Inorganica Chimica Acta 362 (2009) 2189–2199

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis and characterization of metal complexes of Calcein Blue: Formation of monomeric, ion pair and coordination polymeric structures

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ARTICLE INFO

Article history:
Received 6 August 2008
Accepted 22 September 2008
Available online 1 October 2008

Keywords:
Calcein Blue
Ion-pair complexes
Hydrogen bonding
Solid-state fluorescence

ABSTRACT

A series of metal complexes containing the 4-methylumbelliferone-8-methyleneiminodiacetic acid (H_3muia, also named as Calcein Blue) has been synthesized and characterized. Complexes of Cu(II), Ni(II), Mn(II), Zn(II) and Mg(II) have been structurally characterized while Ca(II) and Al(III) complexes by elemental analysis and thermogravimetry. The Cu(II) and Ni(II) complexes are neutral and mononuclear in the solid state. Interestingly, the Mn(II), Zn(II) and Mg(II) muia complexes exist as ion-pairs containing hydrated or solvated metal cations and dimeric metal(II) muia anions. Owing to the presence of hydrogen-bond donors and acceptors in the ligand, hydrogen bonding interactions are dominant along with π–π stacking in their solid-state structures. The solid-state fluorescence studies indicate that the family of muia complexes exhibit comparable emission properties as in solution state, in which only main group and post-transition complexes show bright blue fluorescence while transition metal complexes do not fluoresce.

1. Introduction

Crystal engineering of coordination polymers and supramolecules have attracted lot of attention due to their potential applications as functional materials, as well as their fascinating architectures and topologies [1–7]. A successful strategy in the construction of such networks is to utilize appropriate multidentate ligands with flexible backbone that are capable of binding metal ions in different modes. One such class of ligands is the amino acid moiety in which both amino and carboxylate groups can take part in the supramolecular interactions. Considerable efforts have been made to study the coordination chemistry of various transition metal complexes derived from salicyaldehyde and amino acid Schiff base [8–14] and reduced Schiff base ligands [15–20]. Our laboratory has been interested in the coordination chemistry of Cu(II) and Zn(II) complexes containing reduced Schiff base ligands derived from substituted salicylaldehyde and amino acid for the construction of supramolecular network structures. X-ray crystal structures of these complexes revealed that the *N*-(2-hydroxybenzyl)-amino acid ligands mainly act as tridentate moiety, coordinating through the phenolato oxygen, amine nitrogen and carboxylate oxygen. The other exodentate carboxylate oxygen atom coordinating to metal ions intermolecularly is responsible for the fascinating supramolecular architectures [21,22]. We have successfully demonstrated that incorporation of yet another carboxylate group to the reduced Schiff base ligand, *viz.*, *N*-(2-hydroxylbenzyl)-glutamic acid has led to an interesting 1D coordination polymer which encapsulated helical water channel [23]. Thus, it is promising that the additional functional group such as carboxylate is essential for furnishing structurally interesting coordination polymers by these ligands.

Hence, we have chosen 4-methylumbelliferone-8-methyleneiminodiacetic acid (H_3muia) or Calcein Blue which has two carboxylic acid groups as shown in Scheme 1. This commercially available ligand has coumarin group instead of phenyl group. The coumarin derivatives are advantageous as they show remarkable absorption and luminescence properties [24]. Furthermore, the presence of extra ring may induce the π–π interactions in the solid-state structures of the resulting complexes. Owing to the presence of coumarin group, Calcein Blue has been employed as an indicator in the EDTA titration of calcium and some transition metals based on its fluorescence properties [25–27]. However, this tetradentate ligand with flexible amino dicarboxylate functional group and multi-hydrogen bonding functionalities has never been exploited for its coordination behaviour in the solid state. While much research has been devoted to natural product chemistry, biological application [28,29] and photophysical properties [24] of organic coumarin derivatives, little information is available on solid-state structures of transition metal complexes of coumarin derivatives [30–42].

