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Synthesis, structure and DFT calculations of the first bioctahedral chalcohalide rhenium cluster complex $(Et_4N)_4(Me_2NH_2)_2[Re_{12}CS_{17}Br_6]$

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The first example of dodecanuclear chalcohalide rhenium cluster complex, $(Et_4N)_4(Me_2NH_2)_2[Re_{12}CS_{17}Br_6]$ (**1**), has been synthesized by reaction of polymeric cluster solid $Re_{12}CS_{17}$ with excess of Et_4NBr in boiling DMF. The compound was characterized by a set of methods, including IR and UV–Vis spectroscopy, elemental analysis, EDS, mass-spectrometry, single-crystal X-ray diffraction analysis, and quantum-chemical calculations. The crystal structure presents an interesting case of 1D supramolecular architecture based on notably short Br···Br interactions of 3.432 Å between the terminal bromide *trans*-ligands of adjacent $[Re_{12}CS_{17}Br_6]^{6-}$ cluster anions. The DFT calculations performed for the $[Re_{12}CS_{17}Br_6]^{6-}$ anion showed good agreement between calculated and experimental data.

1. Introduction

Over the last 15 years, the research and development in the field of properties modification of rhenium cluster complexes have been closely related to the investigation of solution chemistry of tetra- and hexanuclear rhenium chalcogenide clusters. The compounds containing the cluster units $[Re_4Q_4L_{12}]^n$ and $[Re_6Q_8L_6]^n$ (Q = S, Se; L = terminal ligand) possess significant interest because of their structural, electronic and photochemical properties, all of which depend largely on the type of terminal ligand L [1–3].

Since the discovery in 2005 of the first compounds containing the thiocyanide anions $[Re_{12}CS_{17}(CN)_6]^{8-/6-}$ [4], the chemistry of μ_6-C-centered bioctahedral rhenium clusters, the largest discrete rhenium clusters known, has been the object of our attention. As a result of systematic studies, the series of $\{Re_{12}CS_{17}\}$ core compounds has been supplemented with new members such as hydroxo- and sulfito-derivatives, isolated as $K_6[Re_{12}CS_{17}(OH)_6]\cdot 4H_2O$ and $Na_{12}[Re_{12}CS_{17}(SO_3)_6]\cdot 48.5H_2O$, respectively [5]. The chalcohalide clusters, being of considerable practical interest as versatile precursors for many other derivatives, are usually found among the earliest members of low-nuclearity rhenium cluster families. However, they have never been successfully synthesized for the dodecanuclear core. Unlike the hexanuclear rhenium clusters, whose numerous chalcohalides are easily prepared by high-temperature synthesis [1], typical ampoule synthesis from stoichiometric amounts of the Re and S elements in the molten mixtures of alkali metal halides/cyanides does not afford the $[Re_{12}CS_{17}X_6]^{6-}$ (X = Cl, Br, and I) thiohalide anions. On the other hand, numerous water-soluble hexanuclear rhenium cluster compounds can be obtained through the reaction of depolymerization (so-called excision reaction [6–11]), which involves the breaking of M–X/Q–M linkages connecting cluster cores by incorporation of additional X/Q atoms in the starting insoluble polymeric phase. In this context, the recently reported amorphous material $Re_{12}CS_{17}$ [12] has promising potential. It was assumed that $Re_{12}CS_{17}$ adopts a polymeric structure in the solid state, which consists of one-dimensional zigzag chains based on the Re···S bridging interactions. The main aim of the present study was to examine the synthetic utility of the $Re_{12}CS_{17}$ as a precursor for further modification of ligand environment in $\{Re_{12}CS_{17}\}$ core compounds.

Here we report the successful use of the $Re_{12}CS_{17}$ polymer to synthesize the first dodecanuclear thiobromide rhenium cluster complex, $(Et_4N)_4(Me_2NH_2)_2[Re_{12}CS_{17}Br_6]$ (**1**), the crystal structure of which revealed a supramolecular architecture based on short Br···Br bridging interactions between the cluster anions.

