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A new octupolar material for quadratic nonlinear optics: tris(2,2′-bipyridyl)Zn(II) tetrakis(2-chloro-4-nitrophenolate)Zn(II)

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Tris(2,2′-bipyridine)Zn(II) tetrakis(2-chloro-4-nitrophenolate)Zn(II), $[Zn(bpy)_3][Zn(CNP)_4]$ **1**, is a new octupolar material for quadratic nonlinear optics. **1**, a chiral metal–organic complex, crystallizes in space group *C*2. Refinement of the Flack parameter supports the description of the $[Zn(bpy)_3]^{2+}$ cation as the Δ enantiomer. The counterion is an octupolar, tetrahedral assembly of 2-chloro-4-nitrophenolate chromophores around a Zn^{2+} ion. A second harmonic generation signal equal to 5 × urea is observed. A complex having a slightly different stoichiometry, bis(2,2′-bipyridine)-bis(2-chloro-4-nitrophenolate)Zn(II), crystallizes in the centrosymmetric space group $P\bar{1}$. The structure of bis(2-chloro-4-nitrophenolate)Zn(II) pentahydrate, a precursor of **1** with $P\bar{1}$ symmetry, is described.

Introduction

Several characteristics of metal–organic coordination compounds favor their investigation as potential materials for nonlinear optics (NLO).[1–6] *Via* metal-to-ligand or ligand-to-metal charge transfer, a metal may act as either a strong donor or acceptor of electrons. Relative to organic NLO materials, metal–organic complexes offer increased synthetic flexibility for the optimization of hyperpolarizability. The identity of the metal, as well as its oxidation state, could tunably alter the electronic properties of surrounding ligands. Furthermore, these ligands can be arranged in octahedral,[7] tetrahedral,[8,9] or other geometries[10–13] that are less frequently observed in organic materials. Such coordination geometries can afford three-dimensional charge transfer and octupolar materials.[14,15]

These advantages have been exploited in the investigation of metal–2,2′-bipyridine (bpy) complexes for second harmonic generation (SHG). A relatively large value of the molecular hyperpolarizability, β, was calculated for a substituted $Ru(bpy)_3^{2+}$ complex[16] from harmonic light scattering (HLS) experiments.[17–19] While this calculation and other HLS experiments[20–22] neglected the possibility of two-photon induced luminescence at twice the incident frequency, electric field poling studies[23] and Kurtz and Perry powder tests,[24] in which luminescent intensity is negligible relative to the direct, second harmonic beam, have demonstrated the utility of several other bipyridyl complexes for SHG.[25,26]

Here, we describe the frequency doubling capability and crystal structure of tris(2,2′-bipyridine)Zn(II) tetrakis(2-chloro-4-nitrophenolate)Zn(II), $[Zn(bpy)_3][Zn(CNP)_4]$ **1**. The three bpy molecules of the cation assemble in a Δ configuration around a Zn center. Charge balance is provided by the four CNP moieties that are tetrahedrally arranged around Zn in an octupolar orientation of NLO chromophores. To our knowledge, a study of the NLO properties of CNP has not been published. However, the calculated hyperpolarizability β_{zzz} of a related material, 4-nitrophenolate, is 18.2×10^{-30} esu[27] and single crystals of noncentrosymmetric salts containing this anion have been grown with both organic[27] and inorganic[28–31] counterions. In addition to **1**, we also describe the centrosymmetric crystal structure of *cis*-bis(2,2′-bipyridyl)-bis(2-chloro-4-nitrophenolate)Zn(II), $Zn(CNP)_2(bpy)_2$ **2**, in which there is only one unique zinc atom in the asymmetric unit. The structure of $Zn(CNP)_2 \cdot 5H_2O$ **3**, bis(2-chloro-4-nitrophenolate)Zn(II) pentahydrate, a precursor of $[Zn(bpy)_3][Zn(CNP)_4]$, is also described.

