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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*-[VCl_3(diglyme)] (**1**) resulted from the reaction of VCl_3 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*-[$VOCl_2$(diglyme)] (**2**) in the presence of air.

The synthesis of iron(II), iron(III) complex [FeCl(diglyme)(THF)]$_2$[$FeCl_4$)]$_2$ (**3**) was achieved by the reaction of yellow-green, partly oxidized $FeCl_2 \cdot 4H_2O$, 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 [$FeCl_2$(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 prevailingly chelate bonding of digyme 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 [MCl_3(diglyme)] (M(III) = Sc, Ti),[11–12] [MX_2(diglyme)] (X = Cl, M(II) = Zn, X = I, M(II) = Co, Zn) complexes,[13–14] dinuclear [MX_2(diglyme)]$_2$ (X = Cl, M(II) = Mn, Co, Ni; X = Br, I, M(II) = Ni) or 1-D polymeric [Co_2Cl_4(diglyme)]$_n$.[13–16] 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 M^{2+} or M^{3+} 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]

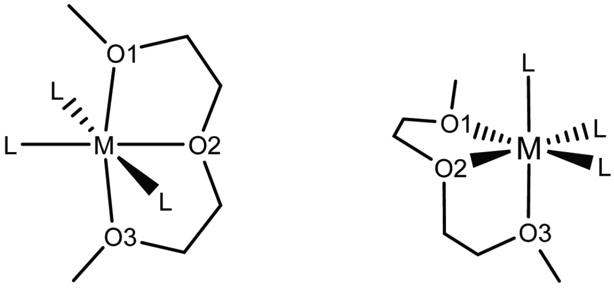

Chart 1. A *mer*– and a *fac*– isomer of [M(diglyme)L_3] complexes.

Dinuclear octahedral M(II) complexes (M = Mn, Co, Ni and Mg) with bridging halides and coordinated diglyme crystallize as *mer* isomers.[13–17] Mononuclear scandium(III) and titanium(III) chloride complexes with diglyme crystallize as *fac* isomers,[11–12] and a complex of a smaller[18] Al^{3+} is the *mer*-[$AlBr_3$(diglyme)].[19]

We prepared vanadium and iron chloride complexes with diglyme to continue our investigation of nuclearity and isomerism in the first row *d*-block metal halide complexes with this polyether. A correlation between structure and interesting magnetic properties of these compounds will be in focus of our research in the future.

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%), iron (Kemika, 95%), hydrochloric acid (Riedel-de Haën, 32%), diglyme (Fluka, 99.5%) and chlorotrimethylsilane (Aldrich, 97.0%) were used as delivered. Solvents were dried (CH_2Cl_2 over calcium hydride, THF over Na/K) and distilled before use.

Suspensions of ground samples in Nujol were prepared in a dry box. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer from 400 to 4000 cm^{-1}.

Chlorine contents were determined by potentiometric titrations of chloride ions with silver nitrate. Elemental analyses were carried out on a Perkin-Elmer 2400 Series II CHN micro analyzer at the University of Ljubljana (Department of Organic Chemistry).

Powdered samples were sealed into tubes in a dry box and room temperature magnetic susceptibility measurements were performed by a Sherwood Scientific MBS-1 balance using Hg[$Co(NCS)_4$] as a standard. Diamagnetic corrections were applied using Pascal's constants and the magnetic moments were calculated.[20]

2. 2. Synthesis of [VCl_3(diglyme)], 1

Method A)

Solvent (THF, 30 mL) and diglyme (1.484 g, 11.05 mmol) were added to VCl_3 (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 VCl_3 in the resulting powder product was detected by a CHN analysis and IR spectroscopy. In order to complete the reaction of VCl_3 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 VCl_3 according to results of CHN analysis, a recrystallization of the product from dichloromethane resulted in crystals of **1**.

Method B)

Solvent (CH_2Cl_2, 30 mL) and diglyme (0.601 g, 4.48 mmol) were added to VCl_3 (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 $C_6H_{14}Cl_3O_3V$ (M_r = 291.46) are: C, 24.72; H, 4.84; Cl, 36.49; found: C, 24.50; H, 4.78; Cl, 36.51. IR (**1** in Nujol) 1302 m, 1275 w, 1258 w, 1240 m, 1199 m, 1098 s, 1070 s, 1040 s, 1014 s, 919 m, 879 w, 856 s, 825 m, 588 w cm^{-1}. Recrystallization from dichloromethane resulted in crystals of **1**.

