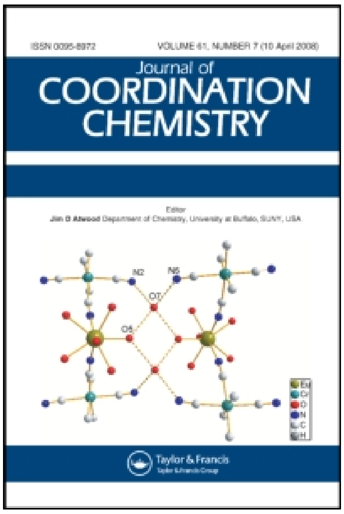

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Synthesis, crystal structure and third-order non-linear optical properties of a cobalt(II) one-dimensional supramolecular compound

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A cobalt(II) thiocyanate complex $[Co(py)_4(NCS)_2]$ **1** (py = pyridine) has been synthesized by low-temperature solid-state reaction. Single crystal X-ray analysis reveals that **1** possesses a one-dimensional (1-D) zigzag chain structure. Each Co ion is symmetrically coordinated by four pyridine ligands and also coordinates with two NCS^- anions. Compound **1** was characterized by elemental analyses, IR spectra and UV-visible spectra. The third-order non-linear optical (NLO) properties were also investigated and they exhibit non-linear absorption and self-defocusing performance with modulus of the hyperpolarizability 9.46×10^{-30} esu for **1** in a 3.6×10^{-4} mol dm^{-3} DMF solution.

Keywords: Cobalt (II) complex; Supramolecular compound; Third-order NLO behavior

1. Introduction

In recent years, self-assembly has been the most efficient approach to organic–inorganic composite materials [1]. The research in metal-directed supramolecular complexes has been rapidly expanding. One aspect is their fascinating structural diversity. So far, a wide region of infinite one-, two- and three- dimensional coordination frameworks have been found, including halicates [2], diamond [3], honeycomb [4], square or rectangular grids [5], T-shaped [6], ladder [7], zigzag [8], brick wall [9], octahedral [10], linear [11], and other frameworks [12]. Another aspect is their potential application as functional materials in catalysis, magnetism, superconductor and non-linear optical materials [13], as well as their potential antibiotic and anti-tumour applications [14].

Supramolecular compounds are one- or poly-dimensional aggregates with extended structures joined by non-covalent interactions [15] in which hydrogen bonding is the most dominant intermolecular force [16]. In supramolecular structures, several types of hydrogen bonds exist, conventional hydrogen bonds O–H–N, O–H–O and N–H–N

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have widely been used in supramolecular assemblies [17–20]. Moreover, unconventional weak bonds such as O–H–C and S–H–C have played a dominant role in some supramolecular assemblies [21]. There are many reports on supramolecular chemistry mostly organic systems; inorganic-organic assemblies are another type of supramolecular compound. In this artilce, we describe an inorganic-organic supramolecular compound $[Co(py)_4(NCS)_2]$ **1** that is formed by unconventional weak hydrogen bonds $C–H \cdots S$.

As a part of our work towards rational design and preparation of functional supramolecular compounds, we carried out a study of cobalt(II) thiocyanate adducts of auxiliary ligands. This compound is synthesized by a low-temperature solid-state reaction, not as traditionally synthesized in solution [22]. Low-temperature solid-state synthesis has potential in reducing environmental pollution. NLO studies have largely focused on semiconductors, conjugated polymers and discrete organic molecules [23, 24], as well as C_{60} [25] while supramolecular compounds (a very promising class of compounds as NLO materials) have not received much attention. We report here the solid-state synthesis, structural characterization and third-order NLO properties of compound **1**.

2. Experimental

2.1. *Starting materials*

The solvents were carefully dried and distilled prior to use and other chemicals from commercial sources were used without further purification.

2.2. *Physical measurements*

Infrared spectra (KBr pellet) were recorded on a Perkin–Elmer SPECTRUM ONE FT–IR spectrometer in 225–4000 cm^{-1} region. Co was determined by a Perkin–Elmer Optima 3300DV spectrometer. Elemental analyses (C, H, S and N) were performed on a Perkin–Elmer 2400 Series IICHNS/O elemental analyzer. Electronic spectra were measured on a Shimadzu UV–3100 spectrophotometer.

