Polyhedron Vol. 12, No. 4, pp. 407–414, 1993
Printed in Great Britain

0277–5387/93 $6.00+.00
Pergamon Press Ltd

DEOXYGENATION OF OXOVANADIUM(IV) COMPLEXES UNDER MILD CONDITIONS: CONVERSION OF VANADYL SPECIES TO THE CORRESPONDING DIHALIDES WITH CARBOXYLIC ACID HALIDES

JOHN G. REYNOLDS* and EDWARD L. JONES

Lawrence Livermore National Laboratory, University of California, Livermore, CA 94550, U.S.A.

and

JOHN C. HUFFMAN and GEORGE CHRISTOU*

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, IN 47405, U.S.A.

(*Received* 5 *June* 1992; *accepted* 5 *October* 1992)

Abstract—A new procedure for the deoxygenation of VO^{2+} complexes utilizing carboxylic acid halides in toluene or methylene chloride has been successfully applied to several vanadyl complexes with different ligand types. Facile conversion of vanadyl β-diketonates, dialkyldithiocarbamates, β-ketiiminates, 8-quinolinolate and porphyrin complexes to the corresponding dihalide complexes has been achieved, demonstrating the general application of the synthetic method. The β-diketonate complexes were studied in the greatest detail. $VX_2(Y)_2$ (X = Cl, Br; Y = $CH_3COCHCOCH_3$, $CH_3COCHCOC_6H_5$) were synthesized in high yield, and the single-crystal X-ray structure of $VCl_2(CH_3COCHCOCH_3)_2$ was obtained. The structure contains a mononuclear unit with *trans*-chloride ligands and distorted octahedral symmetry. The complexes were examined by IR; the spectra exhibited the characteristic loss of the V=O band at approximately 1000 cm^{-1}. For $VX_2(CH_3COCHCOCH_3)_2$ the ligand bands indicate more delocalization of charge onto the ligands compared with the vanadyl starting material, which is consistent with the *trans* octahedral geometry of $VCl_2(CH_3COCHCOCH_3)_2$ and its co-planar chelate ligands. The UV–vis spectra show a weak maximum around 600–700 nm with ε_m of approximately 2000 dm^3 mol cm^{-1}, typical of dihalogenated complexes.

Recently we reported a new, more convenient method of synthesizing V^{IV} dihalide complexes involving the reactions of vanadyl starting materials with acetyl halides.[1] Vanadyl dialkyldithiocarbamates were shown to readily convert to the corresponding dihalide compounds in high yield. For example, vanadyl diethyldithiocarbamate reacts with 3.0 equivalents of acetyl chloride or acetyl bromide to produce dichloro-bis(diethyldithiocarbamate)vanadium(IV) (**1**) or dibromo-bis-(diethyldithiocarbamate)vanadium(IV) (**2**), respectively. Single X-ray examination of these complexes shows the halides to be *cis*, consistent with spectroscopic properties that indicate less ligand–metal interactions due to distortions out of the ligand bonding plane. Although the synthetic method works well with dithiocarbamates, we have felt it important to explore application of the procedure to $VO(acac)_2$ ($acac^- = CH_3COCHCOCH_3^-$) and related species for two reasons: (1) $VO(acac)_2$ is an excellent starting material (cheap and air stable); and (2) even though $VCl_2(acac)_2$ has been known for many years, controversy surrounds the precise arrangement of the chlorine atoms because no single-crystal X-ray

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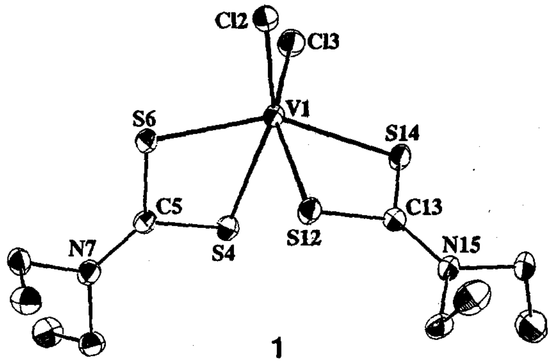
* Authors to whom correspondence should be addressed.



