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New Schiff base zinc(II) complexes exhibiting second harmonic generation

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Four bis(salicylaldiminato)zinc(II) complexes have been synthesized from four Schiff bases obtained by the condensation of chiral (*R*)-(+)-1-phenylethylamine with salicylaldehyde (**1**), 5-nitrosalicylaldehyde (**2**), 3,5-dichlorosalicylaldehyde (**3**) and 5-methoxysalicylaldehyde (**4**). The complexes crystallize in the noncentrosymmetric space groups $P2_12_12_1$ (**1**), $P2_1$ (**2**), and $C2$ (**3**, **4**). The geometry around the zinc(II) metal center is pseudo-tetrahedral with two oxygen and two nitrogen atoms from the ligands and has the Λ absolute configuration. Powders of the four compounds exhibit second harmonic generation (SHG) of intensity between that of 3-methyl-4-nitropyridine-1-oxide (POM) and *N*-(4-nitrophenyl)-(*S*)-prolinol (NPP).

Introduction

In the last decade a growing number of reviews[1–3] and publications have highlighted the utility of organometallic complexes, in which organic chromophores are bound to metal centers, for second harmonic generation (SHG).[4–20] Molecular polarizabilites (*β*) are frequently larger for the metallic complex than for the free chromophore (ligand) because of metal-to-ligand or ligand-to-metal charge transfer and because of the involvement of the orbitals on the metal.[7,8,10,12,18] Another appealing aspect for the design of nonlinear optical (NLO) properties is that metal centers may serve as anchors in the engineering of three-dimensional geometries (tetrahedral, octahedral . . .), giving rise to octupolar molecules.[10,21] Moreover, the combination of organic and inorganic elements affords materials of relatively high mechanical and thermal stability, as is also observed for organic chromophores in inorganic host matrixes.[22]

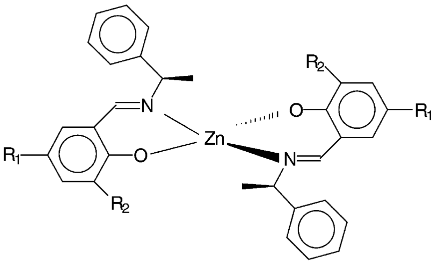

Fig. 1 Chemical structure of the complexes $Zn^{II}(L_n)_2$ (n = 1–4). $R_1 = R_2$ = H (**1**); $R_1 = NO_2$, R_2 = H (**2**); $R_1 = R_2$ = Cl (**3**); R_1 = OMe, R_2 = H (**4**).

However, despite the large molecular hyperpolarizabilities of many organometallic compounds, few organometallic crystals exhibit SHG (nonzero second-order susceptibility χ^2). This is because the molecules are arranged centrosymmetrically in the solid state. One possible way to control the crystallization of organometallic complexes in noncentrosymmetric space groups is to incorporate chiral chromophores.[19] Following this approach we report herein four zinc complexes (**1**–**4**) that exhibit SHG. The complexes were obtained from chiral Schiff bases as schematized in Fig. 1. The synthesis and crystal structure but not the NLO properties of compound **1** were published several years ago.[23] Our aim was to characterize the SHG properties of **1** and to investigate the effect of varying its substituents [$R_1 = R_2$ = H (**1**); $R_1 = NO_2$, R_2 = H (**2**); $R_1 = R_2$ = Cl (**3**); R_1 = OMe, R_2 = H (**4**)] (Fig. 1). The choice of zinc(II) as the metal center was guided by transparency considerations. An important requirement for SHG applications is transparency in a large spectral range in order to avoid absorption of the second harmonic.[24] In this regard Zn(II), Cd(II) and Hg(II) are interesting because of the lack of d–d transitions.[13–15,18] Furthermore, other work has shown that, from a series of complexes with different metal centers, those with Zn(II) generally exhibit the largest hyperpolarizability.[8,18]

Results

Second-order NLO properties

All compounds **1**–**4** give strong SHG signals when incident light is from a 1.064 µm laser. The second harmonic intensities of all four compounds are between those of POM and NPP and increase as **2** < **1** < **3** < **4**.

