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The interconversion of dichlorobis(*N*-*n*-propylsalicylaldimine)zinc(II) and bis(*N*-*n*-propylsalicylaldiminato)zinc(II)

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Abstract

The interconversion of the zinc(II) complex of the neutral ligand adduct of *N*-*n*-propylsalicylaldimine $Zn(L^{pr}H)_2Cl_2$ and its salicylaldiminato counterpart $Zn(L^{pr})_2$ is investigated. The compound $Zn(L^{pr}H)_2Cl_2$ is prepared by the reaction of anhydrous $ZnCl_2$ with 2 equiv. of *N*-*n*-propylsalicylaldimine ($L^{pr}H$) in benzene. A crystallographic study of the distorted tetrahedral $Zn(L^{pr}H)_2Cl_2$ adduct reveals that the oxygen atom of the ligand is deprotonated and bound to the zinc atom while the nitrogen is protonated and non-coordinating. An infrared spectrum of $Zn(L^{pr}H)_2Cl_2$ exhibits a C=N stretch at a higher energy (1658 cm^{-1}) than the free ligand (1632 cm^{-1}) consistent with the presence of the iminium moiety. In contrast, the deprotonated ligand of the crystallographically characterized salicylaldiminato complex $Zn(L^{pr})_2$ coordinates to zinc in its prototypical bidentate monoanionic coordination mode. Deprotonation of $Zn(L^{pr}H)_2Cl_2$ with Et_3N or NaOH forms $Zn(L^{pr})_2$. The reverse reaction, protonation of $Zn(L^{pr})_2$ with anhydrous HCl, produces $Zn(L^{pr}H)_2Cl_2$. These reactions demonstrate the interrelationship between the zinc salicylaldimine adduct and its corresponding salicylaldiminato complex.

Keywords: Schiff bases; Salicylaldimine adducts; Interconversion; X-ray crystal structures; Zinc complexes; Zwitterion

1. Introduction

The salicylaldimine ligand forms the basis of an extensive class of chelating ligands that has enjoyed popular use in the coordination chemistry of transition and main group elements [1–3]. The reaction of the neutral phenol-imine form of the salicylaldimine ligand with a suitable metal starting material in the presence of base is a simple and direct means of preparing metal salicylaldiminato complexes (Scheme 1). In these complexes, the deprotonated phenolate-imine form of the ligand acts as a bidentate monoanionic N/O donor.

Despite the frequent use of this preparative method, comparatively few of the putative precursors or intermediates involved in this reaction prior to deprotonation of the ligand have been structurally characterized [1,2,4–11] and, similarly, the precursors formed by the reverse reaction are not isolated typically [12,13]. We report here an example of the interconversion of a structurally characterized precursor and its corresponding deprotonated salicylaldiminato complex using the zinc(II) dichloride adduct of *N*-*n*-propylsalicylaldimine ($L^{pr}H$). These reactions corroborate the role of neutral salicylaldimine adducts in the formation of salicylaldiminato complexes.

2. Experimental

2.1. Materials and methods

Reagents and solvents were used as received from commercial sources. The ligand *N*-*n*-propylsalicylaldimine ($L^{pr}H$) and the protonated ligand ($L^{pr}H_2$)(CF_3SO_3) were synthesized by generally accepted methods [1,14] and $Zn(L^{pr})_2$ by modification of related literature procedures [15,16]. Infrared and electronic spectroscopic data were collected on a Mattson Satellite FTIR and Perkin–Elmer Lambda 6 instrument, respectively. The ^1H NMR spectroscopic data were obtained on a Bruker AVANCE 300 NMR spectrometer at

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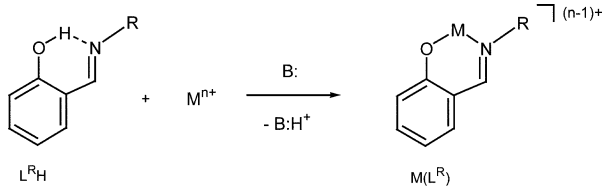


Scheme 1.

ambient room temperature. Chemical shifts are referenced as ppm downfield of tetramethylsilane. A conventional numbering scheme was adopted for ligand aromatic hydrogen atoms attached to carbons for ^{1}H NMR assignments in which the imine moiety was attached to ring C1, the OH to ring C2 and so on. Robertson Microlit Laboratories (Madison, NJ) and Quantitative Technologies Inc. (Whitehouse, NJ) performed the elemental analyses.

