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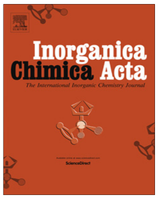

Research paper

A combined experimental and theoretical study on two new dinuclear cadmium(II) Schiff base complexes with selenocyanate-κ-Se

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ABSTRACT

Two new dinuclear cadmium(II) complexes, $[Cd(L^{1})_{2}Cd(SeCN\text{-}\kappa\text{-}Se)_{2}]$ (**1**) and $[Cd(L^{2})_{2}Cd(SeCN\text{-}\kappa\text{-}Se)_{2}]$ (**2**), where HL^{1} = {2-(3-(dimethylamino)propyliminomethyl)-6-methoxyphenol} and HL^{2} = {2-(3-(dimethylamino)propyliminomethyl)-6-ethoxyphenol}, have been prepared and characterized by elemental and spectral analysis and single crystal X-ray diffraction studies. Both complexes contain cadmium-selenium bonds. Non-covalent interactions were also investigated using DFT calculations at the BP86-D3/def2-TZVP level of theory. Both complexes show florescence upon irradiation with visible light.

1. Introduction

Cadmium is an awfully poisonous heavy metal that causes hepato, renal and neurotoxicity even at low concentration levels [1–4]. In spite of its tremendous toxicity, usually some milligrams of it is contained in a normal human adult body [5,6]. Cadmium(II) is also found to serve as the catalytic centre in carbonic anhydrase, discovered recently [7]. On the other hand, cadmium(II) complexes have attracted considerable attention in the past few decades, due to their widely reported bioactivities, such as DNA binding abilities [8–10], antibacterial activities [11,12] and antitumor properties [13,14]. At the same time, cadmium(II) displays a flexible geometry with possible coordination numbers ranging from four to eight [15–17] corresponding to different geometries, due to its d^{10} configuration with no CFSE in any crystal field, the geometries and coordination numbers being mainly governed by the steric demands of the ligands. This makes cadmium(II) very useful in the fields of crystal engineering.

Selenocyanate is an ambidentate ligand [18–20] with two potential donor atoms, nitrogen and selenium, although its complexing ability is much less explored compared to its well known analogue, thiocyanate. Selenocyanate coordinates to hard metal centres through the nitrogen end and soft centres via the selenium end [21–23]. In case of borderline cadmium(II) centres, it may coordinate through either nitrogen {preferably when electron withdrawing ligands decrease the electron density on cadmium (II)} or selenium {when ancillary ligands increase the electron density on cadmium(II)} atoms giving rise to the possibility of linkage isomerism. However, the stability of nitrogen-bonded and selenium-bonded compounds cannot be explained by electronic arguments alone, as the steric effect also plays an important role. Similar ambidentate behaviour of thiocyanate was already addressed in a previous paper [24] where it was shown by theoretical calculations that nitrogen-coordination is preferred over sulphur-coordination for thiocyanate and this finding was in good agreement with the much greater abundance of the reported nitrogen-bonded thiocyanate complexes.

In the present work, we have used two N_2O_2 donor tetradentate salicylaldimine Schiff bases to prepare two dinuclear cadmium(II) complexes, $[Cd(L^{1})_{2}Cd(SeCN\text{-}\kappa\text{-}Se)_{2}]$ (**1**) and $[Cd(L^{2})_{2}Cd(SeCN\text{-}\kappa\text{-}Se)_{2}]$ (**2**). In both complexes, selenocyanates are bonded to cadmium (II) via selenium ends. The importance of such cadmium selenocyanate complexes lie in their strong antibacterial property [25–27]. However, we are interested in the potential ambidentate behaviour of selenocyanate in cadmium(II) complexes. Therefore, a theoretical study has been performed using DFT calculations at the BP86-D3/def2-TZVP level of theory to show that selenium-coordination to cadmium(II) is energetically favoured over

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nitrogen-coordination. Energy of the C-H$\cdots\pi$ interactions observed in the solid state was also calculated using the crystallographic coordinates and at the same time, C-H$\cdots\pi$ interactions were characterized using non-covalent interaction (NCI) plot. Herein, we report the synthesis, spectroscopic characterization, X-ray crystal structures, supra-molecular interaction and DFT study of these two new cadmium(II) complexes. Both complexes show florescence upon irradiation with visible light.

