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Structural and ¹H NMR spectroscopic characterization of bis(*N*-isopropylsalicylaldiminato)iron(II)

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Abstract

Coordinatively unsaturated iron(II) species form reactive organometallic and coordination complexes and are integral to the reactivity of non-heme iron proteins and their synthetic analogues. Iron(II) Schiff base complexes have proven to be easily prepared and useful starting materials for such compounds. Here we report a detailed preparative procedure and the solid-state structure of the iron(II) complex of *N*-isopropylsalicylaldimine ($L^{ipr}H$) based on the compounds first synthesized by Larkworthy (J. Chem. Soc., A (1968) 1048). The title compound is prepared by adding 2 equiv. of salicylaldehyde (salH) to Fe(O₂CCH₃)₂ in KOH–CH₃OH to produce a precursor formulated as Fe(sal)₂ which is reacted subsequently with isopropylamine in THF to form Fe(L^{ipr})₂ in 34% isolated yield. A single crystal X-ray crystallographic study of Fe(L^{ipr})₂ reveals a mononuclear complex with two bidentate salicylaldiminate ligands bound to an iron(II) atom in a tetrahedral coordination geometry. The ¹H NMR spectrum of Fe(L^{ipr})₂ in benzene- d_6 exhibits six paramagnetically shifted ligand resonances ranging from +195 to -31 ppm that are consistent with a mononuclear high spin (S = 2) iron(II) complex in solution. Upon exposure to air, Fe(L^{ipr})₂ forms the oxo-bridged dinuclear iron(III) complex [(L^{ipr})₂Fe]₂O as shown by ¹H NMR spectroscopy. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Iron(II); Zinc(II); Schiff base; X-ray crystal structures; ¹H NMR spectroscopy; Dioxygen reactivity

1. Introduction

The salicylaldimine ligands shown in Scheme 1 are easy to prepare and synthetically versatile and, accordingly, have been popular ligands for the synthesis of transition metal complexes [1-4]. Among metal salicylaldimine compounds, the iron complexes have been prepared extensively to investigate various aspects of their magnetic and spectroscopic properties and wideranging bioinorganic, organometallic, and catalytic chemistry [2,5]. A common approach to prepare these compounds takes advantage of the reactivity of an iron(II) salicylaldimine complex, notably Fe(salen), in concert with the complex being coordinatively unsaturated. By virtue of its ability to be reduced or oxidized as well as to expand its coordination number, Fe(salen) has been employed historically to introduce iron nitrosyl [6], alkyl [7], halide [7], quinone [8], and bridging oxo [9],

sulfido [10], peroxo [11] and imido [12] bonds into iron salicylaldimine compounds. Similarly, widespread recent interest in iron(II) species that possess low coordination numbers has led to unusual coordination or organometallic compounds [13–25]. These compounds frequently exhibit desirable reactions with small molecules, e.g. the activation of dioxygen by non-heme iron(II) proteins and their model complexes [26–28].

Iron complexes of the L^RH and salen ligands shown in Scheme 1 figured early in studies of the magnetic, electronic and Mössbauer properties of iron(II) [5,6,29– 31]. The bis(salicylaldiminato)iron(II) complexes, formulated as Fe(L^R)₂ (R = alkyl or aryl), were first prepared reliably by Larkworthy [6,29]. The compounds were determined to be high spin (S = 2), but their structure was not confirmed. In fact, a four coordinate iron(II) complex of salicylaldimine or a related Schiff base ligand with a N₂O₂ donor set has yet to be characterized by single crystal X-ray crystallography or solution NMR spectroscopy. Herein we describe explicit details of the synthesis of the iron(II) complex of *N*-isopropylsalicylaldimine (L^{*i*pr}H) based on a modifi-

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cation of the general procedure by Larkworthy [29] and show that this complex is a soluble discrete mononuclear complex in the solid state and solution. We also demonstrate that $Fe(L^{ipr})_2$ reacts readily with air to form the corresponding oxo-bridged dinuclear iron(III) complex indicating that it is a useful material for synthetic strategies involving low coordinate iron(II) salicylaldimine compounds.

2. Experimental

2.1. Materials and methods

All reagents were used as received from commercial suppliers. Benzene and tetrahydrofuran were distilled under pre-purified dinitrogen from sodium benzophenone ketyl and stored under dinitrogen. Methanol was dried and distilled over activated molecular sieves under dinitrogen and stored under dinitrogen. The preparation and manipulation of bis(*N*-isopropylsalicylaldiminato)iron(II) was carried out under argon in a glove box and on a vacuum line using standard inert atmosphere methods [32]. Care must be taken to ensure all equipment is fully dried and solvents are de-gassed to successfully prepare bis(*N*-isopropylsalicylaldiminato)iron(II).

