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# 1,3-Dichalcogena-2-vanada-[3]ferrocenophanes *

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## Abstract

The reactions of the half-sandwich compounds $CpV(O)Cl_2$ (**2a**) and $Cp^*V(O)Cl_2$ (**2b**) with dilithio-1,1′-ferrocene dichalcogenates have been used to prepare bimetallic complexes $[Fe(C_5H_4E)_2]V(O)Cp$ (E = S (**3a**), Se (**4a**)) and $[Fe(C_5H_4E)_2]$-$V(O)Cp^*$ (E = S (**3b**), Se (**4b**)). An X-ray diffraction study of **4b** confirms the absence of bonding interactions between the metal centres (Fe ··· V 401.4(2) pm).

## Introduction

Complexes containing two or more different transition metals are of current interest [1], and macrocycles carrying redox-active ferrocene units have been studied in some detail [2]. One way to keep a metal in close proximity to a ferrocene-iron centre is to incorporate it into a ferrocenophane ring. Thus, the use of 1,1′-ferrocene dichalcogenates, $[Fe(C_5H_4E)_2]^{2-}$ (E = S, Se), as bidentate chelate ligands leads to 2-metalla-[3]ferrocenophanes, $Fe(C_5H_4E)_2M$ (**1**), which may contain either main group or transition metal atoms, M, in the bridge.

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* Dedicated to Prof. F.G.A. Stone on the occasion of his 65th birthday.

1

E = S; M = $SnMe_2$ [3]
$SnCl_2$ [4]
Pb [5]
Te [6,7]
$Pt(PPh_3)_2$ [8]
Mo(NO)L * (**1a**) [9]
(L * = $HB(3.5\text{-}Me_2C_3N_2H)_3$)

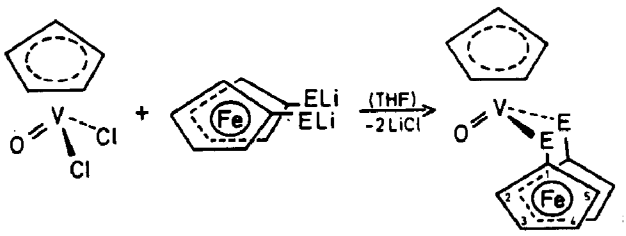
E = Se; M = $SnMe_2$, $SnPh_2$ [5]
$SnCl_2$ [4]
Pb [5]
Te[7]
$Pt(PPh_3)_2$ [8]

Transition metal (M) complexes with a $[Fe(C_5H_4E)_2]^{2-}$ 4-electron chelate ligand were known until now only for M = Pt [8] or Mo [9]. We now report the synthesis of the 2-vanada-[3]ferrocenophanes **3a,b** and **4a,b**, which may be useful bimetallic model compounds, as $^{51}V$ NMR spectroscopy can be used to study intramolecular interactions.

## Results and discussion

### *Preparation and characterization of the complexes*

The complexes **3a,b** and **4a,b** were prepared by mixing THF solutions of the half-sandwich vanadium(V) oxo dichlorides, $Cp^{(*)}V(O)Cl_2$ ($Cp^{(*)}$ denotes cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp *) [10,11]) with THF solutions of dilithio 1,1′-ferrocene dichalcogenate, $Fe(C_5H_4ELi)_2$ [12], in a 1 : 1 molar ratio at −78 °C, and allowing the solutions to warm slowly to room temperature. The products were purified by column chromatography on silica. The sulphur compounds (**3a,b**) are more stable than the selenium compounds (**4a,b**), and the Cp * complexes (**3b**, **4b**) are more stable than the unsubstituted Cp complexes (**3a**, **4a**).



**2a**: $CpV(O)Cl_2$
**2b**: $Cp^{*}V(O)Cl_2$

$Fe(C_5H_4ELi)_2$
E = S, Se

**3a,b**: $[Fe(C_5H_4S)_2]V(O)Cp^{(*)}$
**4a,b**: $[Fe(C_5H_4Se)_2]V(O)Cp^{(*)}$

The [3]ferrocenophanes **3a,b** and **4a,b** are insoluble in hexane and only slightly soluble in toluene, but readily soluble in polar solvents such as dichloromethane and tetrahydrofuran. Both **3b** and **4b** are air-stable in the solid state, although solutions of **4b** tend to deposit red selenium upon standing in the presence of air. The Cp complexes (**3a**, **4a**) are air-sensitive, especially in solution. Chloroform solutions of

