colorless and evaporation of the excess CF_3CF_2I gave an oil which crystallized under methanol.

trans-PtI($CF_3CF_2CF_2I$)Q_2.—$CF_3CF_2CF_2I$ (2 ml) was added to *trans*-PtI(CH_3)Q_2 (0.18 g); the mixture was set aside in the dark for 1 day and then evaporated to dryness and extracted with petroleum ether containing *ca.* 5% chloroform. The red residue did not contain fluorine. The extracts were evaporated to dryness and allowed to crystallize under methanol.

Pyrolysis of PtI(CH_3)$_2CF_3Q_2$.—The complex (0.49 g) was heated at 180° under vacuum. The evolved gas was shown to be mainly ethane by its infrared spectrum. The residue was recrystallized from methanol to give *trans*-PtI(CF_3)Q_2 as white plates (0.40 g).

Pyrolysis of PtI$_2$(CH_3)CF_3Q_2.—The complex (0.32 g) was heated to 225° under vacuum. The evolved gas was shown to be mainly methyl iodide by its infrared spectrum. The residue was recrystallized from methanol to give *trans*-PtI(CF_3)Q_2 (0.22 g).

Reaction of *cis*-Pt(CH_3)$_2L_2$ with (CF_3)$_2$CFI.—To a solution of *cis*-Pt(CH_3)$_2A_2$ (0.31 g) in diethyl ether (6 ml) was added (CF_3)$_2$-CFI (0.5 ml) which had been previously purified by shaking with mercury and distillation. The mixture was set aside in the dark for 2 days and gave a red precipitate of the iodine adduct PtI$_2$-(CH_3)$_2A_2$, configuration V. A sample of (CF_3)$_2$CFI which was

kept next to the reaction vessel did not undergo any decomposition to free iodine during this period of time.

A similar experiment using *cis*-Pt(CH_3)$_2Q_2$ gave a mixture of products which have not yet been fully characterized.

Other Reactions.—CH_3CF_2Cl or CF_3Br did not react with *cis*-Pt(CH_3)$_2Q_2$ using procedure A; however addition of 1% ferric chloride and diethyl ether catalyzed the reaction of CF_3Br and a product was obtained which had the ^1H and ^{19}F nmr spectra expected for PtBr(CH_3)$_2CF_3Q_2$. A satisfactory elemental analysis could not be obtained, however.

CF_2=CFBr reacted with *cis*-Pt(CH_3)$_2Q_2$, using procedure A, to give *trans*-PtBr(CH_3)Q_2.

trans-PtI(CH_3)Q_2 was recovered unchanged from a solution in CF_3CH_2I after 12 days in the dark at room temperature.

The Circular Dichroism of Tetradentate Schiff Base Chelates of Oxovanadium(IV)

BY RICHARD L. FARMER AND F. L. URBACH*

The circular dichroism (CD) and electronic absorption spectra of some oxovanadium(IV) complexes with tetradentate Schiff bases derived from (S)-(+)-propane-1,2-diamine and (SS)-(+)-cyclohexane-1,2-diamine have been measured in several solvents. On the basis of the CD data, both the preferred conformation of the central chelate ring and the absolute configuration of the flattened tetrahedral array of ligand donor atoms about the oxovanadium(IV) ion have been assigned. Improved band resolution occurs in the CD spectra compared to the absorption spectra, and tentative band assignments have been made.

Introduction

Previous studies have established the utility of circular dichroism (CD) measurements for determining the preferred chelate ring conformation and donor atom configuration of tetradentate copper(II),[1] nickel-(II),[2,3] and zinc(II)[4] complexes with optically active Schiff base ligands. In this paper, the results of these prior investigations are applied to elucidate the stereochemical details of several analogous square-pyramidal[5,6] oxovanadium(IV) chelates. The circular dichroism spectrum of a similar oxovanadium(IV) complex, VO(acac)$_2$(−)pn,[7] has been published, but no attempt was made to interpret the data in terms of a particular stereochemical model.

