Characterization of [Bis(acetylacetone) ethylenediiminato]dichlorovanadium(IV), VCl₂(acen), and Its Hydrolysis Product, [Bis(acetylacetone) ethylenediimine]chlorooxovanadium(IV) Chloride, [VO(H₂acen)Cl]Cl

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The dichlorovanadium(IV) compound VCl₂(acen) (H₂acen = the Schiff base of acetylacetone and ethylenediamine) has been isolated for the first time. Upon exposure to the residual water in CH₂Cl₂, an addition product, [VO(H₂acen)Cl]Cl, is formed. This is in contrast to other VCl₂²⁺ and VS²⁺ complexes with Schiff base ligands which upon hydrolysis readily revert to the corresponding VO²⁺ complexes, such as VO(acen) and VO(salen) (H₂salen = the Schiff base of salicylaldehyde and ethylenediamine). [VO(H₂acen)Cl]Cl is the first example of a vanadium(IV) complex in which the acen ligand is bound in the keto form. The IR, UV–visible, and EPR spectra and the electrochemistry of VCl₂(acen) and [VO(H₂acen)Cl]Cl are reported.

Introduction

There has recently been great interest in the chemistry of vanadium(IV) compounds in which the ubiquitous vanadyl ion, VO²⁺, has been converted to VS²⁺,[1-5] VX₂²⁺ (X = Cl⁻, Br⁻),[6-9] or VPh₂²⁺.[10] Callahan and co-workers[1,2] reported the isolation of VS(salen) and VS(acen) (H₂salen = the Schiff base of salicylaldehyde and ethylenediamine; H₂acen = the Schiff base of acetylacetone and ethylenediamine), and the structure of VS(acen) has been determined.[11] Pasquali, Floriani, and co-workers[6,7] made several dichloro compounds of the form VX₂L₂ and VX₂L′ (L = a bidentate ligand; L′ = a tetradentate ligand), including VCl₂(salen). Jezierski and Raynor[8,9] studied numerous VCl₂²⁺ type species in situ, but none were isolated.

Having previously studied the electrochemistry of VO(acen) and VS(acen),[12] we were interested in comparing them to VCl₂(acen). Pasquali and co-workers did not synthesize this compound, and Jezierski's work with VCl₂(acen) was all in situ. Thus, we followed Pasquali's procedure for VCl₂(salen) in order to isolate VCl₂(acen). VCl₂(acen) hydrolyzes faster than VCl₂(salen). Furthermore, the hydrolysis of VCl₂(acen) in CH₂Cl₂ does not yield its oxo analogue, VO(acen), as expected; rather, a bright green solid is obtained. This is quite unusual, since most dichlorovanadium(IV) compounds as well as VS²⁺ compounds revert to their corresponding oxo analogues by abstracting oxygen from water. (For example: VCl₂(salen) + H₂O → VO(salen) + 2HCl.) We report here the characterization of VCl₂(acen) and its unusual hydrolysis product.

Experimental Section

The electrochemical instrumentation used has been described previously.[12] Infrared spectra were recorded in CsI windows on a Perkin-Elmer Model 683 spectrophotometer with data station. UV–visible spectra were recorded on a Hewlett-Packard Model 8450A UV–vis spectrophotometer. All X-band EPR spectra were recorded on a Varian Model E-109 Century Series spectrometer by Dr. Robert Buchanan at the University of Louisville. Spectra at liquid-nitrogen temperature were recorded with the use of an Oxford Instruments temperature controller. The spectra were referenced to DPPH. Elemental analysis for vanadium was done on a Perkin-Elmer Model 560 atomic absorption spectrophotometer using V₂O₅ as the standard. The inert-atmosphere drybox for the synthesis of VCl₂(acen) has been described earlier.[12]

Reagents. All solvents used in the syntheses and spectroscopic studies were spectral grade and deoxygenated before use. CH₂Cl₂ (0.008% water) and Me₂SO (0.011% water) were obtained from Burdick and Jackson Laboratories. Tetraethylammonium perchlorate (TEAP) was prepared as described previously[12] and used as the supporting electrolyte. SOCl₂ (reagent grade) was obtained from Fisher Scientific.

