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The first two-dimensional barium coordination polymer based on neutral and deprotonated 4-formylbenzoic acid

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A two-dimensional barium(II) coordination polymer, $[Ba(4\text{-}FBA)_2(4\text{-}FBAH)]_n$ (4-FBA$^-$ = 4-formylbenzoate), has been synthesized by the reaction of barium carbonate and 4-formylbenzoic acid. The barium(II) ion is nine-coordinated by eight O atoms from six deprotonated 4-FBA$^-$ ligands and one O atom from the terminal 4-FBAH ligand. Adjacent barium(II) ions are linked by the 4-FBA$^-$ ligand to furnish a two-dimensional lamellar structure which exhibits blue fluorescent emission in the solid state at room temperature. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: barium(II) coordination polymer; 4-formylbenzoic acid; fluorescent property; crystal structure

INTRODUTION

Supramolecular chemistry based on metal-ion directed assembly of organic molecular building blocks is receiving increasing attention owing to the potential application in the fields of catalysis, optics, sensors, magnetism and molecular recognition.[1,2] Compared with the extensively investigated transition metal coordination polymers, it is surprising to see the relatively small number of alkali earth coordination polymers in the literature.[3] The oxidation states and atomic radii of alkali earth metals are comparable with those of the late divalent transition metals, which could, in principle, lead to similar networks in the solid state. However, the lack of d-orbital electrons in alkali earth metals could result in coordination numbers greater than six, and for the larger alkali earth metals, a higher coordination number is expected.[4]

In addition, ligand selection is also an important factor which greatly influences the structure of the coordination architecture and the functionality of the complex formed.[5] As is well known, benzoic acid and its derivative with electron-withdrawing groups, such as nitro-, cyano- and halide,[6–8] have been extensively researched. However, there is not much information about metal derivatives of 4-formylbenzoic acid in the literature.[9] Recently, we have synthesized some transition metal complexes containing 4-formylbenzoic acid ligand,[10–14] in which the 4-FBA$^-$ ligand shows a variety of binding modes to metal ions (Scheme 1). Herein, we describe the synthesis, structure, ^{1}H NMR and ^{13}C NMR spectra, and thermal and luminescent properties of a novel two-dimensional Ba^{II} coordination polymer, $[Ba(4\text{-}FBA)_2(4\text{-}FBAH)]_n$, **I**, with the 4-FBA$^-$ ligands showing the $\eta^2:\eta^2:\mu_3$ and $\eta^1:\eta^1:\eta^2:\mu_3$ modes (Scheme 1). To our knowledge, **I** represents the first coordination polymer composed of 4-FBA$^-$.

EXPERIMENTAL

Physical measurements

All chemicals were of analytical reagent grade and used without further purification. Elemental analyses were performed on a Carlo Erba 1106 analyzer. The IR spectra were recorded in the range 4000–400 cm^{-1} on a Bruker Equinox 55 FT-IR spectrophotometer using KBr pellet. ^{1}H and ^{13}C NMR spectra were obtained in deuterated dimethyl sulfoxide (DMSO-d_6) with a Bruker AMX300 spectrometer, operated at 300.13 and 75.48 MHz, using TMS (tetramethlsilane) as

