PAPER

NJC
www.rsc.org/njc

Syntheses, characterization and optical properties of some copper(I) halides with 1,10-phenanthroline ligand†

Jie-Hui Yu, Zheng-Liang Lü, Ji-Qing Xu,* Hai-Ying Bie, Jing Lu and Xiao Zhang

College of Chemistry and State Key Laboratory of Inorganic Synthesis and
Preparative Chemistry, Jilin University, Changchun 130023, P. R. China.
E-mail: xjq@mail.jlu.edu.cn

***Received* (in Montpellier, France) 19th November 2003, Accepted 14th April 2004**
First published as an Advance Article on the web 20th July 2004

The hydrothermal reactions of CuX_2 or CuX with phen (1,10-phenanthroline) have resulted in the syntheses of eight compounds **1**–**8**. In these, 1:1 adducts of CuX/phen are reported: ionic $[Cu(phen)_2][CuX_2]$ (X = Cl **1**, Br **2**) and dimer $[Cu_2I_2(phen)]$ **3**; the trinuclear clusters $[Cu_3X_3(phen)_2]$ (X = Br **5**, I **7**) were first prepared and the structures can be best described as 1:1 adducts of dimers and CuX; the chain compounds **6** and **8** belong to the same series with the formula $[CuX_2L]$ (L = organic ligand), but the chain arrangement is different; the structure of **4** is yet being refined. Compounds **1**–**8** have a high thermal stability. The third-order nonlinear optical properties of compounds **5**, **6** and **8** were investigated and all exhibit a reverse saturable absorption ($\alpha_2 > 0$) and self-defocusing performance ($n_2 < 0$).

Introduction

The structural characterization of 1:1 adducts of copper(I) halides with several chelate organodiimine ligands under ambient conditions has been successfully investigated by White and co-workers. For example, with 2,2′-bipyridine (2,2′-bpy) or 2,9-dimethyl-1,10-phenanthroline (dmphen), from Cl through Br to I, the corresponding products are, respectively, ionic species $[Cu(2,2'\text{-bpy})][CuCl_2]$ and dimers $[Cu_2X_2(2,2'\text{-bpy})_2]$ (X = Br, I)[1] or mononuclear species [CuCl(dmphen)] and dimers $[Cu_2X_2(dmphen)_2]$ (X = Br, I).[2] But to date, the parallel study of 1,10-phenanthroline (phen) is still not quite complete on account of the continued inability to get CuCl/phen crystals, though the remaining two halides have been reported: namely the bromide is ionic $[Cu(phen)_2][CuBr_2]$[3] and the iodine is dimeric with a solvent molecule $[Cu_2I_2(phen)_2]\cdot CH_3OH$.[2] In contrast with the three reported frameworks, the copper(I) ion shows a diversity of coordination geometries and is capable of attaining two-, three-, or fourfold coordination with linear, triangular planar or tetrahedral sites. It should also be noted that the mononuclear species is rather odd and interesting; its formation is possibly determined by composition factors, such as the element Cl with its smaller atomic radius, the phen ligand with a large steric hindrance effect, the substitution groups on the phen ring and the π-π stacking interactions among adjacent phen rings in the solid phase.

One aspect of the current investigation focuses of our group is to hydrothermally synthesize copper halide compounds, characterize the copper-halo clusters and explore their functional properties. Herein, we report the syntheses, characterization and third-order nonlinear optical properties of a range of Cu phen complexes, obtained from the reactions of CuX_2 or CuX with phen.

Experimental

Materials and measurements

The chemicals used to prepare the title compounds include $CuCl_2\cdot 2H_2O$, $CuBr_2$, CuCl, CuBr, CuI, $MnBr_2\cdot 4H_2O$, KBr, KI, 1,2,4-benzenetricarboxylic acid (1,2,4-bta), phen·H_2O and NaOH, used without further purification. The syntheses were carried out in 30 mL Teflon-lined stainless steel vessels under autogenous pressure. The single crystals were collected by filtration, washed with distilled water and dried in air at ambient temperature.

C, H and N analyses were performed with a Perkin–Elmer 2400LS II elemental analyzer. Infrared spectra were recorded with a Perkin–Elmer Spectrum 1 spectrophotometer in the 4000–400 cm^{-1} region using a powdered sample in a KBr plate. Thermogravimetric analyses were determined on a Perkin–Elmer TGA-7 instrument, with a heating rate of 20 °C min^{-1} in air.

X-Ray crystallography

Data were collected with Mo Kα radiation (λ = 0.71073 Å) with a Siemens P4 diffractometer for compound **1**, with a Siemens SMART CCD diffractometer for compound **7**, and with a Rigaku R-AXIS RAPID IP diffractometer for compounds **2**, **3**, **5**, **6** and **8**. Empirical absorption corrections were applied for all compounds. The structures except for compound **3** were solved by direct methods using heavy atom methods with SHELXTL program and refined by full-matrix least-squares techniques. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement and the hydrogen atoms were treated using a riding model. The structure was then refined on F^2 using SHELXL-97. Basic information pertaining to the crystal parameters and structure refinement of the title compounds is summarized in Table 1. The cell dimensions of **2** are a = 17.172(3), b = 13.312(3), c = 10.877(2) Å; β = 115.78(3)°; the structure of **4** is still being refined‡.

---

† Electronic supplementary information (ESI) available: Z-scan data plots for **6**, **11** and **13**. See http://www.rsc.org/suppdata/nj/b3/b314974a/

‡ CCDC reference numbers: **1** 218680, **3** 217161, **5** 171242, **6** 175528, **7** 164222, **8** 224395. See http://www.rsc.org/suppdata/nj/b3/b314974a/ for crystallographic data in .cif or other electronic format.