Elemental analysis of bis(*N*-isopropylsalicylaldiminato)iron(II) was performed by Desert Analytics (Tuscon, AZ). Elemental analysis of *N*-isopropylsalicylaldimine and bis(*N*-isopropylsalicylaldiminato)zinc(II) were carried out by QTI (Whitehouse, NJ). Infrared spectra were recorded on a Mattson Satellite FTIR. The NMR spectroscopic data were obtained on a Bruker AVANCE 300 spectrometer at 23 °C and are reported as positive shifts upfield of tetramethylsilane. The numbering scheme for the aromatic ring protons for the salicylaldimine anion moiety is given in Fig. 2.

2.2. X-ray crystallography of bis(Nisopropylsalicylaldiminato)iron(II)

Single crystals suitable for X-ray crystallographic studies were obtained by dissolving bis(N-isopropylsalicylaldiminato)iron(II) in tetrahydrofuran under argon in a Schlenk tube and cooling to -20 °C in a freezer for several days. The data collection, solution and refine-

Table 1

Crystal data, data collection, and solution and refinement for $Fe(L^{i pr})_2$

Crystal data	
Empirical formula	$C_{20}H_{24}FeN_2O_2$
Crystal habit, color	plate, orange
Crystal size (mm)	0.35 imes 0.30 imes 0.05
Crystal system	orthorhombic
Space group	Pbca
a (Å)	15.0650(6)
b (Å)	13.2631(6)
c (Å)	19.3374(9)
V (Å ³)	3863.8(3)
Ζ	8
Formula weight	380.26
$D_{\text{calc}} (\text{Mg m}^{-3})$	1.307
Absorption coefficient	0.795
(mm^{-1})	
F(000)	1600
Data collection	
Wavelength (Å)	0.71073
Temperature (K)	173(2)
θ Range for data col-	2.11-25.04
lection (°)	
Index ranges	$-17 \le h \le 17, -15 \le k \le 11, -22 \le l \le 22$
Reflections collected	17845
Independent reflec-	$3395 (R_{int} = 0.0763)$
tions	
Solution and refinement	
Solution and rejinement	direct methods
Pofinament method	full matrix least squares on F^2
Weighting scheme	$\int e^{2}(E^{2}) + (AB)^{2} + (BB)^{1-1}$ where
weighting scheme	$W = [0 (F_0) + (AF) + (BF)]$, where $P = (E^2 + 2E^2)/2$ (0.0001 and
	$r = (r_0 + 2r_c)/3, A = 0.0001, and$
A 1	B = 5.2092
Man/min transmission	0.58808 and 0.5272(
Nax/min transmission	0.38808 and 0.33730
Data/restraints/para-	3395/0/254
Einel D indiana	$\mathbf{P} = 0.0(45 \dots \mathbf{P} = 0.0954)$
Final K indices $(I > 2 - (I))$	$R_1 = 0.0043, WR_2 = 0.0834$
$(I \ge 20 (I)]$ <i>D</i> indices (all date)	B 0.0875 B 0.0014
κ modes (an data) Coordinate of fit or F^2	$\kappa_1 = 0.06/3, W \kappa_2 = 0.0914$
Goodness-oi-iit on F	1.240 0.220 and 0.260
heat and hole (e $^{\Lambda}$ ⁻³)	0.229 and -0.209

ment of bis(*N*-isopropyisalicyl-aldiminato)iron(II) summarized in Table 1 were carried out by routine methods using the SHELXTL suite of programs [33]. The ORTEP diagram and selected bond distances and angles are given in Fig. 1 and Table 2, respectively. Full crystallographic details are available as supplementary material.

A crystal of bis(*N*-isopropylsalicylaldiminato)iron(II) was attached to a glass fiber and mounted on the Siemens SMART CCD platform diffractometer system for a data collection at 173(2) K. An initial set of cell constants was 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. This produced orientation matrices determined from 45 reflections. Final cell constants were calculated from a set of 6495 reflections from the actual



Fig. 1. Molecular structure of $Fe(L^{ipr})_2$ shown with 50% probability level thermal ellipsoids.