Table 1

Spectroscopic data

| Compound<br>(colour) | Infrared [a]<br>$\nu$(V=O)<br>[cm$^{-1}$] | ${}^{1}$H NMR [b]<br>$\delta$(Cp$^{(*)}$)<br>($\delta$(Me)) | $\delta$(H$^2$–H$^5$) [c] | ${}^{13}$C NMR [b]<br>$\delta$(Cp$^{(*)}$)<br>($\delta$(Me)) | $\delta$(C$^1$) | $\delta$(C$^2$–C$^5$) | ${}^{51}$V NMR [d]<br>$\delta$(${}^{51}$V)<br>($\Delta\nu_{1/2}$ [Hz]) |
|---|---|---|---|---|---|---|---|
| **2a** $CpV(O)Cl_2$ | 964 | 5.77 | | 103.4 | | | −403 |
| blue | | | | | | | (65) |
| **2b** $Cp^*V(O)Cl_2$ [10] | 967 | – | | 133.7 | | | −25 |
| green | | (2.32) | | (13.3) | | | (66) |
| **3a** $CpV(O)[(SC_5H_4)_2Fe]$ | 960 | 6.37 | 5.74 | 111.4 | 96.7 | 66.1 | 68 |
| green | | | 4.79; 4.29; 3.93 | | | 74.2; 73.8; 73.5 | (144) |
| **3b** $Cp^*V(O)[(SC_5H_4)_2Fe]$ [e] | 950 | – | 5.60 | 124.8 | 101.3 | 65.7 | 117 |
| dark blue | | (2.20) | 4.56; 4.26; 3.88 | (12.4) | | 73.4; 72.9; 71.6 | (172) |
| **4a** $CpV(O)[(SeC_5H_4)_2Fe]$ | 952 | 6.33 | 5.77 | 109.6 | 95.5 | 66.0 | 275 |
| olive-brown | | | 4.82; 4.27; 4.01 | | | 75.5; 75.3; 73.2 | (158) |
| **4b** $Cp^*V(O)[(SeC_5H_4)_2Fe]$ [e] | 956 | – | 5.64 | 123.6 | 93.9 | 65.9 | 338 |
| red-brown | | (2.21) | 4.61; 4.25; 3.95 | (12.7) | | 75.0; 74.8; 71.6 | (174) |
| **5a** $CpV(O)(SPh)_2$ [13,14] | 959 | 6.18 [f] | | | | | (−204) [g] |
| black | | | | | | | |
| **5b** $Cp^*V(O)(SPh)_2$ [13,14] | 954 | – | | | | | (−38) [g] |
| green-black | | (2.20) [f] | | | | | |
| **6a** $CpV(O)(S_5)$ [15] | 961 | | | | | | −46 |
| red | | | | | | | (110) |
| **6b** $Cp^*V(O)(S_5)$ [15] | 961 | – | | 124.1 | | | 44 |
| red | | (2.18) | | (12.3) | | | (140) |

[a] KBr. [b] $CDCl_3$ solution, room temperature, JEOL FX 90Q and Bruker AC 300. [c] Center of the multiplet. [d] $CDCl_3$ solution, 15° C, JEOL FX 90Q. [e] Electrochemical studies of these complexes are in progress. [f] $CD_2Cl_2$ solution, 23° C. [g] $CH_2Cl_2/CDCl_3$ solution, 23° C.

