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Supporting information for the paper entitled "Bimetallic μ-Cyanoimide Complexes Prepared by NCN Group Transfer"

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Introductory Section

Small molecules or ions comprised of combinations of the elements C, N and O hold inherent fascination due to their simplicity and their importance with respect to the global cycles that involve them. Studies in which reactive metal complexes are employed for small molecule activation can shed light on manifolds of processes that permit such substrates to be manipulated. Recent reports involving dinitrogen,[1–9] nitrous oxide,[10–16] carbon monoxide,[17–23] and cyanate[24] ion serve to exemplify this approach. The present work is concerned with cyanoimide ion, $[NCN]^{2-}$, the attributes of which as a ligand in coordination chemistry currently are not well understood.[25–29] To this end has been developed a new reagent for the synthesis of cyanoimide complexes, a reagent based on the bicyclic amine 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene (Hdbabh).[30,31]

References

1 C. E. Laplaza and C. C. Cummins, *Science*, 1995, **268**, 861.

2 C. E. Laplaza, M. J. A. Johnson, J. C. Peters, A. L. Odom, E. Kim, C. C. Cummins, G. N. George and I. J. Pickering, *J. Am. Chem. Soc.*, 1996, **118**, 8623.

3 J. C. Peters, J.-P. Cherry, J. C. Thomas, L. Baraldo, D. J. Mindiola, W. M. Davis and C. C. Cummins, *J. Am. Chem. Soc.*, 1999, **121**, 10053.

4 Y.-C. Tsai, M. J. A. Johnson, D. J. Mindiola, C. C. Cummins, W. T. Klooster and T. F. Koetzle, *J. Am. Chem. Soc.*, 1999, **121**, 10426.

5 G. K. B. Clentsmith, V. M. E. Bates, P. B. Hitchcock and F. G. N. Cloke, *J. Am. Chem. Soc.*, 1999, **121**, 10444.

6 A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1998, **120**, 437.

7 A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1997, **119**, 10104.

8 A. Caselli, E. Solari, R. Scopelliti, C. Floriani, C. Rizzoli and A. Chiesi-Villa, *J. Am. Chem. Soc.*, 2000, **122**, 3652.

9 D. J. Mindiola, K. Meyer, J.-P. F. Cherry, T. A. Baker and C. C. Cummins, *Organometallics*, 2000, **19**, 1622.

10 G. A. Vaughan, G. L. Hillhouse, R. T. Lum, S. L. Buchwald and A. L. Rheingold, *J. Am. Chem. Soc.*, 1988, **110**, 7215.

11 G. A. Vaughan, C. D. Sofield, G. L. Hillhouse and A. L. Rheingold, *J. Am. Chem. Soc.*, 1989, **111**, 5491.

12 G. A. Vaughan, G. L. Hillhouse and A. L. Rheingold, *J. Am. Chem. Soc.*, 1990, **112**, 7994.

13 A. K. List, K. Koo, G. L. Hillhouse and A. L. Rheingold, *Inorg. Chim. Acta*, 1998, **270**, 399.

14 P. T. Matsunaga, G. L. Hillhouse and A. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **115**, 2075.

15 C. E. Laplaza, A. L. Odom, W. M. Davis, C. C. Cummins and J. D.

Protasiewicz, *J. Am. Chem. Soc.*, 1995, **117**, 4999.

16 A. R. Johnson, W. M. Davis, C. C. Cummins, S. Serron, S. P. Nolan, D. G. Musaev and K. Morokuma, *J. Am. Chem. Soc.*, 1998, **120**, 2071.

17 R. E. LaPointe, P. T. Wolczanski and J. F. Mitchell, *J. Am. Chem. Soc.*, 1986, **108**, 6382.

18 D. R. Neithamer, R. E. LaPointe, R. A. Wheeler, D. S. Richeson, G. D. Van Duyne and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1989, **111**, 9056.

19 R. L. Miller, P. T. Wolczanski and A. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **115**, 10422.

20 K. J. Covert, A.-R. Mayol and P. T. Wolczanski, *Inorg. Chim. Acta*, 1997, **263**, 263.

21 M. H. Chisholm, C. E. Hammond, V. J. Johnston, W. E. Streib and J. C. Huffman, *J. Am. Chem. Soc.*, 1992, **114**, 7056.

22 J. C. Peters, A. L. Odom and C. C. Cummins, *Chem. Commun.*, 1997, 1995.

23 A. Caselli, E. Solari and C. Floriani, *J. Am. Chem. Soc.*, 2000, **122**, 538.

24 M. G. Fickes, A. L. Odom and C. C. Cummins, *Chem. Commun.*, 1997, 1993.

25 A. J. L. Pombeiro, *New. J. Chem.*, 1991, **45**, 444.

26 S. Cradock, *Inorg. Synth.*, 1974, **15**, 164.

27 L. A. Pinck and J. M. Salisbury, *Inorg. Synth.*, 1950, **3**, 39.

28 M. T. Schmidt and L. F. Audrieth, *Inorg. Synth.*, 1939, **1**, 97.

29 A. S. Gordetsov, S. V. Zimina, E. Y. Levakova and N. V. Kulagina, *Russ. J. Gen. Chem.*, 1997, **67**, 764.

30 L. A. Carpino, R. E. Padykula, D. E. Barr, F. H. Hall, J. G. Krause, R. F. Dufresne and C. J. Thoman, *J. Org. Chem.*, 1988, **53**, 2565.

31 D. E. Barr, Ph.D. Thesis, University of Amherst, MA, 1965.

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5 The spectrum shows the strong ν_{CN} at 2037 cm^{-1} shifted at higher energy from the ^{13}C isotopomer of (μ-NCN)[**2**]$_2$ at 1982 cm^{-1}. The calculated isotopomer shift using the simple harmonic oscillator model was 41 cm^{-1}. 31

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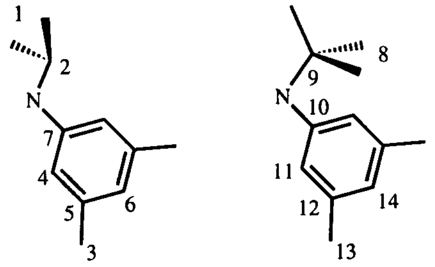

Figure 1: Numbering scheme for the disubstituted $^-$N[^{i}Pr]Ar and the $^-$N[R]Ar anilide derivatives

1 Experimental Procedure

1.1 General Considerations

Unless stated otherwise, all operations were performed in a Vacuum Atmospheres drybox under an atmosphere of purified nitrogen or using Schlenk techniques under an argon atmosphere. Anhydrous OEt_2 was purchased from Mallinckrodt; pentane, *n*-hexane, tetrahydrofuran, and acetonitrile were purchased from EM Science. OEt_2, toluene, benzene, dichloromethane, pentane and *n*-hexane were dried and deoxygenated by the method of Grubbs.[1] THF was distilled under nitrogen from purple sodium benzophenone ketyl and filtered through activated alumina. Distilled solvents were transferred under vacuum into bombs before being pumped into a Vacuum Atmospheres dry box. C_6D_6 was purchased from Cambridge Isotopes and was degassed and dried over 4 Å molecular sieves. $K^{13}CN$ was purchased from Cambridge Isotope Laboratory (CIL). (THF)U(N[R]Ar)$_3$ **3**-THF,[2,3] Mo(H)(η^2-$Me_2C{=}NAr$)(N[^{i}Pr]Ar)$_2$ **1**,[4] V(N[R]Ar)$_3$ **2**,[5,6] N-bromo-7-aza-dibenzonorbornadiene (Br*dbabh*)[7,8] were prepared according to literature procedures.

Solution infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR using CaF_2 or KBr plates. UV-vis spectra were recorded on a Hewlett-Packard 8453 diode-array spectrophotometer. Cyclic voltammetry measurements were collected with the assistance of a Eco-Chemie Autolab potentiostat (pgstat20) and the GPES 4.3 software. ^{1}H, ^{2}H and ^{13}C NMR spectra were recorded on Varian VXR-500, Varian XL-300, or Varian Unity-300 spectrometers. Chemical shifts are reported with respect to internal solvent at 7.16(s) ppm and 128.38 (t) ppm (C_6D_6). The ^{2}H chemical shift is reported with respect to external C_6D_6 (7.16 ppm). Solution magnetic susceptibility measurements were determined by ^{1}H NMR at 300, 400 or 500 MHz using the method of Evans.[9,10] Solid state magnetic susceptibility measurements were determined with a SQuID magnetometer varying the temperature from 5 to 350 K at a constant field of 1000, 3000, or 5000 G. CHN analyses were performed by H. Kolbe Mikroanalytisches Laboratorium (Mülheim an der Ruhr, Germany). Melting points were obtained in sealed glass capillaries.

1.2 Preparation of N-cyano-7-azabicyclo[2.2.1]hepta-2,5- diene (NC*dbabh*)

Method A

Br*dbabh* freshly recrystallized from hot EtOAc/EtOH (1:2) [6.32 g, 23.23 mmol] was dissolved in a minimum of CH_3CN. To the light yellow solution was added an aqueous solution of KCN [0.212 g, 32.52 mmol] (for labeled dbabhCN, $K^{13}CN$ can be conveniently replaced) causing an immediate color change to bright yellow. The yellow suspension was then stirred for 48 h at room temperature. Volatiles were removed under vacuum, and the off-white solids stirred for 1 h with 50 mL of H_2O to dissolve salts. To the suspension, OEt_2 (ca. 100 mL) was added and the mixture stirred for 30 min until two homogeneous and distinguishable layers formed (sometimes excess OEt_2 was required). The organic layer was separated, and the aqueous layered washed with additional OEt_2. The organic extracts were combined, dried with $MgSO_4$ and concentrated. Slow concentration and cooling afforded N-cyano-7- azabicyclo[2.2.1]hepta-2,5-diene (NC*dbabh*) as a white flaky solid [2.58 g, 4.58 mmol, 51% yield]. ^1H NMR (300, $CDCl_3$, 22°C): δ 7.37 (m, aryl), 7.08 (m, aryl), 5.72 (s, bridgehead) ppm. ^{13}C NMR (75.4, $CDCl_3$, 22°C): δ 72.09 (s, bridgehead), 115.8 (s, nitrile), 121.857 (d, aryl), 126.9 (d, aryl), 145.4 (s, aryl) ppm. Solution IR ($CDCl_3$, CaF_2): ν_{CN} 2228 (s), 2198 (s) (^{13}C enriched cyanamide isotopomer) and 2089 (s) cm^{-1}. Anal. calcd. for $C_{15}H_{10}N_2$: C, 82.55; H, 4.62; N, 12.83. Found: C, 82.38; H, 4.55; N, 12.72. Mp: >150°C (decomp).

Method B

To a suspension of Br*dbabh* [3.0 g, 11 mmol] in 20 mL of DMF was added Me_3SiCN [2.0 g, 20.0 mmol]. The mixture was stirred at room temperature for 3 h and poured into 50 mL of water. The white precipitate was collected on a filter frit, washed thoroughly with water and dried under vacuum. Isolated yield of crude NC*dbabh* was 2.33 g [4.14 mmol, 97%]. Powders were dissolved in CH_2Cl_2 and dried over Na_2SO_4. Re-crystallization from CH_2Cl_2/OEt_2 gave 2.01 g [3.57 mmol, 85% yield] of pure white powder.

Method C

A suspension of Br*dbabh* [0.27 g, 1.0 mmol] and AgCN [0.14 g, 1.0 mmol] in 3 mL of CH_3CN was heated to 60°C for 12 h. The resulting mixture was filtered to remove silver salts and the solvent removed under vacuum to give crude (and pure) dbabhCN as a white powder [0.22 g, 0.391 mmol, 100% yield]. Re-crystallization from OEt_2 afforded analytically pure NC*dbabh* [0.154 g, 0.273 mmol, 70% yield]

1.3 Synthesis of (μ-NCN)[2]$_2$

In a 300 mL RBF $V(N[R]Ar)_3$ **2** [0.715 g, 1.196 mmol] was dissolved in 15 mL of THF and NC*dbabh* [125 mg, 0.573 mmol] in 7 mL of THF was added slowly dropwise. The color of the reaction immediately changed from an intense brown-green to a dark-brown violet.

Monitoring of the reaction mixture by ^{2}H NMR indicated complete formation of a new paramagnetic product after 1 h. Two consecutive filtrations of the reaction mixture through activated charcoal were followed to remove generated anthracene. Solvent was removed under vacuum, and the purple-black powder (μ-NCN)[**2**]$_2$ (essentially pure by ^{1}H and ^{2}H NMR spectroscopies) [0.673 g, 0.545 mmol, 91% yield] was extracted with pentane, filtered through Celite, concentrated and cooled to -35°C to afford a dark violet analytically pure microcrystalline powder [0.300 g, 0.242 mmol, 41% yield]. M.pp: 191-193°C. ^{1}H NMR (300, C_6D_6, 22°C): δ 10.05, 5.81 and 2.55 ppm. ^{2}H NMR (46, OEt_2, 22°C): δ 6.36 ppm ($\Delta\nu_{1/2}$ = 17 Hz). Solution IR (C_6H_6, CaF_2): ν_{CN} = 2037 (s), 1982 (s) (^{13}C enriched cyanamide isotopomer) cm^{-1}. Mag. suscep. (Evans' method, 20°C): μ_{eff} = 3.01 μ_B. Mag. suscep. (SQuID, 5-300 K, 5000 G): μ_{eff} = 2.56 μ_B. Anal. calcd. for $C_{73}H_{72}D_{36}N_8V_2$: C, 70.95; H, 8.81; N, 9.07. Found: C, 70.79; H, 8.78; N, 9.15.

