Hydrothermal synthesis, crystal structure and third-order non-linear optical property of a discrete decanuclear iodocuprate(I) $[Cu^{I}_{10}H_2I_{16}]^{4-}$ with $[Ni^{II}(phen)_3]^{2+}$ as a template

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Abstract

The title compound $[Ni^{II}(phen)_3]_2[Cu_{10}H_2I_{16}]$ **1** (phen = 1,10-phenanthroline, $C_{12}H_8N_2$) was hydrothermally synthesized from a simple reaction of CuI–$NiCl_2 \cdot 6H_2O$–phen·H_2O–H_2O. X-ray analysis revealed that it consists of NiN_6^{2+} core cation and decanuclear iodocuprate(I) anion together with two dissociative H^+ ions. In anionic unit, the discrete decanuclear iodocuprate(I) is formed by crystallographically independent five monovalent copper atoms and eight iodine atoms via an inversion center. There exist two types of Cu(I) coordination sites; only one copper(I) atom is in a highly distorted triangular planar site, and the other four copper(I) atoms display the tetrahedral geometries. It deserves to be noted that four types of bridging modes of I^- ions in which two are ordinary μ_2- and μ_3-bonding modes can be found. But the other two are the rectangle planar geometry and the novel μ_4-bridge like an "umbrella", and both of them are rather rare in the halocuprates(I). Compound **1** was crystallized in triclinic space group $P\bar{1}$ with $a = 11.6861(17)$, $b = 14.590(2)$, $c = 14.649(2)$ Å, $\alpha = 76.370(2)$, $\beta = 70.830(2)$, $\gamma = 81.320(3)^{\circ}$, $R = 0.075$, and was characterized by elemental analysis, IR spectrum and UV-VIS spectrum. The third-order non-linear optical property of **1** was also investigated and the compound exhibits the reverse saturable absorption and self-defocusing performance.
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1. Introduction

Copper(I) halides can themselves form halocuprates(I) $Cu_x X_y^{y-x}$ as well as neutral copper halide clusters of stoichiometry $[(CuX)_m L_n]$ (L = organic ligand) [1–10]. The structures of halocuprates(I) are exceptionally varied, very interesting and unpredictable due to the diversity of the Cu(I) coordination geometry and the potential bridging capability of X^- ions. The center ion Cu(I) is capable of attaining two-, three-, or four-fold coordination with linear, triangular planar or tetrahedral geometry. On the other hand, the halide ions can bridge two or more Cu(I) ions besides acting as the terminal ligand. Thus, it is not surprising that halocuprates(I) so far determined in the structural chemistry show a rather wide range from low-molecular-weight units, such as the mononuclear ions $[CuX_2]^-$ [11,12] and $[CuX_3]^{2-}$ [13], the binuclear ones $[Cu_2X_4]^{2-}$ [14], $[Cu_2X_6]^{4-}$ [15] and $[Cu_2Br_5]^{3-}$ [16], and the tetranuclear ones $[Cu_4X_6]^{2-}$ [17] and $[Cu_2Ag_2X_8]^{4-}$ [18], through higher condensed units, such as $[Cu_5I_7]^{2-}$ [19], $[Cu_6Br_9]^{3-}$ [20], $[Cu_6Br_{10}]^{4-}$ [21], $[Cu_6I_{10}]^{4-}$ [22], $[Cu_6I_{11}]^{5-}$ [23], $[Cu_7Cl_{10}]^{3-}$ [24] and $[Cu_8I_{13}]^{5-}$ [25], to

