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Pyridine-2-thiolato Complexes of VII, VIII, and VIV with Unusual Structural Features**

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One of the stimuli for our continuing interest in vanadium-sulfur chemistry is the relevance of this area to industrial petroleum refining. Certain crude oils contain large amounts of vanadyl (VO²⁺) impurities categorized into two types according to their ligands.[1] These are the vanadyl petroporphyrins, which have been well studied and characterized,^[2] and the vanadyl nonporphyrins whose ligand environment is thought to contain S, N, and/or O donor atoms.[3] The presence of these vanadyl impurities leads to the formation of

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vanadium sulfides (primarily V2S3 and V3S4) under the reducing and sulfur-rich hydrotreating conditions.[4] These sulfides have deleterious consequences on the activity and lifetime of the heterogeneous catalyst (e.g., Mo/Co/S on alumina) employed for upgrading crude oil. To model the progressive reduction, sulfide incorporation, and aggregation of VO2+ impurities in crude oil, we have studied a variety of vanadium-sulfur compounds which contain a number of thiolato ligands and range from mono- to tetranuclear in oxidation states from III to v.[5-11] More recently we have used the ligand pyridine-2-thiol (pytH) because it contains functional groups common in crude oils (thiolate S and arene N) and also has the ability to both chelate and bridge transition metals.^[12] We herein report the syntheses of VII, VIII, and VIV complexes with pyt- ligands which have unusual structural features; we also describe an extremely rare example of a thiolatovanadium(II) complex.

The addition of two equivalents of Na(pyt) to a solution of $[VOCl_2(thf)_2]$ in THF yields the vanadium(IV) compound 1.^[13] The structure of 1 (Fig. 1)^[14, 23] displays an unusual

[V2O2(pyt)] 1

bridging arragement of two $\mu_2:\eta^1:\eta^2$ -pyt⁻ ligands in which the N6 atom of pyridine makes up part of the base of the square-pyramidal coordination of V1 (vertices N6, N5, S2, S3', O4) and the sulfur atom S3 of the same pyt⁻ unit occupies a basal position at V1' [V1'–S3 = 2.457(4) Å]. In addi-



Fig. 1. ORTEP representation of complex 1 (ellipsoids at the 50% probability level). Primed and unprimed atoms are related by the inversion center. Selected interatomic distances [Å] and angles [°]: V1···V1' 3.989(2), V1-S2 2.427(3), V1-S3 2.798(3), V1-S3' 2.457(4), V1-O4 1.583(6), V1-N5 2.088(7), V1-N6 2.106(7); V1-S3-V1' 98.65(9), O4-V1-S2 108.92(24), O4-V1-S1 58.92(24), O4-V1-S3' 99.47(22), O4-V1-N5 101.13(28), O4-V1-N6 96.7(3), N5-V1-S3' 158.11(19), S2-V1-N6 150.68(21), S2-V1-N5 68.51(19), S3-V1-N6 62.35(21).

tion, the sixth position of the V1 coordination sphere *trans* to the oxo ligand is occupied by S3 [V1-S3 = 2.798(3) Å]. This complex is an extremely rare example of a compound with an unsymmetrical pyt⁻ bridge.^[15] Two chelating pyt⁻ ligands complete the coordination sphere at each metal center. The V–O distance [1.583(6) Å] is normal for a triply bonded vanadyl unit, and the whole molecule has imposed C_i symmetry. The X-band EPR spectra of 1 dissolved in CH₂Cl₂ or THF recorded at room temperature show only the typical isotropic 8-line signals characteristic of mononuclear VO²⁺ species; this suggests that either the dinuclear arrangement is not retained in solution, or that the metal centers are noninteracting.

