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Binary Vanadium Chalcogenide Complexes

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Contents

- I. Introduction 2601
- II. Mononuclear Complexes 2602
  - A. Inorganometallic Compounds 2602
  - B. Organometallic Compounds 2604
- III. Dinuclear Complexes 2605
  - A. Inorganometallic Compounds 2605
    - 1. $[V_2(\mu\text{-}S_2)_2]$ Core 2605
    - 2. $[V_2S_4E]$ Core E = O, S, Se 2606
    - 3. Other Central Cores 2606
  - B. Organometallic Compounds 2606
    - 1. Multiple E-Bridging Ligands 2606
    - 2. Single E-Bridging Ligands 2608
- IV. Trinuclear Complexes 2608
  - A. $[V_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3]$ Core 2608
  - B. $[V_3(\mu_3\text{-}S)(\mu\text{-}\eta^2\text{-}S_2)_3]$ Core 2608
- V. Tetranuclear Complexes 2608
  - A. Inorganometallic Compounds 2608
  - B. Organometallic Compounds 2609
- VI. Pentanuclear Complexes 2609
- VII. Hexanuclear Complexes 2609
- VIII. ^{51}V NMR Data 2609
- IX. Abbreviations 2610
- X. References 2610

I. Introduction

The preparation and characterization of sulfur-containing architectures represent an exciting challenge for chemists for the implication of those species in many different fields of inorganic chemistry. Thus, thiometalates of group 6, and in this group mainly those based on Mo and W, were extensively studied for their role in crude oil refining,[1−3] inorganic, and bioinorganic chemistry.[4−20] This is not the case of group 5 elements since, so far and at our knowledge, this paper represents the first review exclusively devoted to vanadium−sulfur cluster chemistry, even though some examples of sulfur−vanadium complexes were reported in two quite recent important reviews[21,22] and in two specific papers focused on the reactivity of a terminal M═E bond, (E = O, S, Se, Te).[23,24] This lack of literature is not related to the lower interest brought by chemists to sulfur−vanadium systems but is probably due to the difficulty to develop such a chemistry with a metal having a better affinity for oxygen than for sulfur. The preference of vanadium for oxygen is illustrated by the reactivity of VS_4^{3-}, which dissolves in aqueous bases to give deep violet solutions but spontaneously decomposes to brown oxygen-containing materials. In comparison, MoS_4^{2-} and WS_4^{2-} are stable enough in those media to be at the origin of the huge and well-known development of the chemistry of sulfur-based molybdenum and tungsten binary compounds. The poor stability of VS_4^{3-} probably justifies the wide variety of precursors tentatively used by the different groups involved in sulfur−vanadium molecular chemistry. The same difficulty was encountered with selenium, the nature of the precursor used extending from vanadium metal to soluble vanadates.[25,26] We have limited this review to only binary sulfur-(selenium, tellurium)−vanadium species, the different sections being systematically divided in two parts: one devoted to inorganometallic compounds the other to organometallic species.

The various compounds reported so far are listed in Tables 1, 3, and 4 for sulfur-containing species and in Table 5 for Se and Te compounds, including the precursors and the reaction conditions used for their syntheses. These tables illustrate the diversity of the methods of preparation used together with the large redox range of vanadium precursors involved in those syntheses.

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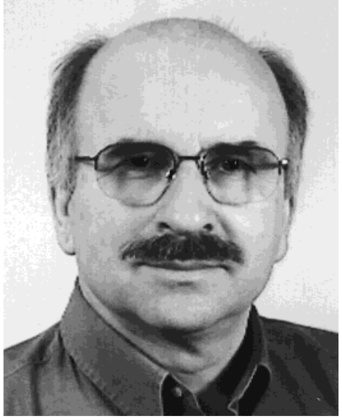
Corine Simonnet-Jégat was born in 1964. She received her Ph.D. degree in 1989 at the University of BORDEAUX I. Her doctoral work dealt with the study by vibrational spectroscopies of carbon dioxide complexes. During her postdoctoral stay at the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr under the supervision of Professor Hoberg in 1990, she studied homogeneous catalytic processes involving carbon dioxide. In 1991 she was appointed Assistant Professor at the University Pierre et Marie Curie in the team of Professor Sécheresse. In 1993 she moved to the University of Versailles. Her current research interest is focused on the reactivity of thiometalates and on the synthesis of new sulfur compounds of transition metals.



Francis Sécheresse was born in 1944. He is a graduate of the University Pierre et Marie Curie (Paris 6). He received his Ph.D. degree in 1973 (complexes Ag–mercaptosuccinic acid) and prepared his thesis (sulfur-based polynuclear complexes of Mo and W) under the supervision of Professor J. Lefebvre in the laboratory of Professor P. Souchay. In 1986 he joined the laboratory directed by Professor Y. Jeannin as Assistant Professor. In 1992 he was appointed Professor of Chemistry at the Université de Versailles St Quentin. His research interests include polyoxo(polythio)anion chemistry and derived inorganic materials chemistry, inorganic polycondensation processes, and reactivity.

II. Mononuclear Complexes

A. Inorganometallic Compounds

$(Me_3NBz)_2[VS_2(S_2)(SPh)]$ was prepared by Christou et al. by oxidation of VCl_3 by elemental sulfur and reaction with NaSPh[27] or LiSPh[28] in MeCN at RT. The product was obtained as black crystals in 30−40% yield after addition of Me_3NBzCl; this yield has been improved to 70% by using LiSPh. The structure of the anion is depicted in Figure 1.

The central vanadium(V) is coordinated to three different types of sulfur: one PhS^-, one disulfido (S_2^{2-}), and two sulfido (S^{2-}) ligands. The overall geometry of the anion can be considered to be tetrahedral, assuming that each disulfido group occupies a single coordination site. Up to now this structure has had no isoelectronic Mo(VI) or W(VI) equivalents. The reactivity of this compound with CS_2 has been studied and reported[28] to give the dinuclear $[V_2(\mu\text{-}S_2)_2(CS_3)_4]^{4-}$ anion described in section III.A.1.

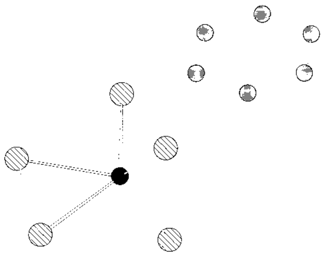


Figure 1. Structure of $[V(S_2)S_2(SPh)]^{2-}$: V atoms, black spheres; S atoms, hatched spheres; C atoms, gray spheres.

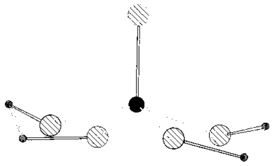


Figure 2. Structure of the pyramidal $[VE(edt)_2]^{2-}$ (E = S, Se) anion. Hatched spheres represent S or Se atoms.

Using almost the same conditions as those for reaction of VCl_3, varying only the proportions of the reagents the three anions, $[VE(SPh)_4]^{2-}$ (E = S, Se) and $[VSe(edt)_2]^{2-}$ have been isolated,[29] while $[VS(edt)_2]^{2-}$ was obtained by reaction of $[VO(edt)_2]^{2-}$ with hexamethyldisilthiane[30] as shown in Tables 1 and 5. These compounds, conversely to the former, contain a vanadium(IV) center in a square-pyramidal environment with a terminal V=E double bond (Figure 2). It can be noticed that the small changes introduced in the syntheses result in completely different arrangements with vanadium in different oxidation states.

The neutral $[V^{IV}(S_2)_2(terpy)]$ was obtained[31] by refluxing $[NH_4]_3[VS_4]$ and terpyridine (terpy) in methanol in a dinitrogen atmosphere. The vanadium(IV) derivative obtained through the reduction in situ of VS_4^{3-} exhibits a distorted pentagonal-bypiramidal geometry, the axial positions being occupied by two nitrogen atoms of the terpyridine while the three equatorial positions are occupied by the remaining nitrogen atom of the terpy and by two disulfido ligands, as represented in Figure 3. The +IV formal oxidation state of vanadium was deduced from the electronic balance.

