

Some new results on the Fischer–Hafner synthesis of vanadium arenes

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Abstract

The biphasic liquid system formed in the Fischer–Hafner reduction of VCl_3 in toluene contains the $[V(\eta^6\text{-MeC}_6\text{H}_5)_2]^+$ cation which has been isolated in the solid state as the tetraphenylborato- (from aqueous solution) or as the $[Al_2Cl_7]^-$, $[Al_4O_2Cl_{10}]^{2-}$ and $[catena\text{-}Al_4O_2Cl_9]^-$ salt (directly from the biphasic liquid system). The crystal structures of $[V(\eta^6\text{-MeC}_6\text{H}_5)_2][Al_4O_2Cl_{10}]$ (**2**), and $[V(\eta^6\text{-MeC}_6\text{H}_5)_2][catena\text{-}Al_4O_2Cl_9]$ (**3**), have been solved representing the first structural report of the $[V(\eta^6\text{-MeC}_6\text{H}_5)_2]^+$ cation (compounds **2** and **3**) and of the polymeric nonachlorodioxoaluminate anion $[Al_4O_2Cl_9]^-$ (compound **3**).

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1. Introduction

The reaction of metal halides with the Al/AlX_3 system in aromatic hydrocarbons has been widely used for the synthesis of η^6 -arene derivatives of typical d-transition elements [1] in low oxidation states.

A common feature to the reaction mixtures deriving from the Fischer–Hafner synthesis of metal-arene compounds is the formation of a biphasic liquid system consisting of a dark-coloured lower layer, containing almost all the transition metal [1a,2]. Atwood [3] has described similar bi-layering phenomena for tetraalkylammonium derivatives of large, aluminium-containing anions; the terminology of “liquid clathrates” was introduced for these systems [3].

Attempts have been made to clarify the nature of the intermediates of the Fischer–Hafner synthesis, mainly concerning vanadium and chromium systems. As far as chromium is concerned, Fischer and Seeholzer [4] showed that the primary product of the reaction between $CrCl_3/Al/AlCl_3$ in benzene had the composition $Cr_3Al_7X_{24}(C_6H_6)_6$ corresponding to the formulation

$\{[Cr(\eta^6\text{-C}_6\text{H}_6)_2]AlX_4\}_3 \cdot 4AlX_3$, $X = Cl, Br$. Recently, the $[Cr(\eta^6\text{-C}_6\text{H}_6)_2][Al_3OCl_8]$ derivative has been isolated from the biphasic liquid system *using commercially available and not purified starting materials* and structurally characterized [5].

Working on the $VCl_3/Al/AlCl_3/1,3,5\text{-Me}_3\text{C}_6\text{H}_3$ system, Calderazzo et al. proposed that the primary product of the Fischer–Hafner reduction of VCl_3 was $[V(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2]Al_2Cl_7$ [1n].

We have recently prepared large amounts of $V(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2$ from commercially available, not further purified, VCl_3 and $AlCl_3$, and in some occasions we observed that solid products formed from the lower, deep brown liquid phase during the cooling of the reaction mixture. In this paper, we report on the solid products obtained thereof as a contribution to the identification of the primary products formed in the Fischer–Hafner reduction.

2. Results and discussion

It is known in the literature that $V(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2$ is obtained in quantitative yields by addition of THF to the biphasic liquid system which forms by reduction of VCl_3 with $AlCl_3$ in $1,3,5\text{-Me}_3\text{C}_6\text{H}_3$ in the presence of excess alu-

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minium [1n]. If the excess aluminium is removed by filtration *before* the addition of THF, the vanadium(I) species $[\text{V}(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)_2]\text{AlCl}_4$ is obtained [1n].

In the case of the Fischer–Hafner system $\text{VCl}_3/\text{Al}/\text{AlCl}_3/\text{toluene}$, the $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2]^+$ cation cannot be isolated in THF due to the disproportionation to the dinuclear, chloride bridging, vanadium(II) derivative $[\text{V}_2(\mu\text{-Cl})_3(\text{THF})_6]\text{AlCl}_4$ and $\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2$ [6], see Scheme 1.

