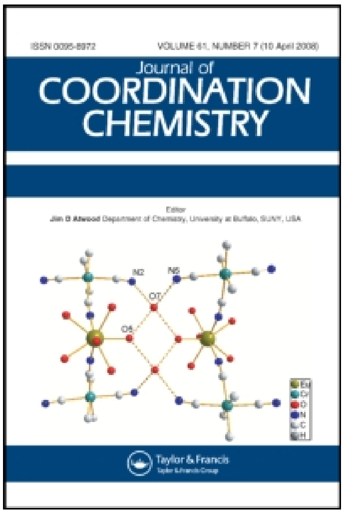

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# SCHIFF BASE COMPLEXES OF OXOCATIONS Part II Oxovanadium(IV) complexes with tetradentate optically active Schiff bases

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# SCHIFF BASE COMPLEXES OF OXOCATIONS
## Part II[†] Oxovanadium(IV) complexes with tetradentate optically active Schiff bases

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The synthesis and properties of oxovanadium(IV) complexes with tetradentate Schiff bases obtained by condensation of two moles of acetylacetone, trifluoroacetylacetone, salicylaldehyde and its 5-chloro and 5-nitro derivatives, with optically active 1,2-diamines, namely (+) propylenediamine, (+) and *meso* butanediamine, (+) and *meso* cyclohexanediamine, (–) and *meso* stilbenediamine, are described. The infrared, circular dichroism and electronic spectra are reported and discussed. The factors influencing the formation of hexacoordinate adducts with donor bases are also discussed.

## INTRODUCTION

We have recently studied uranyl complexes[1] with Schiff bases obtained by condensation of optically active 1,2-diamines with salicylaldehyde, discovering a peculiar conformational behaviour of the chelate ring of the diamine which depends not only on its absolute configuration but also on the nature of the substituents on the carbon atoms of the diamine. Moreover an effect of the coordination number six or seven of the uranyl ion on the whole geometry of the tetradentate ligands was evidenced.

We have therefore extended our investigations to a more simple oxocation, namely the vanadyl ion, which may display pentacoordination and sometimes hexacoordination, with the aim of obtaining information which can be compared with the results obtained in the case of the uranyl ion, and which might give further insight into the conformational behaviour of such tetradentate ligands in oxocation complexes. These latter are of interest since it has been suggested that similar compounds can be used as model systems of biological significance[2,3].

First of all we have to consider the possibility of having two enantiomeric conformations of the "gauche" ethylenediamine chelate ring in a planar or pseudoplanar Schiff base ligand. If an optically active diamine is used the enantiomers become diasteroisomers and the most stable diasteroisomer corresponds to one of the two conformations. It has been reported that in the case of VO acac(+)pn the four possible isomers, are resolvable[4]. Moreover it has been shown[5] that the preferred conformation of the diamine chelate ring does not always depend on the absolute configuration of the optically active diamine; for instance the conformation of the diamine chelate ring appears to be inverted in going from (+) propylenediamine to the configurationally related (+) cyclohexanediamine. The same behaviour has been reported for $Co^{2+}$ and $Ni^{2+}$ complexes[3,6]. However such a clear inversion has not been observed in the case of $UO_2^{2+}$ complexes[1].

Moreover the vanadyl complexes of these Schiff bases are pentacoordinated when in solution and do not show any tendency to coordinate a basic ligand in the free axial coordination position. Only in the case of the trifluoroacetylacetonate Schiff base of ethylenediamine[7] have hexacoordinated species been observed in solution, but these have not been isolated in the solid state. The factors which stabilise hexacoordination were obviously a second aspect worthy of investigation.

We have therefore synthesized and investigated oxovanadium(IV) complexes with some tetradentate Schiff bases, derived from the condensation of two moles of acetylacetone (type A) or salicylaldehyde (type B) with one mole of 1,2-diamine. The general formulae are reported in Fig. 1.

The 1,2-diamines used in this work were (with abbreviations in parentheses) (cf. Fig. 1): $R_1 = R_2 = H$, ethylenediamine (en); $R_1 = CH_3$, $R_2 = H$, (+)

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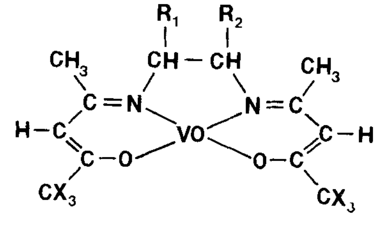
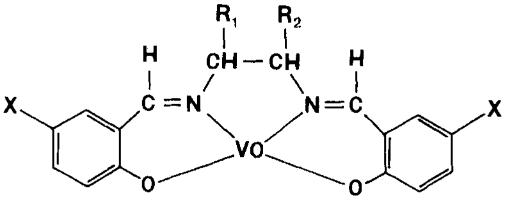
[†] Part I – A. Pasini, M. Gullotti and E. Cesarotti, *J. Inorg. Nucl. Chem.*, 34, 3821 (1972)



type A

(X = H, F)



type B

(X = H, $NO_2$, Cl)

FIGURE 1

propylenediamine (pn); $R_1 = R_2 = CH_3$, (+) and *meso* butanediamine (bn); $R_1 = R_2 = \frac{1}{2}(CH_2)_4$, (+) and *meso* cyclohexane diamine (chxn); $R_1 = R_2 = C_6H_5$, (−) and *meso* stilbenediamine (stien). Abbreviations used throughout this paper are: acac, acetylacetone; tfacac, trifluoroacetylacetone and sal, salicylaldehyde. The loose abbreviations acacen or salen indicate the corresponding Schiff bases. The optically active diamines used in this work are believed to have to same absolute configuration[8,9], though this has been questioned recently[10]. This problem will be briefly discussed in the section on circular dichroism.

## EXPERIMENTAL

Analyses (see Table I) were by the microanalytical laboratory of the University of Milan. Magnetic susceptibility measurements were carried out at room temperature using the Gouy method on a Varian instrument and the diamagnetic contribution was corrected with the Pascal's constants. I.R. spectra were recorded on Perkin Elmer 137 and 237 instruments. Electronic spectra were obtained on a Beckman DK-2A spectrophotometer; C.D. curves on a Jouan dicograph II. The Schiff bases were prepared as described elsewhere[9]. Oxovanadium(IV) complexes of salicylaldiimine were obtained by adding to an aqueous solution of $VOCl_2$ an ethanol solution of an

