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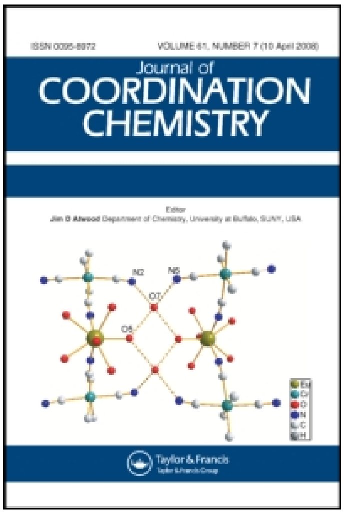

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STRUCTURAL STUDY OF TETRACHLORO-CIS-DIFORMONITRILEVANADIUM (IV)

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STRUCTURAL STUDY OF TETRACHLORO-CIS-DIFORMONITRILEVANADIUM (IV)

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Anhydrous hydrogen cyanide reacts at room temperature on vanadium tetrachloride to give a coordination compound $VCl_4(NCH)_2$. Crystals are orthorhombic with $a = 11.964 \pm 0.007$, $b = 10.647 \pm 0.007$ and $c = 6.503 \pm 0.003$ Å, $Z = 4$, space group $P2_12_12_1$. Crystal structure is resolved by X-ray. Inverting the full matrix of normal equations and using anisotropic temperature factors, the R factor based on 681 reflexions is equal to 0.041 excluding zero values. The vanadium atom is surrounded octahedrally by four chlorine atoms and two nitrogen atoms in the cis position. The coordination octahedron is slightly distorted in agreement with visible and U.V. spectrophotometry. One hydrogen atom of one octahedron is bonded to a chlorine atom of another octahedron.

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INTRODUCTION

Hydrogen cyanide may be considered as a Lewis base since it reacts on covalent transition metal halides, such as $TiCl_4$, to give addition compounds; by infrared,[1,2] NMR[3] spectroscopy, and X-ray diffraction,[4] it has been shown that the hydrogen cyanide molecule is linked to the metal atom through its nitrogen atom. It thus reacts as a nitrile; and indeed hydrogen cyanide is the formonitrile.

Vanadium tetrachloride and hydrogen cyanide vapors react in the same way giving the compound $VCl_4(NCH)_2$.[5] The infrared, ultraviolet and visible spectroscopic study suggests that the complex molecule is octahedral with HCN molecules probably attached in the *cis* position. The infrared spectra of solid $VCl_4(NCH)_2$ and $VCl_4(NCD)_2$ show one band attributed to the V-Cl stretching frequency which is shifted towards lower frequencies: indeed metal-ligand frequencies decrease with an increasing coordination number of the metal. Moreover for $VCl_4(NCD)_2$ the number of bands attributed to $C \equiv N$ and C–D stretching vibrations, and to N–C–D bending vibration, is consistent with a C_{2v} symmetry characteristic of a *cis* MX_4L_2 octahedron.

For safety reasons, synthesis is carried out in a glass apparatus which is entirely sealed.[5] There are two steps in the preparation of single crystals. The contact of the vapors of cyanhydric acid and vanadium tetrachloride, at room temperature, gives a black powder which is separated in a sealed tube. It is then put into a temperature gradient 20°C–80°C; the solid warmed at 80°C is decomposed; vanadium tetrachloride and cyanhydric acid vapors recombine to give single crystals at the cold end.

The deuterated compound is obtained similarly. DCN is prepared by pouring a 18 N D_2SO_4 solution in D_2O on dry potassium cyanide. The infrared spectrum of $VCl_4(NCD)_2$ shows two bands at 1932–1920 cm^{-1} which are attributed to the $C \equiv N$ stretching frequency (Table V). These values are quite different from 2140 cm^{-1}, value which is characteristic of $VCl_4(NCH)_2$. Nothing appears around this last frequency, which leads to the conclusion that the amount of $VCl_4(NCH)_2$ in $VCl_4(NCD)_2$, if any, is negligible.