In an attempt to isolate some species directly from the “liquid clathrate”, we did several, large-scale Fischer–Hafner reductive complexation reactions of VCl_3 in toluene starting from used-as-received reagents. After filtration of excess aluminium, the liquid phase was treated with non polar solvents (chlorinated or aliphatic hydrocarbons) or, alternatively, heated in vacuo at ca. 70 °C, but we never succeeded in the isolation of a solid compound.

We have been able to obtain a solid substance only when the deeply coloured layer was added to a concentrated water solution of NaBPh_4 ; as soon as the addition was complete (10 min) the dark coloured solid which formed was isolated by filtration. The treatment of the solid with heptane, allowed the separation of an insoluble orange compound, identified as the paramagnetic $[\mu_{\text{eff}}(292\text{ K}) = 2.80\text{ BM}] [\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2]\text{BPh}_4$ (**1**), from a soluble dark brown derivative which was characterized as $\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2$, see Scheme 2.

The formation of the vanadium(0) derivative is probably due to the disproportionation of the vanadium(I) cation as observed in THF [6]. We did not make any attempt to characterize the species present in the aqueous solution in order to confirm this hypothesis. Although **1** is obtained in poor yields (6%), its isolation confirms that the $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2]^+$ cation is stable in the presence of water at least for a short time [7] and is probably due to the low solubility of **1** in this medium.

To our surprise, a crystalline compound slowly formed (some weeks) directly from the “liquid clathrate”. This compound was isolated and identified as the paramagnetic $[\mu_{\text{eff}}(292\text{ K}) = 2.72\text{ BM}]$ compound $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2]_2[\text{Al}_4\text{O}_2\text{Cl}_{10}]$ (**2**).

The IR spectrum shows the absorptions typical of the aromatic ring and of the Al–(O)–Cl fragment in the 1000–400 cm^{-1} range [8]. The presence of the decachlorodioxoaluminato dianion is probably due to some water accidentally introduced in the reaction mixture or to some impurities present in the starting materials.

The crystal structure of compound **2** is shown in Fig. 1 and a selection of bond distances and angles is reported in Table 1. The solid consists of centrosymmetric $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2]^+$ cations, reported here for the first time, and $[\text{Al}_4\text{O}_2\text{Cl}_{10}]^{2-}$ anions, organized in alternating layers in the *b* direction. There are two non equivalent cations for each anion showing similar geometries. As imposed by the inversion centre, the toluene rings are parallel with eclipsed ring carbon atoms and with the methyl groups pointing to opposite sides, a conformation which we indi-

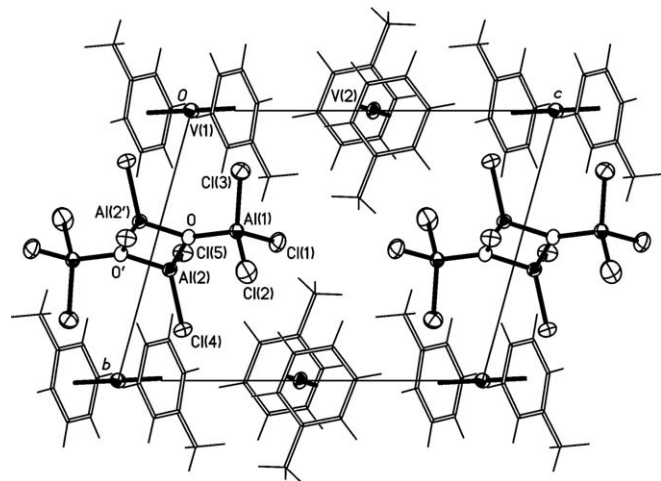


Fig. 1. Projection along *a* of the crystal structure of $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2]_2[\text{Al}_4\text{O}_2\text{Cl}_{10}]$ (**2**). Thermal ellipsoids are at 30% probability. $' = 1 - x$, $1 - y$, $-z$.