TABLE I

| Compound | C calc. | C found | H calc. | H found | N calc. | N found | Magnetic moment at 20°C (B.M.) | M.P. (°C) |
|---|---|---|---|---|---|---|---|---|
| VO salen | 57.6 | 57.6 | 4.2 | 4.2 | 8.4 | 8.2 | 1.80 | 280 |
| VO sal(+)pn | 58.7 | 58.5 | 4.6 | 4.4 | 8.1 | 8.0 | 1.80 | 170 |
| VO sal(+)bn | 59.8 | 59.9 | 5.0 | 5.3 | 7.8 | 7.9 | 1.73 | 240 |
| VO sal *meso* bn | 59.8 | 59.2 | 5.0 | 4.9 | 7.8 | 7.6 | 1.68 | 300 |
| VO sal(+)chxn | 62.0 | 61.4 | 5.2 | 5.2 | 7.2 | 7.1 | 1.70 | 274 |
| VO sal *meso* chxn | 62.0 | 61.7 | 5.2 | 5.2 | 7.2 | 7.3 | 1.69 | 280 |
| VO sal(−)stien | 69.2 | 68.1 | 4.5 | 4.7 | 5.8 | 6.0 | 1.74 | 280 |
| VO sal *meso* stien | 69.2 | 68.8 | 4.5 | 4.8 | 5.8 | 5.8 | 1.81 | 235 |
| VO 5−$NO_2$ salen | 45.6 | 45.7 | 2.8 | 2.5 | 13.2 | 12.7 | 1.84 | >320 |
| VO 5−Clsalen | 47.8 | 48.6 | 3.0 | 2.9 | 7.0 | 7.0 | 1.70 | >320 |
| VO 5−$NO_2$ salen. py | 50.3 | 50.8 | 3.4 | 3.1 | 13.9 | 13.9 | − | dec. |
| VO 5−$NO_2$ salen.DMSO | 43.2 | 42.8 | 3.6 | 2.8 | 11.2 | 11.2 | − | dec. |
| VO acacen | 49.8 | 48.9 | 6.2 | 6.1 | 9.7 | 9.0 | 1.80 | 236 |
| VO acac(+)pn | 51.5 | 51.7 | 6.6 | 6.6 | 9.2 | 9.0 | 1.75 | 177 |
| VO acac(+)bn | 53.0 | 54.0 | 6.9 | 7.0 | 8.8 | 8.7 | 1.85 | 170 |
| VO acac *meso* bn | 53.0 | 53.0 | 6.9 | 7.0 | 8.8 | 9.0 | 1.74 | 190 |
| VO acac *meso* chxn | 55.9 | 56.1 | 7.0 | 7.0 | 8.7 | 8.3 | 1.82 | 283 |
| VO acac( )stien | 65.3 | 64.9 | 5.9 | 6.0 | 6.4 | 6.4 | 1.72 | 275 |
| VO acac *meso* stien | 65.3 | 64.9 | 5.9 | 5.4 | 6.4 | 6.0 | 1.81 | 285 |
| VO tfacacen | 36.2 | 37.5 | 3.0 | 3.0 | 7.1 | 7.3 | 1.83 | 307 |

equimolar amount of the Schiff bases and refluxing the green solution for 15 minutes. After cooling the green crystalline material was collected. The (–)stien derivative precipitated as a yellow-brown powder, and the (+)pn derivative as a grey-green powder. The 5–NO$_2$salen compound was obtained similarly as a brown, very insoluble material.

The acac derivatives were obtained using the exchange method of Martin et al.$^{4,11}$. Equimolar amounts of bisacetylacetone oxovanadium(IV) and of the appropriate Schiff base were intimately mixed together and placed in a distillation apparatus; the mixture was heated to 230° – 240°C for one hour *in vacuo* and then the acetylacetone distilled off. The residue was washed several times with dry ether and crystallized from benzene to give deep green powders.

The trifluoroacetylacetoniminate complex was obtained by the same method from bistrifluoroacetilacetone oxovanadium(IV) and bis-trifluoroacetylacetonethylenediimine as a brown-pink powder, which may be crystallized from acetone.

The adduct of VO 5–NO$_2$salen with pyridine (py) was obtained by refluxing a suspension of the parent compound in anhydrous pyridine for several days. The brown insoluble powder was hot filtered and the pyridine solution evaporated to dryness. Both the materials thus obtained analysed as VO 5–NO$_2$salen.py.

The adduct of VO 5–NO$_2$salen with dimethyl sulphoxide (DMSO) was obtained by precipitation with water from a DMSO solution of the VO 5–NO$_2$salen compound. The VO tfacacen adduct with DMSO, was similarly obtained but on standing overnight it lost the base.

## RESULTS AND DISCUSSION

### *Preparation and Characterization of Compounds*

The preparation of both series of compounds (see experimental) did not present great difficulties. However it must be said that during the preparation of type A compounds, according to the chelate exchange method of Martin$^{4}$ which requires rather high temperatures, sometimes a certain degree of carbonization of the organic ligand was observed, expecially in the (+)chxn case, where the Schiff base could not

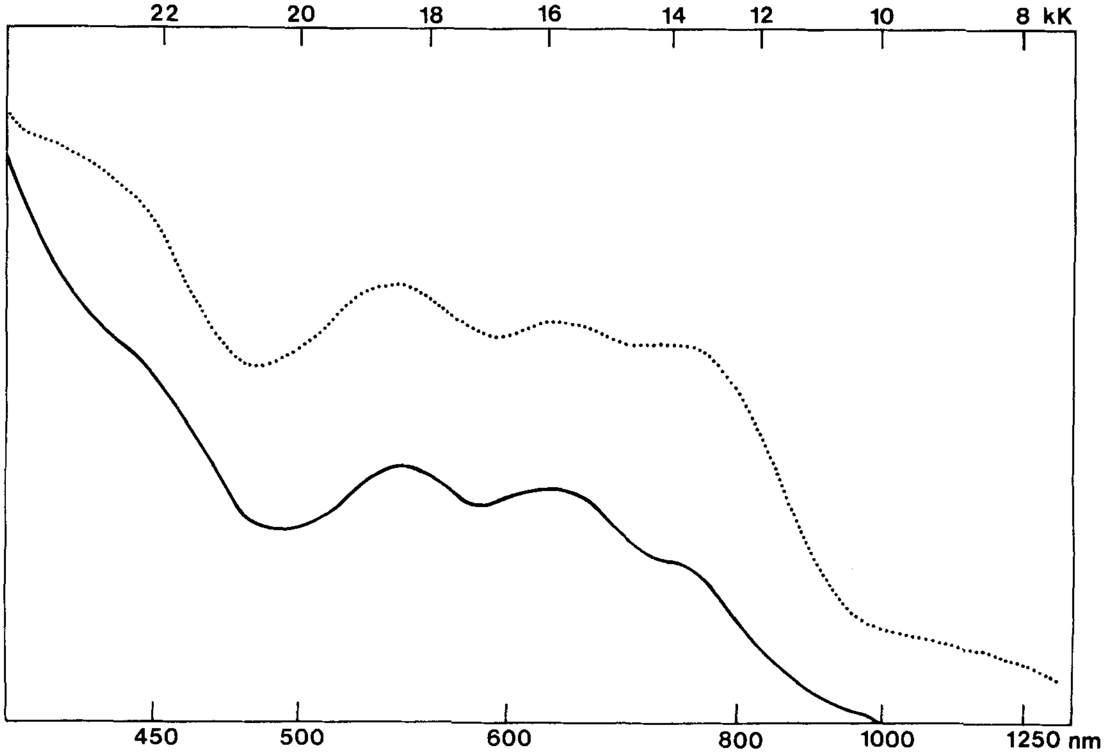


FIGURE 2 Electronic spectra of the type A compound VO acac*meso*chxn. —— Chloroform solution; ..... reflectance. The spectra are all the same throughout the series.

