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SUPPORTING INFORMATION

Copper(II) and Oxovanadium(V) Complexes of Hexaphyrin(1.0.1.0.0.0)

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General Experimental Procedures. Prior to use, all glassware was soaked in KOH-saturated isopropyl alcohol for ca. 12 h and then rinsed with water and acetone before being thoroughly dried. Tetrahydrofuran (THF) was dried by passage through two columns of activated alumina. Methanol, dichloromethane, *n*-pentane and cyclohexanes were purchased from Fisher Scientific and used as received. Deuterated chloroform was purchased from Cambridge Isotope Labs and used as received. $VO(Oi\text{-}Pr)_3$ (Strem) and Cu(OAc)2 (Fisher Scientific) was purchased commercially and used as received. Solutions were stirred magnetically.

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Mercury 400 MHz or on a Varian Inova 500 MHz. UV-visible spectra were recorded on a Beckman DU-640 or a Carey 5000 spectrophotometer. High-resolution mass spectra were obtained at the University of Texas at Austin, Department of Chemistry and Biochemistry, Mass Spectrometry Facility. Elemental analyses were performed by Midwest Microlabs Inc., Indianapolis, IN.

X-ray Experimental

2 [$C_{44}H_{50}N_6Cu_2Cl_2$-$3C_6H_{12}$] Crystals grew as fairly large, dark red needles by slow evaporation from a dichloromethane / cyclohexane solution. The crystal was cut from a cluster of crystals and had approximate dimensions: 0.31 x 0.10 x 0.08 mm. The data were collected on a Nonium Kappa CCD diffractometer using a graphite monochromater with MoKα radiation ($\lambda = 0.71073$Å). A total of 222 frames of data were collected using ω-scans with a scan range of 1.5° and a counting time of 208 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.[1] The structure was solved by direct methods using SIR97[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The Cu complex lies around a crystallographic two-fold rotation axis at ½, y, ¾. There are 1.5 molecules of cyclohexane per asymmetric unit. One molecule of solvent lies around a crystallographic inversion center at 0, ½, ½. The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0421*P)^2 + (12.345*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.106, with R(F) equal to 0.0396 and a goodness of fit, S, = 1.02. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[4] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[5]

3 [$C_{44}H_{53}N_6O_3V$] Crystals grew as small, dark plates by slow evaporation from a dichloromethane solution. The data crystal was a small plate that had approximate dimensions: 0.12 x 0.05 x 0.03 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 140 frames of data were collected using ω-scans with a scan range of 2° and a counting time of 480 seconds per frame. The data were collected at 223 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.[1] The structure was solved by direct methods using SIR97[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). One of the methyl groups on an ethyl group was found to be disordered. The disorder was modeled by assigning the variable x to the site occupancy factor for one methyl position defined by C32 and (1-x) for the site occupancy factor for the alternate position defined by C32A. A common isotropic displacement parameter was refined for both C32 and C32A. In this way, the site occupancy factor for C32 was estimated to be 68(2)%. The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.02*P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_W(F^2)$ refined to 0.128, with R(F) equal to 0.0714 and a goodness of fit, S, = 1.12. Definitions used for calculating R(F), $R_W(F^2)$ and the goodness of fit, S, are given below.[4] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[5]

References

1) Z. Otwinowski and W. Minor, in *Methods in Enzymology,* ed. C. W. Carter, Jr. and R. M. Sweets, Academic Press, 1997, **276**, 307-326.

2) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115-119.

3) G. M. Sheldrick, *SHELXL97. Program for the Refinement of Crystal Structures,* 1994 University of Gottingen, Germany.

4) $R_W(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.

$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

5) *International Tables for X-ray Crystallography* (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

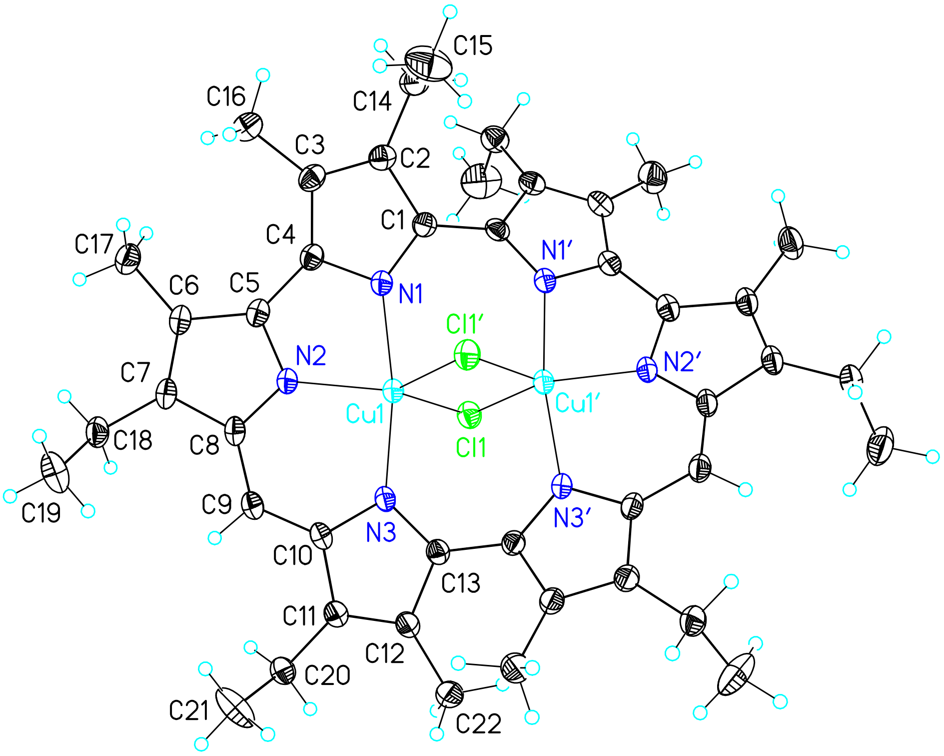

Figure **S1**. View of the Cu complex in **2** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. The complex lies on a crystallographic two-fold rotation axis at ½, y, ¾. Atoms with labels appended by a ‘ are related by 1-x, y, 1½ - z.