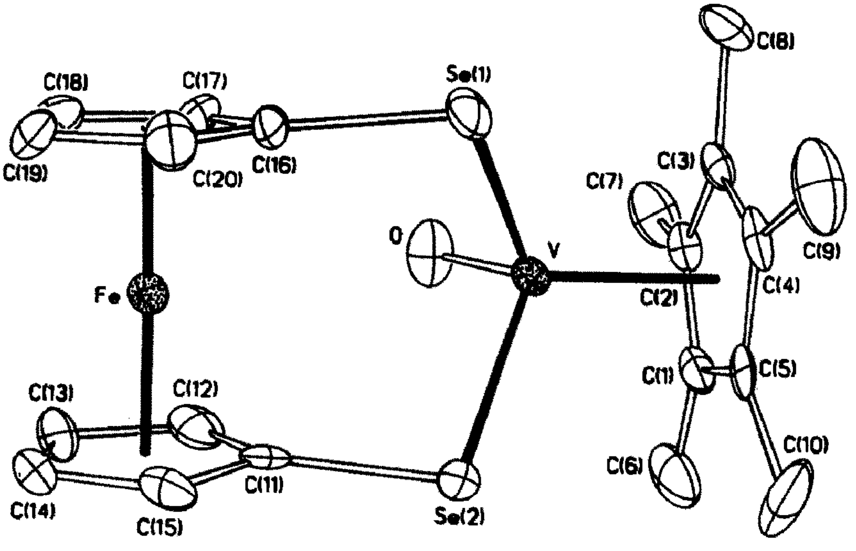


Fig. 1. Molecular structure of $[Fe(C_5H_4Se)_2]V(O)Cp^\star$ (**4b**).

**4a** decompose to give the diselenol, $Fe(C_5H_4SeH)_2$, which is also observed as the most intense fragment ion in the EI mass spectrum of **4a**. The EI mass spectra of the other complexes (**3a,b** and **4b**) contain the molecular ion with the highest intensity and prominent fragment ions resulting from loss of $Cp^{(\star)}$, $C_5H_4E$ and $H_2O$.

The NMR spectroscopic data for the $Cp^{(\star)}V$ complexes **2a,b–4a,b** are given in Table 1, together with those for the related bis(thiophenolato) complexes $Cp^{(\star)}V(O)(SPh)_2$ (**5a,b**) [13,14] and the metallacyclic pentasulfido compounds $Cp^{(\star)}V(O)(S_5)$ (**6a,b**) [15]. The chemical shifts, $\delta(^{51}V)$ are sensitive to the nature of the ligands and the geometry of the coordination sphere of vanadium. In agreement with earlier studies [14,16,17; cf. 18] both introduction of $Cp^\star$ in place of Cp and that of Se in place of S shift the $^{51}V$ signal to lower fields. The $^{13}C$ NMR data of the ferrocenophane complexes (**3** and **4**) clearly indicate that all five carbon atoms of the ferrocene cyclopentadienyl rings are inequivalent. One signal in both the $^1H$ and $^{13}C$ NMR spectra is always separated from the remaining pattern in the $H^2$–$H^5$ and $C^2$–$C^5$ regions, and this is assigned to the 1,1′-ferrocenediyl ring position 2, which is close to the oxo ligand.

### *Molecular structure of $[Fe(C_5H_4Se)_2]V(O)Cp^\star$ (**4b**)*

An X-ray structural determination was carried out in order to confirm the monomeric nature of the complex [19*] and to determine the Fe ··· V distance. As indicated in Fig. 1, the vanadium atom in **4b** is surrounded by the $Cp^\star$ ring, the oxo ligand, and the selenium atoms, in a distorted tetrahedral arrangement. When the $Cp^\star$ ligand is excluded, the molecule contains a mirror plane that includes V, Fe and O, and bisects the 1,1′-ferrocene diselenolate chelate ligand. The two cyclopentadienyl rings of the ferrocene unit are almost exactly eclipsed (torsion angle Se(1)–C(16)–Fe/Fe–C(11)–Se(2) 0.0(1)°) and parallel (dihedral angle 0.8°).

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* Reference number with asterisk indicates a note in the list of references.

Table 2

Selected bond distances and bond angles in $Cp^{*}V(O)[(SeC_5H_4)_2Fe]$ (**4b**)

| Bond lengths [pm] | | Bond angles [°] | |
|---|---|---|---|
| V,O | 158.7(9) | O,V,Se(1) | 102.8(4) |
| V,Se(1) | 239.3(2) | O,V,Se(2) | 103.7(3) |
| V,Se(2) | 240.5(2) | Se(1),V,Se(2) | 100.0(1) |
| V,C(1) | 229.4(13) | CNT $^a$,V,Se(1) | 111.9(4) |
| V,C(2) | 226.6(11) | CNT,V,Se(2) | 110.6(4) |
| V,C(3) | 231.0(11) | CNT,V,O | 124.8(3) |
| V,C(4) | 242.1(12) | CNT,Fe,CNT | 178.3(6) |
| V,C(5) | 239.5(16) | C(11),Se(2),V | 101.5(4) |
| V,CNT(1–5) | 199.5(10) | C(16),Se(1),V | 102.2(4) |
| Fe,CNT(11–15) | 164.3(12) | | |
| Fe,CNT(16–20) | 165.1(12) | | |
| Fe···V | 401.4(2) | | |

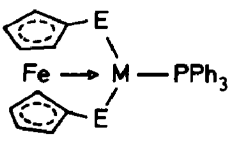
$^a$ CNT = center of the ring ligand.