Description of the structures

Views of the molecular structures of compounds **2**–**4** are shown in Fig. 2–4, respectively. Selected bond lengths (Å) and angles (deg.) for compounds **1**–**4** are listed in Table 1. In the four complexes **1**–**4** the Zn(II) metal center is in a pseudo-tetrahedral environment with two bidentate Schiff base ligands ($L_{1–4}$) acting as chelates through their phenolate oxygen and azomethine nitrogen atoms (Fig. 1–4). All compounds crystallize in noncentrosymmetric space groups and exhibit the same configuration around the metal center. When the geometry is pseudo-tetrahedral, two different optical isomers, Λ and Δ are normally possible. However, for compounds **2**–**4** we found only the Λ configuration. This configuration was also found for **1**, and circular dichroism spectra of this material in chloroform have demonstrated that the Λ configuration is preponderant in solution.[23] The preference for the Λ(*R*,*R*) configuration in compounds **1**–**4** is thought to be driven by the minimization of steric hindrance between the two ligands in the coordination sphere.[23]

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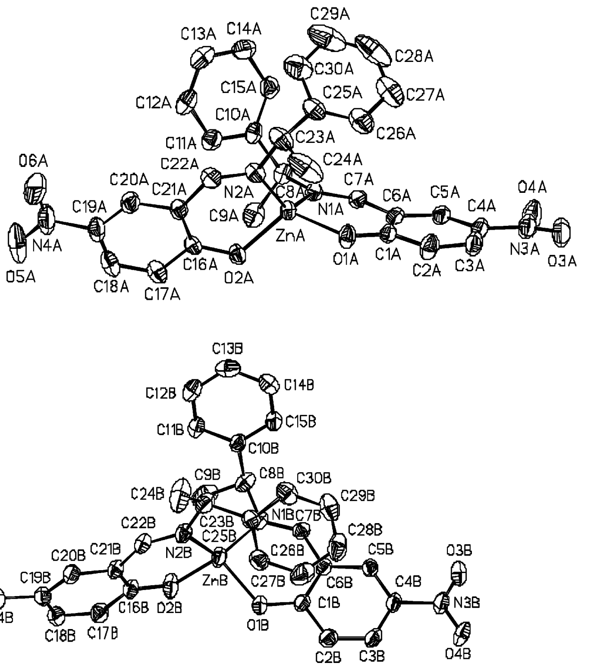

Fig. 2 View of the molecular structures **A** and **B** for complex $Zn^{II}(L_2)_2$ (**2**). Ellipsoids are drawn at the 30% probability level.

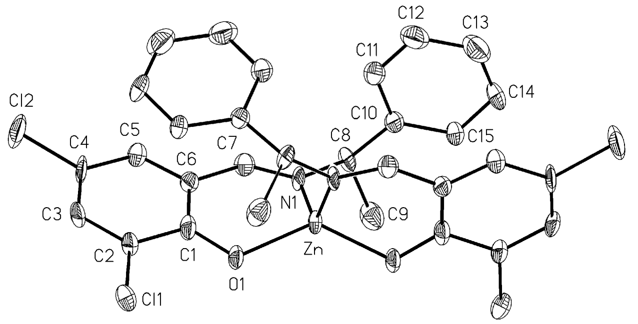

Fig. 3 View of the molecular structure for complex $Zn^{II}(L_3)_2$ (**3**). Ellipsoids are drawn at the 30% probability level.

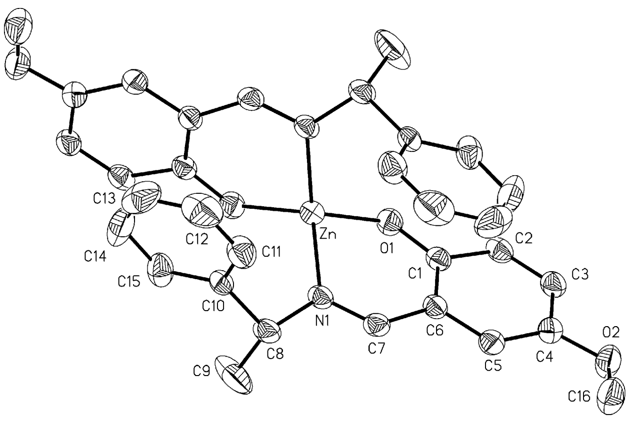

Fig. 4 View of the molecular structure for complex $Zn^{II}(L_4)_2$ (**4**). Ellipsoids are drawn at the 30% probability level.