2.2. X-ray crystallographic structure determination of $Zn(L^{pr})_2$ and $Zn(LH)_2Cl_2$

Data collection, solution and refinement details are given in Table 1 and bond lengths and distances in Figs. 1 and 2 captions and Table 2. Complete crystallographic information is available as supplementary material. Rhomb-shaped single crystals of $Zn(L^{pr}H)_2Cl_2$ suitable for X-ray crystallographic studies could be obtained from slowly evaporating methanol or acetonitrile solutions in air. X-ray quality single crystals of $Zn(L^{pr})_2$ were grown by evaporating the compound dissolved in toluene over a period of 1 week. The crystals were glued to a glass fiber with epoxy and mounted on a Bruker P4 (formerly Siemens) diffractometer equipped with a SMART CCD and the data collected at low temperature under a dinitrogen cold stream.

Data collection, solution and refinement for both compounds were obtained by routine methods using SHELXTL [17] (see Table 1). A data set was collected by obtaining an initial set of cell constants calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. The unit cell was further refined by the inclusion of reflections from the data set and the program SAINT (Bruker AXS). The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2. All hydrogen atom parameters, with the exception of the iminium hydrogens

Table 1
Crystal data, data collection, structure solution and refinement for $Zn(L^{pr}H)_2Cl_2$ and $Zn(L^{pr})_2$

	$Zn(L^{pr}H)_2Cl_2$	$Zn(L^{pr})_2$
Crystal data		
Empirical formula	$C_{20}H_{26}Cl_2N_2O_2Zn$	$C_{20}H_{24}N_2O_2Zn$
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Fdd2$
a (Å)	10.0551(5)	18.172(6)
b (Å)	25.080(1)	39.16(1)
c (Å)	9.1355(5)	5.171(2)
β (°)	109.058(1)	
V (Å^3)	2177.5(2)	3680(2)
Z	4	8
Formula weight	462.70	389.78
D_{calc} (Mg m^{-3})	1.411	1.407
Absorption coefficient (mm^{-1})	1.390	1.350
$F(000)$	960	1632
Data collection		
Wavelength (Å)	0.71073	0.71073
Temperature (K)	213(2)	228(2)
θ Range for data collection (°)	1.62–28.33	2.08–28.28
Index ranges	$-13 \le h \le 7$, $-31 \le k \le 27$, $-11 \le l \le 11$	$-24 \le h \le 16$, $-44 \le k \le 50$, $-6 \le l \le 6$
Reflections collected	16 161	6419
Independent reflections	5027 ($R_{int} = 0.0161$)	2057 ($R_{int} = 0.0440$)
Solution and refinement		
Solution	Direct methods	Direct methods
Refinement method	Full-matrix least-squares F^2	Full-matrix least-squares F^2
Absorption correction	SADABS	SADABS
Max. and min. transmission	0.8735 and 0.6805	0.7740 and 0.6143
Data/restraints/ parameters	5027/0/253	2057/1/117
Final R indices ($I > 2\sigma(I)$]	$R_1 = 0.0229$, $wR_2 = 0.0604$	$R_1 = 0.0423$, $wR_2 = 0.0929$
R indices (all data)	$R_1 = 0.0269$, $wR_2 = 0.0625$	$R_1 = 0.0517$, $wR_2 = 0.0957$
Goodness-of-fit on F^2	1.028	1.115
Largest difference peak and hole (e Å^{-3})	0.37 and -0.295	0.440 and -0.584

