

A novel sheet 4f–3d mixed-metal pyridine dicarboxylate: synthesis, structure, photophysical properties and its transformation to a perovskite oxide†

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The synthesis, characterization and photophysical properties of a 4f–3d mixed metal compound, $\text{Gd}(\text{H}_2\text{O})_3\text{Co}[\text{C}_5\text{N}_1\text{H}_3\text{-(COO)}_2]_3$, are described; the structure is unique, consisting of sheets with large pores (ca. 7 Å diameter) in the sheets and transforms to a perovskite oxide at moderate temperatures.

The growing interest among chemists, physicists and materials scientists to exploit the opportunity to create novel functional materials that combine the stability of the inorganic (extended) and the functionalities of the organic (finite/molecular) entities resulted in new types of compounds in the area of hybrid solids.¹ One of the important developments is the molecular-building block approach, which has been employed extensively by many groups in the design and synthesis of metal–organic frameworks (MOF).^{2–4} Active research during the last few years have given rise

to a spectacular variety of new hybrid compounds with porous structure and interesting properties.^{5–8} Much of this work belongs to the 3d block elements. Mixed metal molecular complexes containing 3d and 4f elements have been studied during the last two decades or so for their interesting interplay of magnetism.^{9–12} There have been some attempts at the preparation of mixed metal hybrid extended structures, especially those belonging to the 4f–3d systems.^{13–16} The synthesis of 4f–3d mixed metal systems with framework structures would be a challenge as the variable coordination preferences of the 4f elements would hinder their introduction into a highly ordered structure. We have been interested in the study of the compounds based on 4f–3d elements

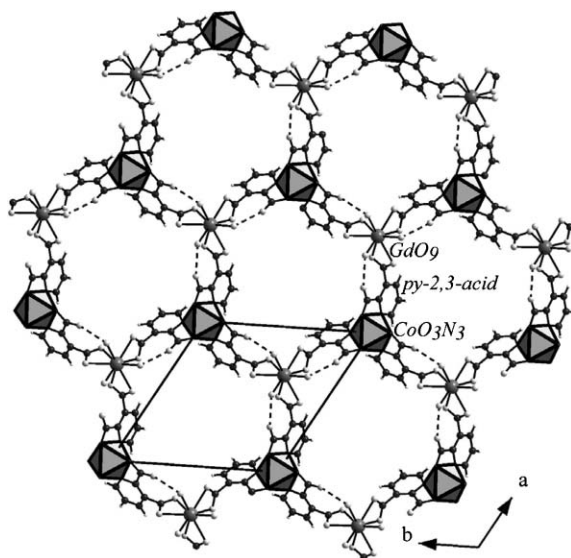


Fig. 1 View of the structure of I in the *ab* plane showing the porous layer. Dotted lines represent possible hydrogen bond interactions.

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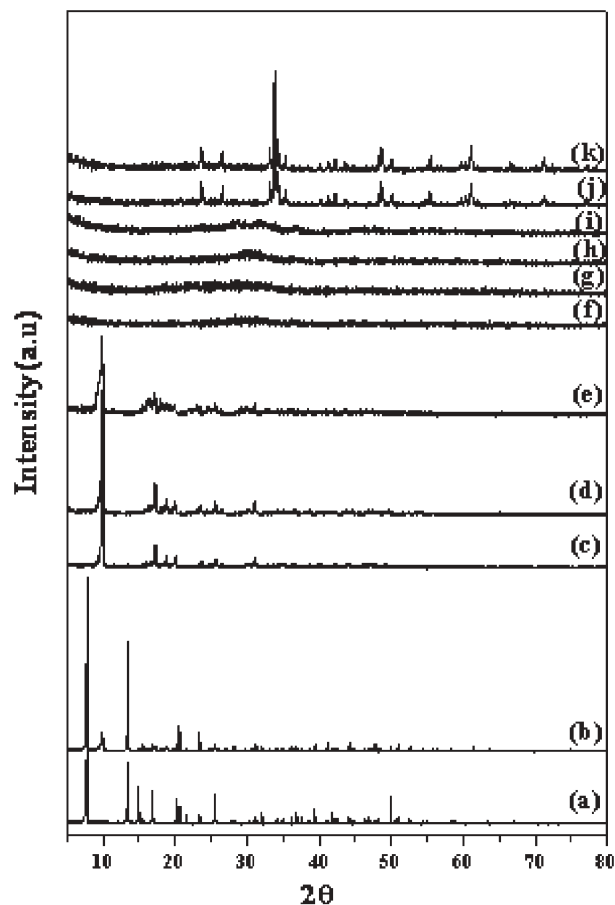


