Chelate Exchange Reactions between Bis(acetylacetonato)oxovanadium(IV) & Salicylidene Benzoyl Hydrazine Schiff Bases

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Depending on the relative amounts of the reactants, chelate exchange between bis(acetylacetonato)oxovanadium(IV) and salicylidene benzoyl hydrazine type Schiff bases provides two types of complexes. In one type the vanadyl-oxygen is retained giving products of the type (salicylidenato benzoyl hydrazonato)oxovanadium(IV). These compounds have subnormal magnetic moments and possess metal-metal interaction in dimeric forms. In the other type abstraction of the vanadyl oxygen occurs to give complexes of the type bis(salicylidenato benzoyl hydrazonato)vanadium(IV). These compounds have normal magnetic moments of 1.7 B.M. These reactions, in general, are valid in acetone and with some ligands also in ethanol. However in ethanol the reaction between bis(acetylacetonato)oxovanadium(IV) and salicylidene benzoyl hydrazine gives a yellow diamagnetic vanadium(V) complex, oxo-hydroxomono(salicylidenato benzoyl hydrazonato)oxovanadium(V). The complexes obtained have been characterised by elemental analyses, infrared and electronic spectra and magnetic moments. The ESR spectra in the powder form are structureless and exhibit only a single band.

Materials and Methods

Bis(acetylacetonato)oxovanadium(IV), [VO(acac)₂], benzoyl hydrazine and other ligands were prepared by standard methods. Solid state magnetic measurements on the complexes were carried out with a Gouy balance. Pascal's constants were taken from standard source. Mono(salicylidenato benzoyl hydrazonato) oxovanadium(IV) — [VO(acac)₂] (0.002 mol) in acetone (100 ml) and salicylidene benzoyl hydrazine (0.002 mol) in acetone (20 ml) were mixed and refluxed for 1 hr. The solution was allowed to stand overnight and the black crystalline product filtered, washed with acetone and dried in air (Found: V, 16.0; N, 8.4; C, 53.8; H, 2.7. [VO(L)] requires V, 16.7; N, 9.1; C, 54.9; H, 3.2%); \( \mu_{\text{eff}} = 0.7 \) B.M.

Mono(5,6-benzo(salicylidenato benzoyl hydrazonato) oxovanadium(IV)) — This was obtained as reddish brown crystals following the above procedure. The total volume of acetone employed was about 120 ml (Found: V, 13.5; N, 7.6; C, 59.4; H, 3.1. [VO(L')] requires V, 14.3; N, 7.8; C, 60.0; H, 3.9%); \( \mu_{\text{eff}} = 1.3 \) B.M.

Bis(salicylidenato benzoyl hydrazonato)vanadium(IV) — [VO(acac)₂] (0.001 mol) in acetone (15 ml) and the ligand (0.002 ml) in acetone (10 ml) were mixed and refluxed for ~ 10 min. The blackish crystalline solid obtained was washed with acetone and dried in air (Found : V, 9.8; N, 10.5; C, 63.7; H, 3.2. [V(L)₃] requires V, 9.7; N, 10.6; C, 63.7; H, 3.8%); \( \mu_{\text{eff}} = 1.7 \) B.M.

Bis(5,6-benzo(salicylidenato benzoyl hydrazonato)vanadium(IV)) — This compound was obtained from appropriate reactants as above using a total volume of acetone ~ 50 ml (Found: V, 8.2; N 8.8; C, 68.7; H, 3.3. [V(L')₃] requires V, 8.1; N, 8.9; C, 68.9; H, 3.8%); \( \mu_{\text{eff}} = 1.7 \) B.M.

Oxo-hydroxomono(salicylidenato benzoyl hydrazonato)vanadium(V) — [VO(acac)₂] (0.002 mol in 100 ml
ethanol) and the ligand (0.002 mol in 20 ml ethanol) were mixed and refluxed for 2 hr. The blackish solution was concentrated in a petri dish to yield a yellow complex. This was dissolved in ethanol on a steam-bath, concentrated in a petri dish to furnish a yellow crystalline product which was filtered, washed with ethanol and dried in air (Found: V, 16.1; N, 8.7; C, 51.9; H, 3.1. \[\text{VO(L)(OH)}\] requires V, 16.7, N, 9.1; C, 52.1; H, 3.7%); this compound was found to be diamagnetic.

Results and Discussion

The compounds are in general insoluble in common organic solvents but dissolved in DMF and DMSO to give nonelectrolyte conductance.

The chelate exchange studies reported in this paper have established the formation of three different types of vanadium complexes: (i) mono (ligand) oxovanadium(IV), (ii) bis(ligand)vanadium(IV) and (iii) oxo-hydroxomono(ligand)vanadium(V).