2. 3. Synthesis of [$VOCl_2$(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 $C_6H_{14}Cl_2O_4V$ (M_r = 272.01) are: C, 26.49; H, 5.19; found: C, 26.51; H, 5.22. IR (**2** in Nujol) 1285 m, 1261 s, 1205 w, 1193 w, 1098 s, 1065 s, 1010 s, 984 s, 924 s, 863 s, 796 s, 550 m, 438 m cm^{-1}.

2. 4. Synthesis of [FeCl(diglyme)(THF)]$_2$[$FeCl_4$)]$_2$, 3

Solvent (THF, 30 mL), diglyme (1.490 g, 11.1 mmol) and $(CH_3)_3SiCl$ (15.103 g, 139 mmol) were added to a yellow-green partly oxidized $FeCl_2·4H_2O$ (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 (**3** in Nujol) 1260 s, 1093 s, 1018 s, 866 w, 799 s, 465 w cm^{-1}.

2. 5. Synthesis of [$FeCl_2$(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 $FeCl_2$. Solvent (CH_2Cl_2, 30 mL), diglyme (1.410 g, 10.5 mmol) and $(CH_3)_3SiCl$ (13.13 g, 121 mmol) were added to the freshly prepared green iron(II) chloride hydrate (1.014 g, 4.72 mmol of Fe^{2+}). 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, 1600 m cm^{-1}) in IR spectrum. Solvent (CH_2Cl_2, 30 mL), diglyme (1.410 g, 10.5 mmol) and $(CH_3)_3SiCl$ (13.13 g, 121 mmol) were added to the white product. The suspension was stirred for a week at room temperature and then dried *in vacuo*, the complex **4** (0.959 g, 77.9% yield) was gained. *Anal.* Calcd. mass fractions of elements, w /%, for $C_{12}H_{28}Cl_4O_6Fe_2$ (M_r = 521.84) are: C, 27.62; H, 5.41; Cl, 27.17; found: C, 27.42; H, 5.35; Cl, 27.28. IR (**4** in Nujol) 1344 m, 1281 m, 1265 m, 1247 m, 1234 m, 1208 w, 1191 w, 1112 s, 1080 s, 1060 s, 1040 s, 1010 s, 950 m, 868 s, 837 s, 828 m, 560 w cm^{-1}. Recrystallization from dichloromethane resulted in colorless crystals of **4**. Magnetic moment of **4**: 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 $K\alpha$ radiation (λ = 0.71073 Å) was employed for all measurements. The data were processed using the program DENZO-SMN.[21] The crystal structures were solved by direct methods implemented in SHELXS-97[22] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-97).[23] 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.[24]

Absolute structures of **1** and **2** cannot be determined reliably (Flack parameter 0.51(3) and 0.53(2) respectively).[25] Figures depicting the structures were prepared by ORTEP3[26] and Mercury.[27]

Table 1 Crystallographic data for the compounds **1**, $[VCl_3(diglyme)]$, **2**, $[VOCl_2(diglyme)]$, **3**, $[FeCl(diglyme)(THF)]_2[FeCl_4]_2$, and **4**, $[FeCl_2(diglyme)]_2$