Preformed vanadium(IV) compounds were also used as precursors. Thus, $[V^{IV}OCl_4]^{2-}$, by reaction with elemental sulfur, Li_2S, and bipyridine (bpy), led to red-black needles identified as the oxidized $[V^{V}O(S_2)_2(bpy)]^-$ monoanion.[32] This compound was also obtained by direct reaction of NH_4VO_3 with bpy in a polysulfur solution.[33] The coordination of the metal center represented in Figure 4 can be described as a pentagonal bipyramid with two disulfido groups and one nitrogen atom of the bpy located in the equatorial positions, the axial positions being occupied by an oxo ligand and the remaining nitrogen atom of the bpy. This molecular architecture was also observed in molybdenum and tungsten complexes[34]

Table 1. Conditions of Preparation of Mononuclear Compounds

compounds	reactants	conditions	yield	ref
$[V(S_2)S_2(SPh)]^{2-}$	$VCl_3/LiSPh/NEt_4Cl/S/Me_3NBzCl$ (1:7:2:3:2)	CH_3CN/RT/1 h	70%	27−28
$[VS(SPh)_4]^{2-}$	$VCl_3/NaSPh/(PhCH_2NMe_3)Cl/S$ (1:5:2:1)	CH_3CN	10%	29
$[VS(edt)_2]^{2-}$	$[VO(edt)_2]^{2-}/(Me_3Si)_2S$	CH_3CN/RT	34%	30
$[V(S_2)_2(terpy)]$	$[NH_4]_3[VS_4]$/terpy	CH_3OH/reflux/24 h	25%	31
$[V(O)(S_2)_2(bpy)]^-$	$VOCl_4^{2-}/S/Li_2S$/bpy (1:2.5:2.5:5)	CH_3CN/EtOH	55%	32
	$[NH_4][VO_3]/bpy/S_x^{2-}$	NH_4OH/RT	60−70%	33
$[V(\eta^5\text{-}C_5Me_5)_2$ $(\eta^2\text{-}S_2)]$	$[V(\eta^5\text{-}C_5Me_5)_2]/S_8$	THF/RT	40%	35, 36
	$[V(\eta^5\text{-}C_5Me_5)_2]$/2 COS	hexane		35
	$[V(\eta^5\text{-}C_5Me_5)_2]/[(Salophen)Co{-}S_2{-}Co{-}(Salophen)(thf)_2Na]^+$	THF		35
	$[V(\eta^5\text{-}C_5Me_5)_2Cl_2]/(NH_4)_2S_5$	acetone/60 °C/2 h	50%	37
$[V(\eta^5\text{-}C_5H_5)_2S_5]$	$[V(\eta^5\text{-}C_5H_5)_2Cl_2]/Na_2S_5$	THF/RT	45%	38
	$[V(\eta^5\text{-}C_5H_5)_2Cl_2]/(NH_4)_2S_5$	acetone/60 °C/2h	74%	39
$[V(\eta^5\text{-}C_5Me_5)(O)(S_5)]$	$[V(\eta^5\text{-}C_5Me_5)_2(O)Cl_2/K_2S_x$	THF/RT/10 min	41%	40

Table 2. Molecular Dimensions (Å) in Some Selected Complexes

compounds	interatomic distances			ref
	V−E (E = S, Se)	S−S or Se−Se	V−V	
$[V(S_2)_2(terpy)]$	2.239(1)-2.448(1)	2.025(1)−2.043(1)		31
$[V(S_2)S_2(SPh)]^{2-}$	V═S: 2.092(2)−2.099(2) $V(\eta^1\text{-}S_2)$: 2.323(2)−2.355(2) V−S: 2.367(2)	2.013(3)		27−28
$[V(O)(S_2)_2(bpy)]^-$	2.344(1)−2.440(1)	2.053(2)−2.055(1)		32−33
$[VS(edt)_2]^{2-}$	2.087(1)			30
$[V(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}S_2)]$	2.415(4)	2.028(4)		36
$[V(\eta^5\text{-}C_5Me_5)(O)(S_5)]$	2.284(2)−2.288(1)	2.038(2)−2.055(2)		40
$[V(\eta^5\text{-}C_5H_5)_2(S)_5]$	2.450(2)−2.464(2)	2.043(3)−2.062(3)		38
$[V_2(\eta^5\text{-}C_5Me_5)_2Cl_2(\mu\text{-}S)_2]$	2.16(2)−2.23(1)		2.829(3)	36
$[V_2(\eta^5\text{-}C_5MeH_4)_2S_5]$	$V{-}(\mu\text{-}S)$: 2.263(1)−2.267(1) $V{-}(\mu\text{-}\eta^1\text{-}S_2)$:2.315(1)−2.316(1) $V{-}(\mu\text{-}\eta^2\text{-}S_2)$: 2.348(1)−2.401(1)	$\mu(\eta^1\text{-}S_2)$: 2.023(2) $\mu(\eta^2\text{-}S_2)$: 1.956(2)	2.658 (1)	63
$[V_2(\eta^5\text{-}C_5MeH_4)_2Se_5]$	$V{-}(\mu\text{-}Se)$: 2.394(2)−2.396(3) $V{-}(\mu\text{-}\eta^1\text{-}Se_2)$:2.450(3)−2.447(3) $V{-}(\mu\text{-}\eta^2\text{-}S_2)$: 2.507(3)−2.549(2)	$\mu(\eta^1\text{-}Se_2)$: 2.290(2) $\mu(\eta^2\text{-}Se_2)$: 2.295(2)		67
$[V_2(\eta^5\text{-}C_5Me_5)_2Se_2S_2]$	$V{-}(\mu\text{-}S)$: 2.231(2)−2.235(3) $V{-}(\mu\text{-}\eta^1\text{-}Se_2)$: 2.404(2)−2.407(2)	$\mu(\eta^1\text{-}Se_2)$: 2.307(1)	2.641(2)	72
$[V_2(\eta^5\text{-}C_5Me_5)_2Se_3O]$	$V{-}(\mu\text{-}Se)$: 2.402(1) $V{-}(\mu\text{-}\eta^1\text{-}Se_2)$: 2.351(1)−2.353(1)	$\mu(\eta^1\text{-}Se_2)$: 2.318(1)	2.502(2)	72
$[V_2(\eta^5\text{-}i\text{-}PrC_5H_4)_2S_4]$	$V{-}(\mu\text{-}S)$: 2.210(2)−2.219(2) $V{-}(\mu\text{-}\eta^1\text{-}S_2)$: 2.268(2)−2.280(2)	2.027(3)	2.610(1)	66
$[V_2OS_4(edt)]^{3-}$	$V{-}(\mu\text{-}S)$: 2.204(2)−2.387(2) V−S: 2.106(2)−2.126(2)		2.977(1)	27−55
$[V_2O_2Se_{10}]^{4-}$	$V{-}(\mu\text{-}Se)$: 2.418(7)−2.502(8) $V{-}(\eta^2\text{-}Se_4)$: 2.465(7)−2.529(8)	2.342(6)−2.447(6)	2.90(1)−2.96(1)	57
$[V_2O_2Se_8]^{4-}$	$V{-}(\mu\text{-}Se)$: 2.402(5)−2.494(5) $V{-}(\eta^2\text{-}Se_2)$: 2.496(6)−2.525(5) $V{-}(\eta^2\text{-}Se_4)$: 2.477(5)−2.482(5)	$(\eta^2\text{-}Se_2)$: 2.358(4) $(\eta^2\text{-}Se_4)$: 2.338(5)−2.473(5)	2.958(7)	57
$[V_2O_2(\mu\text{-}S)_2(Et_2NCS_2)_2]_2{}^{4-}$	$V{-}(\mu\text{-}S)$: 2.258(5)−2.294(6)		2.781(4)−2.813(3)	56
$[V_2(\mu\text{-}S_2)_2(i\text{-}Bu_2NCS_2)_4]$	$V{-}(\mu\text{-}\eta^2\text{-}S_2)$: 2.402(2)−2.403(1)	1.998(2)	2.851(1)	47
$[V_2(\mu\text{-}S_2)_2(Et_2NCS_2)_4]$	$V{-}(\mu\text{-}\eta^2\text{-}S_2)$: 2.374(5)−2.451(4)	1.984(5)	2.884(4)	48
$[V_2(\mu\text{-}S_2)_2(CH_3CS_2)_4]$	$V{-}(\mu\text{-}\eta^2\text{-}S_2)$: 2.366(3)−2.412(3)	1.997(3)	2.800(2)	46
$[V_2(\mu\text{-}S_2)_2(CS_3)_4]^{4-}$	$V{-}(\mu\text{-}\eta^2\text{-}S_2)$: 2.393(3)−2.432(3)	2.012(3)−2.014(3)	2.872(6)−2.841(6)	28
$[V_2Se_{13}]^{2-}$	$V{-}(\mu\text{-}\eta^2\text{-}Se_2)$: 2.518(6) $V{-}(\eta^2\text{-}Se_2)$: 2.403(6)−2.597(9) $V{-}(\mu\text{-}\eta^2\text{-}Se_5)$: 2.505(2)	$(\mu\text{-}\eta^2\text{-}Se_2)$: 2.305(7) $(\eta^2\text{-}Se_2)$: 2.334(3) $(\mu\text{-}\eta^2\text{-}Se_5)$: 2.350(11)−2.428(3)	2.779(5)	54
$[V_3S_4(edt)_3]^{3-}$	$V{-}(\mu_3\text{-}S)$: 2.318(4)−2.363(4) $V{-}(\mu_2\text{-}S)$: 2.229(5)−2.284(4)		2.881(2)- 2.915(2)	55
$[V_3S_7(bpy)_3]^+$	$V{-}(\mu_3\text{-}S)$: 2.314(2)−2.329(2) $V{-}(\mu_2\text{-}S_2)$: 2.354(2)−2.497(2)	2.032(2)−2.040(2)	2.750(1)−2.770(1)	78
$[V_3S_2O_3(Et_2NCS_2)_3]^-$	$V{-}(\mu\text{-}S)$: 2.228(4)−2.263(4)		2.715(3)	83
$[V_4(\eta^5\text{-}C_5MeH_4)_4(\mu_3\text{-}S)_4]$	2.293(3)−2.297(3)		2.868(3)−2.884(3)	94
$[V_4(\eta^5\text{-}C_5MeH_4)_4(\mu_3\text{-}S)_4]^+$	2.276(5)−2.290(5)		2.852(5)−2.855(4)	94
$[V_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]$	2.292(2)−2.300(2)		2.853(2)−2.905(1)	97
$[V_4S_4(C_4H_8NCS_2)_6]^-$	2.273(6)−2.327(5)		2.771(5)−2.999(4)	89
$[V_4S_2(SCH_2CH_2S)_6]^{2-}$	$V{-}(\mu_3\text{-}S)$: 2.315(2)−2.387(2)			88
$[\{V(O)(S_2)_2\}_2(\mu^2\text{-}S_4)\{V(O)(S_2)_2\}_2]^{6-}$	$V(\eta^1\text{-}S_2)$: 2.321(4)−2.460(4)		2.038(5)- 2.051(5)	84
$[V_5(\eta^5\text{-}C_5MeH_4)_5(\mu_3\text{-}S)_6]$	$V_{ax}{-}S$: 2.223−2.229(2) $V_{eq}{-}S$: 2.384−2.406(2)		$V_{ax}{-}V_{eq}$: 3.050−3.081(2) $V_{eq}{-}V_{eq}$: 3.194−3.217(2)	96
$[V_5(\eta^5\text{-}C_5MeH_4)_5(\mu_3\text{-}S)_6]^{2+}$	$V_{ax}\text{-}S$: 2.22(1) $V_{eq}{-}S$: 2.38(1)	2.77(4)		93
$[V_6(Se)_8(O)(PMe_3)_6]$	2.514−2.528(3) 2.525(3)		2.794−2.839(3)	100