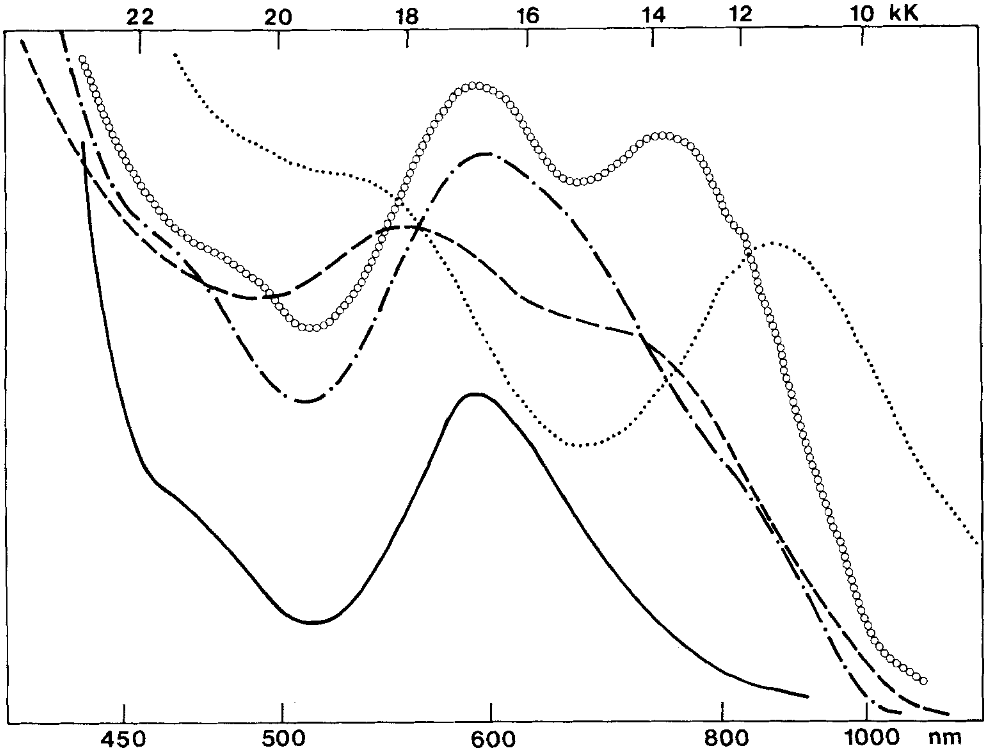


FIGURE 3 Electronic spectra of type B compounds. Chloroform solution; reflectance of VO sal(+)pn; —·—·— reflectance of VO sal(+)chxn; oooo reflectance of VO sal*meso*bn ······· reflectance of VO sal(−)stien. The reflectance spectra of the other compounds are similar to that of the (+)pn derivative.

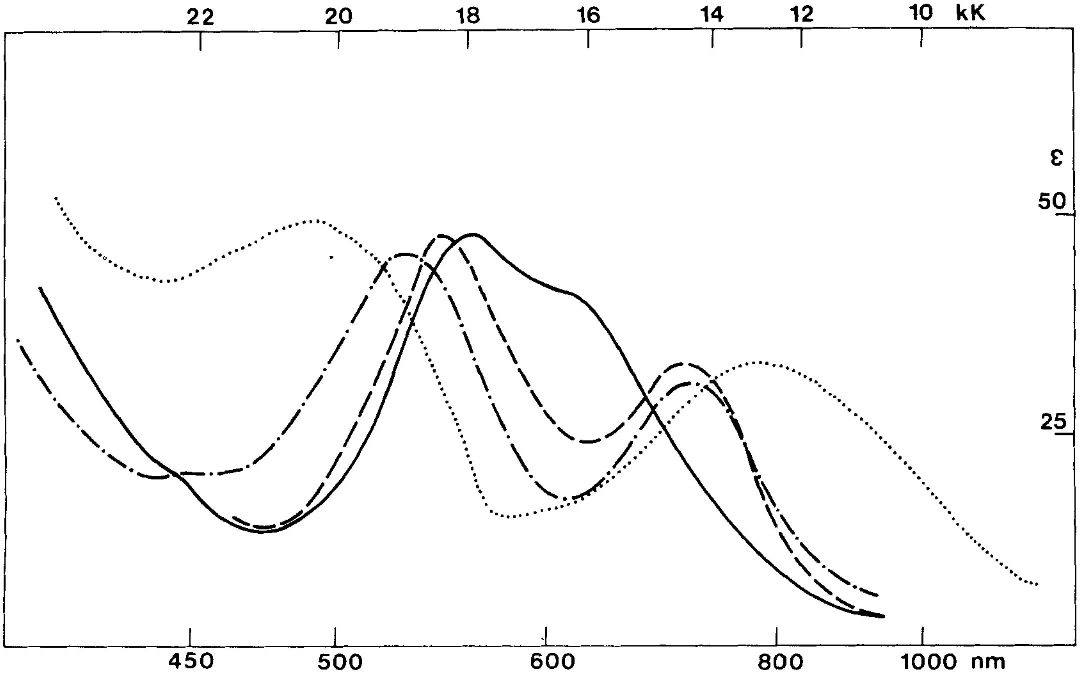


FIGURE 4 Electronic spectra of VO tfacacen. ——— acetone solution; —·—·— acetone solution in the presence of butilamine; — — — pyridine solution; ······ reflectance. The spectrum of a chloroform solution is similar to that of the acetone solution and the spectrum of a dimethylsulfoxide solution is similar to that of the pyridine solution.

be easily crystallized[9]. Consequently the compound corresponding to this Schiff base was not obtained in a pure state; the spectra reported in this paper must be therefore considered as being only indicative.

Compounds of type A and B are green and show the same reflectance spectra with a few notable exceptions; three complexes, VO 5–NO$_2$salen, VO sal(–)stien and VO tfacacen which will be discussed later. (See Figs. 2, 3, 4 and 5 and Table II.)

Green type B compounds show slight differences in the reflectance spectra within the series, while in solution they all have the same type of electronic spectrum (see Fig. 2).

We presume that the differences observed in the reflectance spectra arise from a certain degree of interaction in the solid state, probably between the vanadium atom and the oxygen atoms of the Schiff base of a nearby molecule in the crystalline lattice, to reach a very weak hexacoordination. In agreement with this point some of the reflectance spectra show a splitting of the two absorption bands at about 17 kK which resembles that reported by many authors in the case of hexacoordinate adduct formation in solution of vanadyl complexes (see for instance Ref. 7).

The magnetic moments in the solid state are all around the value of 1.5 B.M. at room temperature, in contrast to the value of 1.5 B.M. found for compounds derived from tridentate Schiff bases[12] for which a polymeric structure must be supposed in order to reach the pentacoordination of the vanadium atom; such a polymeric structure is in the plane of the tridentate ligand thus creating a favourable geometry for an antiferromagnetic coupling. In the case of our compounds this polymeric structure is not necessary and when an interaction occurs, the compounds become hexacoordinated giving rise to a quite different geometrical intermolecular interaction. This may explain the higher values of the magnetic moments, as expected in the case of a very low intermolecular magnetic exchange.

The I.R. spectra (see Table III) do not require much discussion (except as expected in the case of the three anomalous compounds). In particular, the V=O *stretching* always appears, in *nujol* mull, at the expected values (about 1000–970 cm$^{-1}$) despite the fact that one would expect a lowering of its frequency upon hexacoordination[13,14]. Presumably such a hexacoordination, when it exists in the solid state is more a weak *trans* axial perturbation, than a

