Inorganica Chimica Acta, *90* (1984) 111–114

Reaction of Bis(Salicylaldehyde Hydrazone)Vanadium(IV) Dichloride with Aromatic and Heterocyclic Amines

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Received March 6, 1984

Bis(salicylaldehyde hydrazone)vanadium(IV) dichloride undergoes reaction with aromatic amines such as aniline, 1,4-diaminobenzene, heterocyclic amines such as aminopyridine and nucleotides such as adenine. Elemental analysis, magnetic susceptibility measurements, electronic, infrared and esr spectral data indicate that the compound formed in the case of reaction with aniline is bis(salicylaldehyde hydrazone) bis(anilinato)vanadium(IV) with elimination of hydrogen chloride. Similar compounds are formed as a result of reaction with the other amines. In addition, the elimination reaction has been studied using the hydrazone derived from phenylhydrazone which gives similar products on reaction with the aromatic and heterocyclic amines.

Introduction

The facile conversion of oxovanadium(IV) chelates of acetylacetone, 8-hydroxyquinoline and certain Schiff's bases as a result of their reaction with thionyl chloride to the respective vanadium(IV) dichloride has been described [1, 2]. In addition the reaction of thionyl chloride with oxovanadium(IV) porphyrinates which gives dichloro vanadium(IV) porphyrinates has been outlined [3]. The possible uses of these easily available dichlorovanadium(IV) chelates for alkylation, reduction and substitution reactions have been mentioned [2]. The present work sets out to describe the products formed as a result of an elimination reaction involving bis(salicylaldehyde hydrazone)vanadium(IV) dichloride, formed by procedures similar to those alluded to for the other dichlorovanadium(IV) chelates, with certain aromatic and heterocyclic amines.

Experimental

Salicylaldehyde, aniline, 1,4-diaminobenzene, 2-, 3- and 4-aminopyridine were freshly distilled before use. The remaining materials were used as obtained from commercial sources. The UV–visible spectra using glass and silica cuvettes were recorded with a Varian Techtron model 635 spectrophotometer. All e.s.r. measurements were taken with a Varian E-12 spectrometer with samples at the temperature of liquid nitrogen. Infrared spectra of compounds in Nujol mulls were recorded with a Perkin-Elmer 257 (4000–625 cm^{-1}) spectrophotometer calibrated with polystyrene film. Infrared measurements at lower frequencies were made with a Perkin-Elmer 180 Spectrometer.

The oxovanadium(IV) chelates of salicylaldehyde hydrazone and salicylaldehyde phenylhydrazone were prepared as described previously [4, 5]. The elemental analysis data and magnetic susceptibility measurements on the chelates are summarized in Table I.

TABLE I. Analytical Data (Calculated % in brackets).

Compound	(%)			
	C	H	N	μ_{eff}
V(IV)O·(SALHY)$_2$[a]	50.65(49.85)	4.42(4.15)	16.94(16.62)	1.76
V(IV)O·(SALPHENY)$_2$[b]	62.95(63.80)	4.43(4.50)	11.60(11.45)	1.74

[a]SALHY ≡ salicylaldehyde hydrazone. [b]SALPHENHY ≡ salicylaldehyde phenyl hydrazone.

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0020-1693/84/$3.00

TABLE II. Analytical Data (Calculated % in brackets).