Preparation of [Bis(acetylacetone) ethylenediiminato]dichlorovanadium(IV), VCl₂(acen). This procedure is based on the preparation of VCl₂(salen) reported by Pasquali.[7] To a 50-mL deoxygenated CH₂Cl₂ solution of 1.5 g (5.2 × 10⁻³ mol) of VO(acen) was slowly added SOCl₂ (0.84 mL, 1.14 × 10⁻² mol). The blue solution of VO(acen) became

opaque. The reaction mixture was stirred at room temperature for 2–3 h; then a blue-green precipitate was filtered out and discarded. The deep blue filtrate was evaporated to dryness under vacuum and brought into the glovebox. CH₂Cl₂ was put into the flask to dissolve the blue residue, and the solution was filtered again to ensure the complete elimination of undissolved impurities. Mixed hexanes (spectroquality) were added until a blue precipitate began to form. The product was isolated by filtration and washed with hexanes. The blue product was dried under vacuum over P₂O₅. Anal. Calcd for C₁₂H₁₈Cl₂N₂O₂V: C, 41.87; H, 5.23; Cl, 20.64; N, 8.14. Found: C, 40.39; H, 5.44; Cl, 19.85; N, 7.75.

Isolation of [Bis(acetylacetone) ethylenediimine]chlorooxovanadium(IV) Chloride, [VO(H₂acen)Cl]Cl, from VCl₂(acen) in CH₂Cl₂. The isolated VCl₂(acen) was put into CH₂Cl₂, and the solution was stirred in air. The deep blue solution gradually yielded a very bright green precipitate. The green hydrolysis product was filtered and washed with CH₂Cl₂. The solid was dried under vacuum over P₂O₅. Anal. Calcd for C₁₂H₂₀Cl₂N₂O₃V: C, 39.76; H, 5.52; N, 7.73; Cl, 19.60; V, 14.07. Found: C, 39.08; H, 5.60; N, 7.55; Cl, 19.31; V, 13.3.

[VO(H₂acen)Cl]Cl can also be formed directly from a solution of VO(acen) dissolved in acetone containing residual water to which SOCl₂ is added dropwise.

Results and Discussion

Synthesis. While dichloro derivatives of the type VOL₂ (L = a bidentate ligand)[7] were formed quite easily by mixing the oxo analogues with SOCl₂ at room temperature, the synthesis of VCl₂(salen) required heat. Thus, at first, it was assumed that heat would also be necessary to form VCl₂(acen), since acen is a tetradentate ligand like salen. This approach failed, though, while the reaction *without* heat yielded nearly pure VCl₂(acen). This suggests that VCl₂(acen) decomposes upon heating in contrast to VCl₂(salen). The VCl₂(acen) complex is less stable as a solid than VCl₂(salen). After several months in air, VCl₂(acen) became green and the infrared spectrum showed an absorption pattern different from that of the freshly prepared VCl₂(acen), while VCl₂(salen) showed no changes in color or in the infrared spectrum over the same time period.

Since the elemental analysis of the isolated VCl₂(acen) product deviates somewhat from the theoretical value, some decomposition

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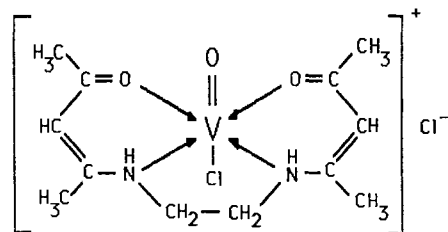
Figure 1. Proposed bonding for [VO(H2acen)Cl]Cl.

must have taken place prior to analysis. But on the basis of its infrared spectrum (vide infra), which shows no V=O stretching band, this decomposition product (probably from reaction with air) is not VO(acen).