Results and discussion

$[Zn(bpy)_3][Zn(CNP)_4]$, 1

When the Kurtz and Perry powder test was performed, crystals of **1** doubled the frequency of a Nd : YAG laser with an efficiency approximately five times that of urea. X-Ray diffraction from a single crystal revealed that the asymmetric unit comprises two distinct Zn atoms (Fig. 1, Table 1). One metal atom is surrounded by three bpy molecules in an octahedral, Δ configuration. The Zn–N bond distances fall in the range 2.14–2.16 Å. All three bpy molecules are nearly planar; the largest dihedral angle between two bonded pyridine rings is 4.6°. The dihedral angle between the entire bpy and half bpy of the asymmetric unit is 86°, close to the 90° angle of an ideal octahedral geometry. In contrast, the CNP chromophores

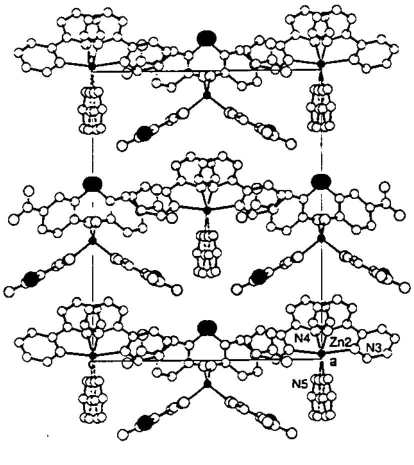

Fig. 1 View along [001] of $[Zn(bpy)_3][Zn(CNP)_4]$. H atoms are omitted.

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Table 1 Selected interatomic distances (Å) and bond angles (°) for Zn coordinations (e.s.d.s in parentheses)

Compound **1**					
Zn1–O4	1.925(2)	O4–Zn1–O4	102.8(1)		
Zn1–O1	1.934(2)	O4–Zn1–O1	114.1(1)		
		O4–Zn1–O1	110.2(1)		
		O1–Zn1–O1	105.8(1)		
Zn2–N3	2.158(3)	N5–Zn2–N5	76.5(1)	N4–Zn2–N4	94.1(1)
Zn2–N4	2.147(3)	N5–Zn2–N4	169.7(1)	N4–Zn2–N3	76.29(9)
Zn2–N5	2.143(3)	N5–Zn2–N4	95.0(1)	N4–Zn2–N3	93.2(1)
		N5–Zn2–N3	98.3(1)	N3–Zn2–N3	164.7(1)
		N5–Zn2–N3	93.7(1)		
Compound **2**					
Zn–O1	2.048(3)	O1–Zn–O4	100.6(5)	O1–Zn–N5	90.2(2)
Zn–O4	2.056(4)	O1–Zn–N3	99.1(3)	O1–Zn–N6	162.8(1)
Zn–N3	2.15(2)	O1–Zn–N4	84.0(6)	N5–Zn–N3	164.34(9)
Zn–N4	2.241(7)	N5–Zn–N6	75.0(4)	N5–Zn–N4	94(1)
Zn–N5	2.144(9)	O4–Zn–N4	165.5(1)	O4–Zn–N5	100(1)
Zn–N6	2.211(3)	O4–Zn–N3	91(1)	O4–Zn–N6	90.6(2)
		N6–Zn–N4	88.4(3)	N3–Zn–N6	93.6(4)
		N3–Zn–N4	75(1)		
Compound **3**					
Zn1–O4	1.96(3)	O4–Zn1–O15	145.5(3)	O4–Zn1–O1	94.6(8)
Zn1–O15	1.982(5)	O4–Zn1–O13	97.6(7)	O4–Zn1–O14	90.7(7)
Zn1–O1	1.985(9)	O15–Zn1–O1	119.6(10)	O15–Zn1–O13	86.2(3)
Zn1–O13	2.137(8)	O15–Zn1–O14	84.0(3)	O1–Zn1–O13	92.3(8)
Zn1–O14	2.143(9)	O1–Zn1–O14	92.1(8)	O13–Zn1–O14	170.22(13)
Zn2–O7	1.976(6)	O7–Zn2–O17	114.4(10)	O7–Zn2–O10	93.6(9)
Zn2–O17	1.998(5)	O7–Zn2–O16	94.9(9)	O7–Zn2–O18	95.8(10)
Zn2–O10	2.00(2)	O17–Zn2–O10	152.0(2)	O17–Zn2–O16	86.0(4)
Zn2–O16	2.123(12)	O17–Zn2–O18	85.2(3)	O10–Zn2–O16	91.5(7)
Zn2–O18	2.131(8)	O10–Zn2–O18	92.7(7)	O16–Zn2–O18	168.3(2)

