Scientific paper

Syntheses and Crystal Structures of Vanadium and Iron Chloride Complexes with Diglyme

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Dedicated to the memory of Prof. Dr. Jurij V. Brenčič.

Abstract

A mononuclear molecular complex fac-[VCl₃(diglyme)] (1) resulted from the reaction of VCl₃ and diglyme (diglyme = di(2-methoxyethyl)ether) in dichloromethane. The violet complex 1 is a sensitive substance which slowly oxidized to a new, blue mononuclear molecular complex, fac-[VOCl₂(diglyme)] (2) in the presence of air.

The synthesis of iron(II), iron(III) complex [FeCl(diglyme)(THF)]₂[FeCl₄] (3) was achieved by the reaction of yellow-green, partly oxidized FeCl₂.₄H₂O, diglyme and chlorotrimethylsilane in tetrahydrofuran. The compound consists of dinuclear cations with octahedral environment of iron(II) and tetrahedral anions of iron(III). A pure iron(II) chloride-diglyme complex [FeCl₂(diglyme)]₂ (4) was gained by the reaction of freshly prepared iron(II) chloride hydrate, diglyme and chlorotrimethylsilane in dichloromethane. Diglyme is coordinated in a meridional mode to octahedral iron(II) in dinuclear cations of 3 and in dinuclear molecules 4.

Keywords: Iron, Vanadium, Chloride, Di(2-Methoxyethyl)ether, mer-isomer, fac-isomer

1. Introduction

Applying a polyether diglyme as a ligand in syntheses of alkaline earth complexes is a common approach to prevent oligomerization by bridging ligands.¹⁻⁴ Saturating a coordination sphere of a metal by the tridentate chelate ligand diglyme hinders ‘metal – metal’ contacts. The formation of two five-membered puckered rings increases the stability of complexes. Minimized intermolecular solid-state interactions in monomeric complexes resulted in an enhanced volatility in comparison to oligomeric complexes, which makes mononuclear alkaline earth complexes superior metal organic chemical vapor deposition (MOCVD) precursors. A prevalingly chelate bonding of diglyme to metal centers in complexes is confirmed by the structural data in the CSD (version 5.35 updated May 2014) listing only about a dozen compounds of alkali metals, aluminum and lead with bridging diglyme molecules among numerous diglyme complexes.

Diglyme is a flexible O-donor ligand able to coordinate to a whole range of metals; not only earth alkaline MOCVD precursors,¹⁻⁴ but also lanthanide(III) halide complexes have been extensively studied.⁵⁻¹⁰ On the other hand, only a few examples of the first row d-block metal halide complexes with diglyme were prepared. They are either mononuclear molecular [MCl₃(diglyme)] (M(III) = Sc, Ti),¹¹⁻¹² [MX₂(diglyme)] (X = Cl, M(II) = Zn, X = I, M(II) = Co, Zn) complexes,¹³⁻¹⁴ dinuclear [MX₆(diglyme)]₂ (X = Cl, M(II) = Mn, Co, Ni; X = Br, I, M(II) = Ni) or 1-D polymeric [Co₃Cl₁(diglyme)]ₙ.¹⁵⁻¹⁶ Metal M(II) ions in polymeric and dinuclear complexes are connected by halides to achieve a preferred octahedral environment. A great flexibility of diglyme is most clearly demonstrated in complexes with octahedral arrangement of donor atoms coordinated to M²⁺ or M³⁺ either in mer or fac geometry (Chart 1). All three oxygen atoms, O₁, O₂, O₃, of diglyme and the central metal atom M are almost in the same plane with O₁–M–O₃ angles in the range from 144 to 156° in mer isomers.¹³⁻¹⁷ In fac isomers are the two planes, each through the central metal atom M, the middle (O₂) and one of terminal oxygen atoms (O₁ or O₃) in diglyme, nearly perpendicular to each other with O₁–M–O₃ angles close to 90°.¹¹⁻¹²

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2. Experimental

2. 1. General

All the manipulations were carried out under an inert atmosphere. Vanadium(III) chloride (Aldrich, 97%), iron(II) chloride tetrahydrate (Merck, 99%), hydrochloric acid (Riedel-de Haën, 32%), diglyme (Fluka, 99.5%) and chlorotrimethylsilane (Aldrich, 97.0%) were used as delivered. Solvents were dried (CH2Cl2 over CaH2, THF over Na/K) and distilled before use.