TABLE I

$VCl_4(NCH)_2$ and $TiCl_4(NCH)_2$ unit cell data

$VCl_4(NCH)_2$	$TiCl_4(NCH)_2$
$a = 11.964 \pm 0.007$	$a = 12.24 \pm 0.01$ Å
$b = 10.647 \pm 0.007$	$b = 10.80 \pm 0.01$
$c = 6.503 \pm 0.003$	$c = 6.469 \pm 0.005$
$P2_12_12_1$	P_{nma}
$d_{exp} = 1.95 \pm 0.04$	$d_{exp} = 1.87 \pm 0.05$
$Z = 4$	$Z = 4$
$d_{calc} = 1.97 \pm 0.01$	$d_{calc} = 1.88 \pm 0.01$

$VCl_4(NCH)_2$ crystals belong to the orthorhombic system (Table I). Lattice constants of $TiCl_4(NCH)_2$ and of $VCl_4(NCH)_2$ are quite similar. However, space groups are different; the space group of $TiCl_4(NCH)_2$ has a mirror plane[6] not present in the space group of $VCl_4(NCH)_2$.

EXPERIMENTAL

The single crystal is shaped like a flat prism with six lateral planes; the height is 0.2 mm and the basal surface is 0.35 mm^2. Because of its extreme sensitivity to humidity, it is put in a sealed glass tube set in a 30 cm diameter eulerian cradle. The MoKα radiation is supplied by a highly stabilized generator C.G.R. Θ60. The beam size obtained with a collimator 0.6 mm in diameter and 70 mm in length, is equal to 3.5 mm at the crystal level. The intensity diffracted is measured with a scintillation counter associated with a pulse height analyser set on MoKα energy in such a way that 90% of the intensity diffracted is counted. Kβ radiation is filtered with a niobium pentoxide pellet set in front of the counter window. 700 independent reflexions are recorded at room temperature after manual setting of the crystal. The symetric Θ–2Θ scan of 100 sec. corresponds to 0.97° in the Bragg angle (2Θ (maximum) $= 46°$). The background is recorded for 30 sec in two fixed positions of the counter before and after the reflexion. 15 data, for which the counting rate goes slightly over 10,000 c/s, are corrected for counting loss.[7] Three reflexions, taken as standard, are recorded every twelve hours, showing no anomaly. No take off angle adjustment is made. Absorption corrections[8] are calculated with an absorption coefficient equal to 25 cm^{-1}. The transmission factor varies between 0.30 and 0.56. For every computed structure factor, a standard deviation is computed.[9] If the observed structure factor is less or equal to its standard deviation, it is then considered as a zero reflexion and the structure factor is made equal to half its standard deviation. During least squares refinement, the reciprocal of the standard deviation is used, as a weighting factor.

For $VCl_4(NCD)_2$ the single crystal used has the shape of a rectangular parallelepiped (1.10 × 0.51 × 0.31 mm). Experimental recording conditions are the same in all but three points. One, the Θ–2Θ scan is made variable as $(\Delta\lambda/\lambda) \tan \Theta$ ($\Delta\lambda/\lambda$ is the dispersion between MoKα_1 and MoKα_2). Two, a take off angle of 2° is used. Three, the beam size obtained with a collimator 0.6 mm in diameter and 120 mm in length, is equal to 1.7 mm at the crystal level. Indeed, in the meantime these three facilities were added on the homemade diffractometer.

RESULTS

Vanadium, chlorine, nitrogen and carbon atoms are easily located from a three dimensional Patterson map. The y coordinate of the vanadium atom is very close to $\frac{1}{4}$. One Cl, one V, one N and one C atoms are nearly in a straight line and these latter all have a y coordinate close to $\frac{1}{4}$.

Atomic coordinates are refined by least squares[10] using the isotropic temperature factors and the atomic scattering factors of Cromer and Waber.[11] The unweighted R excluding zero is equal to 0·085. The introduction of anisotropic temperature factors and anomalous dispersion[11] leads to an R factor equal to 0.041.