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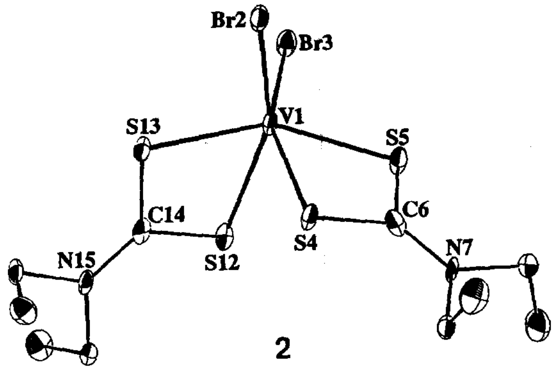

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examination has been reported; spectroscopic studies on dihalide β-diketonates have suggested both *trans* and *cis* arrangements.[2-5]

In this report, we describe the extension of the deoyxgenation reaction of acetyl halides to a broader group of vanadyl complexes, generalizing the utility of the method. In addition we report the single-crystal X-ray analysis of $VCl_2(acac)_2$, the only structurally characterized dichloro V^{IV} β-diketonate complex. The structure is very similar to that of $VCl_2(salen\text{-}N\text{-}Bu^t)_2$ in possessing *trans*-chlorine atoms.[6,7]

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 glove-bag or Vacuum Atmospheres glove-box. IR spectra were recorded as KBr pellets with the Mattson Polaris Model 10410 spectrophotometer. Far-IR spectra were recorded on a Perkin–Elmer Model 283 spectrophotometer. Electronic spectra were recorded in 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 complexes upon exposure to even trace quantities of water, excess acetyl chloride (AcCl) or acetyl bromide (AcBr) was added to the solutions. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Reagents

Spectroanalytical grade methylene chloride (0.006% water), toluene and hexanes were obtained from Burdick and Jackson Laboratories. Methylene chloride and toluene were dried using CaH_2 (Aldrich Chemical Co.) and the hexanes were dried using $LiAlH_4$ (Aldrich Chemical Co.). All solvents were dried under dinitrogen and degassed before use. AcCl, AcBr and benzoyl chloride (BzCl) were purchased from Aldrich Chemical Co. The AcBr was distilled before use and the AcCl and BzCl were used as purchased.

Synthesis of the complexes

The vanadyl complexes $VO(acac)_2$ [acac = acetylacetonate] and VO(TPP) (TPP = 5,10,15,20-tetraphenyl-porphine) were obtained from Aldrich Chemical Co.; VO(PTC) (PTC = phthalocyanine) and $VOOH(8HQ)_2$ (8HQ = 8-hydroxyquinolinate) were obtained from Pfaltz & Bauer Chemicals, Inc.; $VO(bzac)_2$ (bzac = 1-phenyl-1,3-butanedionate) was obtained from Eastman Kodak Co.; $VO(S_2CNMe_2)_2$ (S_2CNMe_2 = dimethyldithiocarbamate), $VO(S_2CNEt_2)_2$ (S_2CNEt_2 = diethyldithiocarbamate) and $VO(S_2CNPy)_2$ (S_2CNPy = pyrrolidinedithiocarbamate) were prepared by the method of McCormick[8] and recrystallized from methylene chloride; $VO(edt)_2(PPh_4)_2$ (edt = ethanedithiolate) was prepared by the method of Wiggins *et al.*;[9] VO(bzen) (bzen = bisbenzoylacetoneethylenediiminate) and VO(acen) (acen = bisacetylacetoneethylenediiminate) were prepared by the method of Boucher *et al.*;[10] $VO(quin)_2$ (quin = 2-methyl-8-quinolinolate) was prepared by the method of Stoklosa *et al.*[11]

