Synthetic Metals 199 (2015) 232–240

Contents lists available at ScienceDirect

Synthetic Metals

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

Syntheses, crystal structures, weak interaction, magnetic and luminescent properties of two new organic–inorganic molecular solids with substituted chlorobenzyl triphenylphosphinium and tetra (isothiocyanate)cobalt(II) anion

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ARTICLE INFO

Article history:
Received 22 September 2014
Received in revised form 10 November 2014
Accepted 12 November 2014
Available online 18 December 2014

Keywords:
Tetra(isothiocyanate)cobalt(II) anion
Crystal structures
Weak interactions
Magnetic properties
Luminescent properties

ABSTRACT

Two new organic–inorganic molecular solids of tetra(isothiocyanate)cobalt(II) dianion and meta-substituted benzyl triphenylphosphinium, [2ClBzTPP]$_2$[Co(NCS)$_4$] (**1**) and [4ClBzTPP]$_2$[Co(NCS)$_4$] (**2**) ([2ClBzTPP]$^+$ = 1-(2′-chlorobenzyltriphenylphosphonium) and [4ClBzTPP]$^+$ = 1-(4′-chlorobenzyltriphenylphosphonium), were prepared and characterized by elemental analysis, FT-IR, UV–vis spectra, ESI-MS and single crystal X-ray diffraction method. Both **1** and **2** crystallize in monoclinic, and the Co(II) ion of the [Co(NCS)$_4$]$^{2-}$ anion shows a distorted tetrahedral coordination geometry. The C—H···Cl, C—H···S hydrogen bonds were found in **1** while C—H···S, C—H···Co, p···π, C—H···π interactions were found in **2** consolidating the stacking of the crystal. Magnetic susceptibility measurement in the temperature range 2–300 K shows that **1** and **2** exhibit a weak antiferromagnetic coupling behavior. Upon excitation at 268 nm, two molecular solids show the luminescent emission peak in the UV-light region in the solid state at room temperature.

1. Introduction

Inorganic complex anions with versatile ligands NCS$^-$ (NCS = isothiocyanate), CN$^-$ (CN = cyano group) and SCN$^-$ (SCN = thiocyanate) have been widely used in the design of organic–inorganic hybrid materials because they have a fascinating structural diversity and may coordinate to metal ions in a number of ways, as terminal ligands or as bridges [1,2]. Those ions can act as a bridging ligand between two metal atoms in end-to-end or end-on coordination modes and the former support an antiferromagnetic interaction while the latter support a ferromagnetic interaction [2–4]. So far a wide range of those various 1D, 2D or 3D structures molecular solids containing [M(NCS)$_4$]$^{2-}$ (M = Mn^{2+}, Co^{2+}, Zn^{2+}), [M(CN)$_6$]$^{n-}$ (M = Co^{3+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Mn^{3+}, n = 3 or 4) have been found and studied [5–10]. It is proven that some weak interactions including non-covalent interactions such as weak p···π/π···π stacking interactions and H-bonding interactions often play an important role in the construction of these molecular materials [9,11–13]. Particularly, the NCS$^-$ ligand has been widely used not only because it can act as bridging ligand and provide a super exchange pathway for magnetic interaction between metal atoms but also because it can coordinate through either nitrogen or sulfur atoms, and more easily formed the weak intermolecular interactions to construct a supra-molecular network [8,9,14–18]. Recent interest in the synthesis of [RBzTPP]$^+$ (R = H, F, Cl, Br, I, NO$_2$, CN, etc. BzTPP = benzyl triphenylphosphinium), originates from wide prospects in their potential applications in hybrid materials. But the literature covering the organic–inorganic hybrid materials containing tetra(isothiocyanate)cobalt(II) anion and substituted benzyl triphenylphosphinium are scarcer. In recent years, our research group has used [RBzTPP]$^+$ (R = H, F, Cl, Br, I, NO$_2$ or CN) as the counter cation and the self-assembly [Co(NCS)$_4$]$^{2-}$ anion to obtain some interesting molecular materials such as [BzTPP]$_2$[Co(NCS)$_4$], [3BrBzTPP]$_2$[Co(NCS)$_4$], [3CNBzTPP]$_2$[Co(NCS)$_4$], [4FBzTPP]$_2$[Co(NCS)$_4$], [4BrBzTPP]$_2$[Co(NCS)$_4$], [4NO2BzTPP]$_2$[Co(NCS)$_4$] [19–21]. Consequently, we have found that the change of the substituted group on the phenyl ring of benzyl group of the cation results in the changes of the crystal system, space group, weak interactions, the stacking mode of the anions and cations, and the magnetic properties. As part of our continuing studies, in

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http://dx.doi.org/10.1016/j.synthmet.2014.11.021
0379-6779/

this paper, two new organic–inorganic molecular solids of [Co$(NCS)_4]^{2-}$ anion and substituted chlorobenzyl triphenylphosphinium, $[2ClBzTPP]_2[Co(NCS)_4]$ (**1**) and $[4ClBzTPP]_2[Co(NCS)_4]$ (**2**) were prepared and characterized by elemental analysis, FT-IR, UV–vis spectra, ESI-MS and single crystal X-ray diffraction. Additionally, some weak interactions, magnetic properties and luminescent properties of **1** and **2** were investigated.