1.4 Synthesis of (μ-NCN)[1]$_2$

Mo(H)(η^2-Me$_2$C=NAr)(N[^{i}Pr]Ar)$_2$ **1** [0.215 g, 0.394 mmol] and NC*dbabh* [43 mg, 0.197 mmol] were mixed together in a vial. To the solid mixture 15 mL of OEt_2 was added and the reaction mixture allowed to stir for 1 h. Upon addition of the solvent, an immediate color change ocurred from orange-brown to orange. ^{1}H NMR of the crude reaction mixture showed clean and quantitative formation of (μ-NCN)[**1**]$_2$ along with anthracene. Solvent was removed under vacuum and the orange powder was extracted with THF and filtered through activated charcoal to remove anthracene generated in the reaction mixture. Solvent was again removed under vacuum, the residue extracted with OEt_2, filtered through Celite, concentrated and cooled to -35°C to afford an orange powder of pure (μ-NCN)[**1**]$_2$ [0.1531 g, 0.123 mmol, 62.6% yield]. Mp: 171-172°C. ^{1}H NMR (300, C_6D_6, 22°C): δ 6.44 (s, 6), 6.29 (s, 4), 4.86 (m, 2), 1.97 (s, 3), 1.62 (m, residual H in d_6-1) ppm. ^{13}C NMR (75.4, C_6D_6, 22°C): δ 176.08 (quintet, N*C*N, J_{CN} = 24 Hz), 151.3 (s, 7), 138.85 (s, 5), 125.84 (aryl), 123.66 (aryl), 61.43 (d, 2), 24.90 (bs, residual H in d_6-1), 21.79 (q, 3) ppm. Solution IR (C_6H_6, CaF_2): ν_{CN} = 2122 (s), 2061 (s) (^{13}C enriched cyanamide isotopomer) cm^{-1}. UV-vis (benzene): 252 nm (ϵ = 53029), 300 nm (ϵ = 26851), 391 nm (ϵ = 26324), sh 475 nm (ϵ = 17180). Anal. calcd. for $C_{67}H_{60}D_{36}N_8Mo_2$: C, 64.81; H, 10.71; N, 9.02. Found: C, 64.89; H, 10.63; N, 9.04.

1.5 Synthesis of (μ-NCN)[3]$_2$

Complex (THF)U(N[R]Ar)$_3$ **3**-THF [0.124 g, 0.148 mmol] was dissolved in 5 mL of THF and the solution frozen. To the thawing uranium solution NC*dbabh* [16.2 mg, 0.074 mmol] in 5 mL of cold THF was added slowly dropwise. The color of the reaction immediately changed from a light brown to a bright yellow. The reaction mixture was stirred for 5 min and volatiles were removed under vacuum. ^{1}H NMR inspection of the reaction showed quantitative formation of (μ-NCN)[**3**]$_2$ along with one equiv of anthracene. The yellow residue was extracted with THF and filtered through activated charcoal to remove anthracene generated in the reaction. Solvent was again removed under vacuum, and the yellow oil re-dissolved in a minimum of

C_6H_6, filtered and dried to a fine orange powder. Cooling of the OEt_2 solution with dissolved orange powder to -35°C for 36 h afforded orange crystals of pure $(\mu\text{-NCN})[\mathbf{3}]_2$ [93.4 mg, 0.059 mmol, 88.2% yield] in two crops. Mp: 181-182°C. ^1H NMR (300, C_6D_6, 22°C): δ 10.938 (s, 8, $\Delta\nu_{1/2} = 16$ Hz), -1.927 (s, 14), -1.93 (s, 14, $\Delta\nu_{1/2} = 5$ Hz) -6.951 (bs, 13, $\Delta\nu_{1/2} = 91$ Hz), -20.399 (bs, 11, $\Delta\nu_{1/2} = 3$ Hz). ^{13}C NMR (75.4, C_6D_6, 22°C): δ 133.4 (bs, N*C*N for ^{13}C enriched isotompomer, $\Delta\nu_{1/2} = 11$ Hz), 117.3, 114.1, 64.60 (s, 8), 14.00 (s, 13). Solution IR (C_6D_6, CaF_2): $\nu_{CN} = 2034$ (s), 1976 (s) (^{13}C enriched cyanamide isotopomer) cm^{-1}. UV-vis (benzene): 254 nm ($\epsilon = 62363$), sh 294 nm ($\epsilon = 20862$). Solid state Mag. suscep. (SQuID, 5-300 K, 5000 G): μ_{eff} (300 K) = 6.90 μ_B. Anal. calcd. for $C_{73}H_{108}N_8U_2$: C, 55.71; H, 6.72; N, 7.12. Found: C, 55.58; H, 7.06; N, 7.04.

1.6 Cyclic Voltammetry Measurements

Cyclic voltammetry study was performed in pre-dried solutions of THF (0.8 M solution containing pre-dried and recrystallized tetrabutylammonium hexafluorophosphate, TBAH, Aldrich). A platinum disk (1.6 mm diameter, Bioanalytical systems), a platinum wire and a silver wire were employed as the working electrode, the auxiliary and the latter as the reference electrode. A one cell compartment was used in the CV measurements. The electrochemical response was collected with the assistance of a Eco-Chemie Autolab potentiostat (pgstat20) and the GPES 4.3 software. An IR correction drop was employed due to the high resistance of this solution (a typical resistance value measured with the positive feedback technique for this solution was 975 ohms). All the potentials were reported against the ferrocenium/ferrocene couple (0 V) measured as an internal standard. All spectra were recorded at a scan rate of 100-200 mV/sec under an N_2 atmosphere. In all instances all reversible waves were subjected to scan rate dependence tests ranging from 40 to 1000 mV/sec. In a typical experiment 8-14 mg of $(\mu\text{-NCN})[\mathbf{2}]_2$, $(\mu\text{-NCN})[\mathbf{1}]_2$ or $(\mu\text{-NCN})[\mathbf{3}]_2$ was dissolved in the solution of *n*-tetrabutylammoniumhexafluorophosphate (TBAH) in THF.

1.7 Electron Paramagnetic Resonance Spectroscopy

The X-band EPR spectra were collected on a Bruker EMX spectrometer equipped with a helium flow cryostat (Oxford Instruments ESP 310) in the temperature range 20-300 K. The EPR spectrum of oxidized $(\mu\text{-NCN})[\mathbf{2}]_2$ was recorded at room temperature in toluene solution or in Et_2O/pentane mixtures. Typical concentrations ranged from 0.1 to 10 mM. To account for the m_I dependency of the linewidths and the asymmetrical hyperfine splitting (increasing hfs with increasing field) a full-matrix-diagonalization of the electron and nucleus Zeeman hyperfine coupling operator ($S = 1/2$, $I = 7/2$) plus an additional quadratic term for the m_I dependency of the linewidths were applied in the simulation. (Weihe and Bendix EPR97, J. Glerup, H. Weihe *Acta Chem. Scand.* **1991**, *45*, 444)

1.8 Density Functional Calculations on (μ-NCN)[1]$_2$

Calculations were performed on a Alpha/Linux machine using Amsterdam Density Functional (ADF) 2.3.0 (Theoretical Chemistry, Vrije Universiteit, Amsterdam).[11–17] The Becke and Perdew gradient corrections (GGA) and the VWN local density approximation (LDA) were used in all calculations. In addition, scalar relativistic corrections were used for the Mo and N atoms and all calculations were performed with unrestricted spins. The N and H atoms were treated using a double zeta basis with polarizations. In all instances, all possible structures were optimized automatically within the program in their corresponding local point group.

2 Crystal Structure Determination

2.1 Crystal structure of (μ-NCN)[1]$_2$

Crystals grown from a concentrated OEt_2 solution were coated with Paratone N oil (Exxon) on a microscope slide. A red-orange plate of approximate dimensions 0.28 x 0.24 x 0.09 mm was selected and mounted with wax on a glass fiber. A total of 15823 reflections ($-16 \leq h \leq 16$, $-19 \leq k \leq 20$, $-20 \leq l \leq 22$) were collected at 183(2) K in the θ range of 2.41 to 20.75 °, of which 10252 were unique (R_{int} = 0.1492). The radiation used was Mo-Kα (λ = 0.71073 Å, μ = 0.422 mm^{-1}). The structure was solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. Two crystallographically independent molecules were present in the asymmetric unit with one of the chemically equivalent molecules possessing an inversion center about the carbodiimide carbon. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated ($d_{\rm CH}$ = 0.96 Å) positions. The residual peak and hole electron density was 1.478 and −1.390 e·Å^{-3}. The least squares refinement converged normally with residuals of R_1=0.0764, wR_2 = 0.1894 and GOF = 1.068 based on $I > 2\sigma I$. No significant extinction coefficient was applied. Crystal and refinement data: Formula = $C_{100.50}H_{144}Mo_3N_{12}$, space group $P\bar{1}$, a = 15.219(2) Å, b = 18.043(3) Å, c = 20.510(3) Å, α = 63.998(2) °, β = 81.112(2) °, γ = 80.611(2) °, Z = 2, V = 4972.1(12) Å^3, D_{calcd} = 1.208 g·cm^{-3}, $F(000)$ = 1914, R (all data based on F) = 0.0953, wR (all data based on F^2) = 0.2153.

2.2 Crystal Structure of (μ-NCN)[3]$_2$

Crystals grown from OEt_2 at −35 °C were coated with Paratone N oil (Exxon) on a microscope slide. A yellow-orange block of approximate dimensions 0.08 x 0.05 x 0.03 mm was selected and mounted with wax on a glass fiber. A total of 12242 reflections ($-12 \leq h \leq 10$, $-21 \leq k \leq 21$, $-19 \leq l \leq 16$) were collected at 183(2) K in the θ range of 2.10 to 21.25 °, of which 4091 were unique (R_{int} = 0.0504). The radiation used was Mo-Kα (λ

$= 0.71073$ Å, $\mu = 4.413$ mm^{-1}). The structure was solved by direct methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated ($d_{\mathrm{CH}} = 0.96$ Å) positions. The residual peak and hole electron density was 0.679 and -0.888 e·Å^{-3}. The least squares refinement converged normally with residuals of R_1=0.0418, $wR_2 = 0.0770$ and GOF = 1.159 based on $I > 2\sigma I$. The extinction coefficient was 0.00024(8). Crystal and refinement data: Formula = $C_{73}H_{108}U_2N_8$, space group $P2_1/n$, $a = 10.9163(8)$ Å, $b = 19.6175(14)$ Å, $c = 17.4079(12)$ Å, $\alpha = 90$ °, $\beta = 96.8390(10)$ °, $\gamma = 90$ °, $Z = 2$, $V = 3701.4(5)$ Å^3, $D_{calcd} = 1.412$ g·cm^{-3}, $F(000) = 1572$, R (all data based on F) = 0.0557, wR (all data based on F^2) = 0.0810.

2.3 Tables for Structures

Table 1. Bond Lengths (Å) for (μ-NCN)[**1**]$_2$.

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Symmetry transformations to generate equivalent atoms:
#1 -x, -y, -z + 1

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Mo(1)-N(11)	1.861(7)
Mo(1)-N(3)	1.939(6)
Mo(1)-N(2)	1.959(7)
Mo(1)-N(1)	1.987(6)
Mo(2)-N(10)	1.864(7)
Mo(2)-N(6)	1.960(6)
Mo(2)-N(5)	1.979(7)
Mo(2)-N(4)	1.991(6)
C(1)-N(10)	1.227(10)
C(1)-N(11)	1.230(10)
C(46)-C(41)	1.384(11)
C(46)-C(45)	1.404(11)
C(151)-C(15)	1.507(12)
N(4)-C(41)	1.396(9)
N(4)-C(47)	1.479(10)
C(451)-C(45)	1.507(12)
C(44)-C(43)	1.390(11)
C(44)-C(45)	1.383(11)
C(42)-C(43)	1.368(11)
C(42)-C(41)	1.425(11)
C(11)-C(16)	1.391(10)
C(11)-N(1)	1.395(9)
C(11)-C(12)	1.395(11)
N(1)-C(17)	1.488(11)

C(61)-C(62)	1.389(11)
C(61)-C(66)	1.404(11)
C(61)-N(6)	1.430(9)
N(2)-C(21)	1.438(11)
N(2)-C(27)	1.511(12)
C(43)-C(431)	1.523(12)
C(31)-C(36)	1.376(12)
C(31)-C(32)	1.398(12)
C(31)-N(3)	1.434(10)
C(16)-C(15)	1.399(11)
N(3)-C(37)	1.492(11)
N(6)-C(67)	1.482(11)
C(34)-C(33)	1.360(14)
C(34)-C(35)	1.377(14)
C(15)-C(14)	1.390(11)
C(32)-C(33)	1.377(12)
C(331)-C(33)	1.537(13)
C(47)-C(49)	1.502(14)
C(47)-C(48)	1.542(14)
C(12)-C(13)	1.376(11)
C(21)-C(26)	1.378(13)
C(21)-C(22)	1.402(13)
C(26)-C(25)	1.46(2)
C(14)-C(13)	1.384(12)
C(51)-C(52)	1.386(13)
C(51)-C(56)	1.393(14)
C(51)-N(5)	1.434(12)
C(131)-C(13)	1.513(12)
N(5)-C(57)	1.519(13)
C(55)-C(54)	1.37(2)
C(55)-C(56)	1.39(2)
C(55)-C(551)	1.54(2)
C(17)-C(18)	1.513(14)
C(17)-C(19)	1.52(2)
C(24)-C(23)	1.35(2)
C(24)-C(25)	1.37(2)
C(52)-C(53)	1.384(13)
C(39)-C(37)	1.49(2)
C(36)-C(35)	1.389(13)
C(22)-C(23)	1.361(14)
C(37)-C(38)	1.47(2)
C(27)-C(29)	1.34(2)
C(27)-C(28)	1.48(2)
C(58)-C(57)	1.45(2)
C(53)-C(54)	1.371(14)

C(53)-C(531)	1.50(2)
C(35)-C(351)	1.50(2)
C(57)-C(59)	1.34(2)
Mo(3)-N(12)	1.852(7)
Mo(3)-N(7)	1.947(6)
Mo(3)-N(9)	1.960(7)
Mo(3)-N(8)	1.994(6)
C(2)-N(12)#1	1.233(7)
C(2)-N(12)	1.233(7)
N(8)-C(81)	1.388(9)
N(8)-C(87)	1.475(10)
C(71)-C(76)	1.385(12)
C(71)-C(72)	1.408(11)
C(71)-N(7)	1.433(10)
N(9)-C(91)	1.445(10)
N(9)-C(97)	1.502(12)
C(85)-C(84)	1.381(11)
C(85)-C(86)	1.388(10)
C(85)-C(851)	1.511(11)
C(78)-C(77)	1.49(2)
C(73)-C(74)	1.375(12)
C(73)-C(72)	1.385(11)
C(73)-C(731)	1.523(12)
C(81)-C(86)	1.409(10)
C(81)-C(82)	1.412(11)
C(831)-C(83)	1.518(12)
C(751)-C(75)	1.496(12)
C(92)-C(93)	1.365(12)
C(92)-C(91)	1.383(12)
C(951)-C(95)	1.512(14)
C(93)-C(94)	1.409(13)
C(93)-C(931)	1.534(13)
N(7)-C(77)	1.499(10)
C(83)-C(84)	1.389(11)
C(83)-C(82)	1.396(11)
C(97)-C(98)	1.49(2)
C(97)-C(99)	1.54(2)
C(95)-C(96)	1.374(12)
C(95)-C(94)	1.380(13)
C(96)-C(91)	1.407(12)
C(76)-C(75)	1.362(11)
C(74)-C(75)	1.413(11)
C(79)-C(77)	1.51(2)
C(62)-C(63)	1.385(11)
C(64)-C(63)	1.377(12)

C(64)-C(65)	1.410(12)
C(66)-C(65)	1.366(11)
C(63)-C(631)	1.498(12)
C(87)-C(88)	1.522(12)
C(87)-C(89)	1.514(12)
C(65)-C(651)	1.511(12)
C(67)-C(69)	1.48(2)
C(67)-C(68)	1.50(2)
C(25)-C(251)	1.49(2)
C(23)-C(231)	1.53(2)

Table 2. Bond Angles (°) for (μ-NCN)[**1**]$_2$.