2.3. *Non-linear optical measurements*

A DMF solution of $3.6 \times 10^{-4}\,mol\,dm^{-3}$ of the title compound was placed in a 1 mm quartz cuvette for optical measurements and non-linear absorption and non-linear refraction were measured with linearly polarized laser light ($\lambda = 532\,nm$, pulse width $= 15\,ns$) generated from a Q-switched and frequency-doubled Nd–YAG laser. The spatial profiles of the optical pulses were nearly Gaussian. The laser beam was focused with a 25 cm focal-length focusing mirror. The radius of the beam waist was measured to be $30 \pm 5\,\mu m$ (half-width at $1/e^2$ maximum). The incident and transmitted pulse energy were measured simultaneously by two Laser precision detectors (RjP–735 energy probes), which were linked to a computer by an IEEE interface [26]. The interval of each transmittance measurement was set to 5 s so that every pulse of light was assured of meeting fresh molecules in the sample to eliminate the influence of any photon degradation. The non-linear optical properties of the samples were manifested by moving the samples along the axis of incident beam (Z-direction) with respect to the focal point instead of being positioned at its focal point, and an identical set-up was adopted in the experiments to measure Z-scan data. An aperture of 0.5 mm radius was placed in front of the detector to assist in measurement of the NLO absorption and refraction effects.

2.4. *Synthesis of [Co(py)$_4$(NCS)$_2$] 1*

A well-ground mixture of $CoCl_2$ (130 mg, 1.0 mmol), NH_4NCS (153 mg, 2.0 mmol) and pyridine (317 mg, 4 mmol) was heated in a sealed glass tube filled with N_2 gas at 90°C for 12 h. The mixture was extracted with the mixed solvent DMF (20 mL) and CH_3OH (35 mL), and then filtered. The thin red filtrate remained in the nitrogen atmosphere at 5°C for 7 days, and thin red crystals were obtained, with yield of 39.2% based on Co. IR (cm^{-1}): 3069(w), 2095(vs), 1594(s), 1500(m), 1455(s), 1075(vs), 705(m), 635(vs), 481(m), 446(m), 428(m). The results of elemental analyses: Anal. Calcd for $C_{11}H_{10}Co_{0.5}N_3S$: C, 53.76; H, 4.10; N, 17.10; Co, 11.99; S, 13.05%. Found: C, 53.78; H, 4.08; N, 17.11; Co, 12.01; S, 13.04%.

2.5. *X-ray crystal structure determination*

Crystal data were collected with Mo-Ka radiation ($\lambda = 0.71073$ Å) using a Siemens SMART CCD diffractometer. The structure was solved using direct methods with the SHEXTL-97 program and refined by full-matrix least-squares techniques. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement; the hydrogen atoms were treated using a riding model. Crystal data and selected parameters are given in tables 1 and 2.

3. Results and discussion

3.1. *Synthesis*

The synthesis of the title complex could be presumed as follows:

$$Co^{2+} + 4by + 2NCS^{-} \longrightarrow [Co(py)_4(NCS)_2]$$

3.2. *Crystal structure of 1*

As shown in figure 1, the Co(II) is symmetrically coordinated by four pyridine ligands [Co–N bond distances: 2.163(3) and 2.170(3) Å] and also coordinates with two SCN^- anions [Co–N bond length: 2.055(3) Å]. The Co atom adopts a nearly octahedral geometry, with the equatorial plane defined by the N(1), N(1)#1, N(2) and N(2)#1 atoms and two axial positions occupied by N(3) and N(3)#1 atoms; the four equatorial N atoms are from four different pyridine ligands, and form a parallel

Table 1. Crystal data and structure refinement for [Co(by)$_4$(NCS)$_2$]. Estimated standard deviations are given in parentheses.

Empirical formula	$C_{11}H_{10}Co_{0.5}N_3S$
Formula weight	245.74
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimension (Å, °)	
a	12.407(3)
b	12.917(3)
c	15.104(4)
β (°)	107.289(4)
Volume (Å^3)	2311.3(10)
Z	8
Density (g cm^{-3})	1.412
F(000)	1012
Absorption coefficient (mm^{-1})	0.944
Crystal size (mm^3)	$0.32 \times 0.28 \times 0.15$
θ range (deg)	2.33–25.07
Limiting indices	$-14 \le h \le 11$, $-14 \le k \le 15$, $-14 \le l \le 17$
T (K)	293(2)
Reflections collected/unique	5184/2048 [$R_{\mathrm{int}} = 0.0584$]
Data/restraints/parameters	2048/0/142
Goodness of fit indicator	1.058
Final *R* indicates [$I > 2\sigma(I)$]	$R_1 = 0.0364$, $wR_2 = 0.1000$
Largest diff. peak and hole (e Å^{-3})	0.246, −0.360

Table 2. Selected bond lengths (Å) and angles (°) for cluster **1**. Estimated standard deviations are given in parentheses.