$VCl_2(acen)$ is soluble in acetone, Me_2SO, and CH_2Cl_2. In Me_2SO, it hydrolyzes (as expected) to VO(acen), as confirmed by absorption spectroscopy (vide infra). In CH_2Cl_2, the hydrolysis product is not VO(acen); rather, H_2O appears to add to VCl_2-(acen) and be tightly bound. The product is bright green and soluble in water, methanol, and Me_2SO, suggesting that it is ionic in character. It is also air-stable. Upon heating at 100 °C overnight, outer-sphere water may have been removed, as the color changed to a different shade of green, but the infrared spectrum did not differ. pH measurement of an aqueous solution of the product shows that the compound is a weak acid.

Infrared Spectroscopy. Infrared spectra of VO(acen), VCl_2-(acen), and the hydrolysis product were taken in Nujol. For VO(acen) the V=O stretching frequency is observed at 979 cm^{-1}, which lies within the range expected for vanadyl complexes. A stretching band for C=N appears at 1586 cm^{-1}. In the infrared spectrum of $VCl_2(acen)$ as expected, no vanadyl stretching band is observed. (A peak at 954 cm^{-1} is one of the vibrational modes of the acen ligand that also appears in the spectrum of VO(acen)). The C=N stretching frequency shifts from 1586 cm^{-1} in VO-(acen) to 1576 cm^{-1} in $VCl_2(acen)$. The same effect has been observed in comparing VO(salen) to VCl_2(salen). A new peak is observed at 317 cm^{-1} in the spectrum of $VCl_2(acen)$ and is assigned as a V—Cl stretching frequency. This is based on the assignment for V—Cl in VCl_2(salen) that occurs at 301 cm^{-1}.[2,10] There is only one V—Cl stretch observed and this suggests trans Cl atoms and a planar coordination of the acen ligand. Jezierski and co-workers[8] also proposed this *trans*-dihalide structure for $VCl_2(acen)$ on the basis of EPR data.

For the atomic formula of the green hydrolysis product from $VCl_2(acen)$, $C_{12}H_{20}C_{12}N_2O_3V$, five possible molecular formulas can be written: [VO(H2acen)Cl]Cl (I), [VO(H2acen)]Cl2 (II), VOCl2(H2acen) (III), VO(acen)·2HCl (IV), VCl2(acen)·H2O (V). On the basis of the IR spectrum of the green compound, formula I is most probable. The proposed bonding in this molecule is shown in Figure 1. The spectrum shows a strong stretching band at 990 cm^{-1} due to V=O. The peak at 317 cm^{-1} is the V—Cl stretching frequency, as also observed for $VCl_2(acen)$. The two broad bands at 3338 and 3135 cm^{-1} could correspond to either –NH or –OH groups. Protonated nitrogen atoms would exist if the H2acen ligand was present in the keto form, as shown for some compounds with Schiff base ligands of salicylaldehyde and alkylamines.[13,14] The H2acen ligand, specifically, has been shown to coordinate this way in some cases with other metals,[15,16] exhibiting two broad bands between 3450 and 3100 cm^{-1}. On the other hand, if the H2acen ligand behaved as a bidentate ligand in the enol form (see formula III), then the two –OH groups would account for the observed bands at 3338 and 3135 cm^{-1}. In our judgment the observed frequencies match more closely those expected for N–H stretches. Furthermore, the hydrolysis product

also exhibits a strong absorption at 1608 cm^{-1}. This frequency has been assigned to the C=O stretch of the keto form of H2acen in previous work.[15-19] This further supports our belief that formula I is correct.