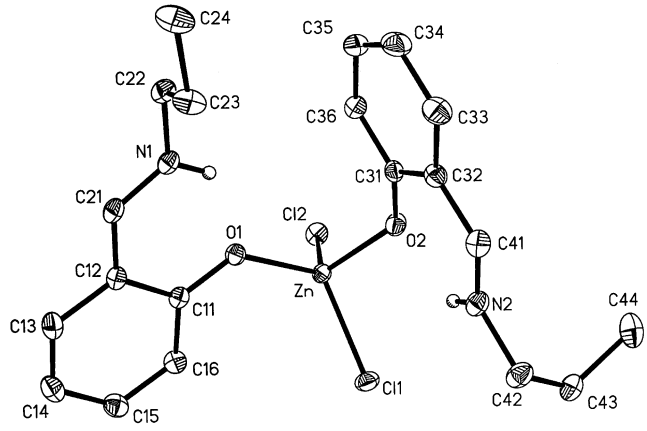


Fig. 1. Molecular structure of $Zn(L^{pr}H)_2Cl_2$. Bond distances (Å): Zn–O(1), 1.9535(9), Zn–O(2), 1.974(1), Zn–Cl(2), 2.2317(4), Zn–Cl(1), 2.2478(4), O(1)–C(11), 1.313(2), O(2)–C(31), 1.3083(17), N(1)–C(21), 1.292(2), N(1)–C(22), 1.467(2), N(2)–C(41), 1.289(2), N(2)–C(42), 1.462(2), C(12)–C(21), 1.422(2), C(22)–C(23), 1.508(2), C(23)–C(24), 1.531(2), C(32)–C(41), 1.428(2), C(42)–C(43), 1.508(2), C(43)–C(44), 1.505(3), average C(ring)–C(ring), 1.398(2), N(1)–H(1), 0.84(2), N(2)–H(2), 0.80(2), O(1)···N(1), 2.674(2), O(2)···N(2), 2.617(2), N(1)···Cl(2), 5.704(2), N(2)···Cl(1), 3.562(2). Bond angles (°): O(1)–Zn–O(2), 102.89(4), O(1)–Zn–Cl(2), 112.31(3), O(2)–Zn–Cl(2), 111.83(4), O(1)–Zn–Cl(1), 116.83(3), O(2)–Zn–Cl(1), 96.30(3), Cl(2)–Zn–Cl(1), 114.73(2), C(11)–O(1)–Zn, 127.01(9), C(31)–O(2)–Zn, 131.69(9), C(21)–N(1)–C(22), 122.6(1), C(41)–N(2)–C(42), 125.8(2), O(1)–C(11)–C(16), 123.4(1), O(1)–C(11)–C(12), 119.6(1), C(21)–C(12)–C(11), 122.3(1), C(13)–C(12)–C(21), 117.6(1), O(2)–C(31)–C(36), 122.4(1), O(2)–C(31)–C(32), 119.7(1), N(1)–C(21)–C(12), 126.0(1), N(1)–C(22)–C(23), 112.3(1), C(22)–C(23)–C(24), 110.7(2), N(2)–C(41)–C(32), 124.4(2), N(2)–C(42)–C(43), 111.6(1), C(44)–C(43)–C(42), 113.7(2), C(33)–C(32)–C(41), 118.9(2), C(31)–C(32)–C(41), 121.6(1), average C(ring)–C(ring)–C(ring), 120.0(2), N(1)–H(1)···O(1), 132(2), N(2)–H(2)···O(2), 134(2), N(2)–H(2)···Cl(1), 143(2).

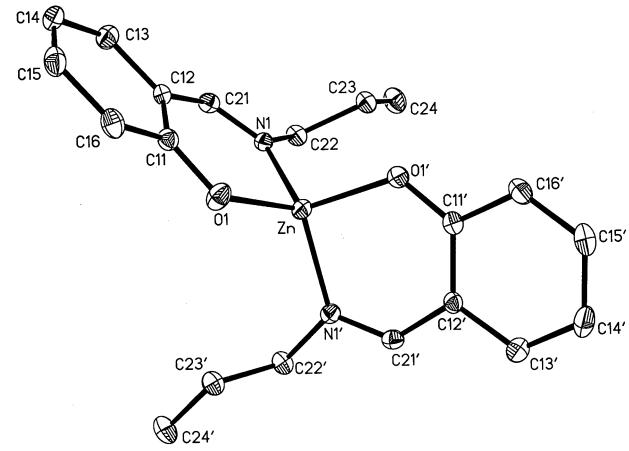


Fig. 2. Molecular structure of $Zn(L^{pr})_2$. Bond distances (Å): Zn–O(1)′, 1.928(2), Zn–N(1)′, 1.998(3), Zn–N(1), 1.998(3), O(1)–C(11), 1.307(4), N(1)–C(21), 1.276(5), N(1)–C(22), 1.483(4), C(12)–C(21), 1.438(5), C(22)–C(23), 1.518(5), C(23)–C(24), 1.524(6), average C(ring)–C(ring), 1.396(6). Bond angles (°): O(1)′–Zn–O(1), 111.26(19), O(1)′–Zn–N(1)′, 95.76(11), O(1)–Zn–N(1)′, 113.34(11), O(1)′–Zn–N(1), 113.34(11), O(1)–Zn–N(1), 95.76 (11), N(1)′–Zn–N(1), 127. 83(16), C(11)–O(1)–Zn, 125.1(2), C(21)–N(1)–C(22), 117.4(3), C(21)–N(1)–Zn, 120.4(2), C(22)–N(1)–Zn, 122.2(2), O(1)–C(11)–C(16), 119.3(3), O(1)–C(11)–C(12), 123.3(3), C(13)–C(12)–C(21), 116.5(3), C(11)–C(12)–C(21), 124.5(3), N(1)–C(21)–C(12), 128.8(3), N(1)–C(22)–C(23), 111.3(3), C(22)–C(23)–C(24), 110.9(4), average C(ring)–C(ring), 120.0(4).