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the polymeric ones, such as one-dimensional $[CuI_2]^-$ [26], $[Cu_2X_3]^-$ [27], $[Cu_3I_4]^-$ [25], $[Cu_4Br_6]^{2-}$ [28], $[Cu_4Cl_6]^{2-}$ [29] and $[Cu_4I_6]^{2-}$ [25]. Furthermore, $[Cu_{36}I_{56}]^{20-}$ is the largest discrete halocuprate(I) ion to date [30]. $[C_5H_7N_2O][Cu_3Br_4]$ ($C_5H_7N_2O^+$ = 2-amino-3-hydroxypyridinium) contains the first example of a two-dimensional Cu(I) halide anionic network [31], and both $[Cu(en)_2][Cu_7Cl_{11}]$ [32] and $[Cu(en)_2][Cu_5Br_7]$ [33] (en = ethylenediamine) exhibit three-dimensional open-framework copper(I) halides with occluded $[Cu(en)_2]^{2+}$ cations. What factors on earth determine anionic configuration, i.e., the coordination number of Cu(I) and the tendency of the anion to form extended structures? A series of systematic studies on halocuprates(I) indicates that the size, form and charge distribution of the cations involved are more significant ones.

In 1997, Martin reported four halometalates possessing mixed metal atoms in anionic frameworks in his paper titled "A New Generation of Zeolite-Type Materials: $[HNMe_3][CuZn_5Cl_{12}]$, $[H_2NEt_2][CuZn_5Cl_{12}]$ and $[H_2NMe_2][Cu_nZn_{6-n}Cl_{12}]$ ($n = 1, 2$)" [34], which provokes our interest in the synthesis of other halometalates. At present, our investigation is focused on the reactions of CuX and the other transition metal halides with the bulky organic chelate ligands as the templating agents, and exploration of correlative functional properties for this kind of solid material. Herein, we report the structural information and the third-order non-linear optical property of a novel iodocuprate $[Ni^{II}(phen)_3]_2[Cu_{10}H_2I_{16}]$ coming from a simple hydrothermal reaction of CuI–$NiCl_2 \cdot 6H_2O$–phen$\cdot H_2O$–H_2O.

2. Experimental section

The synthesis was conducted using regent grade CuI, $NiCl_2 \cdot 6H_2O$ and phen$\cdot H_2O$ from commercial sources without further purification. Infrared spectrum of the title compound was recorded with Perkin–Elmer Spectrum 1 spectrophotometer in the 4000–400 cm^{-1} region using a powdered sample on a KBr plate. Electronic absorption spectrum was obtained on a Rigaku-UV-3100 spectrophotometer in DMF solution. The element analysis was determined using a Perkin–Elmer 2400LS II elemental analyzer.

A mixture of CuI (0.70 g), $NiCl_2 \cdot 6H_2O$ (1.76 g), phen$\cdot H_2O$ (1.10 g) and H_2O (20 mL) in a molar ratio of 1:2:1.5:300 was fully stirred at room temperature, sealed in a 30 mL Teflon-lined autoclave and heated at 160°C for 3 days. Then the autoclave was slowly cooled to ambient temperature. The resulting red column crystals of **1** suitable for X-ray structural analysis were filtered off, and dried. The yields were ca. 30% based on the CuI. IR (cm^{-1}): 1625 (w), 1580 (m), 1517 (s), 1494 (w), 1423 (s), 1339 (m), 1223 (w), 1142 (m), 1103 (m), 868 (m), 843 (s), 769 (m), 724 (s), 645 (w). Anal. Calcd.

for $Cu_{10}Ni_2I_{16}C_{72}H_{50}N_{12}$: C, 22.36; H, 1.30; N, 4.35. Found: C, 23.29; H, 0.95; N, 4.69%.

3. Crystal structure determination

Crystal data and structure refinement details for **1** are given in Table 1. Selected bond lengths and angles for **1** are given in Table 2. Data were collected with MoKα radiation ($\lambda = 0.71073$ Å) using a CCD diffractometer. The sample selected for investigation has dimensions of $0.30 \times 0.25 \times 0.20$ mm^3. A total of 6951 reflections were measured to give 5023 independent reflections. The structure was solved using direct methods with SHELXTL program [35] 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. The structure was then refined on F^2 using SHELXL-97. The final R value (on F) for the 3812 reflections with $I > 2\sigma(I)$ was 0.075.