Figure 1 also suggests that only one chloride atom is covalently bound, while the other forms an ionic bond. This is substantiated by a semiquantitative Fajan titration of the compound with $AgNO_3$. Before the first equivalence point, AgCl is readily precipitated. Near the first equivalence point, the pink color of the reaction indicator is observed where the titrant drops into the solution, but the end point is vague. At 1-2 mL beyond the first equivalence point, the solution suddenly turns gray, indicating that excess silver ion has been reduced. There is no further change when the titration proceeds to the second equivalence point. The solubility of the compound in water, methanol, and Me_2SO also demonstrates its ionic character.

In formula II, [VO(H2acen)]Cl2, H2acen is protonated and acts as a neutral, tetradentate ligand in the keto form, as in formula I. This formula is consistent with most of the data, but fails to account for the observed V–Cl stretching band and the $AgNO_3$ titration data.

Formula III, VOCl2(H2acen), fails to account for several of the data. First, this configuration implies that the ligand is bidentate, in the enol form, binding only through the two nitrogen atoms. This does not agree with the observation of the C=O stretch. Also, two covalently bound chloride atoms are inconsistent with the ionic character of the compound.
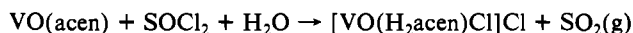
Formula IV, VO(acen)·2HCl, does not account for the V–Cl stretching band. Also, titration of a solution of the compound with NaOH gives a very gradual pH change at the equivalence point, indicating a weak acid. An HCl adduct, however, would give a more definitive break point.

Finally, formula V, VCl2(acen)·H2O, fails to account for the V=O and C=O stretches, as well as the reaction with $AgNO_3$.

In summary, the hydrolysis of $VCl_2(acen)$ results in the addition of one water molecule, the overall reaction being

$$VCl_2(acen) + H_2O \rightarrow [VO(H_2acen)Cl]Cl$$
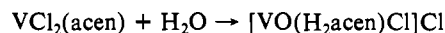
In the direct synthesis the reaction appears to be

$$VO(acen) + SOCl_2 + H_2O \rightarrow [VO(H_2acen)Cl]Cl + SO_2(g)$$

The bonding in this product (Figure 1) is consistent with all of the data. On the basis of the structure of other vanadium–acen compounds, the chloro group is probably trans to the terminal oxygen atom, while the tetradentate ligand is nearly planar.

The trans Cl atom probably affects the V=O stretching frequency slightly by reducing the electron density on the vanadium, thereby increasing its electron-acceptor properties toward oxygen.[20,21] This effect increases the V=O multiple-bond character and its stretching frequency. Although the H2acen ligand has been shown to form complexes with metals in its keto form, [VO(H2acen)Cl]Cl is the first vanadyl–(keto–amine) acen complex. A similar type of complexation has been observed for vanadyl complexes of two neutral bidentate ligands, [VO(bpy)2Cl]Cl and [VO(o-phen)2Cl]Cl.[20,22] Selbin and Holmes measured the equivalent conductances of these compounds in nitrobenzene and concluded that each was composed of two ions, that is, a complex cation and a chloride anion. We expect that the same is true for [VO(H2acen)Cl]Cl.

UV–Visible Spectroscopy. Spectra of $VCl_2(acen)$ were obtained in both CH_2Cl_2 and Me_2SO, with different species arising in the different solvents. $VCl_2(acen)$ in CH_2Cl_2, in the absence of air,

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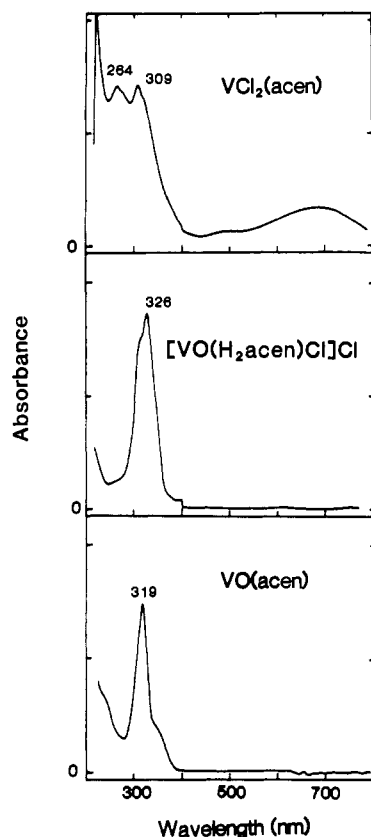(22) Selbin, J.; Holmes, L. H., Jr. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1111.