2. Experimental

2.1. Materials and syntheses

The starting polymeric material $Re_{12}CS_{17}$ was prepared as described in [12]. DMF and Et_4NBr were used as purchased without

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further purification. UV–Vis spectra in the wavelength range 200–1100 nm were recorded on an Ultrospec 3300 pro spectrometer. IR spectra in the range 4000–375 cm^{-1} in KBr pellets were recorded on a Bruker Scimitar FTS 2000 spectrometer. IR spectra in the range 600–80 cm^{-1} were recorded on a Bruker Vertex 80 spectrometer. Energy dispersion spectroscopy (EDS) was performed on a scanning electron microscope (SEM) JEOL 6400. Elemental analysis was made on a Euro EA3000 analyzer. Electrospray ionization mass spectrometry (ESI-MS) was carried out on a mass spectrometer Bruker maXis 4G (negative ion mode, direct injection with syringe, voltage +2.5 kV, nebulizer pressure 0.8 bar, dry gas flow rate 4 L min^{-1}, dry gas temperature 180 °C).

2.2. Synthesis of $(Et_4N)_4(Me_2NH_2)_2[Re_{12}CS_{17}Br_6]$ (**1**)

150 mg (0.054 mmol) of $Re_{12}CS_{17}$ and 400 mg (1.903 mmol) of Et_4NBr was placed in a round-bottom flask. 30 mL of DMF was added as a solvent. The reaction mixture was boiled with reflux during about 20 h. The resulting dark-brown solution was filtered and evaporated to a volume of about 5 mL. Diethyl ether (15 mL) was added to the solution, after that amorphous brown precipitate fell down. The precipitate was filtered off, washed with water and dried in air. The yield: 130 mg (62,0%). λ_{max} (ε, M^{-1} cm^{-1}) 268 (8×10^4), 300 (4.6×10^4), 366 (2.3×10^4) nm. IR (400–4000 cm^{-1}): all bands related to organic cations are observed. Elemental *Anal.* Calc. (% mass) for $C_{37}H_{96}Br_6N_6Re_{12}S_{17}$: C, 11.4; H, 2.5; N, 2.2; S, 14.0. Found: C, 11.8; H, 2.4; N, 2.0; S, 14.0. EDS found Br/Re/S = 6.2/12.0/16.5.

To obtain crystals suitable for X-ray diffraction analysis, a weighing bottle containing the filtered dark-brown reaction mixture was placed into a larger glass with diethyl ether. The glass was tightly closed and the system was kept at about 0 °C for 4 days. After this time, several dark-brown crystals of **1** together with colorless crystals of Et_4NBr and brown amorphous powder were formed on the bottom of weighing bottle.

2.3. X-ray crystallographic data collection and refinement of the structure

The structure of compound **1** was solved by single crystal X-ray diffraction analysis. Suitable single-crystals of **1** were separated and mounted onto the Bruker Nonius X8 Apex 4 K CCD diffractometer fitted with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected at 100(2) K by the standard technique. Crystal data for $C_{37}H_{96}Br_6N_6Re_{12}S_{17}$: brown needle, 0.20 x 0.08 x 0.05 mm^3, M = 3884.08, monoclinic, *C*2/*c*, a =33.311(4) Å, b = 11.8524(15) Å, c = 24.099(3) Å, β = 121.245(2)°, V = 8134.7(18) $Å^3$, Z = 4, D_{calc} = 3.171 g·cm^{-3}. 13871 reflections were measured (φ-scan of narrow frames, $2\theta_{max} = 52.74°$), of which 8276 were unique ($R_{int} = 0.0870$) and 2813 were observed with $I > 2\sigma(I)$. Semi-empirical absorption corrections were applied using the SADABS [13]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [14]. The atoms belonging to the $[Re_{12}CS_{17}Br_6]^{6-}$ anion were refined anisotropically. Because of the failed attempts to adequately resolve the disorder of the Et_4N^+ and $Me_2NH_2{}^+$ cations, they were restrained to idealized geometry using DFIX and DANG instructions and refined in an isotropic approximation. Hydrogen atoms of organic cations were located geometrically and refined as riding. Final *R*-factors were: $R_1 = 0.0670$ for 2813 observed reflections, $wR_2 = 0.1812$ and Good-ness-of fit = 0.817 for all reflections with 258 refined parameters. Min. and max. residual electron densities were −1.817 and 3.187 e $Å^{-3}$ (located 1.42 Å from Re2).