Table 2
Comparative selected crystallographic data for $Zn(L^{pr}H)_2Cl_2$ and $Zn(L^{pr})_2$

$Zn(L^{pr}H)_2Cl_2$		$Zn(L^{pr})_2$	
Bond distances (Å)			
Zn–O(1)	1.9535(9)	Zn–O(1)	1.928(2)
Zn–O(2)	1.974(1)	Zn–N(1)	1.998(3)
Zn–Cl(1)	2.2478(4)		
Zn–Cl(2)	2.2317(4)		
N(1)–C(21)	1.292(2)	N(1)–C(21)	1.276(5)
N(2)–C(41)	1.289(2)		
O(1)–C(11)	1.313(2)	O(1)–C(11)	1.307(4)
O(2)–C(31)	1.308(2)		
Bond angles (°)			
O(1)–Zn–O(2)	102.89(4)	O(1)–Zn–O(1)′	111.3(2)
Cl1–Zn–Cl2	114.73(2)	N(1)–Zn–N(1)′	127.8(2)
O1–Zn–Cl1	116.83(3)	O(1)–Zn–N(1)′	113.3(1)
O2–Zn–Cl1	96.30(3)	O(1)–Zn–N(1)	95.8(1)
O1–Zn–Cl2	112.31(3)		
O2–Zn–Cl2	111.83(4)		
Zn–O1–C11	127.01(9)	Zn–O(1)–C(11)	125.1(2)
Zn–O2–C31	131.69(9)	Zn–N(1)–C(22)	122.2(2)

H(1) and H(2) in $Zn(LH)_2Cl_2$, were placed in ideal positions and refined as riding atoms with individual (or group if appropriate) isotropic displacement. The atoms H(1) and H(2) were found in the difference map and refined to convergence with isotropic displacement parameters.

2.3. Preparation of compounds

2.3.1. N-n-Propylsalicyaldimine ($L^{pr}H$)

A solution of salicylaldehyde (6.106 g, 0.05 mol) in 50 ml of benzene was added to a 100 ml round bottom flask fitted with a Dean–Stark trap and a condenser. To this solution, 2.956 g (0.05 mmol) of *n*-propylamine was added slowly with stirring since the reaction was slightly exothermic and then refluxed for 1 h. After cooling, the reaction mixture was dried over anhydrous magnesium sulfate and gravity filtered. The filtrate was evaporated to yield 7.057 g (78%) of a yellow–brown oil that could be used without further purification. *Anal.* Found: C, 73.30; H, 8.04; N, 8.73. Calc. for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58%. FTIR (neat) 3061(w), 2963(s), 2931(s), 2874(s), 2738(w), 2660(w), 1664(m), 1632(vs), 1582(s), 1497(s), 1461(s), 1416(m), 1382(w), 1338(w), 1279(s), 12059(m), 1150(m), 1115(w), 1054(w), 1031(w), 1013(w), 977(m), 882(m), 850(m, br), 755(s), 640, 553, 463 cm^{-1}. ^1H NMR ($CDCl_3$) δ 13.60 (1H, s br, OH),

8.23 (1H, s, NCH), 7.20 (1H, t, H5), 7.14 (1H, d, H6), 6.87 (1H, d, H3), 6.77 (1H, t, H4), 3.46 (2H, t, NCH_2), 1.63 (2H, m, NCH_2CH_2), 0.89 (3H, t, CH_3) ppm.

2.3.2. $(L^{pr}H)(CF_3SO_3)$

In a 100 ml Schlenk tube, 0.429 g (2.63 mmol) of *N-n*-propylsalicylaldimine was added to 20 ml of anhydrous diethyl ether under argon. To this solution, 0.760 ml (0.448 g, 2.99 mmol) of trifluoromethanesulfonic acid was added in drops with vigorous stirring. The resulting cloudy, slightly pink suspension was stirred for 5 min, then filtered and washed with anhydrous diethyl ether to yield 0.780 g of a white solid after drying under vacuum (95% yield). The compound could be recrystallized from hot chloroform. *Anal*. Found: C, 42.16; H, 4.46; N, 4.45; F, 18.31. Calc. for $C_{11}H_{14}F_3NOS$: C, 42.17; H, 4.50; N, 4.47; F, 18.19%. IR (KBr): 3214(s), 3140(m, br), 3006(m), 2973(m), 2885(w), 1674(m), 1611(m), 1502(w), 1459(w), 1381(w), 1360(w), 1280(vs), 1245(vs), 1223(s), 1151(m), 1061(w), 1031(s), 1000(w), 903(w), 882(w), 758(m), 645(m), 574(w), 517(w), 447(w) cm^{-1}.