crystallized from solutions of polysulfides containing MoO_4^{2-} or WO_3 and bpy.

The geometries of $[V^{IV}(S_2)_2(terpy)]$ and $[V^{V}O(S_2)_2(bpy)]^-$ are based on the same $V(S_2)_2$ central core. The geometrical data of the $M(S_2)_2$ fragment are quite independent of the oxidation state of the vanadium atom and are also independent of the nature of the metallic center since the structural features observed for vanadium are also observed in Mo- and W-related compounds.[34] In the $M(S_2)_2$ groups, two M−S dis-

Table 3. Preparations of Dinuclear Compounds

compounds	reactants	conditions	yield	ref
$[V_2(\mu\text{-}S_2)_2(CS_3)_4]^{4-}$	$[V(S_2)S_2(SPh)]^{2-}/CS_2$ (1:10)	CH_3CN/RT/1 h	60−70%	28
$[V_2(\mu\text{-}S_2)_2(i\text{-}Bu_2NCS_2)_4]$	$[VS_4]^{3-}/(i\text{-}Bu_2NCS_2)$	toluene/DMF 2%/RT/1 h	22%	47
$[V_2(\mu\text{-}S_2)_2(Et_2NCS_2)_4]$	$[VS_4]^{3-}/(Et_2NCS_2)_2$	toluene/DMF 2%/5 h	64%	48
	$VO(S_2(NEt)_2)_3$/boronsulfide	CH_2Cl_2/RT/48 h		
$[V_2(\mu\text{-}S_2)_2(CH_3CS_2)_4]$	$[V(\eta^6\text{-}C_6H_6)_2]/CH_3CSSH$	toluene/RT/4 days	56/62%	46
$[V_2S_5(edt)]^{3-}$	$VCl_3/edt^{2-}/S/NEt_4Br$ (1:2.5:2:2)	CH_3CN/RT/24 h	30%	27−55
	$VCl_3/edt^{2-}/S/NEt_4Br$ (2:4.5:5:2)	CH_3CN/RT/24 h	25−35%	55
$[V_2OS_4(edt)]^{3-}$	$VCl_3/edt^{2-}/S/NEt_4Br$ (1:2.5:2:1)	CH_3CN/RT/24 h	20%	27−55
$\{[(Me_3Si)_2N]_2V(\mu\text{-}S)\}_2$	$[(Me_3Si)_2N]_2VCl(THF)/S_8$	toluene/RT/30 min	21%	58
$[V_2(\eta^5\text{-}C_5MeH_4)_2(CO)_4(S)_2]$	$[V(\eta^5\text{-}C_5MeH_4)(CO)_4]/H_2S$	THF/photolysis		73
	$[V(\eta^5\text{-}C_5MeH_4)(CO)_3(SMe_2)]/H_2S$	hexane/3 h		
$[V_2O_2(\mu\text{-}S)_2(Et_2NCS_2)_2]_24\text{-}$	$[VS_4]^{3-}/PPh_3/Et_2dtc^-/NEt_4^+$ (1:2:3:2)	CH_3CN/RT/24 h	79.8%	56
$[V_2(\eta^5\text{-}C_5Me_5)_2Cl_2(\mu\text{-}S)_2]$	$[V(\eta^5\text{-}C_5Me_5)_2(Cl)]/S_8$	benzene/reflux/4 days	30%	36
	$[V(\eta^5\text{-}C_5Me_5)_2(Cl)]/S_8$	THF/RT		
$[V_2(\eta^5\text{-}C_5MeH_4)_2(\mu\text{-}S)]_2(\mu\text{-}O)$	$[V(\eta^5\text{-}C_5MeH_4)_2Cl_2]/Na/cyclo\text{-}(CH_3AsS)_{3.4}$	THF/RT/16 h	56%	62
$[V_2(\eta^5\text{-}C_5H_5)_2S_5]_n$	$[V(\eta^5\text{-}C_5H_5)_2(S)_5]$	benzene/reflux/2 days	45%	38
	$[V(\eta^5\text{-}C_5H_5)(CO)_4]/S_8$ or cyclohexene sulfide	toluene/reflux/16 h		70
$[V_2(\eta^5\text{-}i\text{-}PrC_5H_4)_2S_4]$	$[V(\eta^5\text{-}C_5(i\text{-}Pr)H_4)_2Cl_2]$			66
$[V_2(\eta^5\text{-}C_5MeH_4)_2S_5]$	$[(\eta^5\text{-}C_5MeH_4)_2VS_5]$	toluene/reflux/3 h	85%	63−64
$[V_2(\eta^5\text{-}C_5Me_5)_2S_5]$	$[V(\eta^5\text{-}C_5Me_5)(CO)_4]/S_8$	toluene/reflux/28 h	62.2%	71
		THF/photolysis/30 min/0 °C	50.8%	
$[V_2(\eta^5\text{-}C_5Me_5)_2S_3]$	$[V_2(\eta^5\text{-}C_5Me_5)_2(S)_5]/Pn\text{-}Bu_3$	toluene/RT/1 h	95.9%	71
$[V_2(\eta^5\text{-}C_5Me_5)_2S_4]$	$[V(\eta^5\text{-}C_5Me_5)(CO)_4]/S_8$	THF/photolysis/30 min/0 °C	27.7%	71

