# Polyhedron 54 (2013) 300-308

Contents lists available at SciVerse ScienceDirect

# Polyhedron

journal homepage: www.elsevier.com/locate/poly

# Molecular structure and spectroscopy of divalent first row transition metals, Mn–Zn, with salicylaldiminate ligands

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#### ARTICLE INFO

Article history: Received 27 December 2012 Accepted 7 February 2013 Available online 16 February 2013

Keywords: Schiff base First row transition metal complexes X-ray crystallography

# ABSTRACT

The synthesis and spectroscopy of divalent first row transition metals bearing two monoanionic salicylaldiminate ligands is reported. The reaction of MnCl<sub>2</sub>, FeCl<sub>2</sub>, CoBr<sub>2</sub>, 1,2-(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)NiCl<sub>2</sub>, and CuCl<sub>2</sub> with 2 equiv. of the alkali metal salt of  $[OC_6H_2^{tB}u_2C(H)=N(C_6H_3Me_2)]^{1-}$  produces the corresponding  $M[OC_6H_2^{tB}u_2C(H)=N(C_6H_3Me_2)]_2$ , M = Mn, Fe, Co, Ni, and Cu. Reaction of ZnEt<sub>2</sub> with 2 equiv. of the protonated ligand affords Zn[OC<sub>6</sub>H<sub>2</sub><sup>tB</sup>u<sub>2</sub>C(H)=N(C<sub>6</sub>H\_3Me\_2)]\_2. The molecular structure of each complex has been analyzed using IR spectroscopy and X-ray crystallography while UV–Vis, CW–EPR, solution magnetic susceptibilities, and DFT calculations were also used to probe their electronic structure.

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#### 1. Introduction

The importance of first row transition metals in the divalent oxidation state for a variety of applications such as enzymatic [1] and polymerization [2] catalysis cannot be overstated. The molecular and electronic structure of transition metal complexes correspond to their chemical properties and reactivity, therefore, examining the coordination chemistry of transition metals provides insight into their current and future applications. The influence of steric and electronic properties to control structure and reactivity continues to be an exciting avenue of interest for main group [3], transition metals [4], and f elements [5]. This has been beautifully illustrated with a simple change of ligand from  $(C_5Me_5)^{1-}$  to  $(C_5Me_4H)^{1-}$  by the Chirik group in the complex  $[(C_5Me_4H)_2Zr]_2(\mu-N_2)$  which was shown to convert dinitrogen to ammonia while this reactivity did not occur with the analogous  $(C_5Me_5)^{1-}$  ligated complex [6].

Similar to cyclopentadienyl, Schiff base ligands are ubiquitously employed in coordination chemistry and used for a variety of applications [7] mainly because of the ease of their preparation as well as their steric and electronic properties can be readily varied [8]. However, while traditional Schiff base ligands take two valence and four coordination sites, we aimed to prepare complexes with more steric influence around the metal center using two ligands that would produce the same valence and coordination, hence one subset of Schiff base ligands, salicylaldiminates, seemed a logical conclusion. Salicylaldiminates [9] are monoanionic, poly-

\* Corresponding author. E-mail address: walenskyj@missouri.edu (J.R. Walensky). dentate ligands and, typically, transition metal complexes with salicylaldiminate ligands have been used for olefin polymerization activity [9a,b–e,10] as well as epoxide and CO<sub>2</sub> copolymerization [9a,11].

Our focus was to create a sterically demanding ligand framework to isolate transition metal complexes from which further reactivity could be pursued. To our surprise, van der Waals interactions between each salicylaldiminate chelate shields the metal center. Herein, we report the synthesis and structural characterization of new *bis*(salicylaldiminate) complexes of middle to late transition metal complexes with the general formula  $M[OC_6H_2^tBu_2C(H)=N(C_6H_3Me_2)]_2$ , where M = Mn, Fe, Co, Ni, Cu, Zn.

#### 2. Experimental section

# 2.1. General considerations

All manipulations were carried out inside an argon atmosphere Vacuum Atmosphere OMNI glove box with rigorous exclusion of air and water unless otherwise specified. Solvents (Aldrich) were purchased anhydrous and stored over molecular sieves. Benzene- $d_6$  (Cambridge Isotopes) was dried over molecular sieves. Anhydrous MnCl<sub>2</sub>, FeCl<sub>2</sub>, 1,2-(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)NiCl<sub>2</sub>, and CuCl<sub>2</sub> (Strem), as well as CoBr<sub>2</sub> and ZnEt<sub>2</sub> (Fisher) were used as received. The protonated ligands, HOC<sub>6</sub>H<sub>2</sub><sup>t</sup>Bu<sub>2</sub>C(H)=N(C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), **1**, and HOC<sub>6</sub>H<sub>2</sub><sup>t-</sup>Bu<sub>2</sub>C(H)=N(C<sub>6</sub>H<sub>3</sub><sup>t</sup>Pr<sub>2</sub>), **2**, were synthesized following their literature procedures [12].





#### 2.2. General synthesis

To a stirred solution of  $HOC_6H_2^tBu_2C(H)=N(C_6H_3Me_2)$ , **1**, (300 mg, 0.89 mmol) in 10 mL THF was added NaH (23 mg, 0.89 mmol) presumably producing the sodium salt, **3**. As the reaction progressed, effervescing was observed. After 30 min, half an equiv of metal halide was added. After 12 h, insoluble material was removed by centrifugation the supernatant decanted and the solvent removed under vacuum.

