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DEOXYGENATION OF OXOVANADIUM(IV) COMPLEXES UNDER MILD CONDITIONS: SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF *CIS*-DIHALOBIS(DIALKYLDITHIOCARBAMATO)VANADIUM(IV)

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Abstract—A new procedure for the deoxygenation of VO^{+2} complexes is described. The synthesis and properties of mononuclear vanadium complexes $VCl_2(S_2CNR_2)_2$ [R = Me, Et, and Py/2 (Me = CH_3, Et = C_2H_5, and Py = C_4H_4) (pyrrolidyl)] and $VBr_2(S_2CNEt_2)_2$ are reported. The compounds were synthesized in high yield by the general reaction of $VO(S_2CNR_2)_2$ with the appropriate acetyl halide in methylene chloride. Single crystal X-ray analysis was performed on both $VCl_2(S_2CN(C_2H_5)_2)_2$ and $VBr_2(S_2CN(C_2H_5)_2)_2$. The analogous structures consist of a mononuclear unit with distorted C_{2v} symmetry, where the halogen atoms are on the same side of the distorted plane formed by the sulphur atoms. The V—Cl distances are inequivalent at 2.260(1) and 2.247(1) Å, as are the V—Br distances at 2.414(1) and 2.401(1) Å. Two sets of V—S bond lengths are also observed for both complexes. The complexes were examined by IR, and the spectra are similar to the spectra of the vanadyl starting material except for the absence of the V═O band at approximately 1000 cm^{-1}. The ligand C—S and C—N bands are slightly higher in energy in the dihalide complexes than in the vanadyl counterpart, contrary to the effects expected from replacing the oxygen with the electron withdrawing halogen atoms. This behaviour, however is indicative of distortions out of the $d_{x^2-y^2}$ orbital bonding plane causing less π bonding and reducing delocalization of charge among the ligands and the metal centre. This is also seen structurally with the two sets of inequivalent V—S and C—S bond lengths. The UV–vis spectra show a weak maximum at around 570 nm with ε_m of approximately 2000 L mol cm^{-1}, typical of dihalogenated V^{IV} complexes.

It is becoming increasingly apparent that the chemistry of vanadium is of great importance to a wide variety of biological and industrial systems. Recent work in the field of inorganic biochemistry indicates there is a class of nitrogenase metallo-enzymes which have vanadium at the active site.[1,2] In these enzymes, vanadium appears to shuttle between V^{II} and V^{IV}, and is possibly bound to an iron–sulphur cluster. However, few models have been made of this active site. One synthetic difficulty is the problem of directly linking iron–sulphur clusters and V^{IV} compounds. This requires functionality on the vanadium atom which can be synthetically manipulated. Thus, having new V^{IV} compounds with functionality is highly desirable.

Vanadium is commercially important in the conversion of crude oils to transportation fuels.[3] Vanadium occurs naturally and can be of high con-

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centration in heavier crude oils.[4] It impacts the industry because its necessary removal during upgrading[5] poisons heterogenous catalysts used in processing.[6] The intermediate species in this transformation of the naturally occurring VO^{2+} complexes to the vanadium sulphide on the upgrading catalyst surface are not well characterized. Some evidence suggests VO^{2+} is deoxygenated to V^{IV}.[7-10] Characterizing this transformation is critical to the understanding of catalytic poisoning due to metals.

Vanadium compounds have also been used to generate slurry-type catalysts to upgrade heavy oils and assist in coal liquefaction. These catalysts increase the conversion of petroleum and coal to lower boiling materials,[11] and desulphurize the resulting liquids.[12,13] The exact species responsible could be finely dispersed vanadium sulphides. These are often formed by *in situ* preparation from vanadyl model compounds such as $VO(acac)_2$.[14] The transformation chemistry and the active VS_x species have not been well characterized. Clearly, activation of the V=O bond is a critical part of this mechanism.

The strong V=O bond is extremely stable and generally dominates the coordination chemistry of vanadium.[15] The reactivity of this bond has not been widely studied because access to other types of vanadium compounds has been through easier synthetic routes which do not employ vanadyl reagents. This is unfortunate because many vanadyl compounds are easy to prepare as starting materials (many can be purchased commercially).

Of the limited V^{IV} non-oxo species reported in the literature, many are dihalide complexes. These have been characterized by spectroscopic methods which indicate six coordinate V and both *trans* and *cis* configurations to be possible. However, only one of these complexes, $VCl_2(salen\text{-}N\text{-}Bu^t)_2$ [salen-N-Bu^t = N-n-butyl(salicylideniminato)] has been characterized by single crystal X-ray analysis.[16] The structure shows an octahedral V centre with *trans* chlorine atoms. We have also recently synthesized and characterized by single crystal X-ray analysis, $VCl_2(acac)_2$ (acac = acetylacetonato),[17] which has a very similar *trans* structure to $VCl_2(salen\text{-}N\text{-}Bu^t)_2$.

Many methods have been employed to make these types of compounds: (1) by direct halogenation of the corresponding vanadyl complex;[16,19-23] (2) by reactions of VCl_4 and the appropriate free ligand;[18] and (3) by reaction of thiuram disulphides with V^{II} compounds.[24] Although these methods are all adequate, there are some drawbacks. Many of the reagents are difficult to handle, some react with the ligand as well as the vanadium, and some require involved ligand synthesis.