2. Experimental

All starting materials and solvents were commercially available, reagent grade, and used as purchased from Sigma-Aldrich without further purification. **Caution!!!** Perchlorate salts are potentially explosive. Although no problem was encountered in the present study, only small amounts of the materials should be prepared and they must be handled with care.

2.1. Preparations

2.1.1. Preparation of ligands

2.1.1.1. Synthesis of HL^1 {2-(3-(dimethylamino)propyliminomethyl)-6-methoxyphenol}. The tetradentate N_2O_2 donor Schiff base, HL^1, was prepared by refluxing 3-methoxysalicylaldehyde (1 mmol, 0.152 g) and *N,N*-dimethyl-1,3-diaminopropane (1 mmol, 0.125 mL) in methanol solution (20 mL) for ca. 1 h. Methanol was evaporated under reduced pressure to get HL^1 as yellow oily liquid. It was not purified and used directly for the preparation of complex **1**.

IR (KBr, cm^{-1}): 1633 ($\upsilon_{C{=}N}$); 2940–2831 (υ_{CH}); 3432 (υ_{OH}). UV–vis, λ_{max} (nm), [ε_{max} ($L\,mol^{-1}\,cm^{-1}$)] (DMSO), 242 (7.1×10^3); 324 (4.8×10^3); 420 (2.5×10^3).

2.1.1.2. Synthesis of HL^2 {2-(3-(dimethylamino)propyliminomethyl)-6-ethoxyphenol}. The tetradentate N_2O_2 donor Schiff base, HL^2, was prepared in a similar method to that of HL^1, except that 3-ethoxysalicylaldehyde (1 mmol, 0.166 g) was used instead of 3-methoxysalicylaldehyde. Methanol was evaporated under reduced pressure to get HL^2 as yellow oily liquid. It was not purified and used directly for the preparation of complex **2**.

IR (KBr, cm^{-1}): 1632 ($\upsilon_{C{=}N}$); 2980–2825 (υ_{CH}); 3424 (υ_{OH}). UV–vis, λ_{max} (nm), [ε_{max} ($L\,mol^{-1}\,cm^{-1}$)] (DMSO), 251 (8.8×10^3); 325 (6.3×10^3); 422 (3.3×10^3).

2.1.2. Synthesis of complexes

*2.1.2.1. Synthesis of $[Cd(L^1)_2Cd(SeCN\text{-}\kappa\text{-}Se)_2]$ (**1**).* A methanol solution of cadmium(II) nitrate tetrahydrate (1 mmol, 0.308 g) was added to the methanol solution of the Schiff base (HL^1) and refluxed for 1 h. A methanol solution of potassium selenocyanate (1 mmol, 0.144 g) was then added to it and refluxed further for ca. 1 h. Diffraction quality single crystals of complex **1** were obtained after few days on slow evaporation of the solution in open atmosphere.

Yield: 0.48 g (54%). Anal. Calc. $C_{28}H_{38}Cd_2N_6O_4Se_2$ (FW 905.38): C, 37.14; H, 4.23; N, 9.28; Found: C, 37.1; H, 4.2; N, 9.3;%. IR (KBr, cm^{-1}):1627 ($\upsilon_{C{=}N}$); 2115 (υ_{SeCN}); 2994–2840 (υ_{CH}). UV–vis, λ_{max} (nm), [ε_{max} ($L\,mol^{-1}\,cm^{-1}$)] (DMSO), 265 (9.6×10^3); 334 (3.7×10^3); 397 (1.5×10^3). ^1H NMR (DMSO-d_6) δ ppm: 8.425 (s, 2H, $-\mathbf{CH}{=}N$); 6.98 (d, 2H, $J = 7.4$ Hz, Ar-**H**); 6.28 (d, 2H, $J = 5.2$ Hz, Ar-**H**); 6.74 (dd, 2H, $J = 7.4$, 7.3 Hz, Ar-**H**); 3.7 (s, 6H, $-OC\mathbf{H}_3$); 3.615 (m, 4H, $-C\mathbf{H}_2CH_2CH_2-$); 2.77 (m, 4H, $-CH_2CH_2C\mathbf{H}_2-$); 2.19 (s, 12H, $-N(C\mathbf{H}_3)_2$); 1.788 (m, 4H, $-CH_2C\mathbf{H}_2CH_2-$).

