

phase was transferred *via* the vapor phase back onto the maroon solid. This cycle of filtration and distillation was repeated ten times after which the supernatant liquid above the maroon crystals remained colorless. The filtered product was washed by distilling about one-third of the liquid (mostly benzene) back and filtering a final time. The benzene and excess ligand were removed by opening the break seal and pumping. The maroon product constituted 96% of the yield and the dark residue obtained from the soluble portion the remaining 4%. The maroon product analyzed for  $ZrCl_3 \cdot 2(C_7H_5N)$ . *Anal.* Calcd for  $ZrCl_3 \cdot 2(C_7H_5N)$ : Zr, 22.15; Cl, 25.82; C, 40.83; H, 4.40; N, 6.80. Found: Zr, 22.31; Cl, 25.80; C, 40.63; H, 4.51; N, 6.71.

2,4-Lutidine (4.86 mmol) and zirconium trichloride (1.62 mmol) in 50 ml of benzene very slowly yielded a faint red colored solution which deepened to a burgundy red. Decantation of the solution through the filter revealed that substantially all the zirconium trichloride remained. The benzene and 2,4-lutidine were distilled back onto the trichloride leaving a red-brown solid in flask B. The solution above the trihalide again became red although less intense. The recycling process was repeated six more times (7 days) by which time the solid in flask A was an orange powder and the solid recovered from the soluble portion of the reaction system was now a black powder. The yield of orange powder was 0.31 g (28% of the zirconium), and the yield of the black powder was 0.18 g. The orange product analyzed for  $ZrCl_3 \cdot 1.2(C_7H_5N)$ . *Anal.* Calcd for  $ZrCl_3 \cdot 1.2(C_7H_5N)$ : Zr, 27.97; Cl, 32.61; C, 30.93; H, 3.34; N, 5.15. Found: Zr, 29.86; Cl, 32.69; C, 31.39; H, 3.42; N, 5.03. In a second synthesis run over a period of 30 days the product analyzed for  $ZrCl_3 \cdot 4/3(C_7H_5N)$ . *Anal.* Calcd for  $ZrCl_3 \cdot 4/3(C_7H_5N)$ : Zr, 26.82; Cl, 31.27; C, 32.95; H, 3.56; N, 5.48. Found: Zr, 26.65; Cl, 30.90; C, 33.28; H, 3.69; N, 5.44.

**Acknowledgment.** This work was supported in part by

National Science Foundation Grant No. GP-9300. We also acknowledge the contributions of R. Clemmer for the reflectance spectra, D. Hillenbrand for the nmr spectra, and J. Kleppinger for the magnetic measurements. This work was initiated in the laboratories of the Inorganic Institute of the Technical University of Vienna at the time the senior author was Fulbright Lecturer there. He is indebted to the Director, Professor Viktor Gutmann, for making the facilities of the laboratory available, and the American-Austrian Commission, for their financial support.

**Supplementary Material Available.** Tables III and IV, X-ray powder pattern data, and Table V, magnetic susceptibility data, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-581.

**Registry No.**  $ZrCl_3 \cdot 2(3,5-L)$ , 43158-20-9;  $ZrBr_4 \cdot 2(3,5-L)$ , 43158-21-0;  $ZrI_4 \cdot 2(3,5-L)$ , 43158-22-1;  $ZrCl_4 \cdot 2(2,4-L)$ , 43158-23-2;  $ZrBr_4 \cdot 2(2,4-L)$ , 43158-24-3;  $ZrI_4 \cdot 2(2,4-L)$ , 43158-25-4;  $ZrCl_4 \cdot 2(2,6-L)$ , 43158-26-5;  $ZrBr_4 \cdot 2(2,6-L)$ , 43209-03-6;  $ZrI_4 \cdot 2(2,6-L)$ , 43158-27-6;  $ZrCl_3 \cdot 2(3,5-L)$ , 43162-25-0;  $ZrCl_3 \cdot x(2,4-L)$ , 43207-71-2.

Contribution from the Department of Chemistry,  
Case Western Reserve University, Cleveland, Ohio 44106

## Stereochemistry and Electronic Structure of Oxovanadium(IV) Chelates with Tetradentate Schiff Base Ligands Derived from 1,3-Diamines

RICHARD L. FARMER and F. L. URBACH\*

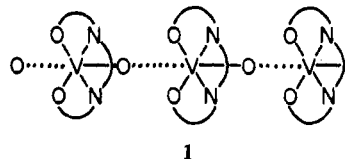
Received April 24, 1973

Oxovanadium(IV) chelates containing the tetradentate Schiff base ligands *N,N'*-bis(salicylidene)propane-1,3-diamine, *N,N'*-bis(7-methylsalicylidene)propane-1,3-diamine, *N,N'*-bis(3-isopropylsalicylidene)propane-1,3-diamine, and *N,N'*-bis(salicylidene)-(S)-(+)-butane-1,3-diamine have been prepared and their properties in the solid state and in donor and nondonor solvents have been characterized. These chelates have a polymeric structure (V-O-V bridging) in the solid state but dissociate to give monomeric five-coordinate species in nondonor solvents and monomeric six-coordinate species in donor solvents such as pyridine or dimethylformamide. The two lowest energy absorption bands are assigned to the  ${}^2B_2 \rightarrow {}^2E(I)$  and  ${}^2B_2 \rightarrow {}^2B_1$  ( $C_{4v}$  symmetry) transitions on the basis of solvent dependent spectral shifts in the electronic and infrared band maxima. The circular dichroism spectrum of [*N,N'*-bis(salicylidene)-(S)-(+)-butane-1,3-diamino]oxovanadium(IV) exhibits exciton components corresponding to the  $\pi \rightarrow \pi^*$  transitions of the coupled azomethine chromophores. On the basis of the relative signs of the exciton components, the Schiff base ligand donor atoms are proposed to have a slight pseudotetrahedral distortion of  $\Delta$  configuration about the V=O moiety.

### Introduction

Oxovanadium(IV) chelates containing tetradentate Schiff base ligands derived from 1,2-diamines have been the subject of several recent reports.<sup>1-5</sup> These square-pyramidal complexes<sup>6</sup> exhibit a strong tendency to remain five-coordinate in both donor and nondonor solvents.<sup>1,3-5,7</sup> Expansion of

the central chelate ring in the tetradentate complexes often leads to an increased ability for adduct formation.<sup>8</sup> For example, X-ray crystallographic data<sup>9</sup> have revealed that [*N,N'*-bis(salicylidene)propane-1,3-diamino]oxovanadium(IV), VO(sal)<sub>2</sub>tn, exhibits a structure containing an infinite chain of square-pyramidal molecules connected by V-O-V bonds, 1.