Dichlorobis(acetylacetonato)vanadium(IV), $VCl_2(acac)_2$. $VO(acac)_2$ (6.00 g, 0.0226 mol) was dissolved in toluene (200 cm^3) to give a dark green solution. The solution was degassed and AcCl (4.8 cm^3, 0.068 mol) was added while stirring. The green solution slowly turned dark blue. The reaction mixture was stirred at room temperature overnight, then layered with hexanes (125 cm^3) and placed in a freezer. Storage at -10°C for 3 days led to the formation of purple–black crystals. The crystals were filtered and dried *in vacuo*. The yield of crude product was 85% based on vanadium. Recrystallization from a CH_2Cl_2/hexanes mixture (layered) led to a pure material as determined by IR, UV–vis and elemental analysis. The preparation was also performed by heating the reaction mixture for 3 h at approximately 100°C, followed by the above crystallizing procedure. Found: C, 37.4; H, 4.6; V, 15.9%. Calc. for $C_{10}H_{14}O_4Cl_2V$: C, 37.5; H, 4.4; V, 15.9%. Mol. wt = 320.07. Electronic absorption maxima, λ(nm) (ε_m, $dm^{-3}\ mol^{-1}\ cm^{-1}$): 628.9 (1849), 396.0sh (2179), 348.0sh (3942).

$VCl_2(acac)_2$ was also prepared by reacting $VO(acac)_2$ (6.00 g, 0.0226 mol) with BzCl (7.9 cm^3, 0.068 mol) in a manner similar to the above procedure. The crude product yield was 60% with respect to vanadium.

The other V^{IV} dihalogen complexes were prepared by the method above described for $VCl_2(acac)_2$, utilizing either AcCl or AcBr with the corresponding vanadyl starting material. The products were identified by comparisons with spectroscopic data found in the literature. For $VBr_2(acac)_2$ [λ (nm), (ε_m, $dm^{-3}\ mol^{-1}\ cm^{-1}$)]: 715.8 (1799), 468.0sh (1689); $VCl_2(bzac)_2$: 638.3 (2183), 384.4sh (6541); $VBr_2(bzac)_2$: 706.4 (2243), 627.0sh (1990), 395.0sh (5626). The products were isolated and recrystallized using the same solvents and procedures as above. Crude yields, with respect to vanadium, were 75, 81 and 65%, respectively.

X-ray crystallography and structure solution

Data were collected on a Picker four-circle diffractometer using standard low-temperature facilities. Details of the diffractometry, low-temperature facilities and computational procedures employed by the Molecular Structure Center are available elsewhere.[12] Data collection parameters are summarized in Table 1 for $VCl_2(acac)_2$. The structures were solved by a combination of MULTAN and Fourier techniques, and refined by full-matrix least-squares.

For $VCl_2(acac)_2$ a systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences indicating the unique space group $P2_1/c$. Subsequent solution and refinement of the structure confirmed this choice. A total of 1870 reflections were collected. Following the usual data processing, 1739 unique reflections remained. Of the 1739 reflections, 884 were considered observed [$F > 2.33\sigma(F)$]. All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. A difference Fourier synthesis revealed the location of some, but not all, hydrogen atoms. All hydrogen atom positions were therefore calculated using ideal geometries and d(C—H) = 0.95 Å, and the hydrogen atoms were included as fixed contributors in the final refinement cycles. The final difference map was essentially featureless, with the largest peak being 1.24 e $Å^{-3}$ at the vanadium site.