Compound	(%)				
	C	H	N	Cl	μ_{eff}
$\mathrm{V(IV)Cl_2(SALHY)_2}$[a]	43.10(42.85)	3.20(3.57)	14.95(14.29)	19.64(18.93)	1.78
$\mathrm{V(IV)Cl_2(SALPHENHY)_2}$[b]	57.10(57.35)	4.25(4.04)	10.71(10.29)	13.84(13.65)	1.79
$\mathrm{V(IV)(SALHY)_2(2\text{-}NHPy)_2}$[c]	56.21(56.80)	4.46(4.73)	22.86(22.09)		1.75
$\mathrm{V(IV)(SALHY)_2(3\text{-}NHPy)_2}$	56.43(56.80)	4.64(4.73)	22.74(22.09)		1.74
$\mathrm{V(IV)(SALHY)_2(4\text{-}NHPy)_2}$	56.29(56.80)	4.21(4.73)	22.94(22.09)		1.75
$\mathrm{V(IV)(SALHY)_2(NHC_6H_5)_2}$	61.95(61.78)	4.83(5.15)	16.41(16.63)		1.76
$\mathrm{V(IV)(SALHY)_2(ADENIL)_2}$	52.07(51.84)	3.74(3.92)	30.15(29.95)		1.72
$\mathrm{V(IV)(SALPHENHY)_2(2\text{-}NHPy)_2}$	65.13(65.55)	4.56(4.86)	17.21(16.99)		1.74
$\mathrm{V(IV)(SALPHENHY)_2(3\text{-}NHPy)_2}$	64.97(65.55)	4.61(4.86)	16.53(16.99)		1.76
$\mathrm{V(IV)(SALPHENHY)_2(4\text{-}NHPy)_2}$	65.32(65.55)	4.27(4.86)	16.59(16.99)		1.74
$\mathrm{V(IV)(SALPHENHY)_2(NHC_6H_5)_2}$	69.12(69.41)	5.63(5.17)	12.71(12.79)		1.75
$\mathrm{V(IV)(SALPHENHY)_2(ADENIL)_2}$	61.09(60.59)	4.42(4.21)	23.17(23.56)		1.72

[a]SALHY ≡ salicyladehyde hydrazone. [b]SALPHENHY ≡ salicyladehyde phenyl hydrazone. [c]NHPy ≡ anion formed by a loss of proton from amino-pyridine.

Preparation of Bis(Salicylaldehyde Hydrazone) Vanadium(IV) Dichloride

Bis(salicylaldehyde hydrazone)vanadium(IV) dichloride was prepared by the addition under nitrogen atmosphere of a dimethylformamide (dmf) (50 cm^3) solution of thionyl chloride (20 mmol, 2.38 g) to a dmf (50 cm^3) solution of bis(salicylaldehyde hydrazone)oxovanadium(IV) (10 mmol, 3.37 g). The reaction which occurred on mixing was marked by an immediate increase in the colour of the reaction mixture. Addition of absolute ethanol (100 cm^3) effects precipitation of the dark brown product which was isolated by filtration under nitrogen atmosphere (yield, 3.2 g, 60%). The corresponding chelate derived from salicylaldehyde phenylhydrazone was synthesized by a similar procedure and the elemental analyses are shown in Table II.

Preparation of Bis(Salicylaldehyde Hydrazone)Bis(Anilinato) Vanadium(IV)

The bis(salicylaldehyde hydrazone)bis(anilinato) chelate of vanadium(IV) was prepared by the addition of a dmf (25 cm^3) solution of aniline (5 mmol, 46 g) to a dmf solution (25 cm^3) containing bis(salicylaldehyde hydrazone)vanadium dichloride (2 mmol, 0.78 g) under nitrogen atmosphere. The black–brown product was isolated by addition of absolute ethanol (50 ml) and filtration under nitrogen atmosphere. (Yield 0.75 g, 48%).

The chelates formed by reaction of bis(salicylaldehyde hydrazone)vanadium(IV) dichloride with the heterocyclic and other amines were isolated by a similar procedure. The elemental analysis data and magnetic susceptibility measurements on the chelates are summarised in Table II. Table II also shows a similar set of compounds using bis(salicylaldehyde phenylhydrazone)vanadium(IV) dichloride.

Results

Reaction of thionyl chloride with bis(salicylaldehyde hydrazone)oxovanadium(IV) in dimethylformamide solution leads to the formation of bis(salicylaldehyde hydrazone)vanadium(IV) dichloride. After isolation the composition of the material was established by elemental analysis. I.R. spectroscopy shows that the band at 1000 cm^{-1} which occurs in the starting material and is assigned to a vanadium–oxygen stretch vibration is absent in the product while a new band appears at 345 cm^{-1} as expected for the presence of a terminal vanadium–chloride vibration in the product. Reaction of thionyl chloride with bis(salicylaldehyde phenylhydrazone)oxovanadium(IV) leads to the corresponding chelate vanadium(IV) dichloride.