4. Results and discussion

The cationic octahedral structure indicates that the value state for the center nickel ion is divalent, because a Ni(III) complex will show the tetragonal structural distortion in virtue of the presence of an active Jahn-Teller effect in the d^7 electronic system. Moreover, the presence of two hydrogen ions (probably associated with the anion), which have not been detected during the structure refinement, is required to balance the charges

Table 1
Crystal data and structure refinement for compound **1**

Empirical formula	$C_{72}H_{50}N_{12}Cu_{10}Ni_2I_{16}$
Formula weight	3866.46
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit-cell dimensions	$a = 11.6861(17)$ Å, $\alpha = 76.370(2)°$
	$b = 14.590(2)$ Å, $\beta = 70.830(2)°$
	$c = 14.649(2)$ Å, $\gamma = 81.320(3)°$
Volume, Z	2285.3(6) Å^3, 1
Density (calculated)	2.808 g cm^{-3}
Absorption coefficient	8.126 mm^{-1}
F_{000}	1758
Crystal size	$0.30 \times 0.25 \times 0.20$ mm^3
θ range for data collection	4.1 to 23.26°
Limiting indices	$-12 \leqslant h \leqslant 10$, $-15 \leqslant k \leqslant 16$, $-16 \leqslant l \leqslant 16$
Reflection collected	6951
Independent reflections	5023
Data/restraints/parameters	5273/0/502
Goodness-of-fit on F^2	0.979
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0750$. w$R_2 = 0.1761$
R indices (all data)	$R_1 = 0.0929$. w$R_2 = 0.1912$