Fig. 2 XRD of I at various temperatures in °C (a) 25, (b) 150, (c) 175 (d) 200 (e) 250 (f) 350 (g) 400 (h) 500 (i) 600 (j) 700 (k) 800.

to understand the electronic effects and to probe the decomposition behaviour as it is likely to give rise to interesting new mixed-metal oxides that would, probably, be difficult to prepare using conventional methods. Our efforts have been successful and we have now prepared a new series of 3d–4f compounds of the general formula, $\text{Gd}(\text{H}_2\text{O})_3\text{Co}[\text{C}_5\text{N}_1\text{H}_3(\text{COO})_2]_3$, **I**. The compound, on heating at 700 °C, decomposes to give a finely dispersed GdCoO_3 perovskite oxide. In this communication, we present the synthesis, structure and photophysical properties of this unusual solid.

Compound **I** was synthesized employing hydrothermal methods and its structure determined using single crystal X-ray diffraction.† The structure comprises a network of GdO_9 and CoO_3N_3 polyhedral units connected through the pyridine-2,3-dicarboxylate anions. The Gd^{3+} ions are surrounded by nine oxygens, of which three are terminal water molecules, to form a tricapped trigonal prismatic coordination arrangement and the Co^{3+} ions are octahedrally coordinated by three oxygen and three nitrogen atoms. The connectivity between the polyhedral units and the dicarboxylate anions gives rise to a two-dimensional layered structure with large apertures bound by 12-membered rings (3GdO_9 , $3\text{CoO}_3\text{N}_3$ and six pyridine dicarboxylates) (Fig. 1). The

layers are arranged in a $AAAA\cdots$ fashion, giving rise to a solid with a supermesh of apertures of *ca.* 7 Å free diameter. The water molecules, bound to Gd, take part in strong hydrogen bonding with the neighbouring oxygens ($\text{O}\cdots\text{O}$ distance = 2.85 Å). Such is the disposition of the water molecules within the apertures that there appears to be specific sites in the walls of the apertures that are hydrophilic.

The thermal stability of **I** was investigated using thermogravimetric analysis in the temperature range 30–800 °C. The studies indicate that the three water molecules, bound to Gd leave about 200 °C. In order to understand the importance of the bound water molecules for the structural integrity, we have heated **I**, *ex situ*, in air at varying temperatures and followed the decomposition process using powder X-ray diffraction studies (XRD). In addition, this would also give an idea about the nature of the products of decomposition of **I**. The results are shown in Fig. 2. As can be noted, the removal of water molecules brings about a change in the structure of **I**, which unfortunately appears to be irreversible. On heating the sample further, the pyridine dicarboxylate is removed and the material turns amorphous at 350 °C. Further heating of **I** gives rise to a weakly crystalline phase at