The reaction of bis(salicylaldehyde hydrazone)vanadium(IV) dichloride dissolved in dimethylformamide with an excess of aniline leads immediately to the formation of a product which upon isolation elemental analysis indicates no longer contains chloride, but contains two anilide moieties per vanadium ion. The reaction is marked by a darkening in colour of the vanadium(IV) chelate and is represented by eqn. 1. The electronic spectra of the original bis(salicylaldehyde hydrazone)oxovanadium(IV), the bis(salicylaldehyde hydrazone)vanadium(IV) dichloride and its reaction product with aniline are compared in Fig. 1. The formation of the

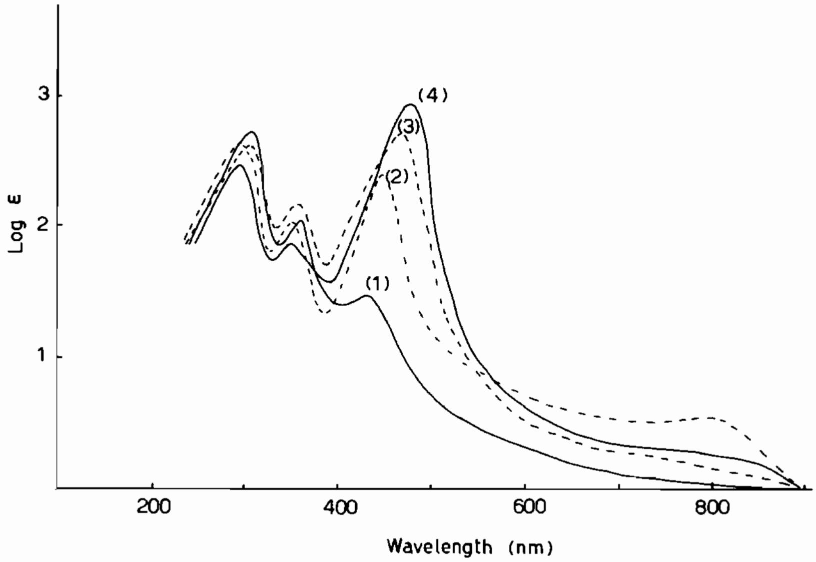
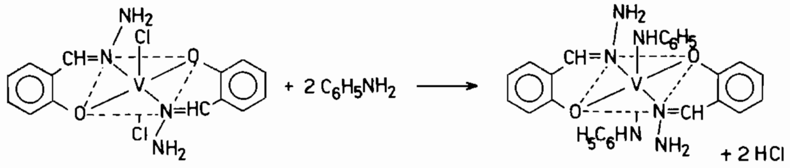


Fig. 1. Absorption spectra in the ultra-violet and visible region of dimethylformamide solutions containing: (1) salicylaldehyde hydrazone, (2) bis(salicylaldehyde hydrazone)oxovanadium(IV), (3) bis(salicylaldehyde hydrazone)vanadium(IV) dichloride, (4) bis(salicylaldehyde hydrazone)bis(anilinato)vanadium(IV).



(1)

anilinato derivative of bis(salicylaldehyde hydrazone)-vanadium(IV) dichloride leaves the infrared spectrum due to the ligand largely the same as that in the bis(salicylaldehyde hydrazone)oxovanadium(IV) though a new band is present at 1150 cm^{-1} attributable to a C–N stretch mode in the anilinato group. group.

Each of the vanadium(IV) compounds have magnetic susceptibilities corresponding to one unpaired election per vanadium ion such that the 3d^1 electronic structure of the vanadium(IV) ion is preserved and there is not any evidence of antiferromagnetic interactions.

