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Donor Properties of the Vanadyl Ion: Reactions of Vanadyl Salicylaldimine β-Ketimine and Acetylacetonato Complexes with Groups 14 and 15 Lewis Acids

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Reactions of organosilicon, -germanium, -tin, -lead, -antimony, and -tin tetrahalide Lewis acids with VO(salen) [H_2salen = *N*,*N′*-bis(salicylidene)ethane-1,2-diamine], related vanadyl salicylaldimines, VO(acacen) [H_2acacen = *N*,*N′*-bis(acetylacetonato)ethane-1,2-diamine], and VO(acac)$_2$ (acac = acetylacetonato) have been investigated, revealing VO(salen) and VO(acacen) to be significantly stronger vanadyl donors than VO(acac)$_2$. The vanadyl donor strength of VO(salen) significantly diminishes with the introduction of electron-withdrawing substituents on the salicylaldimine ligand, and the introduction of methyl substituents on the imine carbon atoms can result in a preference for phenolic over vanadyl oxygen donation. Vanadyl donation results in an increase in the vanadyl bond length, while it leaves the distance of vanadium from the basal plane relatively unaffected. Coordination of water trans to a vanadyl oxygen that is involved in a donor bond to tin or lead has little or no effect on the vanadyl bond length but results in a marked movement of vanadium toward the basal plane and a decrease of the V═O─D (D = Sn or Pb) bond angle by as much as 13°, the latter reflecting a loss of multiple bond character of the vanadyl bond. Formation of a vanadyl donor bond results in a decrease in both the vanadyl stretching frequency (infrared spectrum) and energy of the $e_\pi^* \leftarrow b_2$ transition (electronic spectrum), the latter being intimately related to the strength of the vanadyl donor bond, while the shift of the $b_1^* \leftarrow b_2$ transition to higher or lower energy is relatively small for vanadyl salicylaldimine and β-ketimine complexes. Donation through the phenolic oxygen atoms results in an increase in the vanadyl stretching frequency and energy of the $e_\pi^* \leftarrow b_2$ transition, which can result in $e_\pi^* \leftarrow b_2/b_1^* \leftarrow b_2$ energy crossover.

Introduction

The vanadyl ion ranks among the most stable of diatomic cations and dominates the chemistry of vanadium. While the bulk of the vast literature relating to it dwells on synthetic, structural, spectroscopic, and magnetic aspects, there is now increasing focus on both its biological and catalytic roles. The importance of these latter roles is becoming increasingly clear. For example, vanadyl sulfate functions as an insulin mimetic in diabetic rats, where vanadyl ion acts on a glucose transporter, inducing promotion of glucose uptake and reduction of free fatty acid level release in adipocytes;[1] a range of vanadyl complexes have now been submitted to human trials.[2] A 1/1 vanadyl 1,10-phenanthroline complex is proposed to bind and cleave DNA in the presence of hydrogen peroxide, inhibiting growth of human nasopharyngeal carcinoma cells.[3] Several vanadyl complexes show excellent antibacterial activity against *Streptococcus pneumoniae*, wherein the vanadium complexes inhibit substrate transport through the cell membrane.[4] Examples of catalytic applications by vanadyl complexes relevant to the present study are the use of VO(acac)$_2$ as a catalyst in the stereoselective epoxidation of 2,2-hydrox-δ-sterol side chains using MCPBA or *tert*-butyl hydroperoxide as oxidant, giving the erythro form as the major sterol enantiomer.[5] Polymer-bound VO(acac)$_2$ is a catalyst for the conversion of benzene to phenol. Electronegative vanadyl salicylaldimine complexes bearing electron-withdrawing substituents have been shown to catalyze cyclohexene epoxidation with moderate enantioselectivities of up to 40%.[6]

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In view of the diversity of the investigations of vanadyl complexes, it is surprising how little attention has been focused on the role of vanadyl as a donor group and the potential influence of such donor activity on the structure and reactivity of its complexes. Transient dinuclear species that have been detected in electron-transfer reactions involving vanadyl appear to involve vanadyl donation to the reducing metal.[7] The first report of a stable heterodinuclear complex with a vanadyl donor bond was for $[(NH_3)_5RuOV(H_2O)_4(SO_4)]SO_4$, the evidence for such donation coming from spectroscopic data,[8] while the first crystallographic confirmation of vanadyl donation was for adducts of $VOC_{22}H_{22}N_4$ (a macrocyclic ligand vanadyl complex) with $B(C_6H_5)_3$ and the trimethylsilicon cation.[9] This was quickly followed by crystallographic confirmation from this laboratory of vanadyl donation to tin in the complexes $SnPh_3Cl{\cdot}VO$(sal1,2pn), $SnPh_2Cl_2{\cdot}VO$(salen), and $SnPh_2Cl_2{\cdot}[VO(3\text{-}MeOsalen){\cdot}H_2O]$; in the case of the latter two adducts only preliminary crystallographic details were reported.[10] More recently, crystallographic data have been reported for several other vanadyl salicylaldimine adducts of triphenyltin chloride[11] and for $B(C_6F_5)_3{\cdot}VO(acac)_2$.[12] A very recent study revealed interesting mixed valence vanadium salicylaldimine complexes featuring vanadyl donation to vanadium(V).[13]

The objective of the present work was to obtain a better understanding of the factors that control the basicity of the vanadyl ion and to study the changes in vanadyl coordination geometry resulting from vanadyl donation. To this end, the reactivity of a wide range of vanadyl salicylaldimine and β-ketimine complexes with group 14 and diphenylantimony(V) trihalide Lewis acids was investigated. Crystallographic data were obtained for a number of adducts along with those for parent vanadyl salicylaldimine donors. The data clearly define changes in vanadium coordination geometry associated with vanadyl donation and/or donor bond formation trans to the vanadyl oxygen and provide a sound basis for the assignment of electronic spectra.

Experimental Section

Infrared spectra were recorded as Nujol mulls on a Spectrum 1000 (Perkin-Elmer) spectrometer. Reflectance spectra were recorded on a Cary 1E UV/vis spectrometer. Mössbauer spectra were recorded on a constant-acceleration spectrometer supplied by J & P Engineering (Reading) Ltd. using $Ba^{119}SnO_3$ at room temperature and the sample at liquid nitrogen temperature.

Vanadyl sulfate, acetylacetone, amines, and aldehydes were used without further purification. Tin tetrachloride and *n*-butyltin trichloride were distilled under nitrogen prior to use. Tin tetrabromide was sublimed under vacuum prior to use. Triphenyltin chloride, trimethyltin chloride, diphenyltin dichloride, diphenylgermanium dichloride, and diphenylsilicon dichloride were used without further purification. Diphenyllead dichloride and diethyllead dichloride were prepared from tetraphenyllead (supplied by Aldrich) and tetraethyllead (a gift from Octel), respectively.[14] $SnPh_3(NCS)$ and $SnPh_2(NCS)_2$ were prepared and purified by literature methods.[15] Diphenylantimony trihalides were prepared by literature methods.[16]

Salicylaldimine ligands were prepared using standard procedures. Vanadyl salicylaldimine complexes were prepared by refluxing methanolic solutions of $VO(acac)_2$ and salicylaldimine ligand (these being present in 1/1 molar ratios) for 3 h. The salicylaldimine complexes were isolated from the cooled solutions by filtration and dried under vacuum. VO(acacen) was prepared by a literature procedure.[17]

$VO(3\text{-}MeOsalen){\cdot}H_2O$ was isolated as a crystalline material under the following conditions: $VO(3\text{-}MeOsalen){\cdot}H_2O$ (0.5 g) was reacted with an equimolar quantity of $PbPh_2Cl_2$ in acetonitrile. On addition of the Lewis acid, the solution changed color from a dark green to a brighter green. Diprotonated ethylenediamine was dissolved in a small quantity of acetonitrile and the solution added to the bright green solution. The latter was stirred for 2 h under ambient conditions, after which time a green precipitate had formed. The solid was isolated by filtration and the filtrate transferred to narrow-bore tubes. Golden crystals of suitable quality for X-ray studies were obtained after several days.

$[VO(3\text{-}MeOsalen)/H_3N(CH_2)_2NH_2]Cl$ was obtained as a crystalline material under the following conditions: VO(3-MeOsalen) (0.5 g) was reacted with an equimolar quantity of $PbPh_2Cl_2$ in acetonitrile, giving a bright green solution (as above). Ethylenediamine was dissolved in a small quantity of acetonitrile and the resulting solution added to the bright green solution. The mixture was stirred for 45 min, after which time a green precipitate had formed. The precipitate was isolated by filtration and the filtrate transferred to narrow-bore tubes. Green crystals of suitable quality for X-ray studies were obtained after several days.

