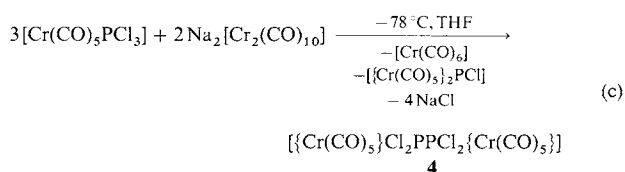


The influence of the $[\text{Cr}(\text{CO})_5]$ complex fragment on the reactions (a) and (b) is of decisive importance. If these reactions are carried out starting from noncomplexed PCl_3 , the percentage of P_2 derivatives formed increases considerably, and in the case of the reaction of PCl_3 with Cp^rMo complexes, **2c** is afforded as the main product. In the corresponding reaction (b) **3** is no longer formed. Thus, the pentacarbonylchromium(0) unit supports the multiple P–P linkage in the coordination sphere of transition metals. Assumptions that metallaphosphaacetylenes of the type $\text{L}_n\text{M}\equiv\text{P}^{[8]}$ ($\text{ML}_n = [\text{Cr}(\text{CO})_n]$ ($n = 3-5$) or $[\text{MCp}^r(\text{CO})_n]$, $\text{M} = \text{Mo}$ or Fe ($n = 3$ or 2)) are intermediates of reactions (a) and (b) were not confirmed by experiments. If the reaction (a) is carried out at various temperatures (-78°C , -40°C , 25°C) in the presence of 2,3-dimethylbutadiene, the same products are formed as from the corresponding reactions without dimethylbutadiene. Thus, a greater importance must be attached to the description of the formation pathway of a stepwise P–P linkage through di- and triphosphorus compounds. The ability of the $[\text{Cr}(\text{CO})_5]$ complex fragments to abstract CO ,^[9] leading to the formation of $[\text{Cr}(\text{CO})_6]$ and thus to the production of $[\text{MoCp}^r(\text{CO})_2]$ or $[\text{FeCp}^r]$ units is also of decisive importance. The results of the reaction of $[\text{Cr}(\text{CO})_5\text{PCl}_3]$ with $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ indicate P–P bond formation since, in addition to $[\{\text{Cr}(\text{CO})_5\}_2\text{PCl}_2]$,^[10] the diphosphane **4** is obtained as the main product [Eq. (c)].



The yellow microcrystalline compound **4** is sparingly soluble in *n*-pentane but readily soluble in CH_2Cl_2 , toluene, and THF. Compound **4** is stable in air for a limited period but should be stored in the dark under an inert gas atmosphere. The spectroscopic data of **4** (Table 1) are in accordance with those given by Fritz et al., who prepared **4** by electrochemical reduction of $[\text{Cr}(\text{CO})_5\text{PCl}_3]$.^[11]

Further investigations starting from $[\text{Cr}(\text{CO})_5\text{PCl}_3]$ have shown that P_x ligands are also formed by reactions with other transition metallates. Furthermore, this method of synthesis also appears to be applicable to the heavier homologues of Group 15.

Experimental Procedure

1-3: $\text{K}[\text{MCp}^r(\text{CO})_n]$ ($\text{M} = \text{Mo}$: $\text{Cp}^r = \text{Cp}$, Cp' , Cp'' , $n = 3$; $\text{M} = \text{Fe}$: $\text{Cp}^r = \text{Cp}''$, $n = 2$) (3.75 mmol) was added to a solution of $[\text{Cr}(\text{CO})_5\text{PCl}_3]$ (1.25 mmol) (prepared from $[\text{Cr}(\text{CO})_5(\text{thf})]$ and PCl_3 at room temperature) in THF (15 mL) and cooled to -78°C . The solution turned red. It was stirred for one hour at this temperature and then slowly allowed to warm up to room temperature. The solvent was then removed under vacuum and the residue was taken up in benzene (15 mL). Subsequently, KCl was filtered off and the solvent was again removed under vacuum.