DOI: 10.1039/b314974a

Table 1 Crystal data and structure refinement for compounds **1**, **3**, **5**, **6**, **7** and **8**

	1	**3**	**5**	**6**	**7**	**8**
Empirical formula	$Cu_2Cl_2C_{24}H_{16}N_4$	$CuIC_{12}H_8N_2$	$Cu_{1.5}Br_{1.5}C_{12}H_8N_2$	$Cu_2Cl_4C_{24}H_{16}N_4$	$Cu_{1.5}I_{1.5}C_{12}H_8N$	$CuBr_2C_{12}H_8N_2$
Formula weight	558.39	370.64	395.38	629.29	465.86	403.56
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	P-1	$C2/c$	Cc	$C2/c$	$P2_1/n$
a/Å	19.627(5)	7.6507(15)	10.040(2)	9.875(2)	10.0495(8)	9.945(2)
b/Å	14.827(3)	9.0871(3)	14.516(3)	17.863(4)	15.0351(12)	6.5064(13)
c/Å	15.196(4)	9.1094(3)	16.319(3)	13.393(3)	16.8237(12)	18.222(4)
α/°		96.74(3)				
β/°	103.057(18)	104.05(3)	94.29(3)	106.84(3)	94.105(2)	91.23(3)
γ/°		109.21(3)				
U/Å^3	4308.1(17)	566.55(8)	2371.7(8)	2263.4(8)	2535.5(3)	1178.8(8)
Z	8	2	8	4	8	4
μ(Mo-Kα)/mm^{-1}	2.243	4.622	7.742	2.375	6.168	8.606
Reflections collected	4655	2476	2302	2591	6074	2700
Independent reflections	3789	2476	2302	2591	1807	2700
R_{int}	0.0258	0.0327	0.0389	0.0397	0.1036	0.0318
R_1 [$I > 2\sigma(I)$]	0.0360	0.0333	0.0390	0.0261	0.0386	0.0285
wR_2 [$I > 2\sigma(I)$]	0.0800	0.0918	0.0772	0.0457	0.0804	0.0600
R_1 (all data)	0.0768	0.0381	0.0760	0.0344	0.0571	0.0479
wR_2 (all data)	0.0890	0.0939	0.0887	0.0470	0.0859	0.0642

Syntheses

[Cu(phen)$_2$][CuCl$_2$] 1. A typical reaction mixture of $CuCl_2 \cdot 2H_2O$ (570 mg, 3.33 mmol), phen·H_2O (660 mg, 3.33 mmol), 1,2,4-bta (700 mg, 3.33 mmol), NaOH (390 mg, 9.99 mmol) and H_2O (18 mL) in a molar ratio of 1:1:1:3:300 was fully stirred until homogeneous, then heated at 160 °C for 3 days to give dark blue plate crystals of **1**. The total yield was approximately 35% based on Cu. IR (KBr) ν: 1621 (w), 1587 (w), 1505 (m), 1423 (s), 1411 (s), 1220 (w), 1136 (w), 846 (m), 837 (s), 775 (m), 761 (m), 722 (s), 415 (m) cm^{-1}. Anal. calcd for $CuClC_{12}H_8N_2$: C, 51.59; H, 2.85; N, 10.07%. Found: C, 51.62; H, 2.87; N, 10.04%.

[Cu(phen)$_2$][CuBr$_2$] 2. A typical reaction mixture of $CuBr_2$ (740 mg, 3.33 mmol), phen·H_2O (990 mg, 4.99 mmol), KBr (990 mg, 8.32 mmol) and H_2O (18 mL) in a molar ratio of 1:1.5:2.5:300 was fully stirred until homogeneous, then heated at 160 °C for 3 days to give dark brownish-red columnar crystals of **2**. The total yield was approximately 50% based on Cu. IR (KBr) ν: 1620 (w), 1581 (w), 1505 (m), 1493 (w), 1421 (s), 1414 (s), 1221 (w), 1139 (w), 841 (s), 767 (w), 725 (s), 637 (w) cm^{-1}. Anal. calcd for $CuBrC_{12}H_8N_2$: C, 44.52; H, 2.49; N, 8.66%. Found: C, 44.99; H, 2.61; N, 8.62%.

[Cu$_2$I$_2$(phen)$_2$] 3. A typical reaction mixture of CuI (630 mg, 3.33 mmol), $MnBr_2 \cdot 4H_2O$ (1910 mg, 6.66 mmol), phen·H_2O (990 mg, 4.99 mmol) and H_2O (18 mL) in a molar ratio of 1:2:1.5:300 was fully stirred until homogeneous, then heated at 160 °C for 3 days to give red columnar crystals of **3**. The total yield was approximately 30% based on Cu. IR (KBr) ν: 1619 (w), 1585 (w), 1570 (w), 1505 (m), 1493 (w), 1420 (s), 1139 (m), 845 (s), 772 (m), 727 (s), 631 (w), 419 (w) cm^{-1}. Anal. calcd for $CuIC_{12}H_8N_2$: C, 38.89; H, 2.18; N, 7.56%. Found: C, 39.77; H, 2.27; N, 7.70%.

Compound 4. A typical reaction mixture of CuCl (330 mg, 3.33 mmol), phen·H_2O (660 mg, 3.33 mmol) and H_2O (18 mL) in a molar ratio of 1:1:300 was fully stirred until homogeneous, then heated at 160 °C for 3 days to give black needle crystals of **4**, weighing *ca.* 300 mg. IR (KBr) ν: 1621 (w), 1504 (m), 1423 (s), 1410 (s), 1219 (w), 1133 (w), 837 (s), 759 (m), 722 (s), 417 (m) cm^{-1}. Anal. found: C, 48.15; H, 2.73; N, 9.26%.