# 2.2.1. $Mn[OC_6H_2^tBu_2C(H)=N(C_6H_3Me_2)]_2$ , **4**

Orange crystals suitable for X-ray diffraction analysis were grown from a saturated toluene solution at  $-35 \,^{\circ}\text{C}$  (223 mg, 70%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.34 (s, C(CH<sub>3</sub>)<sub>3</sub>,  $v_{1/2} = 11.0$  Hz), 1.41 (s, C(CH<sub>3</sub>)<sub>3</sub>,  $v_{1/2} = 13.3$  Hz), 2.00 (s, CH<sub>3</sub>,  $v_{1/2} = 21.0$  Hz), 2.13 (s, CH<sub>3</sub>,  $v_{1/2} = 16.0$  Hz). IR (KBr):  $v_{\text{N=C}}$  1613 cm<sup>-1</sup>. UV–Vis (THF, 10<sup>-4</sup> M): 338 nm (831 M<sup>-1</sup> cm<sup>-1</sup>), 487 nm (130 M<sup>-1</sup> cm<sup>-1</sup>). *Anal.* Calc. for C<sub>46</sub>H<sub>60</sub>MnN<sub>2</sub>O<sub>2</sub>: C, 75.90; H, 8.31; N, 3.85. Found: C, 75.89; H, 8.67; N, 3.67%.

# 2.2.2. $Fe[OC_6H_2^tBu_2C(H)=N(C_6H_3Me_2)]_2$ , **5**

Red crystals suitable for X-ray diffraction analysis were grown from a saturated toluene solution at 0 °C (210 mg, 69%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.24 (s, C(CH<sub>3</sub>)<sub>3</sub>,  $v_{1/2}$  = 39.8 Hz), 1.34 (s, C(CH<sub>3</sub>)<sub>3</sub>,  $v_{1/2}$  = 75.1 Hz), 3.74 (s, CH<sub>3</sub>,  $v_{1/2}$  = 82.9 Hz). IR (KBr):  $v_{N=C}$  1611 cm<sup>-1</sup>. UV–Vis (THF, 10<sup>-4</sup> M):  $\lambda_{max}$  = 353 nm (1500 M<sup>-1</sup> - cm<sup>-1</sup>), 517 nm (180 M<sup>-1</sup> cm<sup>-1</sup>). Anal. Calc. for C<sub>46</sub>H<sub>60</sub>FeN<sub>2</sub>O<sub>2</sub>: C, 75.81; H, 8.30; N, 3.84. Found: C, 75.93; H, 8.54; N, 3.24%.

#### 2.2.3. $Co[OC_6H_2^tBu_2C(H)=N(C_6H_3Me_2)]_2$ , 6

Red crystals suitable for X-ray diffraction analysis were grown from a saturated toluene solution at 0 °C (205 mg, 67%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.93 (s, C(CH<sub>3</sub>)<sub>3</sub>,  $v_{1/2}$  = 181.1 Hz), 1.32 (s, C(CH<sub>3</sub>)<sub>3</sub>,  $v_{1/2}$  = 141.5 Hz), 3.78 (s, CH<sub>3</sub>,  $v_{1/2}$  = 162.0 Hz). IR (KBr):  $v_{N=C}$  1613 cm<sup>-1</sup>. UV–Vis (THF, 10<sup>-4</sup> M):  $\lambda_{max}$  = 385 nm (2400 M<sup>-1</sup> - cm<sup>-1</sup>), 515 nm (170 M<sup>-1</sup> cm<sup>-1</sup>). *Anal.* Calc. for C<sub>53</sub>H<sub>68</sub>N<sub>2</sub>O<sub>2</sub>Co: C, 77.25; H, 8.32; N, 3.40. Found: C, 76.89; H, 8.29; N, 3.35%.

# 2.2.4. $Ni[OC_6H_2^tBu_2C(H)=N(C_6H_3Me_2)]_2$ , 7

Red crystals suitable for X-ray diffraction analysis were grown from a saturated THF solution at room temperature (162 mg, 49%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.68 (s, C(CH<sub>3</sub>)<sub>3</sub>,  $v_{1/2}$  = 4.5 Hz,), 3.78 (s, CH<sub>3</sub>,  $v_{1/2}$  = 2.0 Hz). IR (KBr):  $v_{N=C}$  stretch 1612 cm<sup>-1</sup>. UV–Vis (THF, 10<sup>-4</sup> M):  $\lambda_{max}$  = 390 nm (1920 M<sup>-1</sup> cm<sup>-1</sup>), 514 nm (200 M<sup>-1</sup> cm<sup>-1</sup>).  $\mu_{eff}$  = 2.25 BM. *Anal.* Calc. for C<sub>54</sub>H<sub>76</sub>N<sub>2</sub>NiO<sub>4</sub>: C, 74.05; H, 8.75; N, 3.20. Found: C, 73.69; H, 8.53; N, 3.05%.

