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Crystal Structure and Spectral Characterization of a Rare Example of a Salen-Type Zinc Complex with Neutral Monodentate Oxygen Donor Ligands Coordination

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Summary. The new zinc complex of the *N*,*N*′-bis(salicylidene)-4-methyl-1,3-phenylenediamine ligand as a product of the [2 + 1] *Schiff* base condensation process was synthesized in the one-step metal-promoted reaction between salicylaldehyde and 4-methyl-1,3-phenylenediamine in ethanol in the presence of zinc chloride. The two potentially tetradentate N_2O_2 *Schiff* bases function as neutral monodentate ligands involving only one oxygen atom in coordination. This rare coordination pattern of a mononuclear salen-type zinc complex was revealed by X-ray crystallography and correlated with spectroscopic characterization.

Keywords. Crystal structure; Zinc; Salicylaldimines; *Schiff* base complexes; O-Salen-type ligand.

Introduction

Salicylaldimine metal complexes constitute a family of one of the most important systems due to the number of applications in catalysis, material, and biomimetic chemistry. Among them the zinc salen complexes can be used as models for active sites of hydrolytically active zinc enzymes, in asymmetric *Lewis* acid-catalyzed reactions, and as components for the assembly of supramolecular architectures displaying interesting structures and properties [1–14]. Therefore, there has been a considerable interest in the synthesis of new salen-type complexes. In this paper we wish to report the preparation and crystal structure correlated with spectral characterization of the new symmetrical *Schiff* base zinc complex derived from salicylaldehyde and 4-methyl-1,3-phenylenediamine. The metal-promoted one-step condensation reaction which we have been using for many years in the synthesis of

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Schiff base macrocyclic and acyclic complexes [15] has been found to be a very efficient method for the synthesis of salicylaldimine complexes derived from salicylaldehyde and suitable amines [16, 17].

Results and Discussion

Treating salicylaldehyde with 4-methyl-1,3-phenylenediamine in ethanol in the presence of zinc chloride yields a $Zn(C_{21}H_{18}N_2O_2)_2Cl_2$ complex containing *N*,*N*′-bis(salicylidene)-4-methyl-1,3-phenylenediamine as a result of the [2 + 1] *Schiff* base condensation. The solubility of this complex, not a common feature for neutral salen-type zinc complexes [18], allows us to unambiguously establish the coordination arrangement and correlate the crystal structure with its spectral characterization.

In the crystal structure the Zn(II) ion is four-coordinated and bound to two chlorides and two neutral salicylaldimine ligands in a slightly distorted tetrahedral arrangement (Fig. 1); the X–Zn–X angles (X=Cl or O) are in the range 99.78(7)–116.67(4)°. The two potentially tetradentate mixed N/O donor *Schiff* base ligands are monodentate: only one oxygen atom is involved in the coordination. Neither the second oxygen atom nor any of the nitrogen atoms interact with the Zn ion; they are involved in intramolecular hydrogen bonds.

The two salicylaldimine molecules differ in their conformations (Fig. 2): molecule A is approximately planar; the dihedral angles between the central aromatic

