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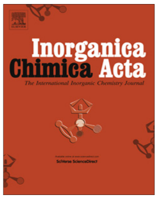

Oxalato-bridged oligonuclear complexes of cadmium(II)/lead(II) with bipyridine coligands: Synthesis, crystal structure, electronic spectra, density functional theory calculation and effect of organic compounds on the fluorescence property

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ABSTRACT

A trinuclear $[Cd_3(ox)_2(bipy)_5](ClO_4)_2$ (**1**) and a dinuclear $[Pb_2(ox)(bipy)_2(NO_3)_2(H_2O)_2]$ (**2**) oxalato-bridged complex, where ox = oxalate dianion and bipy = 2,2′-bipyridine, have been synthesized and characterized by elemental analysis, IR spectroscopy and X-ray crystallography. Structural determination for complex **1** reveals a cationic species of C_2 symmetry having two $Cd(bipy)_2$ fragments connected through bridging oxalate to a central Cd(bipy) unit. Complex **2** is a neutral centrosymmetric species having two Pb(bipy)$(NO_3)(H_2O)$ units connecting through the bridging oxalate. The dinuclear fragments through H-bonding as well as π–π interactions result in a 2D supramolecular network. Since complex **1** exhibits intense fluorescence (λ_{ex} = 284 nm, λ_{em} = 315, 329 and 356 nm) in methanol at room temperature with a fluorescence quantum yield Φ_s = 0.41, it was tested in association with several aromatic compounds. The results show a pronounced fluorescence quenching and enhancement in presence of nitrobenzene and *m*-toluidine, respectively. The outcome from DFT calculations is discussed and compared with the experimental electronic, IR spectral and X-ray structural data.

1. Introduction

Design and synthesis of coordination compounds have been an active area in inorganic chemistry owing to their potential applications [1]. The most efficient and widely used approach for designing such compounds is the self-assembly of organic ligands and metal ions. Aliphatic dicarboxylates have been used as potential building blocks [2], owing to their conformational and coordination versatility. Crystalline organic–inorganic hybrid oxalate has gained a large interest in materials science due to its intrinsic properties. Moreover the type of co-ligands and counter anions used can lead to different dimensionalities, namely 1D chains, 2D layers and 3D open frameworks [3]. Although oxalate anion has a rigid structure, a variety of coordination geometries can be obtained due to its multifunctional behavior [3b]. Literature survey shows either oligonuclear and polynuclear complexes with oxalate are common for 3d metals [4–8], but complexes of low nuclearity are less common for heavy metals.

Over the last few years we have been actively engaging in the design and synthesis of metal-carboxylate coordination compounds [9]. The divergent coordination sites and potential high-denticity of the oxalate anion stimulated us to use this organic species with heavier metals such as Cd(II) and Pb(II). The present contribution reports the syntheses, crystal structures, electronic spectra, DFT calculation, fluorescence property of oxalato-bridged oligonuclear complexes of Cd(II) and Pb(II) with chelating 2,2′-bipyridine ligand, $[Cd_3(ox)_2(bipy)_5](ClO_4)_2$ (**1**) and $[Pb_2(ox)(bipy)_2(NO_3)_2(H_2O)_2]$ (**2**) [ox = oxalate dianion and bipy = 2,2′-bipyridine]. The IR and electronic spectral properties of complexes are explained by DFT computation using optimized geometries. The fluorescence of complex **1** in MeOH has been investigated in presence of various organic molecules.

2. Experimental

2.1. Materials and physical measurements

High purity cadmium perchlorate monohydrate, 2,2′-bipyridine (Aldrich), and lead nitrate (Merck-India) were purchased and used as received. All other chemicals used were of analytical grade. Potassium tris(oxalato)chromate(III) trihydrate ($K_3[Cr(ox)_3]{\cdot}3H_2O$) was prepared by a reported method [10]. Solvents used for

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spectroscopic studies were purified and dried by standard procedures before use [11].