In this report, we describe a useful new method for the mild deoxygenation of VO^{2+} complexes. We present the synthesis and characterization of $VCl_2(S_2CNEt_2)_2$, $VCl_2(S_2CNMe_2)_2$, $VCl_2(S_2CNPy)_2$ and $VBr_2(S_2CNEt_2)_2$ from the reaction of the corresponding vanadyl dithiocarbamates with acetyl halides. In addition, we present the structural characterization by single crystal X-ray analysis of $VCl_2(S_2CNEt_2)_2$ and $VBr_2(S_2CNEt_2)_2$. The described procedure is a new, more facile and direct synthetic method which gives clean products. The crystal structures are the first reported for vanadium dihalodithiocarbamates, and the structures are surprising in as much as the halogen atoms are unexpectedly *cis*.

EXPERIMENTAL

All syntheses were carried out in a dry/inert atmosphere of purified dinitrogen employing standard Schlenk glassware. Air-sensitive samples for spectroscopic study were prepared in a dinitrogen glovebag or Vacuum Atmospheres glove box. IR spectra were recorded as KBr pellets with the Mattson Polaris Model 10410 spectrophotometer. Electronic spectra were recorded on CH_2Cl_2 solutions using a Varian Model 503 spectrophotometer and Spectrochem quartz anaerobic cells. Because the dihalide complexes readily convert back to the corresponding vanadyl complex upon exposure to even trace quantities of water, excess AcCl or AcBr were added to the solutions. Elemental analyses were perfomed by the Lawrence Livermore National Laboratory analytical department and Galbraith Laboratories, Inc., Knoxville, TN.

Reagents

Spectroanalytical grade methylene chloride (0.006% water) and hexanes were obtained from Burdick and Jackson Laboratories, and were dried over CaH_2 and $LiAlH_4$, respectively, under a dinotrogen atmosphere and degassed before use. Ethanol was obtained from Gold Shield Chemical company. Dimethyldithiocarbamic acid, sodium salt dihydrate; diethyldithiocarbamic acid, sodium salt trihydrate; acetyl chloride; and acetyl bromide were purchased from Aldrich. The pyrrolidinedithiocarbamate derivative was purchased from Matheson Coleman and Bell Manufacturing Chemists. The acetyl bromide was distilled before use and the acetyl chloride used as purchased.

Synthesis of complexes

The vanadyl complexes $VO(S_2CNMe_2)_2$, $VO(S_2CNEt_2)_2$ and $VO(S_2CNPy)_2$ were prepared by the method of McCormick[25] and recrystallized from methylene chloride.

Dichlorobis(dimethyldithiocarbamato)vanadium(IV) [$VCl_2(S_2CNMe_2)_2$] (**1**). $VO(S_2CNMe_2)_2$ (0.971 g, 0.00358 mol) was dissolved in methylene chloride (125 cm^3) to give a green–brown solution. This was degassed, and acetyl chloride (0.762 cm^3, 0.0107 mol) was added with stirring. The $VO(S_2CNMe_2)_2$ solution slowly turned black. The reaction solution was stirred at room temperature overnight, and then layered with hexanes (125 cm^3) and placed in a freezer. Storage at -10°C for 3 days led to the formation of black crystals. The crystals were filtered and dried *in vacuo*. The yield of crude product was 45% based on vanadium. Recrystallization from a CH_2Cl_2/hexanes mixture (layered) led to pure material as determined by IR, UV–vis and elemental analysis. Found: C, 19.3; H, 4.2; N, 7.4. Calc. for $C_6H_{12}N_2S_4Cl_2V$: C, 19.9; H, 3.3; N, 7.7%. Electronic absorption maxima = λ, nm (ε_m, L mol cm^{-1}); 578.1(1814), 485.9(1575), 379.9^{sh}(6060).

Dichlorobis(diethyldithiocarbamato)vanadium(IV) [$VCl_2(S_2CNEt_2)_2$] (**2**). This black complex was prepared and purified from $VO(S_2CNEt_2)_2$ (2.06 g, 0.00567 mol) and acetyl chloride (1.21 cm^3, 0.0170 mol) by a similar procedure as above. The yield of the crude product was 56% based on vanadium. Found: C, 28.7; H, 5.6; N, 6.9. Calc. for $C_{10}H_{20}N_2S_4Cl_2V$: C, 28.7; H, 4.8; N, 6.7%. Electronic absorption maxima = λ, nm (ε_m, L mol cm^{-1}); 570.1(1258), 455.2(1459).

Dibromobis(diethyldithiocarbamato)vanadium(IV) [$VBr_2(S_2CNEt_2)_2$] (**3**). This black complex was prepared and purified from $VO(S_2CNEt_2)_2$ (0.502 g, 0.00138 mol) and acetyl bromide (0.295 cm^3, 0.00415 mol) by similar procedures as above. The yield of the crude product was 58% based on vanadium. Found: C, 23.0; H, 4.1; N, 5.2. Calc. for $C_{10}H_{20}N_2S_4Br_2V$: C, 23.7; H, 4.0; N, 5.5%. Electronic absorption maxima = λ, nm (ε_m, L mol cm^{-1}); 571.4(2023), 484.6(2064), 357.6^{sh}(4314).