Table 4. Polynuclear Vanadium Complexes

compounds	reactants	conditions	yield	ref
$[V_3S_7(bpy)_3]^+$	$[V(SPh)_2(bpy)_2]^+/4S$ (1:4)	CH_3CN/65 °C/2−3 h	37%	78
$[V_3S_7(Me_2NCS_2)_3]^-$	$VS_4{}^{3-}/Me_2NCS_2{}^-/PhS^-/NEt_4Cl/CuCl$ (1:2:2:2:2)	DMF/24 h	3%	79
$[V_3S_7(Et_2NCS_2)_3]^-$	$VS_4{}^{3-}/3Et_2NCS_2{}^-/NEt_4{}^+/H_2S/C_4H_{10}O_2S_2$	CH_3CN/RT/16 h	45%	80
$[V_3S_2O_3(Et_2NCS_2)_3]^-$	$VCl_3/NaS_2CNEt_2\cdot 3H_2O/2\ Li_2S/NEt_4Br$	CH_3CN/RT/overnight		83
$[V_3S_4(edt)_3]^{3-}$	$VCl_3/S/edt^{2-}/NEt_4Br$ (1:0.5:2:1)	CH_3CN/RT/2.5 h	20%	55
	$VCl_3/S/edt^{2-}/NEt_4Br$ (1:1.5:2:2)	CH_3CN/RT/3−4 h		
$[V_4S_2(SCH_2CH_2S)_6]^{2-}$	$VCl_3/Li_2S/NEt_4Br/edt^{2-}$ (3:4:6:3)	CH_3CN		88
$[\{V(O)(S_2)_2\}_2(\mu^2\text{-}S_4)\{V(O)(S_2)_2\}_2]^{6-}$	$[NH_4][VO_3]/bpy/S_x{}^{2-}$	NH_4OH/RT	40%	84
$[V_4(\eta^5\text{-}C_5MeH_4)_4(\mu_3\text{-}S)_4]$	$[V(\eta^5\text{-}C_5MeH_4)_2]/H_2S$	THF/RT/72 h		98
	$[V(\eta^5\text{-}C_5MeH_4)_2]/Me_3CSH$	heptane/reflux/3 h	59.9%	95−96
	$[V_2(\eta^5\text{-}C_5MeH_4)_2S_4]/2\ Pn\text{-}Bu_3$	CH_2Cl_2/1 h	43%	93−94
$[V_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]$	$[V(\eta^5\text{-}C_5H_5)_2]/MeCSSH$	THF 75%/toluene 25%/4 days	47%	97
	$[V_2(\eta^5\text{-}C_5H_5)_2S_4]/2\ Pn\text{-}Bu_3$	CH_2Cl_2/RT/30 min	27%	94
$[V_4(\eta^5\text{-}C_5MeH_4)_4(\mu_3\text{-}S)_4]^+$	$[V_4(\eta^5\text{-}C_5MeH_4)_4(\mu_3\text{-}S)_4]/BF_4{}^-$	CH_2Cl_2/RT/1 h	72%	94
$[V_4(C_4H_8NCS_2)_6(\mu_3\text{-}S)_4]^-$	$VS_4{}^{3-}/C_4H_8NCS_2NH_4/PPh_3/NEt_4Cl$	CH_3CN/RT/16 h	67%	89
$[V_5(\eta^5\text{-}C_5MeH_4)_5(\mu_3\text{-}S)_6]$	$[V(\eta^5\text{-}C_5MeH_4)_2]/Me_3CSH$	heptane/reflux/3 h	13.5%	95−96
	$[V_2(\eta^5\text{-}C_5MeH_4)_2S_4]/Pn\text{-}Bu_3$			93
$[V_5(\eta^5\text{-}C_5MeH_4)_5(\mu_3\text{-}S)_6]^{2+}$	$[V_5(\eta^5\text{-}C_5MeH_4)_5(\mu_3\text{-}S)_6]/2\ TCNQ$	toluene		93

Table 5. Conditions of Preparation of Selenium and Tellurium Compounds

compounds	reactants	conditions	yield	ref
$[VSe(SPh)_4]^{2-}$	$VCl_3/NaSPh/(PhCH_2NMe_3)Cl/Se$ (1:6:2:1)	CH_3CN	50%	29
$[VSe(edt)_2]^{2-}$	$VCl_3/Na_2edt/NEt_4Br/Se$ (1:3:2:1)	CH_3CN	50−55%	30
$[V_2Se_{13}]^{2-}$	$[NH_4][VO_3]/NEt_4Cl/[(CH_3)_2(C_8H_{17})Si]_2Se$	CH_3CN/NEt_3		54
$[V_2O_2Se_{10}]^{4-}$	V/K_2Se_4/0.3 mL CH_3OH	CH_3OH/135 °C/4 days		57
$[V_2O_2Se_8]^{4-}$	V/K_2Se_4/1.5 mL CH_3OH	CH_3OH/135 °C/24d		57
$\{[(Me_3Si)_2N]_2V(\mu\text{-}Se)\}_2$	$[(Me_3Si)_2N]_2VTeSi(SiMe_3)_3/Se$	toluene/RT/2 days	89%	59
	$[(Me_3Si)_2N]_2V(Br)(THF)/(DME)LiSeC(SiMe_3)_3$	hexane/1.5h	26%	59
$[V_2(\eta^5\text{-}C_5MeH_4)_2(CO)_4(Te)_2]$	$[V(\eta^5\text{-}C_5MeH_4)(CO)_4]/TePn\text{-}Bu_3$	hexane/photolysis		73
$[V_2(\eta^5\text{-}C_5MeH_4)_2(Se)_5]$	$[V(Se)_5(\eta^5\text{-}C_5MeH_4)_2]$	THF/reflux		67
$[V_2(\eta^5\text{-}C_5Me_5)_2Se_5]$	$[V(\eta^5\text{-}C_5Me_5)(CO)_4]/Se$	THF/photolysis/90 min/0 °C	31.1%	71
$[V_2(\eta^5\text{-}C_5Me_5)_2Se_4]$	$[V(\eta^5\text{-}C_5Me_5)(CO)_4]/Se$	THF/photolysis/90 min/0 °C	13%	71
$[V_2(\eta^5\text{-}C_5Me_5)_2Se_3]$	$[V_2(\eta^5\text{-}C_5Me_5)_2Se_5]/Pn\text{-}Bu_3$	toluene	94.9%	71
$[V_2(\eta^5\text{-}C_5Me_5)_2Se_2S_2]$	$[V_2(\eta^5\text{-}C_5Me_5)_2(CO)_4(\mu\text{-}S)_2]/Na_2Se_5$	THF	52%	72
$[V_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}Se)_4]$	$[V_2(\eta^5\text{-}C_5H_5)_2Se_5]/Pn\text{-}Bu_3$	CH_2Cl_2/2 h	72%	73
$[V_4(\eta^5\text{-}C_5Me_5)_4(\mu_3\text{-}Te)_4]$	$[V_2(\eta^5\text{-}C_5Me_5)_4(CO)_4(\mu\text{-}Te)_2]$	toluene/60 min/60 °C	86%	
$[V_4(\eta^5\text{-}C_5MeH_4)_2(\mu_3\text{-}Te)_4]$	$[V_2(\eta^5\text{-}C_5MeH_4)_2(CO)_4(\mu\text{-}Te)_2]$	toluene/45 min/50 °C	quant.	73
$[V_4(\eta^5\text{-}C_5MeH_4)_2(\mu_3\text{-}Se)_4]$	$[V_2(\eta^5\text{-}C_5MeH_4)_2(Se)_4]/Pn\text{-}Bu_3$	CH_2Cl_2/4 h	46%	73
$[V_6(Se)_8(O)(PMe_3)_6]$	$[V(\eta^5\text{-}C_5H_5)Cl_2(PMe_3)_2]/Se(SiMe_3)_2$	THF/RT/2 days	40%	100

tances are quite long, about 2.45 Å, trans to each other, the other two being significantly shorter, about 2.32 Å. In $[V^VO(S_2)_2(bpy)]^-$, the axial position is occupied by an oxygen atom doubly bonded to vanadium (V═O, 1.60 Å), while in $[V^{IV}(S_2)_2(terpy)]$ this site is occupied by a nitrogen of the trichelating terpy ligand, see Figure 3.

B. Organometallic Compounds

Organometallic chemistry of vanadium−sulfur derivatives has been developed on the basis of CpV and Cp_2V fragments owing to the ability of these units to bind S_n polysulfides. Only two representative types of molecular architectures have been reported so far:

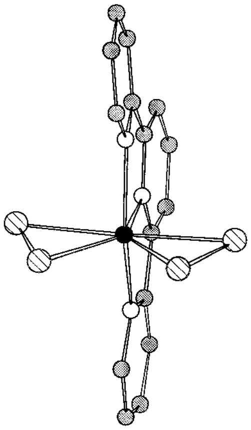


Figure 3. Representation of $[V(S_2)(terpy)_2]$ showing the pyramidal environment of the vanadium atom: N atoms, white spheres.

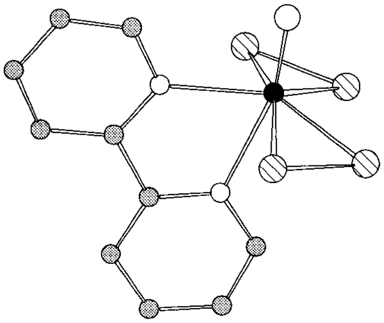


Figure 4. Structure of the $[VO(S_2)_2(bpy)]^-$ monoanion showing the bonding scheme of the bpy ligand: O atom, white sphere.

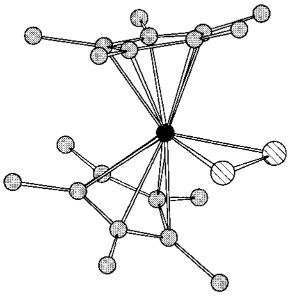


Figure 5. Structure of $[V(\eta^5\text{-}C_5Me_5)_2(\mu^2\text{-}S_2)]$. The equatorial plane contains the central V atom and the S_2 group.

(a) $[V(Cp^*)_2(\eta^2\text{-}S_2)]$[35,36,37] and $[V(Cp)_2(S_5)]$[38,39] and (b) $[V(Cp^*)(O)(S_5)]$.[40] Structure a represented in Figure 5 consists of two cyclopentadienyl ligands η^5-bonded to the metal in a bent arrangement which defines a cavity between the two Cp groups located at the opposite of the η^2-bonded disulfur or pentasulfur ligands.