Adduct Preparation. Adducts were prepared (generally in at least 80% yield) by reacting the vanadyl salicylaldimine, or VO(acacen), with the Lewis acid in the solvent of choice at room temperature. Generally, 0.5 g of the vanadyl salicylaldimine complex was dissolved in 50 cm^3 of the solvent, and either 1 or 2 molar equivalents of the Lewis acid was added. After at least 6 h the adduct was isolated by filtration and dried under vacuum. Adducts of tin tetrachloride and tin tetrabromide were prepared and isolated (by filtration) under dry conditions. Samples of the tin tetrahalide adducts were maintained under dry conditions for all spectroscopic measurements.

Both dichloromethane and acetonitrile were employed as solvents, and acid/base ratios of 1/1 and 1/2 were used for each acid base combination in each of the solvents. Generally, the 1/2 adducts

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Table 1. Crystal Data[a]

	1	**2**	**4**	**5**	**6**	**7**	**8**	**10**
empirical formula	$C_{20}H_{27}ClN_4O_5V$	$C_{19}H_{20}Cl_2N_2O_6V$	$C_{28}H_{23.5}Cl_3N_2O_3SnV$	$C_{30}H_{28}Cl_2N_2O_6SnV$	$C_{44}H_{42}Cl_8N_2O_6SnV$	$C_{32}H_{32}Cl_4N_2O_3SnV$	$C_{62}H_{66}Cl_6N_6O_{10}Pb_2V_2$	$C_{50}H_{49}Cl_2N_5O_{11}PbV_2$
fw	489.85	494.21	711.97	753.07	1266.72	804.03	1784.17	1275.91
temp, K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
λ, Å	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069
cryst syst	triclinic	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	*Pnma*	$P2_1/c$	$C2/c$	$P\bar{1}$
a, Å	8.4499(12)	13.803(2)	11.662(2)	13.986(2)	12.959(3)	11.184(4)	26.785(2)	12.0059(11)
α, deg	76.029(14)	90	67.097(15)	90	90	90	90	71.559(11)
b, Å	11.939(2)	10.505(2)	11.757(2)	21.584(2)	15.783(4)	17.181(3)	13.7530(10)	12.872(2)
β, deg	80.759(12)	97.35(1)	82.549(16)	109.800(2)	90	92.178(18)	125.3490(10)	82.276(8)
c, Å	12.0129(19)	15.210(2)	12.113(2)	12.110(2)	24.795(7)	17.528(2)	22.3710(10)	19.360(2)
γ, deg	71.224(14)	90	71.384(15)	90	90	90	90	66.166(10)
V, Å^3	1109.0(3)	2187.8(5)	1449.8(4)	3439.5(8)	5071(2)	3365.6(13)	6721.6(8)	2596.2(5)
Z	2	4	2	4	4	4	4	2
ρ_{calcd}, Mg/m^3	1.467	1.500	1.631	1.454	1.659	1.587	1.763	1.632
μ, mm^{-1}	0.607	0.735	1.492	1.194	1.626	1.372	5.562	3.753
$R\ [I > 2\rho(I)]$[b]	$R1 = 0.0472$ $wR2 = 0.1173$	$R1 = 0.0485$ $wR2 = 0.1208$	$R1 = 0.0390$ $wR2 = 0.1132$	$R1 = 0.0640$ $wR2 = 0.2221$	$R1 = 0.0385$ $wR2 = 0.1189$	$R1 = 0.0966$ $wR2 = 0.2356$	$R1 = 0.0255$ $wR2 = 0.0727$	$R1 = 0.0214$ $wR2 = 0.0503$
R (all data)[b]	$R1 = 0.1068$ $wR2 = 0.1319$	$R1 = 0.1255$ $wR2 = 0.1400$	$R1 = 0.0476$ $wR2 = 0.1176$	$R1 = 0.0702$ $wR2 = 0.2291$	$R1 = 0.0492$ $wR2 = 0.1252$	$R1 = 0.1430$ $wR2 = 0.2628$	$R1 = 0.0272$ $wR2 = 0.0735$	$R1 = 0.0231$ $wR2 = 0.0509$

[a] **1** = VO(3-MeOsalen)/$H_3N(CH_2)_2NH_2Cl$. **2** = VO(3-MeOsalen)•H_2O. **4** = $SnPh_2Cl_2$•VO(salen). **5** = $SnPh_2Cl_2$•[VO(3-MeOsalen) •H_2O]. **6** = $SnPh_2Cl_2$•H_2O/[$SnPh_2Cl_2$•VO(3-MeOsalen)]. **7** = $SnPh_2Cl_2$ •VO(acetophen1,2pn). **8** = $H_3N(CH_2)_2NH_3$•[$PbPh_2Cl_3$•VO(MeOsalen)]$_2$. **10** = $PbPh_2Cl_2$•VO(3-MeOsalen)•VO(3-MeOsalen)•H_2O. [b] $R1 = [\sum||F_o| - |F_c||]/\sum|F_o|$. $wR2 = [[\sum w(|F_o{}^2 - F_c{}^2|)^2]/[\sum w(F_o{}^2)^2]]^{1/2}$. $w = 1/[(\sigma F_o)^2 + (aP)^2]$. The value of *aP* was obtained from structure refinement.

were obtained from acetonitrile, and in these instances they tended to form even when an acid/base ratio of 1/1 was employed.

Attempts were made to grow crystals of all adducts from the solvents methanol, acetone, acetonitrile, and dichloromethane. Crystals of $SnPh_2Cl_2$•VO(salen) and $SnPh_2Cl_2$•H_2O/$SnPh_2Cl_2$•VO(3-MeOsalen) were obtained from dichloromethane, and all other crystals (Table 1) were obtained from acetonitrile. Reaction of $PbPh_2Cl_2$ with VO(3-MeOsalen)•H_2O in a 1/1 molar ratio in acetonitrile gives rise to a light green solution from which golden crystals of $PbPh_2Cl_2$•VO(3-MeOsalen)•[VO(3-MeOsalen)•H_2O] generally form quite rapidly (after the green precipitate is removed). On occasions, green crystals of the 1/1 adduct are formed, but they are small and of poor quality. Precise conditions leading to the exclusive formation of the 1/1 adduct could not be defined. When acetonitrile solutions containing both the Lewis acid and base are left aside without any protection from the atmosphere for more than a month, green crystals of $H_3N(CH_2)_2NH_3$[$PbPh_2Cl_3$•VO(3-MeOsalen)]$_2$ may form. Several crystals of the complex were obtained, but the complex was not isolated in bulk.

Analytical data for key complexes of the discussion are as follows. Anal. Calcd for $SnPh_3Cl$•VO(salen) ($C_{34}H_{29}ClN_2O_3SnV$): C, 56.82; H, 4.07; N, 3.90. Found: C, 56.71; H, 3.98; N, 4.04. Anal. Calcd for $SnPh_2Cl_2$•VO(salen) ($C_{28}H_{24}Cl_2N_2O_3SnV$): C, 49.67; H, 3.57; N, 4.14. Found: C, 49.55; H, 3.51; N, 4.16. Anal. Calcd for VO(3-MeOsalen)•H_2O ($C_{18}H_{20}N_2O_6V$): C, 52.56; H, 4.90; N, 6.81. Found: C, 52.62; H, 4.87; N, 4.22. Anal. Calcd for ($SnPh_2Cl_2$•H_2O)/$SnPh_2Cl_2$•VO(3-MeOsalen) ($C_{42}H_{40}Cl_4N_2O_6Sn_2V$): C, 45.90; H, 3.67; N, 2.55. Found: C, 45.62; H, 3.8; N, 4.06. Anal. Calcd for $SnPh_2Cl_2$•VO(3-MeOsalen)•H_2O ($C_{30}H_{30}Cl_2N_2O_6Sn$): C, 47.72; H, 4.00; N, 3.71. Found: C, 47.95; H, 4.22; N, 3.65. Anal. Calcd for [VO(3-MeOsalen)/$H_3N(CH_2)_2NH_2$]Cl ($C_{20}H_{27}ClN_4O_5V$): C, 49.04; H, 5.56; N, 11.44. Found: C, 48.88; N, 5.70. Anal. Calcd for $PbPh_2Cl_2$•VO(3-MeOsalen)•H_2O ($C_{30}H_{30}Cl_2PbN_2O_6V$): C, 42.71; H, 3.58; N, 3.32. Found: C, 41.92; H, 3.70; N, 3.17. Anal. Calcd for $PbPh_2Cl_2$•VO(3-MeOsalen)•[VO(3-MeOsalen)•H_2O] ($C_{48}H_{48}Cl_2N_4PbO_{11}V_2$): C, 46.61; H, 3.91, N; 4.53. Found: C, 46.53; H, 3.67; N, 4.25. Anal. Calcd for $SnPh_2Cl_2$•VO(acetophen1,2pn) ($C_{31}H_{30}Cl_2N_2O_2SnV$): C, 51.77; H, 4.21; N, 3.90. Found: C, 51.55; H, 4.19; N, 3.75. Anal. Calcd for $H_3N(CH_2)_2NH_3$[$PbPh_2Cl_3$•VO(3-MeOsalen)]$_2$ ($C_{62}H_{66}Cl_6N_6O_{10}Pb_2V_2$); C, 41.74; H, 3.73; N, 4.71. Found: C, 41.25; H, 3.55; N, 4.32.