The electronic structures of oxovanadium(IV) com-

plexes have been the subject of many investigations,[8,9] and several recent reports[10-12] have dealt specifically with the absorption spectra of complexes of the type reported here. The application of circular dichroism measurements to these complexes offers the possibility of revealing more detailed band splittings than are obtained from absorption spectra. This advantage of CD, which arises because of the signed bands, narrower band widths, and differences in selection rules, is sometimes limited by the adverse effects of overlapping bands of opposite sign.[13] By a careful comparison of the absorption and CD spectra of a series of related complexes in several solvents, the ambiguities caused by band overlap can be minimized and additional spectral information may be obtained.

* To whom correspondence should be addressed.
(1) R. S. Downing and F. L. Urbach, *J. Amer. Chem. Soc.*, **91**, 5977 (1969).
(2) R. S. Downing and F. L. Urbach, *ibid.*, **90**, 5344 (1968).
(3) R. S. Downing and F. L. Urbach, *ibid.*, in press.
(4) B. Bosnich, *ibid.*, **90**, 627 (1968).
(5) L. J. Boucher, D. E. Bruins, T. F. Yen, and D. L. Weaver, *Chem. Commun.*, 363 (1969).
(6) D. Bruins and D. L. Weaver, *Inorg. Chem.*, **9**, 130 (1970).
(7) K. M. Jones and E. Larsen, *Acta Chem. Scand.*, **19**, 1210 (1965).

(8) J. Selbin, *Chem. Rev.*, **65**, 153 (1965).
(9) J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966).
(10) L. J. Boucher, E. C. Tyman, and T. F. Yen, *Inorg. Chem.*, **7**, 731 (1968).
(11) L. J. Boucher and T. F. Yen, *ibid.*, **7**, 2665 (1968).
(12) L. J. Boucher and T. F. Yen, *ibid.*, **8**, 689 (1969).
(13) R. D. Gillard in "Physical Methods in Advanced Inorganic Chemistry," H. A. O. Hill and P. Day, Ed., Wiley-Interscience, New York, N. Y., 1968, Chapter 5.

Experimental Section

A. Diamines. (S)-(+)-**Propane-1,2-diamine, (+)pn.**—Using the method of Dwyer, *et al.*,[14] propane-1,2-diamine (Aldrich Chemical Co.) was resolved to give the (+),(−) antipodes: $[\alpha]^{21}$D for (S)-(+)pn +33.7° (benzene); lit.[14] +34.0°.

(SS)-(+)-**Cyclohexane-1,2-diamine, (+)chxn.**—Cyclohexane-1,2-diamine (Aldrich) was separated into cis and trans isomers by fractional crystallization of the isomeric hexahydro-2,3-diphenylquinoxalines.[15] The trans isomer was resolved by the method of Asperger:[16] $[\alpha]$D for (+)chxn +34.6° (benzene); lit.[17] 32–34°.

B. Schiff Bases.—Bis(7-methylsalicylidene)-(+)-propane-1,2-diamine, (H-7-Mesal)₂(+)pn; bis(salicylidene)-(+)-propane-1,2-diamine, (H-sal)₂(+)pn; and bis(salicylidene)-(+)-cyclohexane,1,2-diamine, (H-sal)₂(+)chxn, were prepared using the methods reported by Terent'ev, *et al.*[18]

C. Metal Complexes.—[N,N'-**Bis(salicylidene)-(S)-(+)-propane-1,2,diamino]oxovanadium(IV),** VO(sal)₂(+)pn, was obtained using the procedure outlined by Pfeiffer, *et al.*[19] *Anal.* Calcd for C₁₇H₁₆O₃N₂V: C, 58.8; H, 4.66; N, 8.08. Found: C, 58.89; H, 4.44; N, 8.16.