- (1) L. J. Boucher, E. C. Tynan, and T. F. Yen, *Inorg. Chem.*, **7**, 731 (1968).
- (2) L. J. Boucher and T. F. Yen, *Inorg. Chem.*, **7**, 2665 (1968).
- (3) L. J. Boucher and T. F. Yen, *Inorg. Chem.*, **8**, 689 (1969).
- (4) D. L. Daughdrill, D. F. Martin, and J. S. Binford, Jr., *J. Inorg. Nucl. Chem.*, **32**, 2885 (1970).
- (5) (a) R. L. Farmer and F. L. Urbach, *Inorg. Chem.*, **9**, 2562 (1970); (b) R. L. Farmer and F. L. Urbach, *Chem. Commun.*, 1515 (1970).
- (6) D. Bruins and D. L. Weaver, *Inorg. Chem.*, **9**, 130 (1970).
- (7) R. G. Garvey and R. O. Ragsdale, *Inorg. Chim. Acta*, **2**, 191 (1968).

- (8) S. Yamada, *Coord. Chem. Rev.*, **1**, 415 (1966).
- (9) M. Mathew, A. J. Carty, and G. J. Palenik, *J. Amer. Chem. Soc.*, **92**, 3197 (1970).

Table I. Microanalytical and Magnetic Susceptibility Data for the Oxovanadium(IV) Complexes

Compd	% C		% H		% N		$\mu_{\text{eff}},^a$ BM	$10^6 \chi_M,^a$ cgsu
	Calcd	Found	Calcd	Found	Calcd	Found		
VO(sal) <sub>2</sub> tn	58.81	59.08	4.65	4.75	8.07	8.52	1.79 (1.68 <sup>b</sup> )	3.30
VO(sal) <sub>2</sub> (+)tnCH <sub>3</sub>	59.67	60.24	5.02	5.06	7.73	8.00	1.84	3.37
VO(3-ipsal) <sub>2</sub> tn	64.02	63.81	6.49	6.49	6.55	6.35	1.80	2.54
VO(7-CH <sub>3</sub> sal) <sub>2</sub> tn	60.79	60.98	5.38	5.29	7.47	7.31	1.85	3.27
(H-7-CH <sub>3</sub> sal) <sub>2</sub> (+)tnCH <sub>3</sub>	74.03	74.38	7.47	7.52	8.64	8.70		

<sup>a</sup> At 22°. <sup>b</sup> Reference 16.

In this paper we report the solid-state and solution properties of a series of oxovanadium(IV) complexes with tetradentate Schiff base ligands derived from 1,3-diamines. A preliminary account of this work has appeared.<sup>5b</sup> The structural information cited above<sup>9</sup> provided a basis for the interpretation of many of the unique properties of these oxovanadium(IV) chelates.

### Experimental Section

**Materials.** (S)-(+)-Butane-1,3-diamine, (+)tnCH<sub>3</sub>, was supplied by Campbell.<sup>10</sup>  $[\alpha]_D^{25}$  for (+)tnCH<sub>3</sub> was +15.2° (benzene) and  $[\alpha]_D^{26}$  was +19.11° (neat, 2 dm); lit.<sup>11</sup>  $[\alpha]_D^{25}$  +1.80° (neat, 2 cm). 3-Isopropylsalicylaldehyde was prepared by the Duff reaction:<sup>12</sup> yield ~30%; bp 60–66° (4 mm); lit.<sup>13</sup> bp 86–94° (7 mm). All other chemicals were reagent quality and were used as received.

**Schiff Bases.** *N,N'*-Bis(salicylidene)propane-1,3-diamine, (H-sal)<sub>2</sub>tn, *N,N'*-bis(7-methylsalicylidene)propane-1,3-diamine, (H-7-CH<sub>3</sub>sal)<sub>2</sub>tn, and *N,N'*-bis(3-isopropylsalicylidene)propane-1,3-diamine, (H-3-ipsal)<sub>2</sub>tn, were prepared by literature methods.<sup>14</sup> *N,N'*-Bis(salicylidene)-(S)-(+)-butane-1,3-diamine, (H-sal)<sub>2</sub>(+)tnCH<sub>3</sub>, and *N,N'*-bis(7-methylsalicylidene)-(S)-(+)-butane-1,3-diamine, (H-7-CH<sub>3</sub>sal)<sub>2</sub>(+)tnCH<sub>3</sub>, were prepared as follows. A benzene solution containing 8.8 mmol of the aldehyde and 4.4 mmol of (+)tnCH<sub>3</sub> was heated until the benzene-water azeotrope had distilled off. The remaining benzene was removed under reduced pressure. The residual yellow oil was dissolved in absolute methanol and placed in a freezer. (H-7-CH<sub>3</sub>sal)<sub>2</sub>(+)tnCH<sub>3</sub> precipitated as yellow crystals but (H-sal)<sub>2</sub>(+)tnCH<sub>3</sub> failed to crystallize and was used as a methanolic solution.

**Metal Chelates.** [*N,N'*-Bis(salicylidene)propane-1,3-diamino]oxovanadium(IV), VO(sal)<sub>2</sub>tn, [*N,N'*-bis(salicylidene)-(S)-(+)-butane-1,3-diamino]oxovanadium(IV), VO(sal)<sub>2</sub>(+)tnCH<sub>3</sub>, and [*N,N'*-bis(3-isopropylsalicylidene)propane-1,3-diamino]oxovanadium(IV), VO(3-ipsal)<sub>2</sub>tn, were prepared as follows. The ligand (3 mmol) and triethylamine (7 mmol) were dissolved in 20 ml of absolute methanol. This solution was added, with stirring, to 100 ml of warm methanol containing a stoichiometric amount (3 mmol) of VOSO<sub>4</sub>·2H<sub>2</sub>O. The reaction mixture was stirred at room temperature for 40 min whereupon the small orange needles which formed were suction filtered from the solution. VO(sal)<sub>2</sub>tn and VO(3-ipsal)<sub>2</sub>tn were digested in warm methanol for 20 min to remove impurities. VO(sal)<sub>2</sub>(+)tnCH<sub>3</sub> was recrystallized from absolute methanol. All of the metal chelates were dried in a vacuum desiccator prior to analysis. [*N,N'*-Bis(7-methylsalicylidene)propane-1,3-diamino]oxovanadium(IV), VO(7-CH<sub>3</sub>sal)<sub>2</sub>tn, was prepared in the same manner as the previous complexes. A few minutes after the metal salt solution and ligand solution were mixed, an orange precipitate began to form. If the reaction was allowed to continue for longer than 20 min, the product began to disappear. The complex was obtained as small orange needles upon suction filtration and dried *in vacuo*. Analytical data and magnetic susceptibilities for the complexes are presented in Table I.