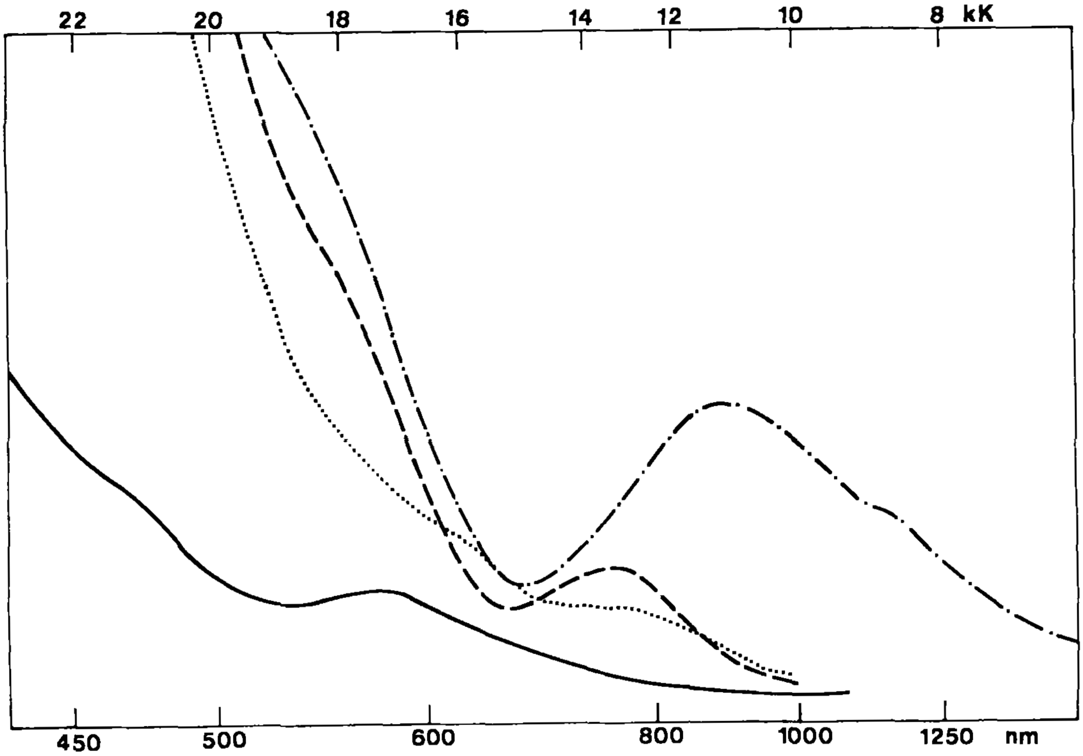


FIGURE 5 Electronic spectra of VO 5–NO$_2$salen. —— acetone solution; ······ pyridine solution; – – – – DMSO solution, –·–·– reflectance.

TABLE II
Electronic absorption spectra (kK)

| Compound | Reflectance | Solution (ε in parentheses) | |
|---|---|---|---|
| VO salen | 12.67(sh); 15.61; 17.10;<br>21.25(sh) | ($CHCl_3$) | 13.33(sh 45); 16.74(164);<br>20.82 (sh 92);<br>27.00(10,000); 35.20 (25,000) |
| VO sal(+)pn | 13.70(sh); 18.20;<br>21.25(sh) | ($CHCl_3$) | 12.90(sh 28); 16.95(202)<br>20.55(sh 137);<br>27.00(6,500); 35.20(16,000) |
| VO sal(+)bn | 12.50(sh); 15.62(sh); 16.70;<br>21.25(sh) | ($CHCl_3$) | 13.90(sh 70); 16.70(193)<br>20.55(sh 84)<br>27.10(9,400); 35.20(23,000) |
| VO sal *meso* bn | 11.78(sh); 13.70; 17.10;<br>21.25(sh) | ($CHCl_3$) | 13.90(sh 70); 16.80(167)<br>21.25(sh 85)<br>27.10(13,000); 35.20(31,000) |
| VO sal(+)chxn | 12.50(sh); 15.40(sh); 16.97<br>21.25(sh) | ($CHCl_3$) | 13.15(sh 27); 16.97(144)<br>21.25 (sh 86)<br>27.20(9,100); 35.20(22,000) |
| VO sal *meso* chxn | 12.50(sh); 15.40(sh); 16.80<br>21.25(sh) | ($CHCl_3$) | 13.25(sh 15); 16.80(156)<br>21.25(sh 77)<br>27.00(12,000); 35.20(30,000) |
| VO sal(−)stien | 11.11; 19.25(sh) | ($CHCl_3$) | 14.70(sh 90); 16.97(157)<br>21.25(sh 83)<br>26.65(11,000); 35.20(36,000) |
| | | (DMSO) | 12.05(sh 50); 15.40(sh 90); 16.77(160)<br>20.08(sh 85) |
| VO sal *meso* stien | 12.70(sh); 15.17(sh); 16.70<br>21.25(sh) | ($CHCl_3$) | 14.30(sh 70); 16.80(156);<br>21.25(sh 77)<br>26.65(12,000); 35.20(30,000) |
| VO 5−$NO_2$ salen | 8.34(sh); 11.10;<br>20.00(sh) | (acetone[a]) | 13.90 (sh); 17.55[b];<br>21.25(sh)<br>29.40 |
| | | (DMSO) | 13.50(63); 17.55(180) |
| VO 5−$NO_2$ salen.py | 12.82; 17.25(sh)<br>20.04(sh); 25.00 | (pyridine[a]) | 13.70; 16.40 (sh);<br>28.00 |
| VO 5−Clsalen | 11.62(sh); 14.70(sh); 16.86<br>20.04(sh) | ($CHCl_3$) | 11.78(sh 40); 15.14(sh 80); 16.78(185)<br>20.08(sh 90)<br>26.30(9,400); 34.50(28,000) |
| | | (DMSO) | 13.60(sh 58); 17.55(170)<br>21.03(sh 75) |
| VO acacen | 13.10(sh); 15.50; 18.40;<br>22.70(sh) | ($CHCl_3$) | 13.50(sh 70); 15.92(sh 130)<br>18.35 (140); 23.22(sh 240)<br>28.80(20,000); 30.50(17,000) |
| VO acac(+)pn | 10.00(sh); 13.20(sh); 16.00<br>17.55; 22.75(sh) | ($CHCl_3$) | 12.50(sh 18); 16.40(sh 81)<br>23.75(sh 198);<br>28.80(5,000); 31.20(19,000) |
| VO acac(+)bn | 9.53(sh); 16.55<br>17.92; 23.00(sh) | ($CHCl_3$) | 12.60(sh 44); 16.04(115)<br>17.91(122); 23.30(sh 238)<br>28.80(6,300); 31.40(18,000) |
| VO acac *meso* bn | 9.53;[b]<br>22.70 | ($CHCl_3$) | 13.90(sh 80); 15.61(90)<br>18.52(100); 22.70(sh 150)<br>28.20(sh 6,100); 31,20(29,000) |
| VO acac(+)chxn[c] | c | ($CHCl_3$ [c]) | 13.70(sh); 16.15(sh)<br>19.05(sh);<br>27.40(sh); 30.50 |
| VO acac *meso* chxn | 8.85(sh); 13.35(sh); 15.90<br>18.70; 22.75(sh) | ($CHCl_3$) | 13.70(sh 40); 16.13(69);<br>18.77(75); 22.82(sh 115)<br>28.20(sh 8,600); 31.03(20,000) |
| VO acac(−)stien | 10.00(sh); 13.33(sh); 15.62<br>17.85(sh); 23.25(sh) | ($CHCl_3$) | 15.75(123)<br>17.88(sh 108); 23.30(sh 162)<br>29.00(8,600); 31.00(22,000) |

TABLE II (continued)

| Compound | Reflectance | Solution ($\epsilon$ in parentheses) | |
|---|---|---|---|
| VO acac *meso* stien | 9.1(sh); 12.75; 16.00<br>18.85; 22.75(sh) | ($CHCl_3$) | 15.78(109)<br>17.38(109); 22.80(sh 145)<br>29.10(10,000); 30.70(18,000) |
| VO tfacacen | 10.55(sh); 13.10<br>20.00; 23.80(sh);<br>26.30(sh) | (acetone[d]) | 13.33(sh 20); 15.88(41)<br>18.05(48); 25.00(sh 65)<br>30.03(sh 4,100) |
| | | (pyridine[e]) | 14.30(35);<br>18.50(57); 22.20(sh 27)<br>28.60(2,700); 32.20(12,000) |

[a] These spectra are only qualitative because of the low solubility of the compound.

