

Isonitrile complexes of vanadium(II)

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Abstract

Reaction between $[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$, halogen and isonitrile in tetrahydrofuran (THF) yielded the complexes $\text{VX}_2(\text{CNR})_4$ ($\text{X} = \text{Br}$; $\text{R} = ^t\text{Bu}$ (**1**) or Cy (**2**)) ($\text{X} = \text{I}$; $\text{R} = ^t\text{Bu}$ (**3**) or Cy (**4**)). $[\text{V}(\text{CO})_6]^-$, I_2 and CN^tBu , when reacted in CH_2Cl_2 , form $[\text{VI}(\text{CN}^t\text{Bu})_5]\text{I}$ (**5**). Replacement of Br_2 by pyridinium bromide leads to the formation of $\text{VBr}_2(\text{py})_4$ (**6**). The X-ray structures of **1**, **3** and **5** are reported. Crystal data are as follows. For $\text{VBr}_2(\text{CN}^t\text{Bu})_4 \cdot 2\text{THF}$ (**1** $\cdot 2\text{THF}$): monoclinic; $P2_1/n$; $a = 9.775(5)$ Å, $b = 10.160(5)$ Å and $c = 18.43(2)$ Å; $\beta = 104.93^\circ$; $Z = 2$; $R_1 = 0.0693$ and $wR_2 = 0.1445$. For $\text{VI}_2(\text{CN}^t\text{Bu})_4(\cdot 2\text{THF})$ (**3** $\cdot 2\text{THF}$): monoclinic; $P2_1/n$; $a = 9.860(2)$ Å, $b = 10.329(2)$ Å and $c = 18.686(4)$ Å; $\beta = 104.39(3)^\circ$; $Z = 2$; $R_1 = 0.0479$ and $wR_2 = 0.0982$. For $[\text{IV}(\text{CN}^t\text{Bu})_5]\text{I}$ (**5**): orthorhombic; $Pnma$; $a = 20.259(6)$ Å, $b = 11.503(2)$ Å and $c = 19.325(10)$ Å; $Z = 4$; $R_1 = 0.0793$ and $wR_2 = 0.1699$.

Keywords: Isonitrile complexes; Vanadium halides

1. Introduction

Halide compounds of vanadium(II) have attracted increasing interest because they open up a potentially wide field as precursors in the generation of structural models for the vanadium site in the cofactor of vanadium nitrogenase. An example for such a reaction is the formation of $\text{V}^{\text{II}}\text{S}_4(\text{tmeda})$ ($\text{H}_2\text{S}_4 \equiv 1,2\text{-bis}(2\text{-mercaptophenylthio})\text{ethane}(2\text{-})$) from $\text{VCl}_2(\text{tmeda})_2$ and Na_2S_4 [1]. Recently, V^{II} halides carrying a supporting phosphine ligand set, namely $\text{VX}_2(\text{p}_2)_2$ (where p_2 is $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ or $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$ and X is Cl , Br or I) have been reported [2]. We present here the first examples of V^{II} halides supported by isonitriles.

Furthermore, isonitrile complexes, similar to carbonyl complexes, are attractive precursor compounds in reductive C–C coupling reactions. Thus it has been shown by Lippard and co-workers [3] that the cationic complexes $[\text{M}(\text{CNR})_6]^+$ undergo coupling, leading to coordinated bis(alkylamino)acetylenes. The corresponding chemistry with the Group 5 metals has not yet been exploited, although the potential precursors for such a reaction, namely $\text{XTa/Nb}(\text{CNR})_2(\text{dmpe})_2$, have been

described [4] and cross-coupling between CO and CNR in mixed carbonyl–isonitrile complexes of Nb and Ta has been shown to occur [5]. Better documented than coupling reactions with CNR are those involving CO [6]. The only example for the vanadium chemistry so far is the formation of a bis(silyloxy)acetylene complex in the presence of Zn and SiCl_3 [6b]. It is anticipated that, owing to the smaller interligand C–C distances in the V than in the Nb and Ta complexes (with larger metal centres and hence more expanded ligand systems), C–C coupling should be facilitated.