Figure 2. Absorption spectra in CH_2Cl_2 of $VCl_2(acen)$, [VO(H_2acen)-Cl]Cl, and VO(acen).

Figure 3. EPR spectra of frozen glasses (69 K, CH_2Cl_2/2% DMF) of (a) VO(acen) and (b) [VO(H_2acen)Cl]Cl.

stayed blue long enough to record its spectrum. It then gradually changed to a green solution of [VO(H_2acen)Cl]Cl. $VCl_2(acen)$ exhibits a broad and very intense ($\epsilon = 5 \times 10^4$) d–d transition at about 690 nm. The chlorine atoms are believed to account for the high molar absorptivity of this band, since the same effect was observed for $VCl_2(salen)$. [VO(H_2acen)Cl]Cl exhibits a similar band near 700 nm, but the intensity is less ($\epsilon = 2 \times 10^3$). Both compounds have smaller absorbance peaks at lower wavelength: $VCl_2(acen)$, 500 nm, $\epsilon = 2 \times 10^4$; [VO(H_2acen)Cl]Cl, 450 nm, shoulder. Absorptions in the ultraviolet region are most distinct. For comparison, the UV spectra of $VCl_2(acen)$, [VO-(H_2acen)Cl]Cl, and VO(acen) in CH_2Cl_2 are shown in Figure 2. $VCl_2(acen)$ shows high-intensity absorptions at 264 and 309 nm and a shoulder at 326 nm. The hydrolysis product exhibits an absorption peak at 326 nm and a shoulder at 309 nm. An absorption at 264 nm is not observed. The spectrum of H_2acen (not shown) shows the same absorption bands in the ultraviolet region as those of the hydrolysis product. This further suggests that the same form of H_2acen exists in [VO(H_2acen)Cl]Cl as in the free H_2acen molecule, i.e. the keto form.[16] VO(acen) has a peak at 319 nm, which is different from that of either of the other compounds.

$VCl_2(acen)$ in Me_2SO immediately decomposed, also to a green solution, but this was identified as VO(acen) by UV–visible spectroscopy and electrochemistry.

EPR Spectroscopy. EPR spectroscopy was used to differentiate among VO(acen), $VCl_2(acen)$, and [VO(H_2acen)Cl]Cl. The EPR spectrum of VO(acen) in CH_2Cl_2 at room temperature shows a typical eight-line splitting pattern, as expected for ^{51}V ($I = 7/2$; $n = 2I + 1$). The isotropic hyperfine coupling constant is about 100 G, as has been reported for numerous other vanadyl complexes.[23] The spectrum of [VO(H_2acen)Cl]Cl was recorded in CH_2Cl_2/2% DMF (due to low solubility in CH_2Cl_2) and showed a similar eight-line pattern, but with a coupling constant of 55