[Cu$_3$Br$_3$(phen)$_2$] 5. A typical reaction mixture of CuBr (480 mg, 3.33 mmol), phen·H_2O (660 mg, 3.33 mmol) and H_2O (18 mL) in a molar ratio of 1:1:300 was fully stirred until homogeneous, then heated at 160 °C for 3 days to give red columnar crystals of **5**. The total yield was approximately 30% based on Cu. IR (KBr) ν: 1620 (w), 1572 (w), 1509 (s), 1492 (w), 1444 (w), 1424 (s), 1415 (m), 1222 (w), 1137 (m), 842 (s), 765 (s), 725 (s), 636 (w), 423 (w) cm^{-1}. Anal. calcd for $Cu_{1.5}Br_{1.5}C_{12}H_8N_2$: C, 36.45; H, 2.04; N, 7.09%. Found: C, 36.76; H, 1.70; N, 6.94%.

[CuCl$_2$(phen)] 6. A typical reaction mixture of $CuCl_2 \cdot 2H_2O$ (570 mg, 3.33 mmol), phen·H_2O (990 mg, 4.99 mmol) and H_2O (18 mL) in a molar ratio of 1:1.5:300 was fully stirred until homogeneous, then heated at 160 °C for 3 days to give light green columnar crystals of **6**. The total yield was approximately 40% based on Cu. IR (KBr) ν: 1625 (w), 1607 (w), 1586 (w), 1514 (m), 1423 (s), 1349 (m), 1146 (m), 1108 (m), 855 (s), 736 (m), 721 (s), 643 (w), 428 (w) cm^{-1}. Anal. calcd for $CuCl_2C_{12}H_8N_2$: C, 45.80; H, 2.56; N, 8.90%. Found: C, 44.87; H, 1.98; N, 8.24%.

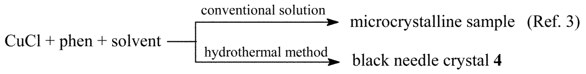
[Cu$_3$I$_3$(phen)$_2$] 7. A typical reaction mixture of CuI (630 mg, 3.33 mmol), phen·H_2O (660 mg, 3.33 mmol), KI (1.38 mg, 8.32 mmol) and H_2O (18 mL) in a molar ratio of 1:1:2.5:300 was fully stirred until homogeneous, then heated at 150 °C for 5 days to give red rhombic crystals of **7**. The total yield was approximately 25% based on Cu. IR (KBr) ν: 1619 (w), 1572 (w), 1508 (m), 1492 (w), 1423 (s), 1221 (w), 1138 (m), 866 (m), 841 (s), 765 (m), 725 (s), 637 (w), 423 (w) cm^{-1}. Anal. calcd for $Cu_{1.5}I_{1.5}C_{12}H_8N_2$: C, 30.94; H, 1.73; N, 6.01%. Found: C, 30.44; H, 1.70; N, 6.21%.

[CuBr$_2$(phen)] 8. A typical reaction mixture of CuI (630 mg, 3.33 mmol), $CuBr_2$ (1480 mg, 6.66 mmol), phen·H_2O (990 mg, 4.99 mmol) and H_2O (24 mL) in a molar ratio of 1:2:1.5:400 was fully stirred until homogeneous, then heated at 160 °C for 4 days to give dark green rectangle crystals of **8**. The total yield was approximately 30% based on Cu. IR (KBr) ν: 1607 (w), 1585 (w), 1515 (m), 1423 (s), 1348 (m), 1146 (m), 1106 (m), 854 (s), 776 (w), 734 (w), 720 (s), 644 (w), 430 (w) cm^{-1}. Anal. calcd for $CuBr_2C_{12}H_8N_2$: C, 35.71; H, 2.00; N, 6.94%. Found: C, 35.44; H, 1.70; N, 6.21%.

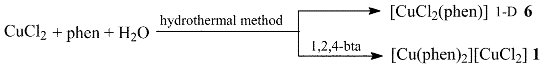
Results and discussion

Syntheses

With the conventional solution [see eqn. (1)], only a microcrystalline sample of CuCl/phen unsuitable for X-ray analysis could be prepared,[3] while black needle crystals of **4** were isolated under hydrothermal conditions. The elemental analysis of **4** revealed that it is not the desired ionic or dimeric species, so we investigated the reaction of $CuCl_2$ and phen, because it has been reported that Cu(II) halides have the tendency to be reduced to Cu(I) ones in the presence of organic species.[4,5] Based on this idea, compound **1** has been synthesized successfully from the simple reaction of $CuCl_2$, phen and 1,2,4-bta, where 1,2,4-bta acts as the reductive reagent [see eqn. (2)]. For comparison, just the Cu(II) chain polymer $[CuCl_2(phen)]$ **6** is produced without 1,2,4-bta.

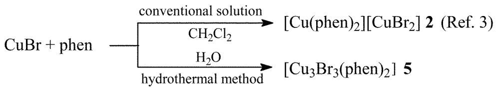


(1)

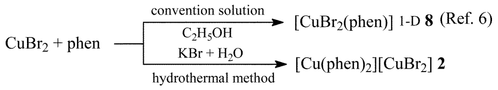


(2)

As far as the Br system is concerned, the product of the reaction of CuBr with excess phen in dichloromethane under ambient temperature has proved to be ionic $[Cu(phen)_2][CuBr_2]$ **2**.[3] But the same precursors under hydrothermal conditions give birth to the novel trinuclear species $[Cu_3Br_3(phen)_2]$ **5** [see eqn. (3)]. How on earth can one prepare compound **2** with the hydrothermal method? The answer is the same as for compound **1**; $CuBr_2$ is used as one of the raw materials (herein the reductive reagent is excess phen), whereas Cu(II) halide is not reduced with conventional solution so that the outcome is the chain polymer $[CuBr_2(phen)]$ **8** [see eqn. (4)].[6]

