Vanadium(IV) Complexes with N,N,S-Donor Systems

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Research interest in V/O chemistry derives from its utility in several biological and industrial processes.[1] Vanadium is an essential element in biological systems, taking part in some enzymic reactions, such as nitrogen fixation.[2] Its insulinomimetic properties[3] in the therapeutics of diabetes, using oxovanadium species have attracted even more attention. The distinct preference of this metal center for N-, O- and S-coordination environments has prompted the synthesis of numerous model vanadium compounds containing N/O/S donor ligands. Our interest in this area is concentrated on the riches of structure types of the V/O complexes and studies on synthetic systems and clustering mechanisms. V/O complexes, such as $VO(L)_2 \cdot H_2O$ (L = picolinic or pyridine-2-carboxylic acid),[4] $[VO(Hhida)(H_2O)] \cdot CH_3OH$,[5] and VO(SALIMH)(acac),[6] have been synthesized and structurally characterized. We recently reported Mn(II-IV) and Mo(V-VI) of schiff base ligands containing ONS, ONO, NNS donor systems.[7] This paper reports further study on the V/O synthetic systems, in which two novel oxovanadium(IV) complexes with 2-acetylpyridine-S-methyldithiocarbazate (acpy-mdtcH) and 2-acetylpyridine-4-phenylthiosemicarbazate (acpy-phtscH) comprising mixed hard-soft N,N,S-donor systems have been obtained.

Experimental Section

All procedures were performed under aerobic conditions. Acpy-mdtcH was prepared as described in the literature.[8]

C, H, N, S elemental analyses were performed using a Carlo Erba 1106 automatic analyzer. Positive-ion FAB mass spectra were obtained using a JEOL JMS 700 high resolution mass spectrometer in a *m*-nitrobenzyl alcohol matrix. Melting point determinations were carried out with a Laboratory Devices Inc. Mel-Temp II. The IR spectra in the range 4,000-500 cm^{-1} and UV-Vis spectra in DMSO were recorded using a Mattson Polaris FT-IR spectrophotometer and a Milton Roy Spectronic Genesys 2 spectrophotometer, respectively.

[VO(acpy-mdtc)(acac)] [1]. To a methanol solution (15 mL) of 1.91 mmol (0.43 g) of acpy-mdtcH was added 1.89 mmol (0.53 g) of $VO(acac)_2$. The solution was refluxed for 30 min. and cooled to room temperature to yield a green solid. The solid was filtered, washed with diethyl ether, and dried under vacuum. Yield: 84% (0.62 g) (based on V). mp 196 °C (dec.). Anal. Calcd. for $\mathbf{C_{14}H_{17}N_3O_3S_2V}$: C, 43.08; H, 4.39; N, 10.76; S, 16.43. Found: C, 43.60; H, 4.58; N, 10.31; S, 17.02. FAB^+, m/z 390. IR (cm^{-1}): 1587 ($\nu_{C=N}$), 952 ($\nu_{V=O}$). UV-Vis. {nm, log ε (M^{-1} cm^{-1})}: 753 (1.76), 591 (2.01), 411 (3.99), 339 (4.20).

[VO(acpy-phtsc)(acac)] [2]. A methanol solution (15 mL) of 1.91 mmol (0.231 g) of 2-acetylpyridine, 1.91 mmol (0.320 g) of 4-phenyl-3-thiosemicarbazide, and a drop of c-HCl was heated to reflux for 1 h. After the yellow solution was cooled, 1.89 mmol (0.53 g) of $VO(acac)_2$ was added with stirring and refluxed further for 30 mim. The resulting brown solid was filtered, washed with methanol and diethyl ether, and then dried in vacuum. Yield: 89 % (0.74 g) (based on V). mp 210 °C (dec.). Anal. Calcd. for $\mathbf{C_{19}H_{20}N_4O_3SV}$: C, 52.41; H, 4.63; N, 12.87; S, 7.36. Found : C, 51.73; H, 4.83; N, 12.80 S; 7.78. FAB^+, m/z 435. IR (cm^{-1}): 3374 (ν_{N-H}), 1597 ($\nu_{C=N}$), 952 ($\nu_{V=O}$). UV-Vis. {nm, log ε (M^{-1} cm^{-1})}: 750 (1.71), 573 (2.01), 420 (4.31), 414 (4.30).

X-ray quality brown crystals of molecular unit, $[VO(acpy-phtsc)(acac)] \cdot CH_2Cl_2$ were obtained by slow diffusion of diethyl ether into a dichloromethane solution (CH_2Cl_2 : $(C_2H_5)_2O$ = 1 : 3).