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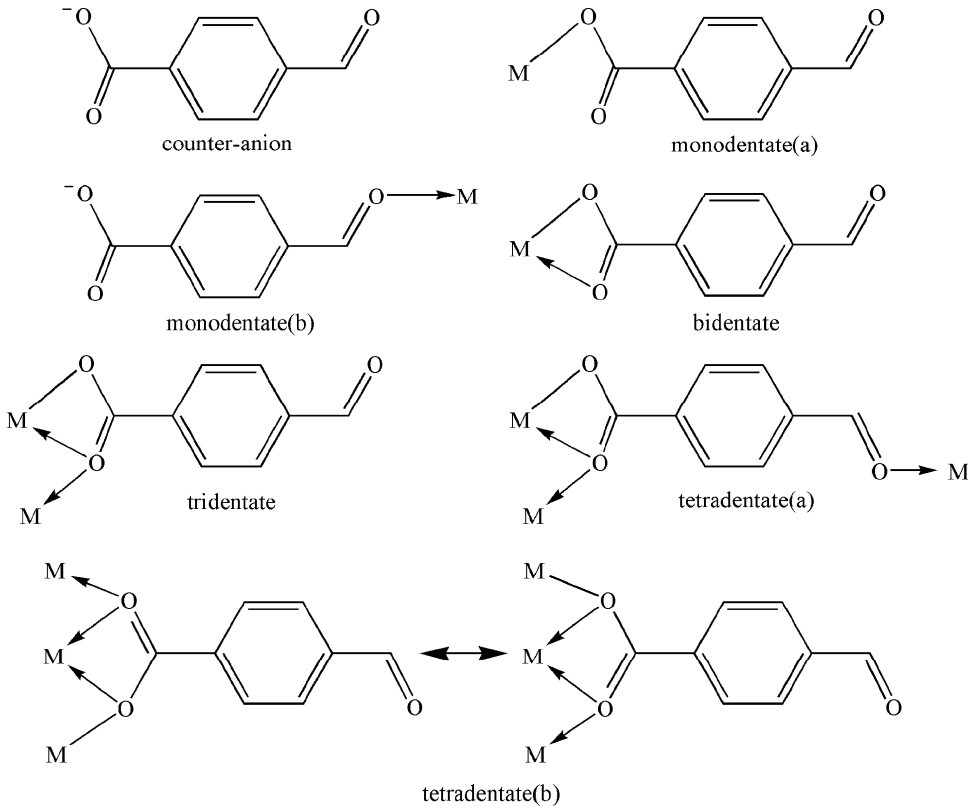

Scheme 1. The coordination modes of 4-FBA$^-$ ligands: tetradentate (a) $\eta^1 : \eta^1 : \eta^2 : \mu_3$; tetradentate (b) $\eta^2 : \eta^2 : \mu_3$.

standard. The thermogravimetry (TG) analyses were carried out on a Perkin Elmer TG/DTA 6300 thermal analyzer under flowing N_2 atmosphere, with a heating rate of 10 °C/min. Luminescence spectra were measured on an Perkin Elmer LS 55 luminance spectrophotometer. Crystallographic data were collected at 295 K on a Rigaku Raxis-Rapid diffractometer using Mo–K_α radiation ($\lambda = 0.71073$ Å). $C_{24}H_{16}O_9Ba$, $M =$ 585.71, monoclinic, $P2_1/c$, $a = 11.6039(3)$, $b = 26.3131(5)$, $c =$ 7.3092(2) Å, $\beta = 78.694(1)°$, $V = 2188.44(9)$ Å^3, $Z = 4$; 5001 unique data ($\theta = 27.5°$), 4614 data with $I \geq 2\sigma(I)$. $R = 0.031$, $wR = 0.094$; $\Delta\rho_{max} = 1.64$ e$^\bullet$ Å^{-3} (located near Ba). The structure resolution was carried out using the SHELXS-97 and SHELXL-97 programs.[15,16] Molecular graphics were obtained using ORTEP III.[17] CCDC reference number 642549 contains the supplementary crystallographic data for this paper.

Synthesis

An aqueous solution of barium carbonate (3.95 g, 20 mmol) was slowly added to an aqueous solution of 4-formylbenzoic acid (6 g, 40 mmol). The mixture was stirred for 30 min and then filtered. Colorless crystals were isolated from the filtered solution over several days in a yield of 69% based on barium. Anal. found: C, 49.17; H, 2.77. Calcd for $C_{24}H_{16}O_9Ba$: C, 49.22; H, 2.75%. IR (KBr, cm^{-1}): 3465s[ν(O–H)]; 1698s[ν(C═O)]; 1592s, 1405s[$\nu_{as}(COO^-) + \nu_s(COO^-)$].