Table 2
Selected bond lengths (Å) and angles (deg) for compound **1**

Cu(1)–I(4)	2.835(4)	Cu(2)–I(2)	2.580(4)
Cu(1)–I(5)	2.643(3)	Cu(2)–I(4)	2.969(4)
Cu(1)–I(7)#1	2.608(4)	Cu(2)–I(5)	2.620(4)
Cu(1)–I(8)#1	2.741(5)	Cu(2)–I(6)	2.657(5)
Cu(1)–Cu(5)#1	2.900(4)	Cu(3)–I(1)	2.632(4)
Cu(4)–I(1)	2.490(3)	Cu(3)–I(2)	2.528(3)
Cu(4)–I(3)	2.520(3)	Cu(3)–I(6)	3.095(6)
Cu(4)–I(6)	2.706(4)	Cu(3)–I(8)	2.628(3)
Cu(4)–Cu(3)	2.583(5)	Cu(3)–Cu(2)	3.017(6)
Cu(5)–I(3)	2.714(3)	Ni(1)–N(1)	2.083(12)
Cu(5)–I(6)	2.780(3)	Ni(1)–N(2)	2.124(11)
Cu(5)–I(7)	2.563(3)	Ni(1)–N(3)	2.089(11)
Cu(5)–I(8)	2.732(3)	Ni(1)–N(4)	2.077(12)
Cu(5)–Cu(4)	2.593(4)	Ni(1)–N(5)	2.033(12)
Cu(5)–Cu(1)#1	2.900(4)	Ni(1)–N(6)	2.117(13)
I(5)–Cu(1)–I(7)#1	122.47(17)	I(1)–Cu(4)–I(3)	141.64(16)
I(7)#1–Cu(1)–I(8)#1	110.82(13)	I(1)–Cu(4)–I(6)	110.58(14)
I(5)–Cu(1)–I(8)#1	115.11(15)	I(3)–Cu(4)–I(6)	106.61(12)
I(4)–Cu(1)–I(7)#1	103.07(13)	I(7)–Cu(5)–I(3)	119.42(11)
I(4)–Cu(1)–I(5)	98.39(12)	I(7)–Cu(5)–I(8)	112.51(10)
I(4)–Cu(1)–I(8)#1	103.12(13)	I(3)–Cu(5)–I(8)	107.38(10)
I(2)–Cu(2)–I(4)	100.56(13)	I(7)–Cu(5)–I(6)	110.29(10)
I(2)–Cu(2)–I(5)	119.82(16)	I(3)–Cu(5)–I(6)	99.48(9)
I(2)–Cu(2)–I(6)	116.05(15)	I(8)–Cu(5)–I(6)	106.36(10)
I(5)–Cu(2)–I(4)	95.67(13)	Cu(3)–I(8)–Cu(5)	79.39(13)
I(6)–Cu(2)–I(4)	101.75(12)	Cu(3)–I(8)–Cu(1)#1	109.42(13)
I(2)–Cu(3)–I(1)	114.71(15)	Cu(5)–I(8)–Cu(1)#1	64.00(9)
I(8)–Cu(3)–I(2)	121.03(14)	Cu(5)–I(7)–Cu(1)#1	68.23(11)
I(1)–Cu(3)–I(8)	114.77(14)	Cu(2)–I(6)–Cu(4)	115.02(12)
I(6)–Cu(3)–I(1)	96.20(14)	Cu(2)–I(6)–Cu(5)	107.14(10)
I(6)–Cu(3)–I(2)	103.96(16)	Cu(4)–I(6)–Cu(5)	56.39(10)
Cu(2)–I(5)–Cu(1)	81.42(13)	Cu(2)–I(6)–Cu(3)	62.73(10)
Cu(1)–I(4)–Cu(1)#1	180.0	Cu(4)–I(6)–Cu(3)	52.36(11)
Cu(1)–I(4)–Cu(2)	72.48(11)	Cu(5)–I(6)–Cu(3)	71.08(9)
Cu(1)–I(4)–Cu(2)#1	107.52(11)	Cu(4)–I(3)–Cu(5)	59.26(10)
Cu(2)–I(4)–Cu(2)#1	180	Cu(3)–I(2)–Cu(2)	72.41(16)
Cu(4)–I(1)–Cu(3)	60.50(13)	N(2)–Ni(1)–N(1)	79.3(5)
N(1)–Ni(1)–N(3)	170.1(5)	N(2)–Ni(1)–N(3)	94.0(5)
N(1)–Ni(1)–N(4)	92.7(5)	N(2)–Ni(1)–N(4)	89.6(4)
N(1)–Ni(1)–N(5)	94.1(4)	N(2)–Ni(1)–N(5)	94.5(5)
N(1)–Ni(1)–N(6)	92.7(5)	N(2)–Ni(1)–N(6)	169.7(4)
N(3)–Ni(1)–N(4)	79.9(5)	N(5)–Ni(1)–N(4)	172.6(5)
N(3)–Ni(1)–N(5)	93.6(5)	N(6)–Ni(1)–N(3)	94.8(5)
N(6)–Ni(1)–N(4)	97.3(5)	N(6)–Ni(1)–N(5)	79.6(5)

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

Fig. 1. Cationic structural unit for compound **1**.
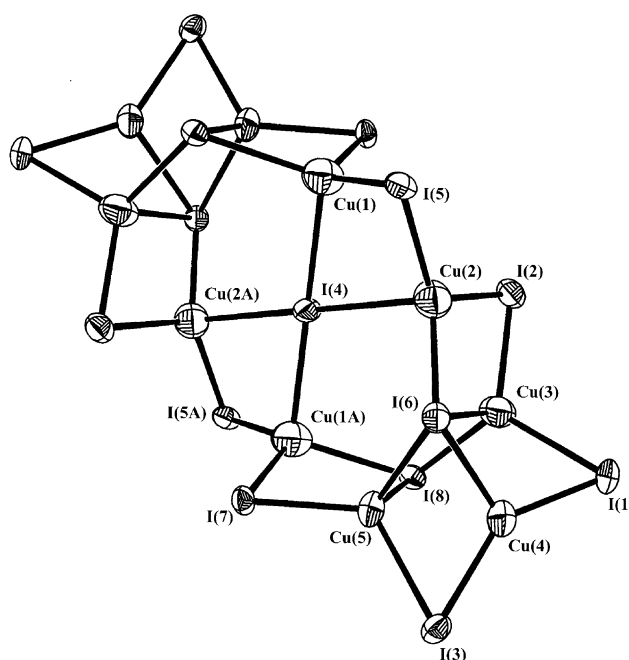
Fig. 2. Anionic structural unit for compound **1**.

of the crystal structure. The stoichiometry of the complex would then be $[Ni^{II}(phen)_3]_2[Cu_{10}H_2I_{16}]$.