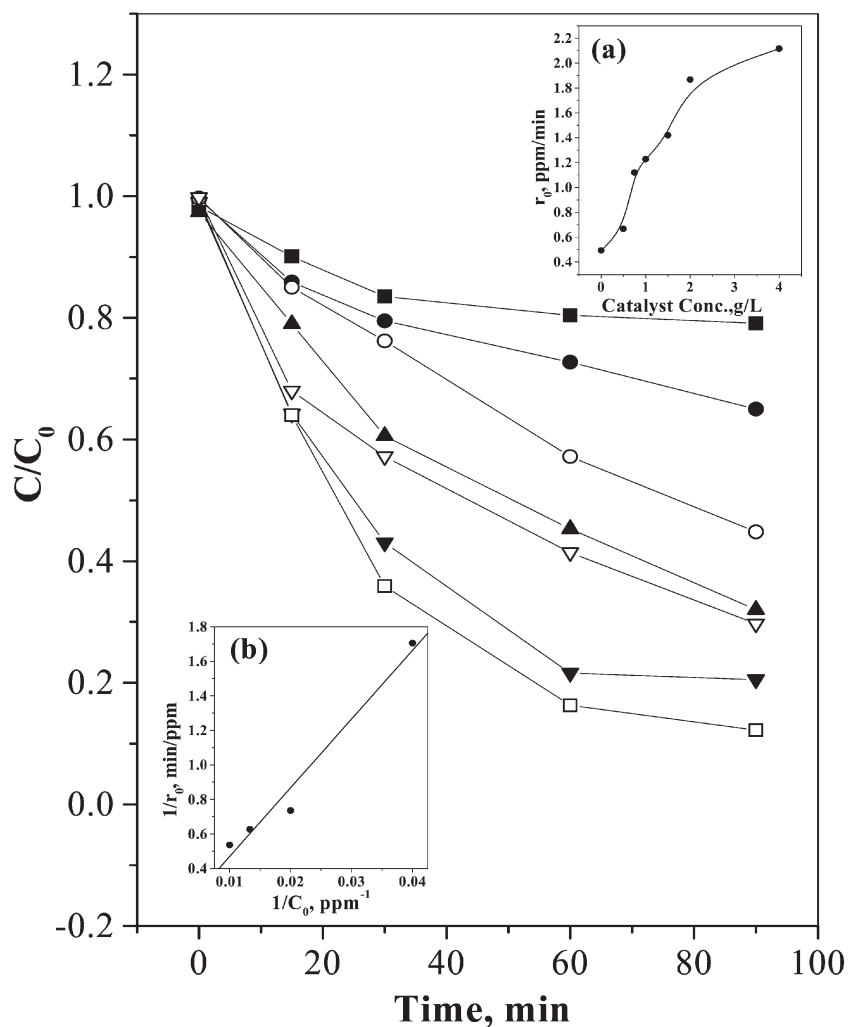


Fig. 3 Degradation profiles for 100 ppm RBBR without **I** (■), with 0.5 g L⁻¹ (●), 1 g L⁻¹ (▲), 1.5 g L⁻¹ (▼), 2 g L⁻¹ (▼), 4 g L⁻¹ of **I** (□), with 1 g L⁻¹ of Degussa P-25 (○). Inset (a) Variation of the degradation rate with catalyst concentration. (b) Linear variation of the initial rate with the initial concentration of RBBR.

600 °C, and to a good crystalline compound at 700 °C identified as a simple perovskite oxide, GdCoO₃. The formation of GdCoO₃ at this low temperature is really intriguing, considering that a routine ceramic method generally employs temperatures >1200 °C for the preparation of perovskite oxides. It is likely that the strictly alternating arrangement of Gd and Co in **I** (1 : 1 ratio of Gd/Co) might have helped in the formation of the perovskite oxide, by acting as a precursor. Precursor routes for the preparation of perovskite oxides have been discussed before.¹⁷