Table 1. Crystallographic data for *trans*-$VCl_2(acac)_2$

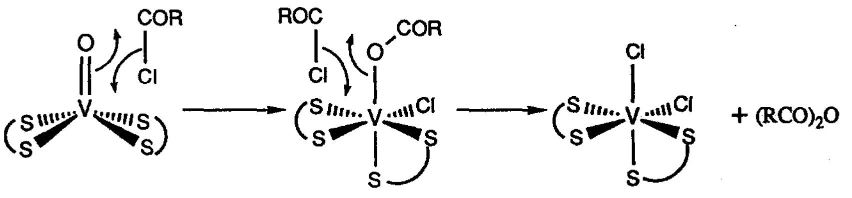
Space group	$P2_1/c$
a (Å)	7.964(5)
b (Å)	12.454(8)
c (Å)	13.341(9)
β (°)	93.80(4)
Z	4
V ($Å^3$)	1320.35
Formula	$V_{10}H_{14}O_4Cl_2$
M_r ($g\ mol^{-1}$)	320.07
ρ_{calc} ($g\ cm^{-3}$)	1.610
μ (cm^{-1})	11.339
T (°C)	−155
λ (Å)	0.71069
Range	$6° \leqslant 2\theta \leqslant 45°$
Observed data	884
$R(R_w)$ (%)	8.45(8.69)
Crystal dimensions (mm)	0.35 × 0.15 × 0.20
Colour of crystal	Brown

RESULTS AND DISCUSSION

Synthesis

Vanadyl complexes can be deoxygenated by a variety of reagents ($SOCl_2$, $SOBr_2$, PCl_5, $SeOCl_2$ and $COCl_2$)[3,7,13,14] to yield the corresponding dihalide derivatives. 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,[5] and by less direct methods including via thiuram disulphide intermediates.[15] We have now discovered carboxylic acid halides can also be used to synthesize V^{IV} dihalide complexes. The cheap and relatively easy-to-handle RX reagents (X = Cl, Br; R = CH_3CO, $C_6H_5CH_2CO$) directly afford the dihalide complexes, overcoming potential side-reactions of the other reagents. As a result we have recently reported the synthesis of, directly from the corresponding vanadyl complexes, $VCl_2(S_2CNMe_2)_2$, $VCl_2(S_2CNEt_2)_2$, $VBr_2(S_2CNEt_2)_2$ and $VCl_2(S_2CNPy)_2$ 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.

Although we have reported the characterization of the dihalodithiocarbamates, our original development of carboxylic acid halides as vanadyl deoxy-



Scheme 1.

genation reagents was with the vanadyl β-diketonates. $VCl_2(acac)_2$, $VBr_2(acac)_2$, $VCl_2(bzac)_2$ and $VBr_2(bzac)_2$ can all be successfully prepared by eq. (1). The procedure yields very clean products, which has made single-crystal growth facile. All the complexes are relatively easily isolated and may be purified by recrystallization from CH_2Cl_2/hexanes (layered). As a result, a single-crystal X-ray analysis of $VCl_2(acac)_2$ has been performed to unequivocally establish the geometry around the metal.

$$VO(L)_2 + 2RX \longrightarrow VX_2(L)_2 + R_2O \quad (1)$$

$$(X = Cl, Br; R = CH_3CO, C_6H_5CH_2CO)$$

An excess (50%) of RX has been routinely employed after observation of incomplete conversion with stoichiometric amounts of reagents (probably due to hydrolysis by adventitious water) in preliminary experiments.

Although we have not experimentally verified the mechanism of the reaction, it probably involves electrophilic attack by the carboxylic acid halide at the VO^{2+} oxygen atom to lead to a bound acetate group that can then undergo attack by a second acid halide molecule (Scheme 1). This sequence would suggest a *cis* isomer might result, as found in the dithio carbamate complexes, but it is likely that *cis*/*trans* isomerization will be rapid, allowing for the formation of the observed *trans* isomer for the β-diketonate complexes. The extreme rapidity of the reaction and the paramagnetic nature of the V^{IV} species have precluded attempts to probe this point further by normal spectroscopic methods.