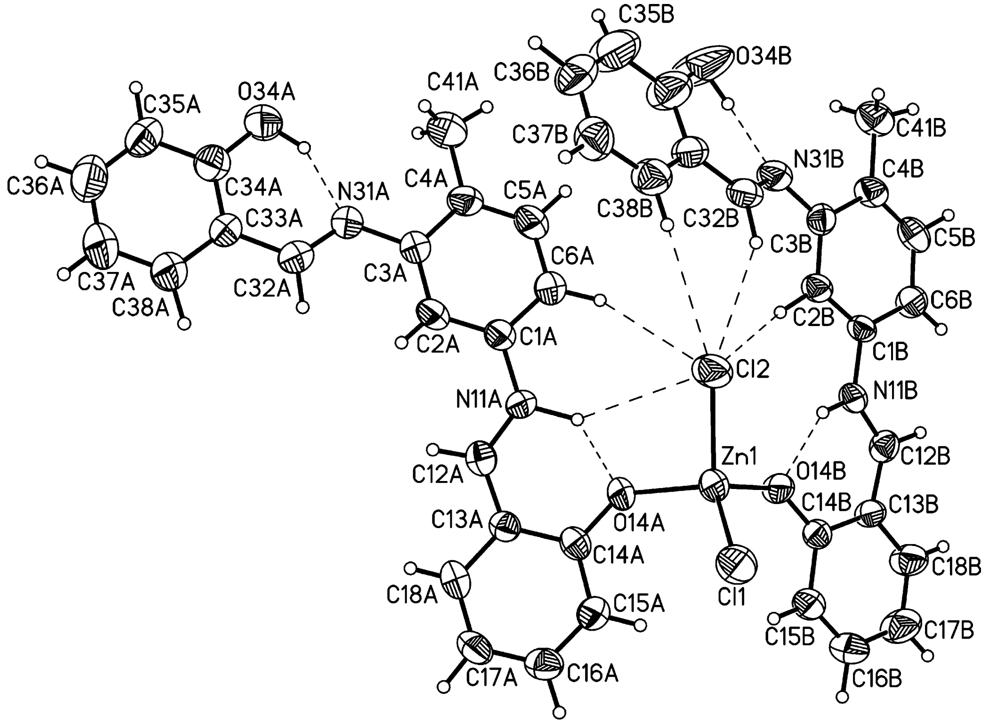

Fig. 1. Anisotropic displacement ellipsoid representation of the complex $ZnCl_2(C_{21}H_{18}N_2O_2)_2$; the ellipsoids are drawn at 50% probability level, hydrogen atoms are represented by spheres of arbitrary radii; strong and weak intramolecular hydrogen bonds are depicted as dashed lines

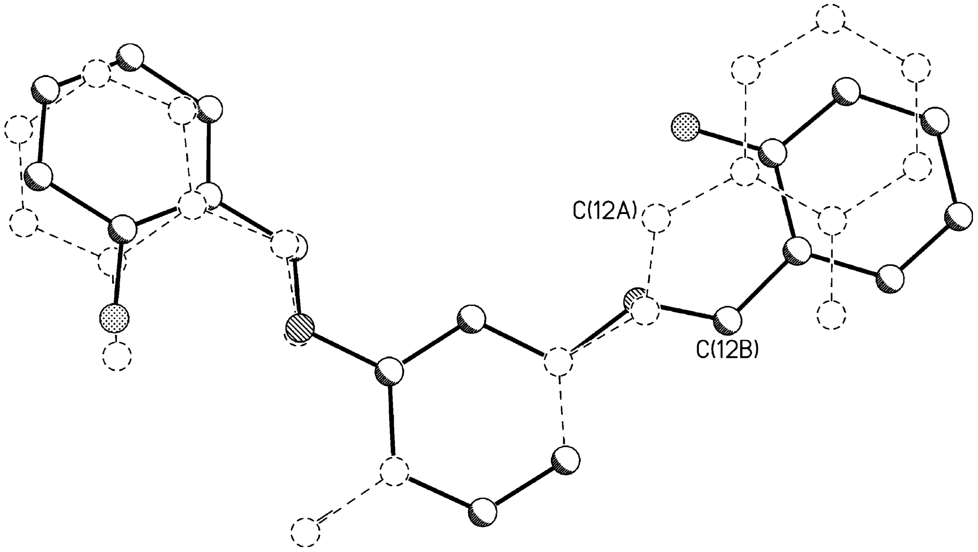

Fig. 2. A comparison of the conformation of two symmetry-independent molecules: A (solid lines) and B (dashed lines); the central phenyl rings were fitted by the least-squares procedure

ring and the terminal ones are 8.1(1) and 7.1(1)°. In molecule B one of the terminal rings (the one involved in coordination) is also coplanar with the central ring, the dihedral angle between their planes is 4.0(1)°, but the other one is significantly rotated, the appropriate dihedral angle is as high as 26.8(1)°. This difference can be related to the different interactions in which both ligands take part. Ligand B participates in three relatively short and directional intramolecular C–H···Cl hydrogen bonds with one chlorine atom (Cl2); ligand A participates only in one such interaction. The H···Cl distances are in the range 2.64(3)–3.01(3) Å, and C–H···Cl angles are between 142(2) and 154(2)°. On the other hand, ligand A forms two equally short and directional intermolecular C–H···Cl hydrogen bonds (H···Cl: 2.80(2)–3.06(3) Å, C–H···Cl: 122(2)–178(2)°) with the other chlorine, Cl1 (symmetry code $-x$, $1-y$, $1-z$). These intermolecular interactions build hydrogen-bonded dimers of complex molecules (Fig. 3).

