



Ag^I and Zn^{II} complexes with possible application as NLO materials – Crystal structures and properties

Bojidarka Ivanova, Michael Spiteller*

Institute of Environmental Research of the Faculty of Chemistry, Chair of Environmental Chemistry and Analytical Chemistry, Dortmund University of Technology, Otto-Hahn-Str. 6, D-44227 Dortmund, Germany

ARTICLE INFO

Article history:

Received 5 October 2010

Accepted 14 October 2010

Available online 30 October 2010

Keywords:

Ag^I- and Zn^{II}-complexes

Squaric acid

DL-mandelic acid

3-Pyridin aldehyde

2-Amino-8-hydroxyquinoline

ABSTRACT

Four novel Ag^I-complexes with DL-mandelic acid (*MA*) (**1**), squaric acid (*H₂Sq*) (**2**), 3-pyridin aldehyde (*3PyA*) (**3**) and 2-amino-8-hydroxyquinoline (*2A8H*) (**4**) as well as two Zn^{II}-ones with *3PyA* (**5**) and *2A8H* (**6**) are synthesized, isolated, spectroscopic and structural characterized by single crystal X-ray diffraction, UV–vis–NIR, and IR-spectroscopy. The experimental data of the complex (**1**) were compared with the analogous of the neutral *MA*. Quantum chemical calculations are carried out, and the electronic structures and optical properties of neutral *MA* and its anion, with a view to assign the vibrational properties of (**1**).

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The possible application of the Zn^{II}- or Ag^I-complexes as optical limiting (OL) materials has been demonstrated in series of studies recent years [1–3]. OL compounds are kind of nonlinear optical (NLO) materials that can limit the transmitted light intensity to a maximum value, i.e., render transparency to weak signals and opaqueness to strong signals. OL materials can protect sensitive photo detectors from undesired high-intensity radiation hazards. Therefore, they have received considerable attentions due to growing needs for optical techniques. For an ideal OL material, it could be exhibit a high, linear transmission below a certain “limiting” threshold, and above this threshold the transmission becomes highly nonlinear. Thus far, researchers have made great efforts to search for such OL materials [4–6]. Metal–organic polymers are new class of promising OL compound have attracted extensive attentions due to their OL merit and large OL capabilities [7–16]. Recent investigations have been focused on metal–organic polymers with metal ions on OL performance become unapparent, such as in Co^{II}, Zn^{II}, Cd^{II}, Hg^{II}, Ag^I and Pb^{II} [3,7,9,17–19], due to insignificant contribution of metals to delocalization of π -electron cloud or the relatively poor orbital overlap between metal ions and organic ligands. For the Ag^I-bridged metal–organic polymers have been found ultra fast OLs-responses both toward nanosecond and picoseconds laser pulses [3]. By comparing the optical nonlinearities of these polymers and homogeneous metal–organic polymers have

been found that that Ag^I-ions as connectors, making the resultant polymers exhibit a significant improvement of OL responses relative to organic ligands.

The application of the *H₂Sq* and *MA* themselves as well as their organic salts as NLO materials, has been demonstrated [20–26]. In metal complexes usually the *H₂Sq*, stabilized as its squarate dianion (*Sq*²⁻) acts as bidentate 1,4-O-containing ligand, forming polymer complexes [27–29]. For catena-tetra-aqua-(μ_2 -squarato-O,O′)-Zn^{II} has been reported non-centrosymmetric space group *Cc* [27]. The studies of Ag^I-complexes of *H₂Sq* are relatively rare. In crystal structure of catena-(bis((μ_8 -squarato)-di-Ag^I)) [30], the *Sq*²⁻-acts as tetradentate ligand. Heterocyclic chemicals as ligands are also attractive, featuring the π -conjugated system and the possibility for tuning of their polydentate ability.

For these reasons the further validation of the Ag^I- and Zn^{II}-metal–organic compounds have great potential for optical limiters as well as NLO materials. Herein is presented the theoretical and experimental study of six novel complexes of with *MA*, *H₂Sq*, *3PyA*, and *2A8H*, respectively.

2. Experimental

2.1. Synthesis

The (**1**) and (**2**) were obtained by mixing of AgNO₃ (0.1691 g) with *H₂Sq* (0.1140 g, Sigma) or *MA* (0.1522 g, Sigma–Aldrich) acid in 20 ml solvent mixture methanol:water 1:1 under stirring for 30 min at 70 °C. Yields 90% (**1**) and 96% (**2**). *Anal. Calc.* for [(C₈H₇O₃Ag)_{*n*}]: C, 37.10; H, 2.72. Found (**1**): C, 37.40; H, 2.38%.

* Corresponding author. Tel.: +49 231 755 4080.