Addition of four equivalents of Na(pyt) to a solution of $[VCl_3(thf)_3]$ in THF yields the vanadium(III) complex 2.^[16]

 $[Na(thf)_2V(pyt)_4]$ 2

The crystal structure of **2** (Fig. 2)^[17, 23] shows a rare example of a vanadium(III) center with sevenfold coordination^[18] which consists of three chelating py^- ligands and a fourth bound to the V atom by its sulfur atom (S23). The nitrogen



Fig. 2. ORTEP representation of complex **2** (ellipsoids at the 50% probability level). Selected distances [Å] and angles [°]: V-S2 2.526(1), V-S9 2.567(1), V-S16 2.543(1), V-S23 2.495(1), V-N8 2.121(3), V-N15 2.178(3), V-N22 2.187(3), Na-S9 3.042(2), Na-S16 2.887(2), Na-S23 2.951(2), Na-N29 2.400(3), Na-O31 2.286(3), Na-O36 2.325(3); S9-V-N15 64.39(9), S2-V-N8 66.59(9), S16-V-N22 64.57(9); Na-S9-V 77.15(7), Na-S16-V 80.44(7), Na-S23-V 79.96(7); N8-V-S23 168.14(9).

atom (N29) of this fourth pyt⁻ ligand is bound to a second metal center, the Na atom. There are also bonding interactions between the Na atom and S9, S16, and S23. Two THF molecules complete the coordination sphere of the Na atom. Complex **2** may best be described as a triply bridged heterobimetallic species because of the ligation mode of three of the four pyt⁻ ligands (particularly that containing S23 and N29). The formulation as an ion pair, $[Na(thf)_2]^+[V(pyt)_4]^-$, would be less accurate. In **2** the three pyt⁻ ligands are also in the rare μ_2 : $\eta^1: \eta^2$ ligation mode.

Addition of two equivalents of Na(pyt) to a solution of $[VCl_2(tmeda)_2]$ (tmeda = tetramethylethylenediamine)^[19] in CH₂Cl₂ or THF yields the vanadium(II) complex 3,^[20] an

[V(pyt)₂(tmeda)] 3

extremely rare example of a thiolatovanadium(II) complex.^[22] Compound 3 (Fig. 3)^[21, 23] is a mononuclear trischelate which has a distorted octahedral geometry because of the small bite angle of the pyt⁻ ligand. The molecule has imposed C_2 symmetry, and the S2-V-S2' angle is 156.05(4)° rather than 180°. X-band EPR spectra of 3 dissolved in toluene recorded at room temperature show a broad signal near g = 2. At 115 K, an additional broad signal at g = 4 is observed, consistent with an S = 3/2 ground state.

The pyt⁻ complexes of V^{II}, V^{III}, and V^{IV} display unusual structural features and provide a useful family of related compounds for reactivity studies. Preliminary results show that both compounds 2 and 3 react with O_2 and S_8 to yield complex 1 and $[V_2S_2(pyt)_4]$, respectively. Also, dissolution of

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²ig. 3. ORTEP representation of complex 3 (ellipsoids at the 50% probability evel). Selected distances [Å] and angles [°]: V-S2 2.547(1), V-N8 2.124(2), V-N9 .252(2); S2-V-S2' 156.05(4), S2-V-N8' 97.24(6), S2-V-N8 66.85(8), S2-V-N9 '7.63(6), S2-V-N9' 100.45(6), N8-V-N8' 99.89(13), N8-V-N9 90.65(9); N8-V-49' 164.27(8), N9-V-N9' 81.64(12).

ompound 2 in CH_2Cl_2 yields a white precipitate [Na(pyt) ccording to IR spectroscopy]. Efforts are currently undervay to characterize this material, since mononuclear $[V(pyt)_3]$ " may be unstable with respect to aggregation.