Mono(ligand)oxovanadium(IV)—Both salicyliden benzoyl hydrazone \[LH_2\] and 5,6-benzo salicyliden benzoyl hydrazone \[L'H_2\] react with bis (acetylacetonato)oxovanadium(IV) in refluxing acetone to give blackish crystals of the complexes of the type \[\text{[VO(L)]} \] and \[\text{[VO(L')]} \]. The ligands \[LH_2\] and \[L'H_2\] exhibit in their IR spectra (KBr) characteristic bands at 3250, 1250, due to \[vC-O\] (OH phenolic) are shifted to give nonelectrolyte conductance. In the complexes, \[\text{[VO(L)]} \] and \[\text{[VO(L')]\} \] \[vNH\] is absent and strong bands appear at 1595 and 1590 cm\(^{-1}\) respectively attributable to \(-C=\ddot{N}-N-C-\) moiety. This implies that the ligands function as dibasic tridentate ones. The free ligand bands \(\sim 1250\), due to \[vC-O\] (OH phenolic) are shifted to higher wave numbers and appear at 1280 cm\(^{-1}\) (ref. 5) indicating deprotonation and attachment to the metal.

The above infrared bands are comparable to those exhibited by mono(ligand)lead(II) complexes reported recently from this Laboratory\(^4\). The vanadyl band\(^7\) in bis(acetylacetonato)oxovanadium(IV) appears about 995 cm\(^{-1}\). The complexes \[\text{[VO(L)]}\] and \[\text{[VO(L')]\}] exhibit medium intensity bands at 980 and 990 cm\(^{-1}\) respectively. The two compounds show subnormal magnetic moments\(^8\) of 0.7 and 1.3 B.M. respectively.

All the above observations taken together justify dimeric formulation \[\text{[VO(L)]}\] and \[\text{[VO(L')]\}] respectively. The tridentate salicylidene benzoyl hydrazone and 5,6-benzo salicyliden benzoyl hydrazone are known to function as tridentate dibasic bridging ligands giving copper(II) complexes of subnormal magnetic moments\(^9\).

Electronic spectra of oxovanadium(IV) complexes are usually characterised by three absorption bands corresponding to the transitions\(^10\) : \(d_{xy} \rightarrow d_{xz}, d_{yz} \); \(d_{xy} \rightarrow d_{x^2-y^2}\); and \(d_{xy} \rightarrow d_{z^2}\). The complex, \[\text{[VO(L)]}\] exhibits two distinct bands at 15.3 and 23.5 kK and \[\text{[VO(L')]\}] displays a shoulder at 14.9 and a broad band in the region 22.2-33.3 kK.

Bis(ligand)vanadium(IV)—Using two molar proportions of \[LH_2\], \[L'H_2\] and \[L'H_2\] for one molar proportion of bis(acetylacetonato)oxovanadium(IV) in refluxing acetone, black crystalline products of the compositions corresponding to \[\text{[V(L)]}_2\], \[\text{[V(L')]_2}\] and \[\text{[V(L')_2]}\] are obtained. The infrared spectra of \[\text{[V(L)]}_2\] and \[\text{[V(L')_2]}\] do not exhibit any \[vNH\] but they do exhibit a strong composite band at 1600 cm\(^{-1}\), attributable\(^4\) to \(-C=\ddot{N}-N-C-\) moiety, indicating that the ligands \[LH_2\] and \[L'H_2\] coordinate to vanadium(IV) as dibasic ONO donor in the enol form. The free ligand band at 1250 cm\(^{-1}\) is shifted upwards\(^8\) to 1275 cm\(^{-1}\) indicating the absence of the V=O bond in these complexes. Since the infrared characteristics of the coordinated ligands in \[\text{[V(L)]}_2\] and \[\text{[V(L')_2]}\] are very similar to those found for \[\text{[VO(L)]}\] and \[\text{[VO(L')]\}] complexes, it is believed that both the ligands \[LH_2\] and \[L'H_2\] function as tridentate dibasic ONO donors. The complex \[\text{[V(L')_2]}\] does not reveal any worthwhile infrared band in the region 850-1000 cm\(^{-1}\). The free ligand \[L'H_2\] exhibits \[vC-O\] at 1650 and \[vC-N\] at 1620 cm\(^{-1}\). Its complex, \[\text{[V(L')_2]}\] displays \[vC-O\] at 1620 and \[vC-N\] at 1595 cm\(^{-1}\). Since there are two phenolic \(-OH\), which are stronger acid than enolic \(-OH\), it is likely that the ligand is attached to vanadium as ONO donor in its keto form while both the phenolic \(-OH\) undergo deprotonation to satisfy the charge of vanadium(IV). The magnetic moments \[\text{[V(L)]}_2\], \[\text{[V(L')_2]}\] and \[\text{[V(L')_2]}\] are quite normal (1.7 B.M.). As there are two tridentate ligands coordinated to vanadium (IV) possibility of dimerisation through bridging oxygen donor atoms may be ruled out.

