

Investigation of electronic structure of $\{\text{Nb}_2\text{S}_4\}^{4+}$ clusters by XES, XPS and DFT calculations

Lev N. Mazalov^{a,b}, Anastasiya D. Fedorenko^a, Artem L. Gushchin^{a,b,*}, Maxim N. Sokolov^{a,b}, Pavel A. Petrov^{a,b}, Svetlana A. Dalmatova^{a,b}, Artem V. Gusel'nikov^a, Alexander V. Kalinkin^c

^a Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 Lavrentiev Av., Novosibirsk 630090, Russia

^b Novosibirsk State University, 2 Pirogov Str., Novosibirsk 630090, Russia

^c Borekov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 5 Lavrentiev Av., Novosibirsk 630090, Russia

ARTICLE INFO

Article history:

Received 6 June 2018

Accepted 10 July 2018

Available online 19 July 2018

Keywords:

Dinuclear niobium complexes

Disulfide bridging ligands

Electronic structure of complexes

X-ray emission spectroscopy

X-ray photoelectron spectroscopy

ABSTRACT

For the following compounds $[\text{Nb}_2\text{S}_4(\text{acac})_4]$ (acac = acetylacetonate), $\text{K}_4[\text{Nb}_2\text{S}_4(\text{ox})_4]$ (ox = oxalate) and $\text{Nb}_2\text{S}_4\text{Br}_4$ containing dinuclear cluster core $\{(\text{Nb}^{4+})_2(\mu\text{-S}_2^{2-})_2\}^{4+}$ (simply $\{\text{Nb}_2\text{S}_4\}^{4+}$) the electronic structure has been experimentally and theoretically investigated through X-ray emission (XES), X-ray photoelectron (XPS) spectroscopies and Density functional theory (DFT). The bonding and antibonding highest occupied molecular orbitals (HOMOs) observed in the X-ray emission spectra have been characterized by the analysis of overlap populations and the partial atomic composition considering the nature of the electron density distribution. Furthermore, the effective atomic charges have been determined.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Transition metal chalcogenides are one of the most employed classes of inorganic compounds due to their versatile chemical, electrophysical, magnetic, optical and catalytic properties. For the theoreticians, they are convenient models to investigate new physical phenomena, physical and chemical properties inherent in inorganic materials of the metal cluster nature and low-dimensional systems [1–8].

A remarkable feature for a large series of transition metal polychalcogenides is the presence of dichalcogenide groups X_2 (X = S, Se, Te) in their structure. Such groups are present in metal trichalcogenides (MX_3) and extended chain structures $[\text{M}_n\text{X}_{4(n-1)}]$ of IV–VI group transition metals. They determine the features of their electronic structure: due to the interaction (X–X) the dichalcogenide group forms a system of σ and π bonds made of ns and np AOs of chalcogen atoms, which in turn can interact with nd AOs of transition metal atoms and act both as π -donor and π -acceptor. This situation is different from simple metal–chalcogen (M–X) bonding where only π -donation is possible. In this

way the dichalcogenide bridges allow better tuning of the electron density on the metal centers.

Discrete dinuclear niobium chalcogenide complexes are convenient model structures for studying electronic interaction of the dichalcogenide group (X_2) with transition metal atoms in one-dimensional chain structures of transition metal chalcogenides [10,15,16]. The common structural fragment in all these compounds is the dinuclear cluster $\{\text{Nb}_2(\text{X}_2)_2\}^{4+}$ (X = S, Se, Te) in which two dichalcogenide groups (X_2) bridge the Nb–Nb bonded dimers. Photocatalytic and nonlinear optical properties of some $\{\text{Nb}_2\text{S}_4\}$ complexes have been reported [15].