	1	**2**	**3**	**4**
Formula	$[VCl_3(O_3C_6H_{14})]$	$[VOCl_2(O_3C_6H_{14})]$	$[FeCl(O_3C_6H_{14})(OC_4H_8)]_2[FeCl_4]_2$	$[FeCl_2(O_3C_6H_{14})]_2$
Color	violet	blue	yellow	colorless
For. mass (g mol^{-1})	291.46	272.01	990.45	521.84
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P\ 2_1\ c\ n$ (no. 33)	$C\ c$ (no. 9)	$P\ 2_1/c$ (no. 14)	$P\ 2_1/c$ (no. 14)
a (Å)	6.9987(1)	6.9947(2)	12.2851(3)	10.3118(4)
b (Å)	11.2312(2)	11.8436(3)	13.6297(3)	7.5431(2)
c (Å)	28.4482(6)	13.0738(4)	12.2931(3)	14.3736(5)
β (°)	90.0	92.918(2)	109.519(1)	110.547(2)
V (Å^3)	2236.14(7)	1081.66(5)	1940.09(8)	1046.90(6)
Z (form.)	8	4	2	2
$D_{cal.}$ (g cm^{-3})	1.732	1.670	1.695	1.655
μ (mm^{-1})	1.577	1.392	2.191	1.919
Crystal size (mm)	0.22 0.20 0.18	0.07 0.06 0.05	0.15 0.14 0.14	0.20 0.20 0.17
θ Range (°)	1.43–27.48	3.78–27.40	3.5–27.5	3.43–27.44
Total numb. of collected reflections	4941	2381	13188	4474
Number of unique reflections	4941	2375	4415	2387
R_{int}	0.045	0.0155	0.0245	0.029
Number of reflections used	4419	2301	3857	1899
Threshold	[I>2.0 $\sigma(I)$]	[I>2.0 $\sigma(I)$]	[I>2.0 $\sigma(I)$]	[I>2.0 $\sigma(I)$]
Number of parameters	239	121	192	111
R^a (obs.)	0.0333	0.0248	0.0229	0.027
wR_2^b	0.0692	0.0591	0.0557	0.055
S	1.044	1.027	1.015	1.034
Maximum/minimum res. elec. d. (e Å^{-3})	0.296, –0.401	0.217, –0.339	0.624, –0.294	0.289, –0.354

$^aR = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $^b\ wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^2)^2)^{1/2}$

3. Results and Discussion

3. 1. Syntheses of Vanadium Chloride Complexes with Diglyme, [VCl$_3$ (diglyme)], 1, and [VOCl$_2$(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 VCl$_3$ 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.

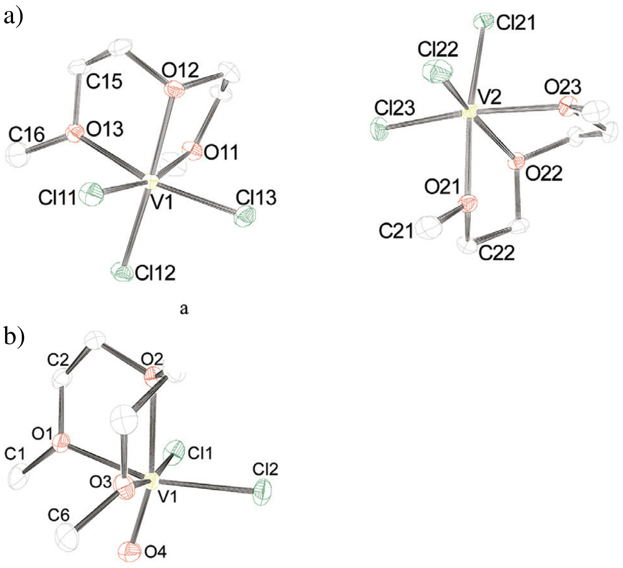

Figure 1. a) Two molecules of [VCl$_3$(diglyme)] in the asymmetric unit of **1**. b) The crystal structure of **2**, [VOCl$_2$(diglyme)], with the numbering scheme adopted. Hydrogen atoms are omitted for clarity. The probability of the thermal ellipsoids is 50%.

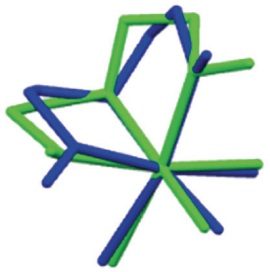

Figure 2. Two molecules of [VCl$_3$(diglyme)] in the asymmetric unit of **1** are overlaid. Hydrogen atoms are omitted for clarity.

