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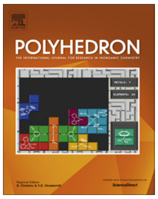

Ligand substitution in *cis*-bis(acetonitrile)tetrachlororhenium(IV) complex with *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide

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ABSTRACT

The preparation, crystal structures, and magnetic properties of two novel mononuclear Re^{IV} complexes of formula *cis*-$[Re^{IV}Cl_4(dmf)_2]$ (**1**) and *cis*-$[Re^{IV}Cl_4(dma)_2]$ (**2**) (dmf = *N*,*N*-dimethylformamide and dma = *N*,*N*-dimethylacetamide) have been studied. Both Re^{IV} systems were synthesized through ligand substitution reactions from the *cis*-$[Re^{IV}Cl_4(MeCN)_2]$ precursor, upon heating in the employed solvent. **1** and **2** crystallize in the monoclinic crystal system with space group *C*2/*c*. Each Re^{IV} ion exhibits a distorted octahedral environment, being bonded by two oxygen atoms from two dmf (**1**) and dma (**2**) molecules and four chloride ions. In the crystal lattice of **1** and **2**, the mononuclear Re^{IV} complexes are placed generating short intermolecular $Re^{IV}\text{-Cl}\cdots\text{Cl-}Re^{IV}$ contacts. The magnetic properties of **1** and **2** were investigated through variable-temperature magnetic susceptibility measurements, which reveal significant antiferromagnetic exchange interactions between neighboring Re^{IV} ions. In **1**, these interactions account for a maximum in the magnetic susceptibility curve at *ca*. 5.0 K.

1. Introduction

The synthesis and development of new magnetic systems based on the paramagnetic Re^{IV} metal ion has intensively been investigated in the field of molecular magnetism, because of the broad variety of interesting magnetic phenomena that these systems can display [1–7]. Re^{IV} is a $5d^3$ ion with a ground electronic state $^4A_{2g}$ containing three unpaired electrons (t_{2g}^3 configuration), and a large value of the spin–orbit coupling constant ($\lambda \sim 1000\ cm^{-1}$ for the free ion) that accounts for the high magnetic anisotropy that Re^{IV} compounds generally exhibit [6]. Many of these compounds have been prepared from mononuclear Re^{IV} complexes containing potential bridging ligands [8–30], which in turn originate from ligand substitution processes of the well-known hexahalorhenate(IV) salts, $[ReX_6]^{2-}$ (X = F, Cl, Br and I) [31–44].

Although to a much lesser extent than hexahalorhenate(IV) salts, *cis*-$[Re^{IV}Cl_4(MeCN)_2]$ complex has also been used as a starting material to obtain Re^{IV} systems that can exhibit interesting magnetic behaviors [45]. The synthetic procedure of this Re^{IV}-based precursor is known since 1968 [46]. However, the study of its magnetic properties was recently reported, which revealed a magnetic ordering through spin canting at 6.5 K [47]. Hence, it seems that $[Re^{IV}Cl_4(MeCN)_2]$ complex could be a good candidate to prepare mononuclear Re^{IV} systems that can exhibit interesting magnetic behaviors, just by replacing the MeCN molecules by another commercial solvent.

In this work, we present our first results concerning this investigation, namely, the synthesis and magnetostructural characterization of two novel Re^{IV} complexes of general formula *cis*-$[Re^{IV}Cl_4L_2]$, with L = *N*,*N*-dimethylformamide (dmf, **1**) and *N*,*N*-dimethylacetamide (dma, **2**). Remarkably, **2** is the first example of crystal structure containing *N*,*N*-dimethylacetamide molecules coordinate to a paramagnetic 5d metal ion.

2. Experimental

2.1. Materials

All manipulations were performed under aerobic conditions, using chemicals as received. *cis*-$[ReCl_4(MeCN)_2]$ precursor was prepared following a literature procedure [46]. *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide solvents were dried and kept with molecular sieves (type 4 Å) before use.