TABLE II

VCl_4 $(NCH)_2$ atomic parameters and anisotropic thermal vibration components

$\exp[-2\pi^2(U_{11}(ha^*)^2 + U_{22}(kb^*)^2 + U_{33}(lc^*)^2 + 2U_{12}(hka^*b^*) + 2U_{13}(hla^*c^*) + 2U_{23}(klb^*c^*))]$

Atome	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	0.13881 (9)	0.2529 (1)	0.2914 (1)	0.0298 (7)	0.0280 (6)	0.0249 (7)	−0.0017 (8)	0.0014 (3)	−0.001 (6)
Cl (1)	0.0306 (1)	0.2354 (2)	0.0118 (3)	0.046 (1)	0.057 (1)	0.026 (8)	−0.009 (1)	0.0044 (9)	0.002 (1)
Cl (2)	0.2464 (2)	0.0916 (2)	0.2124 (4)	0.057 (1)	0.039 (1)	0.048 (1)	0.015 (1)	0.009 (1)	−0.007 (1)
Cl (3)	0.0285 (1)	0.3862 (1)	0.4569 (4)	0.040 (1)	0.034 (1)	0'039 (1)	0.0081 (9)	0.005 (1)	−0.009 (1)
Cl (4)	0.2461 (2)	0.4011 (2)	0.1534 (4)	0.048 (1)	0.042 (1)	0.042 (1)	−0.016 (1)	0.009 (1)	0.005 (1)
N (1)	0.2356 (5)	0.2584 (6)	0.567 (1)	0.035 (3)	0.040 (3)	0.033 (3)	−0.003 (3)	0.001 (3)	−0.005 (4)
N (2)	0.0401 (5)	0.1147 (6)	0.452 (1)	0.040 (4)	0.040 (4)	0.029 (4)	−0.06 (4)	−0.002 (4)	−0.003 (4)
C (1)	0.2888 (7)	0.252 (1)	0.709 (1)	0.044 (5)	0.086 (7)	0.037 (5)	−0.006 (7)	−0.010 (4)	−0.019 (7)
H (1)	0.343 (8)	0.262 (9)	0.84 (2)						
C (2)	−0.0094 (7)	0.0469 (9)	0.554 (1)	0.060 (6)	0.049 (5)	0.049 (6)	−0.005 (5)	−0.009 (6)	−0.002 (5)

Standard deviations, given in parentheses, are related to the last figure.

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TABLE III

Interatomic distances (Å)

	$VCl_4(NCH)_2$	$VCl_4(NCD)_2$		$VCl_4(NCH)_2$	$VCl_4(NCD)_2$
V–Cl (1)	2.239 (3)	2.242 (2)	N (1) - C (1)	1.12 (1)	1.112 (8)
V–Cl (2)	2.207 (3)	2.206 (2)	N (2) - C (2)	1.14 (1)	1.144 (7)
V–Cl (3)	2.216 (2)	2.215 (2)	C (1) - H (1)	1.11 (9)	
V–Cl (4)	2.222 (3)	2.223 (2)	C (1) - D (1)		0.96 (7)
V–N (1)	2.135 (7)	2.124 (5)	H (1) - Cl (1)	2.42 (9)	
V–N (2)	2.157 (7)	2.153 (5)	D (1) - - - Cl (1)		2.64 (8)
			C (1) - - - Cl (1)	3.39 (1)	3.43 (1)
			C (2) - - - Cl (4)	3.51 (1)	3.51 (1)

Bond Angles (°)

Cl (1)–V–Cl (2)	94.8 (1)	94.67 (8)	Cl (2)–V–N (2)	84.3 (2)	84.3 (2)
Cl (1)–V–Cl (3)	95.9 (2)	95.86 (5)	Cl (3)–V–Cl (4)	94.8 (1)	94.85 (7)
Cl (1)–V–Cl (4)	93.82 (9)	93.82 (7)	Cl (3)–V–N (1)	84.1 (2)	84.7 (1)
Cl (1)–V–N (1)	175.8 (2)	175.7 (1)	Cl (3)–V–N (2)	82.8 (2)	82.8 (1)
Cl (1)–V–N (2)	91.1 (2)	91.5 (2)	Cl (4)–V–N (1)	90.3 (2)	90.4 (1)
Cl (2)–V–Cl (4)	97.0 (1)	96.94 (8)	Cl (4)–V–N (2)	174.7 (2)	174.4 (1)
Cl (2)–V–Cl (3)	163.4 (1)	163.61 (8)	N (1)–V–N (2)	84.7 (3)	84.3 (2)
Cl (2)–V–N (1)	84.3 (2)	83.9 (1)	V–N (1)–C (1)	174.7 (9)	177.0 (6)
N (1)–C (1)–H (1)	170 (6)		V–N (2)–C (2)	173.6 (8)	174.8 (5)
N (1)–C (1)–D (1)		175 (5)			

Values in parentheses are the errors in the last figure.