1 crystallizes in the $P2_12_12_1$ orthorhombic space group.[23] The asymmetric unit comprises two independent molecules, **A** and **B**, which show slight differences in the Zn(II) coordination sphere (Table 1). For both molecules there is a pseudo-*C*2 axis running through the Zn(II) ion and bisecting the N–Zn–N and O–Zn–O angles. In molecules **A** and **B** the dihedral angles between the two planes O_1ZnN_1 and O_2ZnN_2 are 81.7° and 84.9°, respectively, so that the geometry around Zn is nearly tetrahedral with a slight distortion toward a *cis*-planar geometry.

2 crystallizes in the $P2_1$ monoclinic space group. As for **1**, the asymmetric unit comprises two different molecules, **A** and **B**. The dihedral angles between the two planes O_1ZnN_1 and O_2ZnN_2 are 80.47° and 94.61°, respectively, in molecule **A** and molecule **B**. The conformation around the zinc is nearly tetrahedral with distortion toward a *cis*-planar geometry for molecule **A** and a *trans*-planar geometry for molecule **B**.

3 crystallizes in the *C*2 monoclinic space group. The asymmetric unit is comprised of a half molecule with the zinc(II) metal ion located on the two-fold axis bisecting the N–Zn–N and O–Zn–O angles. The dihedral angle between the two planes O_1ZnN_1 is 77.07°. The conformation around the zinc has a strong distortion toward a *cis*-planar geometry.

4 crystallizes in the *C*2 monoclinic space group. As in the case of **3**, the asymmetric unit comprises half a molecular complex. The Zn metal ion is in a special position on the two fold axis bisecting the N–Zn–N and O–Zn–O angles. The dihedral angle between the two planes O_1ZnN_1 is 84.67°, corresponding to a slight distortion of the geometry from tetrahedral toward *cis*-planar.

Spectroscopic properties

The UV-visible spectra of the solids (KBr pellets) and solutions (CH_2Cl_2, acetone) of complexes **1**–**4** are very similar. The absorption maxima for the lowest optical transitions are below 400 nm (Table 2). Compound **2** is blue-shifted compared to **1** because of the acceptor effect of the nitro substituent. The maxima of **3** and **4** are red-shifted relative to **1** because the chloro or methoxy substituents act as donors in addition to the phenylato oxygen.

Discussion

All compounds **1**–**4** give strong SHG signals when illuminated with a Nd^{3+} : YAG laser (λ = 1.064 μm). Second harmonic signal intensities are between those of POM and NPP and increase as **2** < **1** < **3** < **4**. This trend is surprising; we had expected compound **2** to give the strongest SHG signal. The intensity of the second harmonic depends on the structure of both the molecules and the crystals they form. In the ligand of **1** there is no substituent, and charge transfer (CT) is along the O(phenolato) ⟶ CN(imino) direction. The substituents NO_2, Cl, and OMe in compounds **2**–**4** tune the CT of **1**. In the ligand of **2** there are two CT directions: O ⟶ NO_2 and O ⟶ CN(imino). The large value of β calculated for the 4-nitrophenolate anion[25] would predict a significant contribution to the hyperpolarizability of **2** from O ⟶ NO_2 CT. However, its effect is weakened by the O ⟶ CN CT. In the chromophores of **3** and **4**, on the other hand, the chloro and methoxy substituents have cooperative effects for the charge transfer directions, which are Cl ⟶ CN and O ⟶ CN (**3**) and MeO ⟶ CN and O ⟶ CN (**4**).

In considering the effect of crystallization of the chromophores, we assume that the Zn(II) ion has an identical impact on the molecular hyperpolarizabilities of compounds **1**–**4** and that its main role is structural anchorage of the chromophore. Then only the polarizabilities of the chromophores and their orientations in point groups 2 and 222 should be taken into account. Compounds **2**–**4** crystallize in point group 2, for which four coefficients d_{ijk} of the χ^2 tensor are nonzero. **1**, on the other hand, crystallizes in point group 222, for which only one coefficient of χ^2 is nonzero.[26] In the crystal structure of **2**, the two chromophores of molecule **B** are nearly in opposition; the angle between the two O ⟶ NO_2 charge transfer directions is 7°. Such a situation may contribute to cancellation of the d_{ijk} coefficients of the χ^2 tensor. This factor, in addition to molecular charge transfer considerations, may explain why **2** exhibits the lowest SHG signal.