N(11)-Mo(1)-N(3)	93.8(3)
N(11)-Mo(1)-N(2)	98.0(3)
N(3)-Mo(1)-N(2)	117.8(3)
N(11)-Mo(1)-N(1)	100.1(2)
N(3)-Mo(1)-N(1)	119.8(3)
N(2)-Mo(1)-N(1)	117.6(3)
N(10)-Mo(2)-N(6)	94.4(3)
N(10)-Mo(2)-N(5)	97.2(3)
N(6)-Mo(2)-N(5)	119.3(3)
N(10)-Mo(2)-N(4)	101.0(3)
N(6)-Mo(2)-N(4)	115.4(3)
N(5)-Mo(2)-N(4)	120.2(3)
N(10)-C(1)-N(11)	178.5(8)
C(41)-C(46)-C(45)	121.7(7)
C(41)-N(4)-C(47)	118.8(6)
C(41)-N(4)-Mo(2)	104.3(5)
C(47)-N(4)-Mo(2)	132.3(5)
C(1)-N(10)-Mo(2)	177.7(6)
C(43)-C(44)-C(45)	120.7(7)
C(1)-N(11)-Mo(1)	176.8(6)
C(43)-C(42)-C(41)	120.5(7)
C(16)-C(11)-N(1)	115.8(6)
C(16)-C(11)-C(12)	117.5(7)
N(1)-C(11)-C(12)	126.5(7)
C(11)-N(1)-C(17)	117.2(6)
C(11)-N(1)-Mo(1)	107.2(4)
C(17)-N(1)-Mo(1)	130.6(5)
C(62)-C(61)-C(66)	118.4(7)

C(62)-C(61)-N(6)	120.9(7)
C(66)-C(61)-N(6)	120.7(7)
C(46)-C(41)-N(4)	116.6(7)
C(46)-C(41)-C(42)	117.9(7)
N(4)-C(41)-C(42)	125.5(7)
C(21)-N(2)-C(27)	112.5(8)
C(21)-N(2)-Mo(1)	120.8(5)
C(27)-N(2)-Mo(1)	126.4(7)
C(42)-C(43)-C(44)	120.4(7)
C(42)-C(43)-C(431)	121.0(8)
C(44)-C(43)-C(431)	118.6(7)
C(36)-C(31)-C(32)	118.2(8)
C(36)-C(31)-N(3)	120.3(8)
C(32)-C(31)-N(3)	121.4(8)
C(11)-C(16)-C(15)	121.8(7)
C(31)-N(3)-C(37)	114.2(6)
C(31)-N(3)-Mo(1)	118.2(5)
C(37)-N(3)-Mo(1)	127.5(5)
C(44)-C(45)-C(46)	118.6(7)
C(44)-C(45)-C(451)	123.2(7)
C(46)-C(45)-C(451)	118.1(7)
C(61)-N(6)-C(67)	115.6(6)
C(61)-N(6)-Mo(2)	117.1(5)
C(67)-N(6)-Mo(2)	126.9(5)
C(33)-C(34)-C(35)	121.7(9)
C(14)-C(15)-C(16)	118.3(7)
C(14)-C(15)-C(151)	121.3(7)
C(16)-C(15)-C(151)	120.3(7)
C(33)-C(32)-C(31)	120.5(9)
N(4)-C(47)-C(49)	112.9(8)
N(4)-C(47)-C(48)	109.2(9)
C(49)-C(47)-C(48)	111.4(8)
C(13)-C(12)-C(11)	121.8(7)
C(26)-C(21)-C(22)	119.5(10)
C(26)-C(21)-N(2)	120.3(9)
C(22)-C(21)-N(2)	120.2(8)
C(21)-C(26)-C(25)	117.8(11)
C(13)-C(14)-C(15)	120.8(7)
C(52)-C(51)-C(56)	118.3(9)
C(52)-C(51)-N(5)	122.6(9)
C(56)-C(51)-N(5)	119.1(10)
C(51)-N(5)-C(57)	111.0(9)
C(51)-N(5)-Mo(2)	123.3(5)
C(57)-N(5)-Mo(2)	125.7(8)
C(12)-C(13)-C(14)	119.5(8)

C(12)-C(13)-C(131)	120.6(8)
C(14)-C(13)-C(131)	119.8(7)
C(54)-C(55)-C(56)	117.3(10)
C(54)-C(55)-C(551)	121.0(12)
C(56)-C(55)-C(551)	121.6(12)
N(1)-C(17)-C(18)	109.6(8)
N(1)-C(17)-C(19)	112.4(8)
C(18)-C(17)-C(19)	113.4(8)
C(23)-C(24)-C(25)	123.7(11)
C(55)-C(56)-C(51)	121.3(11)
C(34)-C(33)-C(32)	119.7(9)
C(34)-C(33)-C(331)	119.8(9)
C(32)-C(33)-C(331)	120.5(10)
C(51)-C(52)-C(53)	121.7(10)
C(31)-C(36)-C(35)	121.6(9)
C(23)-C(22)-C(21)	122.9(11)
C(38)-C(37)-C(39)	115.6(11)
C(38)-C(37)-N(3)	113.6(10)
C(39)-C(37)-N(3)	113.8(10)
C(29)-C(27)-C(28)	127.0(12)
C(29)-C(27)-N(2)	117.4(12)
C(28)-C(27)-N(2)	113.6(10)
C(54)-C(53)-C(52)	117.3(10)
C(54)-C(53)-C(531)	121.6(10)
C(52)-C(53)-C(531)	121.1(10)
C(34)-C(35)-C(36)	118.2(9)
C(34)-C(35)-C(351)	121.9(10)
C(36)-C(35)-C(351)	119.8(11)
C(59)-C(57)-C(58)	130(2)
C(59)-C(57)-N(5)	117(2)
C(58)-C(57)-N(5)	112.2(14)
N(12)-Mo(3)-N(7)	94.3(2)
N(12)-Mo(3)-N(9)	95.6(3)
N(7)-Mo(3)-N(9)	118.2(3)
N(12)-Mo(3)-N(8)	98.0(2)
N(7)-Mo(3)-N(8)	117.5(3)
N(9)-Mo(3)-N(8)	121.1(3)
N(12)#1-C(2)-N(12)	179.996(2)
C(81)-N(8)-C(87)	118.7(6)
C(81)-N(8)-Mo(3)	105.7(4)
C(87)-N(8)-Mo(3)	131.0(5)
C(2)-N(12)-Mo(3)	176.6(4)
C(76)-C(71)-C(72)	118.2(7)
C(76)-C(71)-N(7)	121.4(7)
C(72)-C(71)-N(7)	120.4(7)

C(91)-N(9)-C(97)	113.2(7)
C(91)-N(9)-Mo(3)	120.3(5)
C(97)-N(9)-Mo(3)	126.2(5)
C(84)-C(85)-C(86)	119.5(7)
C(84)-C(85)-C(851)	120.6(7)
C(86)-C(85)-C(851)	119.8(8)
C(74)-C(73)-C(72)	119.6(8)
C(74)-C(73)-C(731)	120.0(8)
C(72)-C(73)-C(731)	120.4(8)
N(8)-C(81)-C(86)	116.8(7)
N(8)-C(81)-C(82)	125.7(7)
C(86)-C(81)-C(82)	117.3(7)
C(85)-C(86)-C(81)	121.4(8)
C(93)-C(92)-C(91)	122.2(8)
C(92)-C(93)-C(94)	118.5(8)
C(92)-C(93)-C(931)	122.8(9)
C(94)-C(93)-C(931)	118.7(9)
C(71)-N(7)-C(77)	115.4(6)
C(71)-N(7)-Mo(3)	118.3(5)
C(77)-N(7)-Mo(3)	126.4(5)
C(73)-C(72)-C(71)	120.0(8)
C(84)-C(83)-C(82)	119.0(8)
C(84)-C(83)-C(831)	121.9(7)
C(82)-C(83)-C(831)	119.0(8)
C(98)-C(97)-N(9)	112.8(12)
C(98)-C(97)-C(99)	112.7(12)
N(9)-C(97)-C(99)	113.4(11)
C(96)-C(95)-C(94)	119.2(9)
C(96)-C(95)-C(951)	121.3(9)
C(94)-C(95)-C(951)	119.3(9)
C(83)-C(82)-C(81)	121.4(8)
C(95)-C(96)-C(91)	121.2(8)
C(75)-C(76)-C(71)	123.4(8)
C(73)-C(74)-C(75)	121.6(7)
C(92)-C(91)-C(96)	118.1(7)
C(92)-C(91)-N(9)	121.3(8)
C(96)-C(91)-N(9)	120.6(7)
C(76)-C(75)-C(74)	117.1(8)
C(76)-C(75)-C(751)	122.4(8)
C(74)-C(75)-C(751)	120.5(8)
C(78)-C(77)-N(7)	113.5(9)
C(78)-C(77)-C(79)	111.0(10)
N(7)-C(77)-C(79)	112.9(8)
C(85)-C(84)-C(83)	121.2(7)
C(61)-C(62)-C(63)	121.2(8)

C(63)-C(64)-C(65)	122.6(8)
C(65)-C(66)-C(61)	122.2(8)
C(64)-C(63)-C(62)	118.4(8)
C(64)-C(63)-C(631)	119.9(8)
C(62)-C(63)-C(631)	121.8(8)
C(55)-C(54)-C(53)	124.0(10)
N(8)-C(87)-C(88)	109.3(7)
N(8)-C(87)-C(89)	111.2(7)
C(88)-C(87)-C(89)	112.2(7)
C(95)-C(94)-C(93)	120.9(8)
C(66)-C(65)-C(64)	117.2(8)
C(66)-C(65)-C(651)	121.8(8)
C(64)-C(65)-C(651)	121.0(8)
N(6)-C(67)-C(69)	113.4(8)
N(6)-C(67)-C(68)	113.9(9)
C(69)-C(67)-C(68)	110.6(9)
C(24)-C(25)-C(26)	118.2(10)
C(24)-C(25)-C(251)	123.4(14)
C(26)-C(25)-C(251)	118.2(14)
C(22)-C(23)-C(24)	117.7(12)
C(22)-C(23)-C(231)	121.3(13)
C(24)-C(23)-C(231)	121.0(12)

Table 3. Atomic Coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for the structure of (μ-NCN)[**1**]$_2$. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Mo(1)	8286(1)	6239(1)	2634(1)	36(1)
Mo(2)	11781(1)	6954(1)	584(1)	37(1)
C(1)	10036(6)	6571(5)	1610(4)	42(2)
C(46)	13484(5)	6619(5)	-27(4)	42(2)
C(151)	5596(6)	5778(6)	4291(5)	61(2)
N(4)	12490(4)	5846(4)	961(3)	45(2)
C(451)	14421(6)	7578(5)	-1072(5)	58(2)
N(10)	10735(4)	6730(4)	1212(3)	44(2)
C(44)	14307(5)	6098(5)	-860(4)	41(2)
N(11)	9329(5)	6432(4)	2004(3)	40(2)

C(42)	13394(5)	5220(5)	160(4)	47(2)
C(11)	7024(5)	7402(4)	2852(4)	36(2)
N(1)	7673(4)	7386(4)	2296(3)	45(2)
C(61)	11693(5)	7612(5)	-978(4)	40(2)
C(41)	13122(5)	5876(5)	380(4)	38(2)
N(2)	7845(5)	5471(4)	2351(3)	48(2)
C(43)	13980(5)	5334(5)	-445(4)	46(2)
C(31)	8422(5)	5706(5)	4176(4)	44(2)
C(16)	6601(5)	6685(5)	3242(4)	41(2)
N(3)	8918(4)	5772(4)	3502(3)	51(2)
C(45)	14058(5)	6749(5)	-664(4)	47(2)
N(6)	11184(4)	7242(4)	-290(3)	46(2)
C(34)	7450(6)	5598(8)	5462(5)	68(3)
C(15)	6021(5)	6575(5)	3869(4)	42(2)
C(431)	14287(6)	4634(6)	-681(5)	61(2)
C(32)	8055(5)	4977(6)	4662(5)	53(2)
C(331)	7185(7)	4122(7)	5845(6)	92(4)
C(47)	12275(6)	5027(6)	1534(5)	65(3)
C(12)	6801(5)	8040(5)	3078(5)	50(2)
C(21)	7141(7)	4977(5)	2794(5)	57(2)
C(26)	7321(8)	4279(6)	3423(5)	73(3)
C(14)	5814(5)	7231(5)	4069(5)	52(2)
C(48)	12096(7)	5073(7)	2277(5)	92(4)
C(51)	12937(6)	8168(6)	572(6)	63(3)
C(131)	5917(8)	8689(6)	3870(6)	84(3)
N(5)	12082(5)	7852(5)	790(4)	59(2)
C(13)	6191(5)	7967(5)	3667(4)	49(2)
C(55)	14518(7)	7952(8)	737(7)	79(3)
C(17)	7994(6)	8192(5)	1766(5)	66(3)
C(24)	5739(10)	4097(8)	3621(8)	90(4)
C(18)	8154(8)	8214(6)	1012(5)	92(4)
C(56)	13667(7)	7689(7)	946(6)	72(3)
C(49)	11506(6)	4721(6)	1379(7)	86(4)
C(33)	7581(6)	4927(6)	5306(5)	58(2)
C(52)	13078(7)	8915(6)	-23(5)	61(2)
C(39)	10101(8)	4598(9)	4036(8)	133(6)
C(36)	8276(6)	6374(6)	4350(5)	56(2)
C(22)	6264(7)	5206(6)	2591(6)	68(3)
C(37)	9894(6)	5498(8)	3557(6)	89(4)
C(27)	8229(10)	5260(7)	1720(6)	99(4)
C(19)	8796(7)	8380(6)	2001(7)	88(4)
C(58)	11562(11)	7901(11)	1972(8)	147(7)
C(53)	13913(7)	9199(6)	-236(6)	67(3)
C(35)	7797(7)	6329(7)	4998(6)	65(3)
C(57)	11463(9)	8293(12)	1196(11)	143(7)