# 2.2.5. $Cu[OC_6H_2^tBu_2C(H)=N(C_6H_3Me_2)]_2$ , 8

Red crystals suitable for X-ray diffraction analysis were grown from a saturated toluene solution at 0 °C (269 mg, 85%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.18 (s, C(CH<sub>3</sub>)<sub>3</sub>),  $v_{1/2}$  = 37.5 Hz), 1.42 (s, C(CH<sub>3</sub>)<sub>3</sub>,  $v_{1/2}$  = 30.3 Hz), 3.58 (s, CH<sub>3</sub>  $v_{1/2}$  = 25.2 Hz). IR (KBr):  $v_{N=C}$  stretch 1615 cm<sup>-1</sup>. UV–Vis (THF, 10<sup>-4</sup> M):  $\lambda_{max}$  = 407 nm (2800 M<sup>-1</sup> - cm<sup>-1</sup>), 535 nm (100 M<sup>-1</sup> cm<sup>-1</sup>).  $\mu_{eff}$  = 1.06 BM. *Anal.* Calc. for C<sub>67</sub>-H<sub>84</sub>N<sub>2</sub>O<sub>2</sub>Cu: C, 79.44; H, 8.36; N, 2.77. Found: C, 78.67; H, 8.24; N, 3.06%.

#### 2.2.6. Synthesis of $Zn[OC_6H_2^tBu_2C(H)=N(C_6H_3Me_2)]_2$ , **9**

ZnEt<sub>2</sub> (0.3 mL, 0.296 mmol) was added to a stirred solution of **1** (300 mg, 0.668 mmol) in 8 mL THF. The color changed immediately from yellow to orange. After 1 h, the volatiles were removed under vacuum to yield an orange microcrystalline solid (310 mg, 94%). Orange crystals suitable for X-ray diffraction analysis were grown from a saturated toluene solution at 0 °C. <sup>1</sup>H NMR: (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.83 (s, imine H, 2H), 7.50–6.72 (m, Ar-H, 10H), 2.46 (s, CH<sub>3</sub>, 6H), 1.81 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H) 1.40 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.18 (s, CH<sub>3</sub>, 6H). <sup>13</sup>C

NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  174.9 (imine C), 170.4 (ArC-O), 148.7 (Ar-C), 142.1 (Ar-C), 135.5 (Ar-C), 131.4 (Ar-C), 131.2 (Ar-C), 131.0 (Ar-C), 130.3 (Ar-C), 129.0 (Ar-C), 128.5 (Ar-C), 117.4 (Ar-C), 35.7 (C(CH<sub>3</sub>)<sub>3</sub>), 33.8 (C(CH<sub>3</sub>)<sub>3</sub>), 31.3 (C(CH<sub>3</sub>)<sub>3</sub>), 29.5 (C(CH<sub>3</sub>)<sub>3</sub>), 18.7 (CH<sub>3</sub>), 17.0 (CH<sub>3</sub>). IR (KBr):  $v_{N=C}$  stretch 1602 cm<sup>-1</sup>. UV–Vis (THF, 10<sup>-4</sup> M):  $\lambda_{max}$  = 401 nm (3200 M<sup>-1</sup> cm<sup>-1</sup>). Anal. Calc. for C<sub>53</sub>H<sub>68</sub>N<sub>2</sub>-O<sub>2</sub>Zn: C, 76.65; H, 8.25; N, 3.85. Found: C, 76.47; H, 8.13; N, 3.27%.

#### 2.2.7. $Cu[OC_6H_2^tBu_2C(H)=N(C_6H_3^iPr_2)]_2$ , **10**

To a stirred solution of  $HOC_6H_2{}^tBu_2C(H)=N(C_6H_3{}^iPr_2)$ , **2**, (300 mg, 0.762 mmol) in 10 mL THF was added NaH (20 mg, 0.83 mmol) presumably producing the sodium salt. As the reaction progressed, effervescing was observed. After 30 min, CuCl<sub>2</sub> (102 mg, 0.759 mmol) was added. After 12 h, insoluble material was removed by centrifugation the supernatant decanted and the solvent removed under vacuum yielding a red powder (504 mg, 79%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.46 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 2.58 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.55 (s, 12H, CH(CH<sub>3</sub>)<sub>2</sub>). UV–Vis (THF, 10<sup>-4</sup> M):  $\lambda_{max} = 346$  nm (2920 M<sup>-1</sup> cm<sup>-1</sup>),  $\lambda_{max} = 394$  nm (2560 M<sup>-1</sup> cm<sup>-1</sup>),  $\lambda_{max} = 548$  nm (140 M<sup>-1</sup> cm<sup>-1</sup>). Anal. Calc. for C<sub>68</sub>H<sub>92</sub>N<sub>2</sub>O<sub>2</sub>Cu: C, 79.06; H, 8.98; N, 2.71. Found: C, 78.94; H, 8.76; N, 2.86%.

#### 2.3. Crystallographic data collection and structure determination

The selected single crystal was mounted on nylon cryoloops using viscous hydrocarbon oil. X-ray data collection was performed at 173(2) K. The X-ray data were collected on a Bruker CCD diffractometer with monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The data collection and processing utilized Bruker APEX2 suite of programs [13]. The structures were solved using direct methods and refined by full-matrix least-squares methods on  $F^2$  using Bruker SHELEX-97 program [14]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were added on idealized positions and not allowed to vary. Thermal ellipsoid plots were prepared by using X-seed [15] with 50% of probability displacements for non-hydrogen atoms. Crystal data and detail for data collection for complexes **4–9** are provided in Table 1, and significant bond distances and angles are gathered in Table 2.