Deconvolution of UV/Vis Spectra. The UV/vis spectra of most parent vanadyl salicylaldimine complexes and those of several of their adducts consisted of overlapping peaks in the region 19000−12000 cm^{-1}. Curve fitting of such spectra was carried out in each case using the program PeakFit (Jandel Scientific). In the curve-fitting procedure, the peaks were assumed to be Gaussian in character. The complex charge-transfer region was fitted to a number of Gaussian peaks, but no physical significance was attached to these peaks apart from the fact that their presence results in satisfactory curve fitting. However, since, in the UV/vis spectrum of Zn(salen), the intensity of the charge-transfer peaks drops off quite abruptly below approximately 19000 cm^{-1}, care was taken in the curve-fitting procedure that the fitted peaks in the charge-transfer area did not trail significantly into the lower region (thus affecting the positions of other fitted peaks in this region). In the case of the reflectance spectra of VO(salen) and VO(sal1,2pn), it was necessary to include a peak in the 12000−13000 cm^{-1} region to obtain a satisfactory fit. These peaks are not considered for two reasons. First, the peaks are of very low intensity relative to the peaks in the 14000−19000 cm^{-1} region. Second, the spectra of these complexes in noncoordinating solvents, while retaining the peaks in the 14000−19000 cm^{-1} region (albeit in positions slightly different from those in the solid-state spectra), no longer exhibit the low-intensity band.

Single-Crystal X-ray Diffractometry. Crystallographic details are in Table 1. Diffraction data for **1**, **2**, and **4**−**7** were collected on an Enraf Nonius CAD-4 diffractometer, and those for **8** and **10** were collected on a Marr Research image plate. In the case of **8** the unit cell parameters were obtained from the diffractometer. The structures were solved by direct methods using SHELX-86[18] and refined by full-matrix least-squares using SHELXL-97.[19] SHELX operations were rendered paperless using ORTEX,[20] which was also used to obtain the drawings. Data were corrected for Lorentz and

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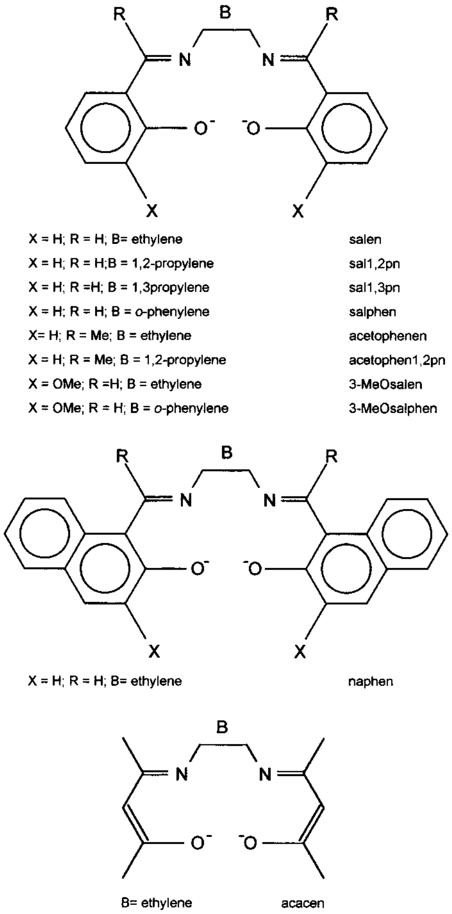

Figure 1. Schiff base ligands of the investigation.

polarization effects but not for absorption. Apart from the case of VO(3-MeOsalen)/$H_3NCH_2CH_2NH_2Cl$, hydrogen atoms were included in the calculated positions with thermal parameters 30% larger than that of the atom to which they were attached. In the case of VO(3-MeOsalen)/$H_3NCH_2CH_2NH_2Cl$, the three hydrogen atoms of the protonated nitrogen were located and these positions refined, and other hydrogen atoms were included in calculated positions. The non-hydrogen atoms were refined anisotropically. The crystals of $PbPh_2Cl_2$•VO(3-MeOsalen)•H_2O were small and of poor quality, and this may have a bearing on the fact that efforts to refine the structure to a final *R* value of less than approximately 16% failed. In view of the low level of refinement, complete crystal data are not included in Table 1. Crystals belong to the space group $P\bar{1}$. The unit cell dimensions are $a = 11.7273(14)$ Å, $b = 13.153(2)$ Å, $c = 13.295(5)$ Å, $\alpha = 99.90(2)°$, $\beta = 113.70(2)°$, $\gamma = 105.235(11)°$, and $V = 1720.2(7)$ Å^3 ($Z = 2$). All calculations were carried out on a Pentium PC.

Results and Discussion

The investigation focused on a fairly wide range of vanadyl salicylaldimine complexes as well as a related β-ketimine complex, VO(acacen), and $VO(acac)_2$ (see Figure 1). Furthermore, an extensive range of groups 14 and 15 Lewis acids were included in the study. A listing of the characterized adducts, along with selected infrared and Mössbauer spectroscopic data, are available (Supporting Information).

Limitations and subtlies of vanadyl donation are clearly apparent from the study. $SnMe_3Cl$, $PbEt_2Cl_2$, and $GePh_2Cl_2$ failed to react with any of the vanadyl complexes, and only hydrolysis products were identified from reactions with $SiMe_2Cl_2$ and $SiPh_2Cl_2$. Replacement of the ethylene bridge of the Schiff base ligand by a phenylene group (the ligands salphen and 3-MeOsalphen) or the introduction of naphthyl groups in the place of phenyl groups (the ligand naphen) dramatically reduced the vanadyl basicity to the point that vanadyl donation was only observed in reactions with diphenylantimony(V) Lewis acids (the strongest of the organometallic Lewis acids of the study). The failure of the relatively weak Lewis acid triphenyltin chloride to form an adduct with VO(sal1,3pn), even though it readily formed an adduct with VO(salen), can be attributed to the stability of the associated polymeric structure of VO(sal1,3pn).[21] VO(acac)$_2$ behaved as a much weaker vanadyl donor than VO(acacen) and the vanadyl salicylaldimines, forming adducts only with $SbPh_2Cl_3$ and $SbPh_2Br_3$. Most surprisingly, it does not form donor bonds to either $SnCl_4$ or $TiCl_4$.

In the case of the vanadyl salicylaldimine complexes, both the phenolic and vanadyl oxygen atoms compete as potential donor atoms. Crystallographic data (discussed later) revealed both modes of donation. In the absence of crystallographic data, vanadyl stretching frequency data proved particularly useful in establishing the mode of donation since, as would be anticipated, donation by the vanadyl group results in a decrease in the vanadyl frequency whereas donation by the phenolic oxygens results in an increase in the vanadyl frequency. In the case of organotin and -lead Lewis acids, donation through the phenolic oxygen atoms was only observed in the case of VO(acetophenen) and VO(acetophen1,2pn). This can be attributed to the increased electron density on the phenolic oxygen atoms resulting from the methyl groups on the imine carbon atoms. In most instances, donation to tin tetrachloride occurred through the phenolic oxygens.