Dichlorobis(pyrrolidyldithiocarbamato)vanadium(IV) [$VCl_2(S_2CNPy)_2$] (**4**). This black complex was prepared and purified from $VO(S_2CNPy)_2$ (1.16 g, 0.00324 mol) and acetyl chloride (0.690 cm^3, 0.00971 mol) by similar procedures as above. The yield of the crude product was 46% based on vanadium. Found: C, 26.5; H, 3.5; N, 5.6. Calc. for $C_{10}H_8N_2S_4Cl_2V(CH_2Cl_2)$: C, 26.9; H, 2.0; N, 5.7%. Electronic absorption maxima = λ, nm (ε_m, L mol cm^{-1}); 578.1(1106), 489.9(959), 417.0^{slsh} (1288).

X-ray crystallography and structure solution

Data were collected on a Picker four-circle diffractometer by using standard low-temperature facilities. Details of the diffractometry, low-temperature facilities, and computational procedures

Table 1. Crystallographic data for *cis*-$VCl_2(S_2CNEt_2)_2$ and *cis*-$VBr_2(S_2CNEt_2)_2$

Property	*cis*-$VCl_2(S_2CNEt_2)_2$	*cis*-$VBr_2(S_2CNEt_2)_2$
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.136(2)	9.233(1)
b (Å)	14.620(4)	14.829(2)
c (Å)	7.186(2)	7.222(1)
α (°)	98.57(1)	98.72(1)
β (°)	110.49(1)	110.12(1)
γ (°)	95.82(2)	95.90(1)
Z	2	2
V (Å^3)	876.77	904.78
Formula	$VC_{10}H_{20}N_2S_4Cl_2$	$VC_{10}H_{20}N_2S_4Br_2$
M_r (g mol^{-1})	418.37	507.27
ρ_{calc} (g cm^{-3})	1.585	1.865
μ (l cm^{-1})	13.028	53.492
T (°C)	-131	-172
λ (Å)	0.71069	0.71069
Range	$6° \leqslant 2\theta \leqslant 55°$	$6° \leqslant 2\theta \leqslant 45°$
Observed data	3424	2161
$R(R_w)$ (%)	3.56(3.70)	4.23(4.31)
Crystal dimensions	0.25 × 0.25 × 0.25 mm	0.28 × 0.32 × 0.30 mm
Colour of crystal	Black–green	Black

employed by the Molecular Structure Center are available elsewhere.[26] Data collection parameters are summarized in Table 1 for $VCl_2(S_2CNEt_2)_2$ and $VBr_2(S_2CNEt_2)_2$. The structures were solved by a combination of MULTAN and Fourier techniques, and refined by full-matrix least-squares.

For both complexes, **2** and **3**, a systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences indicating a triclinic space group. Subsequent solution and refinement of the structure confirmed the centrosymmetric choice $P\bar{1}$. For **2**, a total of 4825 reflections were collected. Following the usual data processing 4033 unique reflections remained. Of the 4033 reflections, 3424 were considered observed $[F > 2.33\sigma(F)]$. For **3**, a total of 2390 reflections were collected. Following the usual data processing 2366 unique reflections remained. Of the 2366 reflections, 2161 were considered observed $[F > 3\sigma(F)]$. All non-hydrogen atoms were readily located and refined anisotropically for both complexes. All hydrogen atoms were clearly visible in subsequent difference Fourier maps, and were included in the final refinement cycles with isotropic thermal parameters. The final difference maps were essentially featureless, with the largest peak being 0.45 e Å^{-3} near the vanadium atom for complex **2** and 1.02 e Å^{-3} in the immediate vicinity of a bromine atom for complex **3**.

RESULTS AND DISCUSSION

Synthesis

Vanadyl complexes can be deoxygenated by a variety of reagents ($SOCl_2$, $SOBr_2$, PCl_5, $SeOCl_2$, and $COCl_2$)[19,21,23,27] to yield the corresponding dihalide derivative. These reagents, however, are caustic and often react with the ligands. In addition, some dihalide complexes can be made by the direct reaction of VCl_4 (which is difficult to handle) with the ligand,[18] and by less direct methods including going through thiuram disulphide intermediates.[24] We have now discovered acetyl halides can also be used to synthesize V^{IV} dihalide complexes. The cheap and relatively easy to handle AcX reagents (X = Cl, Br) directly afford the dihalide complexes, overcoming the potential side reactions of the other reagents. As a result, we have successfully synthesized, directly from the corresponding vanadyl complexes, $VCl_2(S_2CNMe_2)_2$ (**1**), $VCl_2(S_2CNEt_2)_2$ (**2**), $VBr_2(S_2CNEt_2)_2$ (**3**), and $VCl_2(S_2CNPy)_2$ (**4**) by eq. (1). Previous attempts in the literature to synthesize such compounds using the other halogenating agents mentioned above often led to poorly characterized, impure products, probably due to the halogenating agent reacting with the ligand. The present procedure yields very clean products, and this has also made single crystal growth easy. As a result, single crystal X-ray analyses on **2** and **3** have been performed.