of the anion are tetrahedrally arranged around the second Zn of the asymmetric unit (Fig. 1 and 2). The Zn–O bonds have lengths of 1.92–1.93 Å, and the O–Zn–O angles range from 102.8 to 114.1°. The tetrahedral $[Zn(CNP)_4]^{2-}$ anions and octahedral $[Zn(bpy)_3]^{2+}$ cations assemble through Coulombic and C–H(bpy)···π(CNP) interactions into two-dimensional layers that stack along the [010] direction (Fig. 1).

$Zn(CNP)_2(bpy)_2$, 2

$[Zn(bpy)_3][Zn(CNP)_4]$, a frequency-doubling material, crystallized from an aqueous methanol solution containing Zn, bpy, and CNP in a molar ratio of 1 : 2 : 2. However, the previous four harvests from the same solution yielded a racemic, centrosymmetric phase, $Zn(CNP)_2(bpy)_2$. X-Ray diffraction from a single crystal of this material revealed that the asymmetric unit comprises a single Zn atom surrounded by two CNP anions and two bidentate bpy molecules in an octahedral arrangement (Fig. 3). The two Zn–O bonds of the asymmetric unit have lengths of 2.05 and 2.06 Å. There is greater variation in the lengths of the Zn–N bonds (2.14–2.24 Å). The two bpy molecules of the asymmetric unit have dihedral angles of 4.8° and 11.2° between the least squares mean planes of the pyridine rings. Calculation of the planes of each bpy molecule reveals an 88.3° dihedral angle between the ligands. The $Zn(CNP)_2(bpy)_2$ units assemble *via* C–H(bpy)···π(bpy or CNP) interactions and the antiparallel alignment of CNP dipoles.

$Zn(CNP)_2{\cdot}5H_2O$, 3

$Zn(CNP)_2{\cdot}5H_2O$ was investigated as a precursor to **1** in an alternative route to the noncentrosymmetric material. The hydrate is grown from an aqueous solution containing Zn^{2+} and CNP. Two crystallographically inequivalent zinc atoms with similar environments comprise the asymmetric unit of this material (Fig. 4). Each zinc is pentacoordinated by oxygen atoms in a distorted trigonal bipyramidal geometry. Two water molecules are axial ligands, and the equatorial sites are occupied by a third water molecule and two CNP anions coordinated *via* the phenolate O. Equatorial Zn–O bonds have lengths 1.96–2.00 Å, while axial Zn–O bonds are longer (2.12–2.14 Å). Outside the coordination sphere of Zn, four water molecules are incorporated into the asymmetric unit *via* hydrogen bonding. The Zn atom, CNP anions, and equatorial water ligand lie in a plane parallel to (010). These two-

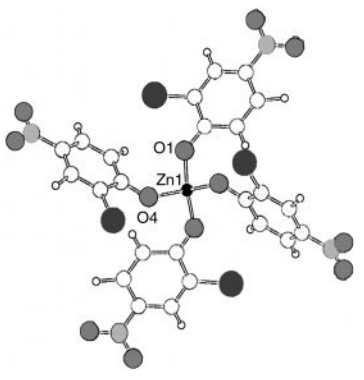

Fig. 2 $[Zn(CNP)_4]^{2-}$ tetrahedral anion, octupolar chromophore with C_2 degenerate symmetry.