For the workup of the molybdenum complexes the solid was taken up in CH_2Cl_2 (15 mL) and adsorbed onto silica gel (10 cm^3). This mixture was dried under vacuum and then applied to a column (silica gel, 35×2.5 cm). The *cyclo-P*₃ complexes **1a-c** were eluted as yellow fractions with *n*-hexane or *n*-hexane/toluene (2:1). After recrystallization from *n*-pentane these fractions precipitated in the form of yellow needles (**1a**: 30 mg (23%), m.p. 125°C ; **1b**: 43 mg (22%), m.p. 112°C ; **1c**: 60 mg (26%), m.p. 98°C). With *n*-hexane/toluene (1:1) **2a-c** were obtained as a mixture with $[\{\text{MoCp}^r(\text{CO})_2\}_2]$. Compound **2c** could be isolated from this mixture by recrystallization from *n*-pentane in the form of orange crystals (15 mg; 4%).

To isolate the green needlelike crystals of **3**, the *n*-pentane extract from the reaction mixture was evaporated to dryness and sublimed at $120^\circ\text{C}/10^{-4}$ Torr (**3**: 25 mg (10%), m.p. $115-118^\circ\text{C}$).

4: $[\text{Cr}(\text{CO})_5\text{PCl}_3]$ (6 mmol) was allowed to react with $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ (1.7 g, 4 mmol) as described above and then worked up. The residue was suspended in *n*-pentane (30 mL), transferred to a frit and extracted with hot *n*-pentane until the filtered extracts were colorless. 0.6 g of a mixture of **4** and $[\text{Cr}(\text{CO})_6]$ was recrystallized from this solution at 5°C . This mixture was filtered and the solid dried. The chromium hexacarbonyl was sublimed off at $40^\circ\text{C}/10^{-3}$ Torr, leaving microcrystalline, yellow **4** (0.55 g, 30%). The filtrate contained $[\{\text{Cr}(\text{CO})_5\}_2\text{PCl}_2]$ as the main component.

Received: November 12, 1992 [Z 56781E]
German version: *Angew. Chem.* **1993**, *105*, 641

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Novel V^{III} Complexes with a Central $[\text{V}_3(\mu_3\text{-S})-(\mu\text{-S}_2)_3]^+$ or $[\text{V}_2(\mu\text{-O})(\mu\text{-SPh})_2]^2+$ Unit**

By Norman S. Dean, Kirsten Folting, Emil Lobkovsky, and George Christou*

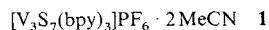
There are two main reasons for our continuing interest in V–S and V–O chemistry. Firstly, the mechanistic details behind the conversion of vanadyl impurities in crude oil into polymeric V^{III} sulfides during hydrodemetallation (HDM) and hydrodesulfurization (HDS) in the processing of crude oil is not understood.^[1] Oxo-bridged V^{III} compounds and multinuclear V^{III} -S aggregates are likely intermediates in the early and late stages, respectively, of this transformation. Secondly, the comparison of V–S chemistry with the much better explored Mo–S chemistry is instructive. Despite the many similarities, V–S chemistry is proving sufficiently different from Mo–S chemistry that the study of the former is not a routine extension of the latter. In this report we describe two new structural types for vanadium compounds and contrast them with Mo compounds.

Treatment of $[\text{V}(\text{SPh})_2(\text{bpy})_2]\text{PF}_6$ ($\text{bpy} = 2,2'$ -bipyridine) with four equivalents of sulfur in hot MeCN gives a dark

[*] Prof. Dr. G. Christou, N. S. Dean, Dr. K. Folting, Dr. E. Lobkovsky
Department of Chemistry and Molecular Structure Center
Indiana University
Bloomington, IN 47405 (USA)

[**] This work was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy (Grant DE-FG02-87ER13702).

green solution from which complex **1**^[2, 16] can be isolated in 35–40% yield. The structure of the cation of **1** (Fig. 1) consists of a $[V_3(\mu_3-S)]$ unit with three edge-bridging $\eta^2:\eta^2:\mu S_2^-$ groups and three chelating bipyridine ligands.