The bond lengths and angles pattern indicate that upon coordination the hydrogen atom of the hydroxy group is transferred to the nitrogen atom. These hydrogen atoms were found in differential *Fourier* maps and successfully refined (Fig. 1). The hydrogen atoms from the OH groups not involved in the coordination are located (also from the ΔF map) in the vicinity of oxygen atoms. As a consequence, there are profound changes in the neighbouring N–C, C–C, and C–O bond lengths. The N–C bonds in the protonated imine (N(11)–C(12)) are elongated to 1.317(4) and 1.300(4) Å for molecules A and B compared to 1.282(4) and 1.291(4) Å (N(31)–C(32)) found in noncoordinated parts of these ligands, while the adjacent C–C bonds are shortened (1.403(4) and 1.412(4) Å for C(12)–C(13) of A and B *vs.* 1.445(4) and 1.435(4) Å for C(32)–C(33)). There are also changes in the C–N–C bond angles; these angles widen upon protonation: 126.6(3) *vs.* 122.9(3)° and 131.1(3) *vs.* 119.1(3)°, in molecules A and B, respectively. In addition, the phenolic C–O bonds (C(14)–O(14)) coordinated to the zinc ion are considerably shorter (1.326(3) Å

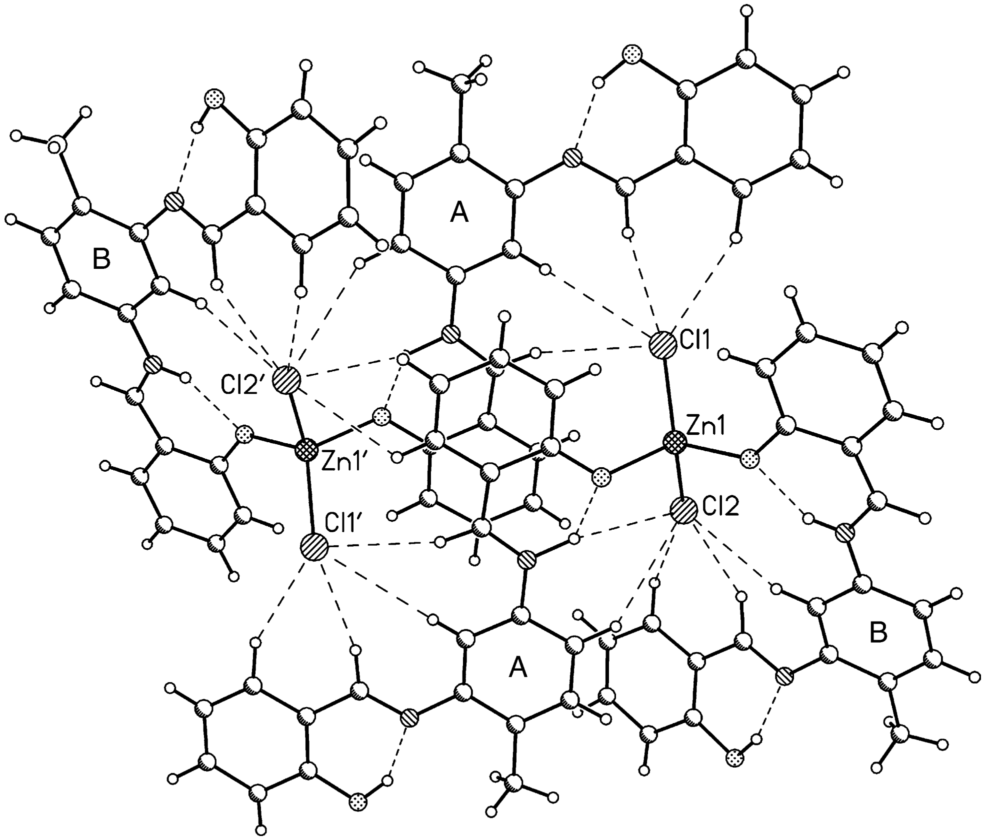

Fig. 3. Centrosymmetric dimer of complex molecules, kept by C–H$\cdots$Cl hydrogen bonds; hydrogen bonds are depicted as dashed lines; prime denotes the symmetry code ($-x$, $1-y$, $1-z$)