To explore the scope of the deoxygenation reaction further, several other representative vanadium(IV) complexes and one vanadium(V) species were mixed with AcCl, AcBr or BzCl in CH_2Cl_2. (We assume the reactivity displayed when only AcCl was used will extend to other carboxylic acid halides.) Table 2 summarizes the results. The identification of products was either by full analysis, including X-ray crystallography, or in some cases,

Table 2. Summary of products from the reaction of vanadyl complexes with carboxylic acid halides in CH_2Cl_2

Vanadium starting complex	Acid halide	Vanadium product	Evidence	Purified yield (%)[a]
$VO(S_2CNEt_2)_2$	AcCl	$VCl_2(S_2CNEt_2)_2$	X-ray, IR, UV–vis	41
$VO(S_2CNEt_2)_2$	AcBr	$VBr_2(S_2CNEt_2)_2$	X-ray, IR, UV–vis	42
$VO(S_2CNEt_2)_2$	BzCl	$VCl_2(S_2CNEt_2)_2$	IR, UV–vis	39
$VO(S_2CNMe_2)_2$	AcCl	$VCl_2(S_2CNMe_2)_2$	IR, UV–vis	33
$VO(S_2CNPy)_2$	AcCl	$VCl_2(S_2CNPy)_2$	IR, UV–vis	34
$VO(acac)_2$	AcCl	$VCl_2(acac)_2$	X-ray, IR, UV–vis	56
$VO(acac)_2$	AcBr	$VBr_2(acac)_2$	IR, UV–vis	50
$VO(bzac)_2$	AcCl	$VCl_2(bzac)_2$	IR, UV–vis	54
$VO(bzac)_2$	AcBr	$VBr_2(bzac)_2$	IR, UV–vis	42
$VO(edt)_2^{2-}$	AcCl	$VOCl_4^-$	X-ray, IR	[b]
VO(PTC)	AcCl	No reaction	Insoluble	[c]
VOOH(8HQ)	AcCl	Partial reaction	IR	[d]
VO(acen)	AcCl	VCl_2(acen)	IR	[d]
VO(bzen)	AcCl	VCl_2(bzen)	IR	[d]
$VO(quin)_2$	AcCl	$VCl_2(quin)_2$	IR	[d]
VO(TPP)	AcCl	VCl_2(TPP)	UV–vis	[d]

[a] Per cent yield based on moles of vanadium in starting material.

[b] Not measured.

[c] Does not apply.

[d] Reactions performed on spectroscopic scale for identification only.

by diagnostic spectroscopic changes. As can be seen in Table 2, the reaction by eq. (1) is able to efficiently convert several different types of vanadyl compounds to the corresponding dihalide complexes. The vanadyl β-diketonate, dialkyldithiocarbamate, β-ketiiminate, 8-quinolinate and tetrapyrrole complexes demonstrate the utility of the reaction. However, VO(PTC) did not exhibit any reactivity, probably due to its low solubility (higher temperatures were not used); $VOOH(8HQ)_2$ appeared to only partially react as evidenced by IR; $VO(edt)_2{}^{2-}$ was extremely reactive, producing $VOCl_4{}^-$. In the sequence of the latter reaction a dark blue intermediate was formed, which could possibly be the dihalide product.[16] This intermediate was so short-lived that it could not be isolated by standard techniques. Further attempts to isolate this material are in progress.

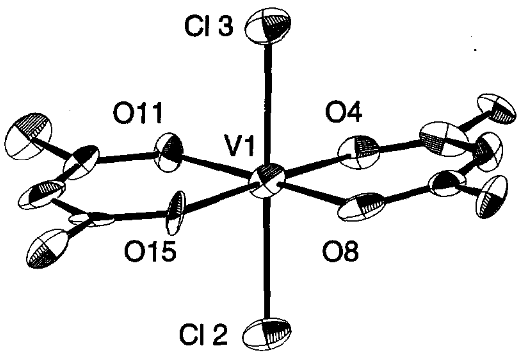


Fig. 1. ORTEP drawing of *trans*-$VCl_2(acac)_2$ showing the appropriate atom numbering scheme.