$$VO(S_2CNR_2)_2 + 2AcX \longrightarrow VX_2(S_2CNR_2)_2 + Ac_2O \quad (1)$$

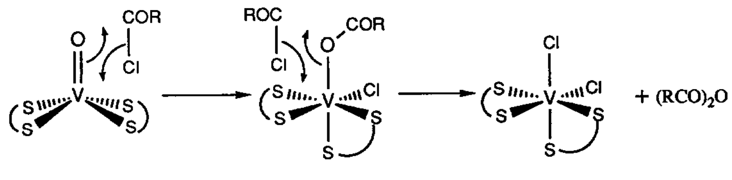
$$(X = Cl, Br;\ R = Me, Et, Py/2).$$

An excess (50%) of AcX was routinely employed after observing incomplete conversion with stoichiometric amounts of reagents (probably due to hydrolysis by adventitious water). Isolation of **4** was difficult because crystals turned to powder upon vacuum drying due to loss of solvent. This was overcome by drying under N_2 purge. However, even under these conditions, the crystals would gradually turn to a powder, making analysis difficult. The inclusion of solvent was verified by elemental analyses which indicated one CH_2Cl_2 in the molecular formula.

Although we have not experimentally studied the mechanism of the reaction, it probably involves electrophilic attack at the VO^{2+}. Reaction Scheme 1 shows a possible pathway.

Description of structures

Figure 1 shows the structure of **2** with the atom numbering scheme. Selected structural parameters are collected in Table 2. The crystal is composed of discrete molecules of $VCl_2(S_2CNEt_2)_2$ with the expected six coodination at vanadium. The geometry around the metal can be described as highly distorted octahedral, with the chlorine atoms



Scheme 1.

Table 2. Selected bond distances (Å) and angles (°) for *cis*-$VCl_2(S_2CNEt_2)_2$

V(1)—Cl(2)	2.2595(10)	N(7)—C(5)	1.309(3)
V(1)—Cl(3)	2.2467(10)	N(7)—C(8)	1.474(3)
V(1)—S(4)	2.4517(11)	N(7)—C(10)	1.481(3)
V(1)—S(6)	2.3777(11)	N(15)—C(13)	1.319(4)
V(1)—S(12)	2.4506(10)	N(15)—C(16)	1.473(4)
V(1)—S(14)	2.3860(11)	N(15)—C(18)	1.477(4)
S(4)—C(5)	1.7126(28)	C(10)—C(11)	1.515(4)
S(6)—C(5)	1.7338(28)	C(16)—C(17)	1.515(5)
S(12)—C(13)	1.709(3)	C(18)—C(19)	1.506(5)
S(14)—C(13)	1.7328(28)		
Cl(2)—V(1)—Cl(3)	98.26(4)	S(4)—V(1)—S(12)	86.11(3)
Cl(2)—V(1)—S(4)	155.63(3)	S(4)—V(1)—S(14)	88.75(4)
Cl(2)—V(1)—S(6)	83.77(4)	S(6)—V(1)—S(12)	86.14(4)
Cl(2)—V(1)—S(12)	92.30(4)	S(6)—V(1)—S(14)	151.63(3)
Cl(2)—V(1)—S(14)	113.86(4)	S(12)—V(1)—S(14)	71.71(4)
Cl(3)—V(1)—S(4)	93.01(4)	V(1)—S(4)—C(5)	87.63(10)
Cl(3)—V(1)—S(6)	116.99(4)	V(1)—S(6)—C(5)	89.56(9)
Cl(3)—V(1)—S(12)	155.37(3)	V(1)—S(12)—C(13)	87.92(10)
Cl(3)—V(1)—S(14)	83.66(4)	V(1)—S(14)—C(13)	89.48(10)
S(4)—V(1)—S(6)	71.86(3)		

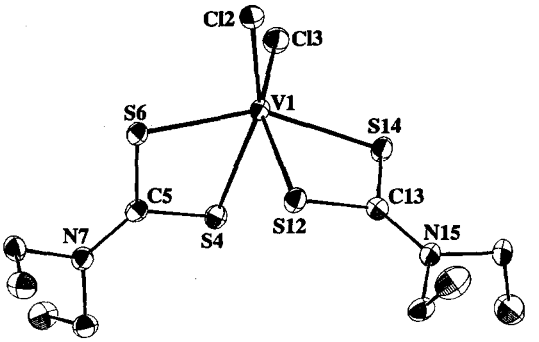


Fig. 1. ORTEP representation of *cis*-$VCl_2(S_2CNEt_2)_2$ showing the atom labelling scheme.

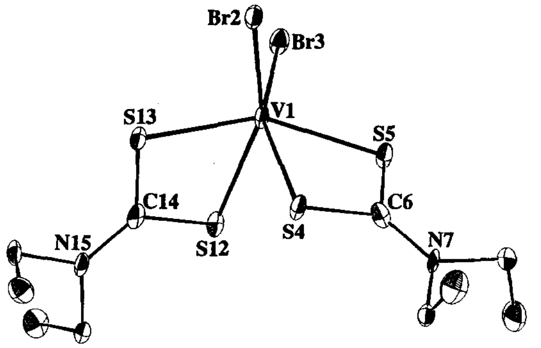


Fig. 2. ORTEP representation of *cis*-$VBr_2(S_2CNEt_2)_2$ showing the atom labelling scheme.