C(351)	7665(10)	7066(8)	5170(7)	113(4)
C(38)	10384(8)	6068(10)	3668(7)	127(6)
Mo(3)	1699(1)	267(1)	3923(1)	36(1)
C(2)	0	0	5000	36(3)
N(8)	2573(4)	-37(4)	4655(3)	39(2)
N(12)	664(4)	103(4)	4554(3)	34(1)
C(71)	2002(5)	1937(5)	2843(4)	44(2)
N(9)	1517(4)	-513(5)	3539(4)	58(2)
C(85)	4291(5)	615(5)	3107(4)	42(2)
C(78)	-25(7)	2215(8)	2738(6)	102(4)
C(73)	2717(5)	2541(5)	1614(4)	50(2)
C(81)	3357(4)	280(4)	4258(4)	38(2)
C(831)	5230(6)	1485(6)	4216(5)	63(3)
C(86)	3581(5)	231(5)	3584(4)	41(2)
C(751)	3842(6)	3146(6)	2813(6)	70(3)
C(92)	2801(6)	-1308(6)	3158(5)	55(2)
C(951)	2763(9)	476(7)	934(6)	102(4)
C(93)	3414(6)	-1428(6)	2643(5)	59(2)
N(7)	1346(4)	1442(4)	3359(3)	47(2)
C(731)	2800(7)	2685(6)	819(5)	72(3)
C(72)	2085(5)	2057(5)	2111(4)	48(2)
C(83)	4651(5)	1052(5)	3982(5)	47(2)
C(97)	712(7)	-974(9)	3716(7)	99(5)
C(95)	2744(7)	-164(6)	1718(5)	64(3)
C(82)	3916(5)	692(5)	4448(4)	46(2)
C(96)	2140(6)	-58(6)	2250(5)	57(2)
C(76)	2581(5)	2299(5)	3047(4)	46(2)
C(74)	3280(5)	2883(5)	1845(5)	48(2)
C(91)	2154(5)	-634(5)	2984(4)	49(2)
C(931)	4135(8)	-2172(7)	2828(7)	102(4)
C(75)	3223(5)	2763(5)	2578(5)	46(2)
C(79)	457(8)	2580(9)	3649(8)	122(5)
C(77)	441(6)	1898(6)	3411(5)	70(3)
C(84)	4823(5)	1013(5)	3312(4)	49(2)
C(62)	12068(5)	7148(5)	-1362(4)	47(2)
C(64)	12677(5)	8330(6)	-2306(4)	50(2)
C(66)	11833(5)	8453(5)	-1279(4)	48(2)
C(63)	12564(5)	7502(5)	-2028(4)	48(2)
C(54)	14607(7)	8701(8)	153(6)	73(3)
C(87)	2433(5)	-217(5)	5435(4)	52(2)
C(94)	3388(6)	-838(6)	1913(5)	59(2)
C(851)	4498(7)	562(6)	2382(5)	67(3)
C(65)	12317(6)	8826(5)	-1934(4)	50(2)
C(67)	10228(6)	7198(7)	-322(5)	67(3)
C(89)	1908(6)	510(7)	5553(5)	68(3)

C(25)	6580(11)	3805(6)	3852(6)	84(4)
C(88)	1982(6)	-1010(6)	5853(5)	72(3)
C(23)	5565(8)	4780(9)	3000(7)	86(4)
C(631)	12996(7)	7002(6)	-2436(5)	70(3)
C(651)	12486(8)	9725(6)	-2243(6)	83(3)
C(531)	14052(8)	10021(7)	-872(6)	93(4)
C(69)	10088(8)	6592(8)	-594(7)	104(4)
C(28)	8958(8)	4566(9)	1908(8)	119(5)
C(68)	9721(7)	8023(8)	-728(7)	105(4)
C(231)	4614(8)	5066(10)	2772(9)	131(6)
C(551)	15332(8)	7414(9)	1130(8)	124(5)
C(251)	6763(13)	3063(8)	4546(7)	152(7)
C(98)	163(8)	-676(12)	3090(9)	154(7)
C(29)	8038(11)	5815(16)	1053(7)	250(15)
C(99)	933(11)	-1922(11)	4065(11)	175(8)
C(59)	10984(14)	8999(12)	796(12)	274(17)

Table 4. Anisotropic displacement parameters (Å^2 x 10^3) for (μ-NCN)[**1**]$_2$.

	U11	U22	U33	U23	U13	U12
Mo(1)	31(1)	37(1)	28(1)	-6(1)	-3(1)	2(1)
Mo(2)	29(1)	43(1)	30(1)	-9(1)	-3(1)	3(1)
C(1)	48(7)	47(5)	29(5)	-16(4)	-18(5)	14(4)
C(46)	36(5)	35(5)	50(5)	-13(4)	-14(4)	5(4)
C(151)	64(6)	66(6)	49(5)	-18(5)	4(5)	-22(5)
N(4)	30(4)	47(4)	43(4)	-1(3)	-4(3)	5(3)
C(451)	45(5)	61(6)	55(6)	-19(5)	1(4)	-6(4)
N(10)	32(4)	55(4)	30(4)	-1(3)	0(3)	6(3)
C(44)	36(4)	50(5)	39(5)	-22(4)	-2(4)	0(4)
N(11)	38(4)	40(4)	35(4)	-11(3)	-4(3)	6(3)
C(42)	41(5)	44(5)	49(5)	-9(4)	-9(4)	-5(4)
C(11)	39(5)	35(5)	28(4)	-9(4)	-14(4)	8(4)
N(1)	34(4)	42(4)	46(4)	-1(3)	3(3)	3(3)
C(61)	37(4)	46(5)	28(4)	-9(4)	-8(4)	5(4)
C(41)	32(4)	42(5)	38(5)	-16(4)	-1(4)	2(4)
N(2)	67(5)	38(4)	35(4)	-16(3)	-11(3)	7(4)
C(43)	43(5)	49(6)	42(5)	-19(4)	-9(4)	8(4)
C(31)	38(5)	52(6)	40(5)	-14(5)	-19(4)	3(4)
C(16)	44(5)	34(5)	36(5)	-5(4)	-11(4)	2(4)

N(3)	34(4)	73(5)	39(4)	-19(4)	-13(3)	1(3)
C(45)	32(5)	52(6)	47(5)	-1(4)	-14(4)	-1(4)
N(6)	36(4)	58(4)	39(4)	-13(3)	-12(3)	-4(3)
C(34)	55(6)	98(9)	50(6)	-33(7)	-1(5)	3(6)
C(15)	38(5)	46(5)	40(5)	-13(4)	-13(4)	0(4)
C(431)	54(6)	63(6)	70(6)	-35(5)	-7(5)	1(5)
C(32)	50(5)	57(6)	47(6)	-17(5)	-13(4)	-1(4)
C(331)	69(7)	106(9)	71(7)	-5(7)	-6(6)	-26(6)
C(47)	42(5)	61(6)	51(6)	5(5)	8(4)	6(5)
C(12)	42(5)	41(5)	56(6)	-11(4)	-1(4)	-1(4)
C(21)	85(7)	41(5)	51(6)	-25(5)	-9(5)	-6(5)
C(26)	100(8)	62(7)	62(7)	-25(6)	-6(6)	-22(6)
C(14)	46(5)	59(6)	45(5)	-17(5)	-4(4)	-4(4)
C(48)	86(8)	99(9)	46(6)	-7(6)	1(5)	38(7)
C(51)	56(6)	71(7)	79(7)	-51(6)	-15(5)	1(5)
C(131)	106(9)	60(7)	87(8)	-45(6)	27(7)	-9(6)
N(5)	55(5)	71(5)	65(5)	-46(4)	-3(4)	5(4)
C(13)	38(5)	53(6)	49(5)	-21(5)	3(4)	4(4)
C(55)	74(8)	83(8)	102(9)	-59(8)	-34(7)	12(6)
C(17)	59(6)	47(6)	58(6)	-1(5)	19(5)	0(5)
C(24)	118(11)	77(9)	84(9)	-39(8)	23(8)	-49(8)
C(18)	94(8)	70(7)	57(7)	7(6)	20(6)	1(6)
C(56)	79(8)	73(7)	84(7)	-46(6)	-17(6)	-13(6)
C(49)	60(7)	57(6)	115(9)	-19(6)	16(6)	-11(5)
C(33)	42(5)	76(7)	48(6)	-13(5)	-15(4)	-11(5)
C(52)	71(7)	56(6)	65(6)	-36(6)	-7(5)	0(5)
C(39)	78(9)	143(13)	136(12)	-35(10)	-35(8)	52(9)
C(36)	58(6)	61(6)	51(6)	-21(5)	-26(5)	2(5)
C(22)	67(7)	73(7)	81(7)	-46(6)	-20(6)	-1(6)
C(37)	42(6)	147(12)	55(6)	-31(7)	-19(5)	35(7)
C(27)	169(13)	60(7)	62(7)	-27(6)	9(8)	-7(8)
C(19)	64(7)	48(6)	122(10)	-15(6)	23(7)	-20(5)
C(58)	172(15)	216(18)	116(12)	-124(13)	68(11)	-110(14)
C(53)	70(7)	74(7)	71(7)	-47(6)	0(6)	-8(6)
C(35)	70(6)	76(7)	63(7)	-42(6)	-36(6)	18(6)
C(57)	80(9)	222(19)	225(20)	-195(18)	-31(11)	30(10)
C(351)	153(12)	112(10)	86(9)	-55(8)	-41(8)	23(9)
C(38)	56(8)	176(15)	100(10)	0(9)	-26(7)	-34(8)
Mo(3)	32(1)	45(1)	25(1)	-8(1)	-2(1)	-6(1)
C(2)	34(8)	34(6)	40(7)	-11(5)	-21(7)	-1(5)
N(8)	18(3)	52(4)	35(4)	-6(3)	-9(3)	0(3)
N(12)	22(4)	41(4)	34(4)	-9(3)	-7(3)	-8(3)
C(71)	38(5)	39(5)	39(5)	-2(4)	-8(4)	3(4)
N(9)	48(4)	76(5)	60(5)	-36(4)	-2(4)	-11(4)
C(85)	33(5)	41(5)	41(5)	-9(4)	2(4)	-6(4)

C(78)	69(7)	120(10)	84(8)	-16(7)	-34(6)	22(7)
C(73)	46(5)	45(5)	42(5)	-2(4)	-9(4)	-4(4)
C(81)	21(4)	33(4)	44(5)	0(4)	-11(4)	2(3)
C(831)	48(5)	74(7)	61(6)	-17(5)	-9(5)	-17(5)
C(86)	40(5)	41(5)	32(5)	-8(4)	-12(4)	5(4)
C(751)	66(6)	49(6)	79(7)	-8(5)	-32(5)	1(5)
C(92)	54(6)	62(6)	44(5)	-13(5)	-12(5)	-9(5)
C(951)	154(12)	74(8)	64(7)	-27(6)	11(7)	-1(7)
C(93)	47(5)	66(6)	69(7)	-33(6)	-15(5)	3(5)
N(7)	31(4)	48(4)	42(4)	-3(3)	-3(3)	-1(3)
C(731)	76(7)	79(7)	51(6)	-12(5)	-14(5)	-19(6)
C(72)	37(5)	36(5)	52(6)	2(4)	-13(4)	-7(4)
C(83)	33(5)	44(5)	52(6)	-8(4)	-11(4)	-1(4)
C(97)	63(7)	177(14)	121(10)	-120(10)	31(7)	-54(8)
C(95)	74(7)	59(6)	57(6)	-23(5)	1(5)	-12(5)
C(82)	39(5)	47(5)	39(5)	-7(4)	-11(4)	1(4)
C(96)	62(6)	61(6)	46(6)	-24(5)	-2(5)	3(5)
C(76)	48(5)	41(5)	34(5)	-5(4)	-1(4)	5(4)
C(74)	25(4)	42(5)	53(6)	-1(4)	4(4)	-6(4)
C(91)	53(5)	56(6)	47(6)	-33(5)	-4(4)	-1(4)
C(931)	99(9)	93(9)	119(10)	-55(8)	-40(8)	34(7)
C(75)	40(5)	32(5)	53(6)	-8(4)	-15(4)	11(4)
C(79)	90(9)	119(11)	152(13)	-71(10)	-12(9)	39(8)
C(77)	44(6)	56(6)	70(7)	7(5)	2(5)	-1(4)
C(84)	44(5)	45(5)	46(5)	-8(4)	-1(4)	-3(4)
C(62)	42(5)	46(5)	46(5)	-14(4)	-1(4)	-2(4)
C(64)	47(5)	67(7)	33(5)	-14(5)	-9(4)	-18(4)
C(66)	54(5)	47(6)	33(5)	-8(4)	-7(4)	3(4)
C(63)	42(5)	56(6)	39(5)	-15(4)	-1(4)	-1(4)
C(54)	54(7)	92(9)	88(8)	-53(8)	-7(6)	-6(6)
C(87)	42(5)	70(6)	36(5)	-13(4)	-2(4)	-12(4)
C(94)	61(6)	66(6)	63(7)	-41(6)	9(5)	-15(5)
C(851)	84(7)	64(6)	48(6)	-25(5)	16(5)	-18(5)
C(65)	60(6)	42(5)	42(5)	-5(4)	-19(4)	-9(4)
C(67)	45(6)	104(8)	54(6)	-31(6)	-3(5)	-20(5)
C(89)	44(5)	118(9)	55(6)	-51(6)	-5(4)	0(5)
C(25)	152(12)	52(7)	53(7)	-27(6)	-13(8)	-11(8)
C(88)	52(6)	95(8)	40(5)	5(5)	-12(4)	-19(5)
C(23)	88(9)	100(10)	99(10)	-69(9)	20(7)	-41(8)
C(631)	76(7)	76(7)	62(6)	-40(6)	-6(5)	9(5)
C(651)	123(9)	58(7)	66(7)	-18(5)	-12(6)	-27(6)
C(531)	105(9)	87(9)	97(9)	-48(8)	-7(7)	-16(7)
C(69)	72(8)	133(11)	119(10)	-58(9)	-15(7)	-26(7)
C(28)	73(8)	170(14)	172(13)	-139(12)	13(8)	0(8)
C(68)	45(6)	144(12)	134(11)	-73(10)	-36(7)	35(7)

C(231)	66(9)	200(16)	171(15)	-115(13)	17(9)	-47(9)
C(551)	98(10)	122(11)	163(13)	-70(10)	-72(9)	43(8)
C(251)	265(21)	70(9)	94(10)	-13(8)	6(12)	-36(11)
C(98)	68(8)	283(23)	197(17)	-177(17)	-7(10)	-31(11)
C(29)	121(13)	528(41)	53(9)	-109(16)	-44(9)	85(18)
C(99)	140(14)	142(16)	261(23)	-97(16)	35(15)	-78(12)
C(59)	221(22)	160(18)	279(27)	-37(18)	143(21)	86(17)

Table 5. Bond Lengths (Å) for (μ-NCN)[**3**]$_2$.