[N,N'-**Bis(7-methylsalicylidene)-(S)-(+)-propane-1,2-diamino]oxovanadium(IV),** VO(7-Mesal)₂(+)pn, was prepared as follows. A methanol solution containing 1 ml (0.014 mol) of triethylamine and 1.18 g (0.0038 mol) of (H-7 Mesal)₂(+)pn was added to a warmed methanol solution of 0.755 g (0.0038 mol) of VOSO₄·2H₂O. After stirring the resulting mixture for 40 min at room temperature, a dark green microcrystalline product was obtained. The crystals were washed with methanol and dried *in vacuo* at 160°. *Anal.* Calcd for C₁₉H₂₀O₃N₂V: C, 60.9; H, 5.38; N, 7.48. Found: C, 61.11; H, 5.21; N, 7.34.

[N,N'-**Bis(salicylidene)-(SS)-(+)-cyclohexane-1,2-diamino]-oxovanadium(IV),** VO(sal)₂(+)chxn, was prepared in a manner analogous to the preparation of the previous complex. *Anal.* Calcd for C₂₀H₂₀O₃N₂V: C, 62.3; H, 5.20; N, 7.20. Found: C, 62.6; H, 5.30; N, 7.11.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical Measurements.—Electronic absorption spectra were obtained with a Cary 14 recording spectrophotometer. Circular dichroism data were recorded using a Cary Model 60 recording spectropolarimeter equipped with a Cary Model 6001 circular dichroism accessory. Measurements between 600 and 800 mμ were taken by manually operating the slit. Additional CD measurements were made between 700 and 1000 mμ using a Shimadzu QV-50 spectrophotometer equipped with a VCD-1 circular dichroism attachment. The authors are grateful to Preiser Scientific, Cincinnati, Ohio, for the loan of the Shimadzu instrument. All solutions for spectral measurements were prepared with deaerated solvents; specific rotations were calculated from data obtained with a Rudolph polarimeter, Model 80, equipped with an oscillating polarizer and electronic detection apparatus.

Results and Discussion

Central Chelate Ring Conformation.—Representative circular dichroism spectra for the three oxovanadium(IV) Schiff base chelates are presented in Figures 1 and 2; the CD data for the complexes in several solvents are summarized in Table I. The CD spectra
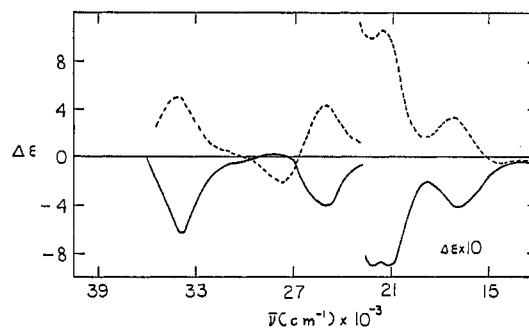
(14) F. P. Dwyer, F. L. Garvan, and A. Schulman, *J. Amer. Chem. Soc.,* **81,** 290 (1959).

(15) A. J. Smith, U. S. Patent 3163675 (1964).

(16) R. G. Asperger and C. F. Liu, *Inorg. Chem.,* **4,** 1492 (1965).

(17) F. M. Jaeger and L. Bijkerk, *Proc. Kon. Ned. Akad. Wetensch.,* **40,** 12 (1937).

(18) A. P. Terent'ev, E. G. Rukhadze, and G. V. Panova, *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).

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

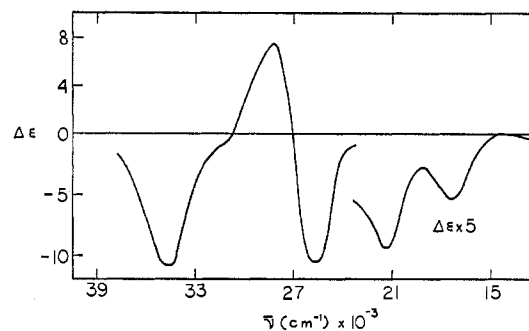Figure 1.—CD spectrum of VO(sal)₂(+)pn (——), and VO(sal)₂-(+)chxn (----) in chloroform.