RESULT AND DISCUSSION

Description of structure

Single-crystal X-ray analysis reveals that **I** has a two-dimensional lamellar structure; the molecular structure and atom labeling of **I** are shown in Fig. 1. The O8 atom of the neutral 4-FBAH species forms an intramolecular hydrogen bond with the $O5^{ii}$ atom of the 4-FBA$^-$ ligand. Each Ba(II) ion is nine-coordinated by eight O atoms from six deprotonated 4-FBA$^-$ ligands and one O atom from the terminal 4-FBAH ligand. The Ba–$O_{carboxyl}$ bond distances fall in the range 2.714(2)–3.046(2) Å, and the Ba–O_{formyl} (Ba1–$O6^{iii}$) distance of 2.851(3) Å is somewhat shorter than that of 2.885(2) Å in $[Ba(4\text{-}FBA)_2(H_2O)_7]$,[18] **II**, in which the Ba^{II} atom is also nine-coordinated by two formyl O atoms and seven water molecules. The carboxylate C–O bond lengths suggest delocalization of π-electron density over the CO_2^- groups.

In the two-dimensional coordination polymer, there are two coordination types of 4-FBA$^-$ ligands that are distinguished by their bridging towards Ba atoms (Fig. 2). On the one hand, adjacent Ba atoms are joined by the carboxylate groups in an $\eta^2 : \eta^2 : \mu_3$ mode to produce a one-dimensional chain, with a Ba···Ba distance of 4.234(2) Å. On the other hand, infinite chains are connected by the carboxylate groups in an $\eta^1 : \eta^1 : \eta^2 : \mu_3$ mode, generating an extended two-dimensional sheet structure parallel to (0 1 0); the adjacent Ba···Ba distance in this direction is 12.442(2) Å. Owing to the

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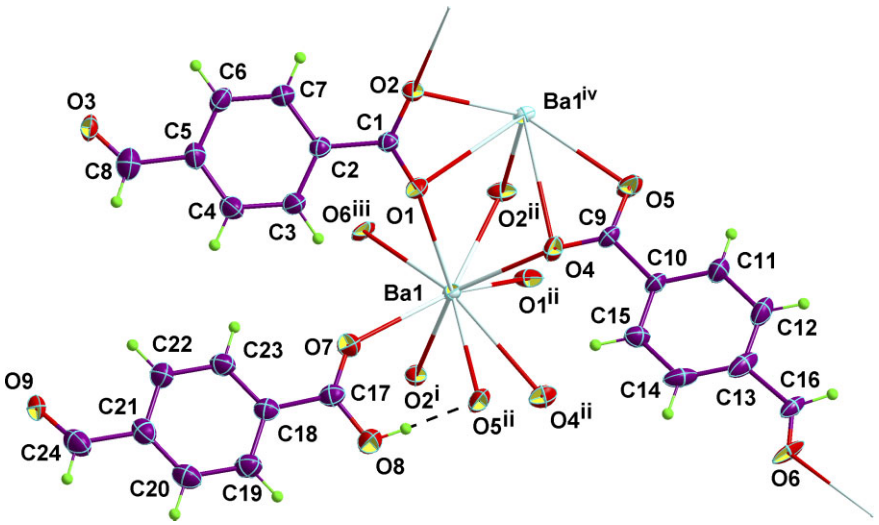

