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Surface modification with multiphilic ligands at detectable well defined active positions of nano-object of giant wheel shaped molybdenum blue showing third-order nonlinear optical properties

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ABSTRACT

The reaction of an aqueous solution of sodium molybdate with L-tyrosine in the presence of reducing agent results in the formation of a new compound of the formula of $Na_8Co_3[Mo^{VI}_{126}\ Mo^{V}_{28}O_{462}H_{14}(H_2O)_{46}(HOC_6H_4CH_2CH(NH_3^+)COO^-)_{12}]$·ca. $200H_2O$. The compound contains nanosized ring-shaped clusters with tyrosine ligands possessing different types of functional groups (one $-CO_2$, one $-NH_3^+$ and one –ArOH) coordinated through the carboxylate groups at the active sites of the inner cavity. Importantly, the result demonstrates that not only active sites/areas of the cluster surface under a specified condition can be directly monitored and detected but also novel type surfaces within the cavity of a nano-structured ring-shaped cluster can be generated simultaneously. The nonlinear optical properties of the new cluster are studied using the well-known Z-scan technique at a wavelength of 532 nm with laser pulse duration of 18 ps. The results show that the new cluster exhibits interesting self-focusing nonlinear optical response with the real and imaginary parts of the third-order nonlinear optical susceptibility $\chi^{(3)}$ being 1.069×10^{-13}(esu) and 2.529×10^{-15}(esu), respectively, which may find application in material science.

1. Introduction

Molybdenum oxide based cluster of the $\{Mo_{154}\}$-type has practically the composition of a protonated reduced molybdenum trioxide with H_2O ligands and the stoichiometry $\{(MoO_3)_{154}H_{14}(H_2O)_{70}\}$ [1]. It belongs to the molybdenum blue family which represents a class of compounds consisting of a large number of Mo atoms with ring shaped nanosized cavities and a variety of sites with different well-defined functional groups [1,2]. The molybdenum blue compounds represent structured nanosensors and nanoreactors that enable chemical processes in several positions. Owing to its perceived structural analogies to the surface of molybdenum oxide [1] which is versatile in catalyzing organic transformations [3], the molybdenum oxide based cluster of the $\{Mo_{154}\}$-type can be viewed as a soluble molybdenum oxide analogue and therefore is of special interest as a model system for the reactions and properties of molybdenum oxide. Given the difficulty in determining the intimate mechanism of these molybdenum oxide involving reactions [4], the study of the stoichiometric reactivity of well-defined surface might contribute toward an understanding of the elementary steps of heterogeneous reactions, particularly with respect to surface-bound intermediates [5]. Therefore, the structural and spectral characterization of organic derivatives of the molybdenum oxide based cluster of the $\{Mo_{154}\}$-type can be thought as a key step to investigate and understand deeply at a molecular level how the molybdenum oxide works as catalysts in various catalytic reactions, especially for an understanding of the elementary steps of heterogeneous reactions taking place at molybdenum oxide surfaces. Furthermore, organic derivatization of molybdenum oxide based cluster of the $\{Mo_{154}\}$-type via either covalent bonding [6] or no-covalent bonding [7] may also produce a new type of organic/inorganic hybrids possessing new type surfaces on a nanostructured ring-shaped cluster, which not only combine the advantages of organic materials so as to realize the so-called value-adding properties, but also contribute to exploring the possible synergistic effects.

Herein we report the preparation, characterization of a new compound containing nanosized ring-shaped clusters with coordinated tyrosine ligands indicating the active sites of the inner wall of their cavities. The measurement of sign and magnitude of both the real and imaginary parts of the third-order nonlinearity $\chi^{(3)}$ at 532 nm with laser pulse duration of 18 ps of the resulting compound is reported for the first time.