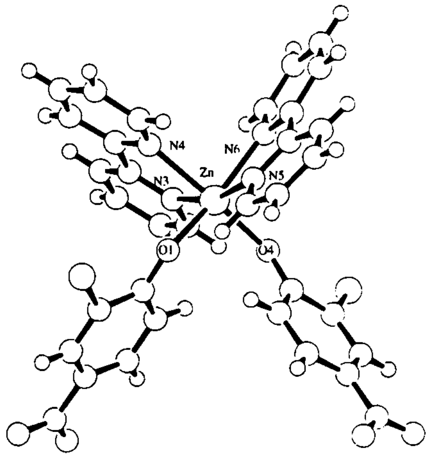

Fig. 3 Asymmetric unit in crystalline $Zn(CNP)_2(bpy)_2$.

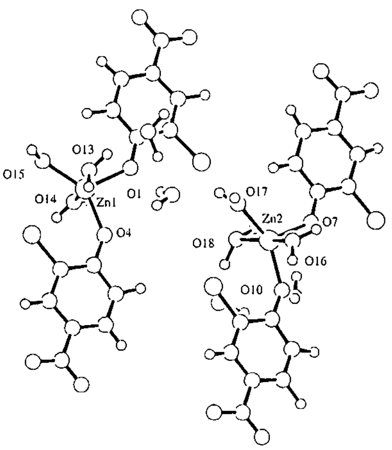

Fig. 4 Asymmetric unit in crystalline $Zn(CNP)_2{\cdot}5H_2O$, showing the pentacoordination of the Zn atoms.

dimensional sheets are separated by the axial water ligands and the outer sphere water molecules. The network of water molecules forms *via* O–H···O and O–H···Cl hydrogen bonds. Chlorine-directing interactions[32] favor the stacking of CNP anions in layers separated by 3.7 Å. The dipole moment, μ, of a CNP anion is parallel to μ of the adjacent CNP anion in the layer above and antiparallel to μ of the adjacent CNP anion in the layer below.

Conclusion

Advantages of 2D or 3D chromophores with respect to conventional rod like chromophores for NLO applications have been already justified[33–36] and their efficiency tested by hyper-Raleigh scattering at the molecular level.[37–40] In the crystalline solid state we know of few routes for crystal engineering of noncentrosymmetric structures including NLO chromophores of D_3, D_{3h} or T_d symmetry.[41–43] Inorganic crystals such as barium trimetaborate ($R3m$), GaAs ($F\bar{4}3m$) or $CdHg(SCN)_4$ ($I\bar{4}$) exemplify 3D frameworks of octupolar chromophores which could be considered as reference models. Crystal engineering using organic chromophores of T_d symmetry (or degenerate D_2, C_2) assembled in noncentrosymmetric structures is currently a challenge, in order to compare the compromise between transparency *versus* NLO efficiency of such crystals to those of well-known organic and inorganic crystals. The $[Zn(bpy)_3][Zn(CNP)_4]$ crystal evidences the noncentrosymmetric packing of two octupolar entities: the octahedral cation $[Zn(bpy)_3]^{2+}$ and the tetrahedral anion $[Zn(CNP)_4]^{2-}$. In this case, only the anion has a contribution to the macroscopic quadratic NLO activity. The efficiency (5 × urea) should be justified by calculation in order to ascertain whether the packing of anions is optimal for a large $\chi(2)$. Replacement of the bpy ligand with a 4,4′-donor substituted bpy should increase the hyperpolarizability of the cation and, thus, its contribution to the bulk NLO properties of the crystal. This route may yield similar metal–organic complex crystals with enhanced SHG responses, since contributions from both the cation and anion chromophores occur. Compound **3** is a precursor which provides a facile synthetic route to **1**.