Bond lengths			
Co–N(1)	2.163(3)	N(1)–C(1)	1.328(4)
Co–N(2)	2.170(3)	N(1)–C(5)	1.335(4)
Co–N(3)	2.055(3)	N(2)–C(6)	1.340(4)
S–C(11)	1.621(3)	N(2)–C(10)	1.340(4)
N(3)–C(11)	1.157(4)		
Bond angles			
N(3)–Co–N(3)#1	180.00(8)	N(3)#1–Co–N(2)#1	90.59(10)
N(3)–Co–N(1)#1	89.05(11)	N(1)#1–Co–N(2)#1	92.68(10)
N(3)#1–Co–N(1)#1	90.96(11)	N(1)–Co–N(2)#1	87.32(10)
N(3)–Co–N(1)	90.95(11)	N(3)–Co–N(2)	90.59(10)
N(3)#1–Co–N(1)	89.04(11)	N(1)#1–Co–N(2)	87.32(10)
N(1)#1–Co–N(1)	180.000(1)	N(1)–Co–N(2)	92.68(10)
N(3)–Co–N(2)#1	89.41(10)	N(2)#1–Co–N(2)	180.0

Symmetry transformations used to generate equivalent atoms: 1 $-x+1/2$, $-y+1/2$, $-z+1$.

quadrilateral with Co at the center of the parallel quadrilateral [N(1)–Co–N(1)#1 = 180.000(1)°, N(2)–Co–N(2)#1 = 180.0°]. The Co–N(1) and Co–N(2) distances in the equatorial plane are 2.163(3) Å and 2.170(3) Å, respectively, comparable with other analogous mononuclear pyridine derivatives of Co(II) [26, 27]. Two N atoms of two SCN$^-$ units occupy the axial positions, and the axial N(3)–Co–N(3)#1 bond angle is also 180.00(8)°. The Co–N(3) distance 2.055(3) Å compares favorably with the Co–N distances of 2.085(6) Å found in the nearly octahedral [Co(NCS)$_2$(bpms)$_2$]$_n$ (bpms = 1,2-*bis*(4-pyridylmethyl)disulfenyl) [28]. The equatorial Co–N bond distances

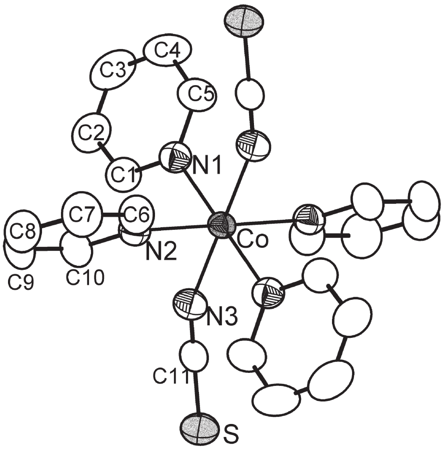

Figure 1. The molecular structure of compound **1**. Thermal ellipsoids are drawn at the 50% probability level.

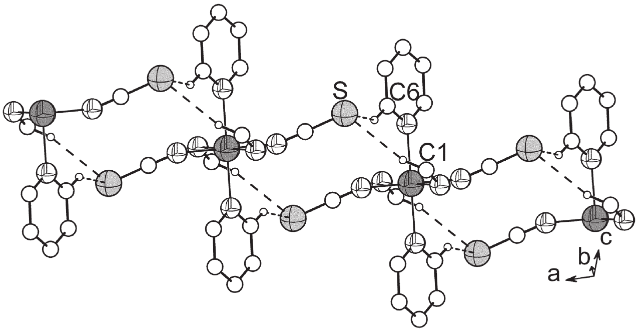

Figure 2. View of the 1-D zigzag chain structure with hydrogen bonds shown as dashed lines for **1** along *a* axis.

are longer than those of the axial Co–N bond distances. In the similar zigzag polymer $[Co(NCS)2(bpms)2]_n$ [28], the coordination sphere around Co is a nearly octahedral with the N_{NCS}–Co–N_{NCS} bond angle 180° and the N_{bpms}–Co–N_{bpms} bond angles also 180°.

Compound **1** is connected into a one-dimensional structure by two types of hydrogen bonds. One type of hydrogen bond C(l)–H(l) $\cdots$ S $[-x, -y, 1-z]$ (figure 2) with S atom as acceptor and H(1) from pyridine as donor occurs. The second type of hydrogen bond C(6)–H(6) $\cdots$ S $[-x, -y, 1-z]$ (figure 2) has S atom as acceptor and H(6) from pyridine as donor. The two types of hydrogen bonds join adjacent molecules along the *a* axis to a one-dimensional zigzag chain structure. The parameters of all the hydrogen bonds are listed in table 3. The C(1) $\cdots$ S and C(6) $\cdots$ S (3.832(6) Å and 3.669(2) Å, respectively) distances are within the range of values found for weak C–H $\cdots$ S hydrogen bonds observed in metal complexes ($d_{C\cdots S} = 3.719 \sim 3.857$ Å) [29]. The existance of unconventional weak-strong hydrogen bonds enhances the stability of complex **1**.