**Physical Measurements.** Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Magnetic susceptibilities were determined at room temperature (22°) by the Faraday method at two field strengths with Hg[Co(NCS)<sub>4</sub>] as the calibrant. Magnetic moments for individual samples were reproducible to ±0.03 BM. Diamagnetic corrections were based on a value of  $\chi_M = 182 \times$

$10^6$  cgsu for *N,N'*-bis(salicylidene)ethane-1,2-diamine, (H-sal)<sub>2</sub>en.<sup>15</sup> Appropriate corrections to this value for substituted ligands were calculated using Pascal's constants.<sup>15</sup> Electronic absorption spectra were obtained with a Cary Model 14 recording spectrophotometer. All samples were dissolved in deaerated solvents, and their spectra were measured as quickly as possible. Circular dichroism spectra of the optically active compound were recorded with a Cary Model 60 recording spectropolarimeter fitted with a Cary Model 6001 circular dichroism accessory. Measurements between 600 and 800 m $\mu$  were taken by manually operating the slit width. Infrared spectra were recorded in the region 4000–625 cm<sup>-1</sup> with a Beckman IR-8 spectrophotometer. Solid-state spectra were measured as Nujol mulls. Solution spectra were obtained using demountable sodium chloride cells with path lengths of 0.5 or 1.0 mm. ESR spectra of the oxovanadium(IV) complexes were measured using a Varian E-3 esr spectrometer. The spectra were calibrated with the diphenylpicrylhydrazyl free radical (DPPH) ( $g = 2.0036$ ). Reflectance spectra were recorded on a Beckman DK-2 ratio recording spectrophotometer with a reflectance unit vs. MgCO<sub>3</sub> reference.

### Results and Discussion

X-Ray crystallography has established that VO(sal)<sub>2</sub>tn has a unique polymeric structure<sup>9</sup> which contains an infinite chain of -V-O-V-O bonds. A complementary determination of the solution properties of this interesting chelate is precluded by its low solubility in most solvents. To overcome this limitation several derivatives of VO(sal)<sub>2</sub>tn were synthesized and found to be sufficiently soluble in chloroform, pyridine, and dimethylformamide (DMF) for spectral measurements. Even these more soluble complexes, VO(sal)<sub>2</sub>(+)tnCH<sub>3</sub>, VO(7-CH<sub>3</sub>sal)<sub>2</sub>tn, and VO(3-ipsal)<sub>2</sub>tn, did not exhibit sufficient solubility to allow molecular weight determinations by vapor pressure osmometry. One of these complexes, VO(7-CH<sub>3</sub>sal)<sub>2</sub>tn, is apparently unstable in solution since the electronic spectrum of this compound in solution changes over a period of hours. The remaining complexes exhibited no evidence of instability.

**Axial Coordination in the 1,3-Diamine Chelates.** The diffuse reflectance spectra (Figure 1) of the tetradentate oxovanadium(IV) chelates derived from 1,3-diamines consist of a broad absorption band at ~11,300 cm<sup>-1</sup> and a shoulder at ~20,000 cm<sup>-1</sup> on the low-energy side of a more intense transition. This is in marked contrast to the solid-state spectra of the analogous chelates derived from 1,2-diamines<sup>1-5,16</sup> which exhibit only a single broad band at ~17,000 cm<sup>-1</sup>. In addition, the infrared spectra of the 1,3-diamine complexes exhibit an unusually low V=O stretching frequency of ~860 cm<sup>-1</sup> (Table II) compared to a value of ~990 cm<sup>-1</sup> for the corresponding 1,2-diamine complexes.<sup>2,16,17</sup> The assignment of  $\nu_{V=O}$  for VO(sal)<sub>2</sub>(+)tnCH<sub>3</sub> and VO(sal)<sub>2</sub>tn was made by comparison with the infrared spectra of the corresponding copper(II) chelates. The anomalously low values of the V=O stretching frequencies in VO(sal)<sub>2</sub>tn<sup>9</sup> and certain mono-

(10) T. G. Campbell, Ph.D. Thesis, Case Western Reserve University, 1970.

(11) E. Balieu, P. M. Boll, and E. Larsen, *Acta Chem. Scand.*, **23**, 2191 (1969).

(12) J. C. Duff, *J. Chem. Soc.*, 547 (1941).

(13) R. H. Holm, *J. Amer. Chem. Soc.*, **83**, 4683 (1961).

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

(15) B. N. Figgis and J. Lewis in "Techniques of Inorganic Chemistry," Vol. IV, H. B. Jonassen and A. Weissberger, Eds., Wiley, New York, N. Y., 1965, p 137.

(16) R. L. Dutta and G. P. Sengupta, *J. Indian Chem. Soc.*, **48**, 33 (1971).

(17) R. L. Farmer, Ph.D. Thesis, Case Western Reserve University, 1971.

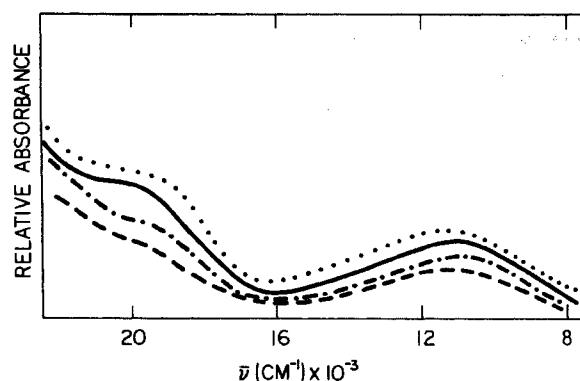


Figure 1. Diffuse reflectance spectra of VO(sal)<sub>2</sub>tn (—), VO(3-ipsal)<sub>2</sub>tn (---), VO(7-CH<sub>3</sub>sal)<sub>2</sub>tn (- · - · -), and VO(sal)<sub>2</sub>(+tn)CH<sub>3</sub> (· · · · ·).

Table II. V=O Stretching Frequencies (cm<sup>-1</sup>) for the Oxovanadium(IV) Complexes in Various Solvents

Complex	Nujol mull	CHCl <sub>3</sub>	DMF	Pyridine
VO(sal) <sub>2</sub> tn	861	<i>a</i>	960	<i>b</i>
VO(sal) <sub>2</sub> (+tn)CH <sub>3</sub>	860	993	961	963
VO(3-ipsal) <sub>2</sub> tn	860	986	960	959
VO(7-CH <sub>3</sub> sal) <sub>2</sub> tn	850	982	<i>c</i>	<i>c</i>

<sup>a</sup> Compound is not sufficiently soluble for the measurement.