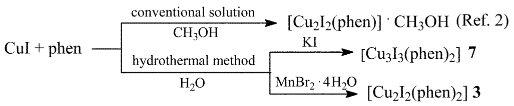


(3)



(4)

As for the I system, the dimer containing a methanol molecule, $[Cu_2I_2(phen)_2]\cdot CH_3OH$, has been reported in the literature.[2] Our significant finding is that we use the hydrothermal method to synthesize two discrete clusters from the reaction of CuI and phen: one is the trinuclear species $[Cu_3I_3(phen)_2]$ **7**, while the other is the dimeric $[Cu_2I_2(phen)_2]$ **3** without any solvent molecule [see eqn. (5)]. It deserves to be noted that the additional soluble salts incorporated in the starting materials, *i.e.*, KI for **7** and $MnBr_2\cdot 4H_2O$ for **3**, play a key role in determining the final framework.



(5)

The TGA analyses show that compounds **1**–**8** possess high thermal stability; the temperatures for the onset of decomposition are 380, 370, 280, 380, 220, 390, 270 and 370 °C for **1**–**8**, respectively.

Some significant conclusions can be drawn from the above results. To begin with, the hydrothermal method is very effective for synthesizing solid inorganic materials. Secondly, identical precursors with different methods may lead to dissimilar products, since the thermodynamic constants of the compounds will change with the changing temperature and pressure of the system and so will the reactive process and mechanism. Thirdly, the hydrothermal setting generally creates a reductive atmosphere and some particular reactions may occur; therefore, we can reasonably design and synthesize new phases by accounting for these remarks. Finally, selecting the right solvent salts and incorporating then into the reactive system may bring on the formation of special clusters; at the least they help in crystal growth as "mineralizers".

Crystal structures

The molecular structure of $[Cu(phen)_2][CuCl_2]$ **1** is similar to those of $[Cu(phen)_2][CuBr_2]$ **2** and $[Cu(2,2'\text{-bpy})_2][CuCl_2]$. As shown in Fig. 1, compound **1** is a new example containing the $[CuN_4]^+$ core. Selected bonding parameters are given in Table 2. In general, the $[CuN_4]^+$ species should approach its ideal *mm* or 222 symmetry (interligand N–Cu–N angles vary from 114.3° to 132.4°[1]) as in complexes $[Cu(tmen)_2]^+$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine)[7] and $[Cu(phen)_2]ClO_4$.[3] But in the $[CuN_4]^+$ core geometry in compound **1**, the tetrahedrally coordinated copper is highly distorted, since the range of interligand angles is 107.62(12)°–149.04(13)°. Moreover, the Cu–N distances, ranging from 2.048(3) to 2.082(3) Å in **1**, are slightly longer than those found in complex $[Cu(2,2'\text{-bpy})_2][CuCl_2]$ [2.005(6)–2.039(6) Å]; the intraligand N–Cu–N angles of **1**, 80.67(11)°–80.71(11)°, compare well with those observed in $[Cu(2,2'\text{-bpy})_2][CuCl_2]$ [80.9(2)–81.4(2)°] and the dihedral angle between the ligand planes is 43.6°. With the $[CuN_4]^+$ core as a template, CuCl forms the mononuclear chlorocuprate $[CuCl_2]^-$. The Cu(2) atom is in a linear site and coordinated by two terminal Cl ions. The Cu–Cl_t distances, 2.0900(15) and 2.0923(15) Å, and the Cl–Cu–Cl angle, 178.71(5)°, are basically in agreement with the values reported for $[Cu(2,2'\text{-bpy})_2][CuCl_2]$ [2.086(2) and 2.091(2) Å, 177.3(1)°].

As shown in Fig. 2(a), compound **3** is a halide-bridged dimer based on the Cu_2I_2 core (selected bonding parameters are listed in Table 3). Because a large number of dimers have been reported before,[8] we just provide some structural information of interest to everyone; for example, is the rhomboid comprising the four atoms Cu(1), Cu(1A), I(1) and I(1A) planar or folded? Here it is planar and displays a dihedral angle of 80.4° with the phen plane; the Cu–I distances and the Cu–N distances are 2.5563(10), 2.6037(8) Å and 2.095(3), 2.103(3) Å, respectively; and the intraligand angle [80.15(12)°] and the

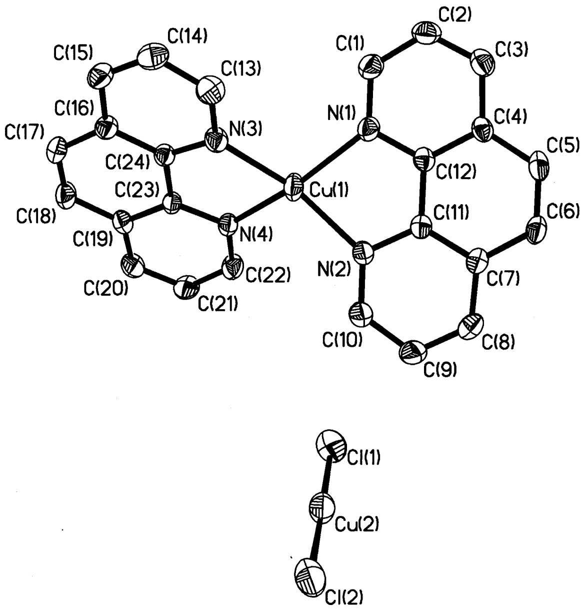


Fig. 1 The molecular structure of ionic $[Cu(phen)_2][CuCl_2]$ **1** (30% probability ellipsoids).