Symmetry transformations to generate equivalent atoms:
#1 -x, -y, -z

U-N(1)	2.219(6)
U-N(2)	2.225(6)
U-N(4)	2.226(7)
U-N(3)	2.291(6)
U-C(21)	2.787(8)
U-C(31)	2.954(8)
U-C(11)	2.968(8)
U-C(32)	2.998(8)
N(1)-C(11)	1.425(10)
N(1)-C(17)	1.479(11)
N(2)-C(21)	1.434(10)
N(2)-C(27)	1.481(10)
N(3)-C(31)	1.384(10)
N(3)-C(37)	1.477(10)
C(31)-C(32)	1.400(11)
C(31)-C(36)	1.428(11)
N(4)-C	1.189(8)
C(11)-C(12)	1.383(11)
C(11)-C(16)	1.408(12)
C(21)-C(26)	1.387(11)
C(21)-C(22)	1.395(11)
C-N(4)#1	1.189(7)
C(32)-C(33)	1.391(11)
C(13)-C(14)	1.395(12)
C(13)-C(12)	1.412(11)
C(13)-C(131)	1.508(13)
C(36)-C(35)	1.379(12)
C(22)-C(23)	1.382(11)
C(16)-C(15)	1.379(13)
C(19)-C(17)	1.525(13)

C(38)-C(37)	1.560(13)
C(33)-C(34)	1.387(12)
C(33)-C(331)	1.494(12)
C(25)-C(24)	1.381(13)
C(25)-C(26)	1.403(12)
C(25)-C(251)	1.533(13)
C(24)-C(23)	1.367(13)
C(210)-C(27)	1.522(12)
C(27)-C(28)	1.495(12)
C(27)-C(29)	1.536(11)
C(35)-C(34)	1.392(12)
C(35)-C(351)	1.525(12)
C(23)-C(231)	1.516(13)
C(17)-C(110)	1.529(13)
C(17)-C(18)	1.534(12)
C(15)-C(14)	1.367(13)
C(15)-C(151)	1.523(13)
C(37)-C(310)	1.509(13)
C(37)-C(39)	1.522(12)

Table 6. Bond Angles (°) for $(\mu\text{-NCN})[\mathbf{3}]_2$.

N(1)-U-N(2)	124.6(2)
N(1)-U-N(4)	94.6(3)
N(2)-U-N(4)	102.6(3)
N(1)-U-N(3)	124.7(2)
N(2)-U-N(3)	105.3(2)
N(4)-U-N(3)	96.4(2)
N(1)-U-C(21)	117.0(2)
N(2)-U-C(21)	30.7(2)
N(4)-U-C(21)	132.7(3)
N(3)-U-C(21)	93.2(2)
N(1)-U-C(31)	100.2(2)
N(2)-U-C(31)	120.0(2)
N(4)-U-C(31)	112.1(2)
N(3)-U-C(31)	27.0(2)
C(21)-U-C(31)	96.7(2)
N(1)-U-C(11)	27.3(2)
N(2)-U-C(11)	97.3(2)
N(4)-U-C(11)	100.9(2)
N(3)-U-C(11)	147.7(2)

C(21)-U-C(11)	94.8(2)
C(31)-U-C(11)	120.8(2)
N(1)-U-C(32)	85.7(2)
N(2)-U-C(32)	112.7(2)
N(4)-U-C(32)	136.7(3)
N(3)-U-C(32)	51.3(2)
C(21)-U-C(32)	83.0(2)
C(31)-U-C(32)	27.2(2)
C(11)-U-C(32)	98.7(2)
C(11)-N(1)-C(17)	119.3(7)
C(11)-N(1)-U	107.1(5)
C(17)-N(1)-U	131.7(6)
C(21)-N(2)-C(27)	118.6(6)
C(21)-N(2)-U	96.9(4)
C(27)-N(2)-U	144.5(5)
C(31)-N(3)-C(37)	122.4(7)
C(31)-N(3)-U	104.3(5)
C(37)-N(3)-U	131.3(5)
N(3)-C(31)-C(32)	117.3(7)
N(3)-C(31)-C(36)	127.9(8)
C(32)-C(31)-C(36)	114.6(8)
N(3)-C(31)-U	48.7(4)
C(32)-C(31)-U	78.1(5)
C(36)-C(31)-U	145.6(5)
C-N(4)-U	162.6(5)
C(12)-C(11)-C(16)	117.9(8)
C(12)-C(11)-N(1)	119.7(7)
C(16)-C(11)-N(1)	122.3(7)
C(12)-C(11)-U	93.4(5)
C(16)-C(11)-U	127.6(6)
N(1)-C(11)-U	45.6(3)
C(26)-C(21)-C(22)	117.7(8)
C(26)-C(21)-N(2)	120.8(8)
C(22)-C(21)-N(2)	121.0(7)
C(26)-C(21)-U	100.5(6)
C(22)-C(21)-U	110.3(5)
N(2)-C(21)-U	52.4(4)
N(4)#1-C-N(4)	179.998(2)
C(33)-C(32)-C(31)	125.2(8)
C(33)-C(32)-U	138.6(6)
C(31)-C(32)-U	74.7(5)
C(14)-C(13)-C(12)	117.9(8)
C(14)-C(13)-C(131)	122.6(9)
C(12)-C(13)-C(131)	119.5(9)
C(35)-C(36)-C(31)	121.4(8)

C(23)-C(22)-C(21)	122.2(8)
C(11)-C(12)-C(13)	121.2(8)
C(15)-C(16)-C(11)	121.9(9)
C(34)-C(33)-C(32)	116.9(8)
C(34)-C(33)-C(331)	121.5(9)
C(32)-C(33)-C(331)	121.5(8)
C(24)-C(25)-C(26)	118.6(9)
C(24)-C(25)-C(251)	122.7(10)
C(26)-C(25)-C(251)	118.7(10)
C(23)-C(24)-C(25)	121.9(9)
N(2)-C(27)-C(28)	107.8(7)
N(2)-C(27)-C(210)	111.5(7)
C(28)-C(27)-C(210)	109.6(8)
N(2)-C(27)-C(29)	109.7(6)
C(28)-C(27)-C(29)	109.8(8)
C(210)-C(27)-C(29)	108.4(7)
C(36)-C(35)-C(34)	120.5(8)
C(36)-C(35)-C(351)	119.5(9)
C(34)-C(35)-C(351)	120.0(9)
C(24)-C(23)-C(22)	118.6(9)
C(24)-C(23)-C(231)	121.3(9)
C(22)-C(23)-C(231)	120.0(9)
C(21)-C(26)-C(25)	121.1(9)
N(1)-C(17)-C(19)	107.0(7)
N(1)-C(17)-C(110)	112.2(8)
C(19)-C(17)-C(110)	108.7(8)
N(1)-C(17)-C(18)	109.2(7)
C(19)-C(17)-C(18)	109.7(9)
C(110)-C(17)-C(18)	109.9(8)
C(14)-C(15)-C(16)	118.7(9)
C(14)-C(15)-C(151)	119.6(10)
C(16)-C(15)-C(151)	121.6(10)
N(3)-C(37)-C(310)	110.9(9)
N(3)-C(37)-C(39)	106.1(7)
C(310)-C(37)-C(39)	108.5(8)
N(3)-C(37)-C(38)	112.9(7)
C(310)-C(37)-C(38)	111.7(9)
C(39)-C(37)-C(38)	106.5(8)
C(33)-C(34)-C(35)	121.0(9)
C(15)-C(14)-C(13)	122.2(9)

Table 7. Atomic Coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for the structure of (μ-NCN)[**3**]$_2$. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U(eq)
U	571(1)	947(1)	1626(1)	33(1)
N(1)	-1399(6)	957(3)	1825(4)	44(2)
N(2)	2072(6)	444(3)	2400(4)	36(2)
N(3)	1520(6)	1787(3)	1000(4)	39(2)
C(31)	862(8)	2371(4)	1127(5)	41(2)
N(4)	288(7)	232(4)	627(4)	52(2)
C(11)	-1500(7)	552(4)	2493(5)	40(2)
C(21)	2318(8)	1001(4)	2929(4)	43(2)
C	0	0	0	38(3)
C(32)	492(8)	2459(4)	1863(5)	42(2)
C(13)	-1169(9)	-535(4)	3161(6)	53(3)
C(36)	431(8)	2885(4)	579(5)	46(2)
C(22)	3221(8)	1484(4)	2826(5)	41(2)
C(12)	-1208(7)	-134(4)	2486(5)	44(2)
C(16)	-1808(9)	833(5)	3190(6)	61(3)
C(131)	-835(10)	-1280(5)	3129(7)	82(4)
C(19)	-2122(9)	1538(6)	633(6)	80(3)
C(38)	1718(10)	1696(6)	-430(5)	90(4)
C(33)	-334(8)	2950(4)	2060(5)	49(2)
C(25)	1693(10)	1717(5)	3952(5)	58(3)
C(24)	2594(11)	2181(5)	3816(6)	67(3)
C(210)	4178(8)	-53(5)	2518(6)	64(3)
C(27)	2809(7)	-188(4)	2536(5)	41(2)
C(35)	-332(8)	3403(4)	768(6)	50(2)
C(331)	-697(9)	2995(5)	2859(5)	66(3)
C(23)	3369(9)	2071(5)	3266(5)	56(3)
C(29)	2630(9)	-486(5)	3331(5)	64(3)
C(26)	1562(8)	1123(5)	3500(5)	50(2)
C(351)	-700(10)	3966(4)	181(6)	71(3)
C(17)	-2531(8)	1152(4)	1319(6)	57(3)
C(15)	-1842(11)	443(6)	3846(6)	72(3)
C(18)	-3231(9)	505(5)	1032(6)	69(3)
C(37)	2386(8)	1753(5)	411(5)	54(3)
C(34)	-734(9)	3427(5)	1497(6)	55(3)
C(28)	2362(11)	-685(5)	1914(6)	76(3)
C(14)	-1502(10)	-227(6)	3829(6)	70(3)
C(39)	3112(9)	1095(5)	569(5)	63(3)
C(310)	3278(10)	2343(5)	495(8)	100(4)
C(110)	-3370(9)	1614(5)	1732(7)	90(4)
C(251)	829(12)	1826(6)	4573(6)	94(4)

C(231)	4321(11)	2597(5)	3102(7)	95(4)
C(151)	-2161(14)	753(6)	4600(7)	115(5)

Table 8. Anisotropic displacement parameters (Å^2 x 10^3) for (μ-NCN)[**3**]$_2$.

atom	U11	U22	U33	U23	U13	U12
U	28(1)	40(1)	31(1)	1(1)	3(1)	-2(1)
N(1)	26(4)	44(4)	62(5)	8(4)	11(4)	2(4)
N(2)	39(4)	36(4)	33(4)	-4(3)	7(3)	-2(3)
N(3)	32(4)	46(4)	39(4)	7(3)	9(3)	4(4)
C(31)	38(6)	46(6)	37(5)	-6(4)	-1(4)	-16(5)
N(4)	59(5)	51(5)	46(5)	-25(4)	2(4)	-13(4)
C(11)	27(5)	37(5)	58(6)	-2(5)	15(4)	-4(4)
C(21)	51(6)	50(6)	29(5)	5(5)	2(4)	16(5)
C	36(8)	35(7)	40(8)	-19(6)	1(6)	-8(6)
C(32)	43(6)	33(5)	46(6)	4(4)	-8(5)	-6(4)
C(13)	53(6)	43(6)	68(7)	12(5)	25(5)	-5(5)
C(36)	39(5)	48(6)	47(6)	21(5)	-8(4)	-16(5)
C(22)	40(6)	43(5)	39(5)	2(5)	-4(4)	0(5)
C(12)	32(5)	50(6)	55(6)	-7(5)	18(4)	-3(4)
C(16)	66(7)	42(6)	82(8)	-12(6)	38(6)	-9(5)
C(131)	86(9)	54(6)	113(10)	30(6)	43(7)	15(6)
C(19)	46(7)	97(8)	90(8)	38(7)	-16(6)	-7(6)
C(38)	79(9)	146(11)	47(7)	30(7)	17(6)	39(8)
C(33)	45(6)	40(5)	60(6)	-3(5)	-3(5)	-4(5)
C(25)	71(8)	66(7)	36(6)	-5(5)	6(5)	20(6)
C(24)	96(9)	50(6)	48(7)	-16(5)	-16(6)	1(7)
C(210)	45(6)	56(6)	93(8)	29(6)	22(6)	16(5)
C(27)	35(6)	37(5)	50(6)	5(4)	4(4)	11(4)
C(35)	37(6)	36(5)	71(7)	4(5)	-16(5)	-4(5)
C(331)	68(7)	66(7)	65(7)	-14(6)	1(6)	12(6)
C(23)	72(7)	47(6)	44(6)	-4(5)	-14(5)	2(6)
C(29)	64(7)	64(7)	64(7)	35(5)	12(6)	14(6)
C(26)	53(6)	60(6)	35(5)	0(5)	-2(5)	8(5)
C(351)	72(7)	47(6)	87(8)	18(6)	-16(6)	-2(6)
C(17)	26(5)	54(6)	88(8)	11(5)	-6(5)	-1(5)
C(15)	93(9)	61(7)	70(8)	6(6)	42(7)	-21(7)
C(18)	47(6)	72(7)	83(8)	1(6)	-11(6)	-9(6)

C(37)	34(6)	70(7)	59(7)	29(5)	8(5)	1(5)
C(34)	42(6)	49(6)	72(7)	-17(6)	-3(6)	-2(5)
C(28)	90(9)	43(6)	95(9)	-9(6)	9(7)	11(6)
C(14)	90(9)	76(8)	53(7)	11(6)	41(6)	-11(7)
C(39)	51(6)	91(8)	50(6)	9(5)	21(5)	4(6)
C(310)	50(7)	79(8)	175(13)	62(8)	37(8)	3(6)
C(110)	46(7)	66(7)	156(12)	2(7)	-1(7)	17(6)
C(251)	124(11)	96(9)	69(8)	-21(7)	33(8)	29(8)
C(231)	106(10)	56(7)	120(10)	-16(6)	0(9)	-43(7)
C(151)	177(15)	109(10)	77(8)	-39(7)	91(10)	-39(9)

