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Acetyl and Benzoyl Cyanide Complexes with Titanium(IV) and Vanadium(IV) Chlorides

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As part of our effort to study the cyanides of the early transition elements we have been investigating a possible Friedel–Crafts route to metal cyanides. In this we had hoped to convert the 'catalyst' $TiCl_4$ into $Ti(CN)_4$ using an acyl or aryl cyanide and an aromatic hydrocarbon. Whilst this has not so far been achieved, we have succeeded in isolating complexes of titanium(IV) and vanadium(IV) chlorides with acetyl and benzoyl cyanides and report on them here. Acyl and aryl cyanides are known to be susceptible to nucleophilic attack [1] but there are no previous reports of them acting as nucleophiles to metal ions.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen or *in vacuo*. Physical measurements were carried out as described elsewhere [2]. Acetyl cyanide was prepared from copper(I) cyanide and acetyl bromide in the presence of acetonitrile [3] and purified by fractionation. Benzoyl cyanide (Aldrich) was used without further purification.

Reactions of $TiCl_4$ and VCl_4 with Acetyl Cyanide

When $TiCl_4$ (3 g, 0.016 mol) in dry petroleum (40–60 °C; 150 cm^3) was treated with CH_3COCN (3 g, 0.043 mol), a yellow precipitate was formed. After removal of all volatiles, the product (Table I) was dried *in vacuo* and removed from the vacuum apparatus under an atmopshere of dried nitrogen. The same product was obtained in the direct reaction between $TiCl_4$ (2 g, 0.010 mmol) which was distilled on to CH_3COCN (8 g, 0.12 mol) at −196 °C. After warming to room temperature, the excess of CH_3COCN was removed *in vacuo* to leave a mixture of lemon yellow crystals and a pale brown solid. The yellow crystals were sublimed at room temperature to give the pure mono-adduct.

Similar reactions between VCl_4 and an excess of CH_3COCN either in petrol or in the absence of a solvent yielded the sublimable, dark red bis-adduct (Table I). When, however, VCl_4 (5 g, 0.031 mol) in petrol (100 cm^3) was treated with CH_3COCN (2 g, 0.028 mol), a brown precipitate formed which could be isolated by the removal of all volatiles *in vacuo* at room temperature as $(VCl_4)_2(CH_3COCN)_3$ (Table I).

Reactions of $TiCl_4$ and VCl_4 with Benzoyl Cyanide

In a typical reaction, VCl_4 (6 g, 0.031 mol) was distilled into a flask containing C_6H_5COCN (2.5 g, 0.019 mol) dissolved in dry petrol (100 cm^3 and the mixture stirred at room temperature to give a homogeneous brown precipitate. The brown solid (Table I) was isolated by removal of excess VCl_4 and petrol *in vacuo* at room temperature. The $TiCl_4$ complex was prepared similarly.

Results and Discussion

The nucleophilicity of acetyl and benzoyl cyanides has been demonstrated by the preparation of their complexes with the stronger electrophiles titanium(IV) and vanadium(IV) chlorides. Acetyl cyanide reacts directly with these halides to give $TiCl_4(CH_3COCN)$ and $VCl_4(CH_3COCN)_2$, respectively; these complexes are also formed using an excess of the ligand in hydrocarbon solvents. When vanadium(IV) chloride is in excess however the complex $(VCl_4)_2$-

TABLE I. Complexes of Acetyl and Benzoyl Cyanides with Chlorides of Titanium(IV) and Vanadium(IV)

Compound	Colour	Analytical data (found (calc.))			
		%C	%H	%N	%Cl
$TiCl_4(CH_3COCN)$	yellow	14.1(13.9)	1.19(1.17)	5.43(5.41)	5.43(54.8)
$VCl_4(CH_3COCN)_2$	dark red	23.4(21.8)	1.96(1.81)	8.87(8.47)	42.2(42.9)
$(VCl_4)_2(CH_3COCN)_3$	brown	18.1(18.2)	1.61(1.53)	6.72(7.09)	47.2(47.8)
$(TiCl_4)_2(C_6H_5COCN)_3$	yellow	36.2(37.3)	2.05(1.96)	5.39(5.44)	36.6(36.7)
$(VCl_4)_2(C_6H_5COCN)_3$	brown	36.0(37.0)	2.01(1.94)	5.40(5.39)	36.1(36.4)