2.2. Synthesis

2.2.1. *cis*-$[ReCl_4(dmf)_2]$ (**1**)

A solution of $[ReCl_4(MeCN)_2]$ (41.0 mg, 0.10 mmol) in 3 mL *N*,*N*-dimethylformamide was heated at 100 °C with continuous stirring

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for 3 h. Once cooled, the resulting green solution was layered with ^{i}PrOH and let to diffuse at room temperature. After complete diffusion, X-ray quality pale green crystals of **1** were formed. Yield: *ca.* 70%. Found: C, 15.0; H, 3.1; N, 5.9. Calc. for $C_6H_{14}N_2O_2Cl_4Re$ (**1**): C, 15.2; H, 3.0; N, 5.9%. X-ray microanalysis gave a Re/Cl molar ratio of 1:4. IR (KBr pellets, ν/cm^{-1}): 2964 (w), 1638 (vs), 1482 (w), 1432 (s), 1345 (s), 1242 (m), 1126 (m), 1056 (w), 863 (w), 708 (s), 430 (m).

2.2.2. *cis-[ReCl$_4$(dma)$_2$] (**2**)*

Compound **2** was prepared as for **1** but using *N,N*-dimethylacetamide instead of *N,N*-dimethylformamide. Yield: *ca.* 50%. Found: C, 19.0; H, 4.0; N, 5.6. Calc. for $C_8H_{18}N_2O_2Cl_4Re$ (**2**): C, 19.1; H, 3.6; N, 5.6%. X-ray microanalysis gave a Re/Cl molar ratio of 1:4. IR (KBr pellets, ν/cm^{-1}): 2945 (m), 1605 (vs), 1477 (m), 1422 (m), 1392 (s), 1365 (w), 1241 (m), 1026 (m), 965 (m), 756 (s), 624 (m), 588 (w), 490 (w), 438 (w).

2.3. *Physical measurements*

Elemental analysis (C, H, N) were performed on a CE Instruments EA 1110 CHNS analyser. Infrared spectra were recorded on a Thermo-Nicolet 6700 FT-IR spectrophotometer in the 4000–400 cm^{-1} region. Re/Cl molar ratio was analyzed for both compounds by means of a Philips XL-30 scanning electron microscope (SEM) equipped with a system of X-ray microanalysis from the Central Service for the Support to Experimental Research (SCSIE) at the University of Valencia. Magnetic susceptibility measurements of **1** and **2** were carried out with a Quantum Design SQUID magnetometer in the temperature range 2.0–300 K and under an applied magnetic field of 0.1 T, in the Institute of Molecular Science (ICMol) at the University of Valencia. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants [48,49].

2.4. *Crystallographic data collection and structure determination*

X-ray diffraction data of single crystals of dimensions 0.20 × 0.13 × 0.11 (**1**) and 0.48 × 0.34 × 0.17 mm^3 (**2**) were collected on a Bruker-Nonius X8APEXII CCD area detector diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Crystal parameters and refinement results for **1** and **2** are summarized in Table 1. The structures of **1** and **2** were solved by Patterson methods and subsequently completed by Fourier recycling using SHELXTL [50–52]. The final full-matrix least squares refinements based on F^2, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, reached convergence with the values of the discrepancy indices given in Table 1. The graphical manipulations were performed with DIAMOND [53].

3. Results and discussion

3.1. *Synthesis of the complexes*

The synthesis of both [Re^{IV}Cl$_4$L$_2$] complexes (**1** and **2**) is quite similar, L being *N,N*-dimethylformamide (dmf, **1**) and *N,N*-dimethylacetamide (dma, **2**). Both Re^{IV} systems were synthesized through ligand substitution reactions from the [Re^{IV}Cl$_4$(MeCN)$_2$] precursor, upon heating at 100 °C for 3 h in the employed solvent. A two-step process is expected to take place and it is represented in Eqs. (1) and (2), which refers to compound **1**.

$$[\mathrm{ReCl_4(MeCN)_2}] + \mathrm{dmf} \leftrightarrow [\mathrm{ReCl_4(MeCN)(dmf)}] + \mathrm{MeCN} \qquad (1)$$

$$[\mathrm{ReCl_4(MeCN)(dmf)}] + \mathrm{dmf} \leftrightarrow [\mathrm{ReCl_4(dmf)_2}] + \mathrm{MeCN} \qquad (2)$$

$$[\mathrm{ReCl_4(MeCN)_2}] + 2\mathrm{dmf} \leftrightarrow [\mathrm{ReCl_4(dmf)_2}] + 2\mathrm{MeCN} \qquad (3)$$

Table 1
Crystal data and structure refinement for [ReCl$_4$(dmf)$_2$] (**1**) and [ReCl$_4$(dma)$_2$] (**2**).