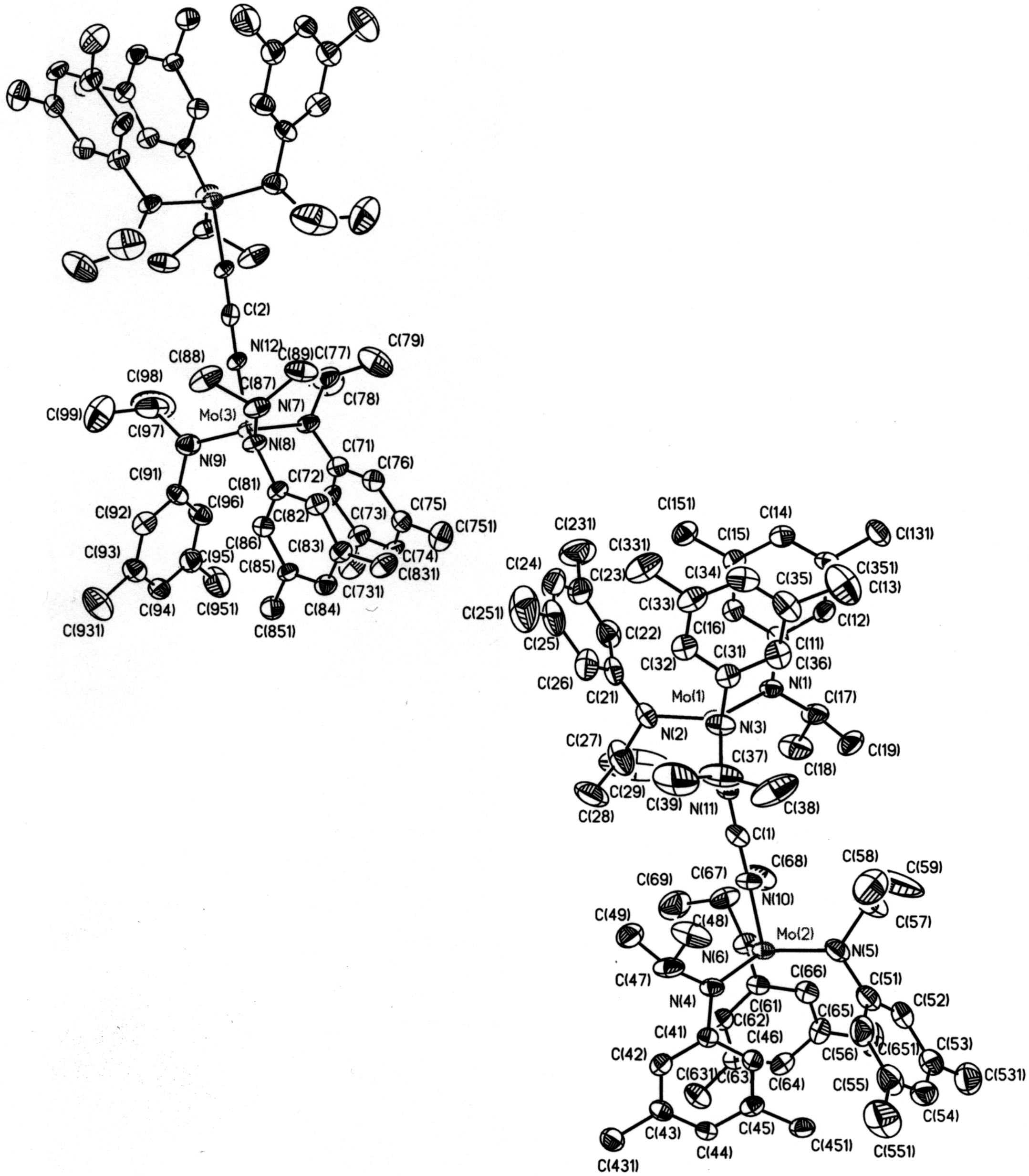


Figure 2: Structural diagram of (μ-NCN)[**1**]$_2$ with thermal ellipsoids at the 35% probability level.

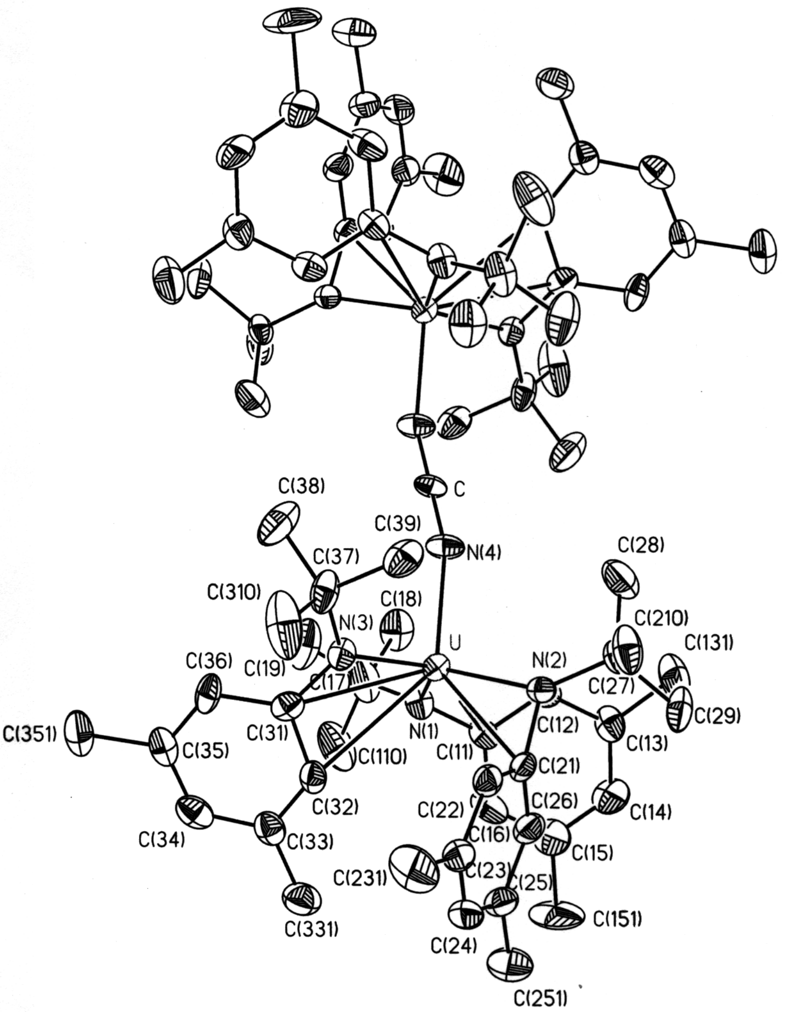


Figure 3: Structural diagram of (μ-NCN)[**3**]$_2$ with thermal ellipsoids at the 35% probability level.

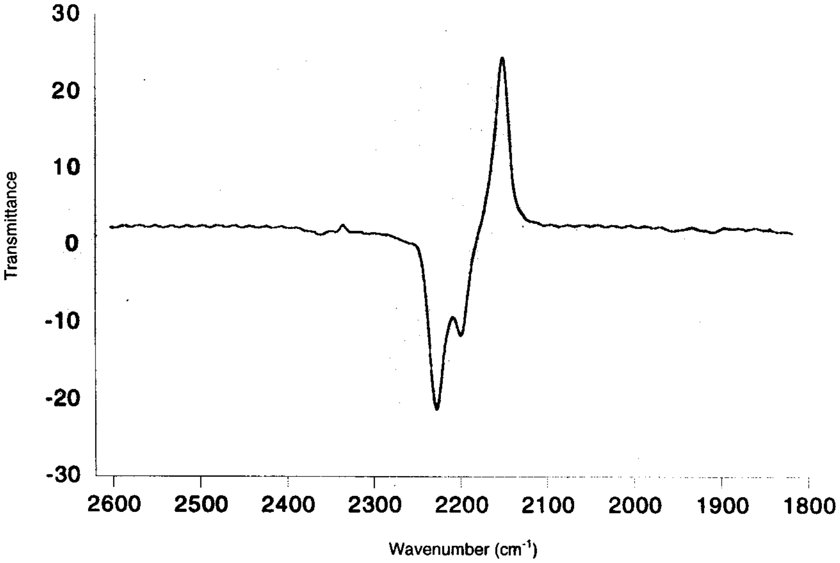


Figure 4: Solution IR spectrum of dbabhCN showing the strong ν_{CN} at 2228 cm^{-1} shifted at higher energy from the ^{13}C isotopomer centered at 2198 cm^{-1}. The calculated isotopomer shift using the simple harmonic oscillator model was 41 cm^{-1}.

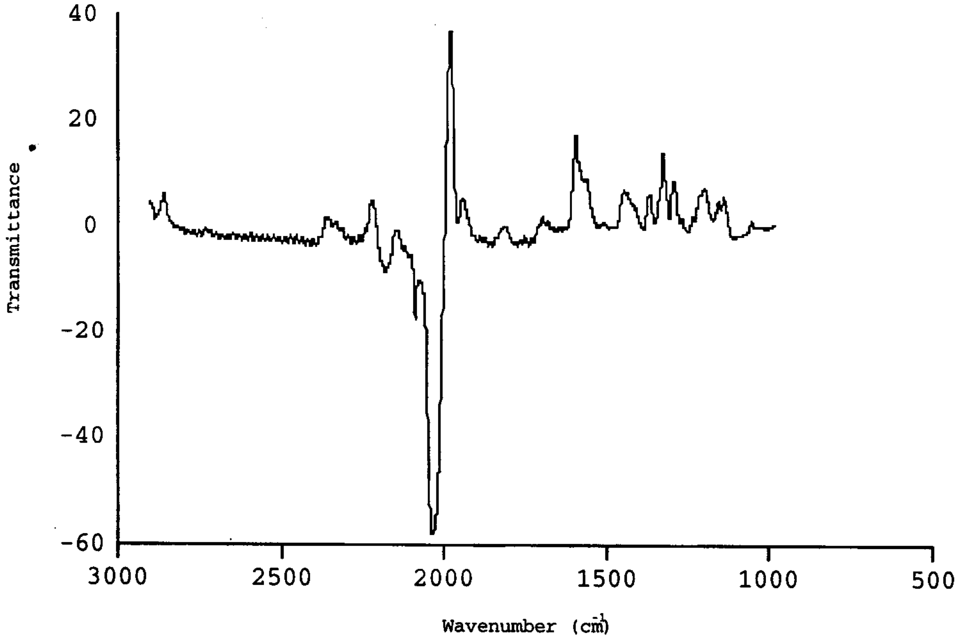


Figure 5: The spectrum shows the strong ν_{CN} at 2037 cm^{-1} shifted at higher energy from the ^{13}C isotopomer of (μ-NCN)[**2**]$_2$ at 1982 cm^{-1}. The calculated isotopomer shift using the simple harmonic oscillator model was 41 cm^{-1}.

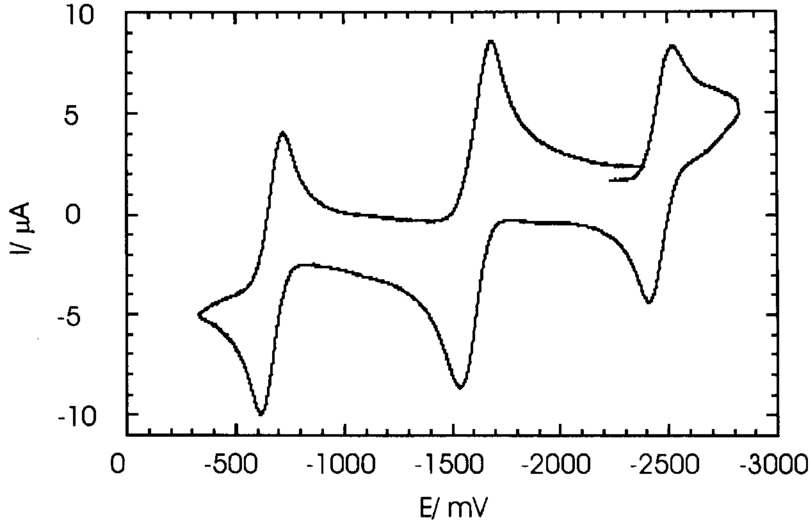


Figure 6: Cyclic voltammagram of (μ-NCN)[**2**]$_2$ in 0.8 M THF solution of [n-Bu_4N][PF_6]. The scan rate for redox cycle was 200 mV/sec giving two reduction waves at -1.61 and -2.42 V, and an oxidation potential at -0.68 V when referenced against an internal [$FeCp_2$]$^{+/0}$ couple.

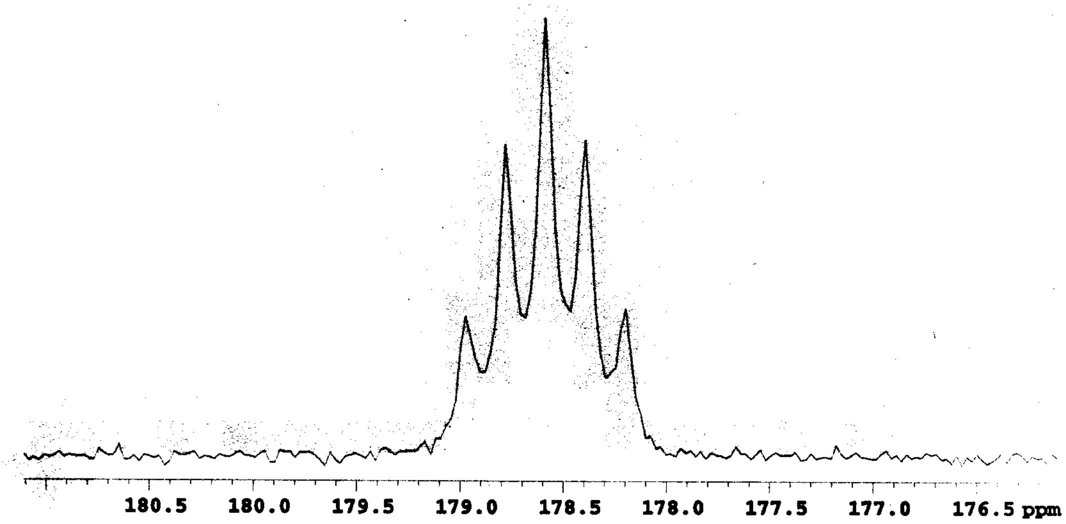


Figure 7: The ^{13}C NMR spectrum of ^{13}C enriched cyanamide (μ-NCN)[**1**]$_2$ showed a well-resolved quintet at 176 ppm due to coupling of ^{13}C to the two adjacent ^{14}N nuclei. The J_{CN} value was 24 Hz.