Not surprisingly, triphenyltin Lewis acids gave rise to adducts of 1/1 stoichiometry exclusively. In the case of diorganotin and diphenyllead Lewis acids, it often proved possible to isolate both the 1/1 and 1/2 adducts by choosing dichloromethane and acetonitrile, respectively, as preparative solvents. A 2/1 stoichiometry was encountered in diphenyltin dichloride adducts with VO(3-MeOsalen)•H_2O and VO(acetophen1,2pn).

A major objective of the present work was to monitor precisely all of the changes in the coordination geometry of vanadium resulting from vanadyl donation to a Lewis acid. With such precise structural information on hand it should be possible to understand accompanying changes in the infrared and, more particularly, the electronic spectra of the vanadyl complexes (discussed later). Thus, efforts were made to obtain crystallographic data not only for key adduct structures but also for the parent vanadyl salicylaldimine Lewis bases of those adducts. Crystallographic data are currently available for VO(salen),[22] and in the absence of crystallographic data for VO(sal1,2 pn) and VO(acetophen1,-

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Vanadyl Complexes[a]

	a	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10a**	**10b**
V−O	1.925(1)	1.9228(16)	1.952(2)	1.886(9)	1.901(3)	1.926(7)	1.917(3)	1.938(5)	1.936(4)	1.924(12)	1.913(3)	1.932(3)
	1.924(1)	1.9287(17)	1.956(2)	1.905(8)	1.899(3)	1.923(7)	1.917(3)	1.936(4)	1.939(4)	1.960(10)	1.902(3)	1.938(3)
V−N	2.055(1)	2.047(2)	2.054(3)	2.038(12)	2.056(3)	2.052(9)	2.039(5)	2.051(6)	2.048(5)	2.058(13)	2.052(3)	2.046(4)
	2.057(1)	2.051(2)	2.058(3)	2.054(10)	2.040(3)	2.056(9)	2.039(5)	2.060(5)	2.059(5)	2.042(16)	2.046(3)	2.045(4)
V═O	1.587(1)	1.5938(18)	1.596(2)	1.617(9)	1.624(3)	1.635(7)	1.616(5)	1.573(5)	1.595(3)	1.627(15)	1.609(3)	1.612(3)
D(V)	0.599	0.590	0.371	0.563	0.598	0.337	0.579	0.657	0.596		0.572	0.322
V−OH$_2$			2.385(2)			2.304(7)				2.344(13)		2.330(3)
V−O−M				175.4(5)	172.0(2)	163.7(4)	174.4(3)		166.2(4)	167.7(9)	169.55(14)	155.49(16)
M−O				2.424(9)	2.331(3)	2.308(7)	2.406(5)	2.435(4) 2.430(4)	2.920(5)	2.616(14)	2.701(3)	2.561(3)

[a] **a** = VO(salen). **1** = VO(3-MeOsalen)/$H_3N(CH_2)_2NH_2Cl$. **2** = VO(3-MeOsalen)·H_2O. **3** = $SnPh_3Cl$·VO(sal1,2pn). **4** = $SnPh_2Cl_2$·VO(salen). **5** = $SnPh_2Cl_2$·[VO(3-MeOsalen)·H_2O]. **6** = $SnPh_2Cl_2$·H_2O/[$SnPh_2Cl_2$·VO(3-MeOsalen)]. **7** = $SnPh_2Cl_2$·VO(acetophen1,2pn). **8** = $H_3N(CH_2)_2NH_3$[$PbPh_2Cl_3$·VO-(MeOsalen)]$_2$. **9** = $PbPh_2Cl_2$·VO(3-MeOsalen)·H_2O. **10** = $PbPh_2Cl_2$·VO(3-MeOsalen)·[VO(3-MeOsalen)·H_2O] (**10a** and **10b** are the anhydrous and hydrated vanadyl salicylaldimines, respectively). *D*(V) is the distance of vanadium from the least-squares plane defined by the Schiff base nitrogen and oxygen atoms. M = Sn or Pb. The oxygen of M−O is the vanadyl oxygen except in the case of **7**, where it is the phenolic oxygen.

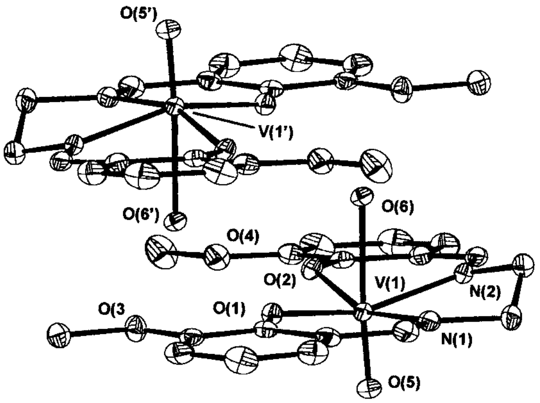

Figure 2. Centrosymmetric hydrogen-bonded dimeric unit of VO(3-MeOsalen)·H_2O. O(6′) contacts with O(1), O(2), O(3), and O(4) are at 2.914, 2.803, 3.264, and 3.199 Å, respectively. There are seven C−C contacts in the range 3.5−3.8 Å between each pair of neighboring aromatic rings, and the centroid−centroid separation is 3.83 Å.

2pn), the vanadium coordination geometry of the former is considered as a reasonable structural model for the latter two complexes. In the case of five adducts whose structures were determined (**5**, **6**, and **8**−**10** in Table 2), the parent vanadyl salicylaldimine Lewis bases are either the hydrogen-bonded dimer [VO(3-MeOsalen)·H_2O]$_2$ with six-coordinated vanadium or VO(3-MeOsalen) with square pyramidal vanadium coordination geometry. Obtaining structural data for these parent vanadyl salicylaldimine complexes proved somewhat problematic.

The monohydrated complex VO(3-MeOsalen)·H_2O is generally the direct synthetic product, but it proved particularly difficult to grow suitable crystals for a crystallographic study. Ultimately, these were obtained from an acetonitrile solution containing VO(3-MeOsalen)·H_2O and an equimolar quantity of $PbPh_2Cl_2$; crystals of a lead−vanadium adduct also resulted from this crystallization. The crystallographic study of VO(3-MeOsalen)·H_2O confirmed that the water was coordinated to vanadium while at the same time it was engaged in hydrogen bonding with Schiff base oxygen atoms of a neighboring molecule. The ensuing centrosymmetric dimer shown in Figure 2 is similar to that observed for Co-(3-MeOsalen)·H_2O,[23] [Fe(3-MeOsalen)(5-phenylimidazole)]-BPh_4·H_2O,[24] and M(NCS)(3-MeOsal1,3pn))·H_2O (M = Fe or Mn).[25] More to the point, it is precisely this dimer which acts as a Lewis base in adducts **5**, **9**, and **10b** of Table 2.

It has recently come to our attention[26] that the highly unstable anhydrous adduct VO(3-MeOsalen) has been isolated and its structure determined. The complex has a weak intermolecular vanadium−phenolic oxygen bond, and in view of this pseudo-six-coordinated vanadium structure coupled with the unstable nature of the complex, an attempt was made to find an alternative model for VO(3-MeOsalen) with five-coordinated vanadium as found in the adduct structures of **6**, **8**, and **10a** (Table 2).

A notable feature of the dimeric structure of VO(3-MeOsalen)·H_2O is the relative weakness of the vanadium−water donor bond (see the discussion of structural parameters later). Since the basicity of the water is augmented by its participation in hydrogen bonding, the possibility was considered that, in the absence of this hydrogen bonding, the vanadium−water donor bond might not exist (the increase of the Lewis acidity of water resulting from its involvement in hydrogen bonding will be discussed in detail elsewhere[27]). Some justification for this view is presented by the crystallographic data for $SnPh_2Cl_2$·VO(3-MeOsalen)·H_2O and ($SnPh_2Cl_2$·H_2O)/[$SnPh_2Cl_2$·VO(3-MeOsalen)] (see Figures 4 and 5, respectively). The absence of a water donor bond to vanadium in the latter (though it exists in the former) may be a consequence of the unavailability of Schiff base oxygens to which the donor water can form hydrogen bonds.