The asymmetrically bridging S_2^- units are found to have one longer (ave. 2.479 Å) and one shorter (ave. 2.372 Å) bond to each V atom; the longer V–S bonds are to the sulfur atoms that are almost coplanar with the V_3 triangle (Fig. 1). The idealized symmetry is C_{3v} , and the metals have the rare coordination number 7. Complex **1** is the first vanadium compound with a central $[M_3S(S_2)_3]$ unit,^[3] although a complex with a $[V_3(\mu_3-S)(\mu-S)_3]$ framework is known.^[4] Several complexes with a central $[Mo_3S(S_2)_3]$ unit have been characterized,^[5] but none analogous to **1** with terminal bipyridine groups have been reported. The $[M_3E(S_2)_3]$ framework is also known for $M = W$, $E = S$ ^[6] and $M = Ti$, $E = O$.^[7]

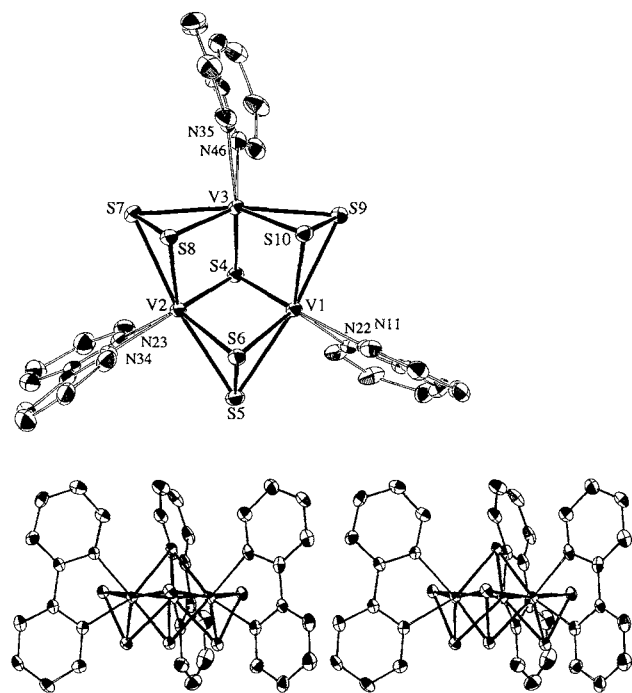


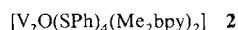
Fig. 1. ORTEP representation and stereoview of the cation of complex **1** (ellipsoids at the 50% probability level). Selected interatomic distances [Å] and angles [°]: V1–V2 2.770(1), V1–V3 2.767(1), V2–V3 2.750(1), S5–S6 2.040(2), S7–S8 2.034(2), S9–S10 2.032(2), V1–S4 2.329(2), V1–S5 2.470(2), V1–S6 2.381(2), V1–S9 2.483(2), V1–S10 2.354(2), V1–N11 2.204(4), V1–N22 2.210(4), V2–S4 2.329(2), V2–S5 2.497(2), V2–S6 2.361(2), V2–S7 2.467(2), V2–S8 2.392(2), V2–N23 2.183(4), V2–N34 2.189(4), V3–S4 2.314(2), V3–S7 2.484(2), V3–S8 2.357(2), V3–S9 2.473(2), V3–S10 2.386(2), V3–N35 2.181(4), V3–N46 2.190(4); V2–V1–V3 59.56(3), V1–V2–V3 60.17(3), V2–V3–V1 60.27(3), V1–S4–V2 72.97(5), V1–S4–V3 73.15(5), V2–S4–V3 72.63(5), V1–S5–V1 67.80(4), V1–S6–V2 71.49(5), V1–S9–V3 67.88(4), V1–S10–V3 71.44(5), V2–S7–V3 67.49(4), V2–S8–V3 70.76(5).