Figure 1. The coordination environments of the Ba^{II} atom in **I** (at 30% probability level). Selected bond distances (Å) and angles (deg): Ba1–O1, 2.757(2); Ba1–O1^{ii}, 2.899(2); Ba1–O2^{i}, 2.714(2); Ba1–O2^{ii}, 2.786(2); Ba1–O4, 2.754(2); Ba1–O4^{ii}, 3.046(2); Ba1–O5^{ii}, 2.778(2); Ba1–O6^{iii}, 2.851(3); Ba1–O7, 2.808(2); O1–Ba1–O4, 72.45(7); O1–Ba1–O2^{ii}, 72.66(7); O2^{ii}–Ba1–O4, 69.68(7); Ba1–O1–Ba1^{iv}, 96.90(7); Ba1–O2^{ii}–Ba1^{iv}, 100.66(7); Ba1–O4–Ba1^{iv}, 93.63(6). Symmetry codes: (i) x, y, $-1+z$; (ii) x, $3/2-y$, $-1/2+z$; (iii) $-1+x$, $3/2-y$, $1/2+z$; (iv) x, $3/2-y$, $1/2+z$. This figure is available in colour online at www.interscience.wiley.com/AOC.

distinct coordination modes, the 4-FBA$^-$ ligands connected adjacent Ba atoms to give rise to three Ba_2O_2 four-membered rings.

It is noteworthy that **I** is the first example of layer coordination polymer covalently constructed by 4-FBA$^-$ ligands, although some other metal complexes have been synthesized, and in all these complexes, the formyl group only coordinated to the Ba atom.[10–14,18]

FT-IR spectroscopy

The band of 1699 cm^{-1} is observed in IR spectra of the free 4-FBAH and assigned to ν(C═O) absorption of carbonyl group. For the title complex, this ν(C═O) absorption still exists at 1698 cm^{-1}, which indicated that there are uncoordinated C═O groups in **I**. The bands of 1592 and 1405 cm^{-1} are shown in IR spectra of the title complex and are related to $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$, respectively. The appearance of two medium intensity bands in the far-IR region 543 and 516 cm^{-1} can be attributed to Ba–O stretching vibrations, indicating the coordination of the metal through the oxygen atoms.[19] In addition, a strong and broad band has been observed at 3465 cm^{-1}, and assigned to ν(OH) absorption with the hydrogen bonds.

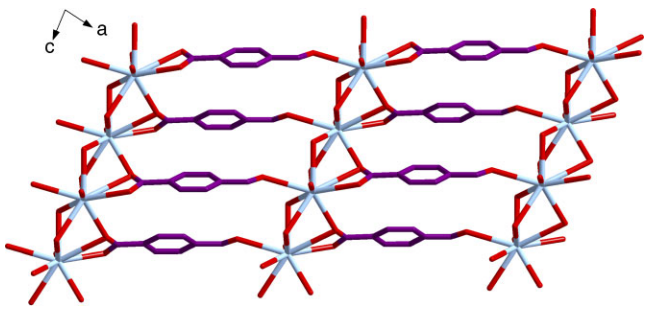

Figure 2. Perspective view of the two-dimensional framework of **I**. The terminal 4-FBA$^-$ and 4-FBAH ligands and the H atoms are omitted for clarity. This figure is available in colour online at www.interscience.wiley.com/AOC.

NMR spectroscopy

The NMR studies were carried out in DMSO-d_6, due to the low solubility of the compound in $CDCl_3$. In the ^{1}H NMR spectrum of the complex, the –COOH proton exhibited a broad singlet at δ 12.83 ppm while the –CHO proton exhibited a singlet at δ 10.05 ppm. The phenyl proton signals present four singlets at δ 8.14, 8.11 7.91 and 7.88 ppm. Regarding the ^{13}C NMR spectrum of the complex, it exhibited two signals at δ 193.53 and 170.34 ppm due to –CHO and –COOH carbon resonances, respectively. The signals at δ 142.46, 137.84, 130.25 and 129.40 ppm were assigned to the phenyl ring carbon resonances.