<sup>b</sup> Not observed. <sup>c</sup> Complex decomposed.

thio-β-diketonate<sup>18</sup> oxovanadium chelates have been attributed to the bridging nature of the VO unit in these compounds. Since the 1,3 complexes reported here also exhibit very low values for  $\nu_{V=O}$  (Table II), and have similar solid-state electronic spectra (Figure 1), we conclude that they also contain bridging V=O groups.

The room-temperature magnetic moments of the tetradentate, 1,3 complexes (Table I) are close to the expected spin-only values of 1.73 BM and do not indicate any anti-ferromagnetic coupling of spins at this temperature.<sup>19</sup> Similar results<sup>18</sup> have been reported for the monothio-β-diketonate complexes which contain bridging V=O groups.

In chloroform solution, the V=O stretching frequencies of VO(sal)<sub>2</sub>(+tn)CH<sub>3</sub>, VO(3-ipsal)<sub>2</sub>tn, and VO(7-CH<sub>3</sub>sal)<sub>2</sub>tn, are shifted from ~860 to ~990 cm<sup>-1</sup> (Table II). This latter value is similar to the values of  $\nu_{V=O}$  observed for the five-coordinate tetradentate salicylaldimine<sup>17</sup> and β-ketimine<sup>1,2</sup> complexes derived from 1,2-diamines. In coordinating solvents such as pyridine or dimethylformamide,  $\nu_{V=O}$  for the 1,3-diamine complexes occurs at ~960 cm<sup>-1</sup>. This shift is similar to the change in the V=O stretching frequency of VO(acac)<sub>2</sub> upon the addition of a ligand into the vacant sixth position.<sup>20,21</sup>

The electronic spectra of the 1,3-diamine complexes in chloroform (Table III and Figure 2) exhibit a single band at ~17,000 cm<sup>-1</sup> with additional inflections at ~14,000 and ~21,000 cm<sup>-1</sup>. These spectra are very similar to the spectra reported for 1,2-diamine tetradentate β-ketimine<sup>1,2</sup> and salicylaldimine<sup>3-5,16</sup> complexes of oxovanadium(IV) which

(18) B. J. McCormick and R. A. Bozis, *Inorg. Chem.*, **10**, 2806 (1971).

(19) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Eds., Interscience, New York, N. Y., 1960, p 400.

(20) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 4533 (1961); K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, pp 112, 221-222.

(21) J. Selbin, H. R. Manning, and G. Cessac, *J. Inorg. Nucl. Chem.*, **25**, 1253 (1963).

Table III. Absorption Spectra of the [N,N'-Bis(salicylidene)-1,3-diamino]oxovanadium(IV) Chelates

Complex	Solvent or phase	$\bar{\nu}$ , cm <sup>-1</sup> ( $\epsilon_{\max}$ )
VO(sal) <sub>2</sub> tn	Solid	11,170 (I); <sup>a</sup> ~20,000 <sup>b</sup> (II)
	DMF	13,160 (26) (I); 19,610 <sup>b</sup> (90) (II); 27,550 (8900)
	Pyridine	12,900 (40) (I); 19,230 <sup>c</sup> (90) (II); 27,030 (8350)
VO(sal) <sub>2</sub> (+tn)CH <sub>3</sub>	Solid	11,340 (I); ~20,000 <sup>b</sup> (II)
	CHCl <sub>3</sub>	13,890 <sup>c</sup> (27) (I); 17,540 (68) (II); 21,280 <sup>c</sup> (95) (III); 27,030 (8250); 34,720 (22,200)
	CH <sub>3</sub> OH	13,160 (30) (I); 19,420 <sup>b</sup> (56) (II); 27,780 (7330); 35,710 (19,700); 42,550 (41,500)
	DMF	13,330 (29) (I); 19,050 <sup>b</sup> (81) (II); 21,740 <sup>c</sup> (90) (III); 27,550 (8630)
	Pyridine	13,070 (38) (I); 19,420 <sup>c</sup> (84) (II); 27,030 (8700)
	VO(3-ipsal) <sub>2</sub> tn	Solid
VO(7-CH <sub>3</sub> sal) <sub>2</sub> tn	CHCl <sub>3</sub>	14,600 (40) <sup>b</sup> (I); 17,770 (65) (II); 26,320 (7750); 36,360 (20,800)
	DMF	13,160 (24) (I); 19,610 <sup>b</sup> (101) (II); 27,030 (8450)
	Pyridine	12,820 (34) (I); 19,230 <sup>c</sup> (110) (II); 26,660 (7920)
(H-7-CH <sub>3</sub> sal) <sub>2</sub> (+tn)CH <sub>3</sub>	Solid	10,990 (I); ~19,400 <sup>b</sup> (II)
	CHCl <sub>3</sub>	13,160 <sup>c</sup> (33) (I); 15,870 (120) (II); 27,780 (6850)
	DMF	13,700 <sup>c</sup> (39) (I); 16,390 (85) (II); 21,740 <sup>c</sup> (218) (III); 28,170 (6500)
	Pyridine	Broad band ranging from 12,000 to 14,900 cm <sup>-1</sup> (~50); 28,170 (7000)
	CHCl <sub>3</sub>	25,100 (2000); 31,000 (7350)

<sup>a</sup> Refers to the numbering of the low-energy bands. <sup>b</sup> Shoulder. <sup>c</sup> Inflection.

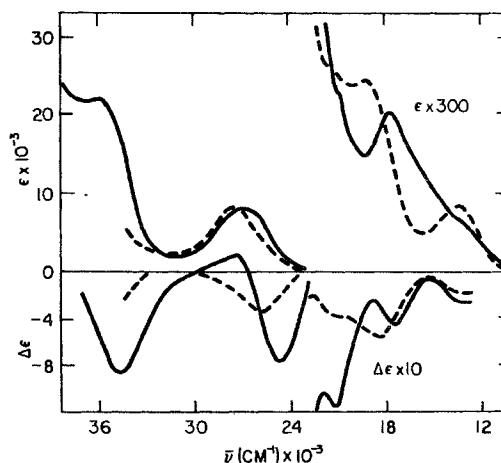


Figure 2. Isotropic absorption and circular dichroism spectra of VO(sal)<sub>2</sub>(+tn)CH<sub>3</sub> in chloroform solution (—) and in dimethylformamide solution (---).

show no solvent dependency and are assigned a five-coordinate, square-pyramidal structure.<sup>6</sup> Unlike the 1,2-diamine analogs, the 1,3-diamine chelates exhibit a different d → d spectrum in coordinating solvents. In the presence of an additional donor, the spectra of the 1,3-diamine complexes consist of an absorption band at ~13,000 cm<sup>-1</sup> and a pronounced shoulder or inflection at ~19,000 cm<sup>-1</sup> (Table III and

Figure 2).<sup>22,23</sup> Similar changes in the electronic spectra of 2,4-pentanedione,<sup>24</sup> fluorinated  $\beta$ -ketimine,<sup>2</sup> and monothio- $\beta$ -diketone<sup>18</sup> complexes of oxovanadium(IV) occur upon axial coordination.