[b] Very broad unresolved bands.

[c] This compound could not be obtained pure; the spectrum reported is only indicative.

[d] The spectrum of a chloroform solution has a very similar pattern, but no quantitative measurement could be made because of the low solubility of the compound.

[e] The spectrum of a DMSO solution is almost superimposable.

true bond. In fact the splitting of the reflectance band at about 17 kK is small, in agreement with a weak axial perturbation of an essentially square pyramidal molecule. The chloroform or benzene solution of both series of compounds are green and their electronic spectra are similar within the two series (Figs. 2 and 3); we conclude that the same species, presumably monomeric, is present. This is also confirmed by the fact that for both type of compounds the V=O stretching frequency lies, in solution, in the expected region 1000–970 cm$^{-1}$.

On the contrary the three anomalous orange-brown compounds, cited above, exhibit an anomalous reflectance spectrum (Figs. 3, 4 and 5) and show, in nujol mull, a low V=O stretching frequency (see Table III)[15]. Such a low V=O stretching frequency occurs in few vanadyl compounds as VO(acetate)$_2$,[17] VO 5–NO$_2$–N(2, hydrophenyl)salicylideneimine[12] and VO sal 1,3 pn[18] (1,3 pn is 1,3 propylenediamine) which has been shown by X ray analysis to possess linear polymeric V=O···V=O ... chains with the vanadyl oxygen atoms involved in bridging two vanadium atoms, thus weakening the vanadium oxygen bond and lowering the vanadyl stretching frequency.

The magnetic moments of these complexes should be around the normal value (ca. 1.80 B.M. at room temperature) as recently pointed out in the case of VO sal 1,3 pn[19], this polymeric arrangement is in fact an unfavourable geometry for any antiferrogmagnetic spin pairing to occur.

As for the reason why only these three compounds show, in the solid state a polymeric structure we propose the following explanation. As will be discussed in the following section, the Schiff base oxovanadium(IV) compounds do not easily form hexacoordinate adducts both for electronic reasons and because of the steric hindrance of the substituents of the ethylenediamine chelate ring which are in axial position. However (see C.D. section) it appears that in the case of VO sal(–)stien, the ethylenediamine substituents are not axial, at least in solution, but equatorial, leaving the vanadium atom more free to *trans* axial coordination. Besides the 5–NO$_2$ salen and tfacacen complexes show a great tendency, in solution to form hexacoordinated species, probably because the vanadium atom becomes a stronger acid in the presence of electronegative groups.

In conclusion, all the compounds which have an anomalous colour in the solid state display a tendency to hexacoordination. Polymerisation in the crystal structure, through V=O···V=O chains (where the oxygen atoms are those of the vanadyl moiety) would correspond to such hexacoordination.

In the case of the less acid VO sal(–)stien the polymeric V=O···V=O chain is less stable. In fact this compound crystallizes as a yellow-brown powder which, on grinding becomes green. The vanadyl stretching frequency changes with the colour of the sample: it lies at 870 cm$^{-1}$ for the yellow-brown form and at a normal value (975 cm$^{-1}$) for the green form. Differently ground samples show both bands with different ratios of intensities, according to their colours. Unfortunately the green form is not stable and eventually becomes brown, making it impossible to record its electronic reflectance spectrum. However we presume, on the ground of the infrared evidence, that its crystal structure corresponds to a monomeric species. As a matter of fact this compound dissolves readily in nondonor solvents giving blue-green solutions, the infrared spectra of which

TABLE III
Relevant infrared absorptions frequencies (cm$^{-1}$)[a]

| | VO$^{2+}$ stretching region | |
|---|---|---|
| Compound | nujol mull | CHCl$_3$ solution |
| VO salen | 990 m | 983 s |
| | 980 sh | 975 m |
| VO sal(+)pn | 982 w | 988 s |
| | 973 sh | 981 sh |
| | 968 s | |
| VO sal(+)bn | 1000 sh | 986 s |
| | 990 s | 980 sh |
| | 978 m | |
| VO sal *meso* bn | 983 s | 985 s |
| | 970 s | |
| VO sal(+)chxn | 988 m | 991 s |
| | 979 sh | 981 sh |
| | 975 s | |
| VO sal *meso* chxn | 997 m | 989 m |
| | 988 s | 978 sh |
| | 973 sh | |
| VO sal(–)stien | 975 s | 993 m |
| (green form) | | 980 s |
| (Brown-yellow form) | 870 s | – |
| VO sal *meso* stien | 1002 m | 988 s |
| | 990 s | 979 s |
| | 980 m | |
| VO 5–NO$_2$ salen | 870 s | – |
| VO 5–Clsalen | 970 s | – |
| VO 5–NO$_2$ salen.py | 947 s | – |
| | 940 sh | |
| VO 5–NO$_2$ salen.DMSO[b] | 940 sh | – |
| | 930 s | |
| VO acacen | 980 s | 985 s |
| VO acac(+)pn | 985 s | 981 s |
| | 975 m | |
| VO acac(+)bn | 985 s | 985 s |
| | 980 s | |
| VO acac *meso* bn | 980 s | 987 s |
| | 970 sh | |
| VO acac(+)chxn | 983 s | – |
| VO acac *meso* chxn | 979 s | 987 s |
| VO acac(–)stien | 991 s | 994 sh |
| | 985 m | 984 sh |
| | 980 sh | |
| VO acac *meso* stien | 990 sh | 989 s |
| | 980 s | |
| VO tfacacen | 900 s | 1000[c] |
| | 890sh | |
| VO tfacacen.DMSO[d] | 900 | |

a = w = weak, m = medium, s = strong, sh = shoulder
b = $\nu_{SO}$ = 1020 cm$^{-1}$
c = acetone solution
d = $\nu_{SO}$ = 1020 cm$^{-1}$

show the VO stretching frequency at the value (c.a. 980 cm$^{-1}$) expected for a monomer.

VO tfacacen dissolves only in donor solvents, such as acetone or acetonitrile ($\nu_{VO}$ = 1000 cm$^{-1}$), while VO 5–NO$_2$ salen dissolves with difficulties even in pyridine and no solution I.R. spectrum could be obtained.

In an alternative description these compounds can be regarded as pentacoordinated vanadium(IV) compounds with a trigonal bipyramidal geometry as is the case of a complex with the (+) tartrate anion[20], but we prefer the other description on the grounds of their striking similarities with VO sal 1,3 pn[18].

### *Adduct Formation*

It is well known that the V=O stretching frequency of VO(acac)$_2$ can be used as a tool for quantitative measurements of the donor strength of a variety of donor bases such as substituted pyridines[14] or pyridine-N-oxides[13] which coordinate in the *trans* axial position.

However little evidence of adduct formation in solution has been reported in the case of VO acacen and VO salen either from I.R.[13] or electronic spectra[16]. A pyridine adduct of VO salen has been isolated[21], but the same authors prefer to describe it as a solvated species rather than a true adduct with a nitrogen-vanadium bond, on the grounds of calorimetric measurements that show only very little (3%) formation of this adduct in benzene solution. Similar solvated species have been found by many authors, including us, in the case of VO salen when crystallized from aromatic solvents.[22]

Spectroscopic evidence for the formation of adducts in solution, has been reported only when the ligand has electronegative groups, such as tfacacen.[7,13] Therefore we have synthesized the 5–NO$_2$salen and the 5–Clsalen complexes in the hope that they would behave similarly because of the presence of electronegative groups in the aromatic ring.