Table 2 Selected bond distances (Å) and angles (°) for $Fe(L^{ipr})_2$

Coordination sphere			
Fe(1)-O(2)	1.912(2)	Fe(1) - N(1)	2.040(3)
Fe(1) - O(1)	1.916(2)	Fe(1) - N(2)	2.053(3)
O(1) - Fe(1) - N(1)	93.4 (1)	O(1) - Fe(1) - N(2)	114.3(1)
O(2) - Fe(1) - N(2)	93.0(1)	O(2) - Fe(1) - N(1)	113.3(1)
O(2) - Fe(1) - O(1)	125.8(1)	ϕ^{a}	82.7
N(1)-Fe(1)-N(2)	119.5(1)	θ^{b}	6.1, 6.9
Ligand geometry			
Ligand 1		Ligand 2	
O(1) - C(1)	1.317(4)	O(2)-C(11)	1.312(4)
C(1) - O(1) - Fe(1)	128.5(2)	C(11) - O(2) - Fe(1)	129.4(2)
N(1)-C(7)	1.293(4)	N(2)-C(17)	1.296(4)
N(1)-C(8)	1.486(4)	N(2)-C(18)	1.483(4)
C(7)-N(1)-Fe(1)	122.0(2)	C(17) - N(2) - Fe(1)	122.1(2)
C(7)-N(1)-C(8)	116.4(3)	C(17)-N(2)-C(18)	117.1(3)
C(8) - N(1) - Fe(1)	121.5(2)	C(18) - N(2) - Fe(1)	120.8(2)
C(6) - C(7)	1.444(5)	C(16)-C(17)	1.442(5)
C(8)-C(9)	1.526(5)	C(18)-C(19)	1.520(5)
C(8) - C(10)	1.522(5)	C(18)-C(20)	1.526(5)
C-C(ring) _{avg}	1.396(6)	C-C(ring) _{avg}	1.398(5)
C-C-C(ring) _{avg}	120.0(4)	C-C-C(ring) _{avg}	120.0(4)

^a The dihedral angle between the mean planes formed by the atoms O(1)-Fe(1)-N(1) and O(2)-Fe(1)-N(2).

^b The two dihedral angles between the mean plane formed by carbon atoms of the aromatic ring of ligand 1 (C1–C6) and O(1)–Fe(1)–N(1) and the carbon atoms of ligand 2 (C11–C16) and the mean plane formed by O(2)–Fe(1)–N(2).

data collection. A semi-empirical absorption correction was carried out using the SHELXTL XPREP absorption routine. The space group *Pbca* was determined based on systematic absences and intensity statistics. A successful direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several fullmatrix least-squares/difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual (or group if appropriate) isotropic displacement parameters. A weak intermolecular hydrogen bond was observed between H(15) and O(2) equal to 2.484 Å.

2.3. Preparation of compounds

2.3.1. N-iso-propylsalicyaldimine $(L^{ipr}H)$

This compound was synthesized by a generally accepted method for the preparation of salicylaldimine ligands [2]. A solution of 16.69 g (0.137 mol) of salicylaldehyde in 150 ml of benzene was added to a 250 ml round bottom flask fitted with a Dean-Stark trap and condenser. To this solution, 12 ml (8.3 g, 0.14 mol) of isopropylamine was added slowly with stirring and then refluxed for 1 h. After cooling, the reaction mixture was dried over anhydrous magnesium sulfate and gravity filtered. The filtrate was rotoevaporated and dried under vacuum to yield 16.8 g (75%) of a yellowbrown oil that could be used without further purification. Anal. Calc. for C₁₀H₁₃NO: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.39; H, 7.84; N, 8.44%. FTIR (neat): 3060, 2969, 2869, 1679, 1631(s), 1582, 1499, 1460, 1420, 1385, 1322, 1279, 1210, 1150, 1032, 977, 951, 905, 846, 755, 738, 632 cm⁻¹. ¹H NMR (CDCl₃) δ 13.72 (1H, s, OH), 8.35 (1H, s, N=CH), 7.26 (2H, m, H3, H4), 6.95 (1H, d, H6), 6.86 (1H, t, H5), 3.52 (1H, septet, NCH(CH₃)₂, 1.29 (6H, d, NCH(CH₃)₂) ppm.

