A Vanadyl Donor Bond to Tin in a Heterobimetallic Complex: the Crystal Structure of $SnPh_3Cl{\cdot}VO$(salpren) (H_2salpren = *N,N'*-1,2-propylenebis-salicylideneamine)

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The title complex has an adduct structure in which the vanadyl salicylaldimine forms a donor bond through the vanadyl oxygen to tin, thereby generating an almost linear V–O–Sn moiety.

It is surprising that, despite the extensive investigations of vanadyl chemistry, little is known about the donor properties of the vanadyl group. It has been proposed that vanadyl donation to bivalent metal ions occurs in heterobimetallic transients which have been detected in a number of electron-transfer reactions and, on spectroscopic grounds, to ruthenium in the stable complex $[(NH_3)_5RuOV(H_2O)_4(SO_4)]SO_4$.[1] However, the literature contains no properly authenticated example of vanadyl forming a conventional donor bond to an element other than vanadium of a neighbouring vanadyl group in auto-associated structures. In this communication we present examples of heterobimetallic complexes in which vanadyl forms donor bonds to tin, and provide crystallographic details for one such complex.

Triphenyltin chloride reacts with VO(L) [L = *N,N'*-ethylenebis(salicylideneaminato), its 3,3'-dimethoxy, and α,α'-dimethyl analogues] and VO(salpren) (H_2salpren = *N,N'*-1,2-propylenebis-salicylideneamine) in acetonitrile to yield air-stable 1 : 1 adducts which have lower vanadyl i.r. stretching frequencies than those of the parent vanadyl complexes. Only in the case of $SnPh_3Cl{\cdot}VO$(salpren) ($\mu_{eff.}$ 1.81 μ_B) did it prove possible to obtain crystals which were suitable for a crystallographic investigation, and in this case the crystals (obtained from acetonitrile) were small and not of favourable dimensions for diffraction studies; this probably contributes to the rather large errors in the molecular parameters from the structure determination.† The most significant feature of this structure (see Figure 1) is that it confirms a vanadyl donor bond to tin. However, it is also significant in that the original five-co-ordination of vanadium is maintained on adduct formation, and thus any resultant structural changes within the vanadyl ligand system can be directly related to vanadyl donation. In this respect the situation differs from that in auto-associated vanadyl structures where the structural geometry within the vanadyl ligand system is a consequence not only of vanadyl donation but also of the concomitant increase in vanadium co-ordination number.

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† *Crystal data*: $C_{35}H_{31}N_2O_3ClSnV$, M = 732.70, monoclinic, space group $P2_1/n$, a = 11.151(3), b = 11.297(3), c = 25.224(5) Å, β = 96.39(2)°, U = 3157.80 Å^3, D_c = 1.54 g cm^{-3}, μ(Mo-K_α) = 11.10 cm^{-1}, 2113 reflections with $I > 3\sigma(I)$, using a Hilger and Watts Y290 diffractometer and Mo-K_α radiation, $2\theta_{max}$ = 48°. The structure was solved by direct methods, SHELX86, and refined with 188 variable parameters using SHELX76.[8] Following full-matrix least-squares refinement with metal and chlorine atoms refined anisotropically, and no absorption correction applied R = 7.33 and R_w = 7.80%. Maximum and minimum excursions in the final $F_0 - F_c$ difference map were 0.45 and −0.73 eÅ^{-3} respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