2. 2. Synthesis of [VCl3(diglyme)], 1

Method A) Solvent (THF, 30 mL) and diglyme (1.484 g, 11.05 mmol) were added to VCl3 (0.810 g, 5.15 mmol) under an inert atmosphere. The suspension was stirred for three days at room temperature and then dried in vacuo. A considerable amount of unreacted VCl3 in the resulting powder product was detected by a CHN analysis and IR spectroscopy. In order to complete the reaction of VCl3 and diglyme additional solvent (THF, 30 mL) and diglyme (0.979 g, 7.29 mmol) were mixed with the powder product and stirred for 20 hours at 65 °C. This suspension was dried in vacuo. Although the powder product still contained unreacted VCl3 according to results of CHN analysis, a recrystallization of the product from dichloromethane resulted in crystals of 1.

Method B) Solvent (CH2Cl2, 30 mL) and diglyme (0.601 g, 4.48 mmol) were added to VCl3 (0.433 g, 2.75 mmol) under an inert atmosphere. The suspension was stirred for a week at room temperature, then dried in vacuo, the complex 1 (0.798 g, 99.6% yield) was gained. Anal. Calcd. mass fractions of elements, w %, for C4H4Cl2O3V (M = 291.46) are: C, 24.72; H, 4.84; Cl, 36.49; found: C, 24.50; H, 4.78; Cl, 36.51. IR (in Nujol) 1302 m, 1275 w, 1258 m, 1196 s, 1093 s, 1018 s, 866 w, 796 s, 550 m, 438 m cm–1. Recrystallization from dichloromethane resulted in crystals of 1.

2. 3. Synthesis of [VOCl2(diglyme)], 2

Air leaking to a closed system during a crystallization of 1 by a slow evaporation of dichloromethane at a reduced pressure resulted in an oxidation of 1 to crystals of the blue complex 2. Anal. Calcd. mass fractions of elements, w %, for C4H6Cl2O2V (M = 272.01) are: C, 26.49; H, 5.19; found: C, 26.51; H, 5.22. IR (in Nujol) 1260 s, 1093 s, 1018 s, 866 w, 796 s, 550 m, 438 m cm–1.

2. 4. Synthesis of [FeCl(diglyme)(THF)]2[FeCl4], 3

Solvent (THF, 30 mL), diglyme (1.490 g, 11.1 mmol) and (CH3)3SiCl (15.103 g, 139 mmol) were added to a yellow-green partly oxidized FeCl3·4H2O (1.092 g, 5.49 mmol). The yellow suspension was stirred five days at room temperature. An attempt to evaporate solvent in vacuo resulted in a highly viscous brownish solution. After a week yellow crystals of the complex 3 grew out of the solution. IR (in Nujol) 1260 s, 1093 s, 1018 s, 866 w, 799 s, 465 w cm–1.