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer. IR spectra were recorded as KBr pellets on a Bruker Vector 22FT IR spectrophotometer operating from 400 to 4000 cm^{-1}. Electronic absorption spectra were obtained with Shimadzu UV-1601 UV–Vis spectrophotometer at room temperature. Quartz cuvettes with a 1 cm path length and a 3 cm^3 volume were used for all measurements. Emission spectra were recorded on a Hitachi F-7000 spectrofluorimeter. Room temperature (300 K) spectra were obtained in methanol solution using a quartz cell of 1 cm path length. The slit width was 2.5 nm for both excitation and emission.

The fluorescence quantum yield was determined using phenol as a reference and water medium for both complexes and reference. Emission spectra were recorded by exciting the complex and the reference phenol at the same wavelength, maintaining nearly equal absorbance (~0.1). The area of the emission spectrum was integrated using the software available in the instrument and the quantum yield was calculated [12] according to the following equation:

$$\Phi_s = \Phi_r \frac{A_s}{A_r} \frac{I_r}{I_s} \frac{\eta_s^2}{\eta_r^2}$$

where Φ_s and Φ_r are the fluorescence quantum yield of the sample and reference, respectively. A_s and A_r are the respective optical densities at the wavelength of excitation, I_s and I_r correspond to the areas under the fluorescence curve; and η_s and η_r are the refractive index values for the sample and reference, respectively. The fluorescence enhancement efficiency (%) was calculated by using equation $[(I - I_0)/I_0] \cdot 100$ and the corresponding quenching efficiency (%) by $[(I_0 - I)/I_0] \cdot 100$, where I_0 and I are the maximum fluorescence intensity of the complex before exposure and in presence of the analyte, respectively.

2.2. Synthesis

2.2.1. [$Cd_3(ox)_2(bipy)_5](ClO_4)_2$ (**1**)

An aqueous solution (5 mL) of potassium tris(oxalato)chromate(III) trihydrate (0.66 mmol, 0.321 g) was added to an aqueous solution (5 mL) of $Cd(ClO_4)_2{\cdot}H_2O$ (1 mmol, 0.329 g) under stirring condition. To this reaction mixture a methanolic solution (10 mL) of 2,2′-bipyridine (1 mmol, 0.156 g) was added. The reaction mixture was refluxed for 1.5 h and filtered; the filtrate was kept in a $CaCl_2$ desiccator. After a few days, colorless crystals suitable for X-ray analysis were obtained. Yield 75%. *Anal.* Calc. for $C_{54}H_{40}Cd_3Cl_2N_{10}O_{16}$ (1493.06): C, 43.43; H, 2.70; N, 9.37. Found: C, 43.44; H, 2.71; N, 9.38%. The infrared spectra exhibited the following absorptions: 2972(s), 1639(s), 1558(vs), 1464 (s), 1429(vs), 1368(s), 1296(s), 1121(vw), 1075(vw), 1003(vw), 879 (w), 814(vw), 645(w) and 506(vw) cm^{-1}.

2.2.2. [$Pb_2(ox)(bipy)_2(NO_3)_2(H_2O)_2$] (**2**)

An aqueous solution (5 mL) of potassium tris(oxalato)chromate (III) trihydrate (0.66 mmol, 0.321 g) was added dropwise to an aqueous solution (5 mL) of $Pb(NO_3)_2$ (1 mmol, 0.331 g) with constant stirring for 5 min until the mixture became turbid. To the resulting mixture a methanolic solution (10 mL) of 2,2′-bipyridine (1 mmol, 0.156 g) was added dropwise. The reaction mixture was stirred for 2 h and filtered; the filtrate was kept in a $CaCl_2$ desiccator. After a few days, colorless crystals suitable for X-ray analysis were obtained. Yield 75%. *Anal.* Calc. for $C_{22}H_{20}Pb_2N_6O_{12}$ (974.82): C, 27.10; H, 2.06; N, 8.61. Found: C, 27.11; H, 2.07; N, 8.60%. The infrared spectra exhibited the following absorptions: 3550–3080(s, br), 2972(s), 1645(vs), 1561(vs), 1465(s), 1416(s), 1370(w), 1336(vw), 1299(s), 1076(w), 880(w), 815(w), 781(w), 645(s) and 513(w) cm^{-1}.

