for this anomalous behavior.

Band Assignments and Solvent Effects. In addition to the results described above concerning the stereochemistry of the chelates, it is possible to attempt a

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(43) R. D. Gillard and R. Wootton, *J. Chem. Soc., B*, 921 (1967).

(44) S. T. K. Bukhari, R. D. Guthrie, A. J. Scott, and A. D. Wrixon, *Chem. Commun.*, 1580 (1968).

(45) J. A. Schellman, *Accounts Chem. Res.*, 1, 144 (1968).

(46) M. J. O'Connor, R. E. Ernst, and R. H. Holm, *J. Amer. Chem. Soc.*, 90, 4561 (1968).

(47) D. W. Urry and H. Eyring, *ibid.*, 86, 4574 (1964).

detailed assignment of the metal ion transitions based on the additional splitting revealed in the d–d region of the CD spectra. In this paper care has been taken not to consider ill-defined "shoulders" as distinct spectral features, since pronounced asymmetry can result from the overlap of oppositely signed bands.[2,24] By comparing the spectra of these related complexes, corresponding bands in the spectra may be identified with reasonable certainty, and bands "missing" from certain individual spectra may be allowed for when making assignments.

It is generally accepted[48] for square-planar copper(II) complexes of the present type that the ground state[49] has the d_{xy} orbital singly occupied. Cotton and Wise[19a] have shown that for copper(II) β-diketonates, whose electronic structures should be similar to those of the present complexes, the four filled d orbitals are closely spaced and lie at about 20,000 cm^{-1} below the d_{xy} orbital. Thus all of the d–d transitions may be expected to occur within the broad low-energy absorption band commonly observed in the absorption spectra of square-planar copper(II) chelates.[17,23]

The appropriate point group for the complexes under discussion is C_2, which allows for the *gauche* central ring and/or a slight pseudo-tetrahedral distortion. In this symmetry all of the d–d transitions are simultaneously electric- and magnetic-dipole allowed, in parallel, thus accounting for the relatively strong CD of these bands.

In the d–d region the CD spectra, in general, reveal three bands, designated I–III in Table III, corresponding bands having been determined by a comparison of the entire series of spectra. Band I is not observed for Cu(sal)$_2$(–)pn or the *o*-aminobenzaldehyde derivatives. In the pyrrole-2-carboxaldehyde Schiff base chelates, the band is not seen in chloroform but appears in pyridine (see Table IV) and methanol (16,390 cm^{-1} for Cu(pca)$_2$(–)pn). It is proposed that bands I and II originate in the $d_{z^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{yz}$ transitions, in agreement with the predictions of simple crystal field theory[18] and the results of epr[48] and single crystal spectral[23,50] studies. CD band III corresponds in energy to the x-polarized band (21,000 cm^{-1}) in the crystal spectrum of Cu(sal)$_2$en.[22] Belford[23] suggested this band could not be a d–d transition, since no d–d transitions are x-polarized in C_{2v} symmetry. In C_2 symmetry, the $d_{xz} \rightarrow d_{xy}$ transition would be x-polarized. This choice of symmetry, however, requires the transitions from the $d_{x^2-y^2}$ and d_{z^2} orbitals (17,300-cm^{-1} band of Cu(sal)$_2$en)[22] to have z, as well as y, components, and this was not found in the crystal spectrum.[22,23] Nevertheless, the transition $d_{xz} \rightarrow d_{xy}$ would be a reasonable assignment for band III on energy grounds, and since its position corresponds to a region of weak electronic absorption it is not likely to be a charge-transfer band. In addition, if band III were an intraligand transition, a corresponding band would be expected in the absorption spectra of the neutral ligands, ligand anions,[40,51] or zinc(II) chelates,[4] but none has been reported. Therefore, pending further crystal spectra on complexes of this type, band III is assigned to the transition $d_{xz} \rightarrow d_{xy}$. In the CD spectrum of Cu(acac)$_2$(–)pn only, a further weak band (25,060 cm^{-1}) and a shoulder (26,670 cm^{-1}) are seen beyond band III, but no evidence is available for the assignment of these bands. It is unlikely on energy grounds that these are d–d transitions, and they may be charge-transfer or spin-forbidden ligand transitions.[17]