2.3.3. $Zn(L^{pr}H)_2Cl_2$

In a 100 ml Schlenk tube, 1.10 g (6.74 mmol) of *N-n*-propylsalicylaldimine was dissolved in 12 ml of dry benzene (distilled over $LiAlH_4$) under Ar. A 3.3 ml solution of 1.0 M $ZnCl_2$ (3.3 mmol) in diethyl ether (Aldrich) was then added via syringe in drops forming a thick orange oil. With vigorous manual agitation the oil slowly changed to a yellow solid after approximately 0.5 h. The reaction mixture was allowed to stir for an additional 1.5 h. The solid was filtered and washed in air with 5 ml of benzene and diethyl ether (3×5 ml) to yield 1.493 g of a yellow powder after drying under vacuum (98% yield). *Anal.* Found: C, 51.57; H, 5.58; N, 6.00; Cl, 14.93. Calc. for $C_{20}H_{26}Cl_2N_2O_2Zn$: C, 51.91; H, 5.66; N, 6.05; Cl, 15.32%. m.p. 151–154 °C. Electronic spectrum ($CHCl_3$, ε M^{-1} cm^{-1}): 316 (7300), 390 (2300) nm. FTIR (KBr): 3060(m, br), 2977(sh), 2957(m), 2935(m), 2877(w), 1658 (vs), 1607(s), 1542(s), 1490(s), 1459(w), 1344(w), 1302(m), 1288(m), 1232(m), 1202(m), 1141(m), 1027(m), 989(w), 911(w), 894(w), 8649w), 787(w), 759(s), 7349(w), 583(m), 514(w), 490(w), 450(w) 434(w), 4169(w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 13.6 (1H, s br, OH), 8.16 (1H, s, NCH), 7.37 (1H, t, H5), 7.23 (1H, d, H6), 7.11 (1H, d, H3), 6.74 (1H, t, H4), 3.61 (2H, t, NCH_2), 1.79 (2H, m, NCH_2CH_2), 0.99 (3H, t, CH_3) ppm.

2.3.4. $Zn(L^{pr})_2$

To a solution of 1.50 g (9.19 mmol) of *N-n*-propylsalicylaldimine in 20 ml of ethanol, 1.01 g (4.60 mmol) of $Zn(O_2CCH_3)_2 \cdot 2H_2O$ was added with stirring. A pale yellow precipitate formed after several minutes and was stirred for an additional 45 min. The precipitate was filtered and dried under vacuum to yield 0.98 g of a light yellow powder (55%). This compound could be recrystallized from acetone and water to obtain a colorless microcrystalline product. *Anal*. Found: C, 61.59; H, 6.08; N, 7.05. Calc. for $C_{20}H_{24}N_2O_2Zn$: C, 61.62; H, 6.21; N, 7.19%. Electronic spectrum ($CHCl_3$, ε M^{-1} cm^{-1}): 316 (6200), 369 (3100) nm FTIR (KBr): 3083(w), 3048(w), 3025(w), 2974(w), 2956(w), 2933(m), 2908(m, br), 2864(m), 1626(vs), 1600(m), 1535(s), 1470(s), 1447(s), 1407(m), 1348(m), 1329(m), 1240(w), 1189(m), 1148(m), 1125(w), 1052(m), 1031(w), 1017(w), 982(w), 922(w), 887(m), 850(w), 795(w), 752(m), 741(m), 654(w), 600(w), 562(w), 512(w), 464(m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 8.17 (1H, s, NCH), 7.29 (1H, t, H5), 7.11 (1H, d, H6), 6.85 (1H, d, H3), 6.60 (1H, t, H4), 3.51 (2H, t, NCH_2), 1.64 (2H, m, NCH_2CH_2), 0.88 (3H, t, CH_3) ppm.

2.3.5. $Zn(L^{pr})_2$ prepared from $Zn(L^{pr}H)_2Cl_2$

In a 125 ml Erlenmeyer flask, 0.179 g (0.387 mmol) of $Zn(L^{pr}H)_2Cl_2$ was added followed by 16.8 ml (0.769 mmol) of aqueous 0.0458 M NaOH with stirring. The solution initially became a light yellow suspension followed by the formation of a white precipitate. After 2 h the product was filtered and dried under vacuum to yield 0.136 g of an off-white solid (90%). Alternatively, solid $Zn(L^{pr}H)_2Cl_2$ (0.110 g, 0.238 mmol) was dissolved in 15 ml of chloroform with stirring in a 25 ml round bottom flask. The slightly cloudy yellow solution became clear and pale yellow after 0.0485 g (0.479 mmol) of Et_3N was added by syringe. The chloroform solution was evaporated on a rotoevaporator and the resulting solid was triturated with deionized water until chloride free (by testing with $AgNO_3$(aq)). The solid was then dried under vacuum to yield 0.083 g of off-white product (89%). This material was judged to be pure based on ^1H NMR and IR spectroscopic measurements.

2.3.6. $Zn(L^{pr}H)_2Cl_2$ prepared from $Zn(L^{pr})_2$

A 2.1 ml (2.1 mmol) aliquot of a 1.0 M solution of HCl in diethyl ether (Aldrich) was added via syringe in drops to a rapidly stirring solution of 0.391 g (1 mmol) of $Zn(L^{pr})_2$ in 20 ml of benzene in a Schlenk tube under argon. The reaction mixture immediately became cloudy and yellow. After several minutes of stirring, a thick orange oil formed. Continued stirring yielded a yellow solid after 1 h. The solvent was decanted and the remaining solid was washed with 5 ml of benzene followed by 3×10 ml of diethyl ether and dried to yield 0.428 g of product (92%). Both preparations yielded material that was pure based on ^1H NMR and IR spectroscopic measurements.