Description of structure

Figure 1 shows the structure of *trans*-$VCl_2(acac)_2$ with the atom numbering scheme. Selected structural parameters are collected in Table 3. The crystal is composed of discrete molecules of $VCl_2(acac)_2$ with the expected octahedral coordination around the vanadium. The molecule has virtual C_{2v} symmetry with the chlorine atoms *trans* to the equatorial plane formed by the oxygen atoms of the acetylacetonate groups. A very similar coordination and geometry is observed in $VCl_2(\text{salen-N-Bu}^t)_2$, the only other reported[6] example of a structurally characterized V^{IV} dihalide with *trans* chlorine atoms. In that case the equatorial plane is formed by two nitrogen and two oxygen atoms. Several studies (EPR and IR) have suggested the existence of both *trans* and *cis* isomers is possible and the geometrical preference seems to be based on the polarity of the solvent medium.[2-5] Whereas the *cis* configuration is predicted in polar solvents, we have isolated the *trans* isomer from CH_2Cl_2.

Table 3 shows the V—Cl bond lengths to be essentially the same. Comparing to other reported dichloride structures, the average V—Cl bond length is longer than those reported for *cis*-$VCl_2(S_2CNEt_2)_2$ (2.25 and 2.26 Å) and is consistent with the argument of a more efficient delocalization of charge onto the chelate ligands in *trans*-type structures.[3] The V—Cl bond lengths of $VCl_2(acac)_2$, however, are slightly shorter than those reported for $VCl_2(\text{salen-N-Bu}^t)_2$ (2.35 Å),[6] probably an effect of the different ligand types. The ligand type[17-19] and substituents on the ligand[20] have been shown

Table 3. Selected bond distances (Å) and bond angles (°) for *trans*-$VCl_2(acac)_2$

V(1)—Cl(2)	2.326(7)	O(15)—C(14)	1.299(25)
V(1)—Cl(3)	2.307(7)	C(6)—C(7)	1.35(3)
V(1)—O(4)	1.904(15)	C(5)—C(6)	1.41(3)
V(1)—O(8)	1.906(15)	C(5)—C(9)	1.45(3)
V(1)—O(11)	1.916(14)	C(7)—C(10)	1.50(3)
V(1)—O(15)	1.904(14)	C(12)—C(13)	1.44(3)
O(4)—C(5)	1.303(24)	C(12)—C(16)	1.497(26)
O(8)—C(7)	1.281(27)	C(13)—C(14)	1.36(3)
O(11)—C(12)	1.242(25)	C(14)—C(17)	1.453(27)
Cl(2)—V(1)—Cl(3)	179.1(3)	O(4)—V(1)—O(8)	87.1(7)
Cl(2)—V(1)—O(4)	91.8(5)	O(4)—V(1)—O(11)	92.0(6)
Cl(2)—V(1)—O(8)	88.3(4)	O(4)—V(1)—O(15)	177.2(7)
Cl(2)—V(1)—O(11)	89.9(5)	O(8)—V(1)—O(11)	178.0(6)
Cl(2)—V(1)—O(15)	89.3(5)	O(8)—V(1)—O(15)	95.5(6)
Cl(3)—V(1)—O(4)	88.5(5)	O(11)—V(1)—O(15)	85.5(6)
Cl(3)—V(1)—O(8)	90.9(5)	V(1)—O(4)—C(5)	132.5(14)
Cl(3)—V(1)—O(11)	90.9(5)	V(1)—O(8)—C(7)	129.7(14)
Cl(3)—V(1)—O(15)	90.4(5)	V(1)—O(11)—C(12)	134.2(13)
		V(1)—O(15)—C(14)	134.5(12)

Table 4. Comparison of selected structural information for $VO(acac)_2$, *trans*-$VCl_2(acac)_2$ and $V(acac)_3^+$

Property	$VO(acac)_2$[17]	$VCl_2(acac)_2$	$V(acac)_3^+$[24]
V—O	1.97 Å	1.91 Å	1.91 Å
C—O	1.28 Å	1.28 Å	1.28 Å[a]
O—V—O[b]	87.2°	85.5°	85.8°

[a] Only average value reported.

[b] Internal ligand angle.