The methyl substituents of the Cp$^{*}$ ring are slightly bent outwards, away from the vanadium atom. The Cp$^{*}$ ring itself is unsymmetrically coordinated; an analogous displacement of the ring ligand with respect to the metal centre is typical of Cp$^{*}$Re half-sandwich complexes such as $Cp^{*}Re(O)X_2$ (X = Cl, I, Me, $CH_2Ph$) [20], $Cp^{*}Re(N^tBu)Cl_2$ [21] or $Cp^{*}Re(CO)(SMe)_2$ [22], and is also found in half-sandwich complexes of vanadium such as $CpV(O)(SPh)_2$ (**5a**) [13,14] and $Cp^{*}V(O)(S_5)$ (**6b**) [15].

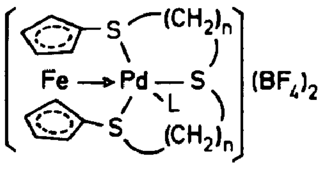
Some bond distances and angles observed for $[Fe(C_5H_4Se)_2]V(O)Cp^{*}$ (**4b**) are given in Table 2. The V=O bond length (158.7(9) pm) corresponds to the expected value for a double bond; very similar V=O distances were reported for $Cp^{*}V(O)Cl_2$ (**2b**) (157.6(8) pm [23]), $[Cp^{*}V(O)Cl]_2(\mu\text{-}O)$ (158.9(3) pm [10]), $[Cp^{*}V(O)]_2(\mu\text{-}O)(\mu\text{-}OCH_2CH_2O)$ (159.8(1) pm [14]), $Cp^{*}V(O)(S_5)$ (**6b**) (159.0(3) and 158.5(4) pm [15]) and $CpV(O)(SPh)_2$ (**5a**) (159.9(1) pm [14]).

The V–Se bond lengths in **4b** (239.3(2) and 240.5(2) pm) are almost identical with the V–Se distances between the metal and the directly bound selenium atom of the $\eta^1$-$Se_2$ ligand in the binuclear complexes $Cp^{*}_2V_2Se_2S_2$ (240.7(2), 240.4(2) pm) and $Cp^{*}_2V_2Se_3O$ (240.2(1) pm) [17]; the corresponding values for $(C_5H_4Me)_2V_2Se_5$ are 244.7(3) and 245.0(3) pm [24]. The Se(1)–V–Se(2) angle in **4b** (100.0(1)°) is slightly smaller than the S–V–S angle in either **5a** (103.06(1)°) [13,14] or **6b** (106.8(1); 106.1(1)°) [15], respectively. The long Fe···V separation (401.4(1) pm) rules out direct bonding interaction between the two metals.

In view of the relatively small Se(1)–V–Se(2) angle, the almost parallel cyclopentadienyl rings of the ferrocene unit and the long V···Fe distance it is obvious, that the 1,1′-ferrocene diselenolate ligand in **4b** plays the part of a conventional anionic 4-electron ligand. There appears to be no tendency for the 18-electron ferrocene iron to act as a donor towards vanadium, which is formally a 14-electron centre. Similarly, no direct interaction is observed between iron and the 16-electron molybdenum centre in $[Fe(C_5H_4S)_2]Mo(NO)L^{*}$ (**1a**) [9]. However palladium(II) and platinum(II) complexes (**7** and **8**) that are assumed to contain weak iron → metal dative bonds have been characterised (cf. [25,26]).



(7)



(8)

E = S; M = Pd [27], Pt [8]
E = Se; M = Pt [8]

$n$ = 2, 3 [28]
(L = acetone, acetonitrile)

Like Cp$^{(*)}$VOCl$_2$ (**2a,b**) other half-sandwich dihalides may be used to prepare 2-metalla-[3]ferrocenophanes, e.g. Cp$^*$W(NO)I$_2$ can be converted into [Fe(C$_5$H$_4$S)$_2$]W(NO)Cp$^*$ [29]. However, attempts to obtain 1,3-dichalcogena-2-metalla-[3]ferrocenophanes derived from Cp$_2^{(*)}$MCl$_2$ (M = Ti, Zr) have been so far unsuccessful [cf. 19 *].

