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Inorganic–organic hybrid compounds exhibiting both magnetic order and non-linear optical properties

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1. Introduction

Hybrid inorganic-organic framework compounds constitute an important class of materials that has been studied extensively over the last few years due to potential applications in catalysis, gas separation and storage [1-3]. Other properties which draw attention to these materials include magnetic, optical and electronic properties [4,5]. Recently a few hybrid compounds with ferroelectric properties have been reported, exhibiting ferroelectric hysteresis at room temperature [6,7]. For example, $\{(HQA)(ZnCl_2)(2.5H_2O)\}_n$ (HQA = 6-methoxyl-(8S,9R)cinchonan-9-ol-3-carboxylic acid) is a one-dimensional compound crystallizing in the non-centrosymmetric, polar space group P1 with a high dielectric constant [8]. Although the magnetic, optical and electronic properties of hybrid materials are of considerable interest, there are very few studies on these aspects, particularly on paired properties. Of great current interest are hybrid compounds possessing multiferroic properties [9]. Known examples of such materials are $[Mn_3(HCOO)_6](C_2H_5OH)$ which exhibits a ferroelectric transition at 165 K and a ferrimagnetic transition at 8.5 K, [10] and the enantiomorphous chiral complexes $[Cu(R)-hmp^*(dca)]_n$ and $[Cu(S)-hmp^*(dca)]_n$

ABSTRACT

Hybrid organic–inorganic framework compounds constitute an important class of materials whose properties, especially paired ones, have not been adequately investigated hitherto. In this communication, we report the non-linear optical properties of hybrid compounds exhibiting interesting magnetic properties.

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 $(hmp^* = R-methyl-2-pyridinemethanol)$, which are reported to be antiferromagnetic and ferroelectric [11]. $(Lig)_2Tb(H_20)_2ClO_4$ (lig = L-lactate), which crystallizes in the polar space group C2, also appears to exhibit interesting ferroic properties [12]. The present work explores hybrid materials that show long range magnetic order combined with non-linear optical (NLO) properties such as second harmonic generation (SHG).

Although SHG is reported in a few hybrid compounds, the coexistence of NLO properties with magnetic properties is not common. We have, therefore, investigated the properties of several hybrid framework compounds containing transition metal ions and crystallizing in non-centrosymmetric space groups. All the compounds are 3-D coordination polymers having $I^0 O^3$ (I, inorganic and O, organic) connectivity [3]. Specifically, we have examined the properties of $[Co_3(2,6-NDC)_3(bipy)_{1.5}]$, (NDC = napahathalenedicarboxylate, bipy = bipyridine), I and $[Ni_3(2,6-NDC)_3(bipy)_{1,5}]$, II, which are reported [13] to be non-centrosymmetric with the space group C2. The magnetic and non-linear optical properties of I and II have not been reported previously. We have also studied the NLO properties of [Mn(1,4 BDC)(1,10 Phen)] (BDC = benzenedicarboxylate, Phen = phenanthroline), **III**, which is reported to crystallize in the non-centrosymmetric polar space group Cc and order antiferromagnetically [14]. Finally, we have measured the NLO properties of { $[Ni(C_4H_4O_5)(H_2O)] \cdot H_2O$ }, **IV**, which is reported to be ferromagnetic [15], with a polar space group, Cc. We have found that three of the compounds, I-III, exhibit NLO properties in combination with



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Fig. 1. Temperature variation of the magnetization of I at 1000 Oe showing the ZFC and FC data.

interesting magnetic properties. We consider this observation to be of interest.

2. Experimental section

 $[{\rm Co}_3(2,6-{\rm NDC})_3({\rm bipy})_{1.5}]$, I, was prepared by taking a mixture of ${\rm Co}({\rm NO}_3)_2 \cdot 6{\rm H}_2{\rm O}$ (0.100 g, 0.344 mmol), 2,6-NDCH₂ (0.025 g, 0.115 mmol), bipy (0.054 g, 0.344 mmol), benzene (1.53 ml, 17.18 mmol), and H₂O (6 ml, 0.333 mol) in the molar ratio of 3:1:3:150:2900 and heating at 180 °C for 3 days. The black crystalline product of $[{\rm Co}_3(2,6-{\rm NDC})_3({\rm bipy})_{1.5}]$ was collected by filtration.