The X-band e.s.r. spectra of bis(salicylaldehyde hydrazone)oxovanadium(IV) and that due to the corresponding chelate derived from phenylhydrazone in frozen (77 K) dimethylformamide solution are similar to those usually encountered for oxovanadium(IV) compounds. The magnetic parameters may be obtained from the e.s.r. spectra by consideration of a spin Hamiltonian as follows:

$$\mathcal{H} = g_{\parallel}\beta H_zS_z + g_{\perp}\beta[H_xS_x + H_yS_y] + A_{\parallel}S_zI_z$$

$$+ A_{\perp}(S_xI_x + S_yI_y) + P[I_z^2 - I/3(I + 1) - g_N\beta_NHI$$

Where S = ½, I = 7/2 and the remaining terms have their usual meaning. Good fits of the experimental spectra using line shape simulation procedures described previously [6] are obtained using the magnetic parameters detailed by Table III.

Bis(salicylaldehyde hydrazone)vanadium(IV) dichloride in frozen (77 K) dimethylformamide does not

TABLE III. ESR Parameters.

Compound	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ × 10^4 cm^{-1}	$A_{\perp}$ × 10^4 cm^{-1}
V(IV)O·(SALHY)$_2$^{a}	1.940	1.971	164	61
V(IV)O·(SALPHENHY)$_2$^{b}	1.941	1.978	170	60

^{a}SALPHY ≡ salicylaldehyde hydrazone. ^{b}SALPHENHY ≡ salicylaldehyde phenylhydrazone.

TABLE IV. Esr Parameters.

Compound	$g_\parallel$	$g_\perp$	$A_\parallel$ × 10^4 cm^{-1}	$A_\perp$ × 10^4 cm^{-1}
$V(IV)(SALHY)_2(2\text{-}NHPY)_2$[a]	1.968	1.987	174	64
$V(IV)(SALHY)_2(3\text{-}NHPY)_2$	1.971	1.985	174	65
$V(IV)(SALHY)_2(4\text{-}NHPY)_2$	1.964	1.988	169	61
$V(IV)(SALHY)_2(NHC_6H_5)_2$	1.977	1.985	172	63
$V(IV)(SALHY)_2(ADENIL)_2$	1.965	1.984	171	65

[a] NHPY ≡ anion formed by loss of proton from amino-pyridine.

give rise to an esr spectrum. The absence of an esr signal due to the porphyrinato vanadium(IV) dihalide has been attributed to a degenerate ground state.

As in the case of porphyrin chelate, magnetic susceptibility measurements indicate a $3d^1$ electronic configuration of the vanadium(IV) dichloride hydrazone chelate with μ_{eff} 1.78 B.M. for bis(salicylaldehyde hydrazone)vanadium(IV) dichloride and μ_{eff} 1.79 B.M. for bis(salicylaldehyde phenylhydrazone)vanadium(IV) dichloride.

The reaction product of bis(salicylaldehyde hydrazone)vanadium(IV) dichloride with aniline gives rise to an esr spectrum in frozen (77 K) dimethylformamide solution. The magnetic parameters associated with the spectrum are detailed in Table IV which includes similar data for the products formed by reaction of bis(salicylaldehyde hydrazone)vanadium(IV) dichloride with 2-aminopyridine and adenine.

Discussion

The reaction of the aromatic, heterocyclic and nucleotide amines with the reactive chloro group of bis(salicylaldehyde hydrazone)vanadium(IV) dichloride leads to elimination of the chloride anion as hydrogen chloride and in the case of aniline the attachment of the anilinato group to the vanadium(IV) centre. Similar products are formed with the other amines. The reaction is not inhibited by the presence of the phenyl group on the hydrazone. The formation of the oxovanadium(IV) chelate of salicylaldehyde hydrazone results in enhancement of the bands in the electronic spectrum of the hydrazone. This effect occurs to a somewhat greater extent when the oxo group on the vanadium(IV) centre is replaced by chloride and the anilinato anion.

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