Figure 2.—CD spectrum of VO(7-Mesal)₂(+)pn in chloroform.

of the two complexes derived from (S)-(+)-propane-1,2-diamine exhibit a mirror-image relationship to the spectrum obtained for the (SS)-(+)-cyclohexane-1,2-diamine analog despite the fact that both parent amines have the same absolute configuration. Similar results have been observed in the CD spectra of the corresponding copper(II)[1] and nickel(II)[2,3] Schiff base complexes and have been attributed to a mirror-image difference in the conformation of the gauche[20] central chelate ring.

In VO(sal)₂(+)chxn, the ligand is stereospecifically coordinated to the vanadyl moiety so that the gauche chelate ring[5,6] is locked in a δ conformation,[21] 1. The

δ
1
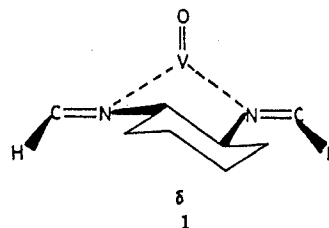
complexes derived from propane-1,2-diamine, however, can undergo a conformational inversion such that the methyl group will occupy either a pseudoaxial or a pseudoequatorial position, depending on whether the chelate ring conformation is λ or δ. The barrier for the ring interconversion from λ to δ is assumed to be quite small,[22] and this interchange is undoubtedly represented by a dynamic equilibrium with one diastereomeric form predominating in solution.

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

(21) Proposed IUPAC nomenclature, *Inorg. Chem.,* **9,** 1 (1970).

(22) A. M. Sargeson, *Transition Metal Chem.,* **3,** 303 (1966).

TABLE I
CIRCULAR DICHROISM SPECTRA OF OXOVANADIUM(IV) CHELATES

Complex	Solvent	ν, cm^{-1} ($\Delta\epsilon$)
VO(sal)$_2$(+)pn	CHCl$_3$	16,850 (−0.39) (II);[a] 21,000 (−0.85) (III); 22,100 (−0.86) (III); 25,000 (−3.84); 33,800 (−5.80)
	CH$_3$OH	17,400 (−0.43) (II); 21,500 (−0.87) (III); 25,700 (−3.02); 34,500 (−6.80); 39,000[b] (−3.3)
	Pyridine	16,800 (−0.42) (II); 21,000 (−1.04) (III); 21,400 (−0.97) (III); 25,300 (−4.11)
VO(7-Mesal)$_2$(+)pn	CHCl$_3$	12,500[c] (−0.07) (I); 17,400 (−1.03) (II); 21,400 (−1.79) (III); 25,500 (−9.4); 28,200 (+6.86); 34,500 (−10.3)
	DMF	12,500[c] (−0.12) (I); 17,300 (−0.92) (II); 21,400 (−1.87) (III); 26,200 (−9.1); 29,000 (+6.1); 36,600 (−9.3)
	Pyridine	17,300 (−1.03) (II); 21,300 (−1.87) (III); 26,000 (−9.4); 28,600 (+7.15)
VO(sal)$_2$(+)chxn	CHCl$_3$	13,300[c] (−0.04) (I); 17,100 (+0.30) (II); 21,400 (+1.03) (III); 25,100 (+3.94); 27,700 (−2.06); 33,500[b] (+5.4)
	DMF	13,300[c] (−0.02) (I); 17,250 (+0.31) (II); 21,400 (+0.94) (III); 25,400 (+3.48); 28,300 (−2.16)
	Pyridine	13,700[c] (−0.03) (I); 17,100 (+0.29) (II); 21,300 (+1.03) (III); 25,350 (+3.66); 27,900 (−2.07)

[a] See text for band designation. [b] Band position and $\Delta\epsilon$ are approximate due to high absorbance compared to rotational strength. [c] Band lies too close to long-wavelength limit of instrument to be fully resolved.