To prepare $[Ni_3(2,6-NDC)_3(bipy)_{1.5}]$, **II**, a mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (0.135 g, 0.403 mmol), 2,6-NDCH₂ (0.100 g, 0.403 mmol), bipy (0.072 g, 0.403 mmol), and H₂O (6.0 ml, 0.333 mol) in the molar ratio of 1:1:1:600 was heated in a 23-ml capacity Teflon-lined reaction vessel at 180 °C for 2 days and then cooled to room temperature. The green crystalline product was collected by filtration using, H₂O (10 ml), ethyl alcohol (15 ml), and acetone (10 ml).

[Mn(1,4-BDC)(1,10 Phen)], **III**, was prepared starting with the mixture of $MnCl_2 \cdot 4H_2O$ (0.1 g, 0.5 mmol), 1,4-dicyanobenzene (0.07 g, 0.5 mmol), 1,10-phenanthroline (0.1 g, 0.5 mmol) and H_2O (16 ml) in the molar ratio of 1 : 1 : 1 : 1777 sealed in a 23 ml capacity Teflon-lined reaction vessel and heated 170 °C for 72 h. The prism-shaped yellow crystals were collected by filtration.

{[Ni(C₄H₄O₅)(H₂O)] \cdot H₂O}, **IV**, was prepared from a mixture of nickel(II) acetate tetrahydrate (0.30 g, 1.5 mmol), malic acid (0.20 g, 2.1 mmol), 4,4-bipyridine dihydrate (0.10 g, 0.7 mmol), KOH (0.9 g 2.24 mmol), distilled water (7 ml) and anhydrous ethyl alcohol (7 ml). The mixture was stirred for 1 h and then heated under autogenous pressure at 160 °C for three days in a 23 ml Teflon-lined stainless steel vessel and finally cooled to room temperature. Purplish-red crystals were filtered, washed with distilled water and dried at ambient temperature.

Magnetic measurements were carried out with a vibrating sample magnetometer in a PPMS instrument (Quantum Design). We also measured the second order nonlinear optical intensity relative to KDP (Kurtz powder test) by employing a pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm with a pulse width 8 ns and repetition rate of 10 Hz and beam energy of 2.2 mJ/pulse. The backward scattered SHG light was collected using a spherical concave mirror and passed through a Czerny–Turner monochromator which transmits only 532 nm radiation.



Fig. 2. Magnetic hysteresis for I and II at 5 K.



Fig. 3. Temperature variation of the magnetization of **II** at 100 Oe showing the ZFC and FC data. Inset shows magnetization vs. temperature plot at 1000 Oe.

3. Results and discussion

The temperature-dependence of the magnetization of **I** (Fig. 1) shows divergence between the field-cooled (FC) and zero-field-cooled (ZFC) data (at 1000 Oe). This behavior, also found at a field of 100 Oe, is similar to that of a spin glass or a frustrated magnetic system. **I** exhibits magnetic hysteresis at low temperatures (<150 K). In Fig. 2(a) we show the hysteresis curve at 5 K. We see that the magnetization approaches saturation and the values of the remnant magnetization and coercive field are 0.339 emu/g and 5500 Oe, respectively. From the high-temperature inverse-susceptibility data recorded at 1000 Oe, we estimate the Curie–Weiss temperature of **I** to be -300 K, suggesting dominant antiferromagnetic exchange interactions.

In Fig. 3, we show the temperature-dependence of the magnetization of **II** (at 100 Oe). **II** also exhibits divergence in the FC and ZFC data and shows a peak in magnetization at low

temperatures. This peak disappears when the data are recorded at 1000 Oe, as can be seen from the inset of Fig. 3. Compound **II** exhibits some magnetic hysteresis at low temperatures (Fig. 2(b)), with small values of the remnant magnetization and coercive field (0.0027 emu/g and 210 Oe respectively). We also notice from Fig. 2(b) the absence of a tendency for saturation. The magnetic behavior of **II** can be considered to be that of a weak canted antiferromagnet at low temperatures.