The title compound $[Ni^{II}(phen)_3]_2[Cu_{10}H_2I_{16}]$ consists of NiN_6^{2+} core cation and decanuclear iodocuprate(I) anion together with two dissociative H^+ ions. As for the cation (Fig. 1), the six-fold coordination Ni(II) center in a distorted octahedral geometry is chelated by six N atoms from three phen ligands. The material parameters associated with the NiN_6^{2+} core cation are comparable with those found in complexes $[Ni(bpy)_3]SO_4$ (bpy = 2,2′-bipyridine) [36], $[Ni(phen)_3]I_2$ [37] and $[Ni(bpy)_3][CdCl_4]$ [38]. The Ni–N distances vary from 2.033(12) to 2.124(11) Å.

There are no apparent bonding interactions between the constituent atoms of the cation and the anion. As shown in Fig. 2, the discrete decanuclear iodocuprate(I) is formed by crystallographically independent five monovalent copper atoms and eight iodine atoms via an inversion center. As to the coordination environment of copper(I) atoms, there exist two types of coordination sites; only one copper(I) atom [Cu(4)] is in a highly

distorted triangular planar site, and the other four copper(I) atoms [Cu(1), Cu(2), Cu(3) and Cu(5)] display the tetrahedral geometries. Indication of the presence of the quite distorted geometry of Cu(4) is the I–Cu(4)–I angles ranging from 106.61(12)° to 141.64(16)°. The tetrahedrally coordinated Cu(I) atoms are also quite distorted because of serious deviation from the normal value (109.5°) of the relevant I–Cu–I angles [95.67(13)–122.47(17)°]. All the Cu–I bond lengths span a rather wide range from 2.490(3) to 3.095(6) Å. Briefly, the anionic framework of compound **1** can also be described as being constructed by two CuI$_3$ units and eight CuI$_4$ tetrahedrons through sharing edges and corners.

Considerable attention is paid to the bridging geometry of the X^- ions. In anionic unit of **1**, four types of bridging modes of I$^-$ ions have been found: two are ordinary μ_2- and μ_3-bonding modes, and the other two are the μ_4-bonding ones being completely different from the tetrahedral and the square pyramidal arrangements. Firstly, five I$^-$ ions [I(1), I(2), I(3), I(5), and I(7)] form μ_2-bridges, with the Cu–I–Cu angles ranging from 59.26(10)° to 81.42(13)°. Secondly, I(8) ion takes on a μ_3-bridge with a trigonal pyramidal geometry. One of Willett's viewpoints is that the X^- anion often favors a trigonal pyramidal geometry with n Cu as the base, when it is involved in a μ_{n^-} ($n = 3$, 4 or 5) bridge, and so does the I(8) ion. The distance from the apical I(8) atom to the plane of the copper atoms [Cu(3), Cu(5) and Cu(1A)] is 1.5494 Å, and the Cu–I(8)–Cu angles are 64.00(9)°, 79.39(13)° and 109.42(13)°, respectively. As for the two μ_4-bridging geometry, one [I(6)] exhibits a novel μ_4-bridge like an "umbrella", which is just found in complex [C$_5$H$_7$N$_2$O][Cu$_3$Br$_4$] [31]. It can be better described that I(6) having adopted the analogous geometry with I(8) further bonds to another Cu ion [Cu(3)] below the plane comprising Cu(2), Cu(4) and Cu(5). The distances between I(6) and each of these three Cu atoms are short [2.657(5)–2.780(3) Å], while the Cu(3)–I(6) separation is considerably longer at 3.095(6) Å. The other [I(4)] is involved in a rectangle planar geometry, which is unique in the halocuprates(I), though it is commonly observed in the Corbett-type rare-earth halide clusters. All the atoms related to this bridge are co-planar (no deviation from the least-squares plane). The formation of this μ_4-geometry is attributed to the special position of I$^-$ ion. I(4) locates on the inversion center of the anionic unit of **1**, and the Cu–I(4) bond lengths are slightly long [2.835(4)–2.969(4) Å]. Moreover, we can find that a majority of acute Cu–X–Cu bridging bond angles exist widely in anionic unit, which results in quite short Cu–Cu separations, i.e., Cu(4)–Cu(3) = 2.583(5) and Cu(5)–Cu(4) = 2.593(4) Å, respectively, which are appreciably larger than those observed in complex [Cu(PhN = NPh)$_2$] (2.45 Å) [39].

