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Preparation of anhydrous vanadium(II) sulfate compounds from aqueous solutions: the synthesis and characterization of $[V(en)_3]SO_4$, $V(bpy)_2SO_4$ and $V(py)_4SO_4$ ☆

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Abstract

An easy way to prepare anhydrous vanadium(II) compounds by reaction of aqueous solutions of $[V(H_2O)_6]SO_4$ with neutral amines is described as well as the X-ray crystal structure determinations of $[V(en)_3]SO_4 \cdot CH_3OH$ (**I**) and $V(bpy)_2SO_4$ (**II**). The air-sensitive compound **I** crystallizes in the trigonal space group $P\bar{3}1c$ with $a=9.009(3)$, $c=9.570(2)$ Å, $V=672.7(3)$ Å^3 and $Z=2$. **II** crystallizes in the monoclinic space group $I2/a$ with $a=11.957(2)$, $b=12.071(2)$, $c=14.614(1)$ Å, $\beta=101.97(1)°$, $V=2063(1)$ Å^3 and $Z=4$.

Keywords: Crystal structures; Vanadium complexes; Amine complexes; Sulfate complexes

1. Introduction

During our studies of the chemistry of vanadium(II) leading to the synthesis and characterization of a dinuclear compound with a short metal-to-metal bond, namely, V_2(di-*p*-tolylformamidinato)$_4$ [1], one of the major difficulties encountered was the lack of well-characterized starting materials [2].

One of the many approaches we explored was that of the stabilization of vanadium(II) by pyridine or pyridine-like ligands. It has been found, by us and others, that vanadium(II) has a high affinity for those types of ligands [3]. Unusually air-stable products were obtained when water was also present in the crystals. Examples of these types of compounds are $[V(saccharinato)_2(H_2O)_4] \cdot 2H_2O$ [4], $[V(picolinato)_2(H_2O)_2] \cdot 2H_2O$ and $V(pyridinesulfonato)_2 \cdot 4H_2O$ [2] which were prepared from aqueous $[V(H_2O)_6]SO_4$ solutions.

Earlier work had shown that hydrated vanadium(II) reacted with heterocyclic and aliphatic amines [5] as well as phosphines [6]. However, there was little work on the structural characterization of such products. In view of the current interest in the chemistry of vanadium(II), including its reactivity towards N_2 and nitrogen containing ligands [7], we now report the syntheses, X-ray crystal structures and other properties of some anhydrous vanadium–amine species obtained from the reaction of aqueous vanadium(II) sulfate and the appropriate amine.

2. Experimental

2.1. Materials and methods

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. The solvents as well as the liquid amines were purified by conventional methods and were freshly distilled under nitrogen prior to use. $[V(H_2O)_6]SO_4$ was prepared as reported earlier [4]. Pyridine and ethylenediamine were purchased from Aldrich and J.T. Baker, respectively. 2,2′-Bipyridine, purchased from Merck, was used as supplied. The IR spectra were recorded on a Shimadzu FT-IR-8101 spectrometer. UV–Vis spectra were obtained on a Shimadzu UV-160 spectrometer. Magnetic measurements were made on a Johnson-Matthey MSB-1 balance. The chemical analyses were done after the samples had been hydrolyzed

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☆ Dedicated to Professor F. Albert Cotton on his 65th birthday and the graduation of his 100th Ph.D. student.

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with acid. For vanadium, the method described in Ref. [8] was used. The sulfate ion was analyzed by a gravimetric method [9]. The amounts of all of the amines were obtained spectrophotometrically from calibration curves of the protonated amines. Satisfactory analyses were obtained. The oxidation state of vanadium in each of the compounds was checked by comparing λ_{max} of a standard vanadium(II) sulfate solution with that of the anaerobic solutions produced by the sulfuric acid hydrolysis on the vanadium products.

2.1.1. $[V(en)_3]SO_4$ (I)

A cold solution of ethylenediamine (11.7 g, 193 mmol) in water (10 ml) was added to 30 ml of a cold aqueous solution of $[V(H_2O)_6]SO_4$ (4.00 g, 15.7 mmol). The reaction mixture was vigorously stirred for 1 min. The light green solid produced was quickly filtered and washed with small amounts of ethanol. After drying in vacuo for 20 min, the yield of $[V(en)_3]SO_4$ was 3.1 g (60%).