We have thus observed in some cases that both electronic (see Figs. 4 and 5) and C.D. (Fig. 6) evidence are consistent with a facile formation of hexacoordinated adducts in solution. In the electronic spectra as already described[7,13], the two bands centered at about 16–17 kK further split. This fact is less evident in the case of the 5–NO$_2$salen derivative because of its low solubility and of the closeness of intense charge transfer bands.

However we have a definitive piece of evidence for adduct formation in solution from the appearance of weak but significant Cotton effects of the d–d transitions of either VO tfacacen or VO 5–NO$_2$salen in the presence of an optically active amine such as (–)l-phenyl, l-aminoethane (see Fig. 6). These Cotton effects are not pure "solvent" effects because they

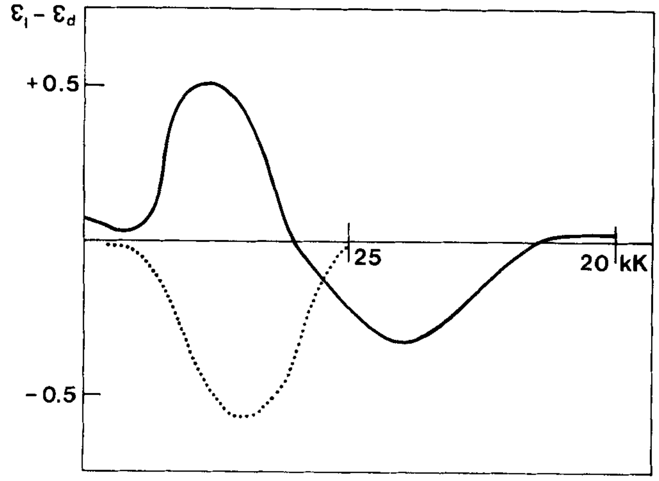


FIGURE 6 Circular dichroism spectra of —— VO 5–NO$_2$salen and ------ VO tfacacen in a 50% solution of (–) 1-phenyl, l-aminoethane in acetonitrile.

were not detected at all under similar conditions in the case of VO acacen and VO salen.

No spectroscopic evidence of hexacoordination was obtained in the case of VO 5–Clsalen.

With pyridine, a solid adduct could be obtained only with VO 5–NO$_2$salen, whereas with stronger bases, white products with irreproducible analysis were isolated. Presumably with strong bases a high degree of hydrolysis or aminolysis takes place. In fact upon addition of an aliphatic primary amine to a solution of VO tfacacen the electronic spectrum changes as described in Fig. 4, but, on standing, a successive slow change, which however we did not investigate in detail, takes place.

With oxygen donor bases such as dimethylsulphoxide (DMSO) we have been able to isolate solid adducts ($\nu_{SO}$ 1020 cm$^{-1}$ in agreement with an electronic donation from oxygen[23]) of both VO tfacacen and VO 5–NO$_2$salen, but only the latter is indefinitely stable; in the case of VO tfacacen the sulphoxide is lost on standing in the air overnight. It has been reported[13,24] that the vanadyl stretching frequency decreases with *trans* axial coordination, however the VO stretching frequency in nujol mull of VO 5–NO$_2$salen. DMSO lies at 930 cm$^{-1}$ that is, some 55 cm$^{-1}$ higher than in the case of the parent compound (872 cm$^{-1}$), whereas that of VO tfacacen. DMSO is practically unchanged, though the appearence of a band at 1020 cm$^{-1}$ is in agreement with the coordination of the sulphoxide (the free sulphoxide absorbs at 1060 cm$^{-1}$). Also in the case of VO 5–NO$_2$salen.py, the V=O stretching frequency in nujol mull is higher than that of the original solid material (943 cm$^{-1}$ as compared to 872 cm$^{-1}$). However we have to recall that the original solid material is probably a polymer, consequently the normal trend could be satisfied also in the case of VO 5–NO$_2$salen when the hypothetical VO stretching frequency of the monomer is considered. Unfortunately VO 5–NO$_2$salen is such an insoluble polymeric material that it has been impossible to record I.R. spectra in solution of non donor solvents, and consequently this frequency is not known.

In agreement with this explanation we may recall that the VO stretching frequency of an acetone solution of the tfacacen derivative is at about 1000 cm$^{-1}$ [13] as expected for monomeric square pyramidal coordination.

In conclusion, both VO tfacacen and VO 5–NO$_2$salen form easily hexacoordinated species of different stabilities both in solution as adducts and in the solid state as polymers. VO 5–Clsalen, on the contrary, is not polymeric in the solid state, as can be inferred from its reflectance spectrum and from its high VO stretching frequency in nujol mull, and consequently does not form adducts with donor ligands, despite the presence of the electronegative chlorine atom in the aromatic ring. The tendency to give a hexacoordinate adducts therefore appears to depend in a subtle way on the true electronegativity of the substituents and on the tendency of the $\pi$ system of the Schiff base to transfer the electronic effect to the vanadium atom. No adduct formation has been detected in the case of the other complexes.

VO sal(–)stien deserves a special discussion. In fact on the grounds of its probable polymeric structure in the solid state, one would expect, by analogy with VO tfacacen and VO 5–NO$_2$salen, a certain tendency to form adducts at least in solution. However we have not been able to obtain any evidence, even in solution, of the formation of adducts by addition of a variety of different donor bases. One is therefore led to conclude that, though this compound does not possess, as already stated, the steric hindrance of the others, it is too weak an acid to form adducts with pyridine and DMSO, but only a weak polymer in the solid state with V=O···V=O chains.

The lack of steric hindrance, which arises because the carbon substituents of the diamine chelate ring are pseudo equatorial, (see C.D. section) is probably the origin of the weak stability of the polymeric structure; increased acidity of the vanadium atom due to the phenyl groups, is not involved; in fact both VO sal*meso*stien and VO acac(–)stien do not display polymerization in the solid state. In particular (see

C.D. section) in VO acac(−)stien the carbon substituents are probably axial as in all the other compounds, while in the case of the compounds with *meso* diamines, one of the carbon substituents is axial and the other is equatorial, but presumably the axial one points in the direction opposite to the V=O moiety and again steric hindrance is operative, no adduct being formed.

In conclusion, the ease of formation of adducts depends on a subtle balance between steric and electronic effects. This point, together with a study of the stereochemical implications of adducts formation, will be the subject of a future paper.

### *Circular Dichroism Spectra*

Circular dichroism (C.D.) spectra were recorded, in chloroform solution, for both types of vanadyl complexes in the 16–33 kK region; results are given in Table IV and Figs. 7 and 8 respectively.

To the best of our knowledge, the only reports on C.D. spectra of vanadyl complexes of this type are those of Farmer and Urbach[5] and a note of Jones and Larsen[25] where the C.D. spectra of some of the compounds described in this paper have been reported. Our spectra are in agreement with those reported; in particular that of the acac(+)pn complex is the mirror image of that reported for the acac(−)pn compound[25], as expected for enantiomers.