Using CuBr as one of the starting materials instead of CuI, only mononuclear [CuCl$_2$]$^-$ anionic unit not the expected bromocuprate(I) is found in the structure of the resulting product with the formula [Ni^{II}(phen)$_3$][CuCl$_2$]$_2$ **2**. Once the CuX is the CuCl, a neutral copper(II) halide coordination polymer [Cu$_2$Cl$_4$(phen)$_2$]$_n$ **3** is separated, displaying a novel 1-D polymeric chain linked alternately by five coordinate and six coordinate Cu(II) via either covalent or semi-coordination Cu–Cl bonds.

Though the size, form and the charge distribution of the cation involved for **1** are the same as those for **2**, why is the anionic constitution of **1** [Cu$_{10}$I$_{16}$]$^{6-}$ different from that of **2** [CuCl$_2$]$^-$? Firstly, the halogen atom is a vital factor, just as one of significant conclusions largely substantiated by earlier work that there is a tendency to form the infinite polymers from Cl through Br to I. Secondly, please see Fig. 3, where the semi-open regions enclosed by adjacent cations because of the so-called $\pi-\pi$ stacking interactions between phen rings should also be a factor. Moreover, the hydrogen-bonded interactions existing widely among the anions and the cations such as the various C–H$\cdots$I hydrogen bonds should also play an important part in influencing the anionic configuration.

Fig. 4 shows the ground state spectrum of the title compound in DMF solution. A strong absorption peak at ~270 nm in the near ultraviolet (UV) wavelength range is attributed to the charge-transfer excitation between Cu$^+$ and I$^-$ ions of anionic segment (the concentration of the sample, 3.40×10^{-6} mol dm^{-3}). In the visible region, there is very weak linear absorption at wavelengths ranging from ~490 nm to ~900 nm (the peak at ~730 nm) assigned as the $d-d$ transfer of the ligand to the Ni center (the concentration, 1.52×10^{-4} mol dm^{-3}).

The third-order non-linear optical (NLO) property of the title compound was investigated at 532 nm with a 15 ns pulse width produced by a frequency-doubled Q-switched Nd:YAG laser in 1.29×10^{-4} mol dm^{-3} DMF solution, and revealed by using a Z-scan technique (Fig. 5). The cell being selected to place the sample is 5-mm-thick quartz one. The open and filled circles depict the non-linear absorptive and refractive properties, respectively. The solid curves were obtained after a reasonably good fit between the experimental data and the theoretical curve (see Fig. 4). In accordance with the observed α_2 and n_2 (α_2 and n_2 are effective third-order NLO absorptive and refractive coefficients, respectively), the modulus of the effective third-order susceptibility $\chi^{(3)}$ can be calculated by