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu(phen)_2][CuCl_2]$ **1**

Cu(1)–N(1)	2.048(3)	Cu(1)–N(4)	2.055(3)
Cu(1)–N(3)	2.079(3)	Cu(1)–N(2)	2.082(3)
Cu(2)–Cl(2)	2.0900(15)	Cu(2)–Cl(1)	2.0923(15)
N(1)–Cu(1)–N(4)	149.04(13)	N(1)–Cu(1)–N(3)	107.62(12)
N(4)–Cu(1)–N(3)	80.71(11)	N(1)–Cu(1)–N(2)	80.67(11)
N(4)–Cu(1)–N(2)	108.14(12)	N(3)–Cu(1)–N(2)	148.41(13)
Cl(2)–Cu(2)–Cl(1)	178.71(5)		

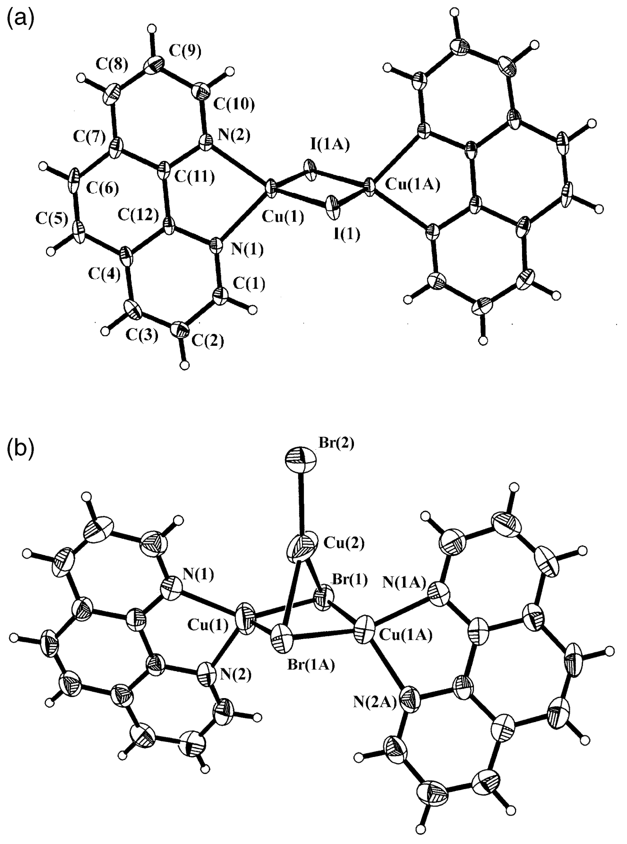


Fig. 2 The molecular structures of dimeric $[Cu_2I_2(phen)_2]$ **3** and trinuclear $[Cu_3Br_3(phen)_2]$ **5** (30% probability ellipsoids).

interligand angles [106.81(8)–123.64(9)°] suggest that the tetrahedral site of the Cu center should be grossly distorted. In addition, the Cu–Cu separation is short [2.6638(16) Å] while the I–I separation (4.419 Å) is close to the usual van der Waals contact distance.

As shown in Fig. 2(b), the trinuclear clusters $[Cu_3X_3(phen)_2]$ (X = Br **5**, I **7**) can be better viewed as 1:1 adducts of CuX with dimers (the selected bonding parameters for **5** and **7** are in Tables 4 and 5, respectively). Here the dimers act as chelating I donor ligands, due to which some of the structural

Table 3 Selected bond lengths (Å) and angles (°) for $[CuI(phen)]_2$ **3**

Cu(1)–N(1)	2.103(3)	Cu(1)–N(2)	2.095(3)
Cu(1)–I(1)	2.5563(10)	Cu(1)–I(1)#1	2.6037(8)
Cu(1)–Cu(1)#1	2.6638(16)		
N(2)–Cu(1)–N(1)	80.15(12)	N(2)–Cu(1)–I(1)	108.35(8)
N(1)–Cu(1)–I(1)	123.64(9)	N(2)–Cu(1)–I(1)#1	114.26(8)
N(1)–Cu(1)–I(1)#1	106.81(8)	I(1)–Cu(1)–I(1)#1	117.85(3)
Cu(1)–I(1)–Cu(1)#1	62.15(3)		

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

Table 4 Selected bond lengths (Å) and angles (°) for $[Cu_3Br_3(phen)_2]$ **5**

Cu(1)–N(1)	2.050(4)	Cu(1)–N(2)	2.069(4)
Cu(1)–Br(1)#1	2.4294(11)	Cu(1)–Br(1)	2.6425(11)
Cu(2)–Br(2)	2.1617(15)	Cu(2)–Br(1)	2.6500(11)
Cu(1)–Cu(2)	2.5522(13)		
N(1)–Cu(1)–N(2)	82.00(14)	N(1)–Cu(1)–Br(1)#1	139.10(11)
N(2)–Cu(1)–Br(1)#1	111.61(11)	N(1)–Cu(1)–Br(1)	105.38(11)
N(2)–Cu(1)–Br(1)	119.92(11)	Br(1)#1–Cu(1)–Br(1)	100.39(4)
Br(2)–Cu(2)–Br(1)	132.64(2)	Cu(1)–Br(1)–Cu(2)	57.66(3)
Br(1)–Cu(2)–Br(1)#1	94.72(5)	Cu(1)#1–Br(1)–Cu(1)	79.01(4)
Cu(1)#1–Br(1)–Cu(2)	60.14(3)		