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TABLE II. Spectroscopic and Magnetic Properties of Acetyl and Benzoyl Cyanide and their Complexes with Titanium(IV) and Vanadium(IV) Chlorides[a]

Compound	Infrared spectrum (cm^{-1})			UV spectrum ($cm^{-1} \times 10^3$)			Magnetic moment
	ν(CN)	ν(CO)	ν(M–Cl)ν(M–N)	$\pi \rightarrow \sigma^*(e_g)$	$\pi \rightarrow \pi^*(t_{2g})$	d–d	μ_{eff} (BM) 20 °C
CH_3COCN	2218	1725					
$TiCl_4(CH_3COCN)$	2272	1725	400(br), 315, 275		31.5		diamagnetic
$VCl_4(CH_3COCN)_2$	2260, 2220	1727	360(br), 310(br)	33.1	20.1	14.8(sh)	2.10
$(VCl_4)_2(CH_3COCN)_3$	2260, 2220	1729	370, 320(sh)	32.8	20.0	14.3(sh), 11.4(sh)	2.09
C_6H_5COCN	2218	1675					
$(TiCl_4)_2(C_6H_5COCN)_3$	2258	1680	380(br)		31.3		diamagnetic
$(VCl_4)_2(C_6H_5COCN)_3$	2258	1686	385, 365	29.9	20.2	12.5(sh)	1.77

[a] br = broad; sh = shoulder.

$(CH_3COCN)_3$ results. A similar formulation arises in the complexes formed by the reactions of benzoyl cyanide with an excess of titanium(IV) or vanadium(IV) chloride. All of these complexes are very moisture sensitive; the acetyl cyanide adducts $TiCl_4(CH_3COCN)$ and $VCl_4(CH_3COCN)_2$ can be purified by vacuum sublimation at room temperature. Pure products were not obtained in reactions of excess of benzoyl cyanide with these halides. Benzoyl cyanide is a solid which is only sparingly soluble in solvents with which the chlorides do not react and it has a similar volatility to the complexes produced so that it is difficult to avoid contamination by excess of benzoyl cyanide.

The magnetic moments of the complexes (Table II) show that there is no reduction of the metals to Ti(III) or V(III) in these reactions. The IR spectra (Table II) show that in the complexes ν(CO) is almost unchanged from that in the free ligand while ν(CN) is in each case shifted to a considerably higher frequency than that in the ligand. In complexes of acetyl chloride such as $TiCl_4(CH_3COCl)$ in which the co-ordination is known to be from the carbonyl oxygen [4], ν(CO) shifts from 1802 cm^{-1} in CH_3COCl to 1625 cm^{-1} in the complex. The increase in ν(CN) upon co-ordination is similar to that observed in complexes of acetonitrile [5]. We conclude therefore that bonding to the metal atoms is via the lone pair on the nitrogen of the cyanide group rather than from the oxygen atom of the carbonyl group.

The most likely structures for these complexes are those containing octahedrally co-ordinated metal atoms. Terminal Ti–Cl stretches in octahedral titanium(IV) compounds occur in the 360–425 cm^{-1} region [6]. Unfortunately because of the broad nature and multiplicity of bands in the far IR region of these compounds we are unable to distinguish ν(M–Cl) and ν(M–N) bands. The UV spectra show the ligand to metal charge transfer bands (Table II) which are in similar positions to the Cl(II) → M(e_g) found in salts of the $[TiCl_6]^{2-}$ and $[VCl_6]^{2-}$ anions [7]. The vanadium(IV) complexes show weak shoulders on the charge transfer absorptions in the region expected for tetragonal VCl_4L_2 complexes [7]. The most likely structures for the complexes are thus a tetragonal monomer for $VCl_4(CH_3COCN)_2$, a doubly halogen bridged dimer for $TiCl_4(CH_3COCN)$ and a singly halogen bridged structure between MCl_4L_2 and MCl_4L units for the complexes of formula $(MCl_4)_2L_3$.

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