From the above observations of the V=O stretching frequencies and the electronic spectra of the 1,3-diamine chelates, we conclude that these complexes have a six-coordinate structure in the solid state (achieved by V-O-V bridging) and a six-coordinate structure in donor solvents (achieved by coordination of a solvent molecule) but exhibit a five-coordinate square-pyramidal structure in nondonor solvents.

The  $g_0$  and  $A_0$  values of the 1,3-diamine complexes (Table IV), obtained by electron spin resonance spectroscopy, are in agreement with published data for other salicylaldimine oxovanadium(IV) complexes.<sup>3,25</sup> A trend in the hyperfine values ( $A_0$ ) as a function of axial coordination has been reported<sup>18</sup> for monothio- $\beta$ -diketonate oxovanadium(IV) complexes. A similar trend is apparent for the 1,3-diamine chelates (Table IV) where the  $A_0$  values are decreased in donor solvents relative to chloroform solutions. This shift cannot be attributed solely to the effect of axial coordination since hydrogen bonding<sup>26,27</sup> and dielectric constant effects<sup>28</sup> also can reduce the value of  $A_0$ .

#### Conformation and Configuration of VO(sal)<sub>2</sub>(+)tnCH<sub>3</sub>.

The circular dichroism spectrum for VO(sal)<sub>2</sub>(+)tnCH<sub>3</sub> in chloroform solution (Table V and Figure 2) is quite similar to the CD spectrum observed<sup>5</sup> for [*N,N'*-bis(salicylidene)-(S)-(+)-1,2-propanediamino]oxovanadium(IV), VO(sal)<sub>2</sub>(+)pn. Both VO(sal)<sub>2</sub>(+)tnCH<sub>3</sub> and VO(sal)<sub>2</sub>(+)pn exhibit Cotton effects of the same sign for comparable electronic transitions. A vicinal effect could account for the similarity in these spectra since both parent diamines have the same absolute configuration.<sup>11,29</sup> We have shown previously, however, that the vicinal effect is not important in chelates of this type and the signs of the Cotton effects are determined by the conformation of the central chelate ring and the configuration of a pseudotetrahedral array of the chelate ligand donor atoms.<sup>5,30</sup>

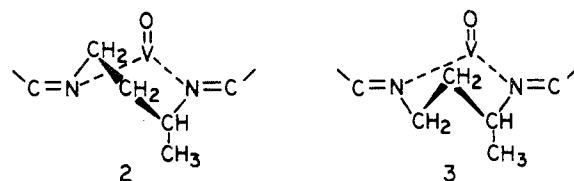
In the tetradentate complexes derived from 1,2-propanediamine the five-membered central chelate ring has a dissymmetric staggered conformation determined by the preference of the methyl substituent for an axial position.<sup>5,30</sup> The possible conformations adopted by a six-membered chelate ring are more complex and may be inherently dissymmetric (skew-boat conformation) or not (chair conformation).<sup>31</sup> The central chelate ring in the Schiff base complex *trans*-diaquo-[*N,N'*-bis(2-pyridylmethylene)-(S)-(+)-butane-1,3-diamine]-nickel(II) has been shown by nmr studies<sup>10,32</sup> to prefer a conformation where the methyl substituent is in a pseudoaxial

Table IV. Isotropic ESR Data for the Oxovanadium(IV) Complexes in Various Solvents

Complex	Solvent	$A_0$ , <sup>a</sup> G	$g_0$ <sup>b</sup>
VO(sal) <sub>2</sub> tn	DMF	94.6	1.973
	Pyridine	95.9	1.973
VO(3- <i>iprsal</i> ) <sub>2</sub> tn	CHCl <sub>3</sub>	96.4	1.973
	DMF	93.3	1.973
	Pyridine	94.6	1.974
VO(7-CH <sub>3</sub> sal) <sub>2</sub> tn	CHCl <sub>3</sub>	95.5	1.973
	DMF	93.7	1.972
	Pyridine	95.9	1.973
VO(sal) <sub>2</sub> (+)tnCH <sub>3</sub>	CHCl <sub>3</sub>	98.6	1.975
	DMF	95.5	1.973
	Pyridine	96.4	1.973
	CH <sub>3</sub> OH	93.7	1.974

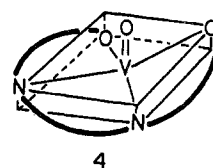
<sup>a</sup> Deviation  $\pm 0.5$  G. <sup>b</sup> Deviation  $\pm 0.001$ .

position. This result suggests that the methyl group in VO(sal)<sub>2</sub>(+)tnCH<sub>3</sub> will also prefer an axial environment and this stereochemistry is strongly supported by the similarity in the circular dichroism spectra of VO(sal)<sub>2</sub>(+)tnCH<sub>3</sub> and VO(sal)<sub>2</sub>(+)pn. VO(sal)<sub>2</sub>(+)pn presumably adopts an axial methyl conformation to avoid steric interaction between the methyl group and substituents at the azomethine carbon.<sup>5</sup> A similar interaction probably dictates the stereochemistry of the (+)tnCH<sub>3</sub> chelate ring as illustrated in 2 and 3 for the



possible skew-boat and chair forms, respectively.

The circular dichroism spectrum of VO(sal)<sub>2</sub>(+)tnCH<sub>3</sub> also provides evidence that a further source of dissymmetry, a configurational effect, is operative. As shown previously,<sup>5,30,33</sup> the observation of two oppositely signed CD bands which correspond to coupled  $\pi$ - $\pi^*$  transitions localized in the azomethine chromophores indicates that the two azomethine bonds are not coplanar and the terminal chelate rings have a skew relationship to one another. This type of exciton couplet, centered at 27,000 cm<sup>-1</sup>, is observed in the CD spectrum of VO(sal)<sub>2</sub>(+)tnCH<sub>3</sub> (Figure 2). The absolute configuration of the pseudotetrahedral arrangement of ligand donor atoms is determined to be  $\Delta$ <sup>34</sup> from the relative signs of the couplet bands. The proposed dominant configuration of VO(sal)<sub>2</sub>(+)tnCH<sub>3</sub> is given by 4.