for A and 1.307(3) Å for B) than the distances (1.356(4) and 1.363(4) Å) in the corresponding bonds (C(34)–O(34)) involved in an intraligand hydrogen bond and not in coordination. This neutral monodentate O-donor type of coordination is in a marked contrast to the dianionic tetradentate N_2O_2 donor-set arrangement typically found in salen-type complexes. Interestingly, an inspection of the available data for the structures of the related bidentate NO or tetradentate N_2O_2 salicylaldiminato zinc complexes [11–14, 17–23] reveals that, despite the obvious difference in the coordination mode, these complexes are crystallographically equivalent to the scarce examples of neutral monodentate oxygen donor atom salicylaldimine ligand zinc complexes [23, 24]. Thus, the effects on the bond lengths of nitrogen protonation and the coordination of the metal ion through oxygen only are remarkably similar to those caused be the removal of protons by ionization and coordination of all oxygen and nitrogen atoms. This point is proved by the results of spectral characterization of this complex. The infrared spectrum clearly reflects this behavior. The proton transfer to the adjacent nitrogen is evidenced by the absorption band at $1636\,cm^{-1}$. The O–H stretching vibrations appear at 3053 and $2729\,cm^{-1}$ as expected for intramolecular hydrogen bonding. The bands associated with νC–O are observed at $1295–1280\,cm^{-1}$. An absorption band in far-infrared at $259–240\,cm^{-1}$ assignable to the M–Cl frequency indicates the interaction of the chloride counterions with the metal. An important feature of the spectrum is the occurrence of two absorption bands at 1611 and 1600 cm^{-1} attributable to the stretching modes of the two different C=N bonds. The higher frequency band corresponds to the C=N groups involved in intramolecular hydrogen bonds, while the lower frequency band corresponds to the protonated C=N groups. It should be pointed out that the decrease in the C=N stretching frequency owing to the lowered double bond character, which is usually ascribed to the involvement of the nitrogen atom in the coordination moiety, is not always the case. Therefore, the coordination mode in salen-type complexes might have been incorrectly inferred from spectroscopic analysis alone. It is apparent that the similarity between the spectroscopic data for the complexes and those for which no crystal data are available does not necessarily provide support to the assumption that these complexes must have analogous structures. The characterization of the salen-type complex by both X-ray crystallography and spectroscopic methods is found to be useful in guiding and confirming interpretations concerning coordination modes in similar complexes. Thank to the ESI mass spectrum performed in ethanol, the identification of the zinc complex in solution was also possible. The presence of a peak corresponding to the metal ion coordinating two salicylaldimine ligands clearly indicates that the integrity of the complex is maintained in solution. The observed loss of counterions and the presence of peaks assignable to the free ligand confirms the formation of a complex with the product of the [2 + 1] (salicylaldehyde + diamine) condensation process. The zinc complex gives a well resolved ^{1}H NMR spectrum. The homonuclear correlation spectroscopy (COSY) experiment in addition to signal integration and linewidth analysis made it possible to identify and assign the signals to corresponding protons. The ^{1}H NMR spectrum of *DMSO*-d$_6$ solution of the zinc complex exhibits the expected splitting patterns and chemical shifts for salicylidene protons. The protons corresponding to the phenylene ring occur as three signals: a dublet (1H) at $\delta = 7.65$ ppm ($J = 6.0$ Hz), a singlet (1H) at $\delta = 7.33$ ppm and another dublet (1H) at $\delta = 7.31$ ppm ($J = 6.0$ Hz). This latter signal is definitely assigned to the proton close to the methyl substituent because it shows COSY cross peak to the signal observed as singlet (3H) at $\delta = 2.37$ ppm corresponding to the protons of this methyl group. The UV-Vis spectra of the complex in both ethanol and *DMSO* confirm the stability of the complex in the two solvents.

In summary, our results extend the number of relatively scarce examples of mononuclear salen-type zinc complexes in which the potentially tetradentate N_2O_2 *Schiff* base functions as a neutral monodentate ligand involving only one oxygen atom in coordination. This rare coordination pattern revealed by X-ray crystallography and correlated with spectroscopic characterization may provide valuable information for the structural studies of other related complexes.