Table 3. The distances (Å) and degrees (°) of hydrogen bonds.

D–H···A	d(D–H)	d(H···A)	d(D···A)	<DHA
C(1)–H (1)···S^{i}	0.930(2)	3.010(4)	3.832(6)	148.24(1)
C(6)–H(6)···S^{i}	0.930(1)	2.910(1)	3.669(2)	139.79(1)

Symmetry operations: i $[-x, -y, 1-z]$.

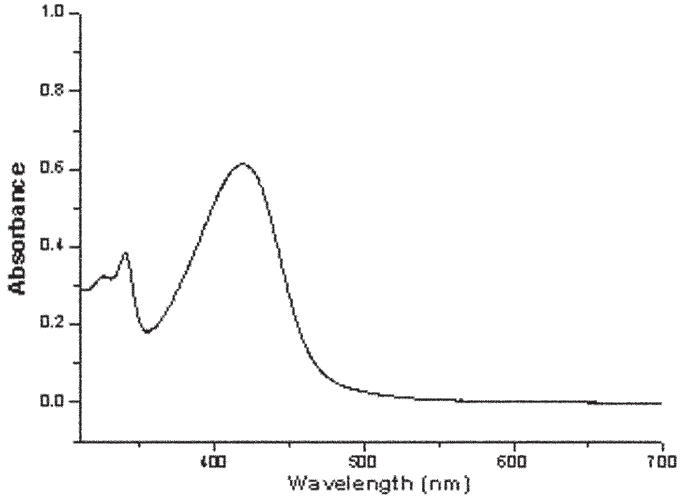

Figure 3. The UV-visible spectra of compound **1** dissolved in DMF.

3.3. *Non-linear optical properties*

The UV-visible absorption spectrum of (**1**) (3.6×10^{-4} mol dm^{-3} in DMF) shown in figure 3 displays two medium-strong absorption peaks (with molar absorption coefficients in dm^{3} mol^{-1} cm^{-1}) at 325 (1.80×10^{3}) nm and 340 (2.12×10^{3}) nm attributed to Co(II) ← ligand charge-transfer transitions, and one strong peak at 421 (3.40×10^{3}) nm from d–d transitions. Figure 3 also shows that the supramolecular compound has potential as optical limiter [30].

The third-order NLO properties of the title compound were investigated by using a Z-scan technique in a 5 mm thick glass cell. The obtained experimental data and theoretical fits [31] are depicted in figure 4. In agreement with the observed effective third-order NLO absorption coefficient α_2 and refractive coefficient n_2, the modulus of the effective third-order non-linear susceptibility $\chi^{(3)}$ can be calculated by

$$|\chi^{(3)}| = \left[\left(\frac{9 \times 10^{8} n_0^2 \varepsilon_0 c \lambda \alpha_2}{8\pi^2}\right)^2 + \left(\frac{n_0 c n_2}{80\pi^2}\right)^2\right]^{1/2} \tag{1}$$

where λ is the laser wavelength, n_0 is the linear refractive index of the sample (n_0 can be replaced by one of the solvents during calculation if the concentration of the sample is