Experimental

Materials and methods

Reagents purchased from commercial sources were used as received without further purification. The compositions of **1**, **2**, and **3** were determined by elemental analysis (CNRS Central Analytical Services, Vernaison, France).

Crystal growth

$Zn(CNP)_2{\cdot}5H_2O$. 200 ml distilled water were added to a mixture of 628.7 mg (5.5 mmol) $ZnCO_3{\cdot}2ZnO{\cdot}3H_2O$ (Merck) and 1.7356 g (10 mmol) 2-chloro-4-nitrophenol (Aldrich, 97%). The reaction mixture was stirred and heated at 65 °C for 4.5 h, allowed to cool, and filtered. The filtrate was allowed to evaporate slowly. Yellow–orange needles formed and were isolated by filtration (yield: 26.1%), decomp. > 200 °C. Calcd for $C_{12}H_{16}Cl_2N_2O_{11}Zn$: C, 28.79; H, 3.22; Cl, 14.17; N, 5.60; Zn, 13.06%. Found: C, 29.12; H, 2.94; Cl, 10.36; N, 5.65; Zn, 11.97%.

$Zn(CNP)_2(bpy)_2$ and $[Zn(bpy)_3][Zn(CNP)_4]$. A crystal of $Zn(CNP)_2(bpy)_2$ of quality suitable for single crystal X-ray diffraction was grown by mixing several stock solutions prepared immediately before use. 1.0 ml of 2.5 M KOH in methanol was added to a mixture of 5.0 ml of 0.2 M $ZnCl_2$ in methanol and 5.0 ml of 0.4 M 2-chloro-4-nitrophenol in methanol. The resulting precipitate was filtered, and 5.0 ml of 0.3 M 2,2′-bipyridyl in methanol was added to the filtrate, which was allowed to evaporate slowly. Two phases, orange crystals and white crystals, were present in both of the two crops isolated from the filtrate. An orange prism was selected from the second crop and was determined by X-ray diffraction to be *cis*-bis(2,2′-bipyridyl)-bis(2-chloro-4-nitrophenolate) Zn(II), **2**, mp 227–229 °C. Calcd for $C_{32}H_{22}Cl_2N_6O_6Zn$: C, 53.17; H, 3.07; Cl, 9.81; N, 11.63; Zn, 9.04%. Found: C, 53.12; H, 2.96; Cl, 9.60; N, 11.57; Zn, 8.97%.

In another experiment, equal volumes of methanol (Normapur, reagent grade) and ammonia (Labosi, 20% aqueous solution) were mixed and used to prepare a 0.2 M solution of 2-chloro-4-nitrophenol. 0.4 M solutions of $ZnCl_2$ (Prolabo, 97%) in methanol and of 2,2′-bipyridyl (Aldrich, 99+%) in methanol were also prepared. 20.0 ml of the 2-chloro-4-nitrophenol solution and 5.0 ml of the $ZnCl_2$ solution were mixed, then 10.0 ml of the 2,2′-bipyridyl solution were added. Slow evaporation of the solvent yielded crystals which were isolated in several batches. Wide angle powder X-ray diffraction revealed that the first four harvests of crystals filtered from the mother liquor had the same lattice parameters as **2**. The fifth filtration, on the other hand, yielded crystals which gave a positive Kurtz and Perry powder test. A crystal selected from this batch was determined by single crystal X-ray diffraction to be tris(2,2′-bipyridyl)Zn(II) tetrakis(2-chloro-4-nitrophenolate)Zn(II), $[Zn(bpy)_3][Zn(CNP)_4]$, mp 247–249 °C. Calcd for $C_{54}H_{36}Cl_4N_{10}O_{12}Zn_2$: C, 50.30; H, 2.81; Cl, 11.00; N, 10.86; Zn, 10.14%. Found: C, 50.04; H, 2.74; Cl, 10.87; N, 10.76; Zn, 10.08%.