2.3. X-ray crystallography

Data collection for complexes 1 and 2 were carried out at room temperature on Nonius diffractometer equipped with KappaCCD detector (Cu Kα radiation, λ = 1.54180 Å) and on an Enraf–Nonius CAD4 (Mo Kα radiation, λ = 0.71073 Å), respectively. Cell refinement, indexing and scaling of the data sets were done by using Denzo and Scalepack package and REFLEX program [13]. The structures were solved by direct methods and subsequent Fourier analyses [14] and refined by the full-matrix least-squares method based on F^2 with all observed reflections [14]. The low accuracy obtained for complex **1** was due to the poor quality of the crystalline material, but attempts to obtain better crystals proved fruitless. This induce to refine a bipy ring as a constrained rigid hexagon and Cl–O perchlorate distances restrained to 1.42 Å. Hydrogen atoms were placed at calculated positions, except those of the water molecule in **2**, which were detected on the ΔFourier map and refined. All the calculations were performed using the WinGX System, Ver 1.80.05 [15]. Crystal data and details of refinements are given in Table 1.

2.4. Theory and computational methods

All computations were performed using the GAUSSIAN 09 (G09) software package, [16] by using the Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr non-local correlation functional (B3LYP) [17]. In the calculation the 6-31G (d-p) basis set was assigned to all elements with the exception of cadmium and lead, for which the Los Alamos ECP plus MBS (LanL2MB) [18] basis set was employed. The geometric structures of the complexes in the ground state (singlet) were fully optimized at the B3LYP level. The vibration frequency calculations were performed to ensure that the optimized geometries represent local minima associated with positive eigen values only. Using optimized geometries (singlet) we performed time dependent density functional theory (TD-DFT) calculations at the B3LYP level to get the theoretically possible absorption character for both the complexes [19]. GAUSSSUM [20] was used to calculate the fractional contributions of various groups to each molecular orbital. Calculated coordination geometries in gas phase are shown in Table 2.

Table 1
Crystal data and details of structure refinement of complexes **1** and **2**.

Complex	1	2
Empirical formula	$C_{54}H_{40}Cd_3Cl_2N_{10}O_{16}$	$C_{22}H_{20}Pb_2N_6O_{12}$
Formula mass (g mol^{-1})	1493.06	974.82
Crystal system	monoclinic	monoclinic
Space group	$P\,2/c$	$P\,2_1/c$
a (Å)	14.3047(10)	9.54440(10)
b (Å)	9.6601(4)	20.5956(3)
c (Å)	22.0345(15)	6.74490(10)
β (°)	94.006(7)	91.8190(10)
Z	2	2
V (Å^3)	3037.4(3)	1325.19(3)
D_{calc} (g cm^{-3})	1.633	2.443
μ(Mo Kα) (mm^{-1})	9.775	12.764
$F(000)$	1480	908
θ (°)	4.02–70.77	3.61–30.51
No. of collected data	13029	16235
No. of unique data	5719	4033
R_{int}	0.0582	0.0301
Observed reflections [$I > 2\sigma(I)$]	2975	3731
Goodness of fit (F^2)	0.988	1.130
Parameters refined	395	196
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0719, 0.2121	0.0298, 0.0698
R_1, wR_2 (all data)	0.1157, 0.2603	0.0337, 0.0718
Residuals (e Å^{-3})	0.769, −0.704	2.448, −1.235

[a] $R_1(Fo) = \Sigma||Fo| - |Fc||/\Sigma|Fo|$, $wR_2(Fo^2) = [\Sigma w\,(Fo^2 - Fc^2)^2/\Sigma w\,(Fo^2)^2]^{1/2}$.