2.3.2. Bis(N-isopropylsalicylaldiminato)iron(II) $Fe(L^{ipr})_2$

This synthetic procedure is a modification of the preparation by Larkworthy [29]. A solution of 4.21 g (34.5 mmol) of salicylaldehyde (salH) dissolved in 20 ml of a 0.14 M KOH methanol solution was added to 3.00 g (17.2 mmol) of Fe(O₂CCH₃)₂ (Aldrich) in 100 ml of methanol with stirring. A dark red solid formed. The solvent was decanted after 10 min. The solid product was dried to yield 2.99 g of a red-purple powder of the iron(II) salicylaldehyde compound 'Fe(sal)₂'. To 0.474 g (1.78 mmol) of Fe(sal)₂ dissolved in 50 ml of tetrahydrofuran, 0.378 g (6.40 mmol) of isopropylamine was added under argon. The opaque solution became dark orange and was allowed to stir for 3 h. The solvent was evaporated under vacuum and the crude product was dissolved in 300 ml of pentane. A small amount of product crystallized immediately as orange flakes along with a substantial amount of a red precipitate, a presumed hydrolysis product. The solution, which is extremely sensitive to moisture and dioxygen, was filtered and cooled in a freezer (-20 °C) for 2 days. The crystalline product was filtered and dried under vacuum to yield 0.23 g of orange flakes (34%). The solid product is comparatively stable when exposed briefly to air. Anal. Calc. for C₂₀H₂₄N₂O₂Fe: C, 63.17; H, 6.36; N, 7.37. Found: C, 62.97; H, 6.24; N, 7.24%. FTIR (KBr): 3447 (br), 3050, 2964, 2924, 2889, 1617, 1599 (s), 1537, 1467, 1442, 1402, 1367, 1331, 1315, 1195, 1143, 1122, 1031, 976, 919, 855, 786, 763, 756, 740, 612, 578, 493 cm⁻¹. ¹H NMR (C₆D₆, 300 MHz, 23 °C) δ 195.4 (1H, s, NCH(CH₃)₂), 67.7 (1H, s, H4), 62.0 (1H, s, H6), – 15.9 (1H, s, H5), –21.8 (1H, s, H3), –30.5 (6H, s, NCH(CH₃)₂) ppm.

2.3.3. Bis(N-isopropylsalicylaldiminato)zinc(II) Zn(L^{ipr})₂

To a rapidly stirring suspension of 4.17 g (25.6 mmol) of N-isopropylsalicylaldimine in 15 ml of deionized water, 1.74 g of ZnCl₂ (12.8 mmol) was added slowly. A 10 ml solution of 1.02 g (24.3 mmol) of NaOH dissolved in deionized water was then added slowly to the slightly yellow solution to produce a white solid. The heterogeneous reaction mixture was stirred for an additional 10 min and filtered. The precipitate was washed with deionized water $(3 \times 5 \text{ ml})$ followed by pentane $(3 \times 5 \text{ ml})$ ml) to remove any unreacted ligand. The product was dried under vacuum to yield 4.12 g of a white powder (83%). The product can be recrystallized from acetonewater. Anal. Calc. for C₂₀H₂₄N₂O₂Zn: C, 61.62; H, 6.21; N, 7.19. Found: C, 61.95; H, 6.10; N, 7.00%. FTIR (KBr): 3051, 2966, 2926, 2901, 1616 (s), 1537, 1466, 1445, 1408, 1333, 1316, 1191, 1145, 1123, 1032, 999, 959, 918, 857, 759, 603, 505, 449 cm⁻¹. ¹H NMR (CDCl₃) δ 8.35 (1H, s, N=CH), 7.29 (1H, t, H4), 7.09 (1H, d, H3), 6.85 (1H, d, H6), 6.59 (1H, t, H5), 3.63 (1H, m, NCH(CH₃)₂), 1.33 (3H, d, NCH(CH₃)₂); 1.21 (3H, d, $NCH(CH_3)_2$ [note: the $NCH(CH_3)_2$ methyl groups are diastereotopic] ppm.

3. Results and discussion

3.1. Synthesis

A general method for the reliable synthesis of bis(salicylaldiminato)iron(II) complexes has been described by Larkworthy [6,29]; these compounds had been prepared prior to this study, but because of their acute air sensitivity the complexes frequently yielded impure oxidized products. As indicated by Larkworthy [29], the optimal procedure for the preparation of bis(salicylaldiminato)iron(II) complexes was the formation of a precursor from salicylaldehyde and iron(II) acetate in the presence of a strong base followed by the addition of a primary amine in alcohol solvents [34]. No preparative details, e.g. amounts of material, yields, etc., however, are given in Larkworthy's or subsequent papers [6,12,29-31]. We have re-examined this synthetic method to render a more detailed experimental procedure for the preparation of the N-isopropylsalicylaldimine derivative, $Fe(L^{ipr})_2$.

The reaction of the *N*-isopropylsalicylaldimine with iron(II) acetate in tetrahydrofuran failed to produce pure product as indicated by 1 H NMR spectroscopy.