Isonitrilevanadium complexes without supporting cyclopentadienyl are scarce. Reported examples are the structurally characterized *mer*- $[\text{VCl}_3(\text{CN}^t\text{Bu})_3]$ [7], $[\text{V}(\text{CN}^t\text{Bu})_6][\text{V}(\text{CO})_6]_2$ [8a], and *trans*- $[\text{V}(\text{CN}^t\text{Bu})_2(\text{dmpe})_2][\text{PF}_6]_2$ [8b]. The complex anions $[\text{V}(\text{CO})_5\text{CNR}]^-$ [9], the complex cations $[\text{V}(\text{NO})_2(\text{CN}^t\text{Bu})_4]^+$ [10], and the neutral compounds $\text{VX}(\text{NO})_2(\text{CNR})_3$ [10b] and $\text{VCl}_3(\text{NPh})(\text{CN}^t\text{Bu})_2$ [11] have also been described.

2. Experimental details

2.1. General

All operations were carried out in absolute solvents under N_2 , using the common Schlenk technique. The UV source was a high pressure mercury lamp, operating

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at 125 W, in a water-cooled quartz immersion well. During the photoreaction, the lamp was placed in the immediate proximity of the Duran Schlenk tube containing the reaction mixture. The starting compounds (VCl_3 , isonitriles, pyridinium bromide and cyclooctatetraene) were obtained from commercial sources. $\text{Mg}[\text{V}(\text{CO})_6]_2$ was prepared by normal pressure synthesis from VCl_3 in tetrahydrofuran (THF), using Mg as a reductant and cyclooctatetraene as a mediator [12a]. After conversion to $\text{Na}[\text{V}(\text{CO})_6]$ with aqueous NaOH, $[\text{Et}_4\text{N}][\text{V}(\text{CO})_6]$ was precipitated from an aqueous–methanolic solution with $[\text{Et}_4\text{N}]\text{Br}$.

IR spectra were obtained with a Perkin–Elmer 1720 FTIR spectrometer either as approximately 0.1 M THF solutions in 0.1 mm CaF_2 cuvettes or as CsI mulls. Susceptibility measurements were carried out with a Johnson Matthey Chemicals Ltd magnetic balance in tubes of 4 mm diameter.

2.2. X-ray crystallography

Data were collected on a Hilger & Watts diffractometer at 153(2) K in the θ – 2θ scan mode using a

graphite monochromator and Mo $\text{K}\alpha$ irradiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved using the SHELXS-86 program system and refined with SHELXL-93. An absorption correction was carried out for **3**. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated in idealized positions and refined isotropically with free (**1** and **3**) or fixed (**5**; 1.5x the methyl-C) temperature factors in the last cycles of refinement. Only in the case of **5** was there a disorder problem; one of the methyl carbon atoms, C(21), was treated with a 1:1 disorder model. No appropriate disorder model was found to treat the apparent disorder of C(11) and C(23). Crystal data and further information on the solution and refinement of the structures are given in Table 1.

Crystals for the X-ray structure determination of **1**·2THF, **3**·2THF and **5**·2THF were taken directly from the mother liquors at -20°C , placed in perfluoropolyether oil and immediately fixed in an N_2 stream at about -120°C .

Tables of displacement parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Table 1
Crystal data, structure solution and refinement for **1**, **3** and **5**

	1 ·2THF	3 ·2THF	5 ·2THF
Cryst dimensions (mm)	$0.3 \times 0.3 \times 0.4$	$0.3 \times 0.3 \times 0.6$	$0.7 \times 0.4 \times 0.4$
Empirical formula	$\text{C}_{28}\text{H}_{52}\text{Br}_2\text{N}_4\text{O}_2\text{V}$	$\text{C}_{28}\text{H}_{52}\text{I}_2\text{N}_4\text{O}_2\text{V}$	$\text{C}_{33}\text{H}_{61}\text{I}_2\text{N}_5\text{O}_2\text{V}$
Molar mass (g mol^{-1})	687.50	781.48	864.61
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$Pnma$
Cell parameter			
a ($\text{\AA}$)	9.775(5)	9.860(2)	20.259(6)
b ($\text{\AA}$)	10.160(5)	10.329(2)	11.503(2)
c ($\text{\AA}$)	18.43(2)	18.686(4)	19.325(10)
β ($^\circ$)	104.93(5)	104.39(3)	
Number of formula units	2	2	4
Cell volume, ($\text{\AA}^3$)	1768(2)	1843.4(7)	4503(3)
Calculated density (g cm^{-3})	1.291	1.408	1.275
Linear absorption coefficient (cm^{-1})	25.7	19.7	16.2
Number of observed reflections	2732	5392	4537
Number of independent reflections	2011	4256	2576
R_{int}	0.0666	0.0217	0.0483
Number of significant reflections ($I > 2\sigma I_o$)	1151	2920	1949
Scan range, ($^\circ$)	2.29–25.05	2.15–27.56	2.27–21.00
Number of refined parameters	201	202	229
hkl region	$-2 < h < 11$, $-5 < k < 12$, $10 < l < 21$	$-1 < h < 12$, $-1 < k < 13$, $24 < l < 23$	$-24 < h < 24$, $-2 < k < 13$, $-2 < l < 23$
$F(000)$	714	786	1756
Difference Fourier synthesis			
Maximum (electrons $\text{\AA}^{-3}$)	0.628	0.981	1.036
Minimum (electrons $\text{\AA}^{-3}$)	–1.030	–0.740	–1.444
Goodness of fit	1.001	1.032	1.099
R_1 (conventional)	0.0693	0.0479	0.0793
wR_2	0.1445	0.0982	0.1699