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In a three-dimensional Fourier series, a peak of about 0.4 e/Å^3 shows up; this value is equal to the error of electron density.[12] However this peak looks like the hydrogen atom of the HCN molecule which is almost located in the plane $y = \frac{1}{4}$. A refinement including this hydrogen atom reduces the R factor from 0.0410 to 0.0406; thermal vibration components of this hydrogen atom are taken to be equal to those of the carbon atom to which it is bonded.[13] Applying Hamilton's test,[14] this decrease of R is significant at the 0.005 level. A Fourier difference map reveals no other peak higher than 0.15 e/Å^3, the second hydrogen atom is not seen.

The final refinement based upon 681 data leads to:

non-weighted R, including 98 zeros	0.048
non-weighted R, excluding 98 zeros	0.041
weighted R, including 98 zeros	0.058
weighted R, excluding 98 zeros	0.052

The non-weighted R factor is defined as $\Sigma(\,|\,|F_c| - |F_o|\,|\,)/\Sigma F_o$ and the weighted one as $[\Sigma[w(|F_c| - |F_o|)]^2/\Sigma[wF_o]^2]^{1/2}$.

Results are in Tables II, III and IV. Figure 1 describes the octahedron $VCl_4(NCH)_2$ and the occupancy of the unit cell.

TABLE IV

Refinement with the two possible chains and values of the isotropic B temperature factor of nitrogen and carbon atoms.

		$VCl_4(HCN)_2$	$VCl_4(DCN)_2$
chain V–N–C	non-weighted R, excluding zeros	0.075	0.072
	B N (1)	2.94	3.13
	B N (2)	2.94	3.23
	B C (1)	4.51	4.68
	B C (2)	4.97	5.02
chain V–C–N	non-weighted R, excluding zeros	0.078	0.078
	B C (1)	1.73	1.85
	B C (2)	1.65	1.99
	B N (1)	6.95	6.82
	B N (2)	7.50	6.88

For $VCl_4(NCD)_2$ the final refinement based upon 684 data leads to:

non-weighted R, including 18 zeros	0.033
non-weighted R, excluding 18 zeros	0.032
weighted R, including 18 zeros	0.050
weighted R, excluding 18 zeros	0.049

Differences in R factors between $VCl_4(NCH)_2$ and $VCl_4(NCD)_2$ are attributed to various factors. First of all, as it has been stated earlier, a take off angle adjustment and a variable Θ–2Θ scanning were added on the diffractometer. Secondly, the crystal of $VCl_4(NCD)_2$ was much larger, leading to higher counts, that is to better accuracy.

Bond lengths and bond angles in $VCl_4(NCH)_2$ and in $VCl_4(NCD)_2$ are equal within the estimated experimental errors (Table III).