In the CD spectra of the tetradentate salicylaldimine oxovanadium(IV) complexes derived from (+)-1,2-propanediamine and (+)-1,2-cyclohexanediamine the values of  $\Delta\epsilon$  are fairly constant in both donor and nondonor solvents.<sup>5</sup> In contrast, the  $\Delta\epsilon$  values of VO(sal)<sub>2</sub>(+)tnCH<sub>3</sub> are significantly lower in donor solvents compared to chloroform solution (Table V). This decrease in  $\Delta\epsilon$  values upon axial coordination may represent a decrease in the configurational contri-

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

(34) The configuration about the metal ion has been assigned by representing the side rings as a pair of nonorthogonal skew lines and viewing them along their common normal; cf. *Inorg. Chem.*, **9**, 1 (1970).

(22) A portion of the solvent dependency observed in the electronic spectrum of VO(sal)<sub>2</sub>(+)tnCH<sub>3</sub> in methanol may be due to hydrogen bonding as well as the coordinating ability of this alcohol.<sup>23</sup>

(23) J. Selbin in "Coordination Chemistry," S. Kirschner, Ed., Plenum Press, New York, N. Y., 1969, p 248.

(24) I. Bernal and P. H. Rieger, *Inorg. Chem.*, **2**, 256 (1963).

(25) J. P. Fackler, Jr., J. D. Levy, and J. A. Smith, *J. Amer. Chem. Soc.*, **94**, 2436 (1972).

(26) R. L. Carlin and F. A. Walker, *J. Amer. Chem. Soc.*, **87**, 2128 (1965).

(27) C. M. Guzy, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc. A*, 2791 (1969).

(28) F. A. Walker, R. L. Carlin, and P. H. Rieger, *J. Chem. Phys.*, **45**, 4181 (1966).

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

(30) R. S. Downing and F. L. Urbach, *J. Amer. Chem. Soc.*, **91**, 5977 (1969); **92**, 5861 (1970).

(31) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley, New York, N. Y., 1971; J. R. Gollgoy and C. J. Hawkins, *Inorg. Chem.*, **11**, 156 (1972).

(32) T. G. Campbell and F. L. Urbach, *Inorg. Chem.*, **12**, 1840 (1973).

Table V. Circular Dichroism Data for VO(sal)<sub>2</sub>(+)*tn*CH<sub>3</sub> in Various Solvents

Compd	Solvent	$\bar{\nu}$ , cm <sup>-1</sup> ( $\Delta\epsilon_{\max}$ )
VO(sal) <sub>2</sub> (+) <i>tn</i> CH <sub>3</sub>	CHCl <sub>3</sub>	13,160 <sup>a</sup> (-0.26) (I); 17,390 (-0.45) (II); 21,280 (-1.18) (III); 24,690 (-7.66); 27,320 (+1.43); 34,480 (-8.5)
	CH <sub>3</sub> OH	13,300 <sup>a</sup> (-0.15) (I); 18,870 (-0.28) (II); 21,280 <sup>b</sup> (-0.19) (III); 27,030 (-2.3)
	DMF	13,300 <sup>a</sup> (-0.18) (I); 18,180 (-0.56) (II); 20,830 <sup>b</sup> (-0.38) (III); 25,640 (-3.54)
	Pyridine	13,300 <sup>a</sup> (-0.10) (I); 17,700 (-0.24) (II); 20,830 (-0.39); 25,320 (-4.1)
(H-7-CH <sub>3</sub> sal) <sub>2</sub> (+) <i>tn</i> CH <sub>3</sub>	CHCl <sub>3</sub>	25,100 (+1.5); 31,100 (+7.0)

<sup>a</sup> Band lies too close to the long-wavelength limit of the instrument to be fully resolved. <sup>b</sup> Shoulder.

tribution to the observed optical activity. In five-coordinate square-pyramidal oxovanadium(IV) chelates the vanadium atom is generally located above the best plane of the four basal ligands toward the oxygen atom.<sup>6,9,35-37</sup> When a sixth donor is added, the vanadium atom moves toward the plane of the basal ligands<sup>35-37</sup> and the tetradentate ligand may adopt a more planar geometry to minimize steric interactions with the axial donor. This explanation also accounts for the apparent loss of the CD couplet in donor solvents (Table V and Figure 2). The decrease in  $\Delta\epsilon$  values could also arise from a greater degree of band cancellation owing to shifts in the electronic transitions upon axial coordination. It is unlikely that such band cancellation would produce the uniform decrease in  $\Delta\epsilon$  which is observed throughout the entire spectrum.

**Band Assignments and Electronic Structure.** The tetradentate 1,3-diamine complexes of oxovanadium(IV) in donor solvents exhibit the following spectral features in the 10,000-21,000-cm<sup>-1</sup> region: a band maximum at ~13,000 cm<sup>-1</sup> (I) and inflections at ~19,000 cm<sup>-1</sup> (II) and ~21,000 cm<sup>-1</sup> (III) (Table III, Figure 2). The latter inflection is better defined in the CD spectrum of VO(sal)<sub>2</sub>(+)*tn*CH<sub>3</sub> in DMF (Figure 2). A comparison of the solid-state reflectance spectra with the donor solution spectra (Figure 2, Table III) reveals that band I is shifted to higher energy with a change from the solid state to coordinating solutions. The observed spectral shifts reflect the changes caused by the replacement of a polymeric V-O-V species by a monomeric complex containing an axially coordinated solvent molecule.

The infrared spectral data discussed above show that the V=O bond order increases when the polymeric 1,3-diamine complexes are dissolved in coordinating solvents. In terms of the Ballhausen and Gray (BG) molecular orbital scheme<sup>38</sup> this observation suggests that the  $\pi$  bonding between the vanadium 3d<sub>xz</sub>, 3d<sub>yz</sub> orbitals and oxygen 2p<sub>x</sub>, 2p<sub>y</sub> orbitals in the VO moiety is enhanced in coordinating solvents relative to the solid state. Increased axial  $\pi$  bonding would result in an increase in the energy of the <sup>2</sup>B<sub>2</sub>(d<sub>xy</sub>) → <sup>2</sup>E(I)(d<sub>xz</sub>, d<sub>yz</sub>) transition (BG scheme) in coordinating solutions compared to the solid state. Band I exhibits this type of behavior and is therefore assigned to the <sup>2</sup>B<sub>2</sub> → <sup>2</sup>E(I) transition. Support

for this interpretation can be gained from solution studies<sup>24</sup> and the polarized crystal spectra of VO(acac)<sub>2</sub>.<sup>39</sup>

