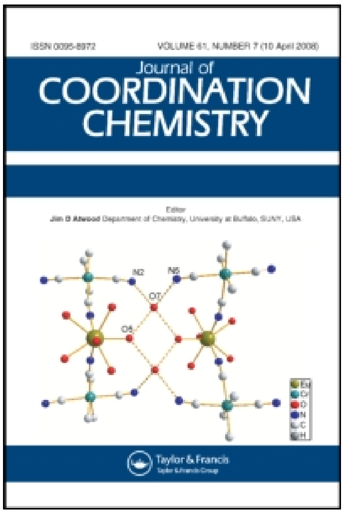

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Synthesis, crystal structure and non-linear optical properties of a new cyanide-containing compound

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SYNTHESIS, CRYSTAL STRUCTURE AND NON-LINEAR OPTICAL PROPERTIES OF A NEW CYANIDE-CONTAINING COMPOUND

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Reaction of $K_3[Fe(CN)_6]$, $NiCl_2$ and diethylenetriamine (dien) resulted in the formation of a cyanide-containing heterometallic compound $[Ni(dien)_2]_2[Fe(CN)_6] \cdot 4H_2O$ **1**. The structure consists of two octahedral $[Ni(dien)_2]^{2+}$ cations, one octahedral $[Fe(CN)_6]^{4-}$ anion and four crystallization water molecules, which are held together by hydrogen-bonding interactions. Its TG curve exhibits two stages of mass loss. Compound **1** in DMF solutions has a very strong third-order non-linear optical (NLO) behavior with an absorption coefficient and refractive index $\alpha_2 = 1.10 \times 10^{-11}\,\mathrm{m\,w^{-1}}$, $n_2 = -3.05 \times 10^{-19}\,\mathrm{m^2\,w^{-1}}$, respectively, and third-order NLO susceptibility $\chi^{(3)}$ 4.34×10^{-13} esu.

Keywords: Crystal structure; Cyanide complexes; Third-order NLO properties

INTRODUCTION

In recent years there has been considerable interest in the design of homo- and heteroleptic cyanometalates as building blocks for cyanide-bridged bimetallic assemblies. This is not only because of their intriguing structural diversity, but also due to their potential applications in magnetic, magneto-optical and zeolitic materials [1]. Among these materials, those prepared from $[M(CN)_6]^{3-}$ ($M = Cr^{III}, Mn^{III}, Fe^{III}, Co^{III}$) and coordinatively unsaturated complexes $M'L$ ($M' = Ni^{II}, Mn^{II}, Cu^{II}$; L = polyamine, Schiff base, etc.) generally have the formulation M'_3M_2, and have been assembled on the basis of the charge ratio 2 : 3 of the cation and anion. Their dimensionality and topology are strongly dependent on the nature of $M'L$ (the degree of coordinative saturation of M'; coordination geometry and volume of ligands, etc.) and the connectivity of the $[M(CN)_6]^{3-}$ building block (number and arrangement of $M'L$ units around M) [2].

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A number of cyanide-bridged complexes have been reported with new and interesting architectures [3]: 1D (zigzag chain, rope-ladder chain [4]), 2D (honeycomb, brick-wall [5] and rectangular-like [6] sheet) and intricate 3D networks [1c].

As a part work of our work towards rational design and preparation of these functional materials, we have synthesized the cyanide-containing heterometallic compound $[Ni(dien)_2]_2[Fe(CN)_6] \cdot 4H_2O$ **1** by reaction of $K_3[Fe(CN)_6]$, $NiCl_2$ and diethylenetriamine (dien) at room temperature. Although such complexes have been extensively studied by crystal structure analyses, their third-order non-linear optical (NLO) properties have been less well examined. Molecular building blocks of coordination compounds may yield bulk materials with third-order NLO properties since some organic compounds have good NLO properties and inorganic compounds have good rigidity and stability. The third-order NLO property of supramolecular compound **1** shows strong third-order non-linear optical absorption and self-defocusing with the α_2 value of $1.10 \times 10^{-11}\,\mathrm{m\,w^{-1}}$ and n_2 value of $-3.05 \times 10^{-19}\,\mathrm{m^2\,w^{-1}}$, respectively.

