# Supporting Information for the Paper Titled: 

Two-electron Reduction of a Vanadium(V) Nitride by CO to Release Cyanate and Open a Coordination Site

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## S1. Synthetic Details

General Considerations. All manipulations were carried out either in a Vacuum Atmospheres model MO-40M glovebox under an atmosphere of $\mathrm{N}_{2}$ or using standard Schlenk techniques. All solvents except for tetrahydrofuran (THF) were degassed and dried using the method of Grubbs. ${ }^{1}$ THF was dried initially using an MBraun SPS and dried further by stirring with Na metal for 24 h followed by filtration through Celite and alumina to remove NaOH . After purification, all solvents were stored under an atmosphere of $\mathrm{N}_{2}$ over $4 \AA$ molecular sieves. Deuterated benzene (Cambridge Isotope Labs) was dried by stirring over $\mathrm{CaH}_{2}$ for 24 h and was subsequently vacuum-transferred onto $4 \AA$ molecular sieves. $\mathrm{KC}_{8}$ was prepared by melting potassium over graphite at $200^{\circ} \mathrm{C}$ under an atmosphere of argon. All other reagents were used as supplied by the vendor without further purification. Celite 435 (EMD Chemicals), alumina (Aldrich) and $4 \AA$ molecular sieves were dried prior to use by heating at $200^{\circ} \mathrm{C}$ for 48 h under dynamic vacuum. All glassware was oven dried at $220^{\circ} \mathrm{C}$ prior to use. NMR spectra were obtained on either a Bruker 400-AVANCE spectrometer equipped with a Magnex Scientific superconducting magnet or a Varian Mercury 300 spectrometer equipped with an Oxford Instruments Ltd. superconducting magnet. UV/Vis spectra were collected on a HP8453 spectrophotometer using 1 cm quartz cells manufactured by Starna. Proton NMR spectra were referenced to residual $\mathrm{C}_{6} \mathrm{D}_{5} \mathrm{H}(7.16$ ppm). IR spectra were collected on a Perkin-Elmer 2000 FT-IR spectrophotometer. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN.

Synthesis of 1-V(NCO). A solution of $1-\mathrm{V}(0.579 \mathrm{~g}, 1.0 \mathrm{mmol})$ in THF $(10 \mathrm{~mL})$ was cooled to -196 ${ }^{\circ} \mathrm{C}$. A slurry of $\mathrm{AgOCN}(0.150 \mathrm{~g}, 1.0 \mathrm{mmol})$ in THF ( 3 mL ) was cooled to $-196{ }^{\circ} \mathrm{C}$. The two mixtures were allowed to partially thaw and were subsequently combined. The reaction mixture was stirred and allowed to warm to an ambient temperature of $23^{\circ} \mathrm{C}$. The color of the mixture changed from green to black as the reaction progressed. After stirring for one hour, the reaction mixture was filtered through a plug of Celite and a sintered glass frit. The filtrate was dried under reduced pressure to give a black residue. The residue was dissolved in a minimum volume of $n$-pentane and stored at $-35^{\circ} \mathrm{C}$. After standing for 18 hours, black crystals had formed and were collected via vacuum filtration on a sintered glass frit. The crystals were dried under reduced pressure. Yield: $0.416 \mathrm{~g}(67 \%) .{ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$, $20^{\circ} \mathrm{C}, 300 \mathrm{MHz}, \delta$ ): 2.20 (br). IR (KBr, thin film): 2974, 2917, 2863, 2207, $1599,1585 \mathrm{~cm}^{-1} . \mu_{\text {eff }}$ (Evans's Method, ${ }^{2}$ benzene $-d_{6}$ ): $2.0 \mu_{\mathrm{B}}$. UV/Vis ( $22{ }^{\circ} \mathrm{C}$, THF) $\lambda_{\text {max }}, \mathrm{nm}(\varepsilon): 360$ (8500), 490 (3200), 600 (2600). Elem. anal. Calcd for $\mathrm{C}_{37} \mathrm{H}_{54} \mathrm{~N}_{4} \mathrm{OV}$ : C, 71.47 ; H, 8.75; N, 9.01. Found: C, 71.24; H, 8.64; N, 9.08.


Figure S1 X-Band EPR spectrum of $1-\mathrm{V}(\mathrm{NCO})$, benzene solution at $20^{\circ} \mathrm{C}, g=1.97, a=6.44 \times 10^{-3} \mathrm{~cm}^{-1}$.