E-mail address: spiteller@infu.tu-dortmund.de (M. Spiteller).

The (3) and (5) were obtained by mixing of AgNO_3 (0.1690 g) or $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1773 g) with 5 ml 3PyA (0.1071 g, Sigma) in 20 ml solvent mixture methanol:water 2:1 under stirring for 1 h at 50 °C. Yields 30% (3) and 44% (5). *Anal. Calc.* for $[\text{C}_{12}\text{H}_{16}\text{O}_5\text{N}_3\text{Ag}]$: C, 36.94; H, 4.13. Found (1): C, 36.90; H, 4.18%. *Anal. Calc.* for $[\text{C}_{12}\text{H}_{10}\text{O}_5\text{N}_2\text{ZnCl}_2]$: C, 48.18; H, 3.37. Found (2): C, 48.19; H, 3.40%. The (4) and (6) were obtained by mixing of 2A8H (0.3451 g) with AgNO_3 (0.1690 g) or $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.1773 g) in 25 solvent mixture methanol:water 1:1 under stirring for 20 min at 70 °C. Yields 55% (4) and 40% (6). *Anal. Calc.* for $[\text{C}_9\text{H}_7\text{ON}_2\text{Ag}]$: C, 40.48; H, 2.64. Found (4): C, 40.67; H, 2.70%. *Anal. Calc.* for $[\text{C}_{18}\text{H}_{24}\text{N}_4\text{O}_4\text{Cl}_4\text{Zn}]$: C, 36.18; H, 3.71. Found (6): C, 36.19; H, 3.77%. The resulting colorless crystals were filtered off, washed with CH_3OH and dried on P_2O_5 at 298 K. The obtained low quality samples of (4) and (6) as well as the observed redox $\text{Ag}^{\text{I}} \rightarrow \text{Ag}^0$ process in the first case difficult the collecting of the resonable crystallographic dataset and a high values of the corresponding R_1 -factors are obtained. (4): $\text{C}_9\text{H}_7\text{N}_2\text{OAg}$; crystal size, $0.11 \times 0.06 \times 0.11$; crystal system, monoclinic; space group Cc; T , 199(2) K; λ , 0.71073 Å; $a = 26.805(11)$, $b = 5.2750(17)$ and $c = 12.062(4)$ Å; $\beta = 114.422(17)^\circ$; $V = 1553.0(10)$ Å³; $Z = 4$; $\mu = 1.319 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.823 \text{ mg m}^{-3}$; goodness-of-fit on $F^2 = 0.998$ and $R_1 [I > 2\sigma(I)] = 0.1049$. The checkcif test (<http://checkcif.iucr.org/>) shows possible or pseudo new space group C2/c, however the refinement is unstable. (6): Triclinic system and $P\bar{1}$ space group; T , 200(2) K; λ , 0.71073 Å; $a = 7.294(3)$, $b = 9.961(5)$ and $c = 16.802(8)$ Å; α , β , γ , 83.528(13)°, 86.584(14)°, and 81.238(14)°; $V = 1197.7(9)$ Å³; $Z = 2$; $\mu = 1.503 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.557 \text{ mg m}^{-3}$ and $R_1 [I > 2\sigma(I)] = 0.1455$.

2.2. Materials, physical and computational methods

The X-ray diffraction intensities were measured on a Bruker Smart X2S diffractometer, using micro source Mo $K\alpha$ radiation

and employing the ω scan mode. The structures in Fig. 1 are presented by PLATON [31]. An absorption correction based on multiple scanned reflections [32]. The crystal structures were solved by direct methods using SHELXS-97 [32,33] and were refined by full-matrix least-squares refinement against F^2 [34]. Anisotropic displacement parameters were introduced for all non-hydrogen atoms. The experimental data are summarized in Table 1.

The IR-spectra were measured on a Thermo Nicolet 6700 FTIR-spectrometer ($4000\text{--}400 \text{ cm}^{-1}$, 2 cm^{-1} resolution, 200 scans) equipped with a Specac wire-grid polarizer. The UV-vis-NIR spectra were recorded on Evolution 300 spectrometer within the 190–1100 nm range. Quantum chemical calculations are performed with GAUSSIAN 98 and DALTON 2.0 program packages [35,36]. The geometry of isolated dication was optimized at Møller-Plesset perturbation theory [37] and 6-31+G(2d,p) basis. The DFT method employed is B3LYP, combining Becke's three-parameter non-local exchange function with the correlation function of Lee, Yang and Parr. Details can be found in [20,21]. The obtained most stable conformer of MA anion ($E = 0.0 \text{ kcal/mol}$) is characterized with an intramolecular $\text{OH} \cdots \text{O}$ hydrogen bond (2.789 Å) leading to the obtained value of 3560 cm^{-1} (ν_{OH}) of the vibration of the OH-group, in contrast to the ν_{OH} value of the COOH-fragment.