Single crystals for X-ray diffraction analysis were produced by reacting a solution of 0.60 ml of ethylenediamine in 10 ml of water and 30 ml of an aqueous 0.10 M solution of $[V(H_2O)_6]SO_4$. After stirring in an ice bath for 2 min the solid was filtered with the aid of Celite. To the light green solution was added a layer of 15 ml of ethanol. After 1 day at 5 °C, light green needle-like crystals were formed. IR (cm^{-1}): 3346(s), 3285(s), 3158(s), 1597(w), 1123(s), 1034(w). UV–Vis (water): λ_{max} (nm): 597. Magnetic susceptibility: 4.18 BM. *Anal.* Calc. for $[V(en)_3]SO_4$: V, 15.6; en, 55.1; SO_4^{2-}, 29.4. Found: V, 15.6; en, 55.1; SO_4^{2-}, 29.3%.

2.1.2. $V(bpy)_2SO_4\cdot CH_3OH$ (II)

2,2′-Bipyridine (4.65 g, 29.4 mmol) dissolved in 15 ml of methanol was added to 5 ml of an aqueous solution of $[V(H_2O)_6]SO_4$ (3.75 g, 14.7 mmol). The dark green solution was stirred for 5 min, and then a layer of 20 ml of acetone was added. After 5 days at 0 °C, deep green microcrystals of **I** were collected by filtration and washed with small amounts of acetone. After drying in vacuo for 20 min the yield of $V(bpy)_2SO_4$ was 5.40 g (80%).

Needle-like single crystals, suitable for X-ray diffraction analysis, were formed from a solution of 0.0352 g of $V(bpy)_2SO_4$ in 6 ml of methanol to which a layer of 6 ml of acetone was added. After 1 week at room temperature the green needle-like crystals were collected. Both dried bulk material as well as the dried crystals show the same physical and chemical characteristics. IR, KBr (cm^{-1}): 3569(s), 1597(m), 1470(w), 1443(m), 1374(w), 1115(s), 774(w), 735(w), 619(w). UV–Vis (water): λ_{max} (nm): 660. Magnetic susceptibility: 4.00 BM. *Anal.* Calc. for $V(bpy)SO_4$: V, 11.1; bpy, 68.0; SO_4^{2-}, 20.9. Found: V, 11.2; bpy, 68.0, SO_4^{2-}, 20.7%.

2.1.3. $V(py)_4SO_4$ (III)

To 1 ml of an aqueous solution of $[V(H_2O)_6]SO_4$ (1.00 g, 3.90 mmol) were added 50 ml of pyridine. The purple color quickly changed to dark red. After stirring the solution for 5 min at room temperature, it was heated and then 30 ml of solvent were distilled. After cooling the solution to room temperature, a burgundy red solid was filtered and washed with hexanes, and dried in vacuo for 3 min. The yield of $V(py)_4SO_4$ was 1.31 g (73%). IR, Nujol (cm^{-1}): 3495(m), 3061(m), 1636(w), 1609(w), 1599(w), 1223(m), 1177(m), 1138(m), 1119(m), 1111(m), 1076(m), 1065(m), 1047(m), 1015(m), 774(m), 768(m), 712(m), 698(m). UV–Vis (pyridine): λ_{max} (nm): 520. Magnetic susceptibility: 3.67 BM. *Anal.* Calc. for $V(py)_4SO_4$: V, 11.0; py, 68.3; SO_4^{2-}, 20.7. Found: V, 11.2; py, 67.9; SO_4^{2-}, 20.6%.

2.2. X-ray crystallography

2.2.1. $[V(en)_3]SO_4$

A pale green, needle-like crystal of **I** was mounted on the tip of a glass fiber. Eleven reflections from a rotation photograph were used to establish an initial orientation matrix. A set of 25 reflections was then chosen from a fast scan of reciprocal space between the 2θ limits of 50 and 80° and used to refine the cell used for data collection. The data were corrected for Lorentz and polarization effects, and an absorption correction based on a series of ψ-scans was applied.