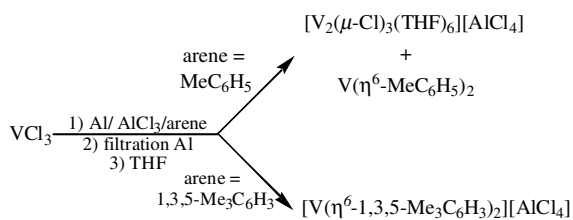
Table 1

Selected bond lengths (Å) and angles (°) in $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2]_2[\text{Al}_4\text{O}_2\text{Cl}_{10}]$ (**2**)

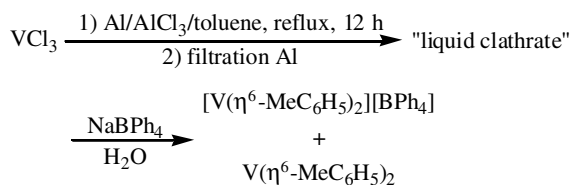
V(1)–C(1)	2.282(6)	V(2)–C(8)	2.283(6)
V(1)–C(2)	2.228(6)	V(2)–C(9)	2.232(6)
V(1)–C(3)	2.217(6)	V(2)–C(10)	2.203(6)
V(1)–C(4)	2.245(6)	V(2)–C(11)	2.240(7)
V(1)–C(5)	2.220(6)	V(2)–C(12)	2.223(7)
V(1)–C(6)	2.232(6)	V(2)–C(13)	2.210(7)
V(1)–Tol1 ^a	1.747	V(2)–Tol2 ^a	1.745
Al(1)–Cl(1)	2.129(2)	Al(2)–Cl(4)	2.106(2)
Al(1)–Cl(2)	2.108(2)	Al(2)–Cl(5)	2.102(2)
Al(1)–Cl(3)	2.128(2)	Al(2)–O	1.801(4)
Al(1)–O	1.768(4)	Al(2)–O'	1.798(4)
O–Al(1)–Cl(1)	106.2(2)	O–Al(2)–O'	86.5(2)
O–Al(1)–Cl(2)	111.0(2)	O–Al(2)–Cl(4)	112.1(2)
O–Al(1)–Cl(3)	106.7(1)	O–Al(2)–Cl(5)	115.7(2)
Al(1)–O–Al(2)	131.8(2)	O'–Al(2)–Cl(4)	114.9(1)
Al(1)–O–Al(2')	133.8(2)	O'–Al(2)–Cl(5)	112.3(2)
Al(2)–O–Al(2')	93.5(2)	Cl(4)–Al(2)–Cl(5)	112.9(1)

Numbers in parenthesis refer to the least significant digits.

^a Tol1 and Tol2 are the centroids of the toluene ligand.



Scheme 1.



Scheme 2.

cate as *trans*-eclipsed. Noteworthy is the fact that such a conformation is frequently observed in the bis(η^6 -toluene) derivatives of Cr(I) [9], while the known structures of methyl-substituted bis(η^6 -arene) derivatives of vanadium show an eclipsed arrangement of either methyl and ring carbon atoms, the examples being $[\text{V}(\eta^6\text{-}1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_2]^{+/0/-}$ species [1n,10].

The tetranuclear, centrosymmetric $[\text{Al}_4\text{O}_2\text{Cl}_{10}]^{2-}$ anion shows the typical [11] structure made of two types of aluminium-containing tetrahedral units, $\{\text{AlCl}_2\text{O}_2\}$ and $\{\text{AlCl}_3\text{O}\}$, arranged in such a way that the two oxygen atoms belong to a common edge in the $\{\text{AlCl}_2\text{O}_2\}$ unit described by Al(2), and are terminal in the $\{\text{AlCl}_3\text{O}\}$ unit described by Al(1). The Al_2O_2 four-membered ring experiences the repulsions between the atoms placed in diagonal positions; the greater charge density on aluminium with respect to that on the oxygen ones causes stronger $\text{Al}(2)\cdots\text{Al}(2')$ repulsions thus reducing the $\text{O}-\text{Al}(2)-\text{O}'$ angle $[86.5(2)^\circ]$ with respect to the $\text{Al}(2)-\text{O}-\text{Al}(2')$ one $[93.5(2)^\circ]$.