We find, as previously determined, that the reaction of the primary amine with the pre-formed iron salicylaldehyde complex forms the desired pure product in an acceptable yield. Two equiv. of salicylaldehyde (salH) are deprotonated in a methanol solution of potassium hydroxide and added to 1 equiv. of iron(II) acetate as shown in Scheme 2, Eq. (1). A precipitate forms, presumed to be bis(salicyaldehydato)iron(II) 'Fe(sal)₂', which is dried under vacuum to yield a purple solid.

The ¹H NMR spectrum of Fe(sal)₂ in CD₃CN exhibits four broad markedly shifted resonances for the ligand aromatic ring protons ranging from +45 to -16 ppm. This shift range is expected since iron(II) complexes with phenolate oxygen donors ordinarily display large upfield and downfield shifts [25,35-37]. The shifts are a consequence of the alternating sign of delocalized unpaired electron spin density from partially filled iron(II) d π symmetry orbitals into ligand π orbitals [38-41]. As a result, alternating upfield and downfield ¹H NMR shifts are observed for one proton attached to a ring carbon atom to the next. On this basis and by analogy to the assignments of other iron(II) phenolate complexes, the ¹H NMR resonances of $Fe(sal)_2$ can be assigned to 6H(+44.8), 4H(+35.3), 5H(-10.4) and 3H(-16.0) in accord with the ring proton numbering scheme for salicylaldimine given in Fig. 2.

Early magnetic studies of $Fe(sal)_2$ suggest it is a high spin iron(II) (S = 2) complex [29], otherwise very little is known about this compound. The most closely related crystallographically characterized salicylaldehyde metal complex is the dinuclear manganese(II) compound, $Mn_2(sal)_4(CH_3OH)_2$ [42], in which phenolate oxygen atoms from two of the salicylaldehyde anions bridge the manganese centers. Our ¹H NMR studies suggest that 'Fe(sal)₂' is mononuclear in solution (though perhaps solvated) since only one set of ring proton resonances is observed for what we presume to be terminally coordinated salicylaldehydato ligands.

The condensation of excess isopropylamine with the coordinated aldehyde moiety in the complex 'Fe(sal)₂' in tetrahydrofuran produced a dark orange solution from which orange microcrystalline $Fe(L^{ipr})_2$ could be isolated in 34% yield (Eq. (2)). While solutions of $Fe(L^{ipr})_2$ are very susceptible to decomposition in air, the solid compound could be handled briefly in air. The com-







Fig. 2. The ¹H NMR spectrum of Fe(L^{ipr})₂ in benzene- d_6 at 23 °C. Chemical shift (δ) in ppm downfield of tetramethylsilane. The schematic indicates the proton assignments (inset). The symbol (\times) indicates solvent or residual solvent impurity.

pound is very soluble in non-polar solvents. The solubility behavior is in marked contrast to its closest analogue, Fe(salen), which requires donor solvents to dissolve due to its assumed polymeric structure [35,43].

For comparative purposes the $Zn(L^{ipr})_2$ analog, a discrete mononuclear tetrahedral complex [45-47], was also prepared. This straightforward synthesis employed ZnCl₂, N-isopropylsalicylaldimine and sodium hydroxide, a general preparative method for zinc(II) Nalkylsalicylaldimines that generally gives good yields in our hands [44]. Both compounds, $M(L^{irp})_2$ (M = Fe, Zn) have very similar solubility characteristics and solidstate infrared spectra, indicative of an analogous structure. The most intense infrared stretch, assigned typically to the imine C=N bond, is found at 1599 (Fe) and 1616 (Zn) cm^{-1} . The value for the energy of the stretch in the iron complex is in excellent agreement with the C=N stretch (1603 cm⁻¹) reported for the tetrahedral iron(II) complex of the nitrogen analogue t- $BuN = C(H)C_6H_4NH^-$ of the salicylaldiminate ligand [18].

3.2. Structure determination by X-ray crystallography

The structure of $Fe(L^{ipr})_2$ shown in Fig. 1 displays a four coordinate iron atom coordinated to two bidentate *N*-isopropylsalicylaldimine anions. The bond distances and angles provided in Table 2 reveal relatively short Fe–O (1.912(2), 1.916(2) Å) and Fe–N (2.040(3), 2.053(3) Å) bond distances and a distorted tetrahedral coordination geometry most likely due to the acute O– Fe–N bite angles (93.4(1)°, 93.0(1)°). Metrical parameters of the ligand, also given in Table 2, indicate that the ligand is coordinated to iron in its characteristic phenolate-imine form [2]. Overall ligand geometry is very similar to generally accepted norms for salicylaldimine ligands in this coordination mode [1,2].