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

where λ is the wavelength of the laser light, n_0 is the linear refractive index of the sample (n_0 can be replaced by one of the solvents if the concentration of the sample
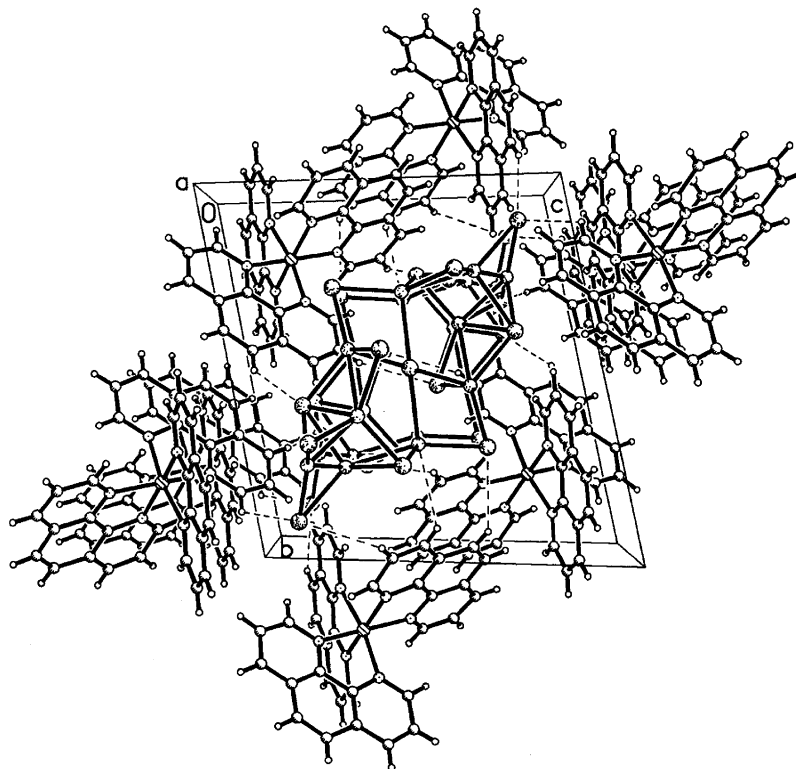
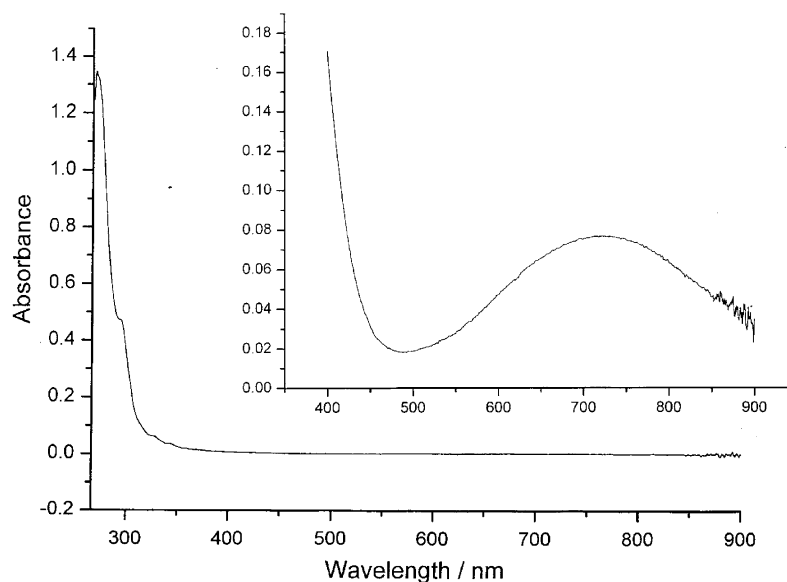Fig. 3. Packing diagram of unit cell structure for compound **1**.

Fig. 4. Electronic spectrum of compound 1 in DMF solution with 1 cm optical path.

is very small during calculation), ε_0 and c are the permittivity and the speed of light in a vacuum, respectively. The corresponding modulus of the hyperpolarizability γ was obtained from $|\gamma| = |\chi^{(3)}|/NF^4$ ($F^4 = [(n_0^2 + 2)/3]^4$), where N is the molecular number density of the compound in the sample and F^4 is the local field correction factor.