On standing, the “liquid clathrate” gave another crop of solid consisting of two vanadium(I) derivatives: $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2][\text{Al}_4\text{O}_2\text{Cl}_9]$ (**3**) and $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2][\text{Al}_2\text{Cl}_7]$ (**4**), whose separation was possible under a microscope due to the crystalline nature of **3**.

The IR spectrum of **3** shows the absorptions typical of the aromatic ring and of the $\text{Al}-\text{O}-\text{Cl}$ fragment in the $1000\text{--}400\text{ cm}^{-1}$ range [8]. Compound **4** has a simpler IR spectrum in the low wavenumber region due to the absence of $\text{Al}-\text{O}$ bonds.

The isolation of $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2][\text{Al}_2\text{Cl}_7]$ represents a further evidence of the presence of heptachlorodialuminate anions in the lower liquid phase from the Fischer–Hafner reduction of VCl_3 , as previously suggested by some of us in the case of the $\text{VCl}_3/\text{Al}/\text{AlCl}_3/1,3,5\text{-Me}_3\text{C}_6\text{H}_3$ system [1n].

The crystal structure of compound **3** is shown in Fig. 2 and a selection of bond distances and angles is reported in Table 2. The structure consists of $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2]^+$ cations and of a polymeric nonachlorodioxoaluminate anion. The vanadium(I) bis(η^6 -toluene) cations are in special positions with the vanadium lying on a twofold axis almost parallel to the toluene plane. Due to the presence of the twofold axis, the two arene rings have a nearly *cis*-eclipsed conformation (the methyl $\cdots\text{Tol}1'\cdots\text{Tol}1''\cdots\text{methyl}'$ torsion angle is 7.8°) and the toluene planes are almost parallel (1.3°). Such a conformation is similar to that observed for $\text{M}(\eta^6\text{-MeC}_6\text{H}_5)_2$, $\text{M} = \text{Ti}$ [12], Nb [13], and in some recently reported species of chromium(I) containing sterically demanding anions [14].

Table 2
Selected bond lengths (Å) and angles ($^\circ$) in $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2][\text{catena-Al}_4\text{O}_2\text{Cl}_9]$ (**3**)

V–C(1)	2.265(14)	Al(1)–Cl(1)	2.071(5)
V–C(2)	2.234(14)	Al(1)–Cl(2)	2.095(5)
V–C(3)	2.216(15)	Al(1)–Cl(3)	2.261(4)
V–C(4)	2.246(15)	Al(1)–O	1.729(8)
V–C(5)	2.210(14)	Al(2)–Cl(4)	2.089(5)
V–C(6)	2.215(14)	Al(2)–Cl(5)	2.092(5)
V–Tol ^a	1.742	Al(2)–O	1.810(8)
		Al(2)–O'	1.816(8)
O–Al(1)–Cl(1)	112.9(3)	O–Al(2)–O'	86.3(4)
O–Al(1)–Cl(2)	109.5(3)	O–Al(2)–Cl(4)	111.4(3)
O–Al(1)–Cl(3)	99.0(3)	O–Al(2)–Cl(5)	114.5(3)
Al(1)–Cl(3)–Al(1'')	117.3(3)	O'–Al(2)–Cl(4)	115.6(3)
Al(1)–O–Al(2)	131.3(5)	O'–Al(2)–Cl(5)	111.4(3)
Al(1)–O–Al(2')	134.0(5)	Cl(4)–Al(2)–Cl(5)	114.7(2)
Al(2)–O–Al(2')	93.7(4)		

Numbers in parenthesis refer to the least significant digits.

^a Tol is the centroid of the toluene ligand.