# 2.4. Computational details

Calculations were performed using the B3LYP [16] (Becke-3 exchange [17] and Lee–Yang–Parr correlation [18] functional) in the GAUSSIAN09 suite of software [19]. Geometry optimizations were initiated from the crystal structure coordinates and found to be minima with no imaginary frequencies. The Stuttgart triple- $\zeta$  quality basis set with corresponding effective core potential (ECP) [20] was used for each metal atom while the Pople double- $\zeta$  quality basis set, 6-31G(d') [21], was used for the remaining atoms.

#### 2.5. Physical measurements

Elemental analyses services were provided by Atlantic Microlab, Inc. (Norcross, Georgia) for C, H and N. Infrared spectra were acquired on a Thermo Nicolet Nexus 670 FT-IR spectrophotometer. Samples were run as KBr pellets prepared under argon in the glove box. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on Bruker AMX-300 MHz superconducting NMR spectrometer. Magnetic susceptibilities in  $C_6D_6$  were determined using Evans method [22]. Continuous wave electron paramagnetic resonance (CW-EPR) spectra were acquired using an X-band Bruker ESP-300E spectrometer equipped with an Oxford Instruments ESR-9 helium cryostat, using a modulation frequency was 100 kHz. Spectra were processed and simulated in the Matlab environment (The Mathworks, Natick, NJ) using the easyspin toolbox [23].

#### Table 1

X-ray crystallographic data for complexes 4-10.

	4	5	6	7	8	9	10
CCDC Deposit Number	916087	884459	884457	884460	884458	884461	887691
Empirical formula	C53H68N2O2Mn	C53H68N2O2Fe	C53H68N2O2C0	C52H68N2O3Ni	C <sub>67</sub> H <sub>84</sub> N <sub>2</sub> O <sub>2</sub> Cu	C53H68N2O2Zn	C68H92N2O2Cu
Formula weight (g/ mol)	820.05	820.94	824.02	875.88	1012.90	830.46	1032.98
Crystal habit, color	plate, orange	plate, red	plate, red	block, red	block, red	block, orange	block, red
Temperature (K)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	Pbcn	I2/a	$P2_1/c$	Pca21
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
Volume (Å <sup>3</sup> )	4791.85	4766.8(10)	4756.4(17)	4962.3(9)	5920(2)	4767.4(14)	6111.0(14)
a (Å)	18.135(2)	18.214(2)	18.250(4)	19.550(2)	20.931(6)	18.279(3)	37.623(5)
b (Å)	14.4053(15)	14.3298(17)	14.272(3)	11.8225(12)	12.2908(19)	14.268(2)	13.3634(17)
c (Å)	19.658(2)	19.577(2)	19.551(4)	21.470(2)	23.030(4)	19.587(3)	12.1548(16)
α (°)	90	90	90	90	90	90	90
β (°)	111.0780(10)	111.1090(10)	110.931(2)	90	92.3130(10)	111.054(2)	90
γ(°)	90	90	90	90	90	90	90
Ζ	4	4	4	4	4	4	4
Calculated density (Mg/m <sup>3</sup> )	1.137	1.144	1.151	1.172	1.137	1.157	1.123
Absorption coefficient (mm <sup>-1</sup> )	0.315	0.356	0.401	0.436	0.413	0.555	0.401
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0452,$ $wR_2 = 0.1292$	$R_1 = 0.0396,$ $wR_2 = 0.1039$	$R_1 = 0.0456,$ $wR_2 = 0.1200$	$R_1 = 0.0554,$ $wR_2 = 0.1590$	$R_1 = 0.0676,$ $wR_2 = 0.1914$	$R_1 = 0.0405,$ $wR_2 = 0.1035$	$R_1 = 0.0456,$ $wR_2 = 0.1128$

#### Table 2

Selected bond distances (Å) and angles (°) for complexes 4-10.

Bond distance/angle	<b>4</b> , Mn	<b>5</b> , Fe	<b>6</b> , Co	<b>7</b> , Ni	<b>8</b> , Cu	<b>9</b> , Zn	<b>10</b> , Cu
M-O(1)	1.968(2)	1.907(1)	1.897(1)	1.896(2)	1.902(2)	1.918(1)	1.893(2)
M-O(2)	1.971(1)	1.910(1)	1.898(2)	1.896(2)	1.902(2)	1.914(2)	1.902(2)
M-N(1)	2.115(1)	2.036(1)	1.984(2)	1.970(2)	1.966(2)	1.991(2)	1.974(2)
M-N(2)	2.107(2)	2.030(2)	1.986(1)	1.970(2)	1.966(2)	2.000(1)	1.988(2)
O(1)-M-N(1)	89.54(6)	91.35(5)	94.83(6)	92.65(8)	93.68(8)	95.43(6)	92.92(8)
O(1)-M-N(2)	133.03(6)	129.23(6)	119.85(6)	129.26(8)	145.36(9)	119.54(6)	96.02(9)
O(2)-M-N(1)	121.28(6)	121.93(5)	124.83(7)	129.26(8)	145.36(9)	125.80(7)	94.62(9)
O(2)-M-N(2)	89.11(6)	91.17(5)	94.82(6)	92.65(8)	93.68(8)	95.24(6)	92.81(9)
O(1)-M-O(2)	112.59(6)	112.64(5)	110.41(6)	108.26(8)	90.33(8)	108.35(6)	152.64(8)
N(1)-M-N(2)	114.85(6)	113.78(5)	114.19(6)	109.16(8)	102.05(9)	114.39(6)	144.89(9)