The V^{III} and Mo^{IV} units are isoelectronic. In analogy to the Mo complexes, **1** is diamagnetic in both the solid state and in solution, exhibiting a sharp 1H NMR spectrum in CD_3CN . An EHMO calculation on the model system $[V_3S_7(NH_3)_6]^+$ also supports a diamagnetic nature for **1**. The calculated HOMO is a filled e set with metal–metal bonding character which is composed primarily ($\approx 70\%$) of metal d

orbitals. The LUMO of a_2 symmetry lies 1.3 eV above the HOMO and is composed ($\approx 80\%$) of an antibonding combination of metal d orbitals.

The cyclic voltammogram of **1** in MeCN displays a reversible one-electron oxidation at -0.47 V (vs. Fc/Fc^+). The oxidized species, generated by controlled potential electrolysis, shows no EPR signal at 298 K or 77 K. On cooling to 5 K a broad, ill-defined EPR signal in the region $g \approx 2$ is observed. This behavior indicating rapid relaxation is consistent with the oxidized species being in a 2E state, as suggested by the EHMO calculation, with low-lying excited states arising from the expected Jahn–Teller distortion. Coupling of the electron to all three vanadium nuclei would also contribute to further broadening of the EPR signal.

Hydrolysis of a solution of $NEt_4[V(Me_2bpy)(SPh)_4]$ ($Me_2bpy = 4,4'$ -dimethylbipyridine) by adventitious H_2O in the MeCN solvent gave small amounts of the green complex **2**.^[8, 16] The complex can be synthesized rationally and



in adequate yield (40–50%) by controlled hydrolysis of a mixture of $[VCl_3(thf)_3]$, NaSPh, and Me_2bpy in THF. The structure of **2** (Fig. 2) consists of two face-sharing octahedra; the bridging ligands are an oxo and two PhS^- groups. The

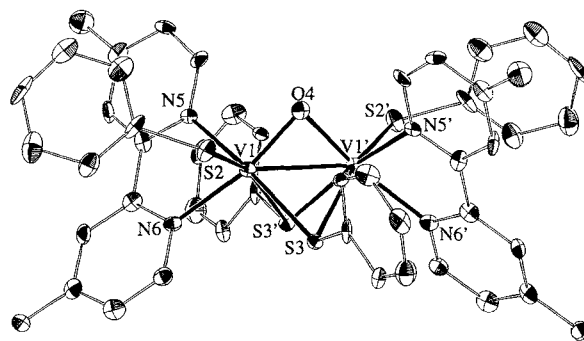
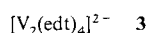


Fig. 2. ORTEP representation of complex **2** (ellipsoids at the 50% probability level). Primed and unprimed atoms are related by a crystallographic C_2 axis. Selected distances [Å] and angles [°]: V1–V1' 2.579(3), V1–S2 2.394(3), V1–S3 2.432(2), V1–S3' 2.493(3), V1–O4 1.841(6), V1–N5 2.152(6), V1–N6 2.184(7); V1–O4–V1' 88.9(3), V1–S3–V1' 63.15(8).

central $[M_2(\mu-O)(\mu-SPh)_2]^{2+}$ unit is unique for vanadium and extremely rare for any other metal; it has been found only in two Mo^{VI} dimers in a highly unsymmetrical form.^[9] An M_2 unit bridged by hydroxo and bis-thiolato ligands is found in $[Cp_2Cl_3Mo_2(OH)(SMe)_2]$,^[10] and a few examples of sulfido/bisthiolato bridged units are known.^[11] The con-facial bioctahedral arrangement is new for $V^{III}-O$ compounds, in which the singly bridged $[V-O-V]^{4+}$ unit is common^[12] and in general linear (or nearly so). In $[V_2O(OAc)_2(tacn)_2]^{2+}$ ($tacn = 1,4,7$ -triazacyclononane) the V–O–V unit is bent with an angle of 130.2° .^[13] The V...V distance in **2** (2.579(3) Å) is shorter than in **1** and comparable with that in **3** (2.60 Å) ($edt = ethane-1,2$ -dithiolate).^[14]