2. 5. Synthesis of [FeCl2(diglyme)]2, 4

In the synthesis of 4 was used the freshly prepared iron(II) chloride hydrate instead of the partly oxidized one. Therefore iron (3.0 g, 53.7 mmol) reacted with hydrochloric acid (22 mL, 18%) at 80 °C for three hours.
Unreacted iron was removed by a hot filtration, a green solution was dried in vacuo and a moist green product resulted. Chlorine content (33.06%) of this product was determined by potentiometric titrations and iron content (25.98%) was calculated according to the molar ratio of iron and chlorine in FeCl₂. Solvent (CH₂Cl₂, 30 mL), diglyme (1.410 g, 10.5 mmol) and (CH₃)₃SiCl (13.13 g, 121 mmol) were added to the freshly prepared green iron(II) chloride hydrate (1.014 g, 4.72 mmol of Fe²⁺). The suspension was stirred for a day at room temperature and then dried in vacuo. The procedure was repeated in the second step, because some water was present in the white product, as proven by characteristic peaks (3419 s, 837 s, 828 m, 560 w cm⁻¹). Recrystallization from dichloromethane resulted in colorless crystals of VOCl₂. Magnetic moment of VOCl₂, µ = 5.48 BM.

### 2.6. Crystal Structure Determination

Details of the crystal data collections and the refinement parameters of the complexes 1–4 are summarized in Table 1.

All studied compounds are hygroscopic. The crystals were mounted on a tip of a glass fiber with a small amount of silicon grease. Diffraction data were collected on a Nonius Kappa diffractometer with a CCD area detector at 150(2) K. Graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) was employed for all measurements. The data were processed using the program DENZO-SMN. The crystal structures were solved by direct methods implemented in SHELXS-97 and refined by a full-matrix least-squares procedure based on F² (SHELXL-97). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the models at geometrically calculated positions and refined using a riding model. The calculations were performed using the WinGX program suite.

Absolute structures of 1 and 2 cannot be determined reliably (Flack parameter 0.51(3) and 0.53(2) respectively). Figures depicting the structures were prepared by ORTEP3 and Mercury.
3. Results and Discussion

3.1. Syntheses of Vanadium Chloride Complexes with Diglyme, [VCl₃(diglyme)], 1, and [VOCl₂(diglyme)], 2

A choice of solvent applied in the reaction of vanadium(III) chloride and diglyme is very important. A reaction is completed in dichloromethane at room temperature, but in tetrahydrofuran even a reaction at elevated temperature (20 hours, 65 °C) resulted in a mixture of unreacted VCl₃ and complex 1. The complex 1 is a sensitive and unstable compound which is oxidized by oxygen to the V(IV) complex 2. The blue color of 2 is characteristic for almost all compounds containing a vanadyl unit.

3.2. Crystal Structures of 1 and 2

A distorted octahedral arrangement of ligands is observed in the mononuclear molecular complexes of 1 and 2 (Figure 1). Three oxygen atoms of a diglyme molecule are coordinated in a facial mode to a central vanadium(III) ion in 1 or to an oxidovanadium(IV) ion in 2. The coordination sphere is fulfilled by three or two chloride ions in 1 and 2, respectively.

The overlay of two molecules in the asymmetric unit of the complex 1 clearly shows a different puckering of coordinated diglyme ligand (Figure 2).

The ring conformation differences of coordinated diglyme in two molecules of an asymmetric unit as in 1 were reported also for the isostructural complex [TiCl₃(diglyme)] (Figure 3).[11] A similar facial geometry of a coordinated diglyme as in 1, 2 and [TiCl₃(diglyme)][11] was found also in [ScCl₃(diglyme)],[12] but the smaller[18]Al³⁺ is coordinated by a diglyme molecule in a meridional mode in [AlBr₃(diglyme)].[19]

Selected geometric parameters (Å, °) in 1 and 2 are summarized in Table 2. Interestingly, the average V–Cl bonding distances in 2 are longer than in 1 in spite of a higher oxidation state of vanadium in 2 than in 1.