These two compounds differ in the size of the cavity: with Cp ligands, the cavity is larger than with Cp* ligands, this difference being illustrated by the values of the ligand−metal−ligand angles: (Cp)V-(Cp), 134.1°; (Cp*) V(Cp*), 141.7°. Smaller L−M−L angles favor larger MS_n rings: this rule is admitted for Cp_2M fragments and can justify the possibility of η^2-bonded disulfur or more bulky η^2-bonded pentasulfur ligands. The influence of the substitution at the Cp groups was also confirmed by the preparation of $[V(Cp^*)_2(\eta^2\text{-}S_2)]$ and $[V(Cp)_2(S_5)]$, respectively, starting from $[V(Cp^*)_2Cl_2]$[37] and $[V(Cp)_2Cl_2]$[38,39] in the presence of soluble polysulfides (in THF or acetone).

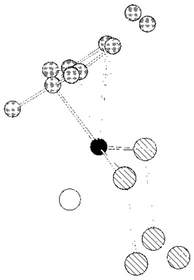


Figure 6. View representing the geometry of $[V(\eta^5\text{-}C_5Me_5)(O)(S_5)]$; the VS_5 cycle has a chair conformation.

The size of the cavity also depends on the ionic radius of the metal. For vanadium, η^2-bonded disulfur and η^2-bonded pentasulfur ligands are obtained, while for molybdenum, only η^2-bonded tetrasulfur ligands[41,42] are observed. $[Mo(Cp)_2(\eta^2\text{-}S_2)]$ has been reported to form, but it spontaneously converts into the more stable $[Mo(Cp)_2(\eta^2\text{-}S_4)]$.[43]

$[V(Cp^*)_2(\eta^2\text{-}S_2)]$ is rather stable for being frequently obtained by quite different methods as given in Table 1. Floriani and co-workers used $[V(Cp^*)_2]$ as the starting material[35,36] in the presence of elemental sulfur or COS. They also described a S−S transfer reaction between $[V(Cp^*)_2]$ and $[(salophen)Co-S_2-Co-(salophen)(THF)_2Na]^+$. The reactivity of $[V(Cp^*)_2(\eta^2\text{-}S_2)]$ with various electrophiles has been studied.[36] With $MeSO_3F$ and [Fe(salen)], $[V(Cp^*)_2)_2(S_2Me)][SO_3F]$ and $[\{Fe(salen)\}_2(\mu\text{-}S)]$ were characterized, the second reaction consisting of a S transfer from $[V(Cp^*)_2)_2(\eta^2\text{-}S_2)]$ to [Fe(salen)].

The molecular structure b is different as it contains only one cyclopentadienyl group instead of two. This different type of coordination, represented in Figure 6, is illustrated by $[V(Cp^*)(O)(S_5)]$, which contains an oxo ligand and a η^2-S_5 ligand occupying the equatorial positions.[40]

$[V(Cp^*)(O)(S_5)]$ was obtained at room temperature by direct reaction of $[V(Cp^*)_2(O)Cl_2]$ with polysulfides in THF.

The V−S dimensions in the $V(S_2)$ and $V(S_2)_2$ groups located in the equatorial plane are independent of the oxidation state of the vanadium as confirmed by the various values summarized in Table 2.

III. Dinuclear Complexes

A. Inorganometallic Compounds

Molybdenum−sulfur chemistry is very rich in dinuclear complexes;[19] this is not the case for vanadium since only five types of dinuclear vanadium−sulfur-containing compounds are known so far, based on different V_2-S_x central cores, see Table 3.

1. $[V_2(\mu\text{-}S_2)_2]$ Core

This central core was obtained stabilized by various coordinating ligands. Different protocols of preparations were successfully used, illustrating the high stability of this fragment. This core, present in the patronit, a natural vanadium sulfide,[44,45] is formed of two vanadium(IV) atoms bridged by two disulfido

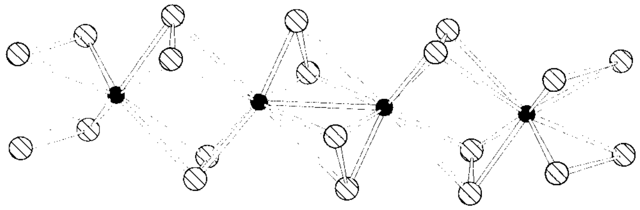


Figure 7. Representation of the structure of the patronit containing the $\{V_2\text{-}(\mu\text{-}\eta^2\text{-}S_2)_2\}$ central core.

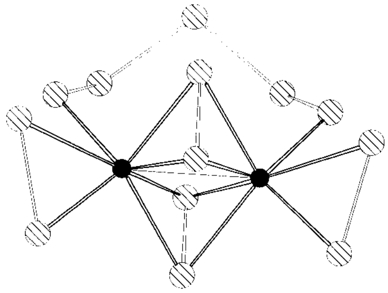


Figure 8. Structure of $[V_2Se_{13}]^{2-}$ showing the central $V_2(Se_2)_4$ core and the Se_5 basket handle.

groups, as represented in Figure 7. The coordination sphere of each vanadium atom is completed by two bidendate ligands. Various binuclear compounds have been reported differing by the nature of the ligands attached to the $\{V_2S_4\}$ core.

$[V_2(\mu\text{-}S_2)_2(CS_3)_4]^{4-}$ was prepared by reaction of $[VS_2(S_2)(SPh)]^{2-}$ with CS_2.[28] Four CS_3^{2-} bidendate ligands are coordinated to the two vanadium atoms of the central $\{V_2S_4\}$ core. Kibala and co-workers[46] described the synthesis and structure of $[V_2(\mu\text{-}S_2)_2(CH_3CS_2)_4]$ obtained from a toluene solution of $[V(\eta^6\text{-}C_6H_6)_2]$ and dithioacetic acid. Stiefel and co-workers[47] reported the synthesis and the structural characterization of $[V_2(\mu\text{-}S_2)_2(\text{i-}Bu_2NCS_2)_4]$ isolated after treatment of a solution of tetrathiovanadate with solid tetraisobutylthiuram disulfide. $[V_2(\mu\text{-}S_2)_2(Et_2NCS_2)_4]$, containing Et_2NCS_2 ligands instead of CH_3CS_2, was obtained by Yang et al.[48] and also by Tiekink et al.[49] The architectures of these four compounds are built on the same $\{V_2S_4\}$ central group with V−V distances of about 2.8−2.9 Å. This short distance together with the diamagnetism observed for these compounds support the possibility of a V−V metal bond. This central core was also observed in molybdenum chemistry in numerous complexes as reported by Shibahara,[19] the closest Mo-related compound being $[Mo_2(\mu\text{-}S_2)_2(Et_2NCS_2)_4]^{2-}$.[50,51] Halides or polysulfides can also complete the coordination of the Mo_2S_4 moiety to give $[Mo_2(S_2)_2Br_8]$[52] and $[Mo_2(S_2)_6]^{2-}$, respectively.[53]

With selenium, $[V_2Se_{13}]^{2-}$ containing the $[V_2(\mu\text{-}Se_2)_2]$ core has been obtained. The geometry is original and unknown in sulfur chemistry. The complex contains both bridging and terminal Se_2 ligand as well as a bridging zigzag Se_5[54] chain as represented in Figure 8.

2. $[V_2S_4E]$ Core E = O, S, Se

Only the two dinuclear compounds $[V_2S_5(edt)]^{3-}$ and $[V_2OS_4(edt)]^{3-}$ were reported to contain the V_2S_4E core. The two complexes were simultaneously obtained from a mixture of VCl_3, Na_2edt, S_8, and NEt_4Br in a 1:2.5:2:1 molar ratio in CH_3CN.[55] The two complexes are readily separable manually and obtained in 30% and 20% yields, respectively. The fully sulfured compound was selectively prepared in 25−35% yield from the same reaction mixture[55] by varying the former molar ratio from 1:2.5:2:1 to 2:4.5:5:2. The structure of $[V_2OS_4(edt)]^{3-}$ was solved by X-ray diffraction, showing two vanadium atoms connected by two $\mu\text{-}S^{2-}$ bridges as represented in Figure 9. The coordination of one of the two vanadium atoms is completed by one edt^{2-} and an oxo ligand, while the coordination of the second vanadium is achieved by two multiply bonded sulfur atoms.

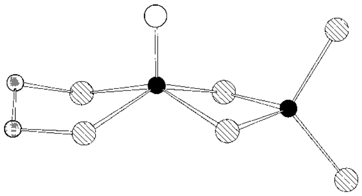


Figure 9. S−S edge connection between the VS_4 tetrahedron and the VOS_4 pyramid in $[V_2(O)(S_4)(edt)]^{3-}$.

The electronic structure of the trianion was described using a mixed $V^{IV}-V^{V}$ valence scheme, the V^{IV} atom being assigned a square-pyramidal geometry and the V^{V} atom a tetrahedral geometry.

3. Other Central Cores

The $[M_2(O)_2(\mu\text{-}S)_2]$ core is often present in molybdenum chemistry; however, only one compound is described, $[V_2O_2(\mu\text{-}S)_2(Et_2NCS_2)_2]_2^{4-}$, in the sulfur chemistry of vanadium.[56] This central core is also known with selenium in $[V_2O_2Se_{10}]^{4-}$ and in $[V_2O_2Se_8]$.[4−57]

Only one inorganometallic compound containing the $\{V_2S_2\}$ core was reported.[58] The analogous selenium derivative $\{[(Me_3Si)_2N]_2V(\mu\text{-}Se)\}_2$ was described by Gerlach et al.[59]

The corresponding $[Mo_2(\mu\text{-}S)_2]$ core attached to various ligands[19] exists in molybdenum chemistry and is observed in a lot of compounds obtained by many different protocols.