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 [TiCl$_3$(diglyme)] (Figure 3).[11]A similar facial geometry of a coordinated diglyme as in **1**, **2** and [TiCl$_3$(diglyme)][11] was found also in [ScCl$_3$(diglyme)],[12] but the smaller[18]Al^{3+} is coordinated by a diglyme molecule in a meridional mode in [AlBr$_3$(diglyme)].[19]

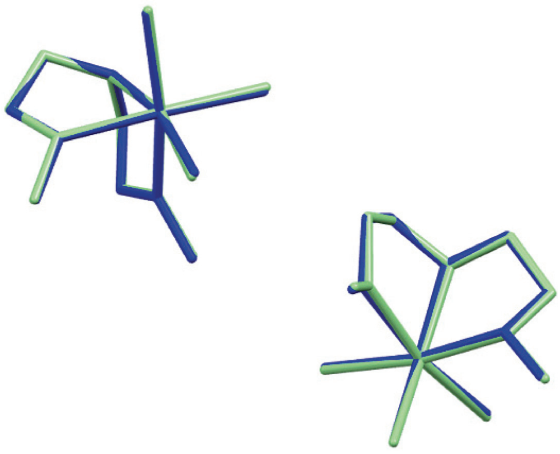

Figure 3. Structure overlay of isostructural complexes **1**, [VCl$_3$(diglyme)], in blue and TiCl$_3$(diglyme)] in green.[11] Hydrogen atoms are omitted for clarity.

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*-[VCl$_3$(DME)(THF)] (2.298(4)–2.306(6) Å)[28] and *mer*-[VCl$_3$(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*-[VCl$_3$(DME)(THF)] (2.03(1) Å)[28] or *mer*-[VCl$_3$(THF)$_3$] (2.062(8) Å).[29]

A comparison of orthorhombic vanadyl complexes [VOCl$_2$(MeOH)$_3$] and [VOCl$_2$(H$_2$O)(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

Table 2. Selected geometric parameters (Å, °) in **1,** [VCl_3(diglyme)], and **2**, [$VOCl_2$(diglyme)]

	1, [VCl_3(diglyme)]		**2, [$VOCl_2$(diglyme)]**	
	n = 1	**n = 2**		
Vn–Cln3	2.3293(10)	2.2834(10)	V–Cl2	2.3174(6)
Vn–Cln2	2.2655(9)	2.3183(9)	V–Cl1	2.3318(6)
Vn–Cln1	2.2798(10)	2.2849(9)	V–Cl_{av}	2.325(1)
Vn–Cl_{av}	2.291(3)	2.296(3)	V–O1	2.102(1)
Vn–On1	2.185(2)	2.108(2)	V–O2	2.237(2)
Vn–On2	2.088(2)	2.088(2)	V–O3	2.146(2)
Vn–On3	2.120(2)	2.102(2)	V–$O_{av.(diglyme)}$	2.162(6)
Vn–On_{av}	2.131(6)	2.099(6)	V–O4	1.592(2)
On1–Vn–On3	88.23(9)	82.43(9)	O1–V–O3	85.98(6)
On2–Vn–On3	76.03(9)	78.37(9)	O3–V–O2	73.83(6)
On1–Vn–On2	74.60(8)	76.80(9)	O1–V–O2	72.60(6)
Cln1–Vn–Cln2	100.57(4)	97.12(3)	Cl2–V–Cl1	93.35(2)
Cln2–Vn–Cln3	97.65(4)	96.45(4)	O4–V–O1	94.82(7)
Cln1–Vn–Cln3	93.54(4)	96.58(4)	O4–V–O3	90.75(7)
On1–Vn–Cln1	168.06(6)	166.60(7)	O4–V–O2	160.46(7)
On2–Vn–Cln2	160.91(7)	167.38(7)	O4–V–Cl2	102.64(6)
On3–Vn–Cln3	170.18(7)	168.36(7)	O3–V–Cl1	166.85(5)

in [$VOCl_2(MeOH)_3$] (2.359(3)–3.386(2) Å) and [$VOCl_2(H_2O)(THF)_2$] (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)]$_2$ [$FeCl_4$)]$_2$, 3, and FeCl$_2$(diglyme)]$_2$, 4

Only a few crystals of iron(II)-iron(III) complex **3** were obtained when partly oxidized $FeCl_2 \cdot 4H_2O$ was used in the synthesis of iron chloride complex with diglyme. A reaction of the freshly prepared green iron(II) chloride hydrate, diglyme and $(CH_3)_3SiCl$ in excess, which should guarantee a formation of a water free complex,[32] 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 $(CH_3)_3SiCl$ and diglyme in dichloromethane. A one step synthesis of **4** was not successful even with a prolonged reaction time and a higher $(CH_3)_3SiCl$ 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 $FeCl_2 \cdot 4H_2O$ by triethyl orthoformate in propan-2-ol yielding [$FeCl_2(PrOH)_2]_n$.[33]