To account for the mirror-image relationship between the signs of the bands in the CD spectra of the (+)pn and the (+)chxn derivatives, it is proposed that the (+)pn complexes prefer a λ conformation, with the pn methyl in a pseudoaxial position. Molecular models lend support to this assignment since they indicate that the least amount of steric interaction between substituents on the azomethine carbon atoms and the pn methyl group occurs when the pn methyl group is pseudoaxial.

In contrast to the corresponding complexes containing monatomic metal ions,[1-3] two possible modes (2, 4) of coordination to the diatomic VO^{2+} cation exist in which the methyl group is pseudoaxial. Structure 2 represents the favored form since it involves the least steric interaction between the vanadyl oxygen and the pn methyl group. The actual situation that exists in

R = H, CH$_3$
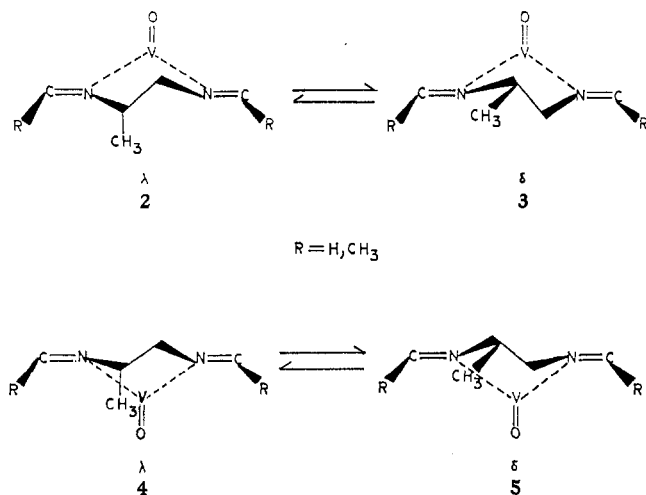
solution is probably an equilibrium mixture of all four isomers with a predominance of the λ conformation described by 2.

Some evidence for the existence of several isomers in solution can be gained from a report of the partial resolution of racemic VO(acac)$_2$pn[23] into four optical isomers (Dd, Ll, Dl, Ld).[24] These isomers were reported to mutarotate and eventually racemize over a period of days.[25-27]

Configuration about the Metal Atom.—Another source of dissymmetry, and hence optical activity, in these complexes occurs if the ligand adopts a preferred flattened tetrahedral geometry about the oxovanadium(IV) ion. Bosnich[4] has assigned the positive–negative couplet[28] centered at 28,700 cm^{-1} in the CD spectrum of the Zn(sal)$_2$(−)pn to $\pi \rightarrow \pi^*$ transitions encompassing the azomethine chromophores. In addition, he has suggested that the transition dipole moment vectors in the two azomethine chromophores are oriented away from the C=N bond axes, toward the phenyl rings, and that the occurrence of the CD couplet demonstrates these transition moment vectors are not coplanar.

The CD spectra of the oxovanadium(IV) chelates

(23) D. L. Martin and K. Ramaiah, *J. Inorg. Nucl. Chem.*, **27**, 2027 (1965).

(24) Here the capital letters refer to the configuration about the vanadium; the lower case letters define the amine configuration.

(25) In the present study, VO(sal)$_2$(+)pn was the only complex that exhibited any spectral change with time. The low-energy bands (10,000–22,000 cm^{-1}) showed a simultaneous increase in rotational strength and absorbance over a period of days. Preliminary studies were not consistent with a mutarotation and racemization process but indicated that oxidation of the metal ion and/or decomposition could be occurring. Oxidation has been reported to occur in solutions of VO(acac)$_2$[26] as well as oxovanadium(IV) dithiocarbamates.[27]

(26) T. R. Ortolano, J. Selbin, and S. P. McGlynn, *J. Chem. Phys.*, **41**, 262 (1964).

(27) B. J. McCormick, *Inorg. Chem.*, **7**, 1965 (1968).