EXPERIMENTAL

Materials and Physical Measurements

All reagents were commercially available and used as received. The infrared spectrum was recorded as a KBr pellet with a Perkin-Elmer spectrophotometer in the 400–4000 $\mathrm{cm^{-1}}$ region. Elemental analysis (CHN) was determined using a Perkin-Elmer 2400 LS II elemental analyzer and inductively-coupled plasma (ICP) analysis was conducted with a Perkin-Elmer Optima 3300 DV ICP spectrometer. The electronic spectrum was measured on a Shimadzu UV-3100 spectrophotometer. A Perkin-Elmer TGA7 thermogravimetric analyzer was used to obtain the TGA curve in O_2 with a temperature increase of 20°C $\mathrm{min^{-1}}$.

Preparation of $[Ni(dien)_2]_2[Fe(CN)_6] \cdot 4H_2O$ 1

An aqueous solution (15 $\mathrm{cm^3}$) of $K_3[Fe(CN)_6]$ (0.329 g, 1.0 mmol) was added dropwise into an aqueous solution (10 $\mathrm{cm^3}$) of $NiCl_2 \cdot 6H_2O$ (0.369 g, 1.0 mmol) and dien (0.22 mL), with stirring for 30 min at 50°C. Purple crystals were obtained in 70% yield after the filtrate was allowed to stand for 1 w. IR ($\mathrm{cm^{-1}}$): 3419(m), 3293(m), 3185(m), 2854(m), 2038(s), 2029(s), 1668(m), 1579(m), 1498(w), 1453(w), 1390(w), 1333(w), 1309(w), 1282(w), 1145(s), 1099(s), 1018(s), 984(s), 889(s), 864(w), 660(w), 610(w), 581(m), 547(m), 522(m), 406(m). Anal. Calcd. for $C_{11}H_{24}Fe_{0.50}N_9NiO_2$ (%): C, 32.95; H, 6.03; N, 31.43; Ni, 14.64; Fe, 6.96. Found: C, 32.74; H, 6.10; N, 31.65; Ni, 14.87; Fe, 6.98.

X-Ray Crystal Structure Determination

Crystallographic data for compound **1** are summarized in Table I. The data were collected with Mo Kα radiation ($\lambda = 0.71073$ Å) using a Siemens SMART CCD diffractometer at 293(2) K. The crystal class, orientation matrix, and cell dimensions were determined according to established procedures [7]. The structure was solved

TABLE I Crystallographic data and structure refinement for compound **1**

Empirical formula	$C_{11}H_{24}Fe_{0.50}N_9NiO_2$
Formula weight	401.03
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimension (Å, °)	$a = 9.243(4)$
	$b = 14.538(4)$ $\beta = 90.94(2)$
	$c = 13.858(5)$
Volume (Å^3), Z	1861.9(11), 4
Density (g/cm^3)	1.431
$F_{(000)}$	840
Absorption coefficient (mm^{-1})	1.439
Crystal size (mm^3)	$0.23 \times 0.20 \times 0.05$
θ range (°)	2.61 to 25.11
Limiting indices	$-10 \le h \le 3$, $-14 \le k \le 16$, $-16 \le l \le 16$
T (K)	293 (2)
Data/restraints/parameters	3017/0/214
Goodness of fit indicator	1.062
Final R indicates $[I > 2\sigma(I)]$	$R1 = 0.0387$, $wR2 = 0.1102$
Largest diff. peak and hole (e/Å^3)	0.621 and −0.577

TABLE II Selected bond lengths (Å) and angles (°) for compound **1**

Ni(1)–N(2)	2.095(3)	Ni(1)–N(3)	2.174(3)
Ni(1)–N(5)	2.097(3)	Fe(1)–C(10)	1.920(3)
Ni(1)–N(1)	2.149(3)	Fe(1)–C(11)	1.925(3)
Ni(1)–N(4)	2.160(3)	Fe(1)–C(9)	1.928(3)
Ni(1)–N(6)	2.168(3)	N(2)–Ni(1)–N(3)	80.61(10)
N(2)–Ni(1)–N(6)	99.89(10)	N(5)–Ni(1)–N(3)	100.19(10)
N(5)–Ni(1)–N(6)	80.45(10)	N(1)–Ni(1)–N(3)	161.77(11)
N(1)–Ni(1)–N(6)	92.80(10)	N(4)–Ni(1)–N(3)	93.31(11)
N(4)–Ni(1)–N(6)	161.90(11)	N(6)–Ni(1)–N(3)	87.81(10)
N(9)–C(11)–Fe(1)	175.7(3)	C(10)#1–Fe(1)–C(11)#1	92.93(11)
N(2)–Ni(1)–N(5)	179.16(9)	C(10)–Fe(1)–C(11)#1	87.07(11)
N(2)–Ni(1)–N(1)	81.34(11)	C(10)–Fe(1)–C(9)	90.51(11)
N(5)–Ni(1)–N(1)	97.88(10)	C(10)–Fe(1)–C(9)#1	89.49(11)
N(2)–Ni(1)–N(4)	98.12(10)	C(11)#1–Fe(1)–C(9)	90.01(12)
N(5)–Ni(1)–N(4)	81.57(10)	C(11)–Fe(1)–C(9)	89.99(12)
N(1)–Ni(1)–N(4)	91.73(11)	N(7)–C(9)–Fe(1)	178.8(3)