3. 4. Magnetic Measurements

The magnetic moment of iron complex **4** (5.48 BM) measured at room temperature suggests a high spin d^6 configuration of octahedrally coordinated Fe^{2+} 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-

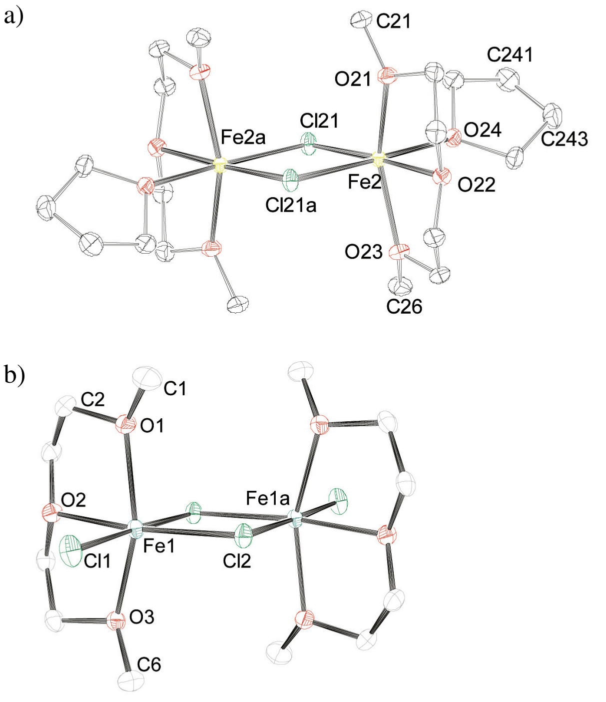

Figure 4. a) A cation of **3**, [FeCl(diglyme)(THF)]$_2^+$. b) The crystal structures of dinuclear molecular complex **4**, [$FeCl_2$(diglyme)]$_2$ with the numbering scheme adopted. Hydrogen atoms are omitted for clarity. The probability of the thermal ellipsoids is 50%.

ging chloride in **4** and by an oxygen atom from THF molecule in cation of **3**.

A rhombus M–Cl–M–Cl is almost the same in **4** and isostructural complexes of manganese(II), nickel(II) and cobalt(II),[13, 15] while ring conformation of coordinated diglyme molecules slightly differs (Figure 5).

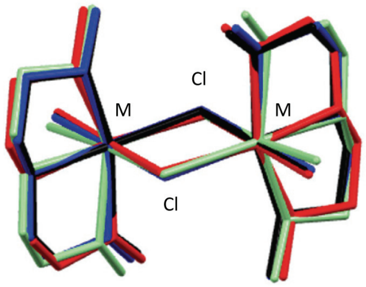

Figure 5. Structure overlay of isostructural complexes $[MCl_2(diglyme)]_2$, (M = Fe in red; Mn in green, Ni in black and Co in blue).[13, 15] Hydrogen atoms are omitted for clarity.

Selected geometric parameters (Å, °) in **3** and **4** are summarized in Table 3.

The average Fe–Cl(bridging), Fe–O(diglyme) bonding distances and distances between two Fe^{2+} ions linked by two μ-bridging chlorides are shorter in a cation of **3** than in a dinuclear complex **4**.

M–O and M–Cl bonding distances in **4** and isostructural $[MCl_2(diglyme)]_2$ (M = Mn, Co and Ni)[13, 15] decrease perfectly in accord to the decreasing ionic radii of the transition metal atoms from manganese to nickel.[18]

Fe–Cl(bridging) and Fe–O bonding distances in cations of **3** are in the same range as in a tetranuclear complex $[Fe_4Cl_8(THF)_6]$ (Fe–(μ^2–Cl) 2.355(1)–2.488(2) Å and average Fe–O 2.135(9) Å).[34] A comparison of geometric parameters in mixed Fe(II), Fe(III) complex **3** and in a Fe(III) complex $[FeCl_2(DME)_2][FeCl_4]$ (Fe–Cl in anion 2.1895(9)–2.200(1) Å)[35] indicates similarity of anions and thus confirming the 3+ oxidation number of iron in anion of **3**. The average Fe–O bonding distances in **3** are longer than in $[FeCl_2(DME)_2]^+$ (2.101(4) Å)[35] due to a lower oxidation number of iron in cation of **3**.