Figure S2. IR spectrum of $\mathbf{1}-\mathrm{V}(\mathrm{NCO})$ as a thin film on KBr plates.

Reduction of $\mathbf{1 - V}(\mathbf{N C O})$ with $\mathbf{N a} / \mathbf{H g}$. A solution of $\mathbf{1 - V}(\mathrm{NCO})(0.575 \mathrm{~g}, 0.92 \mathrm{mmol})$ in THF ( 15 mL ) was prepared. The sodium amalgam ( $0.5 \%$ ) was prepared in a scintillation vial and 5 mL of THF was added. The solution of $1-\mathrm{V}(\mathrm{NCO})$ was added to the stirring amalgam at $23^{\circ} \mathrm{C}$ using a pasteur pipet.

The originally black solution of $1-\mathrm{V}(\mathrm{NCO})$ gradually changed to a deep green color over the course of 30 min . After stirring for one hour, the solution was decanted away for the amalgam and filtered through a plug of Celite on a sintered glass frit. The volatile components of the reaction mixture were removed under reduced pressure. The brown residue was then extracted with n-pentane ( $4 \times 10 \mathrm{~mL}$ ) and filtered through a second plug of Celite on a sintered glass frit. The brown/green filtrate solution was then concentrated to a volume of $\sim 7 \mathrm{~mL}$ and subsequently stored at $-35^{\circ} \mathrm{C}$. After standing for 48 $h$, brown microcrystals had formed. The mother liquor was decanted from the crystals of $\mathbf{1}-\mathrm{V}$ and the solids were dried under reduced pressure. Yield: $0.396 \mathrm{~g}(74 \%)$. Spectroscopic data have been reported previously. ${ }^{3}$ Characterization of the sodium cyanate was not completed due to complications associated with separating the salt by-product from the $\mathrm{Na} / \mathrm{Hg}$.

Reduction of $\mathbf{1 - V}(\mathbf{N C O})$ with $\mathrm{KC}_{\mathbf{8}}$. A solution of $\mathbf{1 - V}(\mathrm{NCO})(0.320 \mathrm{~g}, 0.55 \mathrm{mmol})$ in THF ( 10 mL ) was prepared and cooled to $-108^{\circ} \mathrm{C}$. A suspension of $\mathrm{KC}_{8}(0.075 \mathrm{~g}, 0.55 \mathrm{mmol})$ in THF ( 5 mL ) was prepared and cooled to $-108{ }^{\circ} \mathrm{C}$. The two mixtures were allowed to partially thaw and were subsequently combined. The reaction mixture was stirred and allowed to warm to $23{ }^{\circ} \mathrm{C}$. The color changed from black to a deep turquoise after 1 minute of stirring. The reaction mixture was allowed to stir at $23{ }^{\circ} \mathrm{C}$ for 30 minutes. After stirring, the volatile components of the reaction mixture were removed under reduced pressure. The green residue was extracted with $n$-hexane and subsequently filtered through a plug of Celite on a sintered glass frit. The solvent was removed from the filtrate under reduced pressure, and the resulting green solids were dissolved in a minimum volume of $n$ pentane. The solution was stored at $-35^{\circ} \mathrm{C}$. After standing for 24 h , dark green crystals had formed and were isolated by decanting away the mother liquor and subsequently drying them under reduced pressure. Yield: $0.217 \mathrm{~g}(68 \%)$. The solids that were not soluble in $n$-hexane were removed from the box and extracted into water. A solution of $\mathrm{AgNO}_{3}$ in water was added to give an off-white precipitate. The precipitate was collected on a sintered glass frit washed with ethanol, then acetone, then petroleum ether, and dried in a vacuum desiccator for 12 h . Yield: 0.060 g ( $73 \%$ ). IR ( KBr , Nujol mull): $v_{\mathrm{NCO}}$ $2219 \mathrm{~cm}^{-1}$.