Prompted by this interpretation of the structural data, efforts were made to engage the Schiff base oxygen atoms of VO(3-MeOsalen) in hydrogen bonding alternative to that from a water molecule. This was achieved in the complex [VO(3-MeOsalen)/$H_3N(CH_2)_2NH_2$]Cl (see Figure 3). The three hydrogen atoms of the protonated nitrogen were located in this structure, two being engaged in bifurcated hydrogen bonding with the Schiff base oxygen atoms while the third is engaged in hydrogen bonding with a chloride ion. It is interesting to observe that, as a result of the Schiff base

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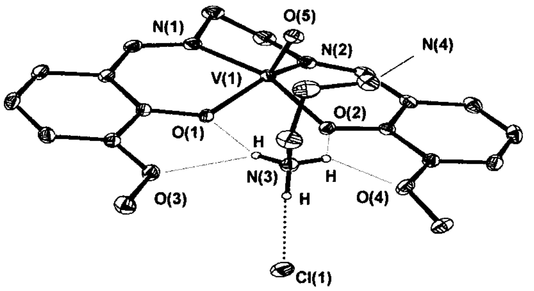

Figure 3. Asymmetric unit of $[VO(3\text{-}MeOsalen)/H_3NCH_2CH_2NH_2]Cl$. N(3) contacts with O(1), O(2), O(3), O(4), and Cl(1) are at 2.995, 3.050, 2.959, 2.900, and 3.114 Å, respectively. There are seven intermolecular C−C contacts in the range 3.37−3.60 Å involving carbon atoms of each pair of directly opposing aromatic groups in centrosymmetrically related neighboring molecules. The centroid−centroid separation is 3.94 Å.

oxygen atoms being engaged in strong hydrogen bonding with the protonated amine, water does not coordinate to vanadium. Since vanadium has square pyramidal geometry in $[VO(3\text{-}MeOsalen)/H_3N(CH_2)_2NH_2]Cl$, it is indeed a good model for the vanadyl salicylaldimine Lewis base in **6**, **8**, and **10a** of Table 2.

All of the adducts containing vanadyl complexes as Lewis bases which have thus far been investigated crystallographically contain organotin(IV), organoboron, or vanadium(V) salicylaldimine Lewis acids, and apart from the 2/1 adduct of diphenyltin dichloride with VO(3-MeOsalen) reported in this paper, they are all of 1/1 stoichiometry. Although a number of 1/2 adducts of diorganotin(IV) with vanadyl salicylaldimine complexes were isolated in the present study, no success was attained in growing crystals suitable for crystallographic studies. On the other hand, a 1/2 adduct was obtained in suitably crystalline form when diphenyllead dichloride was the Lewis acid.

Reaction of diphenyllead dichloride with $VO(3\text{-}MeOsalen)\cdot H_2O$ can lead to the formation of either a 1/1 or a 1/2 adduct (both gold-colored). Only on one occasion did it prove possible to isolate crystals of the 1/1 adduct, but unfortunately the structure did not refine to a satisfactory level ($R = 16\%$). However, at this level of refinement, the broad features of the structure were clear. The structure differs from that of $SnPh_2Cl_2\cdot VO(3\text{-}MeOsalen)\cdot H_2O$ (see Figure 4) only insofar as Pb−Cl intermolecular interactions occur, thus giving rise to six-coordinated lead and an infinite chain structure.

The crystallographic study of the 1/2 adduct confirmed that the two vanadyl salicylaldimine complexes coordinate to lead via the vanadyl oxygen atoms, resulting in a distorted octahedral lead coordination geometry. However, the study revealed two rather surprising features (see Figure 6). First, the vanadyl groups are cis related despite the bulk of the vanadyl complexes, and this is achieved with an O−Pb−O bond angle of 96°. Second, one of the vanadyl salicylaldimine donor ligands is simply VO(3-MeOsalen) with vanadium possessing square pyramidal geometry, while the other is $VO(3\text{-}MeOsalen)\cdot H_2O$. The water has the same dual hydrogen bond donor roles as it has in $SnPh_2Cl_2\cdot VO(3\text{-}MeOsalen)\cdot H_2O$ and $PbPh_2Cl_2\cdot VO(3\text{-}MeOsalen)\cdot H_2O$.

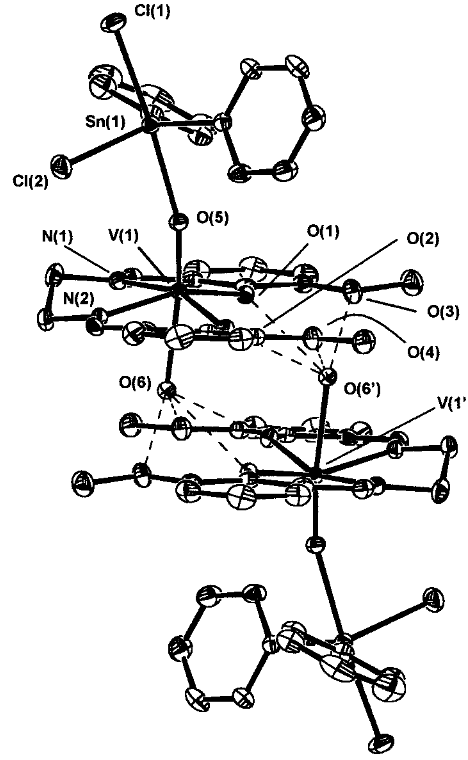

Figure 4. Centrosymmetric dimeric unit of $SnPh_2Cl_2\cdot[VO(3\text{-}MeOsalen)\cdot H_2O]$. O(6′) contacts with O(1), O(2), O(3), and O(4) are at 2.781, 2.915, 3.134, and 3.221 Å, respectively. There are nine C−C contacts between pairs of neighboring aromatic rings in the range 3.39−3.70 Å, and the centroid−centroid separation is 3.65 Å. Selected bonding parameters (Å, deg) about tin: Sn(1)−C, 2.125(10) and 2.128(12); Sn(1)−Cl(1), 2.456(3); Sn(1)−Cl(2), 2.342(3); Sn(1)−O(5), 2.308(7); O(5)−Sn(1)−Cl(1), 175.71(19); Cl(2)−Sn−C, 111.3(3) and 115.7(3); C−Sn(1)−C, 131.4(4).

When solutions of $PbPh_2Cl_2$ and $VO(3\text{-}MeOsalen)\cdot H_2O$ are left aside for prolonged periods, hydrolysis of the Schiff base ligand takes place, and from such solutions green crystals of $[H_3N(CH_2)_2NH_3][PbPh_2Cl_3\cdot VO(3\text{-}MeOsalen)]_2$, **8**, may form. The essential difference between the structure of **8** (see Figure 7) and that of $[VO(3\text{-}MeO\text{-}salen)/H_3N(CH_2)_2NH_2]Cl$, **1** (see Figure 3), is that while one protonated nitrogen of **1** engages in hydrogen bonding with the Schiff base oxygens and chloride, both protonated nitrogens adopt this role in **8**, and furthermore, the chlorides in the latter structure are bound to lead rather than being free chloride as in **1**. The hydrogen bonding in **8** appears, from contact distances (see Figures 3 and 7), to be considerably stronger than in **1**, and the strong hydrogen bonding to Cl(1) in **8** results in the Pb(1)−Cl(1) bond being dramatically longer (by approximately 0.3 Å) than the other two Pb−Cl bonds. A particularly striking feature of this structure, which is difficult to understand, is the weakness of the vanadyl−lead interaction [compare the vanadyl−lead bond length of 2.920(5) Å for this complex with vanadyl−lead bond lengths of 2.561(3) and 2.701(3) Å in **10** and 2.616(14) Å in **9**]. As a result of the weakness of the interaction, the coordination geometry about vanadium is essentially the same as that in $[VO(3\text{-}MeOsalen)/H_3N(CH_2)_2NH_2]Cl$.