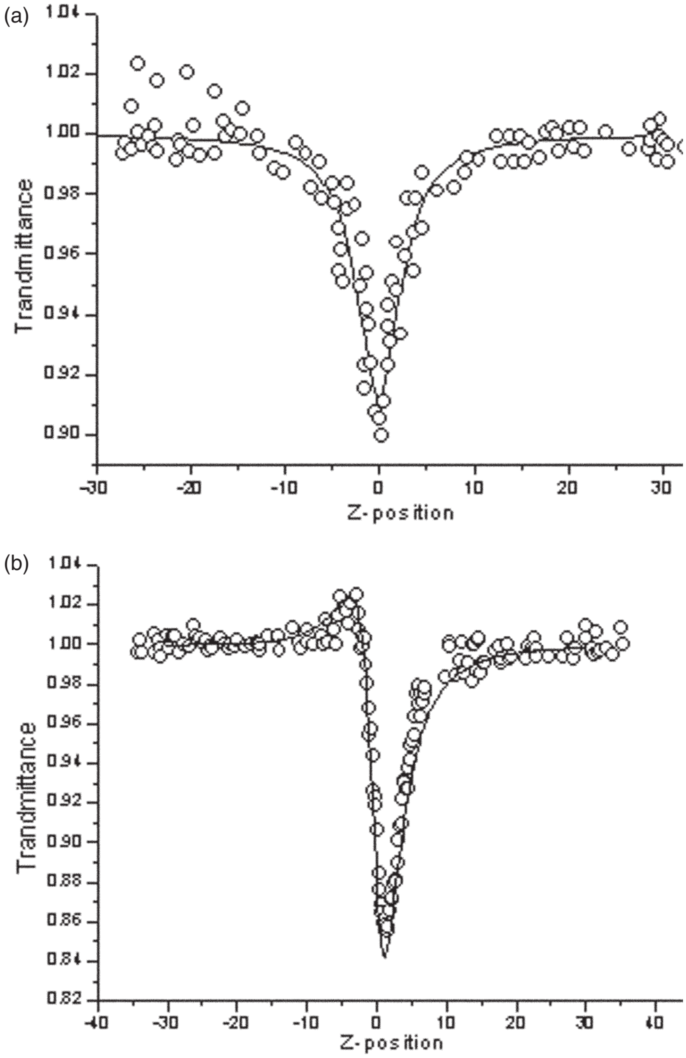

Figure 4. *Z*-scan data of **1** dissolved in DMF with a concentration of 3.6×10^{-4} mol dm^{-3}. The circles represent experimental data and the solid curve is theoretical fit. (a) The data were collected under an open aperture configuration showing NLO absorption. (b) The data were obtained under a closed aperture configuration showing NLO refraction.

very dilute), ε_0 and c are the permittivity and the speed of light in a vacuum, respectively. The corresponding modulus of the third-order non-linear molecular susceptibilities (or hyperpolarizabilities) was

$$|\gamma| = \frac{|\chi^{(3)}|}{\mathrm{NF}^4}$$

where $F^4 = [(n^2 + 2)/3]^4$, N is the molecular number density of the compound in the sample (i.e. molecular number of the solute in each mL of the solution) and F^4 is the

Table 4. Third-order non-linear optical properties of some compounds.

Compounds	Concentrations ($mol\,dm^{-3}$)	α_2 (m/w)	n_2 ($m^2\,W^{-1}$)	$\chi^{(3)}$ (esu)	γ (esu)	Ref.
$[Co(py)_4(NCS)_2]$ **1**	3.6×10^{-4}	3.14×10^{-11}	-8.3×10^{-17}	7.76×10^{-11}	9.46×10^{-30}	This work
$[Co(NCS)_2(bpms)_2]_n$ **2**	4.07×10^{-3}	~	-3.0×10^{-18}	1.07×10^{-11}	1.0×10^{-30}	[27]
$[Cu(im)_2(NCS)_2]$ **3**	7.6×10^{-3}	1.18×10^{-11}	-9.0×10^{-16}	7.00×10^{-10}	4.63×10^{-29}	[31]

py = pyridine; bpms = 1,2-*bis*(4-pyridylmethyl)disulfenyl; im = imidazole.

local Lorentz field correction term. All the calculated results and some literature data on the NLO properties are listed in table 4. The γ value in the table indicates that the title compound has nice third-order NLO performance, and displays the reverse saturation absorption ($\alpha_2 > 0$) and a self-defocusing property ($n_2 < 0$). Materials possessing self-defocusing performance may be excellent for applications in protection of optical sensors.

Compound **1** exhibits a significant NLO absorption property and a refractive effect. The hyperpolarizability γ value (9.46×10^{-30} esu) of the title compound **1** is comparable with that of the compounds, $[Co(NCS)_2(bpms)_2]_n$ **2** (1.0×10^{-30} esu) [28] and $[Cu(im)_2(NCS)_2]$ **3** (4.63×10^{-29} esu) [32]. The three compounds possess similar supramolecular structures but external ligands and center atoms are different. As a result, the three compounds exhibit self-defocusing effects ($n_2 < 0$) with effective n_2 values of $-8.3 \times 10^{-17}\,m^2\,W^{-1}$ for **1**, $-3.0 \times 10^{-18}\,m^2\,W^{-1}$ for **2**, and $-9.0 \times 10^{-16}\,m^2\,W^{-1}$ for **3**, respectively. As for the interrelation between structure and optical performance, we can attribute the NLO properties of these compounds to the presence of large delocalized electron clouds in the supramolecular compounds, strongly implying that compounds may be designed and synthesized to obtain predictable NLO materials. Further work in this field is in progress.

Supplementary data

Supplementary data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 295894 for **1**. Copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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