Disulfide bridges in disulfide transition metal complexes can be coordinated to metal atoms in a different manner: type Ia, side-on coordination; types IIa и IIb, cis and trans end-on bridging coordination, respectively; type III, in which the S–S bond is oriented almost perpendicular to the metal–metal bond, while the sulfur atoms are coordinated to two metal atoms (Fig. 1) [9]. There are four sulfur atoms in the $\{\text{Nb}_2\text{S}_4\}$ cluster which form two disulfide bridges (S_2^{2-}) interacting with two metal atoms to give a structure of type III (Fig. 1). The corresponding disulfide bridges are also present in other transition metal chalcogenide clusters of various types, in particular, in dinuclear $\{\text{V}_2\text{S}_4\}$, trinuclear $\{\text{M}_3\text{S}_7\}$ (M = Mo, W), tetranuclear $\{\text{V}_4\text{S}_9\}$ and $\{\text{Ta}_4\text{S}_9\}$ [10–14].

In this work we report a detailed investigation of the electronic structure of dinuclear complexes $[\text{Nb}_2\text{S}_4(\text{acac})_4]$ and $\text{K}_4[\text{Nb}_2\text{S}_4(\text{ox})_4]$ (acac = acetylacetonate, ox = oxalate), as well as structurally

* Corresponding author at: Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 Lavrentiev Av., Novosibirsk 630090, Russia.

E-mail address: gushchin@niic.nsc.ru (A.L. Gushchin).

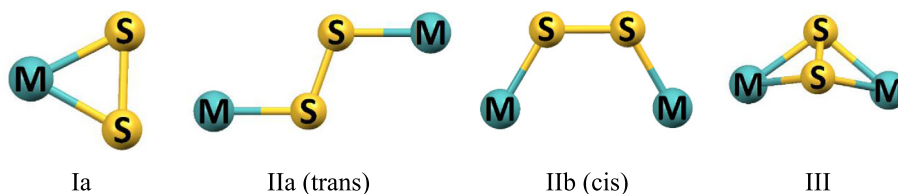


Fig. 1. Different coordination modes of disulfide ligands.

closely related polymeric layered thiobromide $\text{Nb}_2\text{S}_4\text{Br}_4 = {}_2^\infty[\text{Nb}_2\text{S}_4\text{Br}_{8/2}]$ with $\{\text{Nb}_2(\mu\text{-S}_2)_2\}^{4+}$ core by experimental (XES, XPS) and theoretical (DFT) methods.

2. Experimental

The preparations of the dinuclear niobium clusters are described in [16–19].

2.1 X-ray emission spectra (XES)

The S $K\alpha, \beta$ and Nb $L\beta_{2,15}$ spectra were measured on a Stearat X-ray spectrometer [20]. The spectra were obtained under the following conditions: tube mode 10 kV, 0.4 A; (10 1 1) quartz crystal analyzer, $2d = 6.68 \text{ \AA}$; gas proportional counter as an X-ray radiation detector, P-10 (90% argon, 10% methane) working gas mixture [21].

2.2 X-ray photoelectron spectra (XPS)

XPS spectra were measured on a SPECS (Germany) spectrometer. The spectrometer is equipped with a PHOIBOS-150 hemispherical analyzer, a 9-channel electron detector, and an XR-50 characteristic X-ray radiation source with a double Al/Mg anode. The spectra were recorded using non-monochromatic Mg $K\alpha$ radiation. In the energy calibration the carbon C 1s peak at 285.0 eV was used.

3. Computational details

3.1 DFT calculations

The geometry was optimized with the GAUSSIAN09 program package [22] with the B3LYP functional [23] and the def2SVPP basis set [24,25] taking into account the solvent (water) within the CPCM model [26,27]. Calculations of the electronic structure were carried out within the DFT approach with the ADF2017 software package [28–30] with the BHandHLYP functional and the QZ4P basis [31]. Scalar relativistic effects were taken into account in the ZORA approximation [32]. For compensation of the negative charge on the complexes calculations were performed with the COSMO solvent model using the dielectric constant of water [33]. Based on the performed calculations the theoretical $K\beta$ spectra of sulfur atoms and $L\beta_{2,15}$ spectra of niobium atoms were reconstructed, using the S 3p and Nb 4d atomic partial electron density distribution within HOMOs of the niobium complexes.