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

TABLE II
ABSORPTION SPECTRA OF THE OXOVANADIUM(IV) CHELATES

Complex	Solvent	ν, cm^{-1} (ϵ_{max})
VO(sal)$_2$(+)pn	CHCl$_3$	12,990 sh^a (31) (I);^{b} 16,800 (154) (II); 20,960 sh (87) (III); 27,000 (8370); 35,400 (20,700)
	CH$_3$OH	13,500 sh (41) (I); 17,400 (138) (II); 21,500 sh (101) (III); 27,700 (7850); 36,500 (21,500)
	Pyridine	13,000 sh (34) (I); 16,800 (146) (II); 21,200 sh (82) (III); 27,300 (9300)
VO(7-Mesal)$_2$(+)pn	CHCl$_3$	13,160 sh (30) (I); 17,100 (119) (II); 21,350 sh (78) (III); 27,600 (8540); 36,400 (21,400)
	DMF	13,200 sh (33) (I); 17,100 (124) (II); 21,400 sh (81) (III); 28,200 (8950)
	Pyridine	13,200 sh (32) (I); 17,100 (127) (II); 21,000 sh (77); 27,800 (8950)
VO(sal)$_2$(+)chxn	CHCl$_3$	13,160 sh (29) (I); 16,990 (132) (II); 21,300 sh (84) (III); 27,300 (9080)
	DMF	13,330 sh (32) (I); 17,100 (128) (II); 21,400 sh (94) (III); 27,700 (9670)
	Pyridine	13,330 sh (34) (I); 16,950 (135) (II); 21,350 sh (92) (III); 27,400 (9900)

^{a} Shoulder. ^{b} See text for band designations.

exhibit evidence of a similar couplet in the same spectral region. Therefore, by comparison with the zinc(II)[4] and the copper(II)[1] chelates, this couplet is assigned as arising from nondegenerate $\pi \rightarrow \pi^*$ transitions originating in the azomethine chromophores.

For the present complexes, exciton theory[28-31] requires that the azomethine transition moment vectors form a left-handed helix about the pseudo-C_2 axis of the molecules, when the positive component of the CD couplet occurs at lower energy. If it is assumed that the transition moment vectors lie in the plane of the side rings, then the side rings must themselves form a flattened tetrahedral arrangement of Λ configuration[32] (**7**) about the oxovanadium(IV) ion. Similarly, a positive CD component at higher energy requires a

λ, Δ δ, Λ
6   **7**
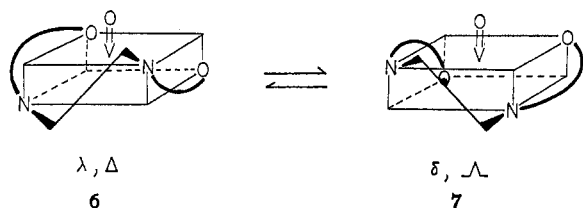
right-handed helical arrangement about the pseudo-C_2 axis, giving rise to a Δ (**6**) configuration.[32] A slight tetrahedral distortion in VO(acac)$_2$en can be inferred from the reported X-ray structure,[5,6] thus lending support to the preceding argument.

The high-energy component of the CD couplet in all of the complexes studied shows a marked asymmetry and lower rotational strength when compared to the low-energy component. This is attributed to the overlap of the high-energy component of the CD couplet

(29) B. Bosnich, *Accounts Chem. Res.*, **2**, 266 (1969).
(30) S. F. Mason, *Contemp. Phys.*, **9**, 239 (1968).
(31) A. S. Davydov, "Quantum Mechanics," N. E. O. Press, Ann Arbor, Mich., 1967, p 514.
(32) The configuration about the metal ion (**6**, **7**) has been assigned by representing the side rings as a pair of nonorthogonal skew lines. When viewed along their common normal, these skew lines describe either a Δ or Λ helicity in accordance with the proposed IUPAC nomenclature.[21]