3. Results and discussion

Each Ag^{I} -ion in (1), of the binuclear Ag^{I} -sub-structure, is coordinated by four O-atoms with Ag–O distances within 2.215–2.492 Å (Fig. 1). The $\text{Ag}^{\text{I}}\text{--Ag}^{\text{I}}$ distance is 2.820 Å, respectively. The MA acts as tridentate ligand by COO^- and OH groups. The COO^- group join two Ag^{I} -ions in a binuclear sub-unit. The OH-group plays role as bridged center, joining each of the binuclear core into infinite polymeric structure. The geometry of the $\text{Ag}^{\text{I}}\text{O}_5$ chromophor could

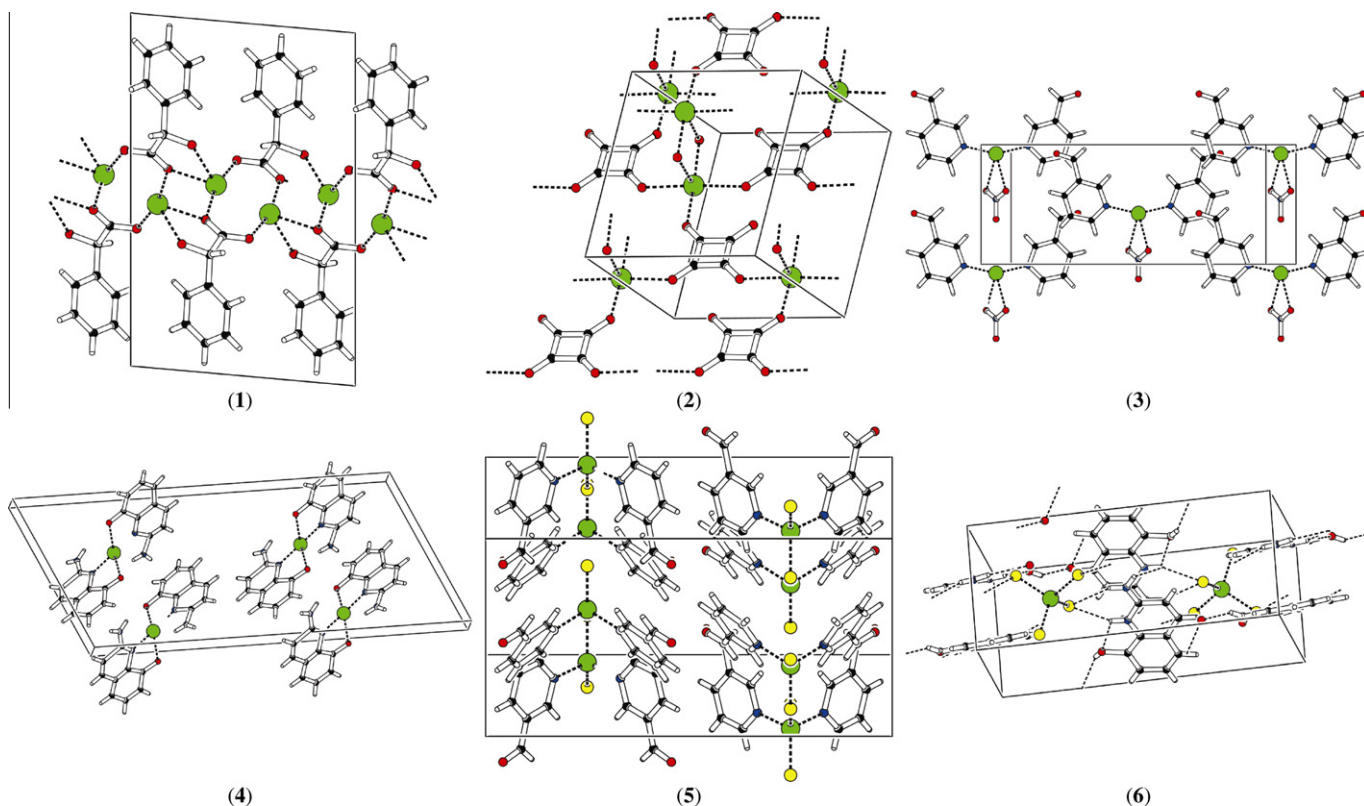


Fig. 1. PLATON diagrams of the hydrogen bonding patterns in the structures (1)–(6).

Download English Version:

<https://daneshyari.com/en/article/10578229>

Download Persian Version:

<https://daneshyari.com/article/10578229>

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