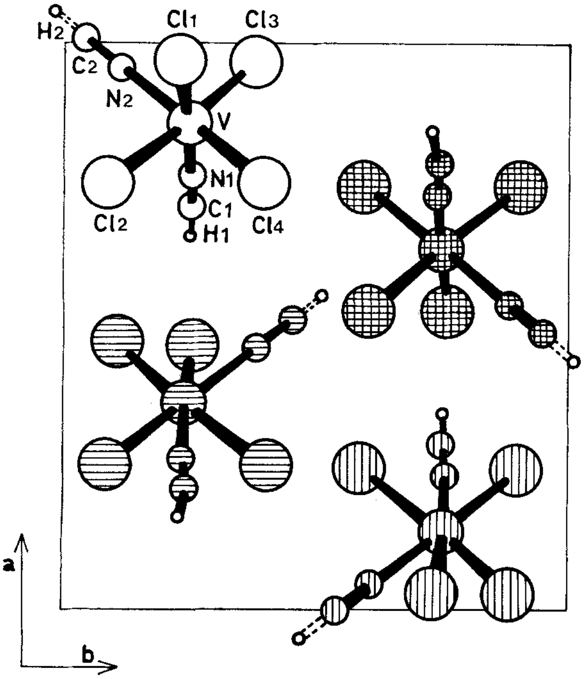

FIGURE 1 Octahedrons $VCl_4(NCH)_2$ and occupancy of the unit cell. (H(2) was not located by X-ray). Projection onto the *ab* plane.

DISCUSSION

The addition compound VCl_4, 2HCN is a molecular octahedral coordination compound with two cyanhydric acid molecules in the *cis* position. It may be questioned whether the carbon atom or the nitrogen atom of the hydrogen cyanide molecule is bound to the vanadium atom. Consideration of infrared spectra[5] may help to answer this question: indeed the increase of the frequency of the CN stretching vibration is typical of coordination by the nitrogen atom.[1, 2, 4] This is particularly obvious when coordination compounds containing RCN are considered. To obtain an answer from X-ray data is not so easy, since carbon and nitrogen electron cores differ by only one electron. However a refinement has been made for both possible chains V–N–C and V–C–N (Table IV). The R factor is slightly lower when the chain is V–N–C: applying Hamilton's test,[14] this decrease of R is significant at the 0.005 level. Another argument may be found in the comparison of the isotropic temperature factors B; in fact, in the V–C–N case, these factors seem anomalously too different: the B factor of the first neighbour which would be C, is too weak, and that of the second neighbour which would be N, is too high. This may be interpreted as an electron lack in the first neighbour and an excess in the second, which would suggest that the correct chain is V–N–C. And indeed in the V–N–C case, B isotropic factors look more realistic.

For $TiCl_4(NCH)_2$[6], $y = \frac{1}{4}$ is a mirror plane which contains the chain Cl–Ti–N–C; moreover a statistical distribution of the other (NCH) molecule with a chlorine atom occurs on both sides of this mirror plane. The origin of this statistical distribution was based upon close similarity of Ti–Cl and Ti–N bond lengths and a close similarity between the Cl atom's diameter and the HCN molecule's total length. The V–Cl and V–N bond lengths appear different enough to prevent such a statistical distribution; consequently there is no mirror plane, and the space group of $VCl_4(NCH)_2$ is different from that of $TiCl_4(NCH)_2$ although lattice constants remain very similar.

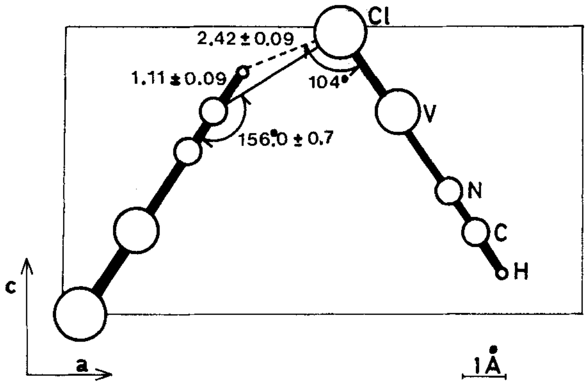

FIGURE 2 Projection on plane $y = \frac{1}{4}$ of ClVNCH chains for which the y coordinate of all atoms is very close to $\frac{1}{4}$. The hydrogen bond is represented by a broken line.