2.3. Preparation of complexes

2.3.1. *trans*-Dibromo-tetrakis(*tert*-butylisonitrile)vanadium(II), *trans*-[VBr₂{CNC(CH₃)₃}₄] (1)

577.5 mg (1.65 mmol) of [Et₄N][V(CO)₆] dissolved in 35 ml of THF was treated with 0.75 ml of ^tBuCN and cooled to –50 °C. 3.2 ml (corresponding to 2.5 mmol of Br₂) from a freshly prepared stock solution containing 2 ml of Br₂ in 48 ml of THF was added. The solution turned red and then black. 15 min after the addition of Br₂, the CO bands had disappeared from the IR spectrum. After removal of the cold bath, the reaction mixture was warmed to room temperature within 1 h. The solution was filtered; the filtrate was concentrated to two thirds of its original volume and allowed to stand at –20 °C. Yellow crystals were isolated after 4 days. These were filtered off and dried in an N₂ stream to yield 0.68 g (1.25 mmol (76%)) of a yellow–green solid material. Anal. Found: C, 44.22; H, 6.63; N, 10.31. C₂₀H₃₆Br₂N₄V Calc.: C, 44.03; H, 6.68; N, 10.41%. IR (THF): $\nu(\text{C}\equiv\text{N})$ 2174 cm^{–1}. The $\nu(\text{V}–\text{Br})$ could not be assigned unambiguously. The magnetic moment is $\mu_{\text{eff}} = 3.98 \mu_{\text{B}}$ (μ_{B} is the Bohr magneton).

trans-[VBr₂(CNcyclo-C₆H₁₁)₄] was prepared accordingly with a 64% yield. Anal. Found: C, 51.26; H, 6.53, N, 8.62. C₂₈H₄₄Br₂N₄V Calc.: C, 51.95; H, 6.85; N, 8.65; IR (THF): $\nu(\text{C}\equiv\text{N})$ 2168 cm^{–1} $\mu_{\text{eff}} = 3.95 \mu_{\text{B}}$.

2.3.2. *trans*-Dibromo-tetrakis(pyridine)vanadium(II), *trans*-[VBr₂(C₅H₅N)₄]

Efforts to prepare **1** with pyridinium bromide as the brominating agent led to the known [13] compound

Table 2
Bond lengths (Å) and bond angles (°) of **1**, **3** and **5**

	1 (X = Br)	3 (X = I)	5 (X = I)
<i>Bond lengths</i>			
V–X(1)	2.598(2)	2.7909(6)	2.74(2)
V–C(1)	2.160(10)	2.141(5)	2.10(2)
V–C(2)	2.145(14)	2.145(5)	2.12(2)
C–C(3)			2.12(2)
C(1)–N(1)	1.139(12)	1.151(6)	1.16(2)
C(2)–N(2)	1.150(14)	1.140(7)	1.16(2)
C(3)–N(3)			1.14(2)
N(1)–C(10)	1.467(11)	1.457(7)	1.45(2)
N(2)–C(20)	1.464(14)	1.460(6)	1.47(2)
N(3)–C(30)			1.49(2)
<i>Bond angles</i>			
X(1)–V–C(1)	90.9(3)	85.93(13)	173.4(5)
X(1)–V–C(2)	85.5(3)	91.2(2)	91.3(3)
C(1)–V–C(2)	93.2(4)	92.6(2)	83.8(5)
V–C(1)–N(1)	177.2(10)	171.3(4)	172(2)
V–C(2)–N(2)	171.3(11)	176.7(5)	169.1(11)
V–C(3)–N(3)			171.6(11)
C(1)–N(1)–C(10)	177.1(10)	168.7(5)	179.8(13)
C(2)–N(2)–C(20)	170.0(14)	176.7(5)	176.0(12)
C(3)–N(3)–C(30)			179.0(13)
Average CMe ₃	109.4	109.5	109.2