Reaction of $\mathbf{C O}$ with $\mathbf{N a}[\mathbf{1 - V N}]$. A solution of $\mathrm{Na}[\mathbf{1 - V N}](3.8 \mathrm{~g}, 6.2 \mathrm{mmol})$ in THF ( 150 mL ) was placed in a 500 mL round bottom Schlenk flask. The flask was partially evacuated and the headspace was backfilled with an atmosphere of CO. The pressure of CO was maintained at an ambient pressure of 1 atm by maintaining a flow of one bubble every two seconds through a mineral oil bubbler that was connected to the Schlenk line. The reaction mixture was stirred at $23^{\circ} \mathrm{C}$ for 24 h using a magnetic stir bar. During the course of the reaction the color of solution changed from bright yellow to a deep forest green. After 24 hours, the volatile components of the reaction mixture were removed under reduced pressure. The green/brown residue was extracted with $n$-hexane ( 200 mL ) and filtered through a sintered glass frit. The gray solids collected on the frit were washed twice with $n$-hexane ( 15 mL ) and then dried under reduced pressure. The filtrate was taken to dryness under reduced pressure. The green/brown residue from the filtrate was dissolved in a minimum of $n$-pentane and stored at $-35^{\circ} \mathrm{C}$ to give green crystals of $\mathbf{1 - V}$. Yield: $2.59 \mathrm{~g}(71 \%)$ in two crops. The sodium cyanate collected in the initial filtration was dissolved in water and filtered through a plug of Celite to give a colorless solution. An aqueous solution of silver nitrate was added to the filtrate to form a white precipitate. The precipitate was collected on a tared, sintered glass frit, washed twice with ethanol ( 10 mL ), twice with diethyl ether ( 10 mL ), and subsequently dried in a vacuum desicator for 24 hours. Yield: 0.713 g (77\%). IR (KBr, Nujol mull): $v_{\mathrm{NCO}} 2199 \mathrm{~cm}^{-1}$.


Figure S3. The ${ }^{13} \mathrm{C}$ NMR spectrum of isolated sodium cyanate in water from the reaction of ${ }^{13} \mathrm{CO}$ with $\mathrm{Na}[1-\mathrm{VN}](100 \mathrm{MHz})$. The resonance at 49.5 ppm is methanol used as an internal reference.

S2. Electrochemical Measurements. Electrochemical measurements were made using a BAS CV-50W potentiostat with a platinum disk working electrode, platinum wire counter electrode, and a silver wire pseudoreference electrode. Potentials were internally referenced to the ferrocene/ferrocenium redox couple at 0 mV . Measurements were made under an atmosphere of dinitrogen using THF solutions of 0.2 M tetra( $n$-butyl)ammonium pentafluorophenylborate, which was synthesized using modified literature methods. ${ }^{4}$ The cyclic voltammogram of $1-\mathrm{V}(\mathrm{NCO})$ was collected at various sweep rates between 10 to $300 \mathrm{mV} / \mathrm{s}$. The cyclic voltammogram of $1-\mathrm{Nb}(\mathrm{NCO})$ was collected at a sweep rate of $300 \mathrm{mV} / \mathrm{s}$.


Figure S 4. CV of $\mathbf{1 - V ( N C O ) , ~} 0.2 \mathrm{M}$ solution of $\left[(n-\mathrm{Bu})_{4} \mathrm{~N}\right]\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}\right]$, sweep rate $=300 \mathrm{mV} / \mathrm{s}$.


Figure S5. CV of 1-V(NCO), 0.2 M solution of $\left[(n-\mathrm{Bu})_{4} \mathrm{~N}\right]\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}\right]$, sweep rate $=10 \mathrm{mV} / \mathrm{s}$.


Figure S6. CV of $\mathbf{1 - N b}(\mathrm{NCO}), 0.2 \mathrm{M}$ solution of $\left[(n-\mathrm{Bu})_{4} \mathrm{~N}\right]\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}\right]$, sweep rate $=300 \mathrm{mV} / \mathrm{s}$. The redox event at -1.8 V is attributed to a low concentration impurity.

S3. Crystallographic Structure Determination. Low-temperature data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated $\mathrm{Mo} / \kappa$ radiation ( $\lambda=0.71073 \AA$ ), performing $\omega$ - and $\varphi$-scans. All structures were solved either by direct or Patterson methods using SHELXS and refined against $\mathrm{F}^{2}$ on all data by full-matrix least squares with SHELXL-97. ${ }^{5}$ A semi-emperical absorption correction (SADABS) was applied to the diffraction data for all structures. ${ }^{6}$ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to ( 1.5 times for methyl groups).

Complex 1-V(NCO) crystallizes in the space group $P 2_{1} / c$, and the structure was solved using direct methods. Refinement proceeded by assigning atom positions according to the electrondensity difference map. No restraints were used in the refinement.

Table 1. Crystal data and structure refinement for $\mathbf{1 - V}(\mathrm{NCO})$.