The positions of the V, S, N and C atoms were taken from a direct-methods E map. The positions of the disordered O atoms of the SO_4 group were later taken from a difference Fourier synthesis. The crystals are essentially homologous with several other tris(ethylenediamine)metal(II) sulfates, such as the compounds of copper and nickel [10,11]. Although the reports of similar structures included up to four unique positions for the oxygen atoms, only two positions could be refined in this case, each position having an occupancy of 1/3. When the other reported positions and the site occupancy factors were included in the refinement, the occupancies for the extra sites approached zero and for the two original sites remained close to 1/3 (as they must, to maintain the proper stoichiometry). Therefore only the two oxygen sites originally found in our determination were included in the final refinement, with occupancies fixed at 1/3. The nature of the disorder and the hydrogen-bonding implications of each orientation have been described in detail [10,11]. The merohedral twinning problem discussed in Ref. [11b] is not of concern here, since the effect was only observed at reduced temperatures (< 190 K). Were a similar effect operating in this case, one would expect violations of the systematic absences and a lack of agreement between *hkl* and *khl* reflections, neither of which were observed in the dataset. Following full anisotropic refinement of the non-hydrogen atoms, the positions of all of the hydrogen atoms were found in a difference Fourier map and included in the refinement (with isotropic thermal parameters). Each pair of H atoms was refined with a common isotropic thermal parameter. Refinement calculations were carried out on a Local Area VAX cluster using the SDP package. For each set of six O–S–O angles possible for a distinct SO_4 group, the angles all range from 102 to 109°.

2.2.2. $V(bpy)_2SO_4 \cdot CH_3OH$

A dark green crystal of **II** was mounted on the tip of a glass fiber with its long axis approximately parallel to the ϕ axis of the diffractometer. A set of nine reflections from a rotation photograph was used to establish an initial orientation matrix, and the resulting primitive cell was transformed to a body-centered monoclinic setting. After confirming the Laue symmetry and cell dimensions with axial photography, 25 reflections were chosen for orientation from a fast scan of reciprocal space ($50 < 2\theta < 62°$). The data were corrected for Lorentz and polarization effects, and an absorption correction based on a series of ψ-scans was applied. Information pertinent to the data collection and structure refinement of both **I** and **II** is presented in Table 1.

The positions of all of the non-hydrogen atoms of the metal complex were found by direct methods. Following full-matrix least-squares refinement of these positions and isotropic temperature factors, a pair of peaks apparently due to the presence of a slightly disordered methanol molecule was found in a difference Fourier map. The solvent molecule refined smoothly with the carbon atom fixed on the two-fold axis and the oxygen atom on a general position at one-half occupancy, although the refined C–O bond distance is unreliable. For the final cycles of refinement, structure factor calculations included hydrogen atoms in calculated positions for the bipyridine ligand. Carbon–hydrogen distances were fixed at 0.95 Å with hydrogen temperature factors set to 1.3 times B_{iso} for the attached carbon atom.

The atomic coordinates for **I** and **II** are given in Tables 2 and 3, respectively. Selected bond distances and bond angles for **I** are given in Table 4 and for **II** in Table 5.

3. Results and discussion

3.1. Compound I

The crystal structure of compound **I** is essentially homologous with that of several other tris(ethylenediamine)metal(II) sulfates, such as the compounds of copper [10] and nickel [11]. An ORTEP drawing of the cation is shown in Fig. 1, which indicates the crystallographic $\bar{3}$ symmetry maintained by the three chelating ethylenediamine groups. There is an extensive hydrogen bonding network formed by the hydrogen atoms of the ligand and the oxygen atoms of the sulfate group. However, unlike those formed in the aqueous saccharinates or picolinate [4,2], this network is not enough to stabilize the product. Crystals of **I** react readily with oxygen and are hygroscopic. Compound **I** forms very rapidly under the reaction conditions described above. However, precautions should be observed to dissipate the heat produced during the reaction. Its properties are consistent with those reported for other $[V(en)_3]^{2+}$ containing compounds, such as in halides [5a] and in the triflate [5b].