Table 3

Atomic coordinates and anisotropic displacement parameters U_{ij} for VBr₂(CN^tBu)₄–2THF

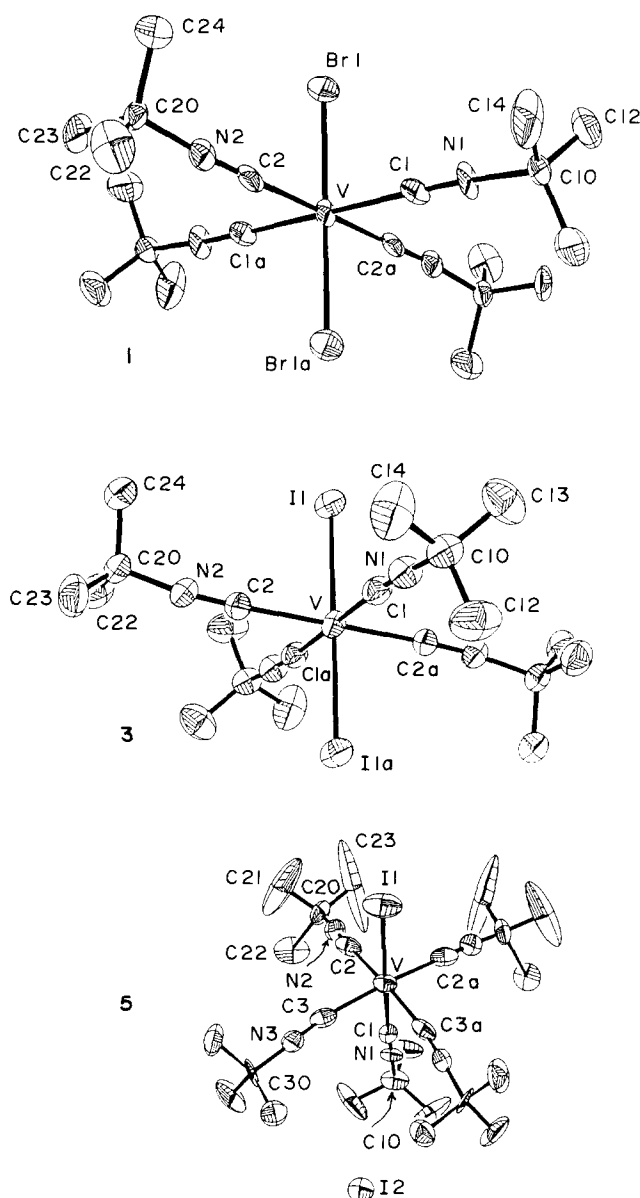
	<i>x</i> (× 10 ^{–4})	<i>y</i> (× 10 ^{–4})	<i>z</i> (× 10 ^{–4})	<i>U</i> _{eq} (× 10 ^{–1} pm ²)
Br(1)	2103(2)	8352(1)	286(1)	44(1)
V(1)	0	10000	0	30(1)
N(1)	1037(12)	11239(8)	1708(4)	41(4)
N(2)	–1765(11)	7494(9)	433(4)	31(3)
C(1)	666(13)	10781(10)	1126(6)	40(5)
C(2)	–1187(12)	8431(12)	324(5)	34(4)
C(11)	1481(13)	11891(10)	2442(5)	38(5)
C(12)	3083(14)	12129(15)	2594(7)	59(6)
C(13)	690(17)	13140(13)	2418(6)	66(6)
C(14)	1199(22)	10938(13)	3010(6)	70(7)
C(21)	–2334(15)	6183(9)	507(6)	36(5)
C(22)	–3612(19)	6313(15)	855(8)	63(6)
C(23)	–2776(21)	5627(11)	–282(7)	65(6)
C(24)	–1138(19)	5401(12)	997(8)	69(6)
O(1)	7030(14)	1339(12)	2145(6)	102(5)
C(3)	5969(15)	–11(13)	1096(7)	57(5)
C(4)	5188(22)	1269(13)	1076(9)	75(7)
C(5)	6269(21)	2161(16)	1582(9)	77(7)
C(6)	7155(20)	119(18)	1806(9)	91(7)

trans-[VBr₂(C₅H₅N)₄]: 716 mg (4.47 mmol) of [Hpy]Br and 524 mg (1.5 mmol) of [Et₄N][V(CO)₆] dissolved in 40 ml of THF were treated with 0.67 ml (6.0 mmol) of ^tBuNC and stirred for 10 min. The reaction mixture was then irradiated with UV until the IR spectrum no longer showed CO bands (about 15 h). The solution was filtered; the filtrate was concentrated to two thirds of its original volume and placed at –20 °C. Compound **6** was isolated as a red–brown solid after 2 days (yield, 76%).