# 3. Results and discussion

# 3.1. Synthesis

The salicylaldimine ligands,  $HOC_6H_2^tBu_2C(H)=N(C_6H_3Me_2)$ , **1**, and  $HOC_6H_2^tBu_2C(H)=N(C_6H_3Me_2)$ , **2**, were synthesized by condensation of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and 2,6-dimethylaniline in refluxing ethanol for 12 h with no addition of formaldehyde as previously reported [12]. Reaction of **1** with NaH generates the sodium salt, **3**. The ionic metathesis reactions

were done *in situ* with the corresponding metal halides to yield the Mn, **4**, Fe, **5**, Co, **6**, Ni, **7**, and Cu, **8**, complexes in good to excellent yields, Eq. (1). In the case of nickel, the insolubility of anhydrous NiCl<sub>2</sub> in THF did not lead to isolation of **7** and only **3** was recovered from this mixture (see Supporting Information). No further characterization was done on **3**. Instead, (dppe)NiCl<sub>2</sub> was used which provided a soluble starting material in THF. The Zn complex, **9**, was made directly from **1** and ZnEt<sub>2</sub>, Eq. (1). Each complex is soluble in THF, CH<sub>3</sub>CN, and arene solvents and only sparingly soluble in aliphatic solvents.



(1)



**Fig. 1.** Molecular structure of **4** with thermal ellipsoids projected at 50% level. Hydrogen atoms and solvent molecule have been omitted for clarity.



**Fig. 2.** Molecular structure of **5** with thermal ellipsoids projected at 50% level. Hydrogen atoms and solvent molecule have been omitted for clarity.

# 3.2. Molecular structure

The solid-state molecular structures of complexes **4–9** were determined using single crystal X-ray diffraction. The solid structures for **4–9** are shown in Figs. 1–6, respectively, and have similar solid state structures. The metal center of each complex is chelated by two salicylaldiminate ligands in a bidentate ( $\kappa^2$ ) fashion. The ligands are coordinated to the metal through nitrogen atoms, N1 and N2, from the imine group and oxygen atoms,



**Fig. 3.** Molecular structure of 6 with thermal ellipsoids projected at 50% level. Hydrogen atoms and solvent molecule have been omitted for clarity.



**Fig. 4.** Molecular structure of **7** with thermal ellipsoids projected at 50% level. Hydrogen atoms and solvent molecule have been omitted for clarity.

O1 and O2, from the phenolate group in such a way that the phenolate oxygen atoms are *cis* to one another; so is the case for the imine nitrogen atoms. Complexes **4**, **5**, **6**, and **9** are isomorphous having nearly identical unit cell parameters with one co-crystallized toluene molecule, while complex **7** co-crystallized with one THF molecule, and **8** with two distorted toluene molecules.

The Mn<sup>2+</sup> derivative, **4**, shows a distorted tetrahedral geometry about the metal center, Fig. 1. With Mn–O bond distances of 1.968(2) and 1.971(1) Å, these are shorter than other Mn<sup>2+</sup> Schiff base complexes which are between 2.110(4) and 2.173(4) Å [24] and have Mn–N dative bonds 2.269(5)–2.380(4) Å while **4** has Mn–N bonds of 2.107(2) and 2.115(1) Å.

Complex **5** crystallizes in a monoclinic crystal system, space group  $P2_1/c$ . While Fe<sup>2+</sup> Schiff base complexes are known [23,24], this appears to be the first monometallic complex with a salicylaldiminate ligand. Complex **5** has a distorted tetrahedral geometry,



**Fig. 5.** Molecular structure of **8** with thermal ellipsoids projected at 50% level. Hydrogen atoms and solvent molecule have been omitted for clarity.



**Fig. 6.** Molecular structure of **9** with thermal ellipsoids projected at 50% level. Hydrogen atoms and solvent molecule have been omitted for clarity.

Fig. 2, with O1–Fe1–O2 of 112.64(5)° and N1–Fe1–N2 of 113.78(5)°. Bond lengths, Fe1–N1 and Fe1–N2 are 2.036(1)Å and 2.030(2)Å, respectively while the Fe1–O1 and Fe1–O2 distances are 1.907(1)Å and 1.910(1)Å, respectively. These bond lengths are slightly shorter than those reported on Fe<sup>2+</sup> complexes with N<sub>4</sub>O dinuclear Schiff base ligands [25,26].

Complex **6**, Fig. 3, crystallizes in monoclinic space group  $P2_1/c$ . The coordination environment of the cobalt ion is best described as distorted tetrahedral with N1–Co1–N2 of 114.19(6)° and O1–Co1–O2 of 110.41(6)°. The bond lengths, Co1–N1 and Co1–N2 are 1.984(2)Å and 1.986(1)Å, respectively. Co1–O1 and Co1–O2 bond distances are 1.897(1)Å and 1.898(2)Å, respectively.