4. Results and discussion

4.1 X-ray spectra and electronic structure of metal compounds with S_2^{2-} groups

The main structural fragment of $\text{Nb}_2\text{S}_4\text{Br}_4$, $\text{K}_4[\text{Nb}_2\text{S}_4(\text{ox})_4]$, and $[\text{Nb}_2\text{S}_4(\text{acac})_4]$ is the $\{\text{Nb}_2\text{S}_4\}$ cluster core. The formal charge distribution within the core can be written as $\{(\text{Nb}^{4+})_2(\text{S}_2^{2-})_2\}^{4+}$. Its idealized shape is a rectangular bipyramid whose base is a rect-

angle (S_4) formed by two disulfide groups (S_2) of covalently bonded sulfur atoms. Two metal atoms are located in the bipyramid opposite vertices, and lie in the axis perpendicular to the rectangular plane (S_4). This leads to idealized D_{2h} symmetry; however, this symmetry can decrease for real compounds. The S_2 group is considered as an electron reservoir playing a significant role in the properties of these compounds and is essential for the overall stability of the cluster core: the $\{\text{Nb}_2\text{S}_4\}$ clusters, unlike other Nb(IV) compounds, are remarkable stable towards hydrolysis and oxidation [15,16].

The electronic structure of the S_2^{2-} disulfide ligand has previously been considered by Jellinek et al. (1974) [34] using the XPS valence band spectra of ZrS_3 with S_2^{2-} bridges, and ZrS_2 for comparison. The authors distinguished characteristic XPS spectrum of the disulfide group. Two maxima A and B related to the structure of MOs are clearly manifested in the spectrum (Fig. 2d).

The MO diagram of disulfide ion S_2^{2-} within $\{\text{M}_2(\text{S}_2^{2-})\}$ unit ($\text{M} = \text{Nb, Zr, Mo, Fe}$ and others), depicted in Fig. 3a, has been proposed by Jellinek et al. [34]. The presence of occupied antibonding orbital $2\pi_g$ is assumed to result in the donor ability of the S_2^{2-} group. The presence of unoccupied antibonding orbital $5\sigma_u$ gives rise to the acceptor properties of the S_2^{2-} group and may cause a shift of electron density from metal atoms to this orbital. Obviously, the appearance of electron density on σ^* -orbital ($5\sigma_u$) will depend on the metal nature, and on the nature of terminal ligands (acac, ox and Br in our case).

According to the proposed interpretation, a low-energy maximum B (Fig. 2) corresponds to the electrons on π_g -antibonding MOs composed of 3p AOs of sulfur atoms. A deeper maximum A is associated to σ_g - and π_u -bonding MOs involving 3p AOs of sulfur atoms. The direct comparison of the experimental (difference) spectrum assigned to the S_2^{2-} group of ZrS_3 (Fig. 2d) with the simplified MO scheme for the S_2^{2-} group (Fig. 3a) provides only qualitative representation of the electronic structure of bridging disulfide groups. In the case of the niobium complexes, in addition to disulfide groups located between the Nb^{4+} ions and involved in the bonding with niobium ions, there are also terminal ligands, interacting with niobium atoms. Consequently, occupied molecular levels involving both 3p AOs of sulfur atoms, 4d AOs of niobium atoms and AOs of terminal ligands will be observed in the experimental XPS valence band spectrum for studied complexes (Fig. 5).

In order to study the character of electronic interactions in the S_2^{2-} group as well as metal–metal, metal–disulfide group and metal–terminal ligand interactions it is necessary to consider the features of the electronic structure by means of highly characteristic X-ray spectra of separate atoms, together with DFT calculations.

4.2 S $K\beta$ XES spectra

S $K\beta$ spectra corresponding to (3p \rightarrow 1s) X-ray transitions are shown in Fig. 2a–c (left). They provide information on the contributions of 3p AOs of sulfur atoms of the disulfide ligands to occupied MOs. XES spectra exhibit two maxima which correspond to those observed in ZrS_3 [34]. Similarly, two maxima are observed in the XPS spectra (see below).

Download English Version:

<https://daneshyari.com/en/article/7762316>

Download Persian Version:

<https://daneshyari.com/article/7762316>

[Daneshyari.com](https://daneshyari.com)