Recently, we reported the self assembly of ion-pair cobalt(II) complexes of Calcein Blue. In one-pot synthesis, concomitant self-assembled monomeric and dimeric ion-pair cobalt(II)

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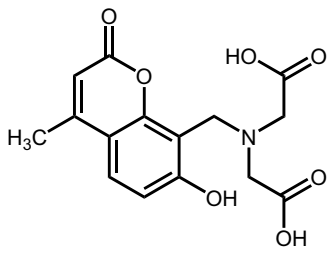
doi:10.1016/j.ica.2008.09.049



Scheme 1. Molecular structure of Calcein Blue.

complexes have been isolated. Both solvated and hydrated cobalt(II) cation interacted with cobalt(II) anion through intermolecular hydrogen bondings. It has been found that solvents play an important part in the condensation of ion-pair complexes to pseudo-supramolecular isomer and led to a 1D coordination polymer [43]. Here in we have further explored the coordination chemistry of Calcein Blue and describe the synthesis, characterization, solid-state structures and fluorescence properties of Cu(II), Ni(II), Mn(II), Zn(II), Mg(II), Ca(II) and Al(III) complexes of the H_3muia ligand.

Table 1
Selected hydrogen bond parameters for **1–6**

D–H	*d*(D–H)	*d*(D···A)	*d*(H···A)	∠DHA	A (symmetry)
Compound **1**					
O1–H1	0.68(5)	1.94(5)	2.615(5)	170(5)	O1S
O1S–H1S	0.76(5)	2.11(5)	2.852(4)	164(5)	O5 (−*x*, 2 − *y*, −*z*)
O2S–H2SB	1.20(3)	2.53(3)	3.430(5)	131(2)	O7 (−*x*, 1/2 + *y*, 1/2 − *z*)
O3S–H3SA	1.23(3)	1.41(4)	2.601(7)	159(3)	O2S
O3S–H3SB	1.22(3)	1.66(3)	2.854(7)	164(3)	O3 (*x*, 1 + *y*, *z*)
O8–H8A	0.80(3)	1.85(3)	2.624(5)	163(3)	O2S
O8–H8B	0.78(4)	1.99(4)	2.740(4)	163(5)	O3 (1 − *x*, 1/2 + *y*, 1/2 − *z*)
Compound **2**					
O1–H1	0.86(3)	1.70(3)	2.558(4)	175(2)	O10 (1 − *x*, 1/2 + *y*, 1/2 − *z*)
O8–H8A	0.86(3)	1.77(3)	2.620(3)	169(4)	O2 (1/2 + *x*, *y*, 1/2 − *z*)
O8–H8B	0.86(4)	1.96(4)	2.806(3)	167(4)	O5 (1 + *x*, *y*, *z*)
O9–H9A	0.86(3)	1.96(3)	2.817(3)	179(4)	O3 (1/2 − *x*, 1/2 + *y*, *z*)
O9–H9B	0.85(3)	1.96(3)	2.793(3)	164(3)	O4 (1/2 + *x*, *y*, 1/2 − *z*)
O10–H10A	0.88(2)	1.91(3)	2.717(4)	153(3)	O11
O10–H10B	0.89(3)	1.94(3)	2.815(3)	171(5)	O3
O11–H11A	0.87(3)	1.90(3)	2.759(4)	171(4)	O5 (−*x*, −1/2 + *y*, 1/2 − *z*)
O11–H11B	0.87(2)	2.03(2)	2.897(4)	176(7)	O7 (*x*, 1/2 − *y*, −1/2 + *z*)
Compound **3**					
O8–H8A	0.83(5)	1.89(5)	2.718(4)	173(5)	O3 (1 − *x*, 1/2 + *y*, 1/2 − *z*)
O8–H8B	0.86(7)	1.88(6)	2.732(4)	170(6)	O7 (−*x*, *y*, *z*)