*2.1.2.2. Synthesis of $[Cd(L^2)_2Cd(SeCN\text{-}\kappa\text{-}Se)_2]$ (**2**).* A methanol solution cadmium(II) perchlorate hexahydrate (1 mmol, 0.419 g) was added to the methanol solution of the Schiff base (HL^2) and refluxed for 1 h. A methanol solution of potassium selenocyanate (1 mmol, 0.144 g) was then added to it and refluxed further for ca. 1 h. Diffraction quality single crystals of complex **2** were obtained after few days on slow evaporation of the solution in open atmosphere.

Yield: 0.55 g (59%). Anal. Calc. $C_{30}H_{42}Cd_2N_6O_4Se_2$ (FW 933.44): C, 38.60; H, 4.54; N, 9.01; Found: C, 38.5; H, 4.5; N, 9.1%. IR (KBr, cm^{-1}):1626 ($\upsilon_{C{=}N}$); 2076, 2120 (υ_{SeCN}); 2991–2833 (υ_{CH}). UV–vis, λ_{max} (nm), [ε_{max} ($L\ mol^{-1}\ cm^{-1}$)] (DMSO), 266 (9.1×10^3); 331 (2.9×10^3); 410 (1.7×10^3). ^1H NMR (DMSO-d_6) δ ppm: 8.129 (s, 2H, $-\mathbf{CH}{=}N$); 6.722 (d, 2H, $J = 3.9$ Hz, Ar-**H**); 6.7 (d, 2H, $J = 4$ Hz, Ar-**H**); 6.26 (dd, 2H, $J = 7.5$ Hz, 7.55 Hz, Ar-**H**); 3.9 (q, 4H, $-C\mathbf{H}_2CH_3$); 3.628 (m, 4H, $-C\mathbf{H}_2CH_2CH_2-$); 2.621 (m, 4H, $-CH_2CH_2C\mathbf{H}_2-$), 2.257 (S, 12H, $-N(C\mathbf{H}_3)_2$); 1.783 (m, 4H, $-CH_2C\mathbf{H}_2CH_2-$); 1.299 (t, 6H, $J = 7$ Hz, $-CH_2C\mathbf{H}_3$).

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectra in KBr (4500–500 cm^{-1}) were recorded using a PerkinElmer FT-IR spectrum two spectrometer. Electronic spectra in DMSO (200–800 nm) were recorded on a PerkinElmer Lambda 35 UV–vis spectrophotometer. Fluorescence spectra in DMSO were obtained on a Hitachi F-7000 Fluorescence spectrophotometer at room temperature. Fluorescence Lifetime measurements were recorded using Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBHDAS6 software. ^1H NMR spectra were measured at room temperature using Bruker DPX-500 MHz NMR spectrometer.

2.3. X-ray crystallography

Single crystals of two complexes having suitable dimensions were used for data collection using a Bruker SMART APEX II diffractometer equipped with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at 150 K. Molecular structures were solved using the SHELX-2014/7 package [28]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Multi-scan empirical absorption cor-

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

	1	2
Formula	$C_{28}H_{38}Cd_2N_6O_4Se_2$	$C_{30}H_{42}Cd_2N_6O_4Se_2$
Formula Weight	905.38	933.44
Temperature (K)	150	150
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a(Å)	11.385(5)	17.3600(5)
b(Å)	17.155(5)	11.4068(3)
c(Å)	18.014(5)	17.8267(5)
β	106.928(5)	92.290(2)
Z	4	4
d_{calc} (g cm^{-3})	1.787	1.758
μ (mm^{-1})	3.464	3.311
F(000)	1776	1840
Total Reflections	47177	49726
Unique Reflections	6372	5986
Observed data[$I > 2\sigma(I)$]	4259	5315
No. of parameters	379	397
R(int)	0.069	0.052
R1, w*R*2 (all data)	0.0818, 0.1051	0.0548, 0.0896
R1, w*R*2 [$I > 2\sigma(I)$]	0.0434, 0.0893	0.0386, 0.0818