4. Conclusions

A chelate η^3, non-bridging coordination of diglyme as characteristic for all complexes of the first row *d*-block metals[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 $[MCl_3(diglyme)]$ (M = Sc, Ti).[11,12] The facial coordination of diglyme molecule is retained in the vanadyl complex *fac*-$[VOCl_2(diglyme)]$, **2**, achieved by an oxidation of $[VCl_3(diglyme)]$, **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 $[FeCl_2(diglyme)]_2$, **4**, coordinated to Fe^{2+} in the meridional mode similarly as in all reported M(II) complexes with an octahedral geometry.[13–17] In the iron(II)-iron(III) complex $[FeCl(diglyme)(THF)]_2[FeCl_4)]_2$, **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.

Table 3. Selected geometric parameters (Å, °) in **3**, $[FeCl(diglyme)(THF)]_2[FeCl_4]_2$, and **4**, $[FeCl_2(diglyme)]_2$

3				**4**	
$[FeCl(diglyme)(THF)]_2^{2+}$		$[FeCl_4]^-$		$[FeCl_2(diglyme)]_2$	
Fe2–Cl21	2.3804(4)	Fe1–Cl11	2.1938(5)	Fe1–Cl1	2.3511(5)
Fe2–Cl21a	2.5098(4)	Fe1–Cl12	2.1966(5)	Fe1–Cl2	2.4348(5)
Fe2–$Cl_{av.}$	2.445(1)	Fe1–Cl13	2.1968(5)	Fe1–Cl2a	2.5154(5)
Fe2–O21	2.1046(12)	Fe1–Cl14	2.1839(5)	Fe2–$Cl_{av.(bridg.)}$	2.475(1)
Fe2–O22	2.1740(11)			Fe1–O1	2.2052(13)
Fe2–O23	2.1378(11)			Fe1–O2	2.1673(13)
Fe1–$O_{av.(diglym)}$	2.139(3)			Fe1–O3	2.1941(13)
Fe2–O24	2.1506(11)			Fe1–$O_{av.(diglyme)}$	2.189(3)
Fe2–Fe2a	3.5506(4)			Fe1–Fe1a	3.6522(5)
Fe2–Cl21–Fe2a	93.07(1)	Cl11–Fe1–Cl12	109.71(2)	Fe1–Cl2–Fe1a	95.07(2)
Cl21–Fe2–O22	177.73(3)	Cl11–Fe1–Cl14	109.98(2)	Cl1–Fe1–Cl2a	177.72(2)
Cl21–Fe2–Cl21a	86.93(2)	Cl12–Fe1–Cl13	110.15(2)	Cl2–Fe1–Cl2a	84.93(2)
O21–Fe2–O22	75.93(4)	Cl12–Fe1–Cl14	109.17(2)	O1–Fe1–O2	76.77(5)
O22–Fe2–O23	75.53(4)	Cl13–Fe1–Cl14	108.85(2)	O1–Fe1–O3	150.20(5)
O21–Fe2–O23	151.44(5)			O2–Fe1–O3	75.83(5)
O21–Fe2–O24	90.61(5)			O2–Fe1–Cl2	171.49(4)
Cl21a–Fe2–O23	91.91(3)				
Cl21a–Fe2–O24	178.28(3)				

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 e-mail deposit@ccdc.cam.ac.uk.

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Povzetek

Enojedrni molekulski kompleks *fac*-[VCl_3(diglyme)] (**1**) je bil sintetiziran z reakcijo med VCl_3 in polietrom diglyme (diglyme = di(2-metoksietil)eter) v diklorometanu. Vijolično obarvani kompleks **1** se v prisotnosti kisika iz zraka počasi oksidira, nastane moder enojedrni kompleks *fac*-[$VOCl_2$(diglyme)] (**2**).

Kompleks [FeCl(diglyme)(THF)]$_2$[$FeCl_4$)]$_2$ (**3**), ki vsebuje železo(II) in železo(III), je nastal z reakcijo rumeno zelenega, delno oksidiranega $FeCl_2 \cdot 4H_2O$, 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 meridialno na centralni železov(II) ion tako v dvojedrnem kationu spojine **3** kot v dvojedrnih molekulah **4**.