B. Organometallic Compounds

1. Multiple E-Bridging Ligands

Regarding the different compounds given in Table 3, three types of molecular architectures containing the CpM fragment can be distinguished. Some sulfur-rich Cp−transition metal complexes have been reported by Wachter.[60]

Floriani and co-workers[36] obtained $[V_2(Cp^*)_2Cl_2(\mu\text{-}S)_2]$ by reacting a solution of $[V(Cp^*)_2(Cl)]$ with excess of S_8. The resulting central $V_2(\mu\text{-}S)_2$ core contains two V^{IV} bridged by two sulfide ligands. $[V_2(Cp)_3Cl(\mu\text{-}S)_2]$ formally derives from the former compound by replacing a Cl by a Cp group.[61] Recently a new tetranuclear compound, resulting from the association via a μ-oxo group of the two $\{Cp_2'V(\mu\text{-}S)_2VCp'\}$ fragments, was characterized by Rheingold et al.[62] The oxidation states of the vanadium atoms were justified either by the presence of a $V^{IV}-V^{IV}$ bond or mixed oxidation states $V^{III}-V^{IV}$.

Table 6. ^{51}V NMR Chemical Shifts for Selected Compounds

compounds	oxidation state of vanadium	solvent	$\delta(^{51}\text{v})$	ref
VS_4^{3-}	V	$NaOH/D_2O$	1400	105
			1574[a]	101
VSe_4^{3-}	V		2570[a]	101
VOS_3^{3-}	V	$NaOH/D_2O$	740	105
$VO_2S_2^{3-}$	V	$NaOH/D_2O$	180	105
VO_3S^{3-}	V	$NaOH/D_2O$	−250	105
VO_4^{3-}	V	$NaOH/D_2O$	−540	105
$[V_2S_7]^{4-}$	V	H_2O	1457	106−28
$[V(\eta^5\text{-}C_5Me_5)OS_5]$	V	$CDCl_3$	44	71
$[V_2(\eta^5\text{-}C_5Me_5)_2S_5]$	IV	$CDCl_3$	596	71
$[V_2(\eta^5\text{-}C_5Me_5)_2Se_5]$	IV	$CDCl_3$	1119	71
$[V_2(\eta^5\text{-}C_5Me_5)_2S_4Se]$	IV		636[b]	72
$[V_2(\eta^5\text{-}C_5Me_5)_2S_4O]$	IV	$CDCl_3$	498	71
$[V_2(\eta^5\text{-}C_5Me_5)_2S_4]$	IV	$CDCl_3$	1541	71
$[V_2(\eta^5\text{-}C_5Me_5)_2Se_4]$	IV	$CDCl_3$	2139	71
$[V_2(\eta^5\text{-}C_5Me_5)_2Se_2S_2]$[b]	IV		1704	72
$[V_2(\eta^5\text{-}C_5Me_5)_2S_3O]$	IV	$CDCl_3$	1266	71
$[V_2(\eta^5\text{-}C_5Me_5)_2Se_3O]$	IV	$CDCl_3$	1647	71
$[V_2(\eta^5\text{-}C_5Me_5)_2Te_3O]$	IV		2240[b]	72
$[V_2(\eta^5\text{-}C_5Me_5)_2Te_2SO]$	IV		1759[b]	72
$[V_2(\eta^5\text{-}C_5Me_5)_2S_3]$	IV	$CDCl_3$	1630	71
$[V_2(\eta^5\text{-}C_5Me_5)_2Se_3]$	IV	$CDCl_3$	2205	71
$[V_2(\eta^5\text{-}C_5Me_5)_2S_2Se]$	IV		1823[b]	72
$[V_2(\eta^5\text{-}C_5MeH_4)_2(CO)_4Te_2]$	IV	C_6D_6	−974	73
$[V_2(\eta^5\text{-}C_5MeH_4)_2(CO)_4S_2]$	IV	C_6D_6	−736	73
$[V_2(\eta^5\text{-}C_5H_5)_2(CO)_4Te_2]$	IV	C_6D_6	−1045	73
$[V_2(\eta^5\text{-}C_5H_5)_2(CO)_4S_2]$	IV	C_6D_6	−747	73
$[V(S_2)S_2(SPh)]^{2-}$	V	$DMSO/CD_3CN$ (1:1)	970	28
$[V(O)(S_2)_2(bpy)]^-$	V	CD_3CN	−402	32
		CH_3CN/C_3D_6O (1:1)	−398	33
$[V_2(\mu\text{-}S_2)_2(CS_3)_4]^{4-}$	IV	$DMSO/CD_3CN$ (1:1)	125	28
		$DMSO/CD_3CN$ (7:1)	135	28
$[V_2(\mu\text{-}S_2)_2(Et_2NCS_2)_4]$	IV	$CDCl_3$	103	28
$[V_2(\mu\text{-}S_2)_2(CH_3CS_2)_4]$	IV	$DMSO/CD_3CN$ (7:1)	173	28
$[V_2(\mu\text{-}S_2)_2(\text{i-}Bu_2NCS_2)_4]$	IV	$CDCl_3$	101	28
$[V_2O_2S_2(Et_2NCS_2)_2]^{2-}$	IV	CH_3CN	−394	56
		DMSO	−390	56
$[V_3S_2O_3(Et_2NCS_2)_3]^-$	IV	DMSO	−385	56
			−519	
$[\{V(O)(S_2)_2\}_2(\mu_2\text{-}S_4)\{V(O)(S_2)_2\}_2]^{6-}$	V	D_2O	−475	84
			−414	

^{51}V NMR chemical shifts are relative to $VOCl_3$. [a] Solid-state shift. [b] Data obtained by coupling ^{51}V NMR with MS experiments.

Dinuclear tetracarbonyl−dichalcogenide complexes $Cp'_2V_2(CO)_4E_2$ and $Cp_2V_2(CO)_4E_2$ (E = S or Te) based on the central core $V_2(\mu\text{-}E)_2$ have been studied by ^{51}V NMR spectroscopy (see Table 6)[73] but have not been structurally characterized.

$[V_2(Cp')_2S_5]$,[63,64] $[V_2(Cp')_2S_4]$,[64,65] and $[V_2(\eta^5\text{-i-Pr-}C_5H_4)_2S_4]$[66] were isolated by Rauchfuss and co-workers. $[V_2(Cp')_2S_4]$ was obtained with different substituted cyclopentadienyl ligands, but only the structure of $[V_2(\eta^5\text{-i-Pr}C_5H_4)_2S_4]$ was established.[66] The V_2S_5 core present in $[V_2(Cp')_2S_5]$ contains three different types of sulfur ligands: a μ-S bridge, a $\mu\text{-}\eta^2\text{-}S_2$ bridge, and a $\mu\text{-}\eta^1\text{-}S_2$ bridge as represented in Figure 10.

The homologue with selenium $[V_2(Cp')_2Se_5]$ was also obtained and described by Rauchfuss et al.[67]

In $[V_2(Cp')_2S_4]$ the V_2S_4 bridge is formed by a $\mu\text{-}\eta^1\text{-}S_2$ bridge and two μ-S bridges. This core has never been observed in molybdenum chemistry since $\{Mo_2S_4\}$ unambiguously represents the most stable core, as shown by the hundreds of dinuclear compounds reported to contain this fragment.[19]

$[V_2(Cp')_2S_5]$[63,64] was prepared by thermal rearrangement of $[V(Cp')(S_5)]$ in refluxing toluene, while the desulfurization of $[V_2(Cp')_2S_5]$ with P*n*-Bu_3 gave $[V_2(Cp')_2S_4]$.[64,65] Reaction of $[Fe(CO)_3]$ with $[V_2(Cp')_4S_4]$ led to $[Fe(CO)_3V_2(Cp')_2S_3]$,[65] while $[(Cp)_2V_2S_4\cdot C_2(CF_3)_2]$ resulted from the reaction of $[V_2(Cp)_2S_4]$ with hexafluoro-2-butyne.[66]

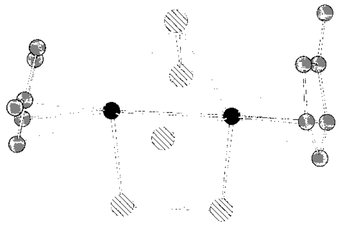


Figure 10. Versatility of sulfur as a bridging ligand: μ-S, $\mu\text{-}\eta^2\text{-}S_2$, and $\mu\text{-}\eta^1\text{-}S_2$ bridges in $[V_2(\eta^5\text{-}C_5MeH_4)_2S_5]$.