In an attempt to assign I and II individually to the $d_{x^2-y^2}$ and d_{z^2} transitions, the CD spectra of the complexes were recorded in pyridine solution. The complexes vary greatly in the effect of solvent changes on their spectra. For example, the CD spectrum of Cu(acac)$_2$(–)pn is virtually identical in hexane, chloroform, ethanol, and pyridine, and the complexes derived from *o*-aminobenzaldehyde are also unaffected by pyridine, whereas this solvent has a marked effect on the salicylaldehyde and pyrrole-2-carboxaldehyde Schiff base complexes. The absorption spectra of Cu(sal)$_2$(–)pn in chloroform solutions containing varying concentrations of pyridine show a single isosbestic point (16,860 cm^{-1}), indicative of the formation of a weak five-coordinate monoadduct. Table IV summarizes the pyridine solution absorption and CD spectra in the d–d spectral region for those compounds which are appreciably affected.

Table IV. Absorption and CD Spectra of the Chelates in Pyridine (d–d Bands Only)

Complex	Absorption spectrum $\bar{\nu}$, cm^{-1} (ϵ_{max})	CD spectrum $\bar{\nu}$, cm^{-1} ($\Delta\epsilon$)
Cu(sal)$_2$(–)pn	16,860 (310)	15,720 (0.32) (II);[a] 19,490 (–0.25) (III)
Cu(7-Mesal)$_2$(–)pn	17,700 (310)	16,000 (–1.45) (I); 18,700 sh (–0.42) (III) 21,740 sh (0.71)
Cu(pca)$_2$(–)pn	16,670 (200)	16,000 (0.28) (I)
Cu(sal)$_2$(–)chxn	16,950 (280)	14,080[b] (0.25) (I); 19,460 (0.70) (III)
Cu(pca)$_2$(–)chxn	16,610 (190)	15,630 (0.77) (I); 18,520 sh (0.18)

[a] See text for band designations. [b] Band lies too close to long wavelength limit of instrument to be fully resolved.

A correlation can be drawn between the extent to which pyridine interacts with the complexes and the steric hindrance offered by the complexes to additional ligands. The *o*-hydroxyacetophenone and acetylacetone derived complexes are expected to be most distorted from planarity, owing to their azomethine methyl groups, and thus will hinder the approach of pyridine along the z axis. In the *o*-aminobenzaldehyde complexes the amine hydrogens presumably project from the molecular plane to some extent, thus causing more hindrance to pyridine approach than with the salicylaldehyde derivatives. The extent of out-of-plane π bonding is probably also important in determining the susceptibility of the complexes to adduct formation; however, epr measurements[48,52] have not yet enabled estimates to be made of the different extents of out-of-plane

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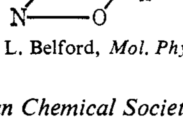
(48) H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).

(49) The coordinate convention for these complexes is



(50) T. S. Piper and R. L. Belford, *Mol. Phys.*, **5**, 169 (1962).

(51) J. Ferguson, *Spectrochim. Acta*, **17**, 316 (1961).

(52) V. C. Swett and E. P. Dudek, *J. Phys. Chem.*, **72**, 1244 (1968).

π bonding among the complexes of the present series.

Returning to the question of the assignment of CD bands I and II, it is significant that, while I is shifted by only from +200 to −300 cm^{-1} in pyridine, II is either shifted toward the red by about 1200 cm^{-1}, as in Cu(sal)$_2$(−)pn, or "disappears," in which case it has probably undergone a larger red shift which causes it to be obscured by band I. This admittedly weak evidence leads to the tentative conclusion that I represents the $d_{x^2-y^2} \rightarrow d_{xy}$ and II the $d_{z^2} \rightarrow d_{xy}$ transition.

Another observation consistent with this assignment is that the magnitude of CD band I is large in those complexes with an azomethine methyl substituent, and small or unobserved in the others. If the principal effect of the azomethine methyl is to increase the distortion of the donors, that is to strengthen the C_2 component of the ligand field, then simple group theory predicts that both the transitions from d_{z^2} and $d_{x^2-y^2}$ would become optically active. However, the $d_{x^2-y^2}$ orbital would be more sensitive to the distortion, which will disrupt the in-plane π bonding, and thus increase the magnitude of the CD band corresponding to the $d_{xy} \rightarrow d_{x^2-y^2}$ hole transition.