Thermal study

TG results show that there are two-step weight losses of **I** in N_2 atmosphere (Fig. 3). The first weight loss of 25.25% from 461 to 623 K corresponds to the release of the terminal 4-FBAH ligand (calcd 25.63%). Then the loss steps are observed continuously with the burning 4-FBA$^-$ ligands in the range of

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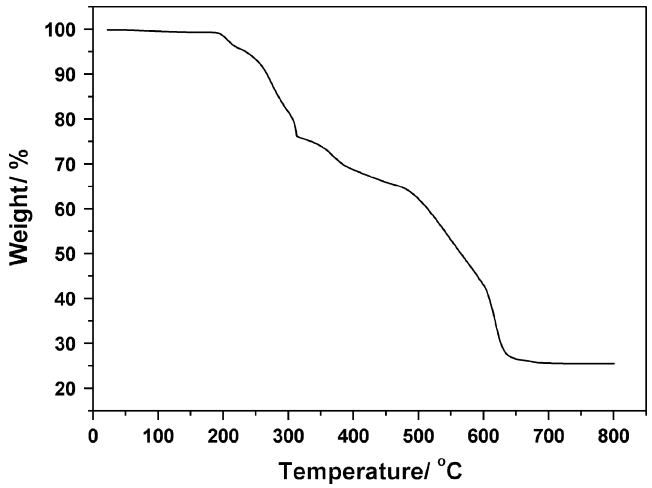

Figure 3. TG curve of complex **I**.

623–947 K. The final residual weight is 25.93% (calcd 26.18%), corresponding to BaO.

Fluorescent property

The luminescent properties of the free 4-formylbenzoic acid and the title complex were investigated in the solid state at room temperature (Fig. 4). Upon photoexcitation at 407 nm, the emission of **I** is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature, and can probably be assigned to the fluorescence from the intraligand emission excited state.[20–23] The most attractive luminescent behavior of **I** is that its high-dimensional condensed polymeric structure leads to significant enhancement of fluorescence intensity compared with the free 4-FBAH ligand at about 476 nm. The enhanced luminescence efficiency is therefore attributed to the chelation of the 4-FBAH ligands to barium ions that effectively increases the rigidity of the ligand and reduces the loss of energy via radiationless decay of the intraligand emission $^1(\pi-\pi^*)$ excited state.[24–26] Thus, results from the present investigation indicate that the complex **I** is capable of producing a blue light in electroluminescent devices.

SUMMARY

In summary, we have successfully constructed a novel two-dimensional Ba(II) polymer, in which nine-coordinated Ba(II) polyhedrons are joined by 4-FBA$^-$ ligands with the $\eta^2:\eta^2:\mu^3$ and $\eta^1:\eta^1:\eta^2:\mu^3$ modes to form a lamellar structure. Its strong blue fluorescent emission of $\lambda_{max} = 476$ nm shows that it may be promising as an optoelectronic device.

Acknowledgments

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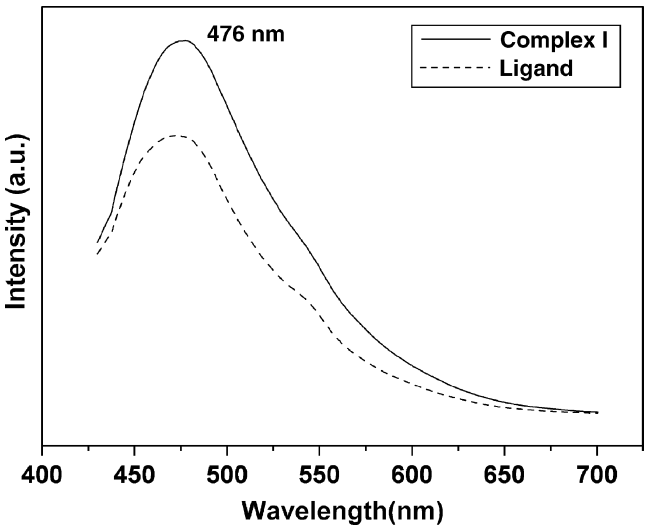

Figure 4. The emission spectrum of **I** measured in solid state at room temperature.

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