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

TABLE III Hydrogen bond parameters

D–H	d(H···A)	<DHA	d(D···A)	A
N4–H4Δ	2.619	139.41	3.319	N8 #1
N6–H6Δ	2.561	165.32	3.399	O2W #1
O1W			2.825(4)	O2W #1

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

using direct methods with SHELXTL 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. Selected bond lengths and angles are listed in Table II; hydrogen bond parameters are listed in Table III.

RESULTS AND DISCUSSION

The crystallographic analysis of **1** shows that its structure consists of one $[Ni(dien)_2]^{2+}$ cation, half a $[Fe(CN)_6]^{4-}$ anion and two water of crystallization molecules, which are linked by hydrogen bond interactions.

As shown in Fig. 1, each nickel(II) exhibits a heavily distorted octahedral coordination of six nitrogen atoms from two chelating dien ligands with *cis* and *trans* angles in the ranges 80.61(10)–100.19(10)°, 166.17(11)–179.16(9)°, respectively. The equatorial positions are occupied by N1, N3, N4 and N6 atoms, the apical positions by N2 and N5 atoms. The nickel atom lies out of the equatorial plane, with an observed deviation 0.3242 Å. The Ni–Ndien bond lengths are in the range 2.095(3)–2.174(3) Å, which are similar to those observed for other Ni–N bonds, $\{Ni(pn)_2 Ni(CN)_4] \cdot H_2O\}_n$ [2.102(5)–2.137(6) Å] [5].

Each Fe(II) exhibits a slightly distorted octahedral coordination geometry with *cis* angles in the range 87.07(11)–92.93(11)°, and *trans* angles 180°. The Fe–C(cyano) bond lengths [1.920(3)–1.928(3) Å] are in good agreement with those reported for the low-spin iron(II) mononuclear complexes, $K_2[Fe(bpy)(CN)_4] \cdot 2.5H_2O$ [1.891(5)–1.936(5) Å] [8] and $[Fe(phen)_2(CN)_2]$ [1.903(6)–1.917(6) Å] [9], but shorter than for $[Fe(bpy)_2(CN)_2]ClO_4$ [1.928(7) and 1.931(7) Å] [10]. The Fe–C–N angles are in the range 175.7(3)–178.8(3)° showing that each cyanide departs somewhat from strict linearity. The cyanide groups exhibit only one type of coordination, as shown from the IR spectrum, which exhibits two strong bands at 2029 and 2038 cm^{-1}, similar to those observed in the low-spin iron(II) species $K_4[Fe(CN)_4]$ (2044 cm^{-1}) and $[Fe(phen)_2(CN)_2]$ (2075 and 2062 cm^{-1}) [9].

As shown in Fig. 2, there are three kinds of hydrogen bond interactions. The first is N(4)–H4A···N(8) through which the $[Fe(CN)_6]^{4-}$ anion is surrounded by two $[Ni(dien)_2]^{2+}$ cation units at a distance of 2.619 Å and angle of 139.4(1)°. The second is N6–H6A···O2W [2.561 Å, 165.32°], which connects one cation to a water molecule. The third, O1W···O2W, occurs between the two water molecules with a distance of 2.825(4) Å. All these hydrogen bond interactions hold the monomeric units and water molecules together to form a $[Ni(dien)_2]_2[Fe(CN)_6] \cdot 4H_2O$ molecule. However, there are no intermolecular hydrogen bond interactions.