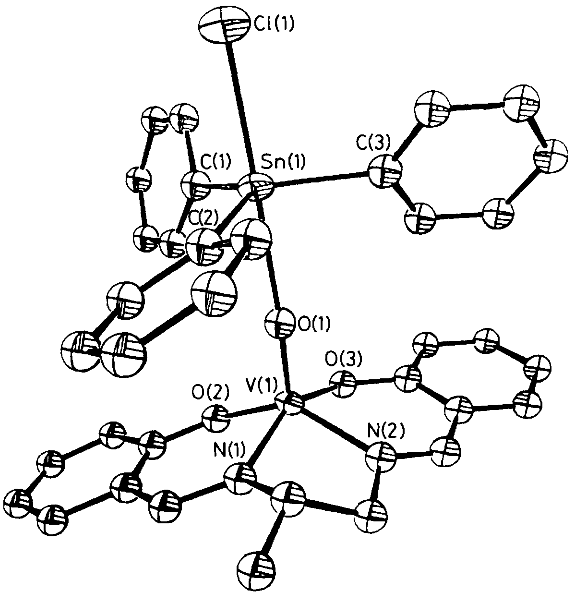

Figure 1. ORTEP[9] plot of the asymmetric unit of $SnPh_3Cl·VO$(salpren). Selected dimensions: V(1)–O(1) 1.617(9), V(1)–O(2) 1.886(9), V(1)–O(3) 1.905(8), V(1)–N(1) 2.038(12), V(1)–N(2) 2.054(10), Sn(1)–O(1) 2.424(9), Sn(1)–Cl(1) 2.484(4), Sn(1)–C(1) 2.139(12), Sn(1)–C(2) 2.152(13), Sn(1)–C(3) 2.138(12) Å. Sn(1)–O(1)–V(1) 175.4(5)°.

We did not succeed in obtaining suitable crystals of VO(salpren) for a comparative structural study, but data are available for the closely related VO(salen) (H_2salen = *N,N'*-ethylenebis-salicylideneamine). The most striking influence of vanadyl donation can be seen in the substantial lengthening of the V=O bond. For example, the average V=O bond lengths in VO(salen)[2] and $[\{VO(salen)\}_2Na]BPh_4$[3] are 1.588 and 1.584(3) Å respectively, compared with a value of 1.617(9) Å for the title complex. There appears to be an associated contraction of the vanadium-to-ligand-oxygen bond lengths. The average V–O bond length of 1.895(9) Å for the title complex compares with the average values of 1.923(1) and 1.925(2) Å for VO(salen) and $[\{VO(salen)\}_2Na]BPh_4$ respectively. On the other hand, the V–N bond lengths do not appear to be significantly affected by the vanadyl donation. In the title complex vanadium is 0.563 Å removed from the least squares plane defined by the ligand oxygen and nitrogen atoms, whereas it is removed from this plane by average distances of 0.599 and 0.606 Å for VO(salen) and $[\{VO(salen)\}_2Na]BPh_4$ respectively. The overall effect of donation to tin is to cause a decrease in the vanadyl i.r. stretching frequency from 976 cm^{-1} [for VO(salpren)] to 939 cm^{-1} [for $SnPh_3Cl·VO$(salpren)].

$SnPh_3Cl·VO$(salpren) provides another example of an M=O moiety forming a donor bond to tin, previous examples being for M = C, N, S, Se, and P.[4] In all these earlier examples the M–O–Sn bond angles were indicative of sp^2 hybridized oxygen. By contrast, the V–O–Sn bond angle of 175.4(5)° is indicative of sp hybridized oxygen, thus confirming substantially different bonding within V=O to that in any of the other M=O systems. The result is consistent with vanadyl possessing partial triple-bond character.[5]

The geometry about tin compares well with that in μ-bis(diphenylphosphino)ethane-bis(chlorotriphenyltin), the most closely related adduct for which crystallographic details are available.[6] The most significant structural difference lies in the Sn–O donor bond lengths; 2.424(9) Å for the title complex compared with a value of 2.357(3) Å for the phosphine adduct. The value of 2.424(9) Å falls well within the range of known Sn–O and Sn–N donor bond lengths and points to quite significant vanadyl donation to tin,[4] but, despite this, the tendency for vanadyl to donate in this fashion is surprisingly limited. For example, sufficient electron delocalization occurs in VO(salphen) (H_2salphen = *N,N'-o*-phenylenebis-salicylideneamine) to render it unreactive to both di- and triphenyltin chlorides. $VO(salpr)_2$ [H_2salpr = *N*-n-propyl(salicylideneamine)], perhaps for reasons related to its trigonal bipyramidal geometry,[7] is also unreactive to both tin Lewis acids, and so also is $VO(acac)_2$ (Hacac = acetylacetone).

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