Identification code
Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group

07214
C37 H54 N4 O V
621.78

100(2) K
$.71073 \AA$
Monoclinic
P2(1)/c


Table 2. Atomic coordinates ( $\mathrm{x} 10^{4}$ ) and equivalent isotropic displacement parameters ( $\AA^{2} \times 10^{3}$ ) for $07214 . \mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| V(1) | 7785(1) | 4653(1) | 985(1) | 11(1) |
| $\mathrm{O}(41)$ | 8071(1) | 2929(1) | -1019(1) | 39(1) |
| $\mathrm{N}(1)$ | 7956(1) | 3072(1) | 1386(1) | 13(1) |
| N(2) | 6855(1) | 5386(1) | 1126(1) | 14(1) |
| N(3) | 8560(1) | 5817(1) | 1237(1) | 13(1) |
| N(4) | 7725(1) | 4202(1) | -45(1) | 18(1) |
| C(11) | 7282(1) | 2440(1) | 1558(1) | 14(1) |
| $\mathrm{C}(12)$ | 7130(1) | 2216(1) | 2282(1) | 15(1) |
| C(13) | 6494(1) | 1557(1) | 2443(1) | 16(1) |
| C(14) | 6006(1) | 1141(1) | 1871(1) | 18(1) |
| C(15) | 6135(1) | 1397(1) | 1149(1) | 18(1) |
| C(16) | 6777(1) | 2045(1) | 996(1) | 16(1) |
| C(131) | 6324(1) | 1316(1) | 3223(1) | 21(1) |
| C(151) | 5575(1) | 1008(2) | 544(1) | 26(1) |
| C(17) | 8620(1) | 2212(1) | 1376(1) | 16(1) |
| $\mathrm{C}(171)$ | 8854(1) | 1740(2) | 2142(1) | 25(1) |
| C(172) | 9271(1) | 2903(1) | 1073(1) | 22(1) |
| C(173) | 8428(1) | 1095(1) | 877(1) | 25(1) |
| C(21) | 6447(1) | 4983(1) | 1729(1) | 15(1) |
| C(22) | 6733(1) | 5231(1) | 2437(1) | 16(1) |
| C(23) | 6353(1) | 4849(1) | 3038(1) | 19(1) |
| C(24) | 5674(1) | 4241(1) | 2920(1) | 19(1) |
| C(25) | 5375(1) | 3976(1) | 2218(1) | 18(1) |
| C(26) | 5768(1) | 4340(1) | 1628(1) | 17(1) |
| C(231) | 4650(1) | 3269(2) | 2105(1) | 24(1) |
| C(251) | 6690(1) | 5089(2) | 3798(1) | 31(1) |
| C(27) | 6485(1) | 6387(1) | 655(1) | 19(1) |
| C(271) | 7076(1) | 7072(2) | 254(1) | 25(1) |
| C(272) | 5926(1) | 5822(2) | 90(1) | 46(1) |
| C(273) | 6099(1) | 7337(2) | 1124(1) | 45(1) |
| C(31) | 8543(1) | 6194(1) | 1986(1) | 14(1) |


| $\mathrm{C}(32)$ | $8846(1)$ | $5417(1)$ | $2539(1)$ | $16(1)$ |
| :--- | ---: | ---: | ---: | ---: |
| $\mathrm{C}(33)$ | $8813(1)$ | $5732(1)$ | $3273(1)$ | $18(1)$ |
| $\mathrm{C}(34)$ | $8473(1)$ | $6844(1)$ | $3448(1)$ | $20(1)$ |
| $\mathrm{C}(35)$ | $8165(1)$ | $7643(1)$ | $2909(1)$ | $19(1)$ |
| $\mathrm{C}(36)$ | $8203(1)$ | $7307(1)$ | $2183(1)$ | $17(1)$ |
| $\mathrm{C}(331)$ | $9134(1)$ | $4866(2)$ | $3858(1)$ | $27(1)$ |
| $\mathrm{C}(351)$ | $7779(1)$ | $8829(2)$ | $3112(1)$ | $32(1)$ |
| $\mathrm{C}(37)$ | $9149(1)$ | $6457(1)$ | $825(1)$ | $15(1)$ |
| $\mathrm{C}(371)$ | $9126(1)$ | $5946(1)$ | $52(1)$ | $17(1)$ |
| $\mathrm{C}(372)$ | $9040(1)$ | $7877(1)$ | $779(1)$ | $21(1)$ |
| $\mathrm{C}(373)$ | $9921(1)$ | $6220(2)$ | $1208(1)$ | $21(1)$ |
| $\mathrm{C}(41)$ | $7900(1)$ | $3557(1)$ | $-525(1)$ | $20(1)$ |