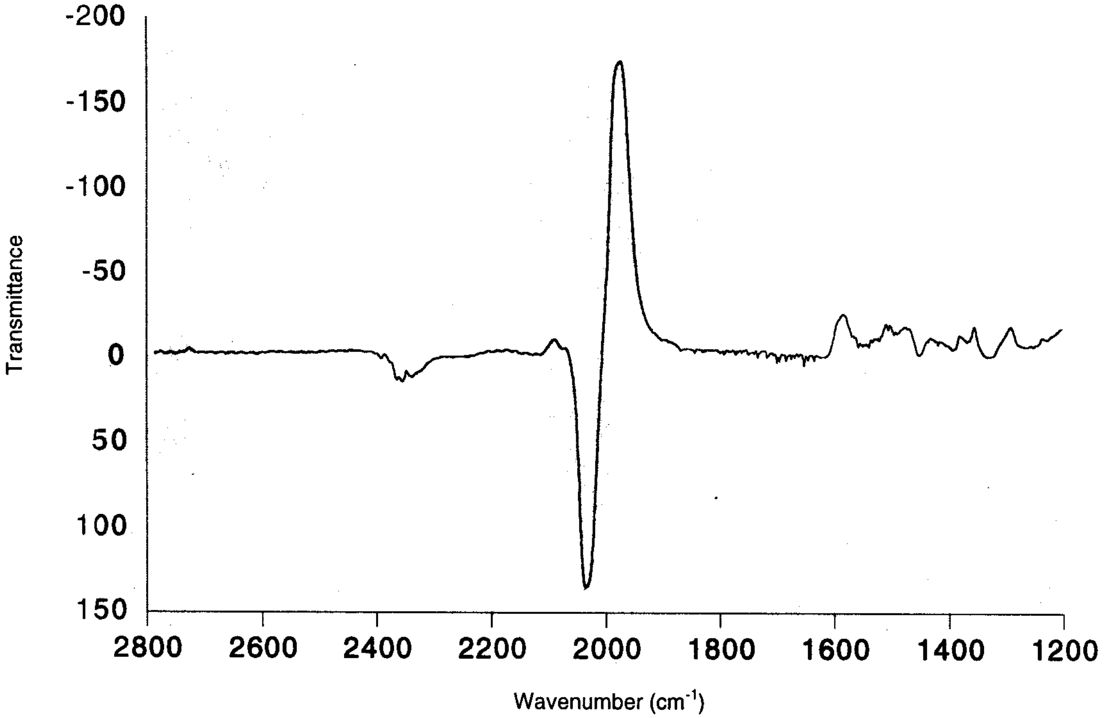
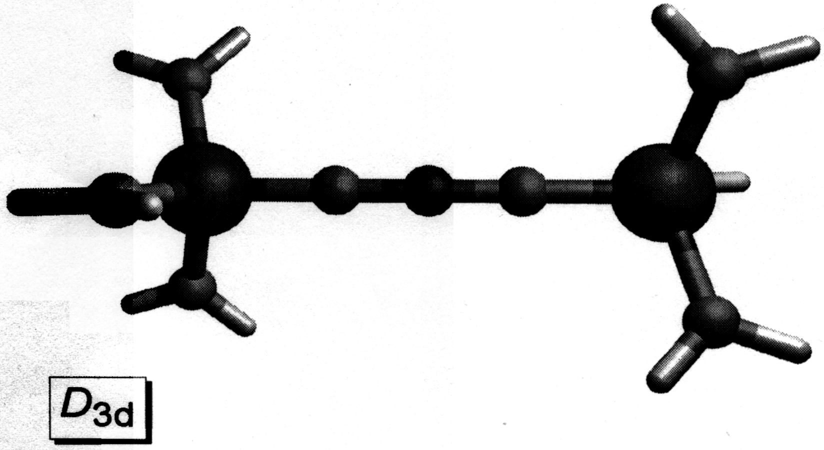


Figure 8: The spectrum shows the strong ν_{CN} at 2034 cm^{-1} shifted at higher energy from the ^{13}C isotopomer of (μ-NCN)[**3**]$_2$ at 1976 cm^{-1}. The calculated isotope effect in the shift using the harmonic oscillator model was 41 cm^{-1}.



Selected Distances and Angles:

V–N_{NCN} = 1.79 Å   N–V–N_{amide} = 105°
N–C = 1.23 Å
V–N_{amide} = 1.88 Å

Figure 9: Geometry from DFT calculations on a simplified model $[V(NH_2)_3]_2(\mu^2;\eta^1,\eta^1\text{-NCN})$ for (μ-NCN)[**2**]$_2$. The model optimized to the local point group D_{3d} even when refining in an idealized C_{2h} bent geometry. The calculated bond lengths are listed along with the most stabilized geometrical model (linear).

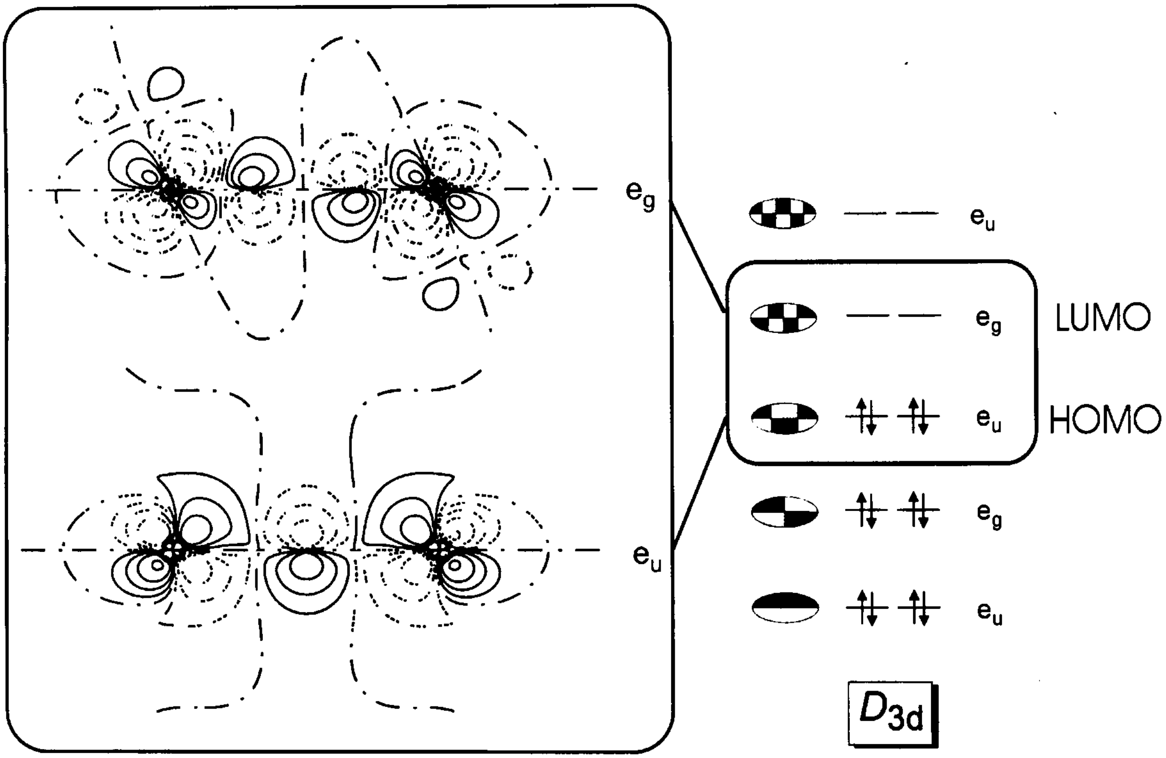


Figure 10: The diagram shows the molecular orbital picture for (μ-NCN)[**2**]$_2$ for the frontier π-orbitals. The 8-π system makes the HOMO fully occupied and thus generates a diamagnetic complex. To the left of the frontier orbitals are depicted their corresponding lobe representation as contour diagrams sliced through the z-axis. The HOMO shows considerable π-bonding (stabilization) of the cyanoimide linkage but in out of phase at the Mo-N$_{cyanoimide}$ linkage. A node at the carbodiimide carbon is also noted in this orbital. The LUMO on the other hand, has pronounced anti-bonding character, with nodes about the Mo-N-C-N-Mo linkages as well as a node centered at the carbodiimide carbon. The bonding e_g orbital for (μ-NCN)[**2**]$_2$ represent the strong Mo-N$_{cyanoimide}$ bonds and thus support the near linear Mo=N=C=N=Mo chain span.

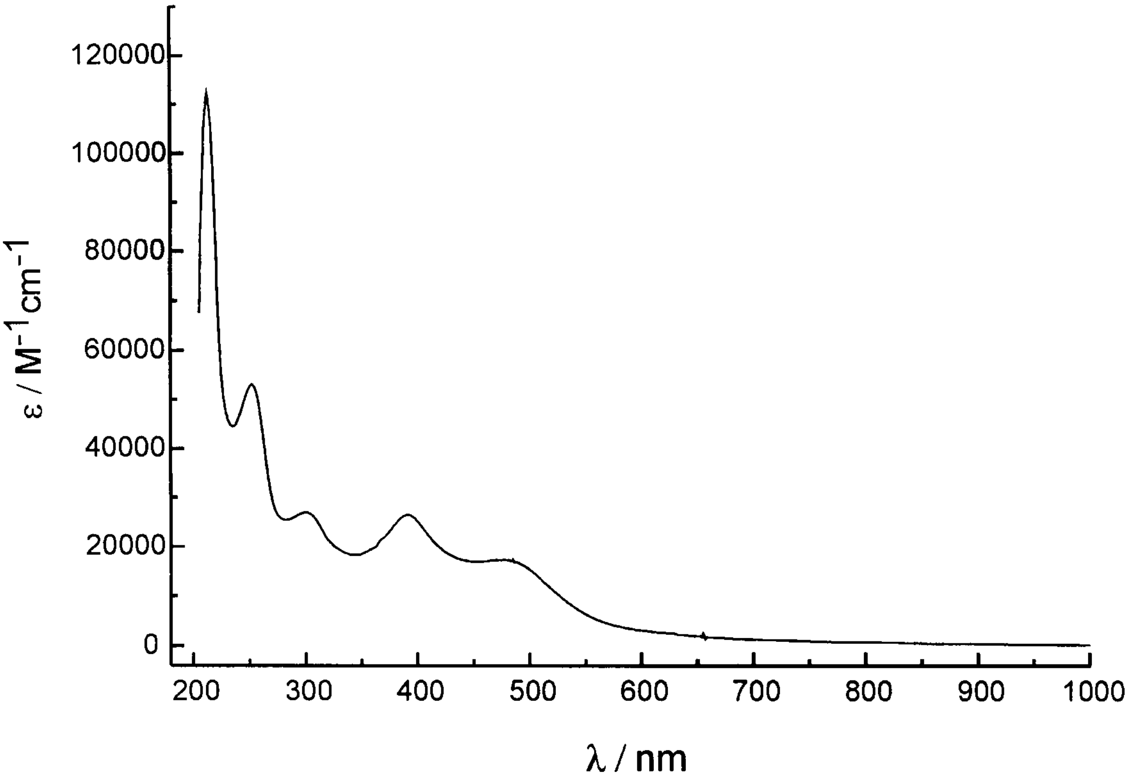


Figure 11: Electronic absorption of the complex (μ-NCN)[**1**]$_2$ in OEt$_2$. The first transition at 475 nm (1.66 eV) is approximate to that calculated by DFT $E_{excited}$-E_{ground} = 1.42 eV. The second transition is found at 2.06 ev at 391 nm. The HOMO-LUMO gap based on DFT calculations is 1.38 eV.

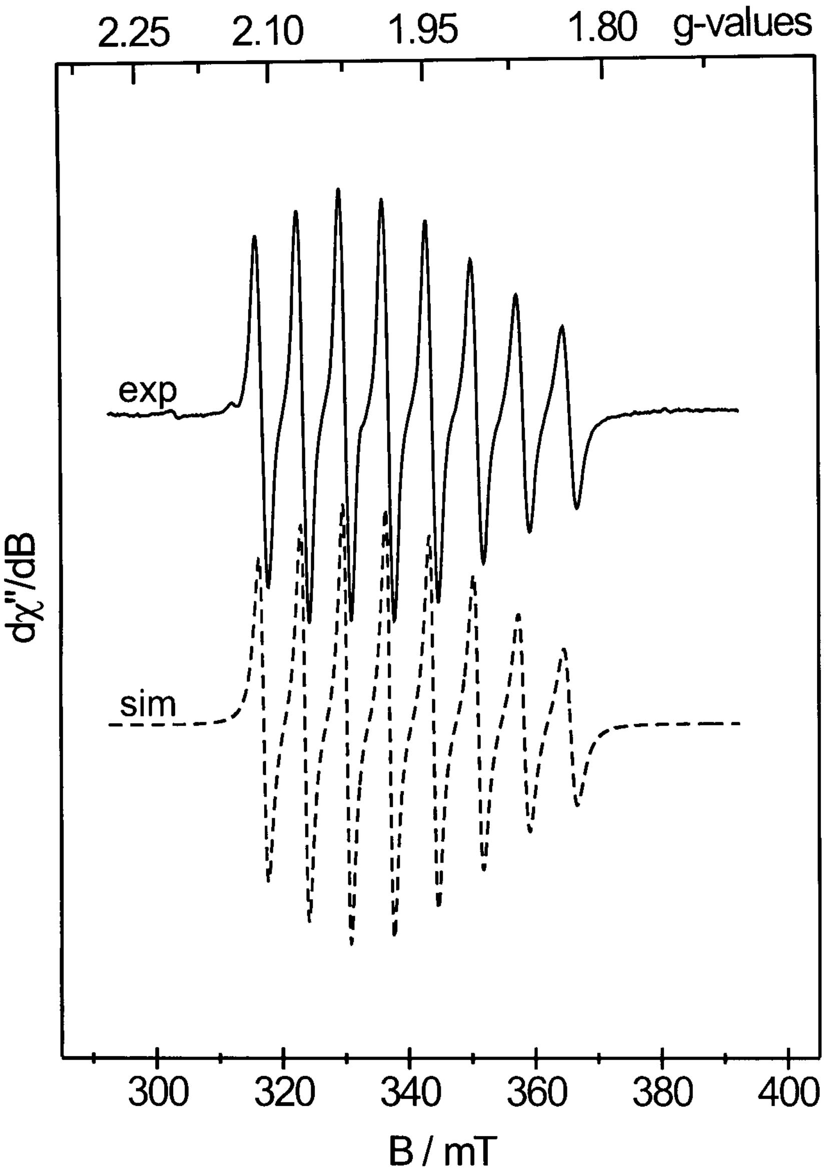


Figure 12: X-band EPR spectrum of oxidized (μ-NCN)[**2**]$_2$ in toluene at 295 K. Experimental Conditions: Frequency ν = 9.355 GHz, Power = 20 mW, Modulation Amplitude = 5 G, Modulation Frequency = 100 kHz. Simulation: g_{iso} = 1.9565, A_{iso} = 0.00635 cm^{-1}, Linewidth W_{corr} = 11.3(1 $-0.07m_I$ + $0.03m_I^2$) G.