with an oppositely signed band at higher energy (Figures 1, 2). Apparently in the case of VO(sal)$_2$(+)pn, the overlap is so extensive that the high-energy CD couplet component is canceled, producing a rotational strength close to zero. Evidence for the existence of exciton splitting in this complex can be inferred from the fact that the well-defined low-energy peak of the CD couplet is displaced 2000 cm^{-1} toward lower energy compared to the position of the azomethine $\pi \rightarrow \pi^*$ band in the absorption spectrum. In the absence of exciton splitting, this band would be expected to occur at similar energies in the absorption and CD spectrum. The position of the lower energy CD component of VO(sal)$_2$(+)pn also compares favorably with the position of the low-energy couplet peak in the other complexes studied, where well-defined CD couplets were observed.

The signs of the CD couplets indicate that, in solution, the predominant configurations for the (+)pn and (+)chxn complexes are Δ and Λ, respectively. It has been proposed[1] that an interdependence exists between the configuration and conformation of these complexes, such that a conformational inversion $\lambda \leftrightarrows \delta$ involves a configurational inversion $\Delta \rightleftarrows \Lambda$. Steric interactions between substituents at the azomethine carbon and those on the central chelate ring provide the driving force for both the preferred conformation and configuration.

The split CD band centered at $\sim$30,000 cm^{-1} in the spectrum of VO(acac)$_2$(−)pn,[7] which was not assigned by Jones and Larsen, is probably the result of nondegenerate $\pi \rightarrow \pi^*$ transitions giving rise to a CD couplet. The signs of this couplet lead to the prediction that the configuration about the metal atom is Λ. The interdependence of configuration and conformation would then require a δ ring conformation with the pn methyl group in a pseudoaxial position, in agreement with the results of the present study.

Band Assignments and Electronic Structure.—The absorption and CD spectral data for the oxovanadium-(IV) Schiff base complexes are presented in Tables I and II. The positions of the absorption band maxima and their solvent dependence are in excellent agreement with those published for the racemic complexes;[12] the molar extinction coefficients differ slightly from previously reported values.[12]

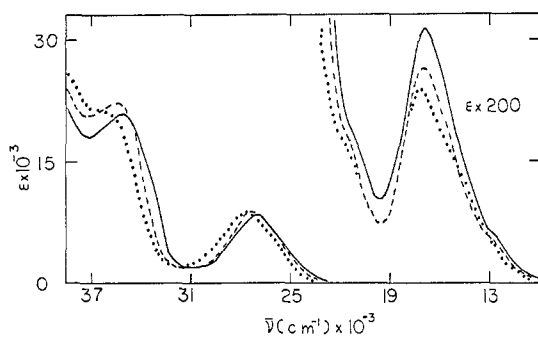The low-energy region (10,000–22,000 cm^{-1}) of the absorption spectra of the present complexes (Figure 3)

Figure 3.—Absorption spectrum of VO(sal)$_2$(+)pn (——), VO(7-Mesal)$_2$(+)pn (·····), and VO(sal)$_2$(+)chxn (----) in chloroform.

contains three weak bands (ϵ 29–160), *viz.*, a shoulder at ~13,000 cm^{-1} (I), a broad peak at ~17,000 cm^{-1} (II), and an additional shoulder at ~21,000 cm^{-1} (III). The circular dichroism spectra reveal three well-defined bands of comparable rotatory strength, corresponding to the three absorption bands. Four CD bands have been reported to occur in the region 10,000–22,000 cm^{-1} of VO(acac)$_2$(−)pn;[7] the additional band has been attributed to low-symmetry splitting of the parent $e\pi^*$ level (*vide infra*). The circular dichroism of VO(7-Mesal)$_2$(+)pn and VO(sal)$_2$(+)pn was measured in the 10,000–14,000-cm^{-1} spectral region using a manual CD instrument, but no additional bands were observed.