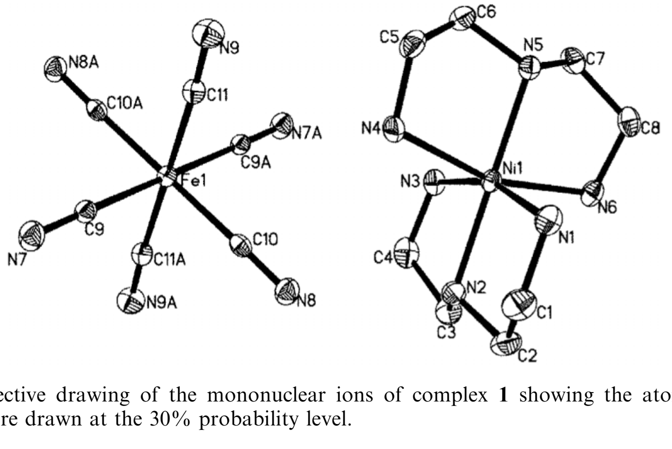

FIGURE 1 Perspective drawing of the mononuclear ions of complex **1** showing the atom numbering. Thermal ellipsoids are drawn at the 30% probability level.

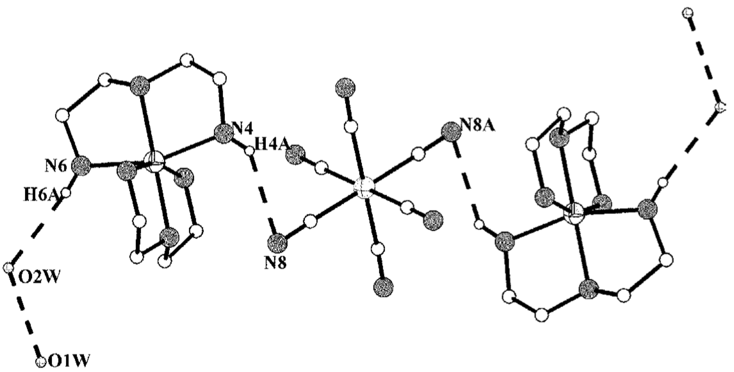

FIGURE 2 Monomeric units connected by hydrogen bond interactions.

Thermal Analysis

To investigate the thermal stability of compound **1**, a thermal analysis study was carried out. The TG curve of compound **1** exhibits two stages of mass loss; the mass loss of the first stage (9.52%) corresponds to the mass of solvent water molecules (9.48%). After removal of the solvent molecule, ash obtained at the final stage of the process in **1** can be regarded as the oxides of iron and nickel (25.90%).

Third-order NLO Properties

Study on coordination polymers is focused on novel structures and magnetic properties [1], with only a few papers reporting second-order NLO properties [11]. Our research interest is in third-order NLO properties of coordination polymers, clusters and supramolcular compounds. The UV-Visible spectrum of compound **1** in DMF solution shows one strong absorption peak at 273 nm in the near ultraviolet (UV) wavelength range indicating the presence of metal–ligand charge transfer (MLCT).

The NLO properties were determined by a *Z*-scan technique with a Q-switched frequency-doubled Nd: YAG laser at 532 nm with 10 ns pulses. The solution was contained on a 1 mm-thick glass cell with a concentration of $6.05 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ in DMF. The non-linear absorption component of compound **1** was evaluated by a *Z*-scan experiment under an open-aperture configuration [Fig. 3(a)] and its non-linear refractive property was assessed under a closed-aperture configuration [Fig. 3(b)], where the open circles represent the experimental data and the solid curves represent theoretical data. Reasonably good fits between the experimental data and theoretical curve were obtained, suggesting that the experimentally obtained NLO effects are third-order. The effective α_2 value of $1.10 \times 10^{-11}\,\mathrm{m\,w^{-1}}$ and self-defocusing performance $n_2 = -3.05 \times 10^{-19}\,\mathrm{m^2\,w^{-1}}$ were derived from the theoretical curves, which shows that compound **1** has strong non-linear optical absorption and self-defocusing effects comparable with some of the best performing organometallic compounds, semiconductors, fullerene and some thiocyanate coordination polymers (Table IV). It should be emphasized that the Z-scan result here did not reveal the origin of the observed non-linearity. Both excited state population (or absorption) and two-photon absorption can be responsible for these measured NLO effects.