$VCl_4(NCH)_2$ octahedra are joined by hydrogen bonds (Figure 2) roughly located in $y = \frac{1}{4}$ and $y = \frac{3}{4}$ planes. These linkages build chains N–C–H . . . Cl–V–N–C–H . . . Cl–V. Indeed, such H– – – –Cl

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and D- - -Cl interatomic distances, equal to 2.42 and 2.64 Å are much smaller than the sum of Van der Walls radii of hydrogen and chlorine atoms equal to 3 Å. A similar chain has been observed in $TiCl_4(NCH)_2$[6] although the hydrogen atom has not been located: the C- - -Cl length is equal to 3.43 Å and N-C- - -Cl angle to 158°; similar values for $VCl_4(NCH)_2$ are 3.41 Å and 156°, which suggests that this hydrogen bond also occurs in $TiCl_4(NCH)_2$. These results are in agreement with the discussion of infrared spectra. The C-H and C-D stretching frequencies shift towards smaller wavelength with respect to hydrogen or deuterium gaseous cyanide (Table V). These shifts increase at the same time as the hydrogen bond becomes stronger. It has been observed that this shift is larger for the vanadium compound than for the titanium or iron compounds. This might explain why a hydrogen atom has been seen on the $VCl_4(NCH)_2$ Fourier map whereas no such observation has been made for $TiCl_4(NCH)_2$[6] and $Fe_3Cl_8(NCH)_6$[4].

TABLE V

C-H and C-N stretching frequencies of HCN and DCN coordination compounds compared with the vibration of free HCN or free DCN. Values in parentheses show the difference with respect to free HCN or DCN.

Compound	*C-H*	*C-N*	*Compound*	*C-D*	*C-N*	*Reference*
HCN (gas)	3311	2097	DCN (gas)	2630	1928	18, 19
$TiCl_4(NCH)_2$	3173 (−138)	2134 (+37)	$TiCl_4(NCD)_2$	2591 (−39)	1926 (−2)	1, 2
$(FeCl_4)_2Fe(NCH)_6$	3180 (−131)	2131 (+34)	$(FeCl_4)Fe(NCD)_6$	2584 (−46)	1920 (−8)	4
$VCl_4(NCH)_2$	3205 (−106)	2140 (+43)	$VCl_4(NCD)_2$	2570 (−60)	1932 (+4)	5
	3155 (−156)			2510 (−120)	1920 (−8)	

Another interesting geometrical feature of the octahedron merits discussion. Bond angles V-N(I)-C(I) and V-N(2)-C(2) which are equal to 174.7 ± 0.9° and 173.6 ± 0.8° depart from 180°. This has already been observed since this angle is equal to 178.1 ± 0.8° in $TiCl_4(NCH)_2$ and 170.7 ± 0.7° in $(FeCl_4)_2Fe(NCH)_6$. Kaufman and Choplin[15] computed electronic distribution in $TiCl_4(NCH)_2$ by a semi-empirical method. They came to the conclusion that some electronic density remains on the nitrogen atom. As a first approximation, this residual electronic density may be correlated to the V-N-C bond angle deformation. Indeed in the $VCl_4(NCH)_2$ molecule, the angle which differs the most from 180°, i.e. V-N(2)-C(2), corresponds to the longest interatomic distance V-N(2). But a long V-N distance can be understood as an incomplete donation of the doublet of the nitrogen atom, which, in other words, means a residual charge on the nitrogen atom. Willet and Rundle[16] who found for $Cu_2Cl_4(NCCH_3)_2$ and $Cu_3Cl_6(NCCH_3)_6$ a Cu-N-C angle equal to 156±4° and 158.8±1.3°, note that the nitrogen atom does not use pure sp^2 character. This is another way of saying the same thing.

This incomplete doublet sharing seems to act on the V-Cl bond in transposition: the lengths found, V-Cl(1) = 2.239 ± 0.003 Å and V-Cl(4) = 2.22 ± 0.003 Å are longer than V-Cl(2) = 2.207 ± 0.003 Å and V-Cl(3) = 2.216 ± 0.002 Å. The longest V-Cl(1) bond length is related to the bond angle V-N(1)-C(1) the nearest to 180°, that is to the smallest V-N(1) bond length, that is to the most complete doublet donation. However this point is difficult to discuss in greater depth since the hydrogen bond necessarily influences also the V-Cl bond length.