2.3.3. *trans*-Diodo-tetrakis(*tert*-butylisonitrile)vanadium(II), *trans*-[VI₂{CNC(CH₃)₃}₄] (3)

560 mg (1.6 mmol) of [Et₄N][V(CO)₆] was dissolved in 30 ml of THF and cooled to about –50 °C. Addition of 0.72 ml (6.4 mmol) of ^tBuNC and 609 mg (2.4 mmol) of I₂ immediately turned the solution red. Stirring for 30 min led to a brown solution and, after further stirring for 12 h and warming to room temperature, a black suspension was obtained, from which [Et₄N]I was removed by filtration. The filtrate was treated with 0.5 ml of *n*-pentane and allowed to stand at –20 °C to yield yellow crystals within 7 days, enveloped by a thin, microscopically visible green layer. The crystals were filtered off and dried in an N₂ stream, whereupon the material turned chrome green (yield, 0.71 g, (1.11 mmol (70%))), Anal. Found: C, 36.62; H, 5.41; N, 8.45. C₂₀H₃₆I₂N₄V Calc.: C, 37.69; H, 5.69; N, 8.79%. IR (THF): $\nu(\text{C}\equiv\text{N})$ 2160, $\nu(\text{V}–\text{I})$ 337 cm^{–1} $\mu_{\text{eff}} = 3.97 \mu_{\text{B}}$.

trans-[VI₂(CNcyclo-C₆H₁₁)₄] (**4**) was prepared accordingly with yields of 54%. Anal. Found: C, 44.88; H, 5.85; N, 8.10. C₂₈H₄₄I₂N₄V: Calc.: C, 45.36; H,



cyclic nitrogen bases HB^+ to act as oxidizing agents towards $[\text{M}(\text{CO})_6]^-$ (where M is mainly V), via the intermediate formation of a contact-ion pair $[\text{HB}][\text{M}(\text{CO})_6]$, has been described in detail by Calderazzo et al. [12b,c]. The reaction according to Eq. 1 is an oxidation of V^{I} to V^{II} by the halogen. The intermediate red colouration of the solution after addition of the halogen has formerly also been observed in the preparation of the seven-coordinated V^{I} and Nb^{I} halides $\text{MX}(\text{CO})_{3/4}(\text{PR}_3)_{3/2}$ and traced back to the intermediate formation of $[\{\text{M}(\text{CO})_3\}_2(\mu\text{-X})_3]^+$ [14].

The complexes show a single CNR stretching frequency at 2160 ($\text{R} = \text{tBu}$) or 2167 ($\text{R} = \text{Cy}$) cm^{-1} , in accord with the *trans* positions of the two halide ligands. As in the V^{II} isonitrile complexes $[\text{V}(\text{tBuNC})_6]^{2+}$ ($\nu(\text{CN}) = 2197 \text{ cm}^{-1}$ [8a]) and $[\text{V}(\text{tBuNC})_2(\text{dmpe})_2]^{2+}$ ($\nu(\text{CN}) = 2150 \text{ cm}^{-1}$ [8b]), the wavenumber ν_{coord} for the coordinated isonitrile is slightly higher than the wavenumber ν_{free} for the free isonitrile. The difference $\Delta\nu = \nu_{\text{coord}} - \nu_{\text{free}}$ amounts to 28 (4) or 26 cm^{-1} (3). This shift to higher wavenumbers is typical for isonitriles bonded to mono and dipositive metal centres and indicative of negligible π back donation and strengthening of the CN bond by the inductive effect of the positively charged metal ion [15]. Compound 5, which

has been obtained in the form of red–brown crystals, shows the expected three $\nu(\text{CN})$ (2195m, 2175s, 2159s cm^{-1}). Coprecipitating with 5 is a blue–black powder with a single $\nu(\text{CN})$ at 2201 cm^{-1} and no band assignable to the V–I stretching frequency (compare $\nu(\text{V–I}) = 337 \text{ cm}^{-1}$ for 3 and 346 cm^{-1} for 4), which possibly represents the cation $[\text{V}(\text{CN}^{\text{tBu}})_6]^{2+}$ (reported [8a] $\nu(\text{CN}) = 2197 \text{ cm}^{-1}$).