$[V_2(Cp')_2S_4]$[68,69] has been used as a starting organometallic ligand. Treatment of $[V_2(Cp')_2S_4]$[68] with an excess of $Hg[Fe(NO)(CO)_3]_2$ in boiling toluene led to the heterobimetallic $[V_2(Cp')_2Fe_2(NO)_2S_4]$. The related compound $[V_2(Cp')_2Co_2(NO)_2S_4]$ was obtained in a similar way by reaction with $[Co(NO)(CO)_3]$ in refluxing CH_2Cl_2. A series of mixed-metal clusters

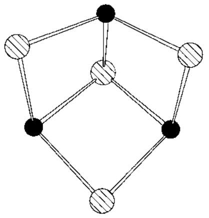


Figure 11. Representation of the V_3S_4 core formed of a V_3 triangle face-capped by a μ_3-S atom.

containing iron, cobalt, nickel, and iridium have also been prepared from $[V_2(Cp')_2S_4]$.[69]

Thermal and photoinduced decarbonylation of $Cp^*V(CO)_4$ in the presence of elemental sulfur or selenium gave $Cp^*_2V_2E_5$ and $Cp^*_2V_2E_4$ (E = S or Se) compounds accompanied with side products identified as $Cp_2^*V_2E_3O$ (E = S or Se) and $Cp_2^*V_2S_4O$.[71] The elemination of chalcogen atoms from $Cp^*_2V_2E_5$ by Pn-Bu_3 results in the formation of $Cp^*_2V_2E_3$ (E = S or Se).[71] Several mixed S/Se compounds ($Cp^*_2V_2SeS_n$, $Cp^*_2V_2Se_2S_n$; $n = 3$ or 2) have been isolated from the reactions of $Cp^*_2V_2E_4$, $Cp^*_2V_2E_3$, or $Cp^*_2V_2(CO)_4S_2$ (E = S or Se) with chalcogenodonors such as polysulfides and polyselenides.[72] Related tellurido complexes were also reported.[72,73] Some ^{51}V chemical shift values for dinuclear pentamethylcyclopentadienyl–vanadium complexes containing various bridged chalcogenide systems are given in Table 6. A complete ^{51}V NMR study on Cp and Cp′ analogous complexes was also reported.[73]

2. Single E-Bridging Ligands

Complexes containing linear V–E–V multiple-bond systems have been obtained by treating $Na[V(CO)_4L]$ (L = diphos, dppe) with Na_2EO_3, Na_2S,[74,75] or H_2S.[75] The reactions lead to $(\mu_2\text{-E})[V(CO)_3L]_2$, the V–E–V bond order lying between double and triple as in the case of related CpCr and CpMo complexes.

IV. Trinuclear Complexes

Five trinuclear compounds are described containing three different V–S fragments also observed in the sulfur chemistry of molybdenum, Table 4.

A. $[V_3(\mu_3\text{-S})(\mu_2\text{-S})_3]$ Core

$[V_3S_4(edt)_3]^{3-}$, represented in Figure 11, contains the $[V_3S_4]$ core formed from three vanadium atoms disposed in a triangular fashion and bridged by a μ_3-sulfur atom.[55] Each edge of the triangle is bridged by a μ_2-sulfur atom.

The coordination geometry at the vanadium atoms is close to that of a trigonal bipyramid, and the trinegative charge of the complex is consistent with the $V^{III}-2V^{IV}$ mixed-valence scheme. In molybdenum chemistry, several examples of species containing $[Mo_3S_4]^{4+}$ cores are known,[19] including $[Mo_3S_4(edt)_3]^{2-}$,[76] which was revealed to be isostructural but not isoelectronic with $[V_3S_4(edt)_3]^{3-}$, obtained from a mixture of VCl_3, Na_2edt, NEt_4Br, and sulfur in different proportions, 1:2:1:0.5 and 1:2:2:1.5, respectively. Recently Saito et al. reported the synthesis and characterization of $[Mo_3S_4Cl_4(py)_5]$.[77]

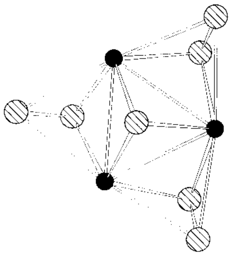


Figure 12. Representation of the V_3S_7 fragment. The edges of the V_3 triangle are S_2-bridged, while a face is μ_3-S capped.

B. $[V_3(\mu_3\text{-S})(\mu\text{-}\eta^2\text{-S}_2)_3]$ Core

The geometry of the $[V_3S_7(bpy)_3]^+$ cation,[78] given in Figure 12, is based on the $[V_3S_7]$ core which can be described as a triangle of vanadium(III) atoms bridged by a μ_3-sulfur atom. Each edge of the triangle is bridged by a disulfido group, and a bipyridine ligand completes the coordination of each vanadium atom. This complex was obtained in 35–40% yield by treatment of $[V(SPh)_2(bpy)_2]^+$ with four equivalents of elemental sulfur in hot acetonitrile.

This V_3S_7 fragment is also present in $[V_3S_7(Me_2NCS_2)_3]^-$ [79] and $[V_3S_7(Et_2NCS_2)_3]^-$,[80] respectively, but the oxidation state of the V_3S_7 core is different, $\{V_3S_7\}^+$ in the former and $\{V_3S_7\}^{2+}$ in the latters.

Several complexes based on the $[Mo_3S_7]$ core have been characterized,[19] but no complexes analogous to this one with a terminal bipyridine and a $\{Mo_3S_7\}^+$ central core have been reported so far. The most ubiquitous oxidation state for $\{Mo_3S_7\}$-based compounds is $\{Mo_3S_7\}^{4+}$ as reported by Fedin et al. for $[Mo_3S_7(Et_2NCS_2)_3]_2(TCNQ)_2$[81] and $[NEt_4][Mo_3S_7Br_5(NH_2Ph)_3]$,[82] respectively. To a lesser extent, some $\{Mo_3S_7\}^{2+}$-containing complexes are also known.[19]

The third type of compound, $[V_3S_2O_3(Et_2NCS_2)_3]^-$, was obtained by Garner and co-workers[83] by reacting VCl_3, Li_2S, NEt_4Br, and $NaS_2CNEt_2\cdot 3H_2O$ in a molar ratio of 1:2:1:1 in acetonitrile. This cluster is composed of a triangle of vanadium(IV) atoms, one of the edges being bridged by two sulfur atoms while the other two are bridged by two oxo ligands. The pentacoordination at the vanadium atoms is achieved by the bidentate ligand.

V. Tetranuclear Complexes

A. Inorganometallic Compounds

$[\{V(O)(S_2)_2\}_2(\mu_2\text{-}S_4)\{V(O)(S_2)_2\}_2]^{6-}$ was obtained by reaction of NH_4VO_3 with a solution of polysulfides in the presence of bpy acting as a templating agent in the solid state.[84]

The typical $\{V(O)(S_2)_2\}$ molecular arrangement, represented in Figure 13, was already observed in molybdenum chemistry with a disulfido instead of a tetrasulfido bridge[85] and also with a μ_2-S_7 bridge and a μ_2-NH_2NH_2 bridge.[86,87]

In $[V_4S_2(SCH_2CH_2S)_6]^{2-}$,[88] four vanadium atoms are bonded to two μ_3-sulfur atoms, the solid-state packing showing strong similarities to the Li_xVS_2 phases.

Recently the new inorganometallic $[V_4S_4(C_4H_8NCS_2)_6]^-$ containing the $\{V_4S_4\}$ core has been de-

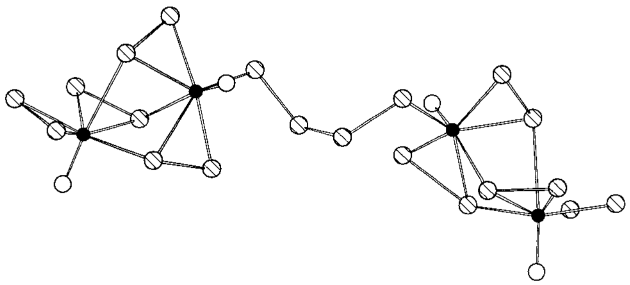


Figure 13. $\{V(O)(S_2)_2\}_2$ fragments linked by a μ_2-S_4 bridge.

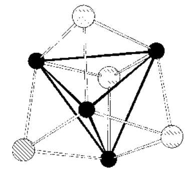


Figure 14. Cubic arrangement of the V_4S_4 core. Mean bond lengths (Å): V−V = 2.854−2.873, V−S = 2.276−2.293.[94]

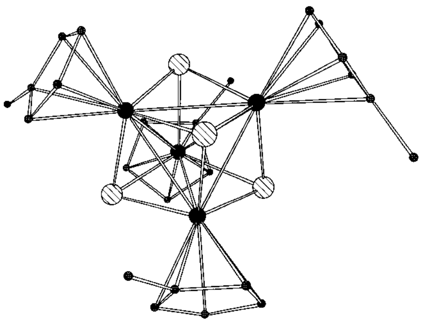


Figure 15. Representation of $[V_4(\eta^5\text{-}C_5MeH_4)_4S_4]$. Each vertex of the V_4S_4 cube is occupied by a η^5-C_5MeH_4 group.

scribed.[89] This compound is the first example of a V_4S_4 cubane containing a highly reduced vanadium (formally 3V(III) + 1V(IV)) without π-acceptor ligands. The corresponding Mo_4S_4 cube is widely spread in the Mo−S chemistry, a nice example being the $[Mo_4S_4(edta)_2]^{n-}$ series published by Shibahara.[90] The most related compound is $[Mo_4S_4(Et_2NCS_2)_6]$, reported by Mak.[91,92]

This cubane core is also frequently encountered in organometallic chemistry, see below.