V–Cl bonding distances in complexes 1 are comparable to those observed in fac-[VCl₃(DME)(THF)] (2.298(4)–2.306(6) Å)[28] and mer-[VCl₃(THF)₃] (2.297(1)–2.333(1) Å).[29] The average V–O(diglyme) distance in 1 is in the same range as V–O(DME) (2.119(8) Å) and longer than V–O(THF) to a sterically less demanding ligand THF in fac-[VCl₃(DME)(THF)] (2.03(1) Å) or mer-[VCl₃(THF)₃] (2.062(8) Å).[29]

A comparison of orthorhombic vanadyl complexes [VOCl₂(MeOH)₃] and [VOCl₂(H₂O)(THF)₂] reveals similar bonding distances as in 2.[30] A pronounced elongation of V–O bonding distance trans to a short vanadyl bond similar as in 2 was found in both compared complexes. V–O distances to monodentate ligands are slightly shorter (V–O(MeOH) 2.056(5)–2.088(5) Å, V–O(THF) 2.064(2) Å) and V–Cl distances slightly longer

Figure 1. a) Two molecules of [VCl₃(diglyme)] in the asymmetric unit of 1. b) The crystal structure of 2, [VOCl₂(diglyme)], with the numbering scheme adopted. Hydrogen atoms are omitted for clarity. The probability of the thermal ellipsoids is 50%.

Figure 2. Two molecules of [VCl₃(diglyme)] in the asymmetric unit of 1 are overlaid. Hydrogen atoms are omitted for clarity.

Figure 3. Structure overlay of isostructural complexes 1, [VCl₃(diglyme)], in blue and TiCl₃(diglyme)] in green.[11] Hydrogen atoms are omitted for clarity.
in [VOCI₂(MeOH)₃] (2.359(3)–3.386(2) Å) and [VOCI₂(H₂O)(THF)₂] (3.3804(6) Å) than in 2.30 Similar, very short V=O distances as in 2 were observed also in oxidovanadium(V) complexes (1.583(3) Å, 1.592(1) Å).31

### 3.3. Syntheses of Iron Chloride Complexes with Diglyme, [FeCl(diglyme)(THF)]₂, 3, and FeCl₂(diglyme)]₂, 4

Only a few crystals of iron(II)-iron(III) complex 3 were obtained when partly oxidized FeCl₂·4H₂O was used in the synthesis of iron chloride complex with diglyme. A reaction of the freshly prepared green iron(II) chloride hydrate, diglyme and (CH₃)₃SiCl in excess, which should guarantee a formation of a water free complex, resulted in an aqua iron chloride complex with diglyme. The complex 4 was gained only in the reaction of the aqua iron chloride complex with (CH₃)₃SiCl and diglyme in dichloromethane. A one step synthesis of 4 was not successful even with a prolonged reaction time and a higher (CH₃)₃SiCl content in a reaction mixture of freshly prepared moist green iron(II) chloride hydrate and diglyme in dichloromethane. A similar two step reaction was reported for a dehydration of FeCl₂·4H₂O by triethyl orthoformate in propan-2-ol yielding [FeCl₂(PrOH)₂]₃.33

### 3.4. Magnetic Measurements

The magnetic moment of iron complex 4 (5.48 BM) measured at room temperature suggests a high spin d⁶ configuration of octahedrally coordinated Fe²⁺ ions.20

### 3.5. Crystal structures of 3 and 4

Two bridging chloride ions and three oxygen atoms of a diglyme molecule in a meridional mode are coordinated to each of two iron centers connected into a cation of 3 or a dinuclear molecule 4 (Figure 4). A distorted octahedral arrangement of iron(II) ions is fulfilled by a non-brid-

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**Table 2.** Selected geometric parameters (Å, °) in 1, [VCl₃(diglyme)], and 2, [VOCI₂(diglyme)]

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**Figure 4.**

a) A cation of 3, [FeCl(diglyme)(THF)]₊. b) The crystal structures of dinuclear molecular complex 4, [FeCl₂(diglyme)]₂, with the numbering scheme adopted. Hydrogen atoms are omitted for clarity. The probability of the thermal ellipsoids is 50%.
ging chloride in 4 and by an oxygen atom from THF molecule in cation of 3.