Symmetry transformation used to generate equivalent atoms: #1 $-x+2, y, -z+3/2$

Table 5 Selected bond lengths (Å) and angles (°) for $[Cu_3I_3(phen)_2]$ **7**

I(1)–Cu(1)	2.5903(12)	I(1)–Cu(2)	2.6962(11)
I(1)–Cu(1)#1	2.7373(13)	I(2)–Cu(2)	2.4323(18)
Cu(1)–N(2)	2.045(6)	Cu(1)–N(1)	2.075(7)
Cu(1)–Cu(2)	2.5501(16)		
Cu(1)–I(1)–Cu(2)	57.64(3)	Cu(1)–I(1)–Cu(1)#1	76.39(4)
Cu(2)–I(1)–Cu(1)#1	55.98(3)	N(2)–Cu(1)–N(1)	82.4(3)
N(2)–Cu(1)–I(1)	111.63(17)	N(1)–Cu(1)–I(1)	135.71(18)
N(2)–Cu(1)–I(1)#1	120.68(18)	N(1)–Cu(1)–I(1)#1	104.99(18)
I(1)–Cu(1)–I(1)#1	102.72(4)	I(2)–Cu(2)–I(1)	129.48(3)
I(1)#1–Cu(2)–I(1)	101.05(6)		

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

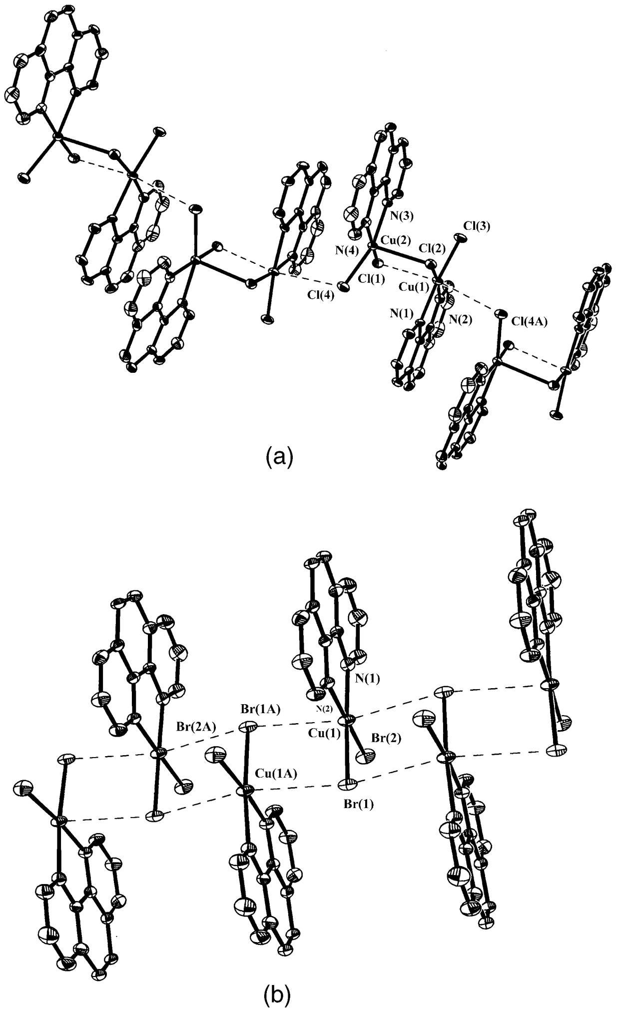


Fig. 3 The one-dimensional chain structures of $[CuCl_2(phen)]$ **6** and $[CuBr_2(phen)]$ **8** (30%.

Table 6 Selected bond lengths (Å) and angles (°) for $[CuCl_2(phen)]$ **6**

Cu(1)–N(1)	2.037(4)	Cu(1)–N(2)	2.039(4)
Cu(1)–Cl(3)	2.2584(13)	Cu(1)–Cl(2)	2.2782(13)
Cu(2)–N(4)	2.034(4)	Cu(2)–N(3)	2.051(4)
Cu(2)–Cl(4)	2.2560(15)	Cu(2)–Cl(1)	2.2752(14)
Cu(2)–Cl(2)	2.7075(16)		
N(1)–Cu(1)–N(2)	81.13(15)	N(1)–Cu(1)–Cl(3)	172.78(11)
N(2)–Cu(1)–Cl(3)	92.92(12)	N(1)–Cu(1)–Cl(2)	92.05(11)
N(2)–Cu(1)–Cl(2)	172.89(13)	Cl(3)–Cu(1)–Cl(2)	94.01(5)
N(4)–Cu(2)–N(3)	80.35(15)	N(4)–Cu(2)–Cl(4)	92.81(12)
N(3)–Cu(2)–Cl(4)	163.80(12)	N(4)–Cu(2)–Cl(1)	170.81(12)
N(3)–Cu(2)–Cl(1)	91.87(11)	Cl(4)–Cu(2)–Cl(1)	93.44(6)
N(4)–Cu(2)–Cl(2)	92.67(12)	N(3)–Cu(2)–Cl(2)	92.40(12)
Cl(4)–Cu(2)-Cl(2)	102.64(6)	Cl(1)–Cu(2)–Cl(2)	92.54(6)
Cu(1)–Cl(2)–Cu(2)	90.99(6)		

Table 7 Selected bond lengths (Å) and angles (°) for $[CuBr_2(phen)]$ **8**

Br(2)–Cu(1)	2.3788(8)	Br(1)–Cu(1)	2.3927(8)
Cu(1)–N(2)	2.027(2)	Cu(1)–N(1)	2.033(3)
N(2)–Cu(1)–N(1)	81.05(11)	N(2)–Cu(1)–Br(2)	174.58(7)
N(1)–Cu(1)–Br(2)	94.00(8)	N(2)–Cu(1)–Br(1)	93.19(8)
N(1)–Cu(1)–Br(1)	173.24(7)	Br(2)–Cu(1)–Br(1)	91.89(3)

parameters of the dimers are changed: (1) the rhomboid Cu_2X_2 core is no longer planar but folded and exhibits a dihedral angle of 167.2° for $[Cu_3Br_3(phen)_2]$ and of 164.0° for $[Cu_3I_3(phen)_2]$; (2) the geometric pattern of the bridging I ions changes from the linear μ_2-I to the triangular pyramidal μ_3-I; (3) the Cu–I_b distances span a by far wider range of 2.5903(12)–2.7373(13) Å than that found in the dimer, owing to the special location of the four atoms. Moreover, the Cu(1) and Cu(2) separation is quite short: 2.5522(13) Å for $[Cu_3Br_3(phen)_2]$ and 2.5501(16) Å for $[Cu_3I_3(phen)_2]$.

