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Spectroscopic properties and the catalytic activity of new organo-lead supramolecular coordination polymer containing quinoxaline

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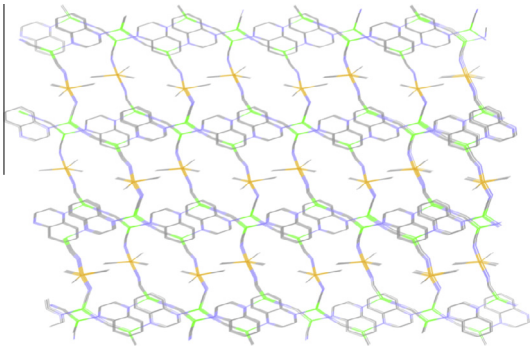
HIGHLIGHTS

- The SCP $^{3}_{\infty}[Cu_2(CN)_3(Me_3Pb)(qox)]$, **1**, consists of parallel $[Cu_2(CN)_3]$ chains connected by quinoxaline.
- 2D-layers are arranged in $(AB\cdots AB)_n$ fashion forming 3D-network. Spectral properties are investigated.
- The SCP **1** exhibits good catalytic and photo-catalytic activities for MB degradation.
- The reaction is first order and the UV-irradiation enhanced the rate of MB mineralization.

GRAPHICAL ABSTRACT

Visualization of the 3D-network structure of the SCP **1** down the projection of *a*-axis showing the methyl groups located in the space between the layers.



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ABSTRACT

The 3D-supramolecular coordination polymer (SCP) $^{3}_{\infty}[Cu_2(CN)_3(Me_3Pb)(qox)]$, **1**, as the first example of the CuCN SCP containing the (Me_3Pb) fragment, was explored to investigate its catalytic and photo-catalytic activities. The structure of **1** contains two chemically identical but crystallographically different $[Cu_2(CN)_3\cdot Me_3Pb\cdot qox]_2$ units with four Cu(I) sites assuming distorted TP-3 geometry. Two non-linear chains of equal abundance are formed producing corrugated parallel chains which are connected laterally by quinoxaline creating 2D-layers which are arranged parallel in an $(AB\cdots AB\cdots AB)_n$ fashion forming 3D-network. IR, mass, electronic absorption and fluorescence spectra are also investigated. The SCP **1** is diamagnetic and exhibits good catalytic and photo-catalytic activities for the degradation of methylene blue (MB). The reaction is first order with respect to MB dye. The irradiation of the reaction with UV-light enhanced the rate of MB mineralization. The efficiency of recycled the **1** and the mechanism of degradation of MB dye were investigated.

Introduction

It is well known that organometallic polymers possess unique properties and potential applications that are dependent on their organic segments and the types of metal complexes incorporated into their backbones or side chains [1]. Also, the cyanide group can be considered as the simplest species containing both carbon

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and nitrogen, which are both bio-essential elements to form amino acids, proteins, nucleotides, and most other known biomolecules. Thus, over the past decades, the synthesis of metal cyanide compounds has become a particularly important area of research and has attracted a growing interest because of potential applications as materials for catalysis, inorganic–organic zeolites, high-Tc molecular based magnets, high-temperature superconductors and luminescent properties [2–14]. In this aspect, the $[Cu_n(CN)_m]_x$ building block approaches are used for the construction of multidimensional SCP by attempting to incorporate the $(R_3Sn)^+$ cation as an essential element of the framework. This strategy allows for the synthesis of uncharged architectures in which channels remain, mostly, blocked by the R groups. A limited number of structural motifs is known for $[Cu_n(CN)_m(R_3Sn)L]$ where L = bipodal organic ligand [15–22]. It is evident that none of these structures contain the $(R_3Pb)^+$ cations or the quinoxaline moiety. The only free organotin example containing qox is $[Cu_2(CN)_2(qox)]$, 2, which exhibits 2D framework [23]. Thus, the aim of this work is the study of the effect of the organo-lead fragment, mainly the $(Me_3Pb)^+$ cation, on the structural variability and flexibility of the self-assembled new SCP **1** to explore its photo-catalytic activity. Most recently, much research has been focused on exploiting new catalytic materials based on MOFs [24–26]. The catalytic and photo-catalytic activities of the SCP **1** towards MB as a pollutant are studied. The spectral characteristics of **1** have been also investigated.

Experimental

All reagents were commercially available and were used as received. $K_3[Cu(CN)_4]$ was prepared following the literature procedure [5]. The dye under investigation namely methylene blue (MB) was obtained from Sigma and used as such. Deionized water was used to make the dye solutions of desired concentration. Hydrogen peroxide (30%) was obtained from Merck. The catalytic activities for the SCP **1** were investigated using MB as a pollutant. Briefly, for every measurement, 0.035 mM of catalyst was dispersed in 50 mL of fresh 5×10^{-6} M MB solution. The catalytic degradation processes were carried out at 30 °C and pH 6 in a reactor The photo-degradation experiments were carried out in a thermostated bath-type photo-reactor using medium pressure mercury lamp (365 nm) as illuminating light source.