3. Results and discussion

3.1. Synthesis and interconversion reactions

In accord with syntheses of zinc(II) adducts of salicylaldimine ligands [6,18], the reaction of 1 equiv. of anhydrous $ZnCl_2$ in diethyl ether with 2 equiv. of *N*-*n*-propylsalicylaldimine in benzene forms $Zn(L^{pr}H)_2Cl_2$ in a nearly quantitative 98% yield. In the presence of 2 equiv. of NaOH(aq) or Et_3N in chloroform, this compound readily forms $Zn(L^{pr})_2$ in excellent yield upon work-up (Eq. (1)). The zinc salicylaldiminato complex prepared in this manner is identical to the commonly reported method that employs $Zn(O_2CCH_3)_2\cdot 2H_2O$ with *N*-alkylsalicylaldimines [15,16,19–21]. The isolated 89–90% yield of $Zn(L^{pr})_2$ from the precursor $Zn(L^{pr}H)_2Cl_2$ is significantly greater than the 55% yield of the reaction by the more conventional preparative method, which is often problematic [22].

$$Zn(L^{pr}H)_2Cl_2 \underset{2HCl}{\overset{2Et_3N:\ or\ 2NaOH}{\rightleftarrows}} Zn(L^{pr})_2 \quad (1)$$

Conversely, the $Zn(L^{pr}H)_2Cl_2$ precursor can be prepared from $Zn(L^{pr})_2$ and 2 equiv. of HCl in benzene/diethyl ether in 92% yield indicating the ready, clean interconversion between the salicylaldimine adduct and its salicylaldiminato counterpart (Eq. (1)). Despite the presence of two nascent equivalents of HCl, this ''reverse'' reaction in the absence of base does not occur. Attempts to affect the elimination of HCl from this complex by heating the neat solid $Zn(L^{pr}H)_2Cl_2$ at 100 °C under vacuum for several days resulted in no reaction. Heating the evidently robust solid to a melt at 155 °C under vacuum or in DMSO under a N_2 purge resulted in no change after 5 h. After prolonged heating over several days, only partial decomposition to the free ligand and unidentifiable products by ^1H NMR and IR spectroscopy was observed.

3.2. Structural characterization

The X-ray crystal structures of $Zn(L^{pr}H)_2Cl_2$ and $Zn(L^{pr})_2$ allow a direct comparison between both compounds of the neutral and deprotonated *N*-*n*-propylsalicylaldimine ligand. The structure of $Zn(L^{pr}H)_2Cl_2$ shown in Fig. 1 reveals a tetrahedral zinc(II) atom bound to two chlorides and two neutral salicylaldimine ligands in their phenolate-iminium (zwitterion) form. Only the phenolate oxygen atom of the potentially bidentate mixed N/O donor ligand binds to zinc in this complex, a rare example of a mononuclear zinc complex with terminal phenolate ligands [23–25]. Notably, the imine nitrogen is non-coordinating and protonated, i.e. an iminium $\{HC{=}NH\}^+$ group. The structure is similar, overall, to the previously reported structure of zinc(II) salicylaldimine adduct $Zn(L^{ipr}H)I_2$ [26], with the exception that $Zn(L^{pr}H)Cl_2$ possesses approximate C_2 symmetry with the phenyl rings of the ligand disposed *trans* to one another rather than *cis* with respect to the normal of the X–Zn–X ($X = Cl^-$ or I^-) plane. In spite of its relative anonymity, this coordination mode has appeared in various reports of Schiff base complexes or adducts [27]. Since the coordinated salicylaldimine zwitterion was first definitively structurally characterized [28], it has appeared in novel compounds [29,30] or useful starting materials for heterobimetallic complexes of multidentate macrocyclic complexes [7–10].

The coordination mode of the monodentate zwitterion salicylaldimine in $Zn(L^{pr}H)_2Cl_2$ is in marked contrast to that of the salicylaldiminato ligand in the structure of the $Zn(L^{pr})_2$ shown in Fig. 2. In this structure, the ligand in its phenolate-imine form uses both N/O donors to bind to tetrahedral zinc(II) in its ubiquitous bidentate monoanionic coordination mode (Scheme 1). The structure of $Zn(L^{pr})_2$ is comparable to analogous bis(salicylaldiminato)zinc (II) complexes [15,16,21,26].