EHMO calculations on the model complex $[V_2O(SH)_4(NH_3)_4]$ suggest the presence of a V–V single

bond in **2** in analogy to **3**. This is also supported by the acute V1-S3-V1' angle ($\approx 63^\circ$). The small magnetic moment of the complex ($\approx 0.6 \mu_B/V$) is thus taken as indicating the coupling of the remaining two electrons by bridge-mediated antiferromagnetic exchange interactions (again in analogy to **3**) to give a singlet ground state and a triplet excited state. Thus, **2** is a rare example of a V^{III} compound with a V–V bond.^[14, 15]

In summary, V–S chemistry continues to be the source of interesting new structural types and new V^{III} compounds with V–V bonds and/or strong interactions. The described work emphasizes both the similarities and differences between V and Mo chemistry. The framework of complex **1** is both structurally and electronically analogous to that of a well-known class of Mo–S compounds, whereas **2** has no exact structural or electronic Mo counterparts.

Experimental Procedure

1: Sulfur (0.128 g, 4.00 mmol) was added to a solution of [V(SPh)₂(bpy)₂](PF₆)^[17] (0.722 g, 1.00 mmol) in MeCN (35 mL), and the solution was heated to 65° for 2–3 h. The initial dark red color gradually changed to dark green and a tan precipitate formed. The solution was filtered and the filtrate volume reduced by 50%. After the addition of Et₂O (30 mL), storage of the solution at 0°C overnight resulted in the precipitation of **1** as a green powder (0.12 g, 37% yield).

2: [VCl₃(thf)₃] (0.711 g, 2.00 mmol), NaSPh (0.798 g, 6.00 mmol), and Me₂bpy (0.368 g, 2.00 mmol) were dissolved with stirring in THF (40 mL). Water (0.018 mL, 1.0 mmol) was added after 1 h, causing the solution to rapidly change color from red/purple to a dark green. After a further hour the solution was filtered and the filtrate volume reduced to 10 mL. Et₂O (40 mL) was added to precipitate **2** as a dark green powder (0.380 g, 41.2% yield).

Received: October 14, 1992 [Z 5625 IE]
German version: *Angew. Chem.* 1993, 105, 623

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The First Unsolvated Chelate and Cubane-Type Barium Complexes: Effective Compounds for the Sol–Gel Process

By Sushil K. Pandey, Alexander Steiner, Herbert W. Roesky,* and Dietmar Stalke

Dedicated to Professor Ulrich Wannagat on the occasion of his 70th birthday

Cyclophosphazenes^[1] are an important class of compounds employed as precursors in polymer chemistry.^[2] Little is known on the chemistry of these compounds, in particular of cyclophosphazenes with Ba–N bonds. To our knowledge, no phosphazene–barium compounds have been reported to date. Before 1990,^[3] molecular barium amides were totally unknown. We were particularly interested in these compounds because they can serve as precursors in the synthesis of complex oxides, which are used in high-temperature superconductors.^[4] The metal oxide hydrates can be prepared by the sol–gel process.

We report here on the first unsolvated chelate and cubane-type barium complexes, which were prepared from barium bis(trimethylsilyl)amide.^[5] Chelate complex **3** was prepared quantitatively from the reaction of amide **1** with **2**^[6] (mol ratio 1:2) in *n*-hexane at 25 °C with elimination of HN-(SiMe₃)₂. Compound **3** is a white, moisture-sensitive, non-volatile solid. When **3** was heated to 110 °C at 0.01 bar it decomposed to **2** ($\delta(^{31}\text{P}) = 18.5$) and further decomposition products in low yield. Single crystals suitable for X-ray crystallography were obtained by storing a supersaturated solu-

[*] Prof. Dr. H. W. Roesky, Dr. S. K. Pandey, Dipl.-Chem. A. Steiner, Dr. D. Stalke
Institut für Anorganische Chemie der Universität
Tammannstrasse 4, D-W-3400 Göttingen (FRG)

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. S. K. P. thanks the Alexander-von-Humboldt Stiftung for a stipend.