Microanalyses (C, H and N) were carried out with a Perkin Elmer 2400 automatic elemental analyzer while copper was determined using Perkin Elmer 2380 atomic absorption spectrometer. The magnetic susceptibility was determined with Johnson-Matthey susceptometer. The IR spectra were recorded on a Bruker Vector 22 spectrophotometer as KBr disks. Mass spectra were recorded on a Finnigan MAT 8222 by FAB spectrometer. Electronic absorption spectra were measured as Nujol mull matrices on a Shimadzu (UV-310PC) spectrometer. Also, it is used to monitor the changes of the MB dye absorbance during the reaction course. It is equipped with an electronically temperature control unit (TCC-260) to maintain constant temperature with an accuracy ± 0.1 °C. Luminescence spectra as solid matrices were recorded at excitation wavelength 310 nm using a Perkin Elmer (LS 50 B) spectrometer.

*Synthesis of $^3_\infty[Cu_2(CN)_3{\cdot}Me_3Pb{\cdot}qox]$, **1***

A solution of 44 mg (0.155 mmol) of $K_3[Cu(CN)_4]$ in 5 mL H_2O was added, with gentle stirring to a mixture of solutions containing 136 mg (0.47 mmol) of Me_3PbCl in 5 mL H_2O and 20 mg (0.155 mmol) of quinoxaline; qox, in 5 mL acetonitrile. Already, after a week, orange needle crystals started growing from the initially clear solution. After filtration, washing with small quantities of cold H_2O and acetonitrile and overnight drying, 39 mg (43% referred to $K_3[Cu(CN)_4]$) of the orange needle crystals were obtained. Anal. Calc. for **1** ($C_{14}H_{15}N_5Cu_2Pb$): C, 28.62; H, 2.56; N, 11.92; Cu, 21.65%. Found: C, 28.58; H, 2.49; N, 11.87; Cu, 21.59%.

X-ray structural determination

Structural measurements for **1**were performed on a Kappa CCd Enraf Nonius FR 590 four cycle goniometer with graphite monochromatic Mo K_∞ radiation source {$\lambda = 0.71073$ Å} at 25 °C. The structure was resolved using direct-methods and all of the non-hydrogen atoms were located from the initial solution or from subsequent electron density difference maps during the initial stages of the refinement. After locating all of the non-hydrogen atoms in each structure the models were refined against F2, first using isotropic and finally using anisotropic thermal displacement parameters. The positions of the hydrogen atoms were then calculated and refined isotropically, and then the final cycle of refinements was performed. Crystallographic data for **1**are summarized in Table 1. Selected bond distances and bond angles are given in Table 2.

Results and discussion

*X-ray diffraction of single crystal and structure of $^3_\infty[Cu_2(CN)_3{\cdot}Me_3Pb{\cdot}qox]$, **1***

The ORTEP drawing of the asymmetric unit of the SCP **1** shows two chemically identical but crystallographically different $[Cu_2(CN)_3{\cdot}Me_3Pb{\cdot}qox]_2$ units exhibiting different bond lengths and bond angles, Fig. 1, Table 2. All the four Cu(I) sites assume distorted TP-3 geometries, where each Cu(I) atom is coordinated to two ordered cyanide groups and one N-atom of qox ligand. Alternatively, the asymmetric unit cell of **1** can be considered as consisting of two crystallographically non-equivalent, non-linear fragments of equal abundance whose three coordinate Cu(3) and Cu(5) atoms serve as crossover points of the two fragments. The angles of the TP-3 around the copper (I) atoms deviate than being 120°, Table 2. Thus, a substantial pyramidal distortion of the essentially TP-3 coordination sphere is apparent which is longer for Cu(3) and Cu(6) than for

Table 1
Crystal data and structure refinement parameters of $^3_\infty[Cu_2(CN)_3{\cdot}Me_3Pb{\cdot}qox]$, **1**.

Empirical formula	$C_{14}H_{15}N_5Cu_2Pb$
Formula weight (g mol^{-1})	587.591
Temperature (K)	298
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	
a (Å)	7.0222(2)
b (Å)	9.8308(3)
c (Å)	13.8538(6)
α (°)	105.3749(14)
β (°)	93.9918(14)
γ (°)	108.139(3)
V (Å^3); Z	864.16(5)/2
$D_{calc.}$ (g cm^{-3})	2.258
F (000)	548
Θ-range (°)	3.09–27.48
Reflections collected/unique	5914/2687
R int	0.032
Data/restraints/parameters	2687/0/207
Goodness-of-fit on F^2	1.661
R indices [$I > 3\ \sigma\ (I)$] R^1/wR^2	0.033/0.064
$W = 1/s^2^ (Fo^2^)+0.10000 \times Fo^2^)$	
R indices (all data)	0.061/0.074
Largest difference peak and hole (e Å^{-3})	1.20/−1.62