Complexes 1 and 2 were studied by electron ionization nass spectrometry to determine gas-phase fragmentation athways and probe possible C-S bond cleavage reactions. hese transformations may serve as a models for some of the igh-energy reactions occurring during hydrodemetallation/ ydrodesulfurization of petroleum. Under normal ionizaon conditions, both compounds show one or more fragientation pathways involving C-S bond cleavage, as reviously detected in $[V(StBu)_4]$, in which the C-S bonds re more easily cleaved.^[11] For example, [VO(C₅H₄NS)₂]⁺ n/z 287; 100% intensity) gives fragment ions assigned to $VO(C_5H_4NS)(C_5H_4N)]^+$ (m/z 255; 4%), $[VO(C_5H_4N)_2]^+$ n/z 223; 38%), and [VO(C₅H₄NS)S]⁺ (m/z 208, 209; 10%) thich appear to form through a one- or two-step process ivolving C-S bond cleavage. The ion $[V(C_5H_4NS)_3]^+$ reponds similarly under the same conditions. Further details f both the mass spectrometric investigation and the reactivy studies will be reported in due course.

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- 142839-69-8; 2, 142865-80-3; 3, 142865-18-9; [VOCl₂(thf)₂], 29666-18-0; 'Cl₃(thf)₃], 19559-06-9; [VCl₂(tmeda)₂], 122116-24-9.
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- [13] A green-blue solution of $[VOCl_2(thf)_2]$ in THF turns dark brown on addition of Na(pyt). The solvent is removed under vacuum, the residue extracted with CH_2Cl_2 , and the resulting solution filtered and placed in a freezer to allow the product to crystallize. Suitable crystals for the X-ray crystallographic study were obtained by filtering the initial reaction mixture through a fine frit and layering the solution with hexanes. Crystals so obtained lose solvent rapidly when removed from the mother liquor.
- [14] Crystal data for $1 \cdot 2$ THF $\cdot 1/3$ C_6H_{12} : $C_{30}H_{36}N_{40}O_4S_4V_2$, 746.76 g mol⁻¹, hexagonal, $R\overline{3}$, a = b = 30.888(21), c = 8.960(6) Å, V = 7402.84 Å³, Z = 9. A total of 1310 unique reflections with $I > 2.33\sigma(I)$ were refined to values of $R(R_*)$ of 0.0613 (0.0563).
- [15] To our knowledge, only one complex with this ligation mode has been reported: M. V. Castano, A. Macias, A. Castineiras, A. S. Gonzalez, E. M. Martinez, J. S. Casas, S. Sordo, W. Hiller, E. E. Castellano, J. Chem. Soc., Dalton Trans. 1990, 1001.
- [16] Addition of Na(pyt) to a red solution of [VCl₃(thf)₃] yields a black solution which slowly turns purple and finally turns blood-red. After overnight stirring, the solution was filtered and placed in a freezer to allow the product to crystallize.
- [17] Crystal data for 2: $C_{28}H_{32}N_4O_2S_4NaV$, 658.76 g mol⁻¹, triclinic, $P\overline{I}$, a = 10.442(2), b = 16.476(4), c = 9.465(2)Å, $\alpha = 100.73(4)^\circ$, $\beta = 109.20(4)^\circ$, $\gamma = 87.86(3)^\circ$, V = 1510.33Å³, Z = 2. A total of 3391 unique reflections with $I > 2.33\sigma(I)$ were refined to values of $R(R_w)$ of 0.0412 (0.0432).
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- [20] A mixture of [VCl₂(tmeda)₂] and two equivalents of Na(pyt) in CH₂Cl₂ or THF immediately turns a deep red-purple color. After several hours of stirring, the mixture is filtered and the solution is layered with hexanes to allow the product to crystallize.
- [21] Crystal data for 3: C₁₆H₂₄N₄S₂V, 387.45 g mol⁻¹, orthorhombic, B22₁2, a = 14.338(5), b = 17.755(7), c = 7.255(2) Å, V = 1846.86 Å³, Z = 4. A total of 1192 unique reflections with I > 2.33σ(I) were refined to values of R(R_w) of 0.0220 (0.0261).
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- [23] All structures were solved by direct methods and refined by full-matrix least-squares. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-56417, the names of the authors, and the journal citation.

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