The reaction of diphenyltin dichloride with VO(acetophen1,2pn) was particularly interesting in that, irrespective of reaction conditions, a 2/1 adduct precipitated rapidly from solution. The Sn-119 Mössbauer spectrum of the adduct consisted of two overlapping doublets corresponding to

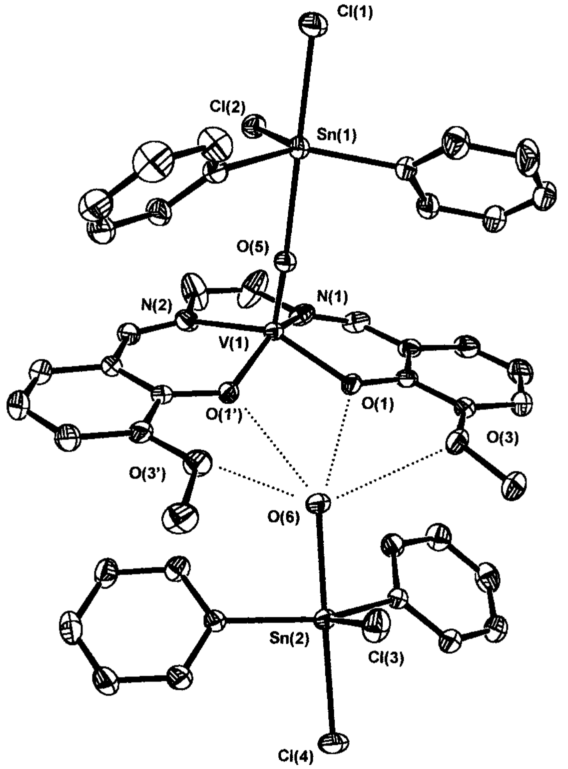

Figure 5. Structure of $SnPh_2Cl_2 \cdot H_2O/SnPh_2Cl_2 \cdot [VO(3\text{-}MeOsalen) \cdot H_2O]$. A mirror plane passes through the tin and vanadium atoms. Distances from O(6) to O(1) and O(3) are 2.832 and 2.992 Å, respectively. Selected parameters (Å, deg) about the tin atoms: Sn(1)−C, 2.121(5); Sn(1)−Cl(1), 2.441(2); Sn(1)−Cl(2), 2.344(2); Sn(1)−O(5), 2.406(5); O(5)−Sn(1)−Cl(1), 179.88(14); Cl(2)−Sn(1)−C; 110.78(15); C−Sn(1)−C, 135.3(3); Sn(2)−C, 2.122(5), Sn(2)−Cl(3), 2.346(2); Sn(2)−Cl(4), 2.464(2); Sn(2)−O(6), 2.293(5); O(6)−Sn(2)−Cl(4), 178.34(17); Cl(3)−Sn(2)−C, 111.50(13); C−Sn(2)−C, 136.1(3).

quadrupole splittings of 3.06 and 3.53 mm·s^{-1}. The larger quadrupole splitting (consistent with six-coordinated tin) is assigned to the tin coordinated to the phenolic oxygen atoms, while the smaller quadrupole splitting (indicative of five-coordinated tin) is assigned to the tin coordinated to the vanadyl oxygen. Long crystallization times from a solution containing diphenyltin dichloride and the Schiff base ligand in a 2/1 molar ratio resulted in the formation of crystals of adduct **7** (Table 2). However, a crystallographic study of **7** revealed it to be a 1/1 adduct rather than the 2/1 adduct that was initially synthesized, but most significantly, it confirmed that it is the phenolic oxygen atoms that coordinate to tin (see Figure 8). Tin achieves a highly distorted octahedral geometry (for example, the O−Sn−O and C−Sn−C bond angles are 63.51° and 165.85°, respectively) that is very similar to that of tin in $SnMe_2Cl_2 \cdot Ni(salen)$,[28] and the Sn−V separation (3.496 Å) is quite similar to the Sn−Ni separation (3.412 Å). However, VO(acetophen1,2pn) does not display the pronounced anisobidentate behavior of Ni(salen). A phenyl group coordinated to tin is located trans to the vanadyl oxygen such that vanadium is 3.569 Å from the α-carbon and 4.012 and 4.102 Å from the β-carbons. The location of this ring is suggestive of a weak interaction between vanadium and the phenyl ring.

Metal salicylaldimine complexes in the solid state very frequently display intermolecular aromatic π-interactions, and most of the structures of this study show such interactions. In the simplest structures where there are no intermolecular hydrogen-bonding or bonding interactions involving the metal, there is a pronounced tendency toward dimerization of the type shown in Figure 9 for $SnPh_2Cl_2 \cdot VO(salen)$. The aromatic ring contacts listed show that the π-interactions are quite significant and the rings involved in the interactions are laterally displaced relative to each other such as typically occurs to minimize repulsive interactions.[29] The adduct $SnPh_3Cl.VO(sal1,2pn)$ (complex **3** in Table 2) shows precisely the same type of dimerization, and so too, in all probability, do the other triphenyltin chloride adducts of vanadyl salicylaldimines that have been reported.[11] When intermolecular hydrogen bonding occurs, π-interactions may still be featured, as suggested by the C−C contacts shown in Figures 2 and 4. The infinite chain structure of **10** (Figure 6) results from a combination of π-interactions and hydrogen bonding.

Table 2 contains structural parameters for the tin and lead adducts of this investigation along with related parameters for some of the vanadyl salicylaldimine complexes (or closely related complexes) that act as Lewis bases in these adducts. The data provide a very clear picture of how the geometry about vanadium is altered both by vanadyl donation and by donor bond formation to vanadium trans to the vanadyl group.

It is generally believed that the formation of a donor bond trans to the vanadyl group results in a movement of vanadium toward the basal plane and an increased vanadyl bond length; the latter is implied by the decrease in vanadyl stretching frequency which generally accompanies such adduct formation. Crystallographic data supporting these observations are largely unavailable, and thus the data in Table 2 are particularly valuable since they clarify the effect of donor bond formation in the case of vanadyl salicylaldimine complexes that have been the focus of many investigations. A major reason for the lack of relevant crystallographic data for the vanadyl salicylaldimines is the difficulty in isolating adducts of the type VO(TSB)·D, where TSB represents a tetradentate salicylaldimine ligand and D represents a donor ligand trans to the vanadyl oxygen. For example, all efforts in this laboratory to isolate adduct VO(salen)·pyridine or VO(salen)·NR_3 were unsuccessful. By contrast, adducts of $VO(acac)_2$ with these strong donor ligands are readily formed.

The long V−OH_2 donor bond of 2.385(2) Å in VO(3-MeOsalen)·H_2O, **2**, points to a relatively weak donor−acceptor interaction. For example, this donor bond length compares with a Co−OH_2 donor bond length of 2.12(2) Å in the very closely related aqua adduct Co(3-MeOsalen)·H_2O.[23] The V−OH_2 donor bond length decreases to a value of 2.330(3) Å in **10b** as a result of the vanadyl oxygen forming a donor bond to $PbPh_2Cl_2$ (resulting in a drain of electron density from vanadium) and further decreases to

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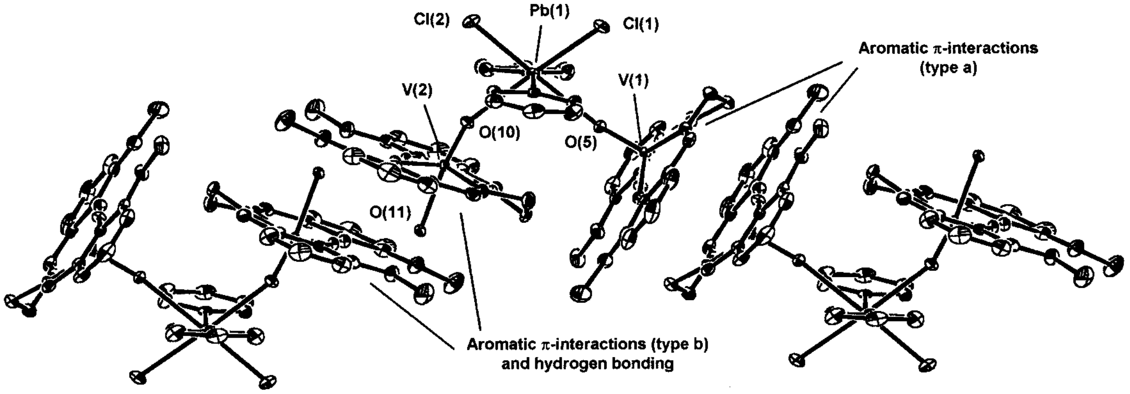

Figure 6. Chain polymeric structure of $PbPh_2Cl_2{\cdot}VO(3\text{-}MeOsalen){\cdot}[VO(3\text{-}MeOsalen){\cdot}H_2O]$ resulting from hydrogen-bonding and aromatic π-interactions. Intermolecular contacts between O(11) and Schiff base oxygen atoms are 2.812, 2.886, 3.130, and 3.209 Å, the first two and latter two values involving phenolic and methoxy atoms, respectively. There are six aromatic C−C intermolecular contacts ranging from 3.29 to 3.59 Å between opposing aromatic groups on neighboring molecules resulting from type a π-interactions. There are seven C−C intermolecular contacts in the range 3.55−3.70 Å between opposing aromatic groups on neighboring molecules resulting from type b π-interactions. All relevant centroid−centroid separations are 3.65 Å. Selected bonding parameters (Å, deg) about lead: Pb(1)−C, 2.168(4) and 2.173(4), Pb(1)−Cl(1), 2.5825(11); Pb(1)−Cl(2), 2.5665(12); Pb(1)−O(5), 2.701(3); Pb(1)−O(10), 2.561(3); C−Pb(1)−C, 163.01(15); O(5)−Pb(1)−O(10), 96.56(9).