Table 1 Selected bond lengths (Å) and angles (deg.) for **1**–**4** (# is for the symmetry related position $-x, y, -z$)

	1A	1B	2A	2B	3	4
Zn–O$_1$	1.907(4)	1.916(4)	1.924(2)	1.927(2)	1.918(7)	1.914(2)
Zn–O$_2$	1.929(4)	1.902(3)	1.937(2)	1.925(2)		
Zn–N$_1$	1.992(4)	1.996(4)	2.017(2)	1.999(3)	2.01(1)	2.017(2)
Zn–N$_2$	1.992(5)	1.986(3)	2.010(2)	1.997(2)		
O$_1$–Zn–O$_2$	117.7(2)	111.6(2)	114.84(9)	104.8(1)		
O$_1$–Zn–O$_1$#					130.1(4)	117.3(1)
O$_1$–Zn–N$_1$	97.6(2)	113.1(2)	95.49(8)	96.60(8)	93.1(3)	96.39(8)
O$_1$–Zn–N$_1$#					110.5(3)	113.00(8)
O$_1$–Zn–N$_2$	112.0(2)	95.5(2)	111.3(1)	118.28(9)		
O$_2$–Zn–N$_1$	110.8(2)	97.1(2)	109.39(9)	117.2(1)		
O$_2$–Zn–N$_2$	94.6(2)	113.5(2)	94.17(9)	97.22(9)		
N$_1$–Zn–N$_2$	125.8(2)	126.6(2)	132.70(9)	122.6(1)		
N$_1$–Zn–N$_1$#					122.5(5)	122.3(1)

Table 2 Absorption maxima (λ_{max}) of compounds **1**–**4** in the solid phase (KBr pellets), and in acetone and dichloromethane (nm). Molecular extinction coefficients (ε_{max}) are given in parenthesis (M^{-1} cm^{-1})

Complex	Solid λ_{max}	Acetone λ_{max} (ε_{max})	CH_2Cl_2 λ_{max} (ε_{max})
1	379	372 (8400)	374 (8300)
2	362	361 (33000)	361 (37000)
3	394	386 (13300)	389 (13000)
4	398	394 (3100)	395 (3000)

Conclusion

This paper reports the synthesis and characterization of four new Schiff base Zn(II) complexes that exhibit intense second harmonic generation. As expected from the chirality of the ligands, these materials crystallize in noncentrosymmetric space groups. Only one optical isomer, Λ, is observed. The compounds are light-colored and show a large range of transparency above 400 nm. The various substituents tune the SHG properties and also the thermal stability of the compounds, as reflected by their melting points.

Experimental

Synthesis of the complexes

All reagents and solvents were reagent grade and were used without further purification. The complexes were synthesized using procedures reported for **1**.[23]

Zn^{II}(L$_1$)$_2$, bis{2-[(*R*)-(+)-1-phenylethyliminomethyl]phenolato-*N*,*O*}zinc(II) (1). A solution of (*R*)-1-phenylethylamine (0.48 g, 4 mmol) and salicylaldehyde (0.48 g, 4 mmol) was refluxed in ethanol (25 mL) for 2 h. To the resulting yellow solution were added powdered $NaHCO_3$ (0.34 g, 4 mmol) and zinc(II) acetate dihydrate (0.44 g, 2 mmol), and the mixture was refluxed for 2 h. Light yellow parallelepiped crystals were obtained by slow cooling of the solution. Mp 190 °C. Anal. Calc. for $C_{30}H_{28}N_2O_2Zn$: C, 70.11; H, 5.49; N, 5.45; O, 6.23; Zn, 12.72. Found: C, 70.28; H, 5.43; N, 5.49; Zn, 12.90.

Zn^{II}(L$_2$)$_2$, bis{2-[(*R*)-(+)-1-phenylethyliminomethyl]-4-nitrophenolato-*N*,*O*}zinc(II) (2). The same procedure as for (**1**) afforded the condensation of (*R*)-1-phenylethylamine (0.48 g, 4 mmol) with 5-nitrosalicylaldehyde (0.67 g, 4 mmol). Contrary to **1**, slow cooling of the resulting solution gave only a microcrystalline powder. Pale yellow needle-like single crystals suitable for X-ray structure determination were obtained after recrystallization from dichloromethane. Mp 226 °C. Anal. Calc. for $C_{30}H_{26}N_4O_6Zn$: C, 59.66; H, 4.34; N, 9.28; O, 15.89; Zn, 10.83. Found: C, 59.09; H, 4.07; N, 9.14; Zn, 10.43.