Table 5. IR data for selected vanadyl and vanadium(IV) β-diketonate complexes (cm^{-1})

Complex	ν(C—O)	ν(C—C)	ν(V═O)
$VO(acac)_2$	1558	1532	998
$VCl_2(acac)_2$	1529		
$VBr_2(acac)_2$	1529		
$VO(bzac)_2$	1588	1521	998
$VCl_2(bzac)_2$	1595	1522	
$VBr_2(bzac)_2$	1596	1539	

to affect the V═O bond distance in vanadyl complexes. Little structural comparison among V^{IV} dihalide complexes to establish this point can be made due to the paucity of comparable structures. However, $VCl_2(acac)_2$ has an O_4Cl_2 first coordination sphere, while VCl_2(salen-N-$Bu^t)_2$ has an $O_2N_2Cl_2$ coordination sphere. The average V—Cl bond length of *trans*-$VCl_2(acac)_2$ is also similar to the average V—Cl bond length in $VOCl_2(C_5H_{12}N_2O)_2$ (2.34 Å)[21] and $VOCl_2(C_4H_8O)_2H_2O$ (2.39 Å),[22] but is longer than that of $VOCl_2(NMe_3)_2$ (2.25 Å).[23] These former two vanadyl dichlorides have square-pyramidal geometry with chlorine atoms on opposite sides of the basal plane (roughly *trans* configuration). The latter vanadyl dichloride has a trigonal bipyramidal structure with the chlorine atoms adjacent to each other similar to the chlorine atoms in *cis*-$VCl_2(S_2CNEt_2)_2$.

The four V—O bonds of $VCl_2(acac)_2$ are essentially equivalent as well as the four C—O bonds, as expected. Since the single-crystal X-ray structure has also been performed on the vanadyl starting material,[17] an interesting comparison can be made to see what effects the chlorine atom substitution for the oxygen atom have on the $[V(acac)_2]^{2+}$ subunit structure. Table 4 lists the comparison for selected bond distances and angles. Also included are some structural features of $[V(acac)_3][SbCl_6]$, another non-vanadyl V^{IV} β-diketonate.[24] The dihalo complex is shown to be more planar as a result of substitution of the chlorine atoms. This is evident in the average V—O bond lengths of the dichloro complex as compared to the average V—O of the vanadyl starting material. The dichloro derivative also exhibits V—O bond lengths similar to $V(acac)_3^+$. However, this difference does not appear to extend past the first coordination sphere, because the average C—O bond lengths are the same for the three complexes.

IR spectra

Table 5 lists the most important and characteristic bands of the IR spectra of $VCl_2(acac)_2$, $VBr_2(acac)_2$, $VCl_2(bzac)_2$ and $VBr_2(bzac)_2$. Included are the same characteristic bands for the corresponding vanadyl starting material. For all the dihalide derivatives, as expected, the strong V═O band is absent, indicating the conversion to the dihalide. We used this method as our best indicator of completeness of reaction.

For $VCl_2(acac)_2$ and $VBr_2(acac)_2$ the principal ligand bands in the 1500–1550 cm^{-1} range combine to form one unresolved peak. This does not agree with the assignments of Behzadi and Thompson[14] for the same compounds. [X-ray powder pattern diffraction data of our preparation of $VCl_2(acac)_2$ were consistent with their reported values.] However, $[V(acac)_3][SbCl_6]$ exhibits only one unresolved peak for these ligand bands.[24] The position of this combined band for both $VCl_2(acac)_2$ and $VBr_2(acac)_2$ is lower in energy than either of those assigned in the vanadyl precursor. This is consistent with the ligand band position of other vanadium(IV) dihalide complexes that have or are considered to have *trans* geometry when compared to the corresponding vanadyl starting materials. In these cases on going from the vanadyl structure (where the metal is somewhat out of the basal plane) to the *trans* structure (where the metal is in the equatorial plane), the σ-bonding d_{xy} orbital is slightly destabilized and the π-bonding $d_{x^2-y^2}$ orbital is greatly destabilized due to increased orbital overlap. This overlap increases delocalization, effectively reducing the charge on the ligand and therefore shifts the position of the diagnostic ligand bands to lower energy.