Mixing stoichiometric quantities of the three stock solutions followed by slow evaporation of the solvent afforded a more direct route to **1**. The noncentrosymmetric phase also formed when 50.9 mg (0.1 mmol) $Zn(CNP)_2{\cdot}5H_2O$ and 15.2 mg (0.1 mmol) 2,2′-bipyridyl were dissolved in boiling methanol, which was then allowed to cool and slowly evaporate.

Kurtz and Perry powder test

A pulsed Nd^{3+} : YAG laser ($\lambda = 1064$ nm) was used to qualitatively determine the efficiency of the crystals for frequency doubling.

X-Ray diffraction

Details of the X-ray diffraction analysis are given in Table 2. Single crystals of **2** and **3** were investigated at 296 K with graphite monochromated Ag-Kα radiation from an Enraf-Nonius FR-590 CCD diffractometer. A single crystal of **1** was examined at 296 K on an Enraf-Nonius CAD-4 four-circle diffractometer with a graphite monochromator and Mo-Kα radiation ($\lambda = 0.71073$ Å). Using TeXsan software,[44] all

Table 2 Crystallographic data for $[Zn(bpy)_3][Zn(CNP)_4]$, $Zn(CNP)_2(bpy)_2$, and $Zn(CNP)_2{\cdot}5H_2O$

Compound	$[Zn(bpy)_3][Zn(CNP)_4]$ **1**	$Zn(CNP)_2(bpy)_2$ **2**	$Zn(CNP)_2{\cdot}5H_2O$ **3**
Formula	$C_{54}H_{36}Cl_4N_{10}O_{12}Zn_2$	$C_{32}H_{22}Cl_2N_6O_6Zn$	$C_{12}H_{16}Cl_2N_2O_{11}Zn$
FW/g mol^{-1}	1289.52	722.85	500.55
Crystal system	monoclinic	triclinic	triclinic
Space group	*C*2 (No. 5)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a/Å	17.776(5)	11.265(1)	13.159(1)
b/Å	18.613(9)	16.725(1)	13.304(1)
c/Å	10.124(3)	9.623(1)	11.999(1)
α/°	90	94.180(3)	94.1(10)
β/°	123.51(3)	109.4(1)	114.6(10)
γ/°	90	106.03(1)	91.107(3)
Cell volume/$Å^3$	2793(2)	1616(6)	1902(9)
Z	4	2	4
Temperature/K	296	296	296
μ/mm^{-1}	1.121	0.517	0.855
No. of reflections			
Collected	32428	3868	6024
Unique	8349	3868	6024
Unique, $I > 3\sigma(I)$	7138	3525	4406
Used in refinement	7138	3525	4406
R $[I > 3\sigma(I)]$	0.0360	0.0310	0.0430
R_w	0.0390	0.0460	0.0520

structures were solved by direct methods[45] and refined with full-matrix least-squares/difference Fourier techniques. Scattering factors for neutral atoms, f' and f'', were taken from the *International Tables for X-Ray Crystallography*.[46] Every non-hydrogen atom was refined with anisotropic displacement parameters. While all but one hydrogen of **3** were found by difference Fourier synthesis, the hydrogen atoms of **1** and **2** were placed in idealized positions and refined as riding atoms with relative isotropic displacement parameters. Data from all three crystals were corrected for Lorentz and polarization factors. An additional psi scan correction for absorption[47] was applied to the data from **1**. The Flack parameter[48,49] was included as a free variable in the refinement of this structure, and the final value, 0.0076(25), supports the given absolute configuration of the $[Zn(bpy)_3]^{2+}$ cation.

CCDC reference number 1145/218. See http://www.rsc.org/suppdata/jm/b0/b000417k/ for crystallographic files in .cif format.

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