The ligands in both complexes impose a distorted tetrahedral coordination geometry with angles about the zinc atom ranging from 96.30(3)° to 116.83(3)° in $Zn(L^{pr}H)_2Cl_2$ and 95.8(1)° to 127.8(2)° in $Zn(L^{pr})_2$ (see Table 2). The Zn–O bond distances of the coordinated neutral ligand in $Zn(L^{pr}H)_2Cl_2$ (1.9535(9), 1.9742(1) Å) are slightly longer than the 1.928(2) Å distance in the corresponding salicylaldiminato complex $Zn(L^{pr})_2$, but in good agreement with the mean Zn–O distance of 1.955 Å for the reported structure of $Zn(L^{ipr}H)_2I_2$ [26]. The Zn–O–C angles (127.01(9)°, 131.69(9)°) in $Zn(L^{pr}H)_2Cl_2$ are within the range (118°–137°) of limited available data for zinc(II) complexes with terminal phenolate ligands [18,23–26,31]. The Zn–Cl bond lengths (2.2478(4), 2.2312(4) Å) of $Zn(L^{pr}H)_2Cl_2$ are comparable to related zinc dichloride adducts [18,31,32] and between those of $ZnCl_4^-$ (range 2.263–2.273 Å) [33] and $Zn(py)_2Cl_2$ (2.215, 2.228 Å) [34].

Despite the obvious difference in coordination mode, the metrical parameters of the zwitterion salicylaldimine ligand in $Zn(L^{pr}H)_2Cl_2$ are crystallographically equivalent to its bidentate anionic counterpart in $Zn(L^{pr})_2$ (see Table 2) and other coordinated salicylaldiminato ligands in general [1,2]. The C–O bond distances in both $Zn(L^{pr}H)_2Cl_2$ (1.308(2), 1.313(2) Å) and $Zn(L^{pr})_2$ (1.307(4) Å) are normal for deprotonated phenols bound to zinc [15,16,18,21–26,31]. The C–N bond distances of the protonated imine in $Zn(L^{pr}H)_2Cl_2$ (1.289(2), 1.292(2) Å) as well as the C–N–C angles (122.6(1)°, 125.8(2)°) compare favorably with the corresponding distances and angles for the imine moiety in $Zn(L^{pr})_2$ of 1.276(5) Å and 117.4(3)° consistent with a sp^2 hybridized nitrogen in a C–N double bond [35].

Of particular relevance to the interconversion of salicylaldimine and salicyclaldiminato complexes is the iminium proton in $Zn(L^{pr}H)_2Cl_2$ shown in Fig. 1. The coordinates of the hydrogen atom attached to nitrogen in the structure of $Zn(L^{pr}H)_2Cl_2$ converge upon refinement to yield N–H bond distances of 0.84(2) (N(1)–H(1)) and 0.80(2) Å (N(2)–H(2)) and positions located well within the ligand plane (the atoms in the $L^{pr}H$ fragment are co-planar with a maximum deviation of 0.05 Å). The N···O distances (2.674(2), 2.619(2) Å) and N–H···O angles (132(2), 134(2)°) in $Zn(L^{pr}H)_2Cl_2$ are consistent with an intraligand hydrogen bond between a protonated nitrogen and a phenolate oxygen [18,26,31]. In addition, the N(2)···Cl(1) distance of 3.562(2) Å and the N(2)–H(2)···Cl(1) angle of 143(2)° approach those of weak hydrogen bonds between N–H and chloride, e.g. $(CH_3NH_3)_2[ZnCl_4]$ (3.210–3.546 Å) [33]. The data suggest that H(2) participates in a three-center hydrogen bond [36] with O(2) and Cl(1).

The protonation of the iminium hydrogen in $Zn(L^{pr}H)_2Cl_2$ results from the reaction of the strong Lewis acid zinc dichloride with the oxygen atom of the phenol-imine form (Scheme 1) of the ligand. This stable hydrogen bonded form of the free ligand, seemingly, converts to the zwitterion form by intermolecular proton transfer from the metalated phenol-imine, {Zn–OH···N}, to form a hydrogen bonded phenolate-iminium species, {Zn–O···H:N}. The iminium proton participates in a moderate strength hydrogen bond [36] to the coordinated phenolate oxygen atom stabilizing this otherwise high-energy zwitterion form (in non-aqueous solvents) of the neutral ligand [2]. An alternative monodentate coordination mode, in which the zinc atom is bound to the imine and the proton resides on the phenol, e.g. {OH···Zn–N}, would lack the O–H···N hydrogen bond and is presumably less stable.