cis to each other on the same side of the distorted plane formed by the four sulphurs of the dithiocarbamate ligands. This is contrary to the structure of $VCl_2(\text{salen-N-Bu}^t)_2$, the only reported[19] single crystal determination of a V^{IV} dihalide, which has octahedral coordination with *trans* chlorine atoms. In addition, our crystallographic determination of the structure of $VCl_2(acac)_2$ shows that the latter also exhibits a *trans* geometry.[17] Figure 2 shows the structure of 3 with the atom numbering scheme. Table 3 lists selected structural parameters. The structure is very similar to $VCl_2(S_2CNEt_2)_2$, being composed of discrete molecules of $VBr_2(S_2CNEt_2)_2$, with distorted octahedral coordination at the vanadium. As in the dichloro complex, the bromine atoms are *cis* to each other and on the same side of the plane formed by the four sulphurs of the dithiocarbamate ligands. The structures of **2** and **3** are the first reported single crystal determinations of a V^{IV} *cis* dihalide complex. This geometry was not expected and is contrary to that predicted by several EPR and IR studies.[21,24]

Table 2 shows that the V—Cl bond lengths of **2** are slightly inequivalent. Table 4 compares these bond lengths with other V—Cl bond lengths in the literature. The V—Cl lengths of **2** are slightly shorter than those for two other V^{IV} dichloro complexes. This is probably due to the differences between the *cis* and *trans* structures. The sulphur atoms of the ligands in the *cis* structure are considerably out of the equatorial bonding plane of the metal. As a result, the σ-bonding d_{xy} and π-bonding $d_{x^2-y^2}$ orbital interactions between the vanadium and the dithiocarbamate ligands in the equatorial

Table 3. Selected bond distances (Å) and angles (°) for *cis*-$VBr_2(S_2CNEt_2)_2$

V(1)—Br(2)	2.4137(14)	N(7)—C(6)	1.312(9)
V(1)—Br(3)	2.4007(14)	N(7)—C(8)	1.466(9)
V(1)—S(4)	2.4528(21)	N(7)—C(10)	1.494(9)
V(1)—S(5)	2.3818(21)	N(15)—C(14)	1.316(9)
V(1)—S(12)	2.4586(22)	N(15)—C(16)	1.488(9)
V(1)—S(13)	2.3786(21)	N(15)—C(18)	1.466(9)
S(4)—C(6)	1.713(7)	C(8)—C(9)	1.497(12)
S(5)—C(6)	1.733(7)	C(10)—C(11)	1.504(12)
S(12)—C(14)	1.721(7)	C(16)—C(17)	1.523(11)
S(13)—C(14)	1.725(7)	C(18)—C(19)	1.531(10)
Br(2)—V(1)—Br(3)	97.97(5)	S(4)—V(1)—S(12)	86.74(7)
Br(2)—V(1)—S(4)	92.00(6)	S(4)—V(1)—S(13)	87.10(7)
Br(2)—V(1)—S(5)	113.34(7)	S(5)—V(1)—S(12)	90.09(7)
Br(2)—V(1)—S(12)	154.90(7)	S(5)—V(1)—S(13)	153.20(8)
Br(2)—V(1)—S(13)	83.04(6)	S(12)—V(1)—S(13)	71.86(7)
Br(3)—V(1)—S(4)	155.13(7)	V(1)—S(4)—C(6)	87.65(25)
Br(3)—V(1)—S(5)	83.26(6)	V(1)—S(5)—C(6)	89.54(25)
Br(3)—V(1)—S(12)	93.46(6)	V(1)—S(12)—C(14)	87.13(24)
Br(3)—V(1)—S(13)	116.61(6)	V(1)—S(13)—C(14)	89.65(23)
S(4)—V(1)—S(5)	71.88(7)		

Table 4. Vanadium–chloride bond lengths of selected vanadyl and V^{IV} complexes

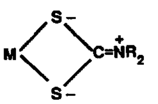
Complex	V—Cl (Å)	Vanadium coordination
$VCl_2(S_2CNEt_2)_2$	2.25–2.26	6
$VCl_2(acac)_2$[17]	2.31–2.33	6
$VCl_2(salen\text{-}N\text{-}Bu^t)_2$[16]	2.35	6
$VOCl_2(NMe_3)_2$[41]	2.25	5
$VOCl_2(C_5H_{12}N_2O)_2$[42]	2.34	5
$VOCl_2(C_2H_5O)_2(H_2O)$[43]	2.39	5

plane are not as extensive as in *trans* structures. Consequently, there is less delocalization of charge onto the ligands, resulting in a stronger V—Cl bond. This change in bonding interaction has been substantiated in EPR[21] and far IR[18] examination of *cis* and *trans* dihalide V^{IV} complexes.