TABLE IV
Circular dichroism spectra (kK; $\epsilon_l - \epsilon_d$ in parentheses)

| | |
|---|---|
| VO sal(+)pn | 17.00(−0.3); 18.70(0); 21.61(−1.0); 25.00(−7.3); 27.80(−0.6); 29.40(−1.2)sh; 33.70(−10.2) |
| VO sal(+)bn | 17.00(−1.3); 18.90(−0.7); 21.20(−0.3); 25.00(−13.6); 28.20(+0.6); 30.03(−0.7)sh; 33.90(−9.2) |
| VO sal(+)chxn | 17.00(+0.3); 18.70(0); 21.40(+1.1); 25.00(+4.0); 27.80(−2.1); 29.40(+1.0); 33.70(+6.5) |
| VO sal(−)stien | 17.15(+0.3); 18.75(0); 21.30(+1.4); 24.60(+5.2); 25.40(0); 27.00(−9.6); 30.03(0); 33.80(+11.5) |
| VO acac(+)pn | 18.30(−0.3); 21.30(−0.1); 23.50(−0.7)sh; 27.80(−11.6); 31.30(+9.0) |
| VO acac(+)bn | 18.55(−0.2); 20.04(0); 22.70(−1)sh; 28.60(−22.0); 31.80(+14.4) |
| VO acac(−)stien | 18.40(−1); 20.08(−0.3); 23.00(−0.4); 28.00(−36.0); 31.40(+25.2) |

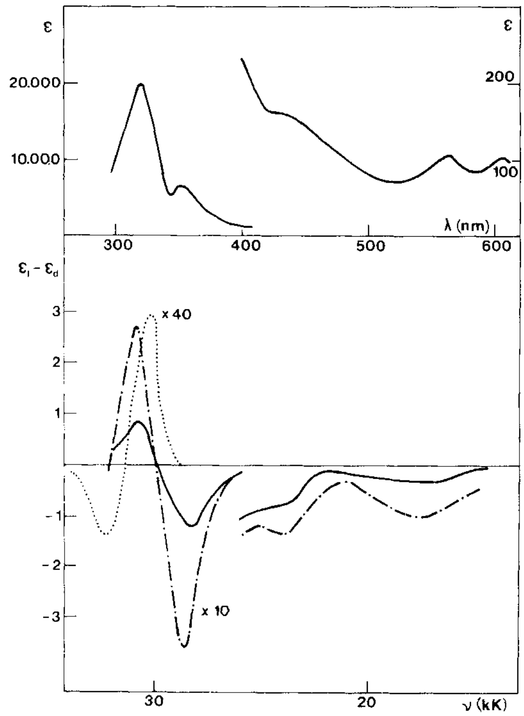


FIGURE 7 Electronic and circular dichroism spectra, in chloroform solution of type A compounds. —— VO acac(+)pn; –.–.– VO acac(−)stien; . . . . . acac(+)pn.

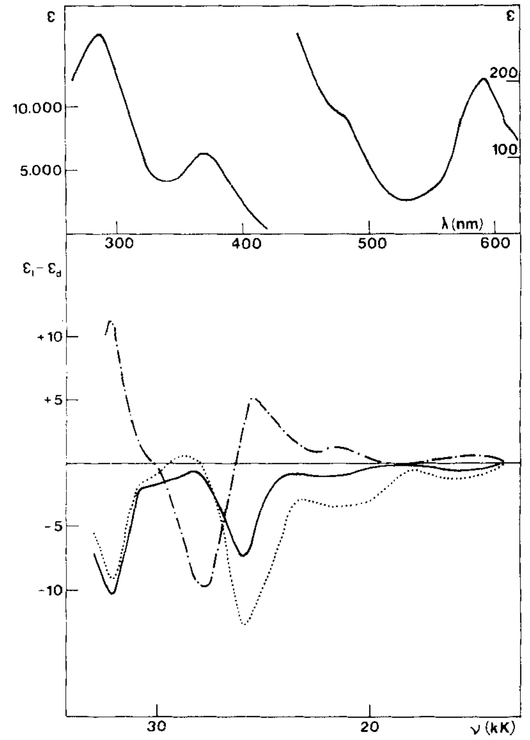


FIGURE 8 Electronic and circular dichroism spectra, in chloroform solution, of type B compound. —— VO sal(+)pn; . . . . . VO sal(+)bn; –.–.– VO sal(−)stien.

In Fig. 8, where spectra of compounds of type B are reported, we may note the almost mirror image relationship of the sal(+)pn and sal(+)bn compounds with respect to sal(−)stien and sal(+)chxn complexes, despite the same absolute configuration[8] of these diamines. Such an inversion has already been reported for the sal(+)chxn and sal(+)pn derivatives, not only in the vanadyl case[5] but also in that of square planar compounds of Cu(II)[26], Ni(II)[6] and Co(II)[3].

Although the C.D. spectra of Cu sal(−)stien and Ni sal(−)stien, have not yet been reported, it is of particular interest that in the case of Cosal(−)stien such an inversion of the C.D. spectrum does not exist, i.e. Co(+)pn and Co sal(−)stien have roughly the same spectrum in chloroform solution.[3,27] However it can be anticipated here that an inversion of some bands can be detected when one compares the C.D. spectra of Co sal(+)pn and Co sal(−)stien in pyridine solution[28], where the compounds are believed to be pentacoordinate.

The inversion of the C.D. spectrum has been explained[5] in the case of chxn derivatives by the existence of two fused rings (that of the cyclohexane and that of the chelate ring) which forces the chelate ring in a conformation which is the opposite to that of the other diamines with the same absolute configuration (see Fig. 9).

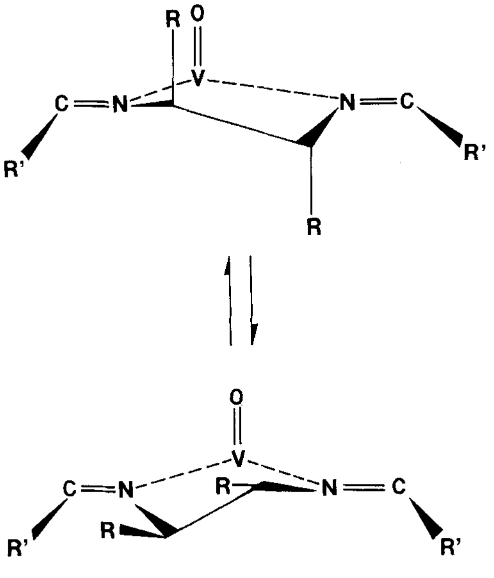


FIGURE 9

The most stable conformation for pn is that with the methyl group axial (see Fig. 9), that is λ for (S)(+)pn, as it has been found by X ray crystallography in the case of Co sal(+)bn[29]; while for chxn is that with the two fused rings strain-free, pseudo coplanar (that is δ for (S,S)(+)chxn).

It might be that the stien derivatives exhibit the same behaviour as the pn and bn compounds when the complex is only tetracoordinate, pseudo planar, as in Co(II) complexes[3]; that is the two phenyl groups of the diamine are axial to minimize the steric hindrance with the azomethine group (λ conformation of the ring for (S,S)(−)stien). When the coordination number of the complex is no longer four but five, as is the case with VO sal(−)stien and Co sal(−)stien.py, it is probable that the phenyl rings cannot remain any longer in an axial position because of steric hindrance with the fifth ligand, e.g. the oxygen atom of the VO group. In such case the conformation of the chelate ring must be inverted (that is δ for (S,S)(−)stien).[30]

The other possible explanation is that VO sal(−)stien has a different coordination geometry (e.g. trigonal bipyramidal instead of square pyramidal), but this can be ruled out since its electronic spectrum in solution is the same as those of all the other compounds in the series (see table II); moreover, one would expect the C.D. spectrum to be quite different and not to display a mirror image relationship.