For $VCl_2(bzac)_2$ and $VBr_2(bzac)_2$ the principal bands are resolved and are shifted to higher energy than the corresponding bands for the vanadyl starting materials. This is not consistent with the observation of Behzadi and Thompson[14] for $VCl_2(bzac)_2$, who reported much lower energies for the C—O and C—C bands. However, our assignments are consistent with their assignment of these bands for $VBr_2(bzac)_2$ and are very similar to assignments of these bands for other vanadium(IV) complexes with bzac as a ligand [for example, V(cat)(bzac)$_2$,[25] [V(bzac)$_3$][$SbCl_6$][24] and V(dtbc)(bzac)$_2$[25]].

The shift of the ligand bands for the bzac cases when going from VO(bzac)$_2$ to the dihalide complexes is opposite to the shift of the corresponding bands in the acac cases discussed above and for the salen-N-Bu^t case. One expectation is that VCl_2(bzac)$_2$ and VBr_2(bzac)$_2$ might have *cis* geometry, based on the behaviour of the analogous dithiocarbamate complexes.[1] [The principal ligand bands of $VCl_2(S_2CNEt_2)_2$ and $VBr_2(S_2CNEt_2)_2$ are shifted to a higher frequency than the corresponding bands for $VO(S_2CNEt_2)_2$ and this has been accounted for by the *cis* geometry reducing delocalization from the ligand plane.] However, Von Dreele and Fay[5] determined the geometry of $VCl_2(t\text{-}C_4H_9COCHCO\text{-}t\text{-}C_4H_9)_2$ by examining the V—Cl bands in the far-IR. Their assignment of 362 cm^{-1} for the *trans* geometry matches ours of 359 cm^{-1} for VCl_2(bzac)$_2$ and 365 cm^{-1} for VCl_2(acac)$_2$. The expected position for the *cis* geometry would be around 385 cm^{-1}. This evidence indicates VCl_2(bzac)$_2$ and VBr_2(bzac)$_2$ also have *trans* geometry and that the shift to higher wave-numbers is probably due to electronic effects of the aromatic ring of the ligand.

CONCLUSIONS

The new and convenient synthetic method of converting vanadyl dialkyldithiocarbamate complexes to the corresponding vanadium(IV) dihalide complexes using carboxylic acid halides has been successfully applied to a wide variety of vanadyl systems. In general, as verified by spectroscopic methods, the reaction was found to work well with β-diketonates, β-ketiiminates, 8-quinolinolate and some tetrapyrroles, as well as dithiocarbamates. In specific, the reaction using VO(acac)$_2$ and AcCl produced a highly crystalline product which, when characterized by single-crystal X-ray analysis, showed the chlorides to be *trans* with respect to the bonding plane formed by the acac ligands. This geometry is similar to that of VCl_2(salen-N-Bu^t)$_2$, but contrary to the *cis* structures of $VX_2(S_2CNEt_2)_2$ (X = Cl, Br). Regardless of the structural differences of these products, the reaction using carboxylic acid halides appears to be a general method to produce dihalide derivatives from vanadyl complexes without the deleterious side-reactions seen for syntheses using some other, more well-known halogenating reagents.

Supplementary material. Complete listings of atomic coordinates, isotropic and anisotropic thermal parameters, bond distances and angles (20 pages); listings of observed and calculated structure factors for VCl_2(acac)$_2$ are available on request. Ordering information is given on any current masthead page. The complete MSC structure report (No. 89164) is available on request from the Indiana Chemistry Library.

Acknowledgements—Work at the Lawrence Livermore National Laboratory was performed under the auspices of the U.S. Department of Energy under contract number W-7405-ENG-48. Work at Indiana University was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy under Grant DE-FG02-87ER13702. We especially thank the Affirmative Action Equal Employment Opportunity Program at Lawrence Livermore National Laboratory for additional support. We also thank Ann M. Murray, Katherine E. Nelson and Melissa Chi-Lin Chu of Lawrence Livermore National Laboratory, Norman R. Dean of Indiana University and Thomas F. Finger of Chevron Research Company for experimental assistance.

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