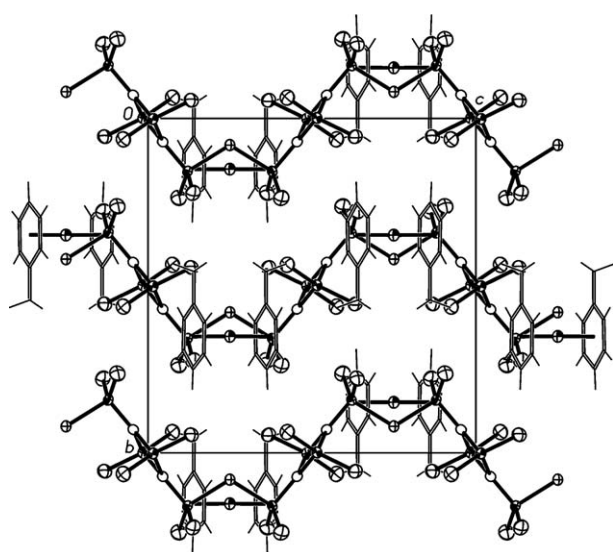


Fig. 2. View of the crystal structure of $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2][\text{catena-Al}_4\text{O}_2\text{Cl}_9]$ (**3**). Thermal ellipsoids are at 30% probability.

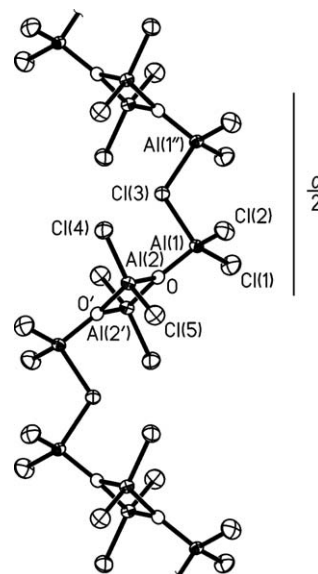


Fig. 3. View of the structure of the polyanion $[\text{catena-Al}_4\text{O}_2\text{Cl}_9]^-$. ' = $-x$, $-y$, $-z$, '' = $-x$, y , $1/2 - z$.

DFT calculations performed on chromium(I)- [14b] and on vanadium(I) bis(η^6 -toluene) cations have shown that the energy gap between the *cis*- and the *trans*-eclipsed conformations in the gas phase is small (0.09 and 1.77 kcal/mol for chromium and vanadium, respectively), thus suggesting that the conformation of the toluene rings in the crystal is mainly dictated by the packing forces.

As far as the anionic part of compound **3** is concerned, the Cl(3) and Cl(3') atoms are placed on twofold axes and bridge two centrosymmetric $[\text{Al}_4\text{Cl}_8\text{Cl}_{2/2}\text{O}_2]^-$ units. As a result, a polymeric anion growing in the *c* direction in a zigzag fashion is obtained, see Fig. 3. As reported in Table 2, the bond distances of the bridging chlorides are longer than the terminal ones by ca. 10%. The presence of bridges makes the O–Al(1)–Cl(3) bond angle [99.0(3)°] smaller than the O–Al(1)–Cl(1) and O–Al(1)–Cl(2) ones [112.9(3) and 109.5(3)°, respectively]. The remaining part of the $[\text{Al}_4\text{Cl}_8\text{Cl}_{2/2}\text{O}_2]^-$ units is substantially similar to that observed in the $[\text{Al}_4\text{O}_2\text{Cl}_{10}]^{2-}$ mononuclear anions.

3. Conclusions

By addition of the deeply coloured, liquid phase formed in the Al/AlCl₃ reduction of VCl₃ in toluene to a concentrated aqueous solution of NaBPh₄, the vanadium(I) bis(η^6 -toluene) cation has been isolated as the tetraphenylborato salt. Although the main reaction is the disproportionation $\text{V(I)} \rightarrow \text{V(0)} + \text{V(II)}$, the isolation of $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2][\text{BPh}_4]$ has definitely proved that the $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2]^+$ cation is the primary product of the cited Fischer–Hafner reduction and that, probably due to its low solubility in water, it can survive in such a medium for short periods of time.

The identification of $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2][\text{Al}_2\text{Cl}_7]$ (**4**), as obtained from the “liquid clathrate”, represents a further evidence of its involvement in the Fischer–Hafner reduction of VCl₃, as previously suggested by some of us in the case of the VCl₃/Al/AlCl₃/1,3,5-Me₃C₆H₃ system.