We have measured the second harmonic generation activity of compounds I–IV. The SHG activity of $[Co_3(2,6-NDC)_3(bipy)_{1.5}]$, I, is 42% with respect to potassium dihydrogen phosphate (KDP), while in the case of $[Ni_3(2,6-NDC)_3(bipy)_{1.5}]$, II, it is 1.4% with respect to KDP. [Mn(1,4-BDC)(1,10Phen)], III, is an antiferromagnet ($T_N = 15$ K) and we find that the SHG activity of this compound is 23% with respect to KDP. The ferromagnetic nickel malate, IV, shows a SHG activity of only 0.5% with respect to KDP.

4. Conclusions

In conclusion, we find significant SHG activity in the three of the hybrid compounds **I–III.** All these three NLO compounds, exhibit dominant antiferromagnetic interactions. They do not show dielectric anomalies or hysteresis in the temperature range 30–300 K. The ferromagnetic compound **IV** does not posses significant SHG activity. The observation of NLO activity in hybrid compounds exhibiting long-range magnetic order is of interest and suggests that it may be possible to find multiferroic hybrid compounds as well.

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References

- [1] A.K. Cheetham, C.N.R. Rao, Science 318 (2006) 58.
- [2] A.K. Cheetham, C.N.R. Rao, R.K. Feller, Chem. Comm. 4780 (2006).
- [3] C.N.R. Rao, S. Natarajan, R. Vaidhyanathan, Angew. Chem. Int. Ed. 43 (2004) 1466.
- [4] C.N.R. Rao, A.K. Cheetham, A. Thirumurugan, J. Phys.: Condens. Matter 20 (2008) 083202.
- [5] S. Kitagawa, R. Kitaura, S. Noro, Angew. Chem. Int. Ed. 43 (2004) 2334.
- [6] P. Jain, N.S. Dalal, B.H. Toby, H.W. Kroto, A.K. Cheetham, J. Am. Chem. Soc. 9 (2008) 130.
 [7] Q. Ye, Y.M. Song, G.X. Wang, K. Chen, D.W. Fu, P.W.H. Chan, J.S. Zhu, S.D. Huang,
- [7] Q. Fe, F.M. Song, G.A. Wang, K. Chen, D.W. Fu, F.W. H. Chan, J.S. Zhu, S.D. Huang, R.G. Xiong, J. Am. Chem. Soc. 128 (2006) 6554.
- [8] Y.Z. Tang, X.F. Huang, Y.M. Song, P.W.H. Chan, R.G. Xiong, Inorg. Chem. 45 (2006) 4868.
- [9] C.N.R. Rao, C.R. Serrao, J. Mater. Chem. 17 (2007) 4931.
- [10] H.B. Cui, Z. Wang, K. Takahashi, Y. Okano, H. Kobayashi, A. Kobayashi, J. Am. Chem. Soc. 128 (2006) 15074.
- [11] Z.G. Gu, X.H. Zhou, Y.B. Jin, R.G. Xiong, J.L. Zuo, X.Z. You, Inorg. Chem. 46 (2007) 5462.
- [12] Q. Ye, D.W. Fu, H. Tian, R.G. Xiong, P.W.H. Chan, S.D. Huang, Inorg. Chem. 47 (2008) 77.
- [13] S.W. Lee, H.J. Kim, Y.K. Lee, K. Park, J.H. Son, Y.U. Kwon, Inorg. Chim. Acta 353 (2003) 151.
- [14] D. Sun, R. Cao, Y. Liang, Q. Shi, W. Su, M. Hong, J. Chem. Soc. Dalton Trans. 2335 (2001).
- [15] F.T. Xie, L.M. Duan, J.Q. Xu, L. Ye, Y.B. Liu, X.X. Hu, J.F. Song, Eur. J. Inorg. Chem. 4375 (2004).