3.2. Compound II

The structure of compound **II** is depicted in Fig. 2. The vanadium atom is surrounded by the two bipyridine ligands as well as a chelating sulfate group. A crystallographic two-fold axis relates two halves of the molecule and includes the V–S vector.

The chelating configuration of the sulfate group, even though not very common, has been found in several compounds of other metal atoms [12]. To our knowledge no other vanadium–bipyridine compound shows that type of ligand arrangement. However, there is at least one compound containing copper which is somewhat similar, namely $[Cu(bpy)_2(ONO)]NO_3$ [13].

The intense green color of the aqueous solutions of **II** is characteristic of those solutions that contain vanadium(II) and bipyridine [5a,14]. However, the reported species giving rise to those colors has always been the $V(bpy)_3{}^{2+}$ entity which is probably true for those cases in which non-coordinating anions were used. We were unable to crystallize a pure sample of $[V(bpy)_3]SO_4$. Even in those cases in which we used bipyridine in more than a 3:1 molar ratio relative to vanadium, the chemical analysis of the isolated crystalline product consistently showed a ratio close to 2:1 (bipyridine:vanadium).

3.3. Compound III

Upon addition of pyridine to concentrated aqueous vanadium sulfate solutions an immediate change in color is produced. Azeotropic distillation of the water afforded a red solid which was insoluble in water, ethanol, acetone, THF or hexanes and only partially soluble in pyridine. The chemical analysis suggests an empirical formula of $V(py)_4SO_4$. Unfortunately all attempts to crystallize the compound from pyridine solutions covered by layers of different organic solvents always produced star-shaped crystals that were unsuitable for single crystal X-ray diffraction studies.

Table 1
Crystal data for $[V(en)_3]SO_4$ (I) and $V(bpy)_2SO_4 \cdot CH_3OH$ (II)

	I	II
Formula	$VSO_4N_6C_6H_{24}$	$VSO_4N_4C_{20}H_{16} \cdot CH_3OH$
Formula weight	327.30	491.42
Space group	$P\bar{3}1c$	$I2/a$
a (Å)	9.009(3)	11.957(2)
b (Å)		12.071(2)
c (Å)	9.570(2)	14.614(1)
β (°)		101.97(1)
V (Å^3)	672.7(3)	2063(1)
Z	2	4
D_{calc} (g cm^{-3})	1.617	1.582
Crystal size (mm)	$0.10 \times 0.11 \times 0.24$	$0.08 \times 0.10 \times 0.29$
μ(Cu Kα) (cm^{-1})	78.68	53.63
Data collection instrument	Rigaku AFC5R	
Radiation (monochromated in incident beam)	CuK$_\alpha$($\lambda_{\bar{\alpha}}$ = 1.54184Å)	
Orientation reflections, 2θ: number, range	25, 51.8–72.7	25, 50.7–61.5
Temperature (°C)	22(2)	
Scan method	ω–2θ	
Data collection range, 2θ (°)	4.0–120.0	
No. total data	341	1555
No. unique data, with $F_o^2 > 3\sigma(F_o^2)$	284	1266
No. parameters refined	55	150
Transmission factors: max., min.	1.0000, 0.9214	0.9999, 0.8989
R [a]	0.028	0.039
R_w [b]	0.040	0.057
Quality-of-fit indicator [c]	1.25	1.63
Largest shift/e.s.d., final cycle	0.02	0.01
Largest peak (e Å^{-3})	0.60(5)	0.16(3)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.
[c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

Table 2
Positional parameters and their e.s.d.s for $[V(en)_3]SO_4$ [a]

Atom	x	y	z	B (Å^2)
V	0.667	0.333	0.250	1.87(2)
N	0.4509(3)	0.3119(2)	0.1264(3)	2.82(5)
C	0.2953(3)	0.1546(3)	0.1714(3)	3.24(7)
H(1)	0.435(4)	0.394(4)	0.144(4)	2.2(5) *
H(2)	0.470(4)	0.308(4)	0.036(3)	2.2(5) *
H(3)	0.297(3)	0.055(4)	0.133(3)	1.0(4) *
H(4)	0.201(3)	0.158(3)	0.139(3)	1.0(4) *
S	0.333	0.667	0.250	2.20(2)
O(1)	0.493(1)	0.790(1)	0.3171(7)	8.2(3)
O(2)	0.439(1)	0.659(1)	0.3548(9)	8.6(2)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: 1/3-$[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. Starred atoms were refined isotropically.