Zn^{II}(L$_3$)$_2$, bis{2-[(*R*)-(+)-1-phenylethyliminomethyl]-4,6-dichlorophenolato-*N*,*O*}zinc(II) (3). The same procedure as for (**1**) afforded the condensation of (*R*)-1-phenylethylamine (0.48 g, 4 mmol) with 3,5-dichlorosalicylaldehyde (0.76 g, 4 mmol). As for **2**, slow cooling of the reaction mixture gave only a microcrystalline powder. Pale yellow parallelepiped single crystals suitable for X-ray structure determination were obtained after recrystallization from dichloromethane. Mp 240 °C. Anal. Calc. for $C_{30}H_{24}N_2O_2Cl_4Zn$: C, 55.29; H, 3.71; N, 4.30; O, 4.91; Cl, 21.76; Zn, 10.03. Found: C, 54.66; H, 3.49; N, 4.29; Cl, 21.14; Zn, 9.62.

Zn^{II}(L$_4$)$_2$, bis{2-[(*R*)-(+)-1-phenylethyliminomethyl]-4-methoxyphenolato-*N*,*O*}zinc(II) (4). The same procedure was used as for (**1**) to accomplish the condensation of (*R*)-1-phenylethylamine (0.48 g, 4 mmol) with 5-methoxysalicylaldehyde (0.61 g, 4 mmol). Single crystals suitable for X-ray structure determination were obtained by slow cooling of the reaction mixture. Mp 100 °C. Anal. Calc. for $C_{32}H_{32}N_2O_4Zn$: C, 66.96; H, 5.62; N, 4.88; O, 11.15; Zn, 11.39. Found: C, 66.62; H, 5.44; N, 4.99; Zn, 11.54.

Crystallography

Data were collected at room temperature (298 K) with a Bruker SMART CCD diffractometer equipped with a normal focus X-ray tube having a molybdenum target. The data were processed through the SAINT reduction software.[27] Empirical absorption corrections were carried out by SADABS.[28] The structures were solved and refined on F^2 using the SHELXTL software.[29] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the final refinement model in calculated positions with isotropic thermal parameters. Crystal structure and refinement data for compounds **1**–**4** are summarized in Table 3.

CCDC reference numbers 165067–165069.

See http://www.rsc.org/suppdata/dt/b1/b104360a/ for crystallographic data in CIF or other electronic format.

Optical measurements

The efficiency of the crystals for frequency doubling was determined by the Kurtz and Perry powder test[30] using a pulsed Nd^{3+} : YAG laser (λ = 1.06 μm). Prior to measurement the crystalline compounds were ground into powders, sieved to an average particle size between 250–300 μm, and packed into pellets of 2 mm path length. The references used were urea, POM [3-methyl-4-nitropyridine-1-oxide] and NPP [*N*-(4-nitrophenyl)-(*S*)-prolinol]. Absorption spectra of KBr pellets and of solutions in acetone and dichloromethane were obtained on a Varian Cary5E spectrometer.

Table 3 Summary of data collection and refinement for crystals **1**–**4**

	1[a]	**2**	**3**	**4**
Formula	$C_{30}H_{28}N_2O_2Zn$	$C_{30}H_{26}N_4O_6Zn$	$C_{30}H_{24}N_2O_2Cl_4Zn$	$C_{32}H_{32}N_2O_4Zn$
M	513.91	603.92	651.68	573.97
T/K	293(2)	298(2)	298(2)	298(2)
Cryst. syst.	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$	$C2$	$C2$
a/Å	17.738(4)	15.4512(8)	13.928(2)	17.569(2)
b/Å	29.632(9)	10.1073(5)	10.949(2)	8.758(8)
c/Å	9.968(2)	18.0725(9)	10.208(2)	11.981(1)
β/deg.	90	90.541(1)	118.246(3)	130.283(1)
V/Å^3	5239(2)	2822.3(2)	1371.4(4)	1406.4
Z	8	4	2	2
μ/mm^{-1}	0.98	0.920	1.318	0.921
d/g cm^{-3}	1.303	1.421	1.578	1.421
λ/Å	0.71073	0.71073	0.71073	0.71073
$R(F)$[b]	0.0725	0.0311	0.0859	0.0312
$R_w(F^2)$[c]		0.0880	0.2006	0.0835

[a] Crystal data obtained from ref. 23. [b] $I > 2\sigma(I)$, $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] All data, $R_w(F^2) = \Sigma[w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

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