The isolation of compounds **2** and **3**, two vanadium(I) bis(η^6 -toluene) cations containing deca- or nonachlorodioxoaluminato anions is noteworthy from a more general point of view. In fact, they represent the first crystallographic report on the $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2]^+$ cation and on the polymeric nonachlorodioxoaluminato anion $[\text{catena-Al}_4\text{O}_2\text{Cl}_9]^-$. Moreover, it has to be noticed that the conformation of the toluene rings is different in the two compounds, i.e., the methyl···Toll···Toll'···methyl' torsion angle is 180° in **2** and 7.8° in compound **3**. The situation is reminiscent of that observed in the structural chemistry of chromium(I) bis(η^6 -toluene) cations [14]: since the DFT calculated energy gap between the *cis*- and the *trans*-eclipsed conformations is small, the conformation of the toluene rings in the crystal is dictated by the packing forces and it can be changed on changing the steric demand of the anion.

4. Experimental

4.1. General procedures

Unless otherwise stated, all the operations were carried out under an atmosphere of prepurified nitrogen. IR spectra were measured with the FT1725X instrument on or nujol and/or polychlorotrifluoroethylene (PCTFE) mulls. Magnetic susceptibility measurements were performed with a Faraday balance using CuSO₄·5H₂O as standard. Pascal contributions were used to calculate the diamagnetic correction [15]. DFT geometry optimization and calculation of the electron spin density distribution were performed using the Linux version of the SPARTAN '02 software [16]. We adopted the BP86 scheme, that uses the functional proposed by Becke [17] and Perdew [18], and the 6-31G** basis set that is appropriate for calculations of split-valence-plus-polarization quality.

VCl₃ (Pechiney), AlCl₃ (Carlo Erba) and finely ground aluminium (C. Erba) were used as received.

4.2. Preparation of $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2][\text{BPh}_4]$ (**1**)

A suspension of VCl₃ (12.75 g, 81 mmol), finely ground aluminium (3.12 g, 115 mmol), AlCl₃ (12.94 g, 97 mmol) in toluene (100 ml) was heated overnight at the reflux temperature. A red suspension was obtained which was filtered at room temperature. The liquid phase consisted of two layers: a pale yellow upper layer, containing only traces of vanadium and chloride, and a deep red lower one containing most of the vanadium introduced (0.059 g/ml of vanadium corresponding to the 93% of vanadium introduced).

A sample of the deeply coloured solution (18 ml, 20.8 mmol of vanadium) was added to a solution of NaBPh₄ (10.61 g, 31 mmol) in water (40 ml) at room temperature. An immediate, exothermic reaction took place with formation of a solid; the solution turned pale violet. The solid was quickly collected by filtration, washed with water and dried in vacuo at room temperature in the presence of P₄O₁₀. The solid (1.144 g), which appeared as a mixture of an orange and a dark brown compounds, was treated with heptane (50 ml) and stirred at room temperature for 2 h. The suspension was filtered and an orange solid was separated from a brown solution. The solid was washed with heptane (2 × 5 ml) and dried in vacuo at room temperature affording $[\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2][\text{BPh}_4]$ (**1**), (0.690 g, 6%) as an orange microcrystalline solid. Anal. Calc. for C₃₈H₃₆BV: C, 82.3; H, 6.5; V, 9.2. Found: C, 82.8; H, 6.3; V, 8.9%. IR (Nujol): $\tilde{\nu}/\text{cm}^{-1}$ 3048m-s, 3035 m-s, 1608w, 1580m, 1151 m-s, 1031s, 742s, 731vs, 709vs, 702s, 603s, 481w. $\chi_{\text{corr}}^{\text{M}} = 3.34 \times 10^{-3}$ cgsu, diamagn. corr. -361.7×10^{-6} cgsu, μ_{eff} (292 K) = 2.80 BM. The filtrate was evaporated to dryness affording $\text{V}(\eta^6\text{-MeC}_6\text{H}_5)_2$ (0.372 g, 8%).