## Experimental

In a typical experiment, a THF solution (10 ml) containing 100 mg (0.37 mmol) Cp$^*$V(O)Cl$_2$ (**2b**) [10,11] was added to a THF solution (30 ml) of 130 mg (0.37

Table 3

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (Å$^2 \times 10^3$)

| | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| Se(1) | 2639.9(15) | 1229.2(8) | 4211.6(12) | 52.9(6) * |
| Se(2) | 3731.9(13) | −502.9(9) | 2432.2(14) | 51.3(6) * |
| Fe | 2544.0(14) | −1190.1(11) | 4891.9(16) | 29.6(6) * |
| V | 2304.4(16) | 640.1(13) | 2175.7(18) | 27.0(7) * |
| O | 1214(7) | 54(6) | 2067(8) | 51(4) * |
| C(1) | 2455(11) | 986(8) | 236(11) | 34(5) * |
| C(2) | 1540(10) | 1478(8) | 497(11) | 32(4) * |
| C(3) | 1988(10) | 2123(7) | 1442(10) | 31(4) * |
| C(4) | 3163(11) | 2059(8) | 1757(10) | 35(5) * |
| C(5) | 3445(12) | 1352(8) | 1001(12) | 45(6) * |
| C(6) | 2395(15) | 252(10) | −688(13) | 73(8) * |
| C(7) | 404(12) | 1368(10) | −125(14) | 67(7) * |
| C(8) | 1324(14) | 2821(9) | 1924(14) | 66(7) * |
| C(9) | 3922(13) | 2648(11) | 2592(13) | 74(7) * |
| C(10) | 4592(12) | 1100(12) | 932(16) | 82(8) * |
| C(11) | 3241(10) | −1385(8) | 3475(11) | 36(5) * |
| C(12) | 2229(12) | −1859(8) | 3252(12) | 45(5) * |
| C(13) | 2320(11) | −2505(8) | 4242(12) | 50(6) * |
| C(14) | 3355(11) | −2418(9) | 5008(12) | 45(5) * |
| C(15) | 3943(12) | −1735(9) | 4551(13) | 49(6) * |
| C(16) | 2295(12) | 192(8) | 5103(12) | 47(6) * |
| C(17) | 1256(11) | −308(9) | 4843(13) | 47(6) * |
| C(18) | 1364(16) | −950(11) | 5834(17) | 69(8) * |
| C(19) | 2403(15) | −866(9) | 6601(13) | 53(7) * |
| C(20) | 2981(15) | −166(8) | 6161(12) | 55(6) * |

* Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

mmol) $Fe(C_5H_4SeLi)_2$ [12] which had been kept at $-78\,^\circ C$. After the mixture had reached room temperature the solvent was removed, the residue extracted with $CH_2Cl_2$ and the concentrated $CH_2Cl_2$ solution chromatographed over silica (in pentane). Some ferrocene was washed out with pentane/$CH_2Cl_2$ (1 : 1) before the red-brown product **4b** was eluted with pentane/$CH_2Cl_2$ (1 : 5). Yield 60 mg (30%).

The analogous reactions with $Fe(C_5H_4SLi)_2$ [12] gave **3b** in 40% yield, but the yields of the CpV complexes **3a** (10%) and **4a** (5%) were low owing to decomposition during the chromatographic purification.

*Crystal data*: **4b**: $C_{20}H_{23}FeOSe_2V$, monoclinic, $P2_1/c$, $a$ 12.491(4), $b$ 14.535(4), $c$ 11.274(3) Å, $\beta$ 103.51(2)°, $V$ 1990.3(10) Å$^3$, $Z = 4$, $D$(calcd) 1.816 g cm$^{-3}$, $\mu(\text{Mo-}K_\alpha) = 51.6$ cm$^{-1}$, $T = 293$ K. Of 3066 data collected and corrected for absorption, 2765 were independent, and 1814 were observed ($3\sigma F_o$). With all non-hydrogen atoms anisotropic and all H atoms idealized: $R(F) = 6.89\%$, $R_w(F) = 6.70\%$ and GOF = 1.701. The atomic coordinates are listed in Table 3. Full details of the crystallographic study along with a complete list of bond lengths and angles and lists of thermal parameters and structure factors are available from ALR.

## Acknowledgements

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