The effect of the ligand type on the length of the V—Cl bond cannot be ruled out, however. V=O bond lengths in the corresponding vanadyl complexes are subject to variations due to both the first coordination sphere[28–30] and substituents on the ligands.[31]

For complex **2**, the four V—S bonds are divided into two short (average 2.382 Å) and two long (average 2.451 Å). This is reflected in the corresponding C—S bond lengths, where the two sulphur atoms with the longer V—S bond lengths have the shorter C—S bond lengths (average 1.711 Å), and the two sulphur atoms with the shorter V—S bond lengths have the longer C—S bond lengths (average 1.733 Å). This can be reasoned by considering the structural deviation from the equatorial plane of the molecule. Starting with the *trans* structure, the two dithiocarbamate ligands in a planar configuration distort to the *cis* structure by bending below this plane and also twisting in opposite directions around the C—N axis of each ligand. This removes one sulphur of each ligand from the plane of the π-bonding orbitals more than the other, therefore yielding two sets of V—S bond lengths, as well as two sets of S—V—S bond angles. Indeed, Fig. 1 shows S(6) and S(14) closer to the perpendicular to the plane formed by Cl(2), V, and Cl(3), and shows the planes formed by the S_2CNC_2 atoms in each of the ligands are also twisted with respect to each other. This behaviour is also seen in **3** (Fig. 2), where the longer V—S bond lengths average to 2.4587 Å and the shorter to 2.3804 Å. The corresponding C—S bond lengths average to 1.717 and 1.729 Å, respectively.

Several investigators have shown canonical form I to be particularly important and predominant in binding many dialkyldithiocarbamates to metals.[24,32,33] The C—N stretching frequencies in the IR support this (see below). However, canonical forms II and III cannot be ignored, particularly in light of the two sets of V—S and C—S bond lengths. When the ligands distort out of the equatorial plane, canonical form I is likely to be less important, and either II or III contribute proportionately more to the bonding. If the contribution of II or III is large enough, this would be reflected in each ligand having one long and short C—S bond, as observed in the structures.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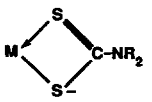
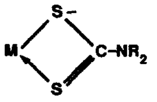

II


III

The single crystal X-ray structure of the vanadyl starting material, $VO(S_2CNEt_2)_2$ is available.[29] Since only the oxygen has been substituted, this allows an interesting comparison of the effects of the chlorine and bromine atom substitution on the $[V(S_2CNEt_2)_2]^{2+}$ subunit structure. The V—S distances reflect more distortion from the equatorial plane in the dihalide complexes than in the vanadyl complex (2.387–2.410 Å). In the vanadyl complex, only one of the four V—S bonds is short, which is considered to be due to crystal packing forces. However, the *average* V—S bond distance for the dichloro complex (2.41 Å), and vanadyl complex (2.40 Å) are similar. These values are slightly shorter than values seen for other vanadium complexes with the $V(S_2C)$ moiety. In these cases, inequivalences in the V—S bond lengths were also seen. $V(S_2CCH_3)_4$,[34] $V(S_2CC_6H_5)_4$,[35] $V(S_2CCH_2C_6H_5)_4$,[35] and $VO(S_2CNEt_2)_3$[36] exhibited the following $V—S_{long}$ distances (Å), $V—S_{short}$ distances (Å), V—S bond ratio (long to short): 2.50, 2.46, 1.02; 2.56, 2.45, 1.05; 2.53, 2.46, 1.03; 2.75, 2.55, 1.08; respectively. These compare to $VO(S_2CNEt_2)_2$, $VCl_2(S_2CNEt_2)_2$ and $VBr_2(S_2CN(Et_2)_2$ with C—S bond ratios of 1.00, 1.03 and 1.03, respectively. The π bonding in $V(S_2CC_6H_5)_4$ and $V(S_2CCH_2C_6H_5)_4$ was also considered weak. Although it is unlikely crystal packing forces would be completely responsible for the V—S bond behaviour described above, it certainly cannot be ruled out and probably accounts for at least some of the distortions in the structures cited.

$VO(S_2CNEt_2)_2$ also exhibits two sets of C—S bond lengths (1.715, 1.727; 1.721, 1.732 Å). Even though the average C—S bond lengths are approximately the same for all three complexes (1.722 Å ± 0.001 Å), the inequivalences seen in the dihalide complexes are greater than the vanadyl complex. This suggests that the canonical form II or III can have significance even when there is less equatorial distortion, as in the vanadyl complex (the vanadium is 0.7 Å above the basal plane formed by the four sulphur atoms of the dithiocarbamate ligands).

IR spectra

Table 5. IR data for selected vanadyl and V^{IV} dithiocarbamate complexes (cm^{-1})

Complex	ν(C—N)	ν(C—S)	ν(V═O)
$VO(S_2CNEt_2)_2$	1514	955	988
$VCl_2(S_2CNEt_2)_2$	1521	994	
$VBr_2(S_2CNEt_2)_2$	1520	996	
$VO(S_2CNMe_2)_2$	1539	970	983
$VCl_2(S_2CNMe_2)_2$	1545	981	
$VO(S_2CNPy)_2$	1494	947	994
$VCl_2(S_2CNPy)_2$	1496	947	

Table 5 lists the most important and characteristic bands of the IR spectra of **1** through **4** and compares them with the corresponding vanadyl starting material. The dihalide derivatives have spectra very similar to the corresponding VO starting material. Both have C—N and C—S bands around 1500 and 950 cm^{-1}, respectively, and a weak C—S stretching band around 850 cm^{-1}. The C—N band is at slightly higher energy than the free ligand (1490 cm^{-1}) for all the complexes.[32] The C—S band is higher for the dihalodialkyldithiocarbamates, and lower or the same for the other complexes compared to the free ligand band (970 cm^{-1}).[32] The most obvious feature of Table 5, however, is the absence of the very intense V═O band in the dihalide complexes. This diagnostic band has been our best indicator of purity during synthesis. The weak C—S absorption which does appear in this region of the dihalide spectra also appears in the vanadyl IR but is partially masked by the very strong V═O stretch.