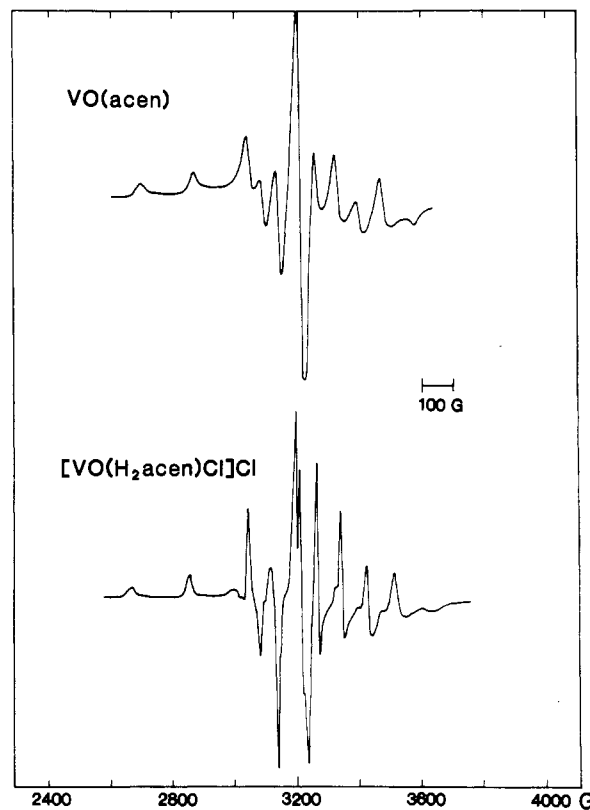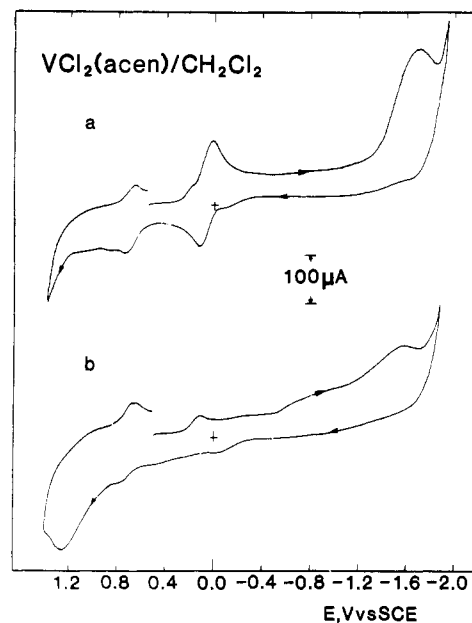**Figure 4.** Cyclic voltammograms in 0.1 M TEAP/CH_2Cl_2 solution of (a) 1.03 mM $VCl_2(acen)$ and (b) solution a after 40 min (scan rate 200 mV/s).

G. This is considerably lower than the usual room-temperature value for VO^{2+} species. Also, Jezierski and Raynor[8,9] recorded the spectrum of $VCl_2(acen)$ at −40 °C and found the coupling constant to be 75 G. Thus, A_{iso} for [VO(H_2acen)Cl]Cl in solution is significantly lower than those for both VO(acen) and VCl_2-(acen).

The spectra of VO(acen) and [VO(H_2acen)Cl]Cl were also recorded as frozen glasses (69 K, CH_2Cl_2/2% DMF) and are shown in Figure 3. The splitting patterns observed under these conditions are similar but not identical. Jezierski and Raynor[8] reported the frozen-glass spectrum of $VCl_2(acen)$ (made in situ;

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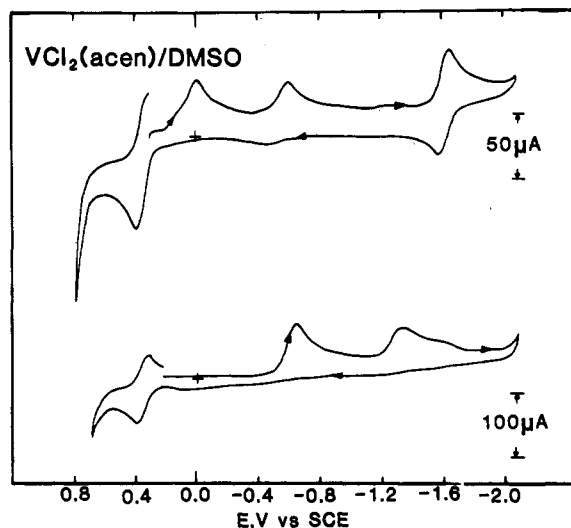
Figure 5. Cyclic voltammograms in 0.1 M TEAP/Me₂SO solution of (a) 1.58 mM VCl₂(acen) and (b) solution a after 30 min (scan rate 200 mV/s).

toluene:CH₂Cl₂:SOCl₂ = 3:7:10). This spectrum is also similar to, but not identical with, the other two. Thus, although no definitive conclusions can be drawn, it appears that the spectrum of [VO(H₂acen)Cl]Cl is consistent with the existence of both V=O and V—Cl groups.