4.3. Isolation of $[V(\eta^6\text{-MeC}_6\text{H}_5)_2]^+$ cations from the “liquid clathrate”

A suspension of VCl_3 (13.72 g, 87 mmol), finely ground aluminium (3.35 g, 124 mmol), $AlCl_3$ (13.94 g, 104 mmol) in toluene (100 ml) was heated overnight at the reflux temperature. A red suspension was obtained which was filtered at room temperature. The liquid phase consisted of two layers: a pale yellow upper layer, containing only traces of vanadium and chloride, and a deep red lower one containing 94% of the vanadium introduced. After some weeks in the dark at room temperature, deep red crystals were present. They were collected by filtration, washed with a small amount of toluene and shortly dried in vacuo at room temperature affording 3.125 g (7.5%) of $[V(\eta^6\text{-MeC}_6\text{H}_5)_2]_2[Al_4O_2Cl_{10}]$ (**2**), as deep red crystals sensitive to oxygen and moisture. Anal. Calc. for $C_{28}H_{32}Al_4Cl_{10}O_2V_2$: C, 34.8; H, 3.3; Al, 11.2; Cl, 36.7; V, 10.6. Found: C, 35.1; H, 3.6; Al, 11.6; Cl, 36.2; V, 10.1%. IR (Nujol): $\tilde{\nu}/\text{cm}^{-1}$ 3059m, 1495w, 1441m, 1383w, 1339w, 1055w, 1039m, 993 w, 823m-br, 765m, 680m-br, 496m-s. $\chi_{\text{corr}}^M = 3.14 \times 10^{-3}$ cgsu, diamagn. corr. -515×10^{-6} cgsu, μ_{eff} (292 K) = 2.72 BM.

After two months, the mother liquor gave another crop of solid, which was collected by filtration, washed with a small amount of toluene and dried in vacuo at room temperature affording 1.096 g yellow-brown solid whose elemental analysis corresponded to the following composition: $\{[V(\eta^6\text{-MeC}_6\text{H}_5)_2][Al_2Cl_7]\}_{0.85} \{[V(\eta^6\text{-MeC}_6\text{H}_5)_2][Al_4O_2Cl_9]\}_{0.15} \cdot C_7H_8$. Anal. Calc. for $C_{21}H_{24}Al_{2.3}Cl_{7.3}O_{0.3}V$: C, 38.6; H, 3.7; Al, 9.5; Cl, 39.6; V, 7.8. Found: C, 38.0; H, 3.4; Al, 10.4; Cl, 39.6; V, 7.6%. IR (Nujol): $\tilde{\nu}/\text{cm}^{-1}$ 3052m, 1493w, 1441m, 1382w, 1336w, 1055w, 1040m, 995w, 828m, 758m, 685m-w, 495s.

A close examination of the solid revealed the presence of a yellow brown microcrystalline solid and some deep red crystals which were carefully separated under the microscope (ca. 0.12 g) from the microcrystalline solid and identified as $[V(\eta^6\text{-MeC}_6\text{H}_5)_2][Al_4O_2Cl_9]$ (**3**). Anal. Calc. for $C_{14}H_{16}Al_4Cl_9O_2V$: C, 24.2; H, 2.3; Al, 15.0; Cl, 46.0; V, 7.8. Found: C, 23.9; H, 2.9; Al, 15.0; Cl, 46.6; V, 7.5%. IR (Nujol): $\tilde{\nu}/\text{cm}^{-1}$ 3059m, 1497w, 1439m, 1380w, 1341w, 1059w, 1042m, 990w, 828m-br, 756m, 685m-br, 493m-s. The yellow brown microcrystalline solid (ca. 950 mg) was identified as $[V(\eta^6\text{-MeC}_6\text{H}_5)_2][Al_2Cl_7]$. Anal. Calc. for $C_{14}H_{16}Al_2Cl_7V$: C, 31.3; H, 3.0; Al, 10.0; Cl, 46.2; V, 9.5. Found: C, 30.7; H, 3.5; Al, 10.8; Cl, 45.5; V, 9.0%. IR (Nujol): $\tilde{\nu}/\text{cm}^{-1}$ 3059m, 1489w, 1435m, 1382w, 1349w, 1062w, 1035m, 491vs.