Single crystal analysis of 7 indicates that the Ni<sup>2+</sup> is in a distorted tetrahedral geometry (Fig. 4). Complex 7 crystallizes in orthorhombic space group Pbcn. The two ligands are arranged in a twisted fashion around the metal with O1-Ni1-O1 of 108.26(8)° and N1-Ni1-N1 of 109.16(8)°. The Ni1-O1 and Ni1-N1 bond lengths are 1.896(2) Å and 1.970(2) Å, respectively, are shorter than those reported by Jarjayes, Thomas, and co-workers [9i] by 0.125 Å (Ni-O) and 0.153 Å (Ni-N) for a high spin octahedral nickel complex with two tridentate salicylaldiminate ligands. In addition, the bond distances in 7 are shorter compared to  $Ni[OC_6H_2^tBu_2C(H)=N(CH_2NMe_2)]_2$ , another pseudo-octahedral complex coordinating two tridentate ligands, in which Ni-O bond distances of 2.0185(16) and 2.0252(14) Å and Ni-N bond distances of 1.9958(17) and 2.0043(17) Å were reported [27]. However, when comparing the bond lengths of 1.905(2)° for Ni-O and  $1.924(2)^{\circ}$  for Ni–N in  $[({}^{i}Pr_{2}H_{3}C_{6})N=C(H)C_{6}H_{2}{}^{t}Bu_{2}$ OlNiPh(NHC), NHC = 1.3-diisoprovlimidazole [9i], the bond distances are similar.

Fig. 5 shows complex **8** that crystallizes in monoclinic space group *I*2/*a* and is best described as a distorted square planar as evidenced by the O1–Cu1–O1 bond angle of 90.33(8)° and 102.05(9)° angle for N1–Cu1–N1. The Cu1–O1 and Cu1–N1 bond length of 1.902(2) Å and 1.966(2) Å, respectively, are geometrically similar to a phenolate–pyrazole Cu<sup>2+</sup> complex recently reported [28] with Cu–O and Cu–N bond lengths of 1.9233(14) Å and 1.9092(19) Å, respectively. The shortening of the bond distances in the phenolate-pyrazole Cu<sup>2+</sup> complex is most likely due to intramolecular hydrogen-bonding.

The geometry around  $Zn^{2+}$  metal center is also distorted tetrahedral with N1–Zn1–N2 and O1–Zn1–O2 bond angles of 114.39(6)° and 108.35(6)°, respectively. Single crystal analysis revealed that **9** (Fig. 6) crystallizes in monoclinic space group  $P2_1/c$ . The 2,6-diisopropyl derivative,  $Zn[OC_6H_2^tBu_2C(H)=N(C_6H_3^tPr_2)]_2$ , **11**, has been reported [9d]. Instead of **9** having a pseudo-square planar conformation as observed in **11**, it is distorted tetrahedral like complexes **4–8**, Fig. 7. The 1.914(2) and 1.918(1) Å Zn–O bond distances in **9** are slightly shorter than those in **11** of 1.9413(22) and 1.9373(22) Å. This is also the case of the Zn–N bond distances which are approximately 0.03 Å shorter in **9** than **11**.

Following the tetrahedral versus square planar moieties observed between ligands **1** and **2** with  $Zn^{2+}$ , we presumed that  $Cu^{2+}$ , with a smaller ionic radius, would produce a similar result. The X-ray crystallography analysis of Cu $|OC_6H_2^tBu_2C(H)=N(C_6H_3^{i-1})|$  $Pr_2$ ]<sub>2</sub>, **10**, confirmed the pseudo-square planar conformation, Fig. 8. Comparing 8 and 10, the Cu-N bond distances are similar, elongating slightly in **10**: 1.966(2) Å in **8**, and 1.974(2) and 1.988(2) Å in **10**, while the Cu–O bonds are statistically equivalent: 1.902(2) Å in 8, and 1.893(2) and 1.902(2) Å in 10. The change in orientation between 8 and 10, as well as 9 and 11, is due to the isopropyl group imposing steric demand on the complex and this is relieved with the pseudo square planar conformation. It should also be noted that similar Ni<sup>2+</sup> and Cu<sup>2+</sup> complexes with isopropyl groups [29], but without tert-butyl groups on the phenoxide also showed a distorted square planar orientation around the metal center [30], indicating that the isopropyl substituents may necessitate this conformation.

Based on the crystal structure data the deviation of each complex from an ideal tetrahedral geometry can be calculated using the four-coordinate geometry index,  $\tau_4$  [31]. This index is described by the equation:  $\tau_4 = \frac{360^\circ - (\alpha + \beta)}{141^\circ}$ , where  $\alpha$  and  $\beta$  represent the two largest bond angles observed in the crystal structure. Perfectly tetrahedral complexes afford  $\tau_4$  of 1.00 while square planar will give zero. As shown in Table 3, complexes **4**, **5**, **6**, **7**, and **9** can all be described as pseudo- or distorted tetrahedral while **8** and **10**, the Cu<sup>2+</sup> compounds, are best described as distorted square planar.