In chloroform solution, the 1,3-diamine chelates are formulated as five-coordinate species and  $\nu_{V=O}$  is shifted approximately 30 cm<sup>-1</sup> toward higher energy (Table II). This result indicates an additional increase in axial V=O  $\pi$  bonding for the chelates in noncoordinating solvents compared to coordinating solvents. X-Ray crystallographic data<sup>6,9,35-37</sup> further show that the loss of a donor molecule from the sixth position gives rise to an increase in the O-V-equatorial ligand bond angle. On the basis of these observations, the <sup>2</sup>B<sub>2</sub>(d<sub>xy</sub>) → <sup>2</sup>E(I)(d<sub>xz</sub>, d<sub>yz</sub>) and <sup>2</sup>B<sub>2</sub>(d<sub>xy</sub>) → <sup>2</sup>B(I)(d<sub>x<sup>2</sup>-y<sup>2</sup>) transitions would be expected to shift to higher and lower energies, respectively, in noncoordinating solvents compared to coordinating solvents.</sub>

The electronic spectra (10,000-22,000 cm<sup>-1</sup>) of the 1,3-diamine complexes in chloroform solution (Table III, Figure 2) are characterized by a single maximum at ~17,500 cm<sup>-1</sup> (II) with inflections at ~13,900 cm<sup>-1</sup> (I) and ~21,400 cm<sup>-1</sup> (III). A comparison of these spectra with those obtained in coordinating solvents indicates that band I shifts ~600 cm<sup>-1</sup> to higher energy and band II 1500 cm<sup>-1</sup> to lower energy upon going from coordinating solvents to chloroform. Band I now becomes a shoulder on the low-energy side of the more intense band II and it is difficult to determine its exact position. The shifts observed for the electronic spectra in chloroform compared to the spectra of pyridine or DMF solutions support the assignment of the lowest energy bands to the <sup>2</sup>B<sub>2</sub> → <sup>2</sup>E(I) and <sup>2</sup>B<sub>2</sub> → <sup>2</sup>B<sub>1</sub> transitions, respectively. The assignments of bands I and II as d → d transitions is in agreement with previous reports.<sup>1-5,16,40</sup> On the other hand, III (~21,000 cm<sup>-1</sup>) has been chosen to represent, alternatively, a d → d band,<sup>5,16,41,42</sup> a spin-forbidden ligand band,<sup>3</sup> and a low-intensity charge-transfer band.<sup>40,43</sup> In a previous study<sup>5</sup> we suggested that the frequent occurrence of similar transitions at about 21,000 cm<sup>-1</sup> for oxovanadium(IV) chelates with a variety of ligands indicates that this transition has its origin in the metal ion chromophore. In accord with this argument, we tentatively assign band III in the present complexes to the <sup>2</sup>B<sub>2</sub> → <sup>2</sup>A<sub>1</sub> transition.

The assignment of the moderately intense absorption band observed at ~27,000 cm<sup>-1</sup> in the electronic spectra of the 1,3-diamine complexes was discussed above. This band and the corresponding CD bands in the spectrum of VO(sal)<sub>2</sub>(+)*tn*CH<sub>3</sub> are assigned to nondegenerate  $\pi$ - $\pi^*$  transitions localized in the coupled azomethine chromophores.<sup>33</sup> The remaining higher energy bands are assigned to intraligand transitions, e.g., phenyl  $\pi$ - $\pi^*$  excitations, since analogous bands are present in the spectra of (H-7-CH<sub>3</sub>sal)<sub>2</sub>(+)*tn*CH<sub>3</sub> (Table V), Zn(sal)<sub>2</sub>(-)*pn*,<sup>33</sup> and Zn(3-*iprsal*)<sub>2</sub>*tn*.<sup>17</sup> Charge-transfer bands are probably masked by these more intense ligand bands.

The isotropic absorption and CD spectra of (H-7-CH<sub>3</sub>sal)<sub>2</sub>(+)*tn*CH<sub>3</sub> (Tables III and V) are similar to observed spectra for other optically active Schiff bases.<sup>30,33</sup> The bands at 25,100 and 31,800 cm<sup>-1</sup> are assigned to an n →  $\pi^*$  transition and an azomethine  $\pi$ - $\pi^*$  transition, respectively. The latter

(35) P. Kierkegaard and J. M. Longo, *Acta Chem. Scand.*, **19**, 1906 (1965).

(36) A. C. Hazell, *J. Chem. Soc.*, 5745 (1963).

(37) B. H. Bersted, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, **7**, 1557 (1968).

(38) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1963); C. J. Ballhausen, B. F. Djurinskij, and K. J. Watson, *J. Amer. Chem. Soc.*, **90**, 3305 (1968).

(39) G. Basu, W. A. Yeranov, and R. L. Belford, *Inorg. Chem.*, **3**, 929 (1964); M. H. Valek, W. A. Yeranov, G. Basu, P. K. Horn, and R. L. Belford, *J. Mol. Spectrosc.*, **37**, 228 (1971).

(40) J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966).

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

(42) S. Yamada and Y. Kuge, *Bull. Chem. Soc. Jap.*, **42**, 152 (1969).

(43) D. Ogden and J. Selbin, *J. Inorg. Nucl. Chem.*, **30**, 1227 (1968); O. Piovesana and J. Selbin, *ibid.*, **31**, 433 (1969).

transition is shifted to lower energy upon complexation with a metal ion.

**Acknowledgment.** This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

**Registry No.** [VO(sal)<sub>2</sub>tn]<sub>x</sub>, 28630-97-9; (DMF)VO(sal)<sub>2</sub>tn,

42578-14-3; (py)VO(sal)<sub>2</sub>tn, 42578-15-4; [VO(sal)<sub>2</sub>(+)(tnCH<sub>3</sub>)<sub>2</sub>]<sub>x</sub>, 42579-14-6; VO(sal)<sub>2</sub>(+)(tnCH<sub>3</sub>), 31929-66-5; (MeOH)VO(sal)<sub>2</sub>(+)(tnCH<sub>3</sub>), 42578-17-6; (DMF)VO(sal)<sub>2</sub>(+)(tnCH<sub>3</sub>), 42578-18-7; (py)VO(sal)<sub>2</sub>(+)(tnCH<sub>3</sub>), 42578-19-8; [VO(3-*i*prsal)<sub>2</sub>tn]<sub>x</sub>, 42579-15-7; VO(3-*i*prsal)<sub>2</sub>tn, 42578-20-1; (DMF)VO(3-*i*prsal)<sub>2</sub>tn, 42578-21-2; (py)VO(3-*i*prsal)<sub>2</sub>tn, 42578-22-3; [VO(7-CH<sub>3</sub>sal)<sub>2</sub>tn]<sub>x</sub>, 42745-97-1; VO(7-CH<sub>3</sub>sal)<sub>2</sub>tn, 42718-93-4; (DMF)VO(7-CH<sub>3</sub>sal)<sub>2</sub>tn, 42578-23-4; (py)VO(7-CH<sub>3</sub>sal)<sub>2</sub>tn, 42578-24-5; (H-7-CH<sub>3</sub>sal)<sub>2</sub>(+)(tnCH<sub>3</sub>), 42530-90-5.