In the dihalobisdialkyldithiocarbamate complexes the C—N and C—S stretches are shifted to higher frequencies or, in the case of the pyrrolidine derivative, stay relatively the same upon deoxygenation of the vanadium and addition of the halides [C—N and C—S bands for $VCl_2(S_2CNMe_2)_2$: 6 and 11 cm^{-1} higher, respectively; $VCl_2(S_2CNEt_2)_2$: 7 and 39 cm^{-1} higher, respectively, than the corresponding bands for the vanadyl complexes]. This is in contrast to the other dihalide complexes reported in the literature. Behzadi and Thompson[27] report, for V^{IV} β-diketonate complexes of the form $VX_2(dik)_2$ (X = Cl, Br; dik = acac, bzac), the dichloro derivatives have C—C and C—O bands which are lower frequencies than the same bands in the corresponding vanadyl complexes. From supporting far IR, EPR, and X-ray powder pattern data, these structures appear to have *trans* halogens. Seangprasertkij and Riechel[37] likewise report that for complexes of the type *trans*-VX_2(salen) (X = Phenyl, Cl), the C—N stretch shifts to a lower frequency on going from the vanadyl to the disubstituted derivative. Cuadrado and

Moran[24] report for $VCl_2(S_2CNMe_2)_2$, C—N and C—S bands to be 28 and 15 cm^{-1} lower, respectively, than the corresponding values for $VO(S_2CNMe_2)_2$. However, for $VCl_2(S_2CNEt_2)_2$, they report the C—N and C—S bands to be the same and 21 cm^{-1} higher than the corresponding values for $VO(S_2CNEt_2)_2$. They also conclude, based on the metal–halogen stretch in the far IR (370 cm^{-1}) that these structures have *trans* halogens.

These differences in IR behaviour with respect to the vanadyl precursor can be rationalized by considering the metal complex symmetry and electronic effects of the substituents on the ligands. Jezierski and Raynor[21] in their EPR study of several V^{IV} dihalide complexes deduce that going from the vanadyl structure (where the metal is somewhat out of the plane of the equatorial ligands) to the *trans*-type structure (where the metal is in the plane of the ligands) stabilizes the σ-bonding d_{xy} orbital slightly and stabilizes the π-bonding $d_{x^2-y^2}$ orbital greatly due to increased orbital overlap. This orbital overlap increases delocalization, effectively reducing the charge on the ligand and therefore decreasing the frequencies of the diagnostic ligand bands.

In the *cis*-type structures, the orbital overlap is reduced because the deviation from the ligand plane is increased. This localizes the charge on the ligand, therefore increasing the frequencies of the diagnostic ligand bands, as observed in complexes **1**–**3**. This is also consistent with the observations of Chatt *et al.*[32] who concluded from examining a large series of metal dithiocarbamate complexes, that the symmetry arrangement in order of decreasing C—N frequencies is planar > tetrahedral > octahedral > distorted octahedral and pyramidal. This is further appreciated if the binding vector of the dithiocarbamates ligand is drawn from the C (on the CS_2) to the metal centre (as opposed to bidentate through the sulphurs), then the coordination around the vanadium in the structures **2** and **3** can be viewed as distorted tetrahedral. The arguments are the same for **4**, except the localized electron density which caused an increase in the C—N and C—S frequencies for **1**–**3** is offset by delocalization onto the pyrrole ring in **4**. The net effect is the frequencies are almost identical in $VCl_2(S_2CNPy)_2$ and $VO(S_2CNPy)_2$.

CONCLUSIONS

A new and convenient synthesis of vanadium dihalodithiocarbamates from vanadyl starting materials has been developed. The dihalodithiocarbamates, $VCl_2(S_2CNMe_2)_2$, $VCl_2(S_2CNEt_2)_2$, $VCl_2(S_2CNPy)_2$ and $VBr_2(S_2CNEt_2)_2$ show definite physical property deviations from previously characterized dihalide derivatives of V^{IV} coordination complexes. The single crystal structures and IR properties definitely indicate a *cis* configuration of the halides which is contrary to all other structurally characterized V^{IV} dihalide complexes. This *cis* configuration can be considered to be a distortion from octahedral coordination to a tetrahedral-type complex with the dithiocarbamate ligand being smaller than acac, acting like a monodentate ligand instead of a bidentate ligand.

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Complete listings of atomic coordinates, isotropic and anisotropic thermal parameters, bond distances and angles (20 pages each structure); listing of observed and calculated structure factors for $VCl_2(S_2CNEt_2)_2$ and $VBr_2(S_2CNEt_2)_2$ are available on request. Ordering information is given on any current masthead page. The complex MSC structure reports (No. 90019 and 90056) are available on request from the Indiana Chemistry Library.