2. Experimental

2.1. General materials and physical measurements

Cobalt dichloride hexahydrate, triphenylphosphine, potassium thiocyanate, 2-chlorobenzyl bromide, 4-chlorobenzyl bromide and all other reagents from commercial sources were of analytical reagent and used without further purification. 1-(2′-Chlorobenzyl) benzyltriphenylphosphonium bromide ([2ClBzTPP]Br) and 1-(4′-chlorobenzyl) triphenylphosphonium bromide ([4ClBzTPP]Br) were synthesized following the literature procedures [22]. Elemental (C, H, N) microanalyses were performed on a Model 240 PerkinElmer elemental analyser. IR spectra were recorded in 400–4000 cm^{-1} range on a Nicolet FT-IR spectrophotometer as KBr pellets. UV–vis spectra in MeCN in the region of 220–800 nm were obtained by Shimadzu UV-2500 spectrophotometer. The electrospray mass spectra [ESI-MS] were determined on a ThermoFisher TSQ Quantum Ultra LC–MS spectrometer. The X-ray powder diffraction (PXRD) measurements were carried out on a PERSEE XD-2 diffractometer using CuKα radiation ($\lambda = 1.5406$ Å).

2.2. Syntheses of *1* and *2*

A methanol solution (15 mL) of KSCN (389 mg, 4 mmol) was added to a methanol solution (15 mL) of $CoCl_2\cdot 6H_2O$ (238 mg, 1 mmol) and the mixture was stirred for 45 min at room temperature, then 30 mL methanol solution of [2ClBzTPP]Br (935 mg, 2.0 mmol) was dropped to the mixture, cooled down after another 1.5 h when all the [2ClBzTPP]Br was added. The product was collected via filtration, wasted with cool methanol and diethyl ether, and air-dried. Yield: 78%. *Anal.* Calc. for $C_{54}H_{42}Cl_2N_4CoP_2S_4$: C, 60.78; H, 3.96; N, 5.25; Found: C, 60.54; H, 4.11; N, 5.16%. ESI-MS (MeCN): 387.2, $[2ClBzTPP]^+$. IR (cm^{-1}): 3045, 2912, 2075, 1591, 1474, 1437, 1389, 1316, 1110, 994, 831, 748, 721, 687, 596, 526. UV–vis spectrum (nm): 268, 317, 623.

The procedure for preparing **2** is similar to that for **1**. Yield: 79.3%. *Anal.* Calc. for $C_{54}H_{42}Cl_2N_4CoP_2S_4$: C, 60.78; H, 3.96; N, 5.25; Found: C, 60.66; H, 4.15; N, 5.12%. ESI-MS (MeCN): 387.2, $[4ClBzTPP]^+$. IR (cm^{-1}): 3057, 2927, 2895, 2071, 1584, 1484, 1437, 1408, 1394, 1112, 997, 840, 740, 720, 689, 646, 536. UV–vis spectrum (nm): 267, 318, 623.

2.3. X-ray single-crystal analysis

Blue–green single crystals suitable for the X-ray structure analysis were obtained by evaporating the solution of **1** and **2** in MeOH about three weeks at room temperature. Diffraction data were performed at 291 K with a Bruker Smart APEX CCD diffractomer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and operating in ω-φ scan mode. Cell parameters of **1** and **2** were obtained and refined using the SAINT [23] program. The structures were solved by direct methods using the SHELXS-97 [24] program. Atom positions were refined using the SHELXL-97 [25] program with anisotropic displacement parameters for all non-H atoms. All H atoms were located on a Fourier difference map. Aromatic carbons were refined with $U_{iso}(H) = 1.2\ U_{eq}\ C(sp^3)$ and the methylene group with $U_{iso}(H) = 1.5\ U_{eq}\ C(sp^2)$. Crystal data, data collection and refinement details for **1** and **2** are given in Table 1. Selected bond parameters for **1** and **2** are listed in Tables 2 and 3.

2.4. Magnetic measurements

Temperature-dependent magnetic susceptibilities were determined in a field of 2000 Oe and in the range of 2.0–300 K on a Quantum Design MPMS-XL SQUID magnetometer. Samples for magnetic data collection were prepared by finely grinding single crystals into a powder and packing the powder into a gelatin capsule, and the weights of the samples used for experiments are 46.81 and 26.77 mg. Corrections were made for the background and diamagnetic contributions of the samples according to Pascal's constants.

2.5. Fluorescent measurements

Solid-state emission spectra were recorded for the solid samples and the corresponding intermediates [2ClBzTPP]Br/

Table 1
Crystal data and structure refinement for **1** and **2**.

Compounds	**1**	**2**
Empirical formula	$C_{54}H_{42}Cl_2CoN_4S_4P_2$	$C_{54}H_{42}Cl_2CoN_4S_4P_2$
Formula weight	1066.93	1066.93
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*C*2/*c*
a (Å)	22.142(3)	18.527(2)
b (Å)	12.638(2)	13.699(2)
c (Å)	21.714(3)	21.189(2)
β (°)	117.12(1)	96.209(2)
Volume ($Å^3$)	5408.3(12)	5346.3(10)
Z	4	4
Density (calculated) (mg/m^3)	1.310	1.326
Absorption coefficient (mm^{-1})	0.669	0.676
F(0 0 0)	2196	2196
Crystal size (mm^3)	0.11 × 0.18 × 0.21	0.11 × 0.15 × 0.22
Reflections collected	39,946	19,047
Independent reflections	10,072 ($R_{int} = 0.065$)	4705 ($R_{int} = 0.038$)
Data/restraints/parameters	10,072/0/604	4705/0/303
Goodness of fit on F^2	1.061	1.008
Final *R*indices [$I > 2\sigma(I)$]	$R1 = 0.0533$, $wR2 = 0.1231$	$R1 = 0.0411$, $wR2 = 0.1078$
Final *R*indices (all data)	$R1 = 0.0951$, $wR2 = 0.1375$	$R1 = 0.0698$, $wR2 = 0.1205$
Largest diff peak and hole (e $Å^{-3}$)	0.48 and −0.47	0.36 and −0.40