2.4. Density functional theory (DFT) calculations

Density functional theory spin-restricted calculations were carried out of the $[Re_{12}CS_{17}Br_6]^{6-}$ cluster anion with D_{3h} symmetry by using ADF2012 code [15–17]. Geometric parameters for the cluster anions were optimized with model Hamiltonians of density functional given by the sum of a local density functional LDA (Vosko et al. [18]) and a gradient exchange functional GGA (Becke [19] and Perdew [20]) in the gas phase. A relativistic valence triple-ζ Slater-type basis set with an augmented polarization function (TZP) without core potential was applied for all elements. The zero-order regular approximation (ZORA [21–25]) Hamiltonian was used in all calculations in this work to take into account the scalar relativistic effects. Electronic energy of model complex was calculated using the method [26,27]. Topological methods of quantum chemistry QTAIM (“Quantum Theory Atoms in Molecules”) [28] and ELF (Electron Localization Function) [29] were used to characterize the charges of the atoms in the $[Re_{12}CS_{17}Br_6]^{6-}$ cluster anion.

The observed electronic transitions in UV–Vis spectra are dipole allowed electronic transitions according to the experimental values of extinction. To model the electronic absorption spectra the 30 lowest-lying dipole-allowed electronic transitions were computed for cluster within time-dependent density functional theory (TD-DFT [30]). From the resulting set of spectral lines, we have chosen the most intensive transitions which fall in the experimental absorption band at 250–600 nm.

3. Results and discussion

3.1. Synthetic procedure and characterization

The reaction between $Re_{12}CS_{17}$ and Et_4NBr in boiling DMF carried out for about 20 h resulted in the formation of compound **1**. It is worth to note that the $Re_{12}CS_{17}$ is quite inert and reacts with Et_4NBr/DMF at relatively high temperatures of 150–160 °C. It is known that DMF undergoes thermal as well as photochemical decomposition. In the presence of water, DMF slowly hydrolyses to give formic acid and dimethylamine, especially at elevated temperatures and in the presence of transition metal ions [31]. Therefore, the presence of dimethylammonium cations in **1** can be explained by hydrolysis of DMF at synthetic conditions.

A UV–Vis spectrum of DMF solution of **1** is characterized by the region with broad absorption bands in a wavelength range of 260–500 nm. The compound shows a high extinction coefficient of the order 10^4–10^5 m^{-1} cm^{-1}. Maximum of absorption appears at 268 nm ($\varepsilon_{268} = 8 \times 10^4$ m^{-1} cm^{-1}).

Raman and IR spectra of the title compound contain few bands in the region 50–300 cm^{-1}, which can be attributed to vibrations of Re–Br bonds. The measured frequencies of these vibrations are: 93.3 (s), 165.5 (m), 240.4 (s), 265.4(s), 272.1 (m) and 290.4 (m) cm^{-1}. These values correspond to the data available for Re–Br bond vibrations in the mononuclear compounds $(PNP)_2[ReFBr_5]$·H_2O and *cis*-$(CH_2Py_2)[ReBr_4Py_2]$·$(CH_3)_2CO$ [32–34]. There are no comparable literature data neither for the tetrahedral, nor for the octahedral rhenium bromide cluster complexes. The IR spectrum shows also bands in the regions of 400–1700 and 2800–3000 cm^{-1} corresponding to the organic cations.

3.2. Mass-spectroscopy

The ESI mass-spectrum (negative mode) of a DMF/water solution of **1** contains a few sets of intense peaks in the area of *m*/*z* 1070–1130 (trianionic forms) and in the area of *m*/*z* 1690–1750 (dianionic forms), as seen in Fig. 1. The most intense peak set for