Crystal Structure Determination of 2. A crystal size 0.22 × 0.16 × 0.14 mm was used for data collection on a STOE STAD14 four-circle-diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.71069 Å) at room temperature. Cell parameters and orientation matrix for data collection were determined by least-squares refinement, using 44 reflections in the range of 9.5° < θ < 10.4°. Data were collected using the ω-2θ scan technique. Three standard reflections monitored every 1 h and decayed 5.1% over the course of the data collection. The intensity data were collected for Lorentz and polarization effects. A numerical absorption correction was made: the transmission factors were 0.8879 (min.) and 0.9248 (max.). The structure was solved by direct method (SHELXS-97, Sheldrick, 1990) and refined by full-matrix least-squares methods (SHELXL-97, Sheldrick, 1997). All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were idealized (d(C-H) = 0.96 Å) and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotropic thermal parameter of 1.2 times that of the attached atom. The data collection and structure solution parameters are listed in Table 1, together with standard discrepancy indicies, *R* and *wR*.

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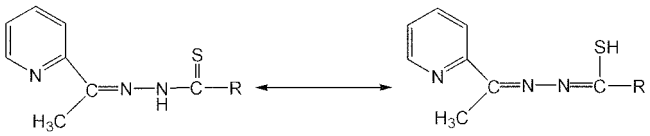
Table 1. Crystal data and structure refinement for compound **2**

Formula	$C_{20}H_{22}Cl_2N_4O_3SV$
Formula weight	520.32
Temperature	293 (2) K
Wavelength	0.71069 Å
Crystal system, space group	Triclinic, *P*-1
Unit cell dimensions	a = 11.882 (5) Å α = 94.29 (5)°
	b = 12.987 (6) Å β = 98.40 (4)°
	c = 8.277 (6) Å γ = 65.79 (3)°
Volume	1167.9 (11) Å^3
Z, calculated density	2, 1.480 Mg m^{-3}
Absorption coefficient	0.772 mm^{-1}
F(000)	534
Crystal size	0.22 × 0.16 × 0.14 mm
Theta range for data collection	1.7-27.5°
Index ranges	h = -15 → 15, k = -16 → 16,
	l = 0 → 10
Reflections collected/unique	5362/5362 [Rint = 0.0000]
Completeness to 2 theta	55.0 100%
Absorption correction	numerical
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5362 / 0 / 280
Final R indices [$I > 2\sigma(I)$]	$R_1{}^a$ = 0.0623, w$R_2{}^b$ = 0.1297
R indices (all data)	$R_1{}^a$ = 0.1075, w$R_2{}^b$ = 0.1612
Goodness-of fit on F^{2,c}	1.112
Largest diff. Peak and hole	0.443 eÅ^{-3} and -0.584 eÅ^{-3}

$^a R = \Sigma(|Fo|-|Fc|)/\Sigma|Fo|$. $^b wR = [\Sigma w(|Fo|^2-|Fc|^2)^2/\Sigma|Fo|^4]^{1/2}$, w = $1/[\sigma^2(Fo^2) + (0.0497P)^2 + 1.5601P$, where P = $(Fo^2+2Fc^2)/3$. ^{c}G.O.F = $[\Sigma w(|Fo|^2-|Fc|^2)^2/(n-p)]^{1/2}$.

Results and Discussion

The reactions of vanadyl acetylacetonate with acpy-mdtcH and acpy-phtscH in methanol afforded the monomeric oxovanadium(IV) complexes, **1** and **2** of VOL(acac) type (L = acpy-mdtc^{-1} and acpy-phtsc^{-1}), respectively. The formulations were in accordance with the data of elemental analysis and physicochemical measurements. The IR spectrum of the free acpy-mdtcH has several prominent bands appearing at *ca* 3149, 1628, and 1059 cm^{-1}, due to ν(N-H), ν(C=N), and ν(C=S) stretching modes, respectively. On complexation for **1**, both bands of ν(N-H) and ν(C=S) disappeared, and the ν(C=N) band shifted to 1587 cm^{-1}. These events indicate NNS coordination mode of the ligand in the thiol form.[9]



In addition, the complexes **1** and **2** exhibited a strong band in the 952 cm^{-1} range due to the terminal V=O stretching,[10] along with a medium-intensity band in the high-frequency region (3374 cm^{-1} for **2**), associated with the N-H stretch of phenyl amine.[4,10,11] The electronic absorption spectra of the complexes exhibited two bands of moderate intensity (log ε = 1.71-2.01 M^{-1} cm^{-1}) at *ca*. 750 and 580 nm due to the ligand field transitions $d_{xy} \rightarrow d_{xz}$, d_{yz} and $d_{xy} \rightarrow d_{x^2-y^2}$, respectively, for the oxovanadium(IV) chromophore. A third d-d band expected at higher energy due to $d_{xy} \rightarrow d_{z^2}$ transition was probably obscured by the tail of the ligand to metal or intraligand CT absorption of *ca*. 400 nm (log ε = 3.99-4.31 M^{-1} cm^{-1}). These transitions are consistent with tetragonally symmetry commonly associated with spectra of the vanadyl complexes.[5,11]