It is generally agreed that bands I and II represent d–d transitions in oxovanadium(IV) complexes of the type studied;[8,9] band III has been assigned both as a d–d band[9,26,27] and as a spin-forbidden ligand band.[7,12] In view of the similarity in extinction coefficients and rotatory strengths of all three low-energy bands we strongly support the assignment of band III as a d–d transition for these complexes. In addition to intensity arguments, the assignment of band III to a spin-forbidden ligand transition in these salicylaldimine chelates is questionable since similar transitions at ~21,000 cm^{-1} have been observed in VO(acac)$_2$,[26] VO(acac)$_2$pn,[7,10] and some oxovanadium(IV) dithiocarbamate complexes.[27] It is unlikely that an intraligand band would occur at such similar energies for these different ligand systems. Finally, no corresponding band occurs in the absorption spectra of Zn(sal)$_2$(−)pn[4] or the free ligands,[4,33] further suggesting that the assignment as an intraligand transition is incorrect.

(33) R. S. Downing, Ph.D. Thesis, Case Western Reserve University, 1969.

The moderately intense absorption band at ~28,000 cm^{-1} and the corresponding couplet in the CD spectrum were previously assigned to nondegenerate $\pi \rightarrow \pi^*$ transitions involving the azomethine chromophores. The remaining higher energy absorption bands may be attributed to $\pi \rightarrow \pi^*$ transitions within the phenyl rings.[1,4] No bands in the spectra of these chelates are assigned as charge-transfer transitions since all of the observed bands may readily be accounted for as either d–d transitions or shifted ligand bands. Existing charge-transfer transitions are probably masked by more intense ligand excitations.

The molecular orbital scheme developed by Ballhausen and Gray[34] (B and G) to rationalize the electronic spectrum of VO(H$_2$O)$_5$$^{2+}$ may be employed as a basis for assigning the d–d spectra of the present chelates. Although this theoretical calculation was developed for a charged species with C_{4v} symmetry, several authors have used it as an approximation for neutral species of lower symmetry.[7,9–12,27] The essential feature of the B and G theory is that it predicts three d–d transitions: $b_2(d_{xy}) \rightarrow e\pi^*$ (d_{xz}, d_{yz}), $b_2(d_{xy}) \rightarrow b_1^*(d_{x^2-y^2})$, and $b_2(d_{xy}) \rightarrow a_1^*(d_{z^2})$. The relative ordering of the $e\pi^*$ and b_1^* orbitals has been questioned,[9,27] and the $e\pi^*$ degeneracy can be removed by inclusion of spin–orbit coupling[26] and/or symmetries lower than C_{4v}. B and G[34] attributed the 50,000-cm^{-1} band in the absorption spectrum of VO(H$_2$O)$_5$$^{2+}$ to the $b_2(d_{xy}) \rightarrow a_1^*(d_{z^2})$ transition; other authors[7,26,27] have assigned this transition as low as 17,000 cm^{-1} in low-symmetry Schiff base chelates. Solvent studies[10,12] indicate that the position trans to the vanadyl oxygen is vacant in the present Schiff base complexes. This absence of additional z-axis perturbation would lower the energy of the a_1^* level of these complexes relative to that found for VO(H$_2$O)$_5$$^{2+}$. The symmetry of the salicylaldime chelates is sufficiently low such that a splitting of the $b_2 \rightarrow e\pi^*$ transition similar to that reported in the CD spectrum of VO(acac)$_2$(−)pn[7] might be expected. No such splitting was observed, but this may have been due to cancellation caused by overlapping bands of opposite sign.

In view of the preceding arguments, the transitions at 13,000 and 17,000 cm^{-1} are assigned to the $b_2 \rightarrow e\pi^*$ and $b_2 \rightarrow b_1^*$ transitions, although no additional support for the relative ordering of these two transitions is obtained from the present study. The highest energy d–d transition will undoubtedly involve a transition to primarily the d_{z^2} orbital, which in terms of the B and G[34] scheme would be the $b_2 \rightarrow a_1^*$ transition. This transition is proposed as the origin of band III.

(34) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).