Table 3. Bond lengths [ $\AA$ ] and angles [ ${ }^{\circ}$ ] for 07214.

| $\mathrm{V}(1)-\mathrm{N}(1)$ | 1.8701(12) |
| :---: | :---: |
| $\mathrm{V}(1)-\mathrm{N}(2)$ | 1.8823(12) |
| $\mathrm{V}(1)-\mathrm{N}(3)$ | 1.9055(11) |
| $\mathrm{V}(1)-\mathrm{N}(4)$ | 1.9552(12) |
| $\mathrm{O}(41)-\mathrm{C}(41)$ | 1.1888(19) |
| $\mathrm{N}(1)-\mathrm{C}(11)$ | 1.4425(17) |
| $\mathrm{N}(1)-\mathrm{C}(17)$ | 1.5093(17) |
| $\mathrm{N}(2)-\mathrm{C}(21)$ | 1.4379(17) |
| $\mathrm{N}(2)-\mathrm{C}(27)$ | 1.5082(18) |
| $\mathrm{N}(3)-\mathrm{C}(31)$ | 1.4399(17) |
| $\mathrm{N}(3)-\mathrm{C}(37)$ | 1.5085(17) |
| $\mathrm{N}(4)-\mathrm{C}(41)$ | 1.1823(19) |
| $\mathrm{C}(11)-\mathrm{C}(16)$ | 1.3962(19) |
| $\mathrm{C}(11)-\mathrm{C}(12)$ | 1.4003(18) |
| $\mathrm{C}(12)-\mathrm{C}(13)$ | 1.3930(19) |
| $\mathrm{C}(13)-\mathrm{C}(14)$ | 1.399(2) |
| $C(13)-C(131)$ | 1.5118(19) |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | 1.392(2) |
| $\mathrm{C}(15)-\mathrm{C}(16)$ | 1.3919(19) |
| $\mathrm{C}(15)-\mathrm{C}(151)$ | 1.511(2) |
| $\mathrm{C}(17)-\mathrm{C}(172)$ | 1.5237(19) |
| $\mathrm{C}(17)-\mathrm{C}(171)$ | 1.532(2) |
| $\mathrm{C}(17)-\mathrm{C}(173)$ | 1.537(2) |
| $\mathrm{C}(21)-\mathrm{C}(22)$ | 1.3956(19) |
| $\mathrm{C}(21)-\mathrm{C}(26)$ | 1.4039(19) |
| $\mathrm{C}(22)$-C(23) | 1.4001(19) |
| $\mathrm{C}(23)-\mathrm{C}(24)$ | 1.388(2) |
| $\mathrm{C}(23)-\mathrm{C}(251)$ | 1.511(2) |
| $\mathrm{C}(24)$-C(25) | $1.396(2)$ |
| $\mathrm{C}(25)$-C(26) | 1.3915(19) |
| $\mathrm{C}(25)-\mathrm{C}(231)$ | 1.511(2) |
| $\mathrm{C}(27)-\mathrm{C}(271)$ | 1.523(2) |
| $\mathrm{C}(27)-\mathrm{C}(272)$ | 1.524(2) |
| C(27)-C(273) | 1.532(2) |