Complex **2** crystallized in triclinic space group P-1 and the unit cell contained one solvate dichloromethane molecule per molecule. **2** consists of vanadyl moiety, one trifunctional acpy-phtsc^{-1}, and the bidentate acac^{-1} ligand that occupies the fifth and sixth metal coordination sites (Figure 1). The V=O bond (1.594 Å) was unexceptional, falling within the range 1.588-1.635 Å.[6] The vanadium atom was displaced out of the best least squares plane (mean deviation was 0.022 Å) formed by the three donors of acpy-phtsc^{-1} and the equatorial donor atom of the bidentate ligand toward the vanadyl oxygen by 0.27 Å. The acpy-phtsc^{-1} is a tridentate meriodional ligand that provides thiolate sulfur (V-S = 2.404 Å), acetyl pyridine nitrogen (V-N = 2.119 Å), and imine nitrogen (V-N = 2.080 Å) donor atoms to the vanadium(IV). This V-S distance is much longer than that observed in [VOL(OMe)] (L = S-methyl 3-((2-hydroxyphenyl)methyl)-dithiocarbazate) (V-S = 2.318 Å).[10] Each of the acetyl pyridine nitrogen and imine nitrogen distance to the vanadium was consistent with values - 2.099-2.121 Å for acetyl pyridine nitrogen and 2.054-2.118 Å for imine nitrogen found in other oxovanadium(IV) complexes.[6,10]

The bidentate acac^{-1} acts as enol form and could have bonded in two orientations either with the neutral carbonyl oxygen in the axial position or in the equatorial position. The carbon-carbon and carbon-oxygen distances suggest that the neutral carbonyl oxygen is in the axial position (Table 2). The long V-O(1) (carbonyl oxygen *trans* to the oxo moiety of the vanadyl ion) distance (2.159 Å) is a direct consequence of the *trans* influence of the oxo ligand and is similar to to the 2.203 distance determined for the complex [VO(SALIMH)-acac-CH_3OH] (SALIMH = 4-(2-(salicylideneamino)ethyl)-imidazolate).[6]

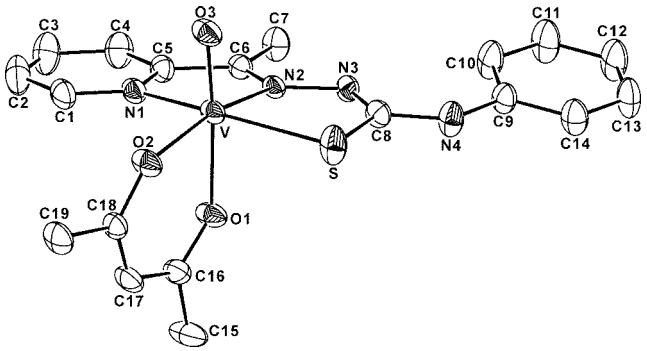


Figure 1. A view of the compound **2** with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms and solvent molecule, CH_2Cl_2 are emitted.

Table 2. Selected geometric parameters (Å, °) for compound **2**

V-O(1)	2.159(3)	N(3)-C(8)	1.303(5)
V-O(2)	1.979(3)	C(8)-S	1.748(4)
V-O(3)	1.594(3)	C(8)-N(4)	1.347(5)
V-N(1)	2.119(4)	N(4)-C(9)	1.412(5)
V-N(2)	2.080(3)	C(9)-C(10)	1.382(6)
V-S	2.40(2)	C(16)-O(1)	1.256(4)
N(1)-C(5)	1.348(5)	C(16)-C(17)	1.401(5)
C(5)-C(6)	1.471(5)	C(17)-C(18)	1.362(6)
N(2)-C(6)	1.295(5)	C(18)-O(2)	1.279(4)
N(2)-N(3)	1.374(4)	C(20)-Cl(2)	1.727(8)
O(1)-V-O(3)	174.2(2)	O(1)-V-O(2)	83.2(1)
O(2)-V-N(2)	162.9(1)	O(2)-V-S	103.0(1)
N(1)-V-S	154.4(1)	O(2)-V-N(1)	97.0(1)
N(1)-V-O(3)	94.3(2)	N(1)-V-N(2)	76.9(1)
N(2)-V-O(3)	99.6(1)	N(2)-V-S	79.4(1)
S-V-O(3)	99.0(1)	C(8)-N(4)-C(9)	131.4(4)
O(2)-V-O(3)	96.8(1)	Cl(1)-C(20)-Cl(2)	113.3(4)

Conclusion

Two novel mononuclear vanadium(IV) complexes **1** and **2** with acpy-mdtcH and acpy-phtscH comprising mixed hard-soft N,N,S-donor systems have been prepared and characterized. Complex **2** consists of vanadyl moiety, one trifunctional acpy-phtsc^{-1}, and the bidentate acac^{-1} ligand that occupies the fifth and sixth metal coordination. The acac^{-1} acts as enol form and the neutral carbonyl oxygen is in the axial position. Continuing studies in our laboratory on these complexes are focusing on the reactivity of the vanadium(IV) analogues of the complexes reported above.

Supporting Information Available: Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-208635). The data can be obtained free of charge via *www.ccdc.cam.ac.uk/conts/retrieving.html* (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: *deposit@ccdc.cam.ac.uk*).

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