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2. Experimental section

2.1. Reagents and apparatus equipments

All chemicals and reagents were analytical grade and without further purification. Elemental analysis for C, H, and N was performed on an Elementar Vario EL elemental analyzer, while that for Co, Na and Mo was performed using an ICPS-7500 model inductively coupled plasma emission spectrometer with samples dissolved in dilute hydrochloric acid. FT-IR spectra were recorded on a Bruker Nicolet-210-FT infrared spectrometer with pressed KBr disk in the range of 400–4000 cm^{-1}. UV–Vis spectra were obtained on a Shimadzu UV-2550 type UV–Vis spectrophotometer. TG/DTA analyses were performed on a Netzsch STA 449 thermogravimetric analyzer in flowing air with a heating rate of 5 °C min^{-1}. The ^1H NMR spectrum was obtained on a Bruker AC-80 MHz NMR system.

The nonlinear refraction and absorption of the solution of the compounds at a concentration of 1.0×10^{-5} mol l^{-1} dissolved in water/ethanol (1:1 in volume) were measured by the Z-scan setup [8]. An EKSPLA NL303 Q-switched Nd:YAG laser with a wavelength of $\lambda = 532$ nm, a pulse duration of $\tau = 18$ ps, a pulse energy $E_0 = 15$ μJ corresponding to an intensity of the light at focus $I_0 (I_0 = E_0/\tau\pi\omega_0^2) = 2.9 \times 10^{14}$ W m^{-2} and a repetition rate of 10 Hz was employed as the light source. The laser beam, after being focused by a 20 cm focal length lens into the sample placed in a $L = 1$ mm path-length quartz cell, was passed through a large-area beam splitter. That part of the beam transmitted through the splitter beam was passed through an aperture in the far field and then measured by a photomultiplier. The portion of the beam reflected by the beam splitter was collected by a large aperture lens (ensuring collection of the total light transmitted through the sample) and then measured by a photomultiplier. The variation of the transmission of the focused laser beam in these two cases, as a function of the sample distance from the focal plane, gave rise to what are called closed- and open-aperture Z-scan measurements, respectively. The beam waist radius at the focus ω_0 was determined to be about 30 μm, and the sample position in respect to the focal plane of the laser beam was controlled by a computer-controlled stepper motor.

2.2. Synthesis of the compound *1*

$CoCl_2{\cdot}6H_2O$ (1.997 g) and $Na_2MoO_4{\cdot}2H_2O$ (1.297 g) dissolved in 60 ml water was stirred for 30 min resulting in the solution A; hydrochloric acid (2 ml, 1 M) was added to a solution of L-tyrosine (0.357 g) dissolved in hydrochloride (4.5 ml, 6 M) under stirring resulting in the solution B. The solution B was then added into the solution A. To the mixed solution hydrazine chloride was added and then the solution was heated at 70 °C for 3.5 h in water bath resulting in a transparent blue solution. The solution was filtered into a 100 ml beaker. After three days, 0.39 g of blue single crystals was obtained. Yield: 38.4% based on Mo. Anal. Calc. for $C_{108}H_{638}Mo_{154}N_{12}Co_3Na_8O_{744}$: C, 4.45; H, 2.21; N, 0.58; Na, 0.63; Co, 0.61; Mo, 50.69. Found: C, 4.8; H, 2.3; N, 0.4; Na, 0.4; Co, 0.4; Mo, 51.3%.

2.3. Single-crystal X-ray diffraction

Suitable crystal ($0.20 \times 0.15 \times 0.10$ mm^3) of **1** was mounted on a glass fiber with vaseline and used for data collection on a Rigaku IP diffractometer with graphite-monochromatized Cu-Kα radiation ($\lambda = 1.54184$ Å) at 183(2) K using $\varphi/2\theta$ scan techniques. An empirical absorption correction and LP correction were applied to the intensity data. The structure was solved by direct methods, successive Fourier difference synthesis, and refined by full-matrix least-squares techniques on F^2 using the SHELXL-97 software [9]. During the anisotropic refinement, some O and C atoms exhibited severe non-positive define (NPD) problems. Therefore, the O and C atoms were just isotropically refined. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 745074). A summary of the crystallographic data and structural determination parameters are given in Table 1.