Contribution from the Departments of Chemistry, University of Kentucky, Lexington, Kentucky 40506, and West Virginia University, Morgantown, West Virginia 26506

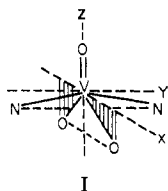
## Electronic Structure of Bis(2-methyl-8-quinolinolato)oxovanadium(IV)

HENRY J. STOKLOSA,<sup>1a</sup> JOHN R. WASSON,<sup>\*1a</sup> and B. JACK McCORMICK<sup>1b</sup>

Received July 18, 1973

The spectral and magnetic properties of bis(2-methyl-8-quinolinolato)oxovanadium(IV), VO(quin)<sub>2</sub>, a low-symmetry complex possessing effective C<sub>2v</sub> symmetry, are described. An explicit phenomenological crystal field model was developed which gave a good account of the electronic and electron spin resonance (esr) spectra of VO(quin)<sub>2</sub>. Iterative extended-Huckel molecular orbital calculations for the model complex ion VOCl<sub>4</sub><sup>2-</sup> yielded results in qualitative agreement with the crystal field model. The esr spectrum of VO(quin)<sub>2</sub> in a toluene glass exhibited three *g* values and yielded spin-Hamiltonian parameters analogous to those found for bis(*N*-methylsalicylaldiminato)oxovanadium(IV) which also contains the VO(N<sub>2</sub>-O<sub>2</sub>) chromophore. Except for the splitting of the d<sub>xz</sub> and d<sub>yz</sub> levels, the Ballhausen-Gray energy level scheme for complexes with C<sub>4v</sub> microsymmetry holds for VO(quin)<sub>2</sub>.

A wide variety of oxovanadium(IV), vanadyl complexes have been prepared and characterized.<sup>2,3</sup> A square pyramidal (C<sub>4v</sub>) geometry has been established or, more frequently, assumed for vanadyl compounds. In recent years two crystal structures<sup>4,5</sup> have appeared which serve to shake confidence in the usual assumptions concerning the structures of vanadyl chelates. Shiro and Fernando<sup>4</sup> have reported the structure of bis(2-methyl-8-quinolinolato)oxovanadium(IV), VO(quin)<sub>2</sub>, which is five coordinate and has a trigonal bipyramidal coordination polyhedron about the vanadium in which the three oxygen atoms and the vanadium are in the equatorial plane and the two nitrogen atoms occupy apical positions, I. Similar structures have been reported for bis-



(trimethylamine)oxovanadium(IV) dichloride<sup>6</sup> and bis(tetramethylurea)oxovanadium(IV) dichloride.<sup>7</sup> It is noted that although these molecules are referred to as being trigonal bipyramidal they are more appropriately considered as having an effective C<sub>2v</sub> distorted square pyramidal geometry.<sup>6</sup> The other unusual structure of importance to vanadyl chemistry is the one found<sup>5</sup> for the 4-phenylpyridine adduct of vanad-

yl acetylacetonate, VO(acac)<sub>2</sub>, in which the 4-phenylpyridine added cis to the vanadyl oxygen atom rather than trans axially as is usually assumed for VO(acac)<sub>2</sub> adduct formation.

Here we address ourselves to the problem of the electronic structure of VO(quin)<sub>2</sub> since it was of interest to characterize the properties of a compound which could not be expected to be interpreted in terms of the familiar Ballhausen-Gray<sup>8</sup> model for vanadyl complexes possessing effective C<sub>4v</sub> symmetry. To this end we have obtained the electronic and esr spectra of VO(quin)<sub>2</sub>. A general crystal field model for complexes of this type was developed and iterative extended-Huckel molecular orbital calculations were performed for the model compound VOCl<sub>4</sub><sup>2-</sup> which was assumed to have bond angles appropriate to VO(quin)<sub>2</sub>.

### Experimental Section

2-Methyl-8-quinolinol was obtained from Aldrich Chemical Co., Milwaukee, Wis. and used without further purification. All other chemicals were of the best available reagent or spectroscopic grades. Optical and infrared spectra were measured with Cary Model 14 and Perkin-Elmer Model 621 recording spectrophotometers, respectively. Electron spin resonance spectra were measured with Varian E-3 and Magnion MVR-12X X-band spectrometers. The Magnion esr spectrometer operates at about 9.4 GHz using 6-kHz field modulation and a 12-in. electromagnet. The frequency was monitored with a calibrated absorption wavemeter incorporated in the microwave unit. Field calibration was checked using diphenylpicrylhydrazyl (DPPH) free radical for which *g* = 2.0036. Esr spectra of saturated (~10<sup>-3</sup> M) toluene solutions of VO(quin)<sub>2</sub> were obtained using quartz capillary tubing. Frozen solution esr spectra were obtained with a finger dewar filled with liquid nitrogen which fit into the instrument sample cavity. Mass spectra were obtained using a double-focusing Hitachi Perkin-Elmer RMU-7 spectrometer. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz.

Bis(2-methyl-8-quinolinolato)oxovanadium(IV), VO(quin)<sub>2</sub>, was prepared by adding an aqueous solution of the sodium salt of the ligand (obtained by adding the ligand to a stoichiometric amount of sodium hydroxide in about 50 ml of warm distilled water) dropwise to a stoichiometric amount of vanadyl sulfate in warm water. A pale green precipitate formed immediately which was collected by

(1) (a) University of Kentucky; (b) West Virginia University.  
 (2) J. Selbin, *Chem. Rev.*, **65**, 153 (1965); *Coord. Chem. Rev.*, **1**, 293 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 712 (1966).  
 (3) B. J. McCormick, J. L. Featherstone, H. J. Stoklosa, and J. R. Wasson, *Inorg. Chem.*, **12**, 692 (1973), and references therein.  
 (4) M. Shiro and Q. Fernando, *Chem. Commun.*, 63 (1971).  
 (5) M. R. Caira, J. M. Haigh, and L. R. Nassimbeni, *Inorg. Nucl. Chem. Lett.*, **8**, 109 (1972).  
 (6) J. E. Drake, J. Vekris, and J. S. Wood, *J. Chem. Soc. A*, 1000 (1968).  
 (7) J. Coetzer, *Acta Crystallogr., Sect. B*, **26**, 872 (1970).

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