In the case of related Schiff base uranyl complexes[1] we did not observe such a simple correlation; in fact the C.D. spectra of the (+)pn, (+)chxn and (−)stien compounds were all rather different in the case of heptacoordinate complexes. This is probably due to the fact that in the uranyl derivatives the changes of conformation of the chelate ring is complicated by a concomitant distortion of all the ligand from planarity.

No inversion was observed for type A derivative acac(−)stien (Fig. 7). This may be due to different factors. Firstly type A compounds are probably less rigid than type B thus leaving the diamine chelate ring strain free. Secondly, it must be remembered that in type A complexes the substituent R' of the carbon of the azomethine groups (see Fig. 9) are methyl groups which are more bulky than the hydrogen atoms of type B derivatives. Consequently one would expect steric hindrance between the substituents of the diamine ring and the methyl groups of acetylacetone to be greater than in the case of the salicylaldehyde derivatives. With such a strong steric hindrance the more stable conformation must always be that with the substituents of the diamine ring in axial position despite the interaction with the ligand in the fifth position[31]

In these and similar complexes the $O_2N_2$ chromophore is not planar but has a slight tetrahedral distortion as was previously proposed[5], and confirmed in the crystal structure of VO acacen[32] and Co sal(+)bn[29].

This distortion introduces a new centre of chiraliry, *i.e.* a dissymmetry about the metal atom itself. Using exciton theory[33] one can infer the chirality of the chromophore by observing the negative-positive couplet due to the exciton splitting of the absorption of the azomethine groups[33,5]. Following Bosnich[33] and Urbach[5], the chirality of the chromophore itself is Δ in the case of VO sal(S)pn and configurationally related diamines but Λ in the case of VO sal(S,S)(+)chxn and VO sal(S,S)(−)stien. On the contrary, type A compounds all have the Δ absolute configuration for diamines of S or SS absolute configuration.

The resolution of the four possible optical isomers of VO acac(±)pn (e.g. λS, δS, λR, δR) has been claimed[4]; this report would thus support that C.D. spectra arise from only the most stable, and consequently the most abundant species in solution.

Another feature of type A compounds deserves further discussion. The Schiff bases derived from acetylacetone are believed to posses a "flyover" structure[9] corresponding to a cyclic structure that can be compared to that of the slightly tetrahedral coordination in the complex. The helicity of the free ligand can be inferred from the exciton couplet at about 30 kK. Surprisingly, (see Fig. 7), it appears from our spectra that the helicities of the free ligand and of the ligand in the complex are not comparable; in fact the Cotton effects are of opposite sign.

In order to rationalize this fact one is led to conclude that the induced helicity of the free ligand in the flyover structure is opposite to that possessed by the same ligand when constrained in the almost planar geometry of the complex. In both cases the methyl group of the propylenediamine must always point away from the methyl group of the azomethine; both in the free ligand and in the complex. From molecular models it appears that this condition is satisfied if the helicity of the complex compounds is opposite of that of the "flyover" ring. Of course the above discussion is valid only if one assumes that the polarization of the transitions of the C=C–C=N chromophore of the Schiff base does not change on complex formation and does not mix with other transitions involving the metal ion moiety.

### *Some Features of Electronic Spectra*

Electronic spectra (see Table II and Figs. 2 to 5) have been recorded both on powders (reflectance) and in solution. As already reported[16] in the case of pentacoordinate compounds, different solvents may give rise to small differences in the spectra, which can only be attributed to a difference in solvation related to the dipole moment of the solvents. However when axial strong interactions are present, as in the case of VO sal(−)stien, VO tfacacen and VO 5-$NO_2$salen both in the solid state and in donor solvents the changes are relevant (see Figs. 3, 4 and 5).

All type A derivatives show four bands in the 7–25 kK region (see Fig. 2), both in the solid state and solution spectra, but sometimes, a fifth, low intensity, band at ca. 8 kK appears in the reflectance spectra. Compounds of type B do not show always similar trends in the solid state spectra, despite the fact that, in solution, the spectra are all the same within the series (Fig. 3). We attribute this fact to a different amount of intermolecular interaction in the crystals, as has been discussed above. In any case, with the exception of VO sal(−)stien, four bands are easily detectable in the solid state in the 7–25 kK region, and though less readily, also in solution. A different situation is presented by the three anomalous compounds, the reflectance spectra of which are quite different, showing a large asymmetric band at about 10 kK and a shoulder at about 20 kK (Figs, 3, 4 and 5).

It has been reported by many authors[16,34] that pentacoordinate oxovanadium(IV) compounds show a complex multiplet of absorption bands between 13 and 20 kK, but only in a few cases three clear absorptions, as in type A compounds, have been observed[16]. These bands have been attributed,[34] to the three low energy *d–d* transitions of the $d^1$ oxovanadium(IV) system, although the relative assignments are rather controversial. Generally speaking the absorption bands centered between 13 and 20 kK are attributed to electronic transitions involving $d_{x^2-y^2}$ and $d_{xz}$, $d_{yz}$ vanadium orbitals as excited states.

However two bands in this region are separated by about 1 kK (see Fig. 2) which may also suggest some vibronic structure due to the V=O stretch.

The very weak absorption at about 8–10 kK has been found only in few cases, for instance Selbin[34,35] has reported one weak band at about 9–10 kK in the solid state spectra at 77°K of some vanadyl bisketoenolate complexes. Its attribution is unclear but it could be related to some spin-forbidden *d–d* transition in agreement with its low intensity and energy.

A rather weak shoulder which we have always observed at about 22 kK in both series of compounds has been attributed to a spin forbidden charge transfer transition[34], however it shows not only an intensity but also a rotational strength which is comparable to that of the *d–d* transitions centered at about 13–20 kK (see Figs. 7 and 8). This latter point may be in contradiction with the assignment to a simple spin forbidden charge transfer since one would expect that such a charge transfer would be strongly magnetically allowed, giving rise to a stronger Cotton effect. Moreover, as pointed out by Farmer and Urbach[5], this absorption band occurs at similar energies not only in both A and B series but also in different ligand systems.

All this evidence would suggest that the assignment as ligand involving transition is incorrect. It could be suggested that the highest energy *d–d* transition involving the $d_z{}^2$ orbital as excited state corresponds to this absorption. This point, which is in contrast to the Ballhausen–Gray[36] localization of this transition at about 50 kK, is however in agreement with other authors[13] who have assigned this transition as low as 17 kK in low symmetry vanadyl complexes.

Of course only a low temperature single crystal investigation, which we hope to undertake as soon as possible, could give a definite solution to this problem.

Finally, in hexacoordinate complexes the large splitting to low and high energy of the bands previously centered at about 13–20 kK, is a trend which needs still a reasonable explanation. Although other authors[7] have already reported this feature their explanation and assignments of the new absorption bands are far from being satisfactory. Also in this case a more refined investigation on monocrystals is required.

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30. As a matter of fact such a hypothesis can also explain the relative ease of polymerization of VO sal(–)stien in the solid state discussed in a previous section.
31. The absolute configuration of (–)stien has recently been questioned by Bosnich[10] who assigned to it the same configuration as that of (–)pn through equilibration studies; the same author however, admitted reservations about this assignment since some Co(III) complexes with (–)stien have circular dichroism spectra which are inverted with respect to what would be expected on the grounds of his assignment. The situation is, therefore, very confused, and only the determination of the absolute configuration, by X-ray methods, will give the final answer. However, at the moment, we prefer to follow Gillard's assignment[8] which has been recently confirmed by the circular dichroism spectra of the free

Schiff bases[9] which show all the same pattern throughout the series (+)pn, (+)bn, (+)chxn, (−)stien. (see also ref. 27).

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