B. Organometallic Compounds

Some molecular architectures containing the $\{V_4S_4\}$ core attached to organometallic ligands have been reported. In those species the $\{V_4S_4\}$ moiety consists of a distorted cube with vanadium and sulfur atoms alternately located at the vertexes of the cube as represented in Figure 14.

Different types of substituted cyclopentadienyl ligands can bind the $\{V_4S_4\}$ core, which can be compared with the $\{Mo_4S_4\}$ homologue.

Rauchfuss and co-workers prepared $[V_4(Cp)_x(Cp')_{4-x}(\mu_3\text{-}S)_4]$ by desulfurization of a mixture containing $[V_2(Cp)_2S_4]$ $[V_2(Cp')_2S_4]$[93,94] with P*n*-Bu$_3$ and characterized it by X-ray diffraction, the $[V_4(Cp')_4(\mu_3\text{-}S)_4]^{+}$ [94] cation is represented in Figure 15.

The same neutral product $[V_4(Cp')_4(\mu_3\text{-}S)_4]$ was isolated by Pasynskii et al. from the reaction of a solution of $[(Cp')_2V]$ with butyl mercaptan in boiling heptane,[95,96] while $[V_4(Cp)_4(\mu_3\text{-}S)_4]$[97] was isolated from a mixture of vanadocene and dithioacetic acid. The corresponding selenido and tellurido derivatives $[V_4(Cp)_4(\mu_3\text{-}Se)_4]$, $[V_4(Cp^*)_4(\mu_3\text{-}Te)_4]$, and $[V_4(Cp')_4(\mu_3\text{-}E)_4]$ (E = Se or Te) were obtained by Herberhold et al. either by chalcogen abstraction with P*n*-Bu$_3$ or by thermal decomposition.[73]

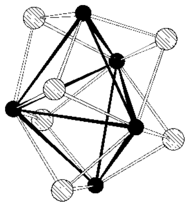


Figure 16. View of the V_5S_6 fragment. The V_5 pyramid is highlighted with bold lines.

Some physical properties of the $\{V_4S_4\}$ core, such as ionization energies and $E_{1/2}$ values, have been reported.[98] Related Mo_4S_4 cubes form the $[Mo_4S_4(\eta^5\text{-}i\text{-}PrC_5H_4)_4]^{n-}$ (n = 0, 1, 2) series.[99]

VI. Pentanuclear Complexes

In Mo−S chemistry, no pentanuclear compound has been reported so far, while with vanadium, different compounds containing the $[V_5S_6]$ core have been isolated, these compounds being relevant to organometallic chemistry. The geometry of the V_5 skeleton, given in Figure 16, consists of a trigonal bipyramid, each face of the pyramid being capped by triply bridging sulfur atoms.

Two compounds containing the V_5 core are described in the literature, $[V_5(Cp')_5(\mu_3\text{-}S)_6][TCNQ]_2$[93] and $[V_5(Cp')_5(\mu_3\text{-}S)_6]$.[93,96] In fact, the already reported[93] desulfurization of $[V_2(Cp')_2S_4]$ with P*n*-Bu$_3$ gives a mixture of $[V_4(Cp')_4(\mu_3\text{-}S)_4]$ and $[V_5(Cp')_5(\mu_3\text{-}S)_6]$. The charge-transfer salt obtained with $[V_5(Cp')_5(\mu_3\text{-}S)_6]$ and TCNQ was crystallographically characterized by Rauchfuss and co-workers in 1986.[93] In 1988, Pasynskii et al. isolated $[V_5(Cp')_5(\mu_3\text{-}S)_6]$ from a solution of $[V(Cp')_2]$ and Me_3CSH. A comparison of the structure of the neutral compound with that of the dication does not reveal any significant difference.[96]

VII. Hexanuclear Complexes

Only the $[V_6Se_8O(PMe_3)_6]$ cluster has been described. The overall geometry consists of an octahedron of vanadium capped by μ_3-Se ligands with an oxygen atom[100] located at the center of the octahedron, Figure 17.

VIII. ^{51}V NMR Data

^{51}V NMR data are dominated by the quadrupole relaxation mechanism (^{51}V, I = 7/2, 99.78% abundance) and depend on the local symmetry and nature of the ligand attached to vanadium. Sharp signals can be obtained, making this an interesting tool for the structural characterization of vanadium-containing complexes. Different review articles have been already devoted to ^{51}V NMR. Thus, Howarth reported

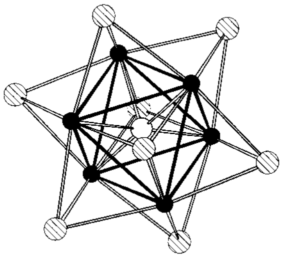


Figure 17. Structure of the V_6Se_8O fragment showing the V_6 octahedron capped by μ_3-Se ligands.

on ^{51}V chemical shifts for selenido and sulfido complexes,[101] while Lapina et al.[102] focused on ^{51}V solid-state NMR studies. In this article, some information on sulfido and seleno compounds are also available. ^{51}V NMR of organovanadium compounds have been reviewed several times.[103] More recent data on compounds containing at least one direct metal-to-carbon bond were reported by Rehder and Rodewald.[104] In Table 6, ^{51}V NMR data are given for some compounds containing vanadium in various oxidation states.

In the series VS_4^{3-}, VOS_3^{3-}, $VO_2S_2^{3-}$, VO_3S^{3-}, and VO_4^{3-}, the vanadium oxide complex has an upfield signal[105] in comparison to the related sulfide compounds. More generally, when a terminal oxygen atom is present in the coordination sphere of the metal center, beside the sulfide ligands, the ^{51}V NMR signal is observed in the upfield region. This is typically the case for $[V(O)(S_2)_2(bpy)]^-$ (−402 ppm), $[V_2O_2S_2(Et_2NCS_2)_2]^{2-}$ (−394 ppm), $[V_3O_3S_2(Et_2NCS_2)_3]^-$ (−389, −519 ppm), and $[\{V(O)(S_2)_2\}_2(\mu_2\text{-}S_4)\{V(O)(S_2)_2\}_2]^{6-}$ (−475, −414 ppm). When sulfur atoms are substituted by selenium in the coordination sphere of the vanadium, chemical shifts are observed in a downfield region: the resonance of VSe_4^{3-} is located at 2570 and 1574 ppm for VS_4^{3-}. The series of dinuclear complexes containing sulfur or selenium in their chalcogenodivanadium frameworks is a good illustration of this behavior (Table 6). Tellurium seems to have the same effect on the chemical shift of ^{51}V as shown by the following three complexes: $[V_2(\eta^5\text{-}C_5Me_5)_2S_3O]$ (1266 ppm), $[V_2(\eta^5\text{-}C_5Me_5)_2Se_3O]$ (1647 ppm), and $[V_2(\eta^5\text{-}C_5Me_5)_2Te_3O]$ (2240 ppm).

The chemical shifts are also dependent on the oxidation state of the vanadium atom. For diamagnetic V^{IV} binuclear complexes (d^1-d^1 coupled electrons), the signal appears upfield compared to that of V^V complexes $[V_2(\mu\text{-}S_2)_2(CS_3)_4]^{4-}$, $[V_2(\mu\text{-}S_2)_2(Et_2NCS_2)_4]$, $[V_2(\mu\text{-}S_2)_2(S_2CSMe)_4]$, and $[V_2(\mu\text{-}S_2)_2(i\text{-}Bu_2NCS_2)_4]$. Only a series of V^{IV} compounds containing cyclopentadienyl ligands has downfield signals relative to V^V complexes.[71−73]

IX. Abbreviations

Cp	$(\eta^5\text{-}C_5H_5)$
Cp*	$(\eta^5\text{-}C_5Me_5)$
Cp′	$(\eta^5\text{-}C_5MeH_4)$
edt	$[SCH_2CH_2S]^{2-}$ ethane-1,2-dithiolate
R_2NCS_2	dialkyldithiocarbamate
edta	ethylenediaminetetraacetate(4-)
salophen	*N,N′-o*-phenyl-enebis(salicylideneaminato)-dianion
salen	*N,N′*-ethylenebis(salicylideneiminate)
TCNQ	tetracyanoquinonedimethane
Ph	phenyl
Bz	benzyl
Me	methyl
Et	ethyl
Bu	butyl
Pr	propyl
THF	tetrahydrofuran
terpy	terpyridine
bpy	bipyridine

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