| $\mathrm{C}(31)-\mathrm{C}(32)$ | 1.3994 (19) |
| :---: | :---: |
| $\mathrm{C}(31)-\mathrm{C}(36)$ | 1.4019(19) |
| $\mathrm{C}(32)-\mathrm{C}(33)$ | $1.3992(19)$ |
| C(33)-C(34) | 1.390(2) |
| C(33)-C(331) | 1.510(2) |
| C(34)-C(35) | 1.400(2) |
| C(35)-C(36) | 1.3910 (19) |
| C(35)-C(351) | 1.510(2) |
| C(37)-C(371) | 1.5250 (19) |
| C(37)-C(373) | $1.5353(19)$ |
| $\mathrm{C}(37)-\mathrm{C}(372)$ | 1.540(2) |
| $\mathrm{N}(1)-\mathrm{V}(1)-\mathrm{N}(2)$ | 116.73(5) |
| $\mathrm{N}(1)-\mathrm{V}(1)-\mathrm{N}(3)$ | 113.68(5) |
| $\mathrm{N}(2)-\mathrm{V}(1)-\mathrm{N}(3)$ | 109.45(5) |
| $\mathrm{N}(1)-\mathrm{V}(1)-\mathrm{N}(4)$ | 98.98(5) |
| $\mathrm{N}(2)-\mathrm{V}(1)-\mathrm{N}(4)$ | 104.15(5) |
| $\mathrm{N}(3)-\mathrm{V}(1)-\mathrm{N}(4)$ | 113.10(5) |
| $\mathrm{C}(11)-\mathrm{N}(1)-\mathrm{C}(17)$ | 113.00(10) |
| $\mathrm{C}(11)-\mathrm{N}(1)-\mathrm{V}(1)$ | 113.31(8) |
| $\mathrm{C}(17)-\mathrm{N}(1)-\mathrm{V}(1)$ | 131.32(9) |
| $\mathrm{C}(21)-\mathrm{N}(2)-\mathrm{C}(27)$ | 115.59(11) |
| $\mathrm{C}(21)-\mathrm{N}(2)-\mathrm{V}(1)$ | 118.90(9) |
| $\mathrm{C}(27)-\mathrm{N}(2)-\mathrm{V}(1)$ | 125.51(9) |
| $\mathrm{C}(31)-\mathrm{N}(3)-\mathrm{C}(37)$ | 114.46(10) |
| $\mathrm{C}(31)-\mathrm{N}(3)-\mathrm{V}(1)$ | 110.91(8) |
| $\mathrm{C}(37)-\mathrm{N}(3)-\mathrm{V}(1)$ | 134.56(9) |
| $\mathrm{C}(41)-\mathrm{N}(4)-\mathrm{V}(1)$ | 150.57(12) |
| $\mathrm{C}(16)-\mathrm{C}(11)-\mathrm{C}(12)$ | 119.74(12) |
| $\mathrm{C}(16)-\mathrm{C}(11)-\mathrm{N}(1)$ | 119.65(12) |
| $\mathrm{C}(12)-\mathrm{C}(11)-\mathrm{N}(1)$ | 120.61(12) |
| $\mathrm{C}(13)-\mathrm{C}(12)-\mathrm{C}(11)$ | 120.32(13) |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(14)$ | 118.89(13) |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(131)$ | 120.66(13) |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{C}(131)$ | 120.43(13) |
| $\mathrm{C}(15)-\mathrm{C}(14)-\mathrm{C}(13)$ | 121.44(13) |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)$ | 118.99(13) |


| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(151)$ | 120.36(13) |
| :---: | :---: |
| $\mathrm{C}(16)-\mathrm{C}(15)-\mathrm{C}(151)$ | 120.62(13) |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(11)$ | 120.54(13) |
| $\mathrm{N}(1)-\mathrm{C}(17)-\mathrm{C}(172)$ | 109.45(11) |
| $\mathrm{N}(1)-\mathrm{C}(17)-\mathrm{C}(171)$ | 111.17(11) |
| $\mathrm{C}(172)-\mathrm{C}(17)-\mathrm{C}(171)$ | 109.14(12) |
| $\mathrm{N}(1)-\mathrm{C}(17)-\mathrm{C}(173)$ | 109.77(11) |
| $\mathrm{C}(172)-\mathrm{C}(17)-\mathrm{C}(173)$ | 107.94(12) |
| $\mathrm{C}(171)-\mathrm{C}(17)-\mathrm{C}(173)$ | 109.31(12) |
| $\mathrm{C}(22)-\mathrm{C}(21)-\mathrm{C}(26)$ | 118.76(12) |
| $\mathrm{C}(22)-\mathrm{C}(21)-\mathrm{N}(2)$ | 119.35(12) |
| $\mathrm{C}(26)-\mathrm{C}(21)-\mathrm{N}(2)$ | 121.90(12) |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(23)$ | 120.95(13) |
| $\mathrm{C}(24)-\mathrm{C}(23)-\mathrm{C}(22)$ | 118.94(13) |
| $\mathrm{C}(24)-\mathrm{C}(23)-\mathrm{C}(251)$ | 121.28(13) |
| $\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{C}(251)$ | 119.78(13) |
| $\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{C}(25)$ | 121.41(13) |
| $\mathrm{C}(26)-\mathrm{C}(25)-\mathrm{C}(24)$ | 118.86(13) |
| $\mathrm{C}(26)-\mathrm{C}(25)-\mathrm{C}(231)$ | 120.69(13) |
| $\mathrm{C}(24)-\mathrm{C}(25)-\mathrm{C}(231)$ | 120.42(13) |
| $\mathrm{C}(25)-\mathrm{C}(26)-\mathrm{C}(21)$ | 121.06(13) |
| $\mathrm{N}(2)-\mathrm{C}(27)-\mathrm{C}(271)$ | 109.18(11) |
| $\mathrm{N}(2)-\mathrm{C}(27)-\mathrm{C}(272)$ | 110.69(13) |
| $\mathrm{C}(271)-\mathrm{C}(27)-\mathrm{C}(272)$ | 108.10(13) |
| $\mathrm{N}(2)-\mathrm{C}(27)-\mathrm{C}(273)$ | 110.41(12) |
| $\mathrm{C}(271)-\mathrm{C}(27)-\mathrm{C}(273)$ | 107.96(14) |
| C(272)-C(27)-C(273) | 110.41(16) |
| $\mathrm{C}(32)-\mathrm{C}(31)-\mathrm{C}(36)$ | 118.37(12) |
| $\mathrm{C}(32)-\mathrm{C}(31)-\mathrm{N}(3)$ | 119.92(12) |
| $\mathrm{C}(36)-\mathrm{C}(31)-\mathrm{N}(3)$ | 121.67(12) |
| $\mathrm{C}(33)-\mathrm{C}(32)-\mathrm{C}(31)$ | 121.38(13) |
| $\mathrm{C}(34)-\mathrm{C}(33)-\mathrm{C}(32)$ | 118.68(13) |
| $\mathrm{C}(34)-\mathrm{C}(33)-\mathrm{C}(331)$ | 121.14(13) |
| $\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{C}(331)$ | 120.18(13) |
| $\mathrm{C}(33)-\mathrm{C}(34)-\mathrm{C}(35)$ | 121.42(13) |
| $\mathrm{C}(36)-\mathrm{C}(35)-\mathrm{C}(34)$ | 118.80(13) |