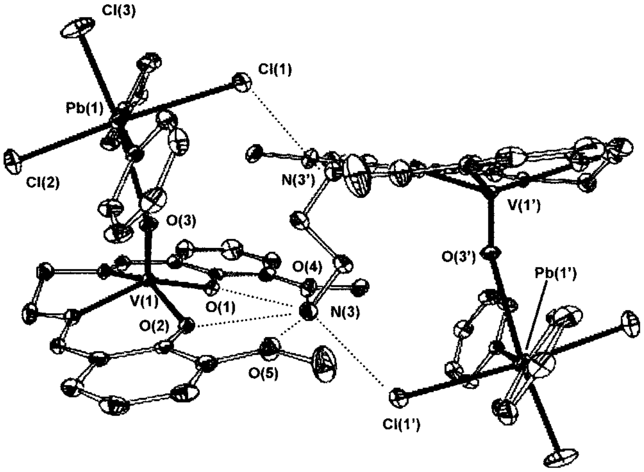

Figure 7. Structure of $H_3N(CH_2)_2NH_3[PbPh_2Cl_3{\cdot}VO(3\text{-}MeOsalen)]_2$. Dotted lines signify hydrogen-bonding contacts. Hydrogen-bonding contact distances (Å): N(3)−O(1), 2.891(7); N(3)−O(2), 2.860(7); N(3)−O(4), 2.851(7); N(3)−O(5), 2.843(7); N(3)−Cl(1), 3.068(5). Selected bonding parameters (Å, deg) about lead: Pb(1)−Cl(1), 2.8913(18); Pb(1)−Cl(2), 2.585(2); Pb(1)−Cl(3), 2.5100(16); Pb(1)−O(3), 2.920(5); Pb(1)−C, 2.173(6) and 2.178(5); C−Pb(1)−C, 166.2(4). There are six C−C contacts in the range 3.54−4.00 Å involving each phenyl of the salicylaldimine ligands and directly opposing phenyl rings of adjacent molecules. The centroid−centroid separation is 4.67 Å.

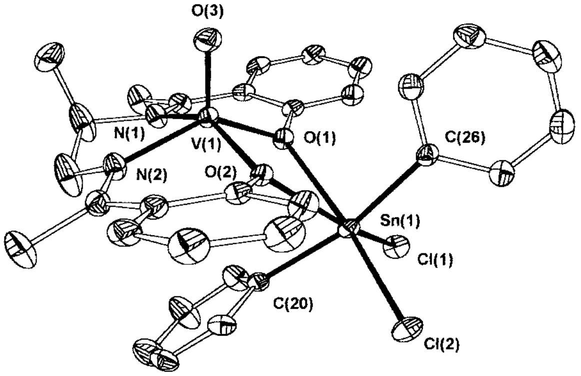

Figure 8. Asymmetric unit of $SnPh_2Cl_2{\cdot}VO(acetophen1,2pn)$. Selected bonding parameters (Å, deg) about tin: Sn(1)−Cl(1), 2.4310(19); Sn(1)−Cl(2), 2.4536(17); Sn(1)−C(20), 2.132(6); Sn(1)−C(26), 2.142(6); Sn(1)−O(1), 2.430(4); Sn(1)−O(2), 2.435(4); C(20)−Sn(1)−C(26), 165.8(2); (O1)−Sn(1)−O(2); 63.45(14).

2.304(7) Å in **5**, where the vanadyl oxygen forms a donor bond to the stronger Lewis acid $SnPh_2Cl_2$.

Complexes **1** and **2** in Table 2 have the same salicylaldimine ligand, and in each case the phenolic oxygen atoms are engaged in fairly strong hydrogen bonding. The significant difference between them is that while **2** has a water molecule coordinated to vanadium, **1** has no such bond. Thus, a comparison of structural data for these complexes provides a valid assessment of the degree to which the V═O bond length and the distance of vanadium from the basal plane, *D*(V), are altered by formation of the donor bond to vanadium. The data confirm the displacement of vanadium toward the basal plane. Despite the weakness of the donor bond, the displacement from 0.590 to 0.371 Å is significant. Surprisingly, however, the V═O bond length is essentially unchanged.

The effect of donor bond formation to vanadium can also be validly assessed by comparing data for the pair of complexes **5** and **6** and especially from a comparison of data for **10a** and **10b** in view of the greater accuracy of crystallographic data for **10**. The conclusions arising from these comparisons are essentially the same as those from the comparison of data for **1** and **2**; i.e., considerable movement of vanadium toward the basal plane but little or no change in the V═O bond length accompany donor bond formation to vanadium. However, while the V═O bond lengths are little affected by the formation of the aqua adduct, considerable changes in the vanadyl donor bond lengths to tin and lead are observed (see Table 2). The changes reflect the expected increased Lewis basicity of the vanadyl oxygen on formation of the donor bond trans to it. For example, by comparing the data for **5** and **6**, it is seen that, as a result of aqua adduct formation, the Sn−O(vanadyl) donor bond length decreases from 2.406(5) to 2.308(7) Å, while in the case of the lead adduct **10** [compare data for **10a** and **10b**] it results in a decrease of the Pb−O(vanadyl) donor bond length from 2.701(3) to 2.561(3) Å.

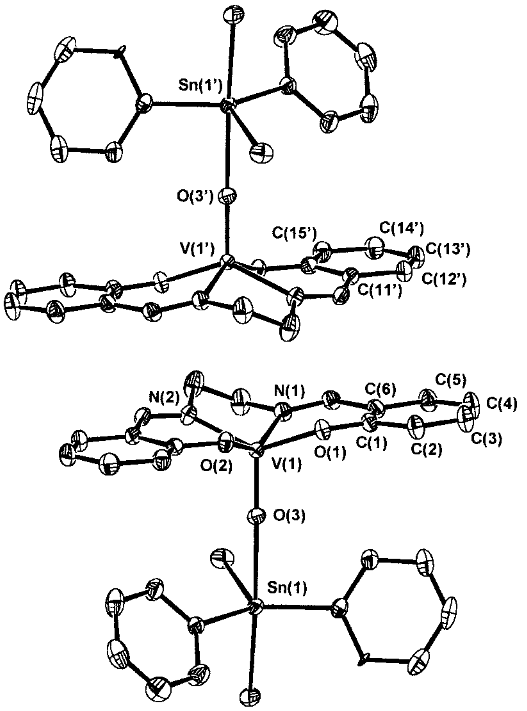

Figure 9. Aromatic π-interactions in $SnPh_2Cl_2 \cdot VO(salen)$. The five closest intermolecular C−C contacts between the centrosymmetrically related neighboring molecules are C(1)−C(11), 3.531; C(5)−C(13), 3.448; C(5)−C(12), 3.478; C(6)−C(11), 3.522; and C(6)−C(12), 3.495. The centroid−centroid separation is 3.99 Å.

There are a number of reliable ways from the data in Table 2 of assessing the effect of vanadyl donor bond formation on vanadium displacement relative to the basal plane and on the V═O bond length. This can be done by comparing structural data for both **3** and **4** with those for **a**, comparing data for both **5** and **10b** with those for **2**, or comparing data for **6** with those for **1**. These comparisons all lead to the same conclusions. The vanadyl bond length increases on formation of the donor bond, and the increase is related to the strength of the Lewis acid. For example, the greatest increase is registered when diphenyltin dichloride, the strongest of the Lewis acids in these structures, is involved. Somewhat surprisingly, little or no change in the vanadium displacement from the basal plane accompanies donor bond formation; slight changes that occur are always toward the basal plane.