REFERENCES

1. R. L. Robson, R. R. Eady, T. H. Richardson, R. W. Miller, M. Hawkins and J. R. Postgate, *Nature* 1986, **322**, 388.
2. J. M. Arber, B. R. Dobson, R. R. Eady, P. Stephens, S. S. Hasnain, C. D. Garner and B. E. Smith, *Nature* 1987, **325**, 372.
3. J. F. Branthaver, *ACS Symp. Ser.* 1987, **344**, 188.
4. J. G. Reynolds and W. R. Biggs, *Acc. Chem. Res.* 1988, **21**, 319.
5. J. G. Speight, *The Chemistry and Technology of Petroleum: Chemical Industries*, Vol. 3. Marcel Dekker, New York (1983).
6. P. W. Tamm, H. F. Harnsberger and A. G. Bridge, *Ind. Eng. Chem. Proc. Res. Dev.* 1981, **20**, 262.
7. B. G. Silbernagel, R. R. Mohan and G. H. Singhal, *ACS Symp. Ser.* 1984, **248**, 91.
8. B. G. Silbernagel, *J. Catal.* 1979, **56**, 315.
9. P. C. H. Mitchell and J. A. Valero, *Inorg. Chem. Acta* 1983, **71**, 179.
10. P. C. H. Mitchell and J. A. Valero, *React. Kinet. Catal. Lett.* 1982, **20**, 219.

11. B. Schuetze and H. Hofmann, *Hydro. Proc.* 1984, **63(2)**, 75.
12. J. G. Reynolds, S. G. Yu and R. T. Lewis, 1985, U.S. Patent 4,559,129.
13. P. A. Montano and B. Granoff, *Fuel* 1980, **59**, 214.
14. W. K. T. Gleim and J. G. Gatis, 1971, U.S. Patent 3,558,474.
15. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn. John Wiley and Sons, New York (1988).
16. M. Pasquali, F. Marchetti and C. Floriani, *Inorg. Chem.* 1979, **18**, 2401.
17. E. L. Jones, J. G. Reynolds, J. C. Huffman and G. Christou, manuscript in preparation.
18. R. B. VonDreele and R. C. Fay, *J. Am. Chem. Soc.* 1972, **94**, 7935.
19. M. Pasquali, A. Torres-Filho and C. Floriani, *J. Chem. Soc., Chem. Commun.* 1975, 534.
20. A. Jezierski and J. B. Raynor, *Inorg. Chim. Acta* 1980, **44**, L153.
21. A. Jezierski and J. B. Raynor, *J. Chem. Soc., Dalton Trans.* 1981, 1.
22. A. Jezierski, *Inorg. Chim. Acta* 1985, **98**, L1.
23. P. Richard, J. L. Poncet, J. M. Barbe, R.Guilard, J. Goulon, D. Rinaldi, A. Cartier and P. J. Tola, *J. Chem. Soc., Dalton Trans.* 1982, 1451.
24. I. Cuadrado and M. Moran, *Trans. Met. Chem.* 1986, **11**, 375.
25. B. J. McCormick, *Inorg. Chem.* 1968, **7**, 1965.
26. M. H. Chisholm, K. Folting, J. C. Huffman and C. C. Kirkpatrick, *Inorg. Chem.* 1984, **23**, 1021.
27. K. Behzadi and A. J. Thompson, *J. Less-Common Met.* 1987, **128**, 281.
28. R. P. Dodge, D. H. Templeton and A. Zalkin, *J. Chem. Phys.* 1961, **35**, 55.
29. K. Henrick, C. Raston and A. White, *J. Chem. Soc., Dalton Trans.* 1976, 26.
30. D. Bruins and D. L. Weaver, *Inorg. Chem.* 1970, **9**, 130.
31. M. Pasquali, F. Marchetti, C. Floriani and S. Merlino, *J. Chem. Soc., Dalton Trans.* 1977, 139.
32. J. Chatt, L. A. Duncanson and L. M. Venanzi, *Suomen Kemistilehti* 1956, **B29**, 75.
33. J. Chatt, L. A. Duncanson and L. M. Venanzi, *Nature* 1956, **177**, 1042.
34. A. L. Fanfani, P. F. Nunzi and A. R. Zanazzi, *Acta Cryst.* 1972, **B28**, 1298.
35. M. Bonamico, G. Dessy, V. Fares and L. Scaramuzza, *J. Chem. Soc., Dalton Trans.* 1974, 1258.
36. J. C. Dewan, D. L. Kepert, C. L. Raston, D. Taylor, A. H. White and E. N. Maslen, *J. Chem. Soc., Dalton Trans.* 1973, 2082.
37. R. Seangprasertkij and T. L. Riechel, *Inorg. Chem.* 1986, **25**, 3121.
38. G. J. M. van der Kerk and H. L. Klopping, *Rec. Trav. Chim.* 1952, **71**, 1179.
39. G. J. M. van der Kerk, M. H. van Raalte, A. K. Sijpesteijn and R. van der Veen, *Nature* 1955, **176**, 308.
40. K. Nakamoto, J. Fujita, R. A. Condrate and Y. Morimoto, *J. Chem. Phys.* 1963, **39**, 423.
41. J. E. Drake, J. Vekris and J. S. Woods, *J. Chem. Soc.* (A), 1968, 1000.
42. J. Coetzer, *Acta Cryst.* 1970, **B26**, 872.
43. J. G. Reynolds, J. C. Huffman and G. Christou. Unpublished data.