Fig. 7. Structural difference between the 2,6-dimethylphenyl, 9, and 2,6-diisopropylphenyl, 11, derivatives is depicted.



**Fig. 8.** Molecular structure of **10** with thermal ellipsoids projected at 50% level. Hydrogen atoms and solvent molecule have been omitted for clarity.

Table 3

Four-coordinate	geometry	index, $\tau_4$	, calculated	for <b>4–10</b> .
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4	5	6	7	8	9	10
$\alpha$ 133.03(6) $\beta$ 121.28(6)	129.23(6) 121.93(5)	124.83(7) 119.85(6)	129.26(8) 129.26(8)	145.36(9) 145.36(9)	125.80(7) 119.54(6)	152.64(9) 144.89(9)
τ <sub>4</sub> 0.75	0.77	0.82	0.72	0.49	0.81	0.44

#### 3.3. Non-covalent interactions

It must be noted in bis(Schiff base) divalent transition metal complexes, the geometry adopted around the metal center is normally square planar with the two 3,5-di-tert-butylphenoxide groups on opposite sides to each other. For example, the 2,6dimethylphenyl derivative has been made without tert-butyl groups and its Cu<sup>2+</sup> and Ni<sup>2+</sup> complexes have a square planar arrangement [30]. In addition, removing the methyl groups and leaving the phenyl off the imine also affords square planar geometries [32]. The reason for these structural inconsistencies are reasoned that in complexes 4-9, the proximity of the phenyl groups stemming from the nitrogen atoms of each ligand may provide stabilization through non-covalent interactions. Indeed, the closest carbon-carbon distances found are 3.583, 3.528, 3.437, 3.403, and 3.577 Å for **4–9**, respectively, and correlate to the ionic radius of the metal ion. These lengths are within the range found in complexes involving  $\pi$ - $\pi$  stacking interactions [33], however closer inspection reveals van der Waals interaction between a methyl proton, H(15B), and the  $\pi$ -system, C(8)–C(13), of the other phenyl ring, Fig. 9, at distances of approximately 2.640 Å. These interactions could stabilize the tetrahedral arrangement in each structure.

# 3.4. Spectroscopy

The IR spectra of complexes **4–9** show a strong and sharp band assigned as the C=N stretch at 1613, 1611, 1613, 1612, 1615 and 1612 cm<sup>-1</sup>, respectively. These are red shifted from the free ligand, which has a stretching frequency of 1625 cm<sup>-1</sup>, demonstrating the weakening of the imine bond with electron density being donated to the metal. The absorptions observed for **4–9** are consistent with the analogous aluminum salicylaldiminate metal complex (1613 cm<sup>-1</sup>) [12].

<sup>1</sup>H NMR spectra obtained in  $C_6D_6$  for complexes **4–8** suggest these complexes are paramagnetic as evidenced by broad <sup>1</sup>H NMR signals, however two resonances were found for each –  $C(CH_3)_3$  group and one for the – $CH_3$  groups. Each singlet is located near the resonances observed for diamagnetic **9** and this is probably due to the distance of the groups from the paramagnetic metal center. For **9**, the <sup>1</sup>H NMR spectrum reveals singlet resonances at 1.81 and 1.40 ppm consistent with – $C(CH_3)_3$ groups. In addition, the resonances at 1.18 and 2.46 ppm can be assigned to – $CH_3$  groups while the singlet observed at 7.83 ppm can be assigned to proton attached to imine carbon. The <sup>13</sup>C NMR spectrum showed resonances at 29.5, 31.3, 33.8, and 35.7 ppm which can be assigned to the – $C(CH_3)_3$  groups. <sup>13</sup>C NMR also revealed a resonance at 174.9 ppm that is characteristic of an imine carbon.

The UV–Vis electronic spectra of complexes **4–9** depicted in Fig. 10 were recorded in THF solution. The electronic spectra show intense UV absorption bands at 338, 353, 385, 390, 407 and 401 nm for complexes **4–9**, respectively. Due to the similarity in absorption bands, especially with respect to the zinc complex, **9**, we attribute these to transitions within the ligand. Another set of transitions were observed between 500 and 540 nm (Fig. 10 inset) with small molar absorptivity and we attribute these to forbidden  $d \rightarrow d$  transitions. However, since the paramagnetic complexes, i.e. **5–8**, are all red in color (**4** is orange), this would suggest that the transitions located in the 500–540 nm region have some ligand character as well.

CW-EPR spectra was obtained for complex **4** in THF at 4 K which showed the typical six-line pattern for a  $S = {}^{5}/{}_{2}$  ground state of tetrahedral Mn<sup>2+</sup>, Fig. 11. Hyperfine splitting was observed with <sup>14</sup>N. CW-EPR spectra were also obtained for the two Cu<sup>2+</sup> complexes, **8** [34] and **10**, Fig. 12, in THF at 77 K. Each spectrum exhibits a characteristic Cu<sup>2+</sup> axial signal for an  $S = {}^{1}/{}_{2}$  ground state. With an isotropic superhyperfine coupling constant,  $A_{||}$ , of 155 *G* and  $g_{||}$  value of 2.24 and 2.25, for **8** and **10**, respectively, this is typical of a distorted square planar geometry [35]. Based on the parameters obtained from the EPR spectra we can calculate the covalency parameter,  $\alpha^{2}$  [36], using the equation:

$$\alpha^2 = -(A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$



Fig. 9. Thermal ellipsoid plot of complex 7 shown at the 50% probability level showing H(15B) interaction with opposing phenyl ring, C(8)-C(13).