The chain compounds **6** and **8** belong to the series with the common formula $[CuX_2L]$, but the chain arrangement is different (see Fig. 3 and Tables 6 and 7). The one-dimensional chain of the former consists alternately of square pyramidal and octahedral Cu(II) linked alternately *via* covalent and semi-coordinate Cu–Cl bonds [Cu(1)–Cl(4A) = 3.15 Å], while the structure of the latter can be described as a staircase chain formed *via* intermolecular semi-coordinate Cu–Br bonds [$Cu–Br_{semi}$ = 3.256 Å].

Optical properties

The structural chemistry of copper halide cluster compounds has been extensively explored, but the studies of their functional properties are still rare to date. Now, we are much interested in the third-order nonlinear optical properties of copper halides.

The third-order nonlinear optical (NLO) properties of the compounds were investigated at 532 nm with a 15 ns pulse width produced by a frequency-doubled Q-switched Nd:YAG laser in DMF solution and revealed by using a *Z*-scan technique. The cell selected to place the sample was a 5 mm thick glass one. Representative plots of the *Z*-scan data are shown in Fig. 4 for **5**. The plots on the left and right depict respectively the nonlinear absorptive and refractive properties. Reasonably good fits between the experimental data and the theoretical curves were obtained, which suggests that the experimentally obtained NLO effects are effectively third-order in nature. The effective α_2 and n_2 values were derived from the theoretical curves (α_2 and n_2 are the effective third-order NLO absorptive and refractive coefficients, respectively). In accordance with the observed α_2 and n_2, the modulus of the effective third-order susceptibility $\chi^{(3)}$ can be calculated by eqn. (6):

$$|\chi^{(3)}| = [(9 \times 10^8 n_0{}^2 \varepsilon_0 c \lambda \alpha_2 / 8\pi^2)^2 + (n_0 c n_2 / 80\pi^2)^2]^{1/2} \quad (6)$$

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 the one

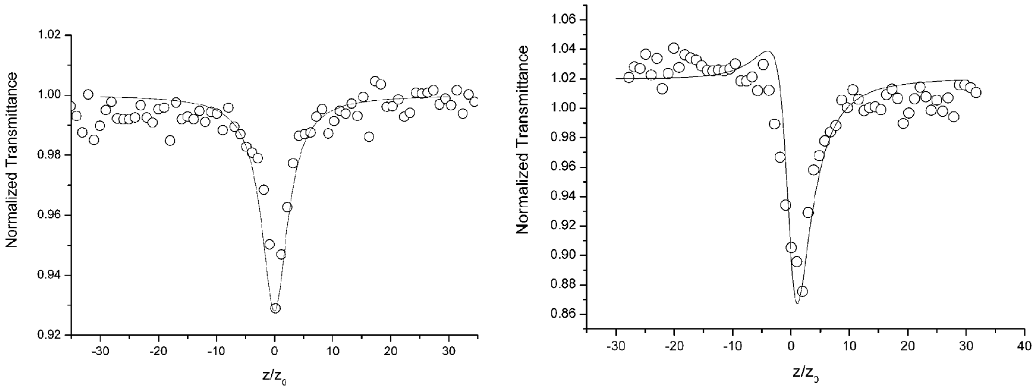


Fig. 4 *Z*-scan data of 8.85×10^{-4} mol dm^{-3} of $[Cu_3Br_3(phen)_2]$ **5** in DMF: (left) collected under the open aperture configuration showing NLO absorption (the solid curve is a theoretical fit); (right) obtained under the closed aperture configuration.

Table 8 Third-order nonlinear optical properties of some copper halide compounds

	α_2/m W^{-1}	n_2/m^2 W^{-1}	χ^3/esu	χ^3/esu mol^{-1} dm^3	γ/esu	Reference
$[Cu_3Br_3(phen)_2]$ **5**	0.12×10^{-11}	-1.25×10^{-19}	1.05×10^{-13}	1.19×10^{-10}	6.50×10^{-32}	This work
$[CuCl_2(phen)]$ **6**	0.10×10^{-11}	-1.75×10^{-19}	1.40×10^{-13}	1.60×10^{-10}	8.05×10^{-32}	This work
$[CuBr_2(phen)]$ **8**	0.08×10^{-11}	-2.00×10^{-19}	1.78×10^{-13}	1.03×10^{-10}	5.62×10^{-32}	This work
$[Ni(phen)_3]_2[Cu_{10}H_2I_{16}]$ **9**	0.20×10^{-11}	-3.10×10^{-19}	2.50×10^{-13}	1.94×10^{-9}	9.77×10^{-31}	Ref. 9
$[Cu_6(CN)_6(phen)_4]$ **10**	0.13×10^{-11}	-2.00×10^{-19}	2.03×10^{-13}	2.27×10^{-9}	1.24×10^{-30}	Ref. 10
$[Cu_2(OH)_2(phen)_2]$ $[Cu_4Br_6]$ **11**	0.80×10^{-11}	-1.55×10^{-18}	1.23×10^{-12}	2.33×10^{-9}	1.17×10^{-30}	First report
$[Cu_4Br_2I_3(phen)_2]$ **12**	0.12×10^{-11}	-1.90×10^{-19}	1.53×10^{-13}	3.21×10^{-10}	1.61×10^{-31}	First report
$[Cu_2Cl_2(phen)]$ **13**	0.12×10^{-11}	-2.00×10^{-19}	1.61×10^{-13}	5.23×10^{-10}	2.63×10^{-31}	First report