| $\mathrm{C}(36)-\mathrm{C}(35)-\mathrm{C}(351)$ | $120.65(14)$ |
| :--- | :--- |
| $\mathrm{C}(34)-\mathrm{C}(35)-\mathrm{C}(351)$ | $120.53(13)$ |
| $\mathrm{C}(35)-\mathrm{C}(36)-\mathrm{C}(31)$ | $121.36(13)$ |
| $\mathrm{N}(3)-\mathrm{C}(37)-\mathrm{C}(371)$ | $109.28(11)$ |
| $\mathrm{N}(3)-\mathrm{C}(37)-\mathrm{C}(373)$ | $109.68(11)$ |
| $\mathrm{C}(371)-\mathrm{C}(37)-\mathrm{C}(373)$ | $109.73(12)$ |
| $\mathrm{N}(3)-\mathrm{C}(37)-\mathrm{C}(372)$ | $112.83(11)$ |
| $\mathrm{C}(371)-\mathrm{C}(37)-\mathrm{C}(372)$ | $108.01(12)$ |
| $\mathrm{C}(373)-\mathrm{C}(37)-\mathrm{C}(372)$ | $107.26(12)$ |
| $\mathrm{N}(4)-\mathrm{C}(41)-\mathrm{O}(41)$ | $178.53(17)$ |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 07214 . The anisotropic displacement factor exponent takes the form: $-2 p^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| V(1) | 12(1) | 11(1) | 12(1) | 0(1) | 2(1) | $0(1)$ |
| $\mathrm{O}(41)$ | $42(1)$ | $49(1)$ | 25(1) | -17(1) | -1(1) | 16(1) |
| $\mathrm{N}(1)$ | $14(1)$ | $12(1)$ | 14(1) | $0(1)$ | 2(1) | $0(1)$ |
| $\mathrm{N}(2)$ | $14(1)$ | $15(1)$ | $13(1)$ | 2(1) | 2(1) | 1(1) |
| $\mathrm{N}(3)$ | $14(1)$ | $13(1)$ | $12(1)$ | 0(1) | 2(1) | -2(1) |
| $\mathrm{N}(4)$ | $21(1)$ | $20(1)$ | $14(1)$ | -1(1) | 3(1) | -2(1) |
| $\mathrm{C}(11)$ | $15(1)$ | $10(1)$ | $17(1)$ | $0(1)$ | $4(1)$ | -1(1) |
| $\mathrm{C}(12)$ | $16(1)$ | $13(1)$ | $16(1)$ | $-1(1)$ | $1(1)$ | $1(1)$ |
| $\mathrm{C}(13)$ | $18(1)$ | 13(1) | $19(1)$ | $2(1)$ | $5(1)$ | 2(1) |
| $\mathrm{C}(14)$ | $16(1)$ | $14(1)$ | $25(1)$ | $0(1)$ | $5(1)$ | -2(1) |
| $\mathrm{C}(15)$ | $17(1)$ | $16(1)$ | $21(1)$ | -4(1) | $1(1)$ | -2(1) |
| $\mathrm{C}(16)$ | 18(1) | $15(1)$ | $16(1)$ | -1(1) | 2(1) | -1(1) |
| $\mathrm{C}(131)$ | $21(1)$ | $21(1)$ | $21(1)$ | 5(1) | 7(1) | $0(1)$ |
| $\mathrm{C}(151)$ | $23(1)$ | 30(1) | 26(1) | -5(1) | -1(1) | -8(1) |
| $\mathrm{C}(17)$ | $16(1)$ | $14(1)$ | 18(1) | 1(1) | 3(1) | 2(1) |
| $\mathrm{C}(171)$ | 22(1) | 29(1) | 23(1) | 7(1) | 2(1) | 8(1) |
| C(172) | 18(1) | 17(1) | 33(1) | 3(1) | 10(1) | 2(1) |
| C(173) | 24(1) | 17(1) | 34(1) | -6(1) | 3(1) | 4(1) |
| C(21) | 14(1) | 14(1) | 16(1) | 1(1) | 4(1) | 2(1) |
| C(22) | 17(1) | 16(1) | 17(1) | -1(1) | 4(1) | $0(1)$ |
| C(23) | 23(1) | 18(1) | 16(1) | -2(1) | 5(1) | 1(1) |
| C(24) | 20(1) | 18(1) | 20(1) | 2(1) | 10(1) | 2(1) |
| C(25) | 15(1) | 15(1) | 24(1) | 2(1) | 5(1) | 2(1) |
| C(26) | 15(1) | 18(1) | 17(1) | 1(1) | 2(1) | 1(1) |
| C(231) | 18(1) | 25(1) | 29(1) | 2(1) | 6(1) | -4(1) |
| C(251) | 37(1) | 41(1) | 15(1) | -3(1) | 6(1) | -11(1) |
| C(27) | 17(1) | 21(1) | 20(1) | 6(1) | 2(1) | 5(1) |
| C(271) | 23(1) | 26(1) | 27(1) | 13(1) | 3(1) | 3(1) |
| C(272) | 39(1) | 55(1) | 40(1) | 26(1) | -24(1) | -19(1) |
| C(273) | 61(1) | 36(1) | 43(1) | 19(1) | 28(1) | 32(1) |
| C(31) | 14(1) | 15(1) | 14(1) | -2(1) | 2(1) | -3(1) |