The photocatalytic activity of hybrid compounds containing f-electron systems are just beginning to emerge.¹⁴ In this regard, we wanted to explore other hybrid structures as potential photocatalysts for degrading organic substrates. For this, we have selected an N-containing dye, Remazol brilliant blue R (RBBR) as a model textile organic pollutant in aqueous media to demonstrate the photocatalytic effectiveness of **I**.¹⁸ The photocatalytic performance of **I** was estimated from the variation of the colour in the reaction system by monitoring the absorbance (at $\lambda = 590$ nm) characteristics of the target RBBR, which directly relates to the structural change of its chromophore. For comparison, the photocatalytic performance of commercial TiO₂ (Degussa P-25) was also assessed under the same experimental conditions. Control experiments without the catalyst were also carried out. The degradation profiles of RBBR with an initial concentration of 100 ppm for different concentrations of **I** varying from 0.5 kg m⁻³ to 4 kg m⁻³ are shown in Fig. 3. The variation of initial rate with the loading of **I** for the degradation of RBBR is shown in inset (a) of Fig. 3. As can be noted, the initial rate of degradation increases with an increase in the concentration of RBBR, but appears to saturate at a catalyst loading of 2 kg m⁻³. This loading of the catalyst was used to investigate the degradation of RBBR of different concentrations (inset (b) of Fig. 3). In order to quantify the reactions, the kinetics can be determined by Langmuir–Hinshelwood (L–H) kinetics written as $1/r_0 = (1/k_0C_0) + (K_0/k_0)$, where r_0 is the initial rate, C_0 is the initial concentration of RBBR, k_0 is the kinetic rate constant and the parameter K_0 represents the equivalent adsorption equilibrium coefficient. The parameters for the photocatalytic degradation of RBBR, k_0 and K_0 , obtained from the slope and intercept of the linear plot of the initial degradation rate ($1/r_0$) with the reciprocal of the initial RBBR concentration ($1/C_0$) (inset (b)) are 0.02514 min⁻¹ and 0.0018 ppm⁻¹, respectively. As K_0 represents the adsorption equilibrium coefficient, the low value of K_0 can be attributed to negligible adsorption. This is also confirmed by powder XRD of the catalyst after the photocatalytic degradation experiments, which clearly indicated that the structure remains the same and no adsorption is observed. In addition, the photocatalytic activity of **I** appears to be higher than that of the commercial TiO₂ (Fig. 3). Although, a more detailed mechanism is yet to be elucidated, it is likely that the water molecules attached to the rare-earth ions play an important role.

In conclusion, the synthesis, structure and the photophysical properties of a new 3d–4f hybrid compound has been accomplished. We anticipate that the successful synthesis of **I** and its photocatalytic activity along with the formation of a perovskite oxide at a reasonable temperature, may help in the design and exploitation of new hybrid compounds for other useful applications.‡

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Notes and references

‡ A mixture of Gd(NO₃)₃ (0.343 g, 1 mM), Co(OAc)₂·4H₂O (0.252 g, 1 mM) and pyridine-2,3-dicarboxylic acid (0.338 g, 2 mM) were dissolved in 14 ml of water and heated at 140 °C for 72 h under autogeneous pressure to result in large quantities of dark pink rod like crystals (yield = 70%). An EDAX analysis on many single crystals revealed a Gd : Co ratio of 1 : 1. C, H, N analysis: obsd. (calcd.) C = 33.15 (33.93)% N = 5.61 (5.49)% H = 2.11 (1.96)%. The compound was characterized by powder XRD, IR, UV-Vis, photoluminescence and magnetic studies. The structure was determined by single crystal XRD using Siemen's SMART-CCD system. The structure was solved and refined using the SHELXTL-PLUS suite of programs.¹⁹ All the hydrogen atoms of the carboxylic acids were initially located in the difference Fourier maps and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The hydrogen atoms of the bonded water molecules were not located in the difference Fourier maps. Crystal data for **I**: C₂₁H₁₅N₃O₁₅GdCo, $M = 765.168$, trigonal, space group $P3$, $a = 13.1879(2)$, $c = 5.9291(1)$ Å, $V = 893.04(2)$ Å³, $Z = 1$, $T = 293(2)$ K, $D_c = 1.401$ Mg m⁻³, $\mu(\text{Mo-K}\alpha) = 2.363$ mm⁻¹, 3745 data, 1689 unique ($R_{\text{int}} = 0.045$), 125 parameters and 1 restraint. Final R_1 and wR_2 (all data) = 0.041 and 0.1066, and $S = 1.142$. CCDC 277358. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b509588c

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