The specific observation of the individual d–d transitions should, in principle, allow a better comparison of the ligand field strengths of this series of ligands than is possible by simply observing the positions of the maxima in the absorption spectra. However, the transition $d_{x^2-y^2} \rightarrow d_{xy}$, which defines Δ_1 for square-planar complexes, is not observed in all of the CD spectra. CD band II, corresponding to the $d_{z^2} \rightarrow d_{xy}$ transition, is observed in all of the spectra, and since the interval II–I is relatively constant, this band position may serve as a measure of the ligand field strength of the tetradentate ligands. Since II corresponds almost exactly with the solution absorption band maxima, a similar ranking is obtained as has been observed previously for some of these ligands, namely, (pca)$_2$pn^{2-} > (7-Mesal)$_2$pn^{2-} ≈ (acac)$_2$pn^{2-} > (sal)$_2$pn^{2-} > (aba)$_2$pn^{2-}. Substitution of chxn for pn does not have much effect on the ligand field strength except for the *o*-hydroxyacetophenone complexes, in which the apparent steric crowding between the cyclohexane residue and the azomethine methyl substituents produces a pronounced weakening of the ligand field, manifested by a shift of band I of 1500 cm^{-1} from the pn chelate.

Charge-Transfer Transitions. It might be expected that low-energy charge-transfer bands would be observed in the absorption and CD spectra of these chelates. Such bands occur at energies between the d–d and intraligand transitions in the corresponding nickel(II) complexes and have been assigned as $d \rightarrow \pi^*$ transitions.[4] The copper(II) chelates, on the other hand, do not consistently display additional bands which may be attributed to charge-transfer transitions. The copper(II) chelates with 2,4-pentanedione and *o*-aminobenzaldehyde Schiff bases do exhibit shoulders (30,000 and 22,000 cm^{-1}, respectively) on the low-energy side of the azomethine $\pi \rightarrow \pi^*$ band (Table II), corresponding to bands in the CD (29,330 and 21,500 cm^{-1}), which overlap the low-energy component of the ligand $\pi \rightarrow \pi^*$ couplet. Also, in the chelates derived from pyrrole-2-carboxaldehyde, the first intense band can be assigned to charge transfer, since the first ligand band is shifted only slightly from its position in the free ligand.[36] In the CD the corresponding band is at ~26,000 cm^{-1}, and the 23,000-cm^{-1} band may also have its origin in a charge-transfer excitation. In the nickel(II) chelates the assignment of charge-transfer bands as $d \rightarrow \pi^*$ transitions is reasonable; however, in the copper(II) chelates the greater stability of the copper d orbitals would place $d \rightarrow \pi^*$ transitions at significantly higher energies, and they may be obscured by intense intraligand transitions. In addition, ligand→metal ion charge transfer ($\pi \rightarrow d$ or $\sigma \rightarrow d$) would occur at lower energies in copper(II) chelates compared to nickel(II) chelates,[53] and thus no unambiguous assignment of charge-transfer bands is possible in the present study.

Concluding Remarks

The effects of solvent and ligand variation on the circular dichroism of tetradentate Schiff base chelates of copper(II) have been interpreted as showing a d-orbital ordering d_{xy} (G.S.) $\gg d_{x^2-y^2} > d_{z^2} > d_{xz}$ with d_{yz} either at higher energy, or, more probably, close in energy to one of the three filled orbitals. This accords with the ordering deduced from epr measurements on related complexes.[48] The observation that the CD of the copper(II) chromophore is most sensitive to subtle conformational and configurational changes shows that the method is potentially capable of giving information on slightly distorted planar copper(II) complexes, which cannot be obtained by magnetic studies or absorption spectroscopy.[54,55]

Acknowledgment. This research was supported in part by an Institutional Grant from Case Western Reserve University sponsored by the American Cancer Society.

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(53) For a comparison of the energy levels in Ni(II) and Cu(II) bis(β-ketoenolate) complexes, see ref 19a.

(54) R. H. Holm, A. Chakravorty, and L. J. Theriot, *Inorg. Chem.*, **5**, 625 (1966).

(55) Note Added in Proof. A CD study of one of the complexes reported here (Cu(acac)$_2$(−)pn) has recently appeared. *Cf.* E. Larsen, Proceedings of the Second International Conference on Coordination Chemisty, 1968, p 193.