The bond lengths N(1)-C(1) = 1.12 ± 0.01 Å and N(2)-C(2) = 1.14 ± 0.01 Å are smaller than those observed for gaseous cyanhydric acid 1.15 Å. This result has been already quoted for several addition compounds prepared with hydrogen cyanide or with acetonitrile. The CN bond length is equal to 1.11 ± 0.01 Å in $TiCl_4(NCH)_2$ and 1.09 ± 0.01 Å in $(FeCl_4)_2Fe(NCH)_6$. The increase of C-N stretching frequency with respect to the $C \equiv N$ frequency of hydrogen cyanide[1,2,4,5] may be correlated with the decrease of the $C \equiv N$ bond length. Nevertheless for $VCl_4(NCD)_2$ such a change in C — N stretching frequency is not observed (Table V); this may be explained by a mechanical coupling between vibrations modes as already pointed out by Kawai and Kanesaka.[1]

This discussion will be concluded by examining bond angles Cl-V-Cl which are, except for Cl(2)-V-Cl(3), greater than 90°. They vary between 93.82 and 97.0 ± 0.1. The repulsion of chlorine atoms may explain this phenomenon. Consequently bond angles Cl-V-N and N(1)-V-N(2) are smaller

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than 90°. This distortion is likely to occur for the octahedron in solution. The ultraviolet and visible spectrum of the $VCl_4(NCH)_2$ solution in liquid hydrogen cyanide shows three bands; the first one located at 16,000 cm^{-1} may be attributed to the $^2Eg \leftarrow {}^2T2g$ transition, the others close to 21,500 and 37,700 cm^{-1}, are explained by two charge transfers. In fact, the molar extinction coefficient of the last two bands are identical and five times larger than that of the first band which is lower than 100; moreover 33,700–21,500 = 16,200 is only slightly different from 16,000 cm^{-1}. This interpretation may be compared with a previous discussion on the UV and the visible spectrum[17] of $VCl_6{}^{2-}$; it shows two bands, the first, located at 14,900 cm^{-1} ($\varepsilon = 65$), is attributed to the $^2Eg \leftarrow {}^2T2g$ transition and the second, located at 21,300 cm^{-1} ($\varepsilon = 310$), is attributed to a charge transfer. If the octahedron is distorted, it is expected that term Eg splits in two terms and that the band attributed to $^2Eg \leftarrow {}^2T2g$ would be double or asymetric. If the band of $VCl_6{}^{2-}$ located at 14,900 cm^{-1} is asymetric,[17] the spectrum recorded for $VCl_4(NCH)_2$ does not clearly show such an asymetry (Figure 3). Therefore $VCl_4(NCH)_2$ dissolved in cyanhydric acid appears to have an octahedral configuration undistorted or weakly distorted.

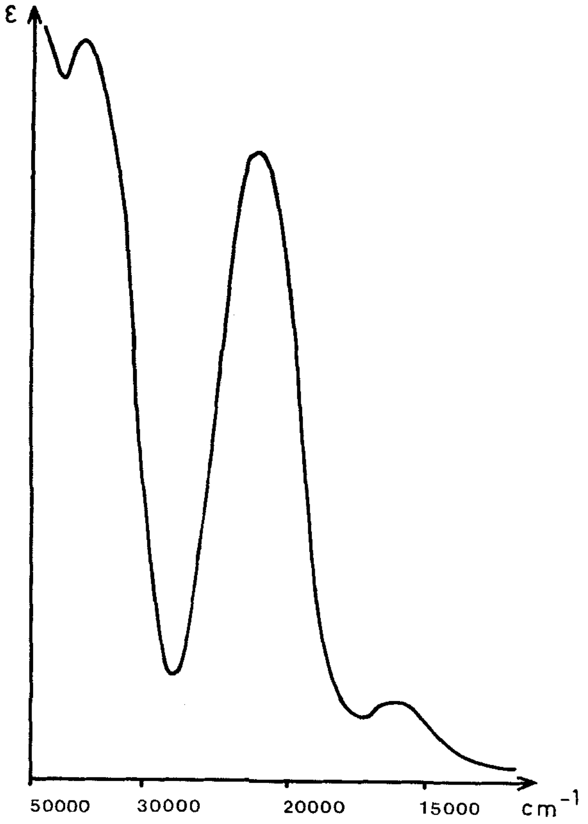

FIGURE 3 Ultraviolet and visible spectrum of $VCl_4(NCH)_2$ dissolved in hydrogen cyanide.

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