Table S1. Crystal data and structure refinement for 2.

Empirical formula	C62 H86 Cl2 Cu2 N6	
Formula weight	1113.35	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 22.6533(3) Å	α= 90°.
	b = 18.5581(3) Å	β= 128.203(1)°.
	c = 17.2459(3) Å	γ = 90°.
Volume	5697.39(15) Å^3	
Z	4	
Density (calculated)	1.298 mg/m^3	
Absorption coefficient	0.885 mm^{-1}	
F(000)	2368	
Crystal size	0.31 x 0.10 x 0.08 mm	
Theta range for data collection	2.19 to 27.47°.	
Index ranges	-29<=h<=29, -24<=k<=24, -22<=l<=22	
Reflections collected	12599	
Independent reflections	6526 [R(int) = 0.0247]	
Completeness to theta = 27.47°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6526 / 18 / 326	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0396, wR2 = 0.0962	
R indices (all data)	R1 = 0.0570, wR2 = 0.1060	
Largest diff. peak and hole	0.841 and -0.497 e.Å^{-3}	

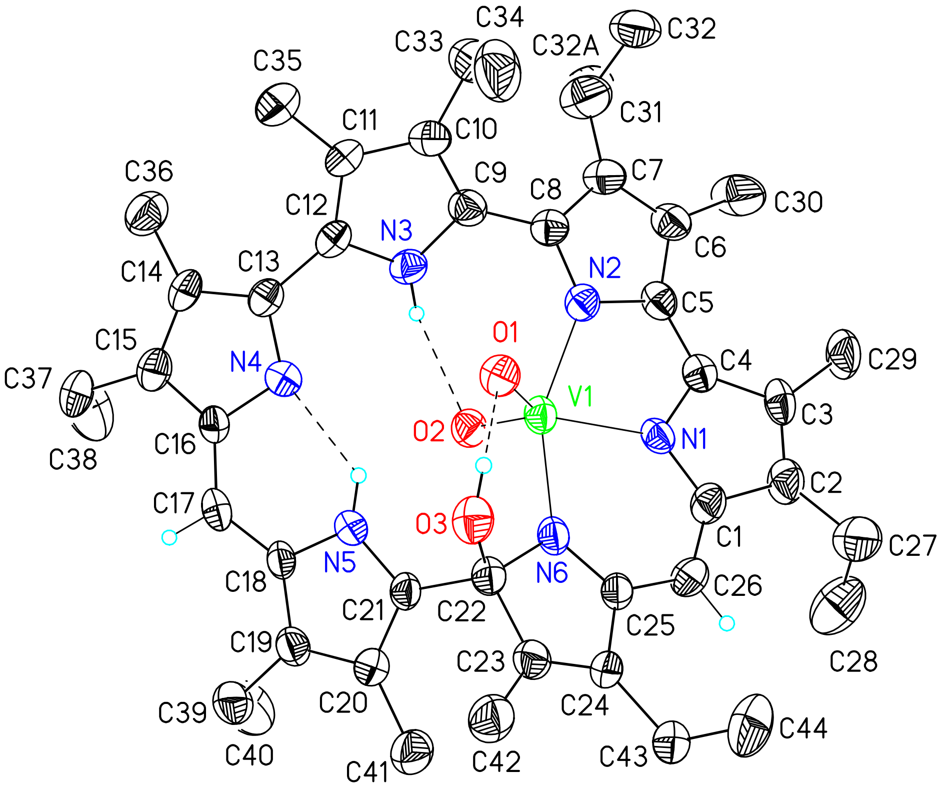

Figure S2. View of the vanadium complex **3** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. Most hydrogen atoms have been removed for clarity. Dashed lines are indicative of H-bonding interactions. The geometry of these interactions is: O1-H1O···O3, O···O 2.668(4) Å, H···O 1.79Å, O-H···O 165°; N3-H3N···O2, N···O 2.875(4)Å, H···O 2.09Å, N-H···O 152°; N5-H5N···O2, N···O 2.706(5)Å, H···N 2.16Å, N-H···N 121°. The disordered methyl carbons, C32 and C32a, are shown.

Table S2. Crystal data and structure refinement for 3.

Empirical formula	C44 H53 N6 O3 V	
Formula weight	764.86	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.6960(5) Å	α= 74.891(2)°.
	b = 12.8190(5) Å	β= 65.9560(19)°.
	c = 13.9100(6) Å	γ = 81.4270(19)°.
Volume	1993.60(14) Å^3	
Z	2	
Density (calculated)	1.274 mg/m^3	
Absorption coefficient	0.296 mm^{-1}	
F(000)	812	
Crystal size	0.12 x 0.05 x 0.03 mm	
Theta range for data collection	2.19 to 24.93°.	
Index ranges	-15<=h<=15, -15<=k<=15, -16<=l<=15	
Reflections collected	10519	
Independent reflections	6900 [R(int) = 0.0644]	
Completeness to theta = 24.93°	99.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6900 / 0 / 508	
Goodness-of-fit on F^2	1.118	
Final R indices [I>2sigma(I)]	R1 = 0.0714, wR2 = 0.1040	
R indices (all data)	R1 = 0.1803, wR2 = 0.1278	
Largest diff. peak and hole	0.327 and -0.290 e.Å^{-3}	