The magnetic behaviour of 1–4, $\mu_{\text{eff}} = (3.95\text{--}3.99)\mu_{\text{B}}$, is that of a high spin d^3 system with spin-only contributions to the susceptibility.

3.2. X-ray structure determinations

Fig. 1 represents ORTEP plots and the numbering schemes for the three complexes. Crystal data are contained in Table 1 in the experimental section. Table 2 summarizes selected bonding parameters. Fractional coordinates and isotropic displacement parameters of the non-hydrogen atoms are given in Tables 3–5.

Compounds 1 and 3 crystallize in the monoclinic space group $P2_1/n$ with almost ideal octahedral geometry and normal bond parameters, i.e. they compare, as far as the V^{II} -isonitrile moieties are concerned, with those of the cations $[\text{V}(\text{tBuNC})_6]^{2+}$ and *trans*- $[\text{V}(\text{tBuNC})_2(\text{dmpe})_2]^{2+}$ [8], and with *trans*- $[\text{VBr}_2(\text{dmpe})_2]$ ($d(\text{V–Br}) = 2.607(2) \text{ \AA}$) and *trans*- $[\text{VI}_2(\text{dmpe})_2]$ ($d(\text{V–I}) = 2.827(2) \text{ \AA}$) with respect to the $\text{V}^{\text{II}}\text{--X}$ bond lengths [2d]. The bonding parameters of 5 fit into this scheme as well. Compound 5 crystallizes in the orthorhombic space group $Pnma$. The molecule is bisected by a mirror plane containing the atoms I(1), V, C(1), N(1), C(10), C(12) and (the ionically bound) I(2). The closest contacts for I(2) are those to H- atoms of neighbouring $^{\text{tBu}}$ groups (3.35–3.58 $\text{\AA}$). In all three complexes, the average angle at the tertiary carbon of the $^{\text{tBu}}$ group is that of an ideal tetrahedron.

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References and notes

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Table 5
Atomic coordinates and isotropic displacement factors for $[\text{VI}_2(\text{CN}^{\text{tBu}})_5]\text{I} \cdot 2\text{THF}$

	<i>x</i> ($\times 10^{-4}$)	<i>y</i> ($\times 10^{-4}$)	<i>z</i> ($\times 10^{-4}$)	<i>U</i> _{eq} ($\times 10^{-1} \text{ pm}^2$)
V(1)	4314(1)	2500	3140(2)	38(1)
I(1)	5377(1)	2500	4019(1)	71(1)
I(2)	3754(1)	2500	150(1)	52(1)
N(1)	2907(8)	2500	2334(7)	37(4)
N(2)	3456(5)	696(10)	4085(6)	43(3)
N(3)	4939(5)	686(10)	2025(6)	41(3)
C(1)	3433(11)	2500	2570(10)	41(5)
C(2)	3816(6)	1262(14)	3760(6)	45(4)
C(3)	4730(6)	1257(13)	2456(7)	45(4)
C(10)	2250(9)	2500	2041(10)	51(6)
C(11)	2202(8)	1412(18)	1612(10)	109(8)
C(12)	1770(10)	2500	2639(10)	76(8)
C(20)	2963(7)	12(11)	4465(7)	50(4)
C(21)	3240(13)	−1019(22)	4742(15)	205(18)
C(22)	2657(18)	−739(32)	3865(17)	88(13)
C(23)	2723(22)	710(22)	5019(23)	410(44)
C(22*)	2310(13)	304(31)	4209(22)	78(13)
C(30)	5224(6)	−53(10)	1469(7)	44(4)
C(31)	5748(8)	−823(12)	1784(8)	69(5)
C(32)	5496(7)	750(13)	925(7)	55(4)
C(33)	4675(8)	−741(14)	1170(8)	80(6)
O(1)	5162(20)	2500	6687(17)	192(15)
C(40)	5069(23)	1538(32)	6253(25)	320(39)
C(41)	4458(9)	1895(18)	6061(9)	202(17)
O(2)	2509(9)	2500(18)	6895(9)	298(25)
C(50)	1921(9)	2500(18)	6708(9)	219(29)
C(51)	1707(9)	1705(18)	7264(9)	262(73)
C(52)	2363(9)	1273(18)	7632(9)	93(13)
C(53)	2824(9)	1993(18)	7420(9)	130(23)

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