2.3.1 Selected Input and Output Parameters for DFT Calculations on Complex (μ-NCN)[1]$_2$

1(INPUT FILE)

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 atoms Z-matrix
 1.  XX 0 0 0
 2.  C  1 0 0 1.0
 3.  N  2 1 0 NC  90.0
 4.  XX 3 2 1 1.0 90.0 180.0
 5.  N  2 1 3 NC  90.0 180.0
 6.  XX 5 2 1 1.0 90.0 180.0
 7.  Mo 3 4 2 NMo 90.0 180.0
 8.  Mo 5 6 2 NMo 90.0 180.0
 9.  N  7 3 4 MoN NMoN 180.0
 10. N  7 3 4 MoN NMoN 60.0
 11. N  7 3 4 MoN NMoN -60.0
 12. N  8 5 6 MoN NMoN 0.0
 13. N  8 5 6 MoN NMoN 120.0
 14. N  8 5 6 MoN NMoN -120.0
 15. H  9 7 3 HN1 HNMo1 0.0
 16. H  9 7 3 HN2 HNMo2 180.0
 17. H 10 7 3 HN1 HNMo1 0.0
 18. H 10 7 3 HN2 HNMo2 180.0
 19. H 11 7 3 HN1 HNMo1 0.0
 20. H 11 7 3 HN2 HNMo2 180.0
 21. H 12 8 5 HN1 HNMo1 0.0
 22. H 12 8 5 HN2 HNMo2 180.0
 23. H 13 8 5 HN1 HNMo1 0.0
 24. H 13 8 5 HN2 HNMo2 180.0
 25. H 14 8 5 HN1 HNMo1 0.0
 26. H 14 8 5 HN2 HNMo2 180.0
 end

 geovar
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 MoN=2.0
 NMoN=100
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 HN2=1.1
 HNMo1=120.0
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 HNMo2=120.0
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 symmetry D(3D)

 relativistic scalar

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 C  4
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 fragments
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 C ../../track/t21r.C.IV
 H ../../track/t21.H.III
 end

 xc
 LDA VWN
 GRADIENTS BECKE PERDEW
 end

 geometry
 optim selected
 end

 end input
1
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 *  -------------------------------------                                      *
 *   Amsterdam Density Functional  (ADF)         2.3.0     April 16, 1997     *
 *  -------------------------------------                                      *
 *                                                                             *
 *   (c) Copyright 1993-1997, Theoretical Chemistry,                           *
 *       Vrije Universiteit, Amsterdam, The Netherlands                        *
 *   All rights reserved.                                                      *
 *                                                                             *
 *   Recommended citation:                                                     *
 *     ADF 2.3.0, Theoretical Chemistry, Vrije Universiteit, Amsterdam         *
 *     E.J.Baerends et.al., Chem.Phys. 2 (1973) 41                             *
 *     G.te Velde, E.J.Baerends, J.Comp.Phys. 99 (1992) 84                     *
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```
 *    C.Fonseca Guerra et.al. METECC-95 (1995) 305                           *
 *                                                                            *
 *   Online information and documentation:                                    *
 *    http://tc.chem.vu.nl/SCM                                                *
 *                                                                            *
 *   E-mail: adf@chem.vu.nl                                                   *
 *                                                                            *
 ******************************************** dec_osf1 ************************

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 X3MoNCNMoX3

==============================
 M O D E L   P A R A M E T E R S
 ==============================

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    Gradient Corrections:                Becke88 Perdew86          == Not Default ==

 SPIN  (restricted / unrestr.)
    Molecule:                            Restricted
    Fragments:                           Restricted

 OTHER ASPECTS
    Relativistic Corrections:            scalar (Pauli,FrozenCore)  == Not Default ==
    Core Treatment:                      Frozen Orbital(s)

    Electric Field:                      ---

    Magnetic Field:                      ---

Orbital Energies, per Irrep and Spin:
 =====================================
                          Occup          E (au)                E (eV)   Diff (eV) with
                          -----   --------------------         ------   --------------
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                3         2.000   -0.84882443669829E+00       -23.098         7.08E-08
                4         2.000   -0.74645679232664E+00       -20.312         4.78E-07
                5         2.000   -0.46529901765217E+00       -12.661         1.18E-07
                6         2.000   -0.42476157610139E+00       -11.558         3.92E-07
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        1     2.000   -0.19852109849093E+00     -5.402       3.30E-07
        2     0.000    0.41095851464420E+00     11.183
        3     0.000    0.53768156168181E+00     14.631
        4     0.000    0.85470538012545E+00     23.258
        5     0.000    0.16929164722548E+01     46.067
        6     0.000    0.17617387115082E+01     47.939
        7     0.000    0.36050975053769E+01     98.100
E1.g
        1     4.000   -0.14611227023409E+01    -39.759      -1.38E-07
        2     4.000   -0.74059038206284E+00    -20.152       4.73E-07
        3     4.000   -0.42816168899003E+00    -11.651       3.92E-07
        4     4.000   -0.34408549239222E+00     -9.363       2.81E-07
        5     4.000   -0.26655496449522E+00     -7.253       1.62E-07
        6     4.000   -0.23838839320157E+00     -6.487       2.97E-07
        7     0.000   -0.90708269444884E-01     -2.468
        8     0.000   -0.27565061915737E-01     -0.750
        9     0.000    0.44787603583800E-01      1.219
       10     0.000    0.11850525894117E+00      3.225
       11     0.000    0.19716692055119E+00      5.365
       12     0.000    0.22515354718315E+00      6.127
       13     0.000    0.30399984024754E+00      8.272
       14     0.000    0.37004476395248E+00     10.069
       15     0.000    0.45299679335661E+00     12.327
       16     0.000    0.53417067006181E+00     14.536
A1.u
        1     2.000   -0.19853697053021E+00     -5.402       3.30E-07
        2     0.000    0.41000943529683E+00     11.157
        3     0.000    0.53717952004654E+00     14.617
        4     0.000    0.85474099986322E+00     23.259
        5     0.000    0.16931716245893E+01     46.074
        6     0.000    0.17609441702475E+01     47.918
        7     0.000    0.36026452190621E+01     98.033
A2.u
        1     2.000   -0.24171477682259E+01    -65.774        1.45E-07
        2     2.000   -0.14646036731163E+01    -39.854       -6.35E-09
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                3        2.000      -0.78645170621782E+00        -21.400         2.92E-08
                4        2.000      -0.74627497574834E+00        -20.307         4.74E-07
                5        2.000      -0.42994650942409E+00        -11.699         1.49E-07
                6        2.000      -0.42427092571689E+00        -11.545         3.61E-07
                7        2.000      -0.35649434268064E+00         -9.701         3.07E-07
                8        0.000      -0.53888614268097E-01         -1.466
                9        0.000      -0.14452545992392E-01         -0.393
               10        0.000       0.10055408254998E+00          2.736
               11        0.000       0.13065860929470E+00          3.555
               12        0.000       0.15508070500000E+00          4.220
               13        0.000       0.19031472862820E+00          5.179
               14        0.000       0.21920344396836E+00          5.965
               15        0.000       0.36996116447603E+00         10.067
               16        0.000       0.47413598869476E+00         12.902
               17        0.000       0.59704258966976E+00         16.246
 E1.u
                1        4.000      -0.14611228912127E+01        -39.759        -1.38E-07
                2        4.000      -0.74059274409717E+00        -20.153         4.73E-07
                3        4.000      -0.42926350919353E+00        -11.681         3.84E-07
                4        4.000      -0.36012247057745E+00         -9.799         1.04E-07
                5        4.000      -0.34375598150944E+00         -9.354         2.77E-07
                6        4.000      -0.23872168334049E+00         -6.496         3.02E-07
                7        4.000      -0.14121103320027E+00         -3.843         2.95E-07
                8        0.000      -0.34031853126276E-01         -0.926
                9        0.000       0.34243804967781E-01          0.932
               10        0.000       0.81737301772674E-01          2.224
               11        0.000       0.98133954618460E-01          2.670
               12        0.000       0.18929708105462E+00          5.151
               13        0.000       0.20814564597375E+00          5.664
               14        0.000       0.28074152616232E+00          7.639
               15        0.000       0.37223435701734E+00         10.129
               16        0.000       0.38285645464621E+00         10.418
               17        0.000       0.47087099484952E+00         12.813

 HOMO :         7 E1.u              -0.14121103320027E+00
 LUMO :         7 E1.g              -0.90708269444884E-01

 =======================================
 M U L L I K E N   P O P U L A T I O N S
 ========================================

 The survey below gives for each atom:
 a) the total charge (Z minus electrons)
 b) the net spin polarization (nr of electrons spin-A minus spin-B)
 c) for each spin the atomic electron valence density (integrated) per L-value.
```

```
Atom               Charge    Spin density        S        P        D        F
----               ------    ------------     ------   ------   ------   ------
1 XX               0.0000                     0.0000   0.0000   0.0000   0.0000
2 C               -0.1004                     1.1434   2.8480   0.1091   0.0000
3 N               -0.4664                     1.5804   3.8144   0.0716   0.0000
4 XX               0.0000                     0.0000   0.0000   0.0000   0.0000
5 N               -0.4664                     1.5804   3.8144   0.0716   0.0000
6 XX               0.0000                     0.0000   0.0000   0.0000   0.0000
7 Mo               1.8785                     1.8573   6.1224   4.1417   0.0000
8 Mo               1.8785                     1.8573   6.1224   4.1417   0.0000
9 N               -0.3698                     1.3845   3.9612   0.0241   0.0000
10 N              -0.3698                     1.3845   3.9612   0.0241   0.0000
11 N              -0.3698                     1.3845   3.9612   0.0241   0.0000
12 N              -0.3698                     1.3845   3.9612   0.0241   0.0000
13 N              -0.3698                     1.3845   3.9612   0.0241   0.0000
14 N              -0.3698                     1.3845   3.9612   0.0241   0.0000
15 H              -0.0312                     0.9018   0.1294   0.0000   0.0000
16 H              -0.0530                     0.9221   0.1309   0.0000   0.0000
17 H              -0.0312                     0.9018   0.1294   0.0000   0.0000
18 H              -0.0530                     0.9221   0.1309   0.0000   0.0000
19 H              -0.0312                     0.9018   0.1294   0.0000   0.0000
20 H              -0.0530                     0.9221   0.1309   0.0000   0.0000
21 H              -0.0312                     0.9018   0.1294   0.0000   0.0000
22 H              -0.0530                     0.9221   0.1309   0.0000   0.0000
23 H              -0.0312                     0.9018   0.1294   0.0000   0.0000
24 H              -0.0530                     0.9221   0.1309   0.0000   0.0000
25 H              -0.0312                     0.9018   0.1294   0.0000   0.0000
26 H              -0.0530                     0.9221   0.1309   0.0000   0.0000
```

References

[1] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.

[2] A. L. Odom, P. L. Arnold, and C. C. Cummins, *J. Am. Chem. Soc.*, 1998, **120**, 5836.

[3] A. L. Odom, *Ph.D. Thesis, Massachusetts Institute of Technology, MA* **1997**.

[4] Y.-C. Tsai, M. J. A. Johnson, D. J. Mindiola, C. C. Cummins, W. T. Klooster, and T. F. Koetzle, *J. Am. Chem. Soc.*, 1999, **121**, 10426.

[5] M. G. Fickes, W. M. Davis, and C. C. Cummins, *J. Am. Chem. Soc.*, 1995, **117**, 6384.

[6] M. G. Fickes, *Ph.D. Thesis, Massachusetts Institute of Technology, MA* **1998**.

[7] L. A. Carpino, R. E. Padykula, D. E. Barr, F. H. Hall, J. G. Krause, R. F. Dufresne, and C. J. Thoman, *J. Org. Chem.*, 1988, **53**, 2565.

[8] D. E. Barr, *Ph.D. Thesis, University of Amherst, MA* **1965**.

[9] S. K. Sur, *J. Magn. Reson.*, 1989, **82**, 169.

[10] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

[11] E. J. Baerends and et. al., *Chem. Phys.*, 1973, **2**, 41.

[12] G. Velde te and E. J. Baerends, *J. Comp. Phys.*, 1992, **99**, 84.

[13] C. F. Guerra and et. al., *METECC-95*, 1995, 305.

[14] T. Ziegler, V. Tschinke, E. J. Baerends, J. G. Snijders, and W. Ravenek, *J. Phys. Chem.*, 1989, **93**, 3050.

[15] T. Ziegler, J. G. Snijders, E. J. Baerends, and J. G. Snijders, *J. Chem. Phys.*, 1981, **74**, 1271.

[16] E. J. Calculations were performed on a Alpha/Linux machine using Amsterdam Density Functional (ADF) 2.3.0, ADF 1999 list of contributors: Baerends, A. Berces, B. C., P. M. Boerrigter, L. Cavallo, L. Deng, R. M. Dockson, D. E. Ellis, L. Fan, T. H. Fischer, C. F. Guerra, S. J. A. v. Gisbergen, J. A. Groeneveld, O. V. Gritsenko, F. E. Harris, P. v. d. Hoek, H. Jacobsen, G. v. Kessel, F. Kootstra, E. v. Lenthe, V. P. Osinga, P. H. T. Philipsen, D. Post, C. Pye, W. Ravenek, P. Ros, P. R. T. Schipper, G. Schreckenbach, J. G. Snijders, M. Sola, D. Swerhone, G. t. Velde, P. Vernooijs, L. Versluis, O. Visser, E. v. Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo, and T. Ziegler.

[17] C. F. Guerra, J. G. Snijders, G. Velde te, and E. J. Baerends, *Theo. Chem. Acc.*, 1998, **99**, 391.