Though no four coordinate iron(II) salicylaldimine complex has been structurally characterized previously, the structure of $Fe(L^{i pr})_2$ and the Zn analog [46,47] are most comparable while those of the other first row d block analogs Co. Ni. and Cu deviate somewhat more significantly [48]. No simple trend is obvious and their differences are likely due to the both the nature of the metal-ligand bonding, the electronic structure of the metal atoms and the structural requirements of the ligand. The average Zn-O (1.913 Å) and Fe-O (1.914 Å) bond lengths are indistinguishable compared with the Co-O (1.905 Å), Ni-O (1.896 Å) and Cu-O (1.805 Å) bond distances. The Zn-N (2.009 Å) bond distance is only slightly shorter than the corresponding Fe-N (2.047 Å) distance while those of Co (1.992 Å). Ni (1.970 Å), and Cu (1.979 Å) are considerably shorter. The average ligand bite angles (O-M-N) for Fe (93.2°), Co (96.4°), Ni (94.4°), Cu (94.9°) and Zn (96.7°) are largely invariant due to the constraints of the ligand. Likewise, the corresponding interligand angles (N-M-O_{avg}, N-M-N, O-M-O) of the Fe complex (113.8°, 119.5°, 125.8°), Co (112.3°, 122.6°, 118.5°), Ni (112.4°, 120.9°, 125.1°), and Zn complex (112.6°, 117.2°, 122.9°) diverge only slightly, while the Cu angles $(100.3^{\circ}, 137.9^{\circ},$ 137.2°) are markedly different because of its very large distortion from tetrahedral geometry. Overall tetrahedral geometry as determined by the dihedral angle, ϕ , between the planes formed by the metal atom and corresponding ligand donor atoms, e.g. N(1)-Fe(1)-O(1), as well as a measure of the deviation of these atoms from the plane formed by ligand aromatic ring (dihedral angle θ), are most similar for the Fe ($\phi =$ 82.7°, $\theta_{avg} = 6.5^{\circ}$) and Zn ($\phi = 84.2^{\circ}$, $\theta_{avg} = 3.9^{\circ}$) complexes, whereas Co, Ni ($\phi = 94^{\circ}$), and Cu ($\phi = 60^{\circ}$) are, again, less comparable.

The most closely related structurally characterized tetrahedral iron(II) complex is that of the salicylaldi-

mine nitrogen analogue, t-BuN=C(H)C₆H₄NH⁻ [18]. The average iron imine nitrogen distance of 2.061 Å in this complex is nearly equivalent to the corresponding distance in Fe(L^{*i*pr})₂. The remaining structural parameters of its coordination sphere, while not as similar to Fe(L^{*i*pr})₂ as Zn(L^{*i*pr})₂, are characteristic of a bidentate monoanionic ligand bound to iron(II) in a tetrahedral coordination geometry. Other similar iron nitrogen imine distances include those of tetrahedral amidinato FeCl₂ adducts (2.100 Å) [24] and the tropocoronand N4 macrocycle (2.020 Å) [16].

An obvious comparison, that of Fe–O bond distances of low coordinate mononuclear complexes (ranging from three to five) with terminal phenolate ligands is more problematic. The number of these complexes is limited and typically have shorter Fe–O bond distances than observed in Fe(L^{*i*pr})₂, for example, the three coordinate homoleptic phenoxide [Fe{O(2,4,6-*t*-BuC₆H₂)}₂]₂ (1.822 Å) [25], four coordinate trispyrazolylborate phenoxide HB{(3,5-*i*pr)pz}₃Fe(OC₆F₅) (1.876 Å) [49], and a five coordinate iron calixarene adduct of THF (1.895 Å) [17].

One can examine the iron ligand bond distances of the four coordinate $Fe(L^{irp})_2$ complex reported here and corresponding examples of five and six coordinate neutral high spin iron(II) salicylaldimine complexes, i.e. 'salen type' ligands with additional donors, N,N'-(3.3'-dipropylmethylamine)bis-(salicylideneimine) (a pentadentate ligand that incorporates one amine donor) [50] and 1,10-bis(5-nitrosalicylaldehyde)-1,4,7,10-tetraazadecane (a hexadentate ligand with two supplementary amines) [51]. The average iron donor bond distances (Fe-N, Fe-O) in this series from coordination number six to four are (2.127, 2.093), (2.045, 2.041), (1.953, 1.914) Å, respectively. Neglecting the differences between the ligands, the change in iron(II)-donor bond distance follows the predictable trend of decreasing bond length with decreasing coordination number.