The complex bis(acetylacetonato benzoyl hydrazono)nato vanadium(IV) has a trigonal prismatic geometry\(^11\) as revealed by X-raycragyraly stollography study. In trigonal prismatic geometry there are likely to be two transitions from \(d_{x^2}, d_{y^2} \rightarrow d_{z^2}^2\); \(d_{xz}, d_{yz} \rightarrow d_{xy}^2\). The complex bis(salicilidenato benzoyl hydrazono)nato vanadium(IV), \[\text{[V(L)]}_2\] exhibits in its electronic spectrum two bands at 14.3 and 18.0 kK. Surprisingly, however, the complex bis(5,6-bensalicylideneato benzoyl hydrazonato)nato vanadium(IV), \[\text{[V(L')_2]}\] exhibits three bands at 16.0; 18.5 and 25.0 kK. This spectrum is more like an oxovanadium(IV) complex although analytical composition and infrared-spectrum do not support an oxovanadium(IV) formulation. The third complex bis(5,6-bensalicylideneato salicyloyl hydrazonato)nato vanadium(IV), \[\text{[V(L')_2]}\] displays two bands, one broad band in the region 16.7-18.1 kK, and a second one at 27.8 kK. The electronic spectra of the bis-complexes are, therefore, not much helpful in deciding the presence or absence of a vanadyl bond in the presently reported complexes.

The somewhat unexpected electronic spectra may indicate some severe distortion in the stereochemistry of these complexes from an ideal octahedral geometry. The electron spin resonance spectra of the bis(ligand)vanadium(IV) complexes in powder form gave one broad, featureless line. No hyperfine splitting due to the \(^{51}V\) nucleus \((I=7/2)\) interaction with the unpaired electron was observed.

Oxo-hydroxomono(salicilidenato benzoyl hydrazo-
nato)vanadium(V)—This yellow complex obtained in ethanol medium by the reaction of salicylidene benzoyl hydrazone and bis(acetylacetonato)oxovanadium(IV) exhibits a sharp band at 1605 cm⁻¹ attributable to -C=N-N=C- moiety. A band at 1275 cm⁻¹ indicates the attachment of phenolic oxygen, a medium intensity band at 975 cm⁻¹ is due to vanadyl bond while a broad band centred ~2800 cm⁻¹ is assigned to νOH. This complex is diamagnetic, indicating the presence of 3d⁵ pentavalent vanadium. In keeping with this the electronic spectrum displays a single absorption band at 22.0 kK, probably arising as a result of charge transfer. The complex may be formulated as a ligand-bridged dimer of the type [VO(OH)(L)₂].

Rationale of chelate exchange reactions—The reaction products obtained via chelate exchange reactions on bis(acetylacetonato)oxovanadium(IV) of Schiff bases of the type salicylidene benzoyl hydrazone are mainly dependent on the reaction stoichiometry rather than on the nature of the solvent. The 1:1 interaction between the reactants leads systematically to monoligand oxovanadium(IV) complexes. Based on their subnormal magnetic moment dimeric, ligand-oxygen bridged structure has been proposed. Interestingly when two molar proportions of the Schiff base are used the products are the bis(ligand) vanadium(IV). In these complexes the vanadyl oxygen bond is abstracted. The ligands used are potentially dibasic in their enol form. It is most likely that the enolic hydrogen of the two tridentate ONO ligands form hydrogen bonds with the vanadyl oxygen. This will certainly lead to weakening of the vanadyl bond and may ultimately effect its abstraction in the form of H₂O.

In ethanol medium between bis(acetylacetonato) vanadium(IV) and salicylidene benzoyl hydrazone affords a product of pentavalent vanadium. Evidently the solvent aids in the oxidation in the presence of air.

The formation of the complexes [VO(L/L')], [V(L/L'/L'/L'')₃] and [VO(OH)(L)₂] may take place by the reactions (1-3).

\[2[VO(acac)₂] + 2LH₂ → [VO(L)₂]₄ + 4acacH \quad \ldots (1)\]
\[[VO(acac)₂] + 2LH₂ → [V(L)₂]₄ + 2acacH + H₂O \ldots (2)\]
\[[VO(acac)₂] + 2LH₂ + H₂O + \frac{1}{2}O₂ → [VO(OH)(L)₂]₄ + 4acacH \ldots (3)\]

References