Experimental

IR spectrum was recorded using CsI pellets in the range 4000–200 cm^{-1} on a Perkin-Elmer 580 spectrophotometer. Electrospray mass spectrum was determined in ethanol using Waters Micromass ZQ spectrometer. The sample was run in the positive-ion mode. The concentration of the compound was about 10^{-4} mol dm^{-3}. Sample solution was introduced into mass spectrometer source with syringe pump with a flow rate of 40 mm^3 min^{-1} with a capillary voltage of +3 kV and the desolvation temperature of 300°C. The source temperature was 120°C. The cone voltage (V_c) was set to 30 V to allow transmission of ions without fragmentation processes. Scanning was performed from $m/z = 100$ to 1000 in 6 s, and 10 scans were summed to obtain the final spectrum. ^{1}H NMR spectra were run in *DMSO*-d$_6$ on a Varian Gemini 300 spectrometer using standard procedures for COSY measurements with *TMS* as an internal reference. The electronic absorption spectra were measured on a Shimadzu UV 2401 PC spectrometer in ethanol and *DMSO*.

The $Zn(C_{21}H_{18}N_2O_2)_2Cl_2$ complex was prepared in the one-pot reaction. To a mixture of zinc(II) chloride (48 mg, 0.2 mmol) in ethanol (10 cm^3) and salicylaldehyde (91 mg, 0.8 mmol) in ethanol (10 cm^3), 4-methyl-1,3-phenylenediamine (24 mg, 0.2 mmol) in ethanol (10 cm^3) was added dropwise with stirring. The reaction was carried out for 3 h. The solution volume was then reduced to 5 cm^3 by roto-evaporation and a orange precipitate formed on addition of a small amount of diethyl ether. This was filtered off, washed with ether, and dried *in vacuo*. Orange single crystals suitable for X-ray diffraction analysis were formed by slow diffusion of the ethyl acetate:ethanol (1:1) mixture into the ethanol solution of powder sample. Yield 78%; ^{1}H NMR and ^{1}H COSY (300 Hz, *DMSO*-d$_6$, 22°C): $\delta = 13.28$, 13.13 (2 s, 2×1H, 2OH), 9.06, 9.03 (2 s, 2×1H, 2HC=N), aryls: 7.68 (d, 2H, $J = 7.9$ Hz), 7.48 (d, 2H, $J = 7.9$ Hz), 7.02 (d, 2H, $J = 7.5$ Hz), 6.97 (d, 2H, $J = 7.5$ Hz), phen-H: 7.65 (d, 1H, $J = 6.0$ Hz), 7.33 (s, 1H), 7.31 (d, 1H, $J = 6.0$ Hz), phen-CH$_3$: 2.37 (s, 3H) ppm; MS (ESI): $m/z = 385$ $(Zn(C_{21}H_{18}N_2O_2)_2 \cdot C_2H_5OH)^{2+}$, 242 $(ZnC_{21}H_{18}N_2O_2 \cdot 2C_2H_5OH)^{2+}$, 331 $(C_{21}H_{18}N_2O_2 + H)^+$; IR (CsI): $\bar{\nu} = 3053$, 2729 (O–H···N), 1636 (N–H), 1611, 1600 (C=N), 1511, 1482, 767, 756 (C=C), 1289 (C–O), 256–240 (M–Cl) cm^{-1}; UV-Vis (*Et*OH): $\lambda_{max} = 212.5$, 257, 331.5 nm; UV-Vis (*DMSO*): $\lambda_{max} = 253$, 275, 302.5(sh), 327.5 nm.

Crystallographic data: $ZnCl_2(C_{21}H_{18}N_2O_2)_2$; triclinic, *P*-1, $a = 8.4430(8)$ Å, $b = 14.4792(13)$ Å, $c = 17.246(2)$ Å, $\alpha = 113.175(9)°$, $\beta = 98.862(9)°$, $\gamma = 96.887(8)°$; $V = 1876.8(4)$ Å^3; $Z = 2$, $d_{calc} = 1.41$ g · cm^{-3}; $\mu(MoK_\alpha) = 0.85$ mm^{-1}, $T = 295(1)$ K; 14,324 reflections collected, 6558 independent ($R_{int} = 0.054$); final $R_1 = 0.047$, $wR_2 = 0.051$, $S = 0.89$; maximum and minimum residuals: 0.26 and -0.35 e · Å^{-3}. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC-272176.

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