| $\mathrm{C}(32)$ | $18(1)$ | $14(1)$ | $17(1)$ | $-1(1)$ | $2(1)$ | $1(1)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{C}(33)$ | $21(1)$ | $18(1)$ | $17(1)$ | $1(1)$ | $0(1)$ | $-2(1)$ |
| $\mathrm{C}(34)$ | $26(1)$ | $19(1)$ | $14(1)$ | $-4(1)$ | $2(1)$ | $-3(1)$ |
| $\mathrm{C}(35)$ | $24(1)$ | $15(1)$ | $19(1)$ | $-3(1)$ | $4(1)$ | $0(1)$ |
| $\mathrm{C}(36)$ | $19(1)$ | $15(1)$ | $17(1)$ | $0(1)$ | $2(1)$ | $0(1)$ |
| $\mathrm{C}(331)$ | $39(1)$ | $24(1)$ | $18(1)$ | $2(1)$ | $-2(1)$ | $4(1)$ |
| $\mathrm{C}(351)$ | $51(1)$ | $22(1)$ | $22(1)$ | $-4(1)$ | $6(1)$ | $13(1)$ |
| $\mathrm{C}(37)$ | $15(1)$ | $15(1)$ | $16(1)$ | $0(1)$ | $4(1)$ | $-4(1)$ |
| $\mathrm{C}(371)$ | $18(1)$ | $18(1)$ | $16(1)$ | $1(1)$ | $6(1)$ | $-3(1)$ |
| $\mathrm{C}(372)$ | $25(1)$ | $14(1)$ | $26(1)$ | $1(1)$ | $6(1)$ | $-5(1)$ |
| $\mathrm{C}(373)$ | $15(1)$ | $26(1)$ | $21(1)$ | $0(1)$ | $2(1)$ | $-5(1)$ |
| $\mathrm{C}(41)$ | $19(1)$ | $23(1)$ | $17(1)$ | $1(1)$ | $-1(1)$ | $1(1)$ |

## S4. References

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