Early studies of bis(salicylaldiminato)iron(II) or related complexes, which included electronic and Mössbauer spectroscopic measurements as well as magnetic measurements, suggested that the compound was either polymeric or monomeric with a coordination number ranging from four to six [6,29-31,52]. These conclusions are reasonable given the tendency for coordinatively unsaturated Schiff base complexes to add donors as well as undergo bridging with the oxygen atom donor portion of the ligand. For example, Fe(salen) is presumably a polymer in the solid state, but readily coordinates to good donor solvents to form soluble species or exogenous anionic ligands to form five coordinate mononuclear species in solution [35]. Likewise, a more soluble Fe(salen) analogue, Fe(acen), is dinuclear in the solid state and mononuclear in benzene [43]. Here, in contrast, we have shown that $Fe(L^{i pr})_2$ is mononuclear and tetrahedral in the solid state.

3.3. Characterization by ¹H NMR spectroscopy

The ¹H NMR spectrum of $Fe(L^{ipr})_2$ shown in Fig. 2 exhibits broad ligand resonances that experience large upfield and downfield shifts ranging from +195 to -31ppm resulting from the paramagnetism of the complex [29]. The observed peaks and their assignment are given in Table 3. The shifts and linewidths of the peaks at 67.7, 62.0, -15.9 and -21.8 ppm in Fig. 2 are similar to those observed previously for high spin iron(II) complexes $[Fe(salen)X]^-$ (X = anion) [35] and are assigned accordingly to the aromatic ring protons H4, H6, H5, and H3. The observation of one set of ligand resonances for the ring protons in $Fe(L^{ipr})_2$ suggests that, like Fe(sal)₂, there is a single static ligand environment consistent with a mononuclear complex (however, we cannot exclude that a rapidly averaged environment is present in either complex).

The large peak observed at -30.5 ppm in Fig. 2 is assigned to the isopropyl methyl protons based on its 6:1 relative intensity compared with each of the aromatic ring protons. The methyl protons, which are diastereotopic in our ¹H NMR spectrum of $Zn(L^{ipr})_2$ [45,53] (see Scheme 3), are either not resolved in the spectrum of Fe($L^{ipr})_2$ or its chirality is lost due ligand exchange or inversion through a square planar intermediate [54]. The anomalously large linewidth (700 Hz) may indicate the former explanation.

The remaining resonance at 195.4 ppm is assigned tentatively to the tertiary hydrogen of the isopropyl group. Hydrogen atoms attached to carbon atoms adjacent to tertiary amines bound to iron(II) have been observed to experience shifts greater than 100 ppm, i.e. in $[FeM(BPMP)(L)_2]^+$ (M = Fe, Zn, Ga, BPMP = 2,6-bis[[bis(2-pyridylmethylamino]methyl]-4methylphenol anion; $L = O_2 CR^-$ or $O_2 P(OR)_2^-$ [37] and (TMEDA)Fe(CH₂Ph)₂ (TMEDA = N, N, N', N'-tetramethyl-ethylenediamine) [23]. The imine hydrogen, HC=N, resonance has not been reported previously in ¹H NMR studies of iron(II) Schiff base compounds [35,36], so its absence is predictable. Since the proton of interest is two bonds away from the iron atom in the delocalized, conjugated imine moiety of the salicylaldiminate ligand, a large proportion of electron spin density would presumably broaden this resonance beyond detection.

The observation that the linewidths (in Hz) of the ring protons H3(254), H6(200), H4(125) and H5(55) for Fe($L^{i pr}$)₂ become progressively smaller the farther the proton is from the iron center, i.e. H3(4.5 Å), H6(5.3 Å), H4(6.3 Å) and H5(6.6 Å), is consistent with their assignment. The nature of the shifts of the isopropyl protons is more difficult to discern. The fact that the proton attached to the tertiary carbon apparently shifts upfield while the methyl group attached to the same carbon shifts downfield implies a contact spin delocali-

Assignment ^a	Chemical shift ^b (δ_{obs} , ppm)	Linewidth ^c (Hz)	Integration (number of H's)	Isotropic shift ^d (δ , ppm)
Н3	-21.8	254	1	-28.9
H4	67.7	125	1	60.4
H5	-15.9	55	1	-22.5
H6	62.0	200	1	55.2
$CH(CH_3)_2$	195.4 ^e	400	1	191.8
$CH(CH_3)_2$	-30.5	700	6	-31.8

Table 3 Tabulated ¹H NMR spectral data of $Fe(L^{ipr})_2$

Concentrated sample in C₆D₆ at 23 °C at 300 MHz.

^a Ligand schematic is shown in Fig. 2.