3.3. Spectroscopic characterization

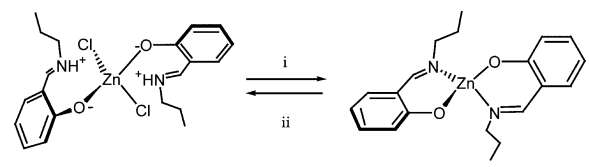
The solid-state infrared spectrum of $Zn(L^{pr}H)_2Cl_2$ displays a distinctive, intense C=N stretch at 1658 cm^{-1}. The C=N stretch occurs at a considerably higher energy than the corresponding frequency in the ligand $L^{pr}H$ (1632 cm^{-1}) or the salicylaldiminato complex $Zn(L^{pr})_2$ (1626 cm^{-1}). A similar positive shift was obtained for the iminium triflate salt $L^{pr}H_2(O_3SCF_3)$ (1674 cm^{-1}) prepared from *N*-*n*-propylsalicylaldimine and trifluorosulfonic acid. This high energy stretch is a well-established characteristic of the iminium ion [14] and substantiates that the salicylaldimine ligand in $Zn(L^{pr}H)_2Cl_2$ coordinates to zinc in its zwitterion form. Infrared spectra of $Zn(L^{pr}H)_2Cl_2$ obtained in chloroform indicate the retention of the iminium C=N stretch at a slightly lower energy (1651 cm^{-1}) in solution. The electronic spectra of the complex substantiate the solution IR data. In chloroform, the lowest energy electronic absorption of $Zn(L^{pr})_2$ shifts from 369 to 390 nm in $Zn(L^{pr}H)_2Cl_2$. This absorption, assigned to a π to π* transition in *N*-alkylsalicylaldimines, is known to shift to lower energy upon formation of the iminium-phenolate form of the free ligand [37].

The iminium proton can also be observed directly as a broad exchangeable resonance at 13.6 ppm in the ^1H NMR spectrum of $Zn(L^{pr}H)_2Cl_2$ in deuterated chloroform. Previously reported NMR spectra of zinc halide salicylaldimine adducts in dimethylsulfoxide were unstable with respect to the salicylaldiminato complexes [6]. We observe, however, we observed no evidence for this in our experiments. Otherwise, the ^1H NMR spectra of $Zn(L^{pr}H)_2Cl_2$ and $Zn(L^{pr})_2$ are alike, with aromatic and propyl protons of the adduct exhibiting small discernible downfield chemical shifts.

3.4. Rationale for interconversion

The presence of the iminium proton in $Zn(L^{pr}H)_2Cl_2$ helps explain how the interconversion reaction occurs (Eq. (1) and Scheme 2). Loss of the iminium proton from $Zn(L^{pr}H)_2Cl_2$ in the form of HCl or deprotonation in the presence of comparatively weak bases to form the salicylaldiminato complex $Zn(L^{pr})_2$ is a reasonable outcome since the iminium proton is fairly acidic ($pK_a \sim 5$) [38,39]. The zwitterion form of the ligand in the adduct, furthermore, provides an explanation for why many salicylaldiminato complexes can be prepared readily from simple metal salts in the absence of base or with bases [1] which are incapable of deprotonating the salicylaldimine ligand ($pK_a \sim 10$–12) [39,40].

The reverse reaction, the protonation of $Zn(L^{pr})_2$ to $Zn(L^{pr}H)_2Cl_2$, can be considered in a similar fashion. In this reaction, the imine nitrogen of the coordinated salicyclaldiminato ligand in $Zn(L^{pr})_2$ is protonated; predictably, this nitrogen is fairly basic given that it is in resonance with the anionic nitrogen of the keto-eneamido form of the ligand [2]. Following protonation of the nitrogen, heterolytic cleavage of the zinc nitrogen bond and formation of the O···H–N hydrogen bond could occur. Under the conditions used here, addition of HCl to $Zn(L^{pr}H)_2Cl_2$, both protonation of the nitrogen and ligand substitution of chloride for imine could take place. The structure of $Zn(L^{pr}H)_2Cl_2$ (Fig. 1) hints at what the intermediate of the addition reaction might look like since it depicts the N(2)–H(2), Zn–O(2) and



i = 2 NaOH, -2 H_2O, -2NaCl or 2 Et_3N, -2 Et_3NHCl
ii = 2 HCl

Scheme 2.

Zn–Cl(1) moieties in close proximity (taking part in a three center hydrogen bond).

The formation/scission of the Zn–N bond would also affect a geometric reorganization of the complex as the ligand changes from a bidentate to a monodentate coordination mode. Examination of the structures of $Zn(L^{pr}H)_2Cl_2$ in Fig. 1 and the representations shown in Scheme 2 indicate that the zinc atom in $Zn(L^{pr})_2$ would have to move out of the same approximate plane as the ligand atoms. This could be accomplished by the rotation of the acute torsion angles in $Zn(L^{pr})_2$ (Zn–O(1)–C(11)–N(1), 16.2°) to the more obtuse corresponding angles about the C–O bond in the adduct (Zn–O(2)–C(31)–C(32), 131.4° and Zn–O(1)–C1(1)–C(12), 174.2°). Inspection of models of the complexes suggests that these rotations as well as other requisite geometric changes are feasible.

4. Supplementary material

Crystallographic data for $Zn(L^{pr}H)_2Cl_2$ and $Zn(L^{pr})_2$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 167224 and 167225. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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