However, the lack of solubility of **III** in most common solvents is probably an indication of the presence of an extended structure in the crystal, presumably by formation of sulfate bridges such as those in $[(H_2O)_2(py)_2CrSO_4Cr(py)_4SO_4]_\infty$, in which infinite chains are present [15]. The well-characterized vanadium(II) tetrapyridine compound $V(py)_4Cl_2$ exhibits a molecular structure [16]. It is considerably more soluble in common organic solvents.

3.4. Other structural relationships

Both compounds for which structures are described here follow the general pattern of most mononuclear vanadium(II) species, in which the metal center is normally octahedrally coordinated [2]. The deviations in the bond angles from the ideal values are just those attributable to the rings formed by the chelating ligands. All V–N bond distances are also in the range of those found for other V-amine containing species [2]. The shorter V–N bond distance in **II** relative to that in **I** (2.110[2] versus 2.199(2) Å), is probably due to the better π-accepting ability of the bipyridine ligand relative to that of the ethylenediamine ligand. The V–N bond distance in **II** is even shorter than that found in other vanadium–bipyridine complexes in which the vanadium atom is in a higher oxidation state [17].

Table 3
Positional parameters and their e.s.d.s for $V(bpy)_2(SO_4)\cdot CH_3OH$ [a]

Atom	x	y	z	B (Å^2)
V	0.250	0.69065(6)	0.000	2.47(1)
S	0.250	0.4668(1)	0.000	3.10(2)
O(1)	0.3111(2)	0.5450(2)	−0.0527(2)	3.13(5)
O(2)	0.3304(3)	0.4000(2)	0.0647(2)	4.60(6)
N(1)	0.2034(2)	0.8113(2)	0.0897(2)	2.80(5)
N(2)	0.3989(2)	0.7067(2)	0.1064(2)	2.74(6)
C(1)	0.1019(3)	0.8636(3)	0.0780(3)	3.70(8)
C(2)	0.0770(3)	0.9397(3)	0.1400(3)	4.29(9)
C(3)	0.1578(3)	0.9635(3)	0.2197(3)	4.02(8)
C(4)	0.2620(3)	0.9118(3)	0.2319(3)	3.49(7)
C(5)	0.2839(3)	0.8381(3)	0.1671(2)	2.79(7)
C(6)	0.3941(3)	0.7797(3)	0.1750(2)	2.78(7)
C(7)	0.4870(3)	0.7979(3)	0.2479(3)	3.50(8)
C(8)	0.5875(3)	0.7409(3)	0.2486(3)	3.88(8)
C(9)	0.5929(3)	0.6684(3)	0.1778(3)	3.80(8)
C(10)	0.4975(3)	0.6522(3)	0.1084(3)	3.36(7)
C(S1)	0.750	0.6187(7)	0.500	7.9(2)
O(S)	0.6693(6)	0.6727(6)	0.4989(7)	8.1(2)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $1/3\text{-}[a^2a^{*2}B_{11}+b^2b^{*2}B_{22}+c^2c^{*2}B_{33}+2ab(\cos\gamma)a^*b^*B_{12}+2ac(\cos\beta)a^*c^*B_{13}+2bc(\cos\alpha)b^*c^*B_{23}]$.

Table 4
Selected bond distances (Å) and angles (°) for $[V(en)_3]SO_4$ (I)

V–N	2.199(2)	S–O(1)	1.455(7)
N–C	1.473(3)	S–O(2)	1.41(1)
C–C′	1.509(5)		
N-V-N′	93.81(8)	N-V-N*	171.27(7)
N-V-N″	92.87(9)	V-N-C	107.5(2)
N-V-N$^+$	80.13(7)	N-C-C′	109.3(2)

Numbers in parentheses are e.s.d.s in the least significant digits.