All the calculated results are listed in Table 3. From the results, the $|\gamma|$ value of **1**, 9.77×10^{-31} esu, is comparable with those of other compounds as discrete clusters [Et$_4$N][MoS$_4$Cu$_4$(SCN)$_4$(2-pic)$_4$] (1.29×10^{-31} esu), [Et$_4$N][WS$_4$Cu$_4$(SCN)$_4$(2-pic)$_4$] (9.42×10^{-32} esu) (2-pic = 2-methyl-pyridine) [40] apart from metal–acetone compounds *trans*-[Mo(CO)$_4$(PPh)$_3$] (3.30×10^{-32} esu) and

Table 3
Third-order nonlinear optical property of compound **1**

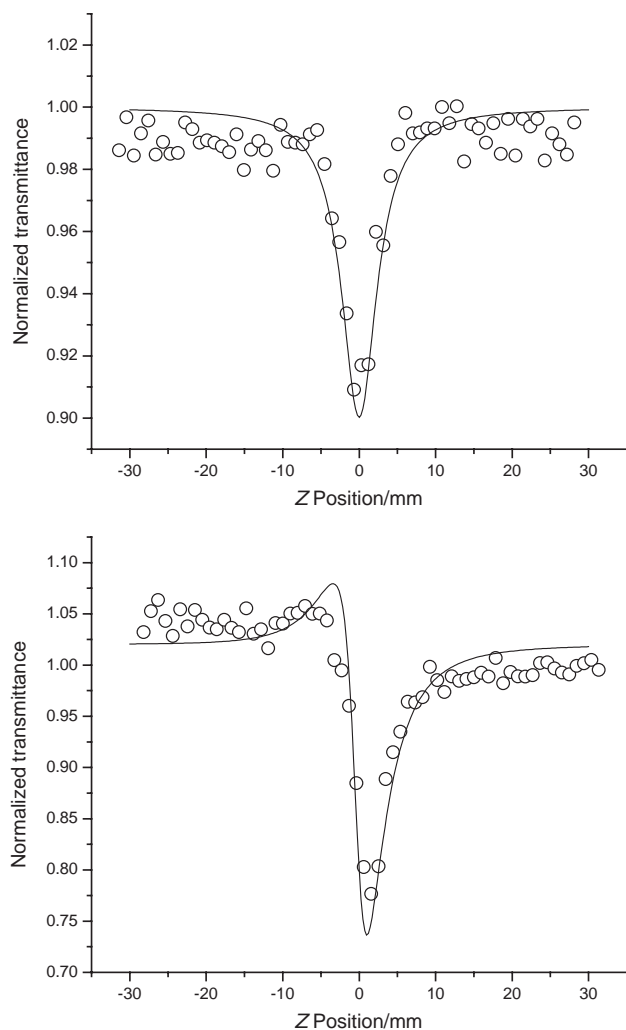|	α_2 (m W^{-1})	n_2 (m^2 W^{-1})	χ^3 (esu)	χ^3 (esu mol^{-1} dm^3)	γ (esu)
[Ni(phen)$_3$]$_2$[Cu$_{10}$I$_{16}$]	0.20×10^{-11}	-3.10×10^{-19}	2.50×10^{-13}	1.94×10^{-9}	9.77×10^{-31}

Fig. 5. Z-scan data of 1.29×10^{-4} mol dm^{-3} of compound **1**: (a) collected under the open aperture configuration showing NLO absorption (the solid curve is a theoretical fit); and (b) obtained by dividing the normalized Z-scan data obtained under the closed aperture configuration by the normalized Z-scan data in (a).

cis-[Mo(CO)$_4$(PPh)$_3$] (1.70×10^{-31} esu) [41]. So, we can state reasonably that the title compound possesses the nicer third-order NOL property, and exhibits the reverse saturable absorption (RSA) ($\alpha_2 > 0$) and self-defocusing performance ($n_2 < 0$). It is said that the material containing the self-defocusing property may be an excellent one for applications in protection of optical sensors. With regard to the interrelation between structure and optical property, we can owe the nicer NLO property of compound **1** to the presence of the

larger delocalized space in the crystal structure provided by the anionic unit, in particular the I$^-$ bridges containing the larger radius and the big π bond of phen ligand around Ni(II) center in cationic part, since these factors help the electronic free movement.

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