A rhombus $\text{M–Cl}–\text{M–Cl}$ is almost the same in 4 and isostructural complexes of manganese(II), nickel(II) and cobalt(II),\textsuperscript{13, 15} while ring conformation of coordinated diglyme molecules slightly differs (Figure 5).

**Table 3.** Selected geometric parameters (Å, °) in 3 and 4,\textsuperscript{13} and isostructural complexes of manganese(II), nickel(II) and cobalt(II),\textsuperscript{13, 15} while ring conformation of coordinated diglyme molecules slightly differs (Figure 5).

4. Conclusions

A chelate $\eta^3$, non-bridging coordination of diglyme as characteristic for all complexes of the first row d-block metals\textsuperscript{13–16} was found in the four novel vanadium and iron complexes 1–4. The new complex of vanadium(III) chloride with diglyme 1 is a mononuclear compound with a facial arrangement of O-donor atoms from diglyme, which has been already reported for \[\text{MCl}_3(\text{diglyme})\] (M = Sc, Ti).\textsuperscript{11, 12} The facial coordination of diglyme molecule is retained in the vanadyl complex $\text{VOCl}_2(\text{diglyme})$, 2, achieved by an oxidation of \[\text{VCl}_3(\text{diglyme})\], 1, in the presence of air.

The new compound of iron(II) chloride with diglyme 4 is a dinuclear complex with two bridging chlorides to achieve a preferred octahedral environment of the central Fe$^{2+}$. Diglyme is in \[\text{FeCl}_2(\text{diglyme})\] and \[\text{FeCl}_2(\text{dme})\]\textsuperscript{13} and \[\text{FeCl}_2(\text{dme})\]\textsuperscript{13} and coordinated to Fe$^{2+}$ in the meridional mode similarly as in all reported M(II) complexes with an octahedral geometry.\textsuperscript{13–17} In the iron(II)-iron(III) complex \[\text{FeCl(diglyme)(THF)}\]\textsuperscript{2, 3}, diglyme is coordinated to Fe$^{2+}$. Two iron(II) ions in the cation are linked by bridging chlorides and diglyme is also coordinated in a meridional geometry.
5. Appendix A. Supplementary Data

Crystallographic data for the structures 1 (CCDC 1031640), 2 (CCDC 1031641), 3 (CCDC 1031639) and 4 (CCDC 1031642) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336033; or email deposit@ccdc.cam.ac.uk.

6. Acknowledgement

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7. References

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Povzetek

Enojedrni molekulski kompleks $\text{fac-}[\text{VCl}_3(\text{diglyme})]$ (1) je bil sintetiziran z reakcijo med $\text{VCl}_3$ in polietrom diglyme (diglyme = di(2-metoksietil)eter) v diklorometanu. Vjolično obarvani kompleks 1 se v prisotnosti kisika iz zraka počasi oksidira, nastane moder enojedrni kompleks $\text{fac-}[\text{VOCl}_2(\text{diglyme})]$ (2).

Kompleks $[\text{FeCl(diglyme)(THF)}]_2[\text{FeCl}_4]$ (3), ki vsebuje železo(II) in železo(III), je nastal z reakcijo rumeno zelenega, delno oksidiranega FeCl$_2$·4H$_2$O, polietra diglyme in klorotrimetilsilana v tetrahidrofuranu. Spojino sestavljajo dvojedrni kationi z oktaedrično koordiniranim železom(II) in tetraedričnimi anioni v katerih je centralni ion železo(III). Kompleks čistega železovega(II) klorida z ligandom diglyme [FeCl$_2$(diglyme)]$_2$ (4) je bil sintetiziran iz sveže pripravljenega železovega(II) klorida hidrata, polietra diglyme in klorotrimetilsilana v diklorometanu. Ligand diglyme je koordiniran meridionalno na centralni železov(II) ion tako v dvojedrnem kationu spojine 3 kot v dvojedrnih molekulah 4.