Table 5
Selected bond distances (Å) and angles (°) for $V(bpy)_2SO_4\cdot CH_3OH$ (II)

V–O(1)	2.110(2)	S–O(1)	1.500(3)
V–N(1)	2.110(3)	S–O(2)	1.446(3)
V–N(2)	2.116(2)		
O(1)-V-O(1′)	67.1(1)	N(1)-V-N(2′)	95.9(1)
O(1)-V-N(1)	163.3(1)	N(2)-V-N(2′)	169.5(1)
O(1)-V-N(1′)	101.1(1)	O(1)-S-O(1′)	102.0(1)
O(1)-V-N(2)	92.44(9)	O(1)-S-O(2)	111.0(1)
O(1)-V-N(2′)	96.3(1)	O(1)-S-O(2′)	110.1(1)
N(1)-V-N(1′)	92.7(1)	O(2)-S-O(2′)	112.2(2)
N(1)-V-N(2)	76.7(1)		

Numbers in parentheses are e.s.d.s in the least significant digits.

4. Supplementary material

The following tables are available (from author L.M.D.) for both I and II: bond distances; bond angles; calculated hydrogen atom positions (for II); anisotropic displacement parameters; a list of observed and calculated structure factors (16 pages).

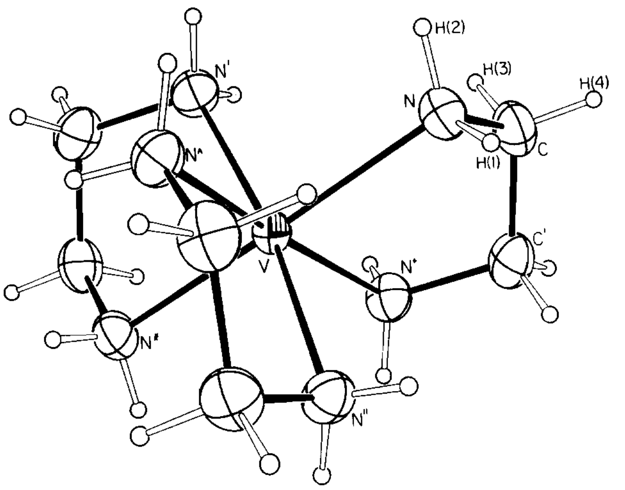

Fig. 1. Thermal ellipsoid plot of the X-ray structure of the cation in $[V(en)_3]SO_4$, showing the atom naming scheme. Non-hydrogen atoms are represented by their 50% probability ellipsoids. Hydrogen atoms are shown as arbitrarily-sized spheres.

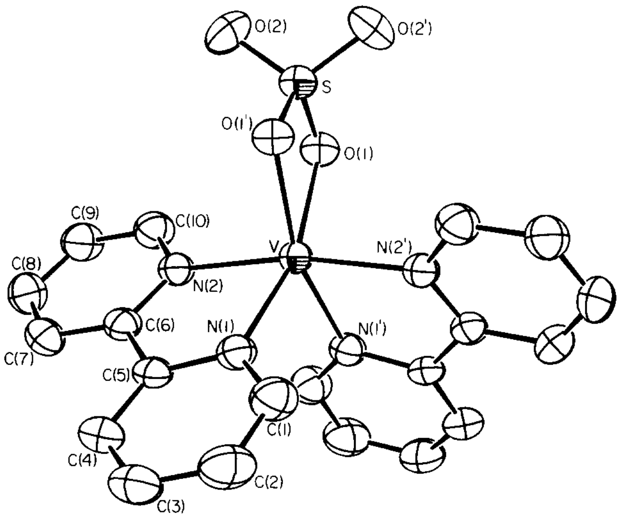

Fig. 2. ORTEP drawing of the molecular structure of $V(bpy)_2SO_4\cdot CH_3OH$ showing the atom labeling scheme. Atoms are represented by their 50% probability ellipsoids.

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