The V−O−M (M = Sn or Pb) bond angle is a particularly interesting parameter. A possible interpretation of these angles, being close to 180° (as can be seen in the data in Table 2 and in all earlier reported data[9,11,12]), is that the vanadyl bond has considerable triple bond character; such an interpretation has theoretical support.[30] In this context, the effect of donor bond formation trans to the vanadyl bond on the V−O−M bond angle is most illuminating. From a comparison of data for **5** and **6** it can be seen that, as a result of aqua adduct formation, the V−O−Sn bond angle decreases by 10.7°. Likewise, a comparison of data for **10a** and **10b** reveals that aqua adduct formation results in the V−O−Pb angle decreasing by 14°. The most immediate and important conclusion to be drawn from these observations is that the original large angles were not dictated by steric considerations (note that as a consequence of water donor bond formation there are no salicylaldimine ligand conformational changes such as to relieve possible steric interactions between the Lewis acid and base molecules). The effect of formation of the water donor bond to vanadium is to increase the electron density on vanadium. This in turn should result in a decrease in the multiple bond character of the vanadyl bond, thus resulting in a decrease in the V−O−M bond angle, as observed. Thus, the data relating to the V−O−M bond angles clearly point to the fact that the multiple bond character of the vanadyl bond is indeed exerting influence on the V−O−M angle and that the angles close to 180° are reflecting vanadyl triple bond character (rather than steric demands).

The effect of the phenolic oxygen coordination to tin on the vanadyl salicylaldimine geometry can be assessed from a comparison of structural data for **7** with those for **a**. As expected, engagement of the phenolic oxygen atoms in donor bond formation results in an increase in the phenolic oxygen−vanadium bond lengths. It also results in a lengthening of the V═O bond (consistent with the increase in vanadyl frequency) and increased displacement of vanadium from the base plane.

Electronic Spectra. There has been a long-running controversy surrounding the electronic spectrum of vanadyl complexes. It is a surprising controversy in view of the simple d^1 electronic configuration involved.[31] Three electronic transitions are possible for complexes having the highest C_{4v} symmetry in five- and six-coordinated complexes, these being

$$3d_{xz}, 3d_{yz} \leftarrow 3d_{xy}\ [e_\pi^* \leftarrow b_2] \qquad \text{(I)}$$

$$3d_{(x2-y2)} \leftarrow 3d_{xy}\ [b_1^* \leftarrow b_2] \qquad \text{(II)}$$

$$3d_{z2} \leftarrow 3d_{xy}\ [a_1^* \leftarrow b_2] \qquad \text{(III)}$$

Controversy exists with respect to the assignment of the highest energy transition (III) with respect to charge-transfer bands, and also with respect to the relative positions of transitions I and II. It is now believed that the relative positioning of these latter two bands can be dictated by the ligands.

In light of the structural changes accompanying vanadyl formation which have been described, a comparison of electronic spectra for the vanadyl salicylaldimines with those for their vanadyl adducts should provide a unique and unambiguous method for distinguishing between transitions I and II. Since on formation of the vanadyl adduct the position of vanadium relative to the basal plane is essentially unchanged, transition II should show minimal movement while transition I is anticipated to move to a significantly

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(30) Di Bella, S.; Lanza, G.; Gulino, A.; Fragalà, I. *Inorg. Chem.* **1996**, *35*, 3885−3890.

(31) (a) Lever, A. B. P. *Inorganic Spectroscopy*, 2nd ed.; Elsevier: Oxford, 1984. (b) Amorós, P.; Ibáñez, R.; Beltrán, A.; Beltrán, D. *J. Chem. Soc., Dalton Trans.* **1988**, 1665−1669 and references therein.

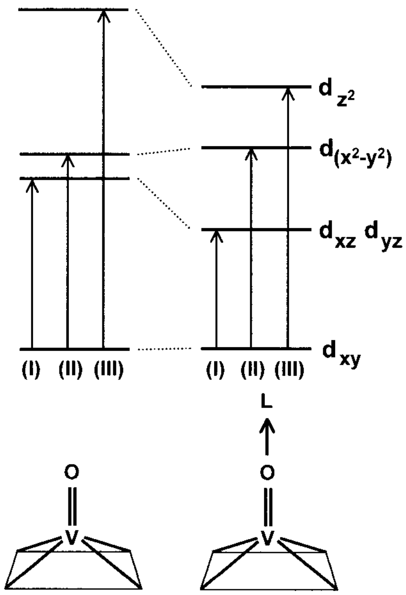

Figure 10. A qualitative representation of d-orbital energy perturbation in vanadyl salicylaldimine complexes resulting from the formation of a vanadyl donor bond (based on crystallographic data in Table 3).

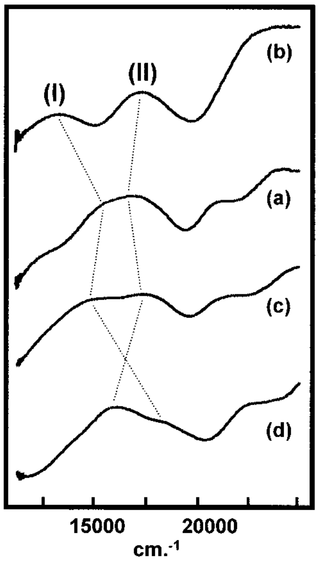

Figure 11. Reflectance spectra of (a) VO(salen), (b) $SnPh_2Cl_2$·VO(salen), (c) VO(acetophenen), and (d) $PbPh_2Cl_2$·VO(acetophenen). Transitions I and II occur at 14500 and 17290 cm^{-1} for (a), 13140 and 17240 cm^{-1} for (b), 14260 and 17420 cm^{-1} for (c), and 18970 and 15760 cm^{-1} for (d), respectively.

lower frequency as a result of the lengthening of the vanadyl bond. The general situation is shown in the energy level diagram of Figure 10. In this diagram, transition II is indicated to move to a slightly higher energy, this being based on the assumption that the slight decrease in bond lengths to the Schiff base oxygen and nitrogen atoms and/or movement of the vanadium toward the base plane raises the energy of the $3d_{xy}$ orbital to a lesser extent than that of the $3d_{x^2-y^2}$ orbital.

The vanadyl salicylaldimines of the study show two overlapping bands in the 14000−17500 cm^{-1} region (see, for example, Figure 11). On formation of a vanadyl donor bond, the lower energy band moves to a significantly lower frequency while the higher energy band is relatively unchanged. A typical case is shown in Figure 11. In actual fact, the movement of this latter band is particularly sensitive to Lewis acidity, increasing acidity resulting in increased band movement toward lower energy (see the Supporting Information). Unquestionably, therefore, the lower energy band in each spectrum is due to transition I. The alternative assignment of the band in either the spectra of the parent adducts or those of associated adducts would be totally at odds with crystallographic observations.

Crystallographic data reveal that considerable shortening of the vanadium bonds to the basal plane atoms occurs on formation of the adduct $B(C_6F_5)$·$VO(acac)_2$.[12] Not surprisingly, therefore, formation of the adducts $SbPh_2X_3$·$VO(acac)_2$ (X = Cl or Br) leads to much greater shifts to higher energy of transition II, compared to analogous shifts observed on formation of adducts with the vanadyl salicylaldimines. Furthermore, in the case of $VO(acac)_2$ and its adducts, transition III is not obscured by charge-transfer bands (as it is in the case of the vanadyl salicylaldimines) and it is observed to undergo the expected shift to lower energy accompanying vanadyl donation. For example, transitions I, II, and III occur at 14500, 16700, and 24500 cm^{-1}, respectively, in the spectrum of $VO(acac)_2$, while they occur at 12500, 18200, and 21300 cm^{-1}, respectively, in the spectrum of $SbPh_2Cl_3$·$VO(acac)_2$.

On the basis of the crystallographic data in Table 2, it is clear that donation through the phenolic oxygen atoms must result in changes in the electronic spectrum significantly different from those that occur as a result of vanadyl donation. In particular, the decrease in vanadyl bond length following phenolic oxygen donation should result in an increase in the energy of transition I, whereas the accompanying movement of vanadium toward the basal plane should result in a decrease in the energy of transition II. Since these transitions are not widely separated in vanadyl salicylaldimine complexes, it is clear that an energy crossover between the two transitions may result. Unfortunately, an insufficient quantity of $SnPh_2Cl_2$·VO(acetophen1,2pn) was available to obtain its reflectance spectrum. However, formation of $PbPh_2Cl_2$·VO(acetophenen) leads to a significant increase in the vanadyl stretching frequency, thus confirming phenolic oxygen donation, and its electronic spectrum shown in Figure 9 confirms the anticipated changes in the electronic spectrum.

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Supporting Information Available: A total listing of characterized adducts along with selected infrared data and Sn-119 Mössbauer parameters (Table 1S), electronic spectral band assignments (Table 2S), electronic spectra of $VO(acac)_2$ and $SbPh_2Cl_3$·$VO(acac)_2$ (Figure 1S), and crystallographic data in CIF file format. This information is available free of charge via the Internet at http://pubs.acs.org.

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