O9–H9B	0.71(5)	2.14(5)	2.813(8)	159(5)	N1S
O10–H10A	0.83(5)	1.85(5)	2.670(4)	169(5)	O4 (1 − *x*, 2 − *y*, 1 − *z*)
O10–H10B	0.91(5)	1.87(5)	2.773(4)	176(7)	O2 (*x*, 1 + *y*, *z*)
O11–H11A	0.69(5)	2.02(5)	2.669(5)	172(5)	O3 (1 − *x*, 1 − *y*, 1 − *z*)
O11–H11B	0.75(7)	1.93(7)	2.653(5)	166(7)	O5 (1 − *x*, 2 − *y*, 1 − *z*)
Compound **4**					
O8–H8A	0.85(5)	1.94(5)	2.735(4)	156(5)	O3 (1 − *x*, 1/2 + *y*, 1/2 − *z*)
O9–H9A	0.86(7)	2.05(7)	2.881(7)	165(7)	N2
O10–H10A	0.91(7)	1.76(7)	2.673(4)	175(7)	O4 (1 − *x*, 2 − *y*, 1 − *z*)
O10–H10B	0.88(7)	1.88(7)	2.733(4)	164(6)	O2 (*x*, 1 + *y*, *z*)
O11–H11A	0.82(7)	1.86(7)	2.679(4)	178(8)	O3 (1 − *x*, 1 − *y*, 1 − *z*)
O11–H11B	0.77(7)	1.89(7)	2.656(5)	178(9)	O5 (1 − *x*, 2 − *y*, 1 − *z*)
Compound **5**					
O15–H15A	1.02(8)	1.68(8)	2.698(6)	179(9)	O4
O15–H15B	0.91(8)	1.87(8)	2.756(6)	167(7)	O2 (1 − *x*, 1 − *y*, 1 − *z*)
O16–H16A	1.11(6)	2.27(8)	2.780(7)	106(4)	O7 (−*x*, −*y*, 1 − *z*)
O16–H16B	0.85(8)	1.89(9)	2.736(7)	172(9)	O11 (−1 + *x*, *y*, *z*)
O17–H17A	0.90(2)	2.04(5)	2.838(8)	148(7)	O3 (1 − *x*, 1 − *y*, 1 − *z*)
O17–H17B	0.90(4)	2.19(5)	3.065(9)	166(6)	O3 (−1 + *x*, *y*, *z*)
O18–H18B	0.94(7)	1.75(7)	2.692(9)	175(8)	O5
O19–H19	0.94	2.07	2.648(6)	118	O9 (1 − *x*, 1 − *y*, 2 − *z*)
O20–H20	0.94	1.81	2.6334	145	O10 (1 − *x*, 1 − *y*, 2 − *z*)
O21–H21A	0.90(5)	1.84(5)	2.731(7)	169(5)	O22
O21–H21B	0.90(6)	1.83(6)	2.694(8)	160(7)	O23
O22–H22A	0.91(6)	1.95(7)	2.849(7)	170(7)	O7 (1 − *x*, −y, 1 − *z*)
O22–H22B	0.90(4)	2.10(3)	2.969(8)	161(6)	O14 (*x*, −1 + *y*, *z*)
O23–H23A	0.89(7)	1.86(7)	2.731(8)	165(6)	O10 (1 − *x*, 1 − *y*, 2 − *z*)
O23–H23B	0.90(5)	2.33(5)	3.052(15)	137(6)	O24 (1 − *x*, 1 − *y*, 2 − *z*)
O24–H24A	0.91(10)	2.30(12)	2.903(17)	124(12)	O14
O24–H24B	0.90(12)	2.22(10)	3.012(16)	146(11)	O19
Compound **6**					
O8–H8A	0.899(10)	1.899(11)	2.761(3)	160.0(11)	O5 (3/2 − *x*, 1/2 + *y*, 1/2 − *z*)
O8–H8B	0.895(11)	1.990(12)	2.828(3)	155.3(14)	O3 (3/2 − *x*, −1/2 + *y*, 1/2 − *z*)
O9–H9	0.894(14)	1.797(16)	2.652(3)	159(3)	O2 (*x*, −1 + *y*, *z*)
O10–H10A	0.899(15)	1.85(2)	2.725(4)	164(2)	O3 (*x*, −1 + *y*, *z*)
O10–H10B	0.905(15)	1.724(19)	2.619(4)	170(3)	O5
O11–H11A	0.908(13)	2.011(14)	2.869(6)	157.0(12)	O4
O12–H12B	0.901(14)	1.84(2)	2.625(7)	144(3)	O7 (−1/2 + *x*, 1/2 + *y*, −1/2 + *z*)