Electrochemistry. The conversion of VCl₂(acen) to [VO-(H₂acen)Cl]Cl in CH₂Cl₂ has been monitored by cyclic voltammetry. Figure 4a shows a cyclic voltammogram of VCl₂(acen) immediately after being dissolved in CH₂Cl₂. The reversible couple at 0.07 V and the reduction at −1.7 V vs. SCE probably correspond to VCl₂(acen) due to their disappearance upon decomposition (Figure 4b). The couple at 0.7 V, which appears on an initial positive scan, corresponds to VO(acen).[12] This is certainly not a major decomposition product due to its small current value. The redox processes of VCl₂(acen) have not been studied in detail, but rather the decomposition products of VCl₂(acen) in various solvents have been investigated. Figure 4b is a cyclic voltammogram of a VCl₂(acen)/CH₂Cl₂ solution taken 40 min after the voltammogram of Figure 4a. There was also a color change from blue

to green. The voltammogram of Figure 4b no longer contains the couple at 0.07 V or the reduction peak at −1.7 V. The reduction peak at −1.6 V is new. A new, broad oxidation peak at 1.4 V probably is due to the oxidation of the H₂acen ligand, since the free ligand in CH₂Cl₂ was observed to exhibit a similar oxidation peak at 1.3 V. Since [VO(H₂acen)Cl]Cl was isolated from a solution of VCl₂(acen) in CH₂Cl₂, we conclude that Figure 4b is due primarily to this species. Also, the UV–visible spectrum of this solution matches that for the isolated product.

As indicated earlier, VCl₂(acen) in Me₂SO decomposes to VO(acen). But electrochemical studies show that the conversion of VCl₂(acen) is not complete; [VO(H₂acen)Cl]Cl is a minor decomposition product. Figure 5 shows cyclic voltammograms of an initial blue solution of VCl₂(acen) in Me₂SO (Figure 5a) and the solution after aging (Figure 5b), which is blue-green. The reduction peak at 0.0 V and the couple at −1.8 V are assumed to correspond to VCl₂(acen). They are both absent from the later voltammogram. The couple at 0.34 V is assigned to the reversible oxidation–reduction [V(IV)–V(V)] process of VO(acen).[12] This verifies that VO(acen) is the major decomposition product in Me₂SO. The green compound [VO(H₂acen)Cl]Cl is believed to be a minor product on the basis of the appearance of the reduction peak at −1.34 V in Figure 5b, which was also observed in the cyclic voltammogram of [VO(H₂acen)Cl]Cl in Me₂SO (not shown). This peak appeared at −1.6 V in CH₂Cl₂. The ligand oxidation peak (1.4 V in CH₂Cl₂) is too far positive to be observed in Me₂SO.

Conclusion

The synthesis of VCl₂(acen) is analogous to that for VCl₂(salen) but requires milder conditions. As a solid, VCl₂(acen) is less stable than VCl₂(salen). In solution, both decompose more rapidly than in solid form. The decomposition of VCl₂(acen) in CH₂Cl₂ apparently involves residual water and results in the formation of [VO(H₂acen)Cl]Cl, which is a green complex. [VO(H₂acen)Cl]Cl is the first example of a (keto–acen)–vanadium(IV) complex, and its structure has been proposed (Figure 1). The decomposition product of VCl₂(acen) in Me₂SO is a mixture of VO(acen) and [VO(H₂acen)Cl]Cl. This is in contrast to the decomposition of VCl₂(salen), which simply yields VO(salen).