Compound	1	2
Formula	$C_6H_{14}N_2O_2Cl_4Re$	$C_8H_{18}N_2O_2Cl_4Re$
Mr. (g mol^{-1})	474.20	502.24
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
a (Å)	16.010(1)	7.680(1)
b (Å)	8.345(1)	13.642(1)
c (Å)	12.488(1)	14.643(1)
α (°)	90.00	90.00
β (°)	125.77	99.89
γ (°)	90.00	90.00
V (Å^3)	1353.7(1)	1511.3(1)
Z	4	4
D_c (g cm^{-3})	2.327	2.207
μ (Mo-K$_\alpha$) (mm^{-1})	9.750	8.739
F(000)	892	956
Goodness-of-fit (GOF) on F^2	1.045	1.107
R_1/wR_2 [$I > 2\sigma(I)$]	0.0164/0.0359	0.0241/0.0573
Largest difference in peak and hole (e Å^{-3})	0.974 and −0.971	0.708 and −1.657

According to Eqs. (1) and (2), an outgoing MeCN group would be substituted by a dmf molecule to generate the intermediate [ReCl$_4$(MeCN)(dmf)] species, which could not be isolated. This [ReCl$_4$(MeCN)(dmf)] complex would react with a second dmf molecule, as an entering ligand, to release another MeCN molecule and form [ReCl$_4$(dmf)$_2$] (**1**). The same process would occur for [ReCl$_4$(dma)$_2$] (**2**). Eq. (3) summarizes Eqs. (1) and (2).

It is interesting to note that in either case the Re^{IV} ion retains the four Cl ligands, which were not substituted even if the reaction time was increased to ca. 45 h, obtaining the same compounds **1** and **2**. It has been previously reported that the inertia to ligand substitution of mononuclear Re^{IV} complexes increases with the substitution degree [54]. The reluctance of hexahalorhenate(IV) anions, [ReX$_6$]$^{2-}$ (X = F, Cl, Br, I), to undergo a full substitution of the ligands in their coordination sphere has been observed in previous studies performed on oxalate-based Re^{IV} complexes [55]. Indeed, in a previous work dealing with the substitution reaction of the [ReCl$_6$]$^{2-}$ precursor in dmf, only the monosubstituted species, [ReCl$_5$(dmf)]$^-$, was isolated and characterized [56]. So that, the reported synthesis constitutes a straightforward preparative method to increase the substitution degree of solvent molecules in mononuclear Re^{IV} complexes.

3.2. *Crystal structure of cis-[ReCl$_4$(dmf)$_2$] (**1**) and cis-[ReCl$_4$(dma)$_2$] (**2**)*

Compounds **1** and **2** crystallize in the monoclinic crystal system with space group *C*2/*c* (Table 1). Their structures are made up of neutral [Re^{IV}Cl$_4$L$_2$] complexes, where L = *N,N*-dimethylformamide (dmf, **1**) and *N,N*-dimethylacetamide (dma, **2**), which are held together mainly by van der Waals interactions. Two chloride ions [Cl(1) and Cl(2)] and a L molecule are present in the asymmetric unit of **1** and **2**, the rhenium(IV) cation being located on a special position.

Each rhenium(IV) ion exhibits a distorted octahedral environment, being bonded by two oxygen atoms from two dmf (**1**) or two dma (**2**) molecules and four chloride ions (Figs. 1 and 2). No significant differences are seen in the Re-Cl and Re-O bond lengths of **1** and **2**, which vary in the ranges 2.319(1)–2.344(1) and 2.058 (2)–2.066(1) Å, respectively (Table 2). In **1**, the O-Re-O angle is 86.55(8)°, whereas it is 91.74(13)° in **2**. The best equatorial plane around rhenium(IV) ion is defined by O(1)-O(1a)-Cl(2)-Cl(2a) set of atoms in **1** and **2**, each rhenium(IV) ion lying in the plane in both compounds. The C–C, C–O, and C–N bond lengths of the dmf and dma ligands exhibit expected values for these molecules [56–59].