Substitution provides  $\alpha^2 = 0.75$  for **8** and 0.77 for **10**. For reference,  $\alpha^2 = 0.50$  suggests complete covalent bonding while 1.0 indicates completely ionic character. Our values are similar to other reported Cu<sup>2+</sup> salicylaldiminate complexes and is consistent with



Fig. 11. X-band EPR spectrum of  ${\bf 4}$  in THF at 4 K is shown. Asteric (\*) indicate spectral features derived solely from  $^{14}N$  hyperfine splittings.

the IR spectra that indicate altered C=N bonding in the metal complexed ligands [9b,36,37]. While **8** shows obvious hyperfine interactions in the  $g_{\perp}$  transition consistent with two inequivalent or *trans*-nitrogen ligands, only a subtle feature is seen in **10** where these nitrogen ligands should be roughly equivalent. However, we cannot rule out that the differences in the hyperfine interaction could also be the result of interactions of the Cu<sup>2+</sup> z-molecular axis with the differing functional groups of each ligand type.

# 3.5. Density functional calculations

One measure of electron density for paramagnetic complexes can be derived from the Mulliken atomic spin densities. This is a more reliable indication of the localization of electron density than Mulliken atomic charges and population analysis since it is basis set independent. The spin density should equate to the total



Fig. 10. UV-Vis spectra of salicylaldimine ligand, 1, and complexes 4-9 are shown.



Fig. 12. X-band EPR spectrum of 8 and 10 in THF at 77 K are shown. Experimental spectrum is in black and simulated spectra in dashed grey. Spectrometer settings: modulation amplitude, 10 G, power was attenuated to 5 mW For 8 and 10 mW for 10.

# Table 4

Mulliken atomic spin densities of the metal, oxygen, and nitrogen atoms in the paramagnetic complexes, **4–8**, are shown.

Mulliken atomic spin density	4	5	6	7	8
Metal	4.793	3.747	2.704	1.636	0.603
O (per atom)	0.0464	0.0868	0.0848	0.0930	0.0977
N (per atom)	0.0013	0.0390	0.0483	0.0765	0.0766
$\langle S^2 \rangle = S(S+1)$	8.7573	6.0264	3.7614	2.0085	0.7543
S	2.5000	2.0053	1.5028	1.0028	0.5021
$S^{2} = S(S + 1)$	0.0464 0.0013 8.7573 2.5000	0.0868 0.0390 6.0264 2.0053	0.0848 0.0483 3.7614 1.5028	0.0930 0.0765 2.0085 1.0028	0.0977 0.0766 0.7543 0.5021

number of unpaired electrons, on the metal center in this case, and should be an integer value. For example, a tetrahedral Fe<sup>2+</sup> complex should have four unpaired electrons and therefore a spin density of 4.000. Shown in Table 4 are spin densities for each of the paramagnetic complexes, 4-8, and Fe<sup>2+</sup> has a spin density of 3.747. As one moves across the series, there is a clear trend of increasing deviation from the integer value, attributed to more electron density being removed from the metal center and donated to the ligand, which is observed in the increase in spin density on the oxygen and nitrogen atoms which should be zero. This is credited to the increasingly electron-rich metal centers donating to the ligand, causing the corresponding increases in ligand atom spin densities. This equates to more covalent bonding from manganese to copper. The amount of Cu-L bonding was estimated using the covalency parameter,  $\alpha^2$ , in the EPR spectrum of **8** and shows a moderate amount of covalent character. We believe this is an accurate representation of the electronic structure of these complexes as no spin contamination was observed since the total spin,  $\langle S^2 \rangle$ , and S values are identical to the anticipated values.

# 4. Summary

We have synthesized and characterized a series of first row transition metal complexes chelated to two monoanionic salicylaldiminate ligands. In particular, we have correlated the molecular structure and spectroscopy of each complex using the four-coordinate index,  $\tau_4$ , and the covalency parameter,  $\alpha^2$ , from the EPR spectrum, as well as observation of hyperfine coupling and lack thereof in the EPR spectrum based on structural differences of the Cu<sup>2+</sup> complexes. Using the ligand with 2,6-dimethylphenyl substituent, **1**, we noticed a structural difference between the previously reported 2,6-diisopropylphenyl, **2**, derivative in which the geometry is tetrahedral in the case of **9**, but square planar in **11**. This was also seen in the Cu<sup>2+</sup> complexes, **8** and **10**. We believe the tetrahedral conformation is stabilized by van der Waals interactions between methyl C–H and  $\pi$ -system of the neighboring phenyl ring. This demonstrates the ability for chelating ligand to adopt unusual binding modes with the assistance of non-covalent interactions.

# Acknowledgments

We gratefully acknowledge financial support from the Nuclear Forensics Education Award Program for startup funds and the University of Missouri College of Arts & Sciences Alumni Association Faculty Incentive Award. A.C.L. thanks the Howard Hughes Fellowship Program at the University of Missouri.

# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.02.011.

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