4.4. Crystal structure of $[V(\eta^6\text{-MeC}_6\text{H}_5)_2]_2[Al_4O_2Cl_{10}]$ (**2**) and $[V(\eta^6\text{-MeC}_6\text{H}_5)_2][catena\text{-}Al_4O_2Cl_9]$ (**3**): solution and refinement

Data were collected at 293 K with graphite-monochromated Mo $K\alpha$ radiation on a Bruker P4 diffractometer on samples sealed in glass capillaries under a nitrogen

atmosphere. The intensity data collection was carried out with the $\omega/2\theta$ scan mode, collecting a redundant set of data. Three standard reflections were measured every 97 measurements to check sample decay. The intensities were corrected for Lorentz and polarization effects and for absorption by the ψ -scan method [19]. The structure solutions were obtained by direct methods [20], and the structural model was refined with full-matrix least-squares on F^2 [20]. Some utilities contained in the WINGX suite [21] were used. A selection of crystal parameters is listed in Table 3.

The asymmetric unit of compound **2** consists of one half of the $[Al_4Cl_{10}O_2]^{2-}$ anion placed near an inversion centre and two half of the $[V(\eta^6\text{-MeC}_6\text{H}_5)_2]^+$ cation, the vanadium atoms being placed on two inversion centres. The hydrogen atoms were in calculated positions and let to “ride” on the corresponding carbon atoms during the refinement. In the last refinement cycles the heavy atoms were refined with anisotropic thermal parameters and the reliability factors listed in Table 3 were obtained.

Due to the instability in the presence of air, crystal of **3** gave broad and irregularly-shaped diffractions, whose intensity rapidly decrease with increasing θ ; this prevented the collection of reflections above $\theta = 22.5^\circ$. The asymmetric unit consists of an infinite polyanion with the repeating modulus $[Al_2Cl_4OCl_{1/2}]^{0.5-}$ – placed between a inversion centre and a twofold axis – and by one half of the $[V(\eta^6\text{-MeC}_6\text{H}_5)_2]^+$ cation, the vanadium being placed on a twofold axis. The hydrogen atoms were in calculated positions and let to “ride” on the corresponding carbon atoms during the final refinement. The final refinement cycle was done with hydrogen atoms in calculated positions, riding on the connected carbon atoms; the heavy atoms were refined with anisotropic thermal parameters. The reliability factors listed in Table 3.

Table 3

Crystal data and parameters of the structure solution of $[V(\eta^6\text{-MeC}_6\text{H}_5)_2]_2[Al_4O_2Cl_{10}]$ (**2**) and $[V(\eta^6\text{-MeC}_6\text{H}_5)_2][catena\text{-}Al_4O_2Cl_9]$ (**3**)

Compound	1	2
Empirical formula	$C_{28}H_{32}Al_4Cl_{10}O_2V_2$	$C_{14}H_{16}Al_4Cl_9O_2V$
Formula weight	964.84	694.18
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no.2)	$C2/c$ (no. 15)
<i>a</i> (Å)	9.470(2)	13.082(3)
<i>b</i> (Å)	9.759(3)	14.900(3)
<i>c</i> (Å)	12.318(3)	14.873(3)
α (°)	102.60(2)	–
β (°)	96.84(2)	101.24(2)
γ (°)	105.59(2)	–
<i>U</i> (Å ³)	1050.8(5)	2843.4(10)
<i>Z</i>	1	4
<i>D</i> _{calc} (Mg m ⁻³)	1.525	1.622
μ (mm ⁻¹)	1.190	1.330
No. measured	3300	2490
No. unique [<i>R</i> _{int}]	2715 [0.0379]	1976 [0.0349]
No. parameters	211	137
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0464, 0.1080	0.0874, 0.2379
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0760, 0.1229	0.1246, 0.2728
Goodness-of-fit on <i>F</i> ²	1.029	1.065

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Appendix A. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 297961 for $[V(\eta^6\text{-MeC}_6\text{H}_5)_2]_2[\text{Al}_4\text{O}_2\text{Cl}_{10}]$ and CCDC 297962 for $[V(\eta^6\text{-MeC}_6\text{H}_5)_2][\text{catena-Al}_4\text{O}_2\text{Cl}_9]$. Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax 44 1223 33 6033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.04.027.

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