3. Results and discussion

3.1. Crystal structure description

The single crystal X-ray diffraction analysis of **1** reveals the tetradecameric ring-shaped structure (Fig. 1) of the anion **1a**, which can be compared to that of the related parent host anion **2a** [1a] formulated as $[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]^{14-} \equiv [(MoO_3)_{154}H_{14}(H_2O)_{70}]^{14-} \equiv [\{Mo^{VI/V}_8O_{26}(\mu_3O)_2H(H_2O)_3Mo^{VI/V}\}\{Mo^{VI}_2O_5(H_2O)_2\}]_{14}{}^{14-} \equiv [\{Mo_8Mo_1\}\{Mo_2\}]_{14}{}^{14-}$, which has 14 $\{Mo_8\}$ basic fragments arranged above and below an equatorial plane of

$Na_8Co_3[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{46}(HOC_6H_4CH_2CH(NH_3^+)COO^-)_{12}]{\cdot}$ ca. $200H_2O$ **1** $\equiv Na_8Co_3$**1a**·ca. $200H_2O$.

$Na_{15}[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]_{0.5}[Mo^{VI}_{124}Mo^{V}_{28}O_{457}H_{14}(H_2O)_{68}]_{0.5}$·ca.$400H_2O$ **2** $\equiv Na_{15}$**2a**$_{0.5}$**2b**$_{0.5}$·ca.$400H_2O$ (**2a** $\equiv [Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]^{14-}$, **2b** $\equiv [Mo^{VI}_{124}Mo^{V}_{28}O_{457}H_{14}(H_2O)_{68}]^{16-}$)

the cluster anion and linked to each other by the O atoms in this plane and the total of 14 equatorial $\{Mo_1\}$ units together with 14 $\{Mo_2\}$ ($\equiv \{Mo_2O_5(H_2O)_2\}$) units in a "circular disposition" with 14 nucleophilic $\{Mo_6O_6\}$ rings on its surface: 7 on the upper surface and 7 on the lower, in between 14 $\{Mo_5O_6\}$ incomplete double-cubane-type compartments spanned by five Mo and six O atoms of the $\{Mo_8\}$ and $\{Mo_1\}$ units and linked by $28 = 14 \times 2$ μ_2O atoms with two 4d electrons delocalized within each compartment.

Table 1
Crystal data and structure refinement for the compound **1**.

Empirical formula	$C_{108}H_{638}Co_3Mo_{154}N_{12}Na_8O_{744}$
Formula weight	29147.77
Temperature (K)	183(2)
Wavelength (Å)	1.54184
Crystal system, space group	Monoclinic, *C2/m*
Unit cell dimensions	
a (Å)	36.1700(6)
b (Å)	42.9182(7)
c (Å)	31.2902(6)
α (°)	90
β (°)	108.405(2)
γ (°)	90
Volume (Å^3)	46088.9(14)
Z, calculated density (mg/m^3)	2, 2.100
Absorption coefficient (mm^{-1})	17.922
F (0 0 0)	27918
Crystal size (mm^3)	0.2 × 0.15 × 0.1
Theta range for data collection (°)	3.83–60.99
Limiting indices	$-40 \leqslant h \leqslant 40$, $-48 \leqslant k \leqslant 44$, $-34 \leqslant l \leqslant 27$
Reflections collected/unique	81603/33564 [*R*(int) = 0.0639]
Completeness to $\theta = 60.99$ (%)	93.8
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.18 and 0.09
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	33564/7/1698
Goodness-of-fit on F^2	1.130
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0902$, $wR_2 = 0.2604$
R indices (all data)	$R_1 = 0.1417$, $wR_2 = 0.3211$
Largest diff. peak and hole	3.412 and −1.769 e Å^{-3}