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

The NLO behavior of compounds **5**, **6** and **8** were investigated and the results are listed in Table 8. In order to explore the relation between structure and function, the NLO properties of other copper halides are also listed in Table 8 {the NLO properties of compounds $[Ni(phen)_3]_2[Cu_{10}H_2I_{16}]$ **9**[9] and $[Cu_6(CN)_6(phen)_4]$ **10**[10] have been reported, and the NLO properties of compounds $[Cu_2(OH)_2(phen)_2][Cu_4Br_6]$ **11**,[11] $[Cu_4Br_2I_3(phen)_2]$ **12**[12] and $[Cu_2Cl_2(phen)]$ **13**[13] are first reported}.

The Z-scan results indicate that all the compounds posses third-order nonlinear optical properties and exhibit reverse saturable absorption (RSA; $\alpha_2 > 0$) and self-defocusing performance ($n_2 < 0$). It is said that materials exhibiting self-defocusing behaviour may be an excellent ones for applications in the protection of optical sensors. However, it should be emphasized that the Z-scan results cannot reveal the origins of the observed nonlinearities. Both the excited state population (or absorption) and two-photon absorption can be responsible for these measured NLO effects.

Comparing the γ values of all the compounds, the chain compound **10** has the largest γ value (1.24×10^{-30} esu). Apart from the presence in the structure of an extended $(CuCN)_\infty$ chain and phen molecules with a large π electronic cloud, the arrangement of the organic ligands, parallel to each other and arrayed regularly on both sides of the parent chain, may be another key factor to significantly enhance the nonlinearity. The γ values of the two-dimensional sheet compound **11** and the decanuclear iodocuprate **9** are basically equal to that of **10**, but are superior to those of the other two chain polymers **12** and **13** infinitely propagated by covalent Cu–X bonds. The γ values of the title chain polymers **6** and **8** are obviously smaller than those of three chain polymers mentioned above, but agree with that of the discrete trinuclear compound **5**. This conclusion can be better explained as follows: once the compounds are dissolved in DMF solution, the intermolecular semi-coordinated Cu–X bonds in compounds **6** and **8** will be broken so that the compounds will exist in the form of asymmetric units and are better viewed as discrete clusters, so the γ values are comparable with that of $[Cu_3Br_3(phen)_2]$ **5**. Thus, the infinite chain, sheet or network compounds, the larger clusters and the compounds with aromatic rings provide the nice optical properties, since these factors help the free movement of electrons.

Acknowledgements

This research was supported by grants from the National Natural Science Foundation of China (No. 20271021 and No. 20333070).

References

1 B. W. Skelton, A. F. Waters and A. H. White, *Aust. J. Chem.*, 1991, **44**, 1207.
2 P. C. Healy, C. Pakawatchai and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 2531.
3 P. C. Healy, L. M. Engelhardt, V. A. Patrick and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 2541.
4 H. Place, B. Scott and R. D. Willett, *Inorg. Chim. Acta*, 2001, **319**, 43.
5 J. H. Yu, J. Q. Xu, L. Ye, H. Ding, W. J. Jing, T. G. Wang, J. N. Xu, H. B. Jia, Z. C. Mu and G. D. Yang, *Inorg. Chem. Commun.*, 2002, **5**, 572.
6 M. T. Garland and D. Grandjean, *Acta Crystallogr., Sect. C.*, 1988, **44**, 1547.
7 L. M. Engelhardt, R. I. Papasergio and A. H. White, *Aust. J. Chem.*, 1984, **37**, 2207.
8 (*a*) P. M. Graham, R. D. Pike, M. Sabat, R. D. Bailey and W. T. Pennington, *Inorg. Chem.*, 2000, **39**, 5121; (*b*) N. P. Rath, E. M. Holt and K. Tanimura, *J. Chem. Soc., Dalton Trans.*, 1986, 2303; (*c*) N. P. Rath, J. L. Maxwell and E. M. Holt, *J. Chem. Soc., Dalton Trans.*, 1986, 2449.
9 J. H. Yu, H. B. Jia, L. Y. Pan, Q. X. Yang, T. G. Wang, J. Q. Xu, X. B. Cui, Y. J. Liu, Y. Z. Li, C. H. Lü and T. H. Ma, *J. Solid State Chem.*, 2003, **175**, 152.
10 J. H. Yu, J. Q. Xu, Q. X. Yang, L. Y. Pan, T. G. Wang, C. H. Lü and T. H. Ma, *J. Mol. Struct.*, 2003, **658**, 1.
11 J. H. Yu, J. Q. Xu, H. Y. Bie, J. Lu and X. Zhang, *Inorg. Chem.*, submitted.
12 J. H. Yu, J. Q. Xu, L. Ye, H. Ding, J. N. Xu, H. B. Jia, T. G. Wang, Z. C. Mu and G. D. Yang, *J. Cluster Sci.*, 2003, **14**, 1.
13 J. H. Yu, Z. Shi, J. Q. Xu, X. B. Cui, H. Ding, W. J. Jing, D. Q. Chu, J. Hua, J. N. Xu and T. G. Wang, *Chin. J. Chem.*, 2002, **20**, 560.