^b Chemical shift positive upfield of tetramethylsilane.

^c Measured at half-height.

^d $(\Delta v/v_0)^{iso} = \delta_{\rm Fe} - \delta_{\rm Zn}.$

^e Tentative assignment.



Scheme 3.

zation mechanism similar to the shifts observed for methylene protons adjacent to a coordinated tertiary amine in $[Fe_2(BPMP)(O_2P(OPh)_2)_2]^+$ [37]. Since tetrahedral iron(II) has an anisotropic ground state (⁵E), it generally experiences a significant dipolar contribution to the isotropic shift which depends on the relative orientation and distance of proton to the iron atom [39– 41]. The isopropyl group protons in $Fe(L^{ipr})_2$ are likely to be very susceptible to dipolar interactions since they can experience close contacts with the iron atom (as close as 2.8 Å estimated from the X-ray structure and model building) as the isopropyl group rotates freely.

3.4. Reactivity

When a solution of $Fe(L^{ipr})_2$ in benzene- d_6 is exposed briefly to air (< 1 min), the ¹H NMR resonances due to the iron(II) complex disappear and less shifted resonances ranging from 28.8 to 1.2 ppm are observed in the spectrum accompanied by peaks due to a small amount of free ligand (< 10% by integration). The five broad resonances are consistent with the formation of the oxobridged dinuclear iron(III) species [Fe(L^{ipr})₂]₂O from $Fe(L^{ipr})_2$ and air (Eq. (3)). The observed ¹H NMR shifts found at 28.8 (very broad), 13.1, 10.1, 2.3 (overlapping), and 1.2 ppm in an approximate 1:1:1:6:1 ratio can be assigned to the (CH₃)₂CH, 4H, 6H, 5H and (CH₃)₂CH (overlapping) and 3H protons, respectively, based on comparison with published spectra of $[Fe(L^R)_2]_2O$ [55] and Fe(salen)₂O [38,56] and their integration. A near identical spectrum was

$$2Fe(L^{ipr})_{2} \underset{C_{6}D_{6}}{\overset{\text{air}}{=}} [Fe(L^{ipr})_{2}]_{2}O$$
(3)

obtained from [Fe(L^{ipr})₂]₂O prepared independently by the literature method [57]. The small exclusively upfield shifts are characteristic of oxo-bridged diiron(III) complexes with strong antiferromagnetic coupling (J > 100)cm⁻¹) between high-spin (S = 5/2) iron(III) centers mediated by an oxo bridge [38]. Since high spin iron(III) has a symmetrical electronic environment $({}^{6}A_{1g})$, the shifts are primarily contact in origin and, therefore, proportional to the magnetic susceptibility of the complex [39-41]. The relatively small magnetic moment $(\sim 1.9 \text{ BM})$ of $[\text{Fe}(L^{R})_{2}]_{2}O$ complexes [55] results in a marked attenuation of their isotropic shift compared with $Fe(L^{ipr})_2$. With the exception of a small amount of ligand, due possibly to ligand dissociation or protonolysis, the reaction did not result in an observable precipitate or any other apparent iron species as monitored by ¹H NMR.

Oxo-bridged diiron(III) species have been observed previously from the reaction of air or dioxygen with mononuclear iron(II) porphyrin [58,59], salen [9], or acen [43] complexes. In contrast to Fe(salen), the reaction with $Fe(L^{ipr})_2$ can be carried out in non-polar, non-coordinating solvents in which both $Fe(L^{ipr})_2$ and $[Fe(L^{ipr})_2]_2O$ are soluble and where $Fe(L^{ipr})_2$ is, plausibly, a discrete mononuclear species. As emphasized previously for Fe(acen) [43], these attributes are essential for studying the reactions of low coordinate iron(II) compounds. A case in point is the reaction of iron(II) porphyrins and dioxygen in toluene to detect the diiron(III) peroxo intermediate by ¹H NMR at low temperature [59].

In addition, tetradentate ligands like acen, salen or porphyrins enforce typically a square planar geometry about the iron center. While this allows for an often critical available coordination site, it may be of interest to probe iron(II) reactions with ligands such as $L^{ipr}H$ that allow access to coordination geometries other than those based on square planar, e.g. as observed in the active sites of iron(II) centers in non-heme iron proteins [28].

4. Supporting information

Full crystallographic information for $Fe(L^{ipr})_2$ is available as deposit number 168259 from the Cambridge Crystallographic Database Center (12 Union Road, Cambridge, CB2 1EZ, UK or on the web at www: http://www.ccdc.cam.ac.uk).

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