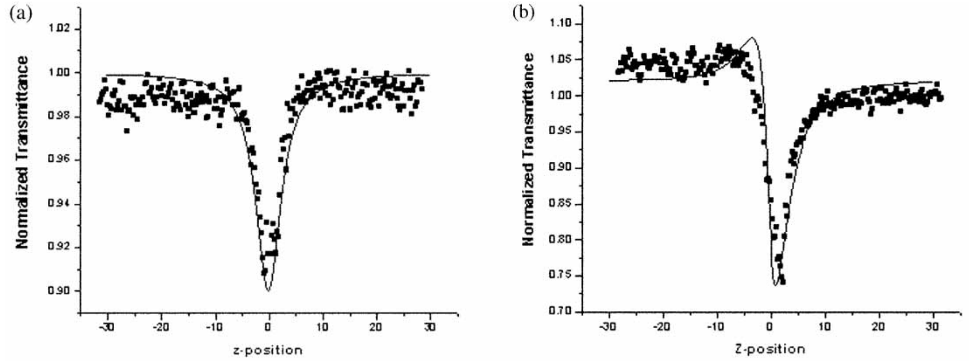

FIGURE 3 Z-scan data of compound **1** (a) collected under an open aperture configuration showing NLO absorption; (b) collected under a closed aperture configuration showing NLO refractive behavior.

TABLE IV Optical parameters of selected NLO chromophores

Compound	α_2/m w^{-1}	n_2/m^2 w^{-1}	$\chi^{(3)}$/esu	γ/esu	Ref.
FeCH=CHC$_6$H$_5$				$(8.55 \pm 1.98) \times 10^{-35}$	12
cis-[Mo(CO)$_4$(PPh$_3$)$_2$]				1.7×10^{-31}	13
Ge				2.3×10^{-33}	14
C$_{60}$				5×10^{-34}	15
[Fe(NCS)$_6$][(Hbpy)(H$_2$bpy)(bpy)]		-2.95×10^{-17}	1.06×10^{-10}		16
[Ni(dien)$_2$]$_2$[Fe(CN)$_6$]$\cdot$4H$_2$O	1.10×10^{-11}	-3.05×10^{-19}	4.34×10^{-13}	3.61×10^{-31}	This work
[Zn(pbbt)$_2$(NCS)$_2$]$_n$		4.53×10^{-18}	1.62×10^{-11}	8.17×10^{-30}	17
[Pb(bpea)(NCS)$_2$]$_n$	1.1×10^{-11}	6.06×10^{-18}			18
[Mn(bbbt)$_2$(NCS)$_2$]$_n$	5.2×10^{-9}	3.6×10^{-19}	1.27×10^{-12}	1.52×10^{-30}	19
[Ni(pbbt)$_2$(NCS)$_2$H$_2$O]$_n$		3.02×10^{-18}	1.08×10^{-11}	1.68×10^{-29}	17

In accordance with the observed α_2 and n_2, the modules of the effective third-order susceptibility $\chi^{(3)}$ can be calculated by the following equation:

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

where λ is the wavelength of the laser, n_0 is the linear refractive index of the sample (n_0 can be replaced by the one of the solvents if the concentration of the sample is very small during calculation), ε_0 and c are the permittivity and speed of light in vacuo, respectively. For compound **1**, the $\chi^{(3)}$ value was calculated to be 4.34×10^{-13}esu. The corresponding module of the hyperpolarizabilities γ of 3.61×10^{-31}esu was obtained from $|\gamma| = |\chi^{(3)}|/\mathrm{NF}^4(F^4 = [(n^2 + 2)/3]^4)$, where n is the linear refractive index of the solvent; N is the molecular number density of the compound in the sample and F^4 is the local Lorenz field correction factor.

Based on the above results, compound **1** exhibits strong non-linear absorption and self-defocusing performance. However, its NLO properties were determined in solution and the effect of the solvent on the compound cannot be ignored. The supramolecular compound may dissociate into oligomeric or monomeric species because secondary bonding interactions are destroyed in DMF solution. Therefore, the result reported here shows the final effect of all monomeric ions in DMF solution, which suggests that compound **1** should have better third-order non-linear optical properties in the solid state.

We have investigated the reported literature concerning third-order NLO properties of coordination polymers. Generally, one-dimensional chain coordination polymers show self-defocusing behavior; all two-dimensional rhombohedral grid coordination polymers possess strong self-focusing behavior; and three-dimensional polymers have either self-defocusing or self-focusing effects. In addition, the valence shell structures of metal ions have some influence on the strength of NLO properties. The strength can be altered by π back-donation of metal ions to ligands. The increased capacity for π back donation of metal ions to ligands may enhance the extension of the electronic π system and improve NLO properties.

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Supplementary data

Supplementary data have been deposited with the Cambridge Crystallographic Centre, CCDC No. 234618. These may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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