

# Synthesis and Spectroscopic Characterization of New $[\text{Cu}(\text{}^t\text{Bu}\text{salpphen})]_2$ , $[\text{MoCl}_2(\text{salpphen})]_2$ Complexes and $\text{Sn}_2\text{Cl}_8(\text{}^t\text{Bu}\text{salpphen}).2\text{HNEt}_3$ Adduct

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Tetradentate Schiff base ligands, which were derived from the condensation of phenylenediamine with salicylaldehyde [salpphenH<sub>2</sub>: N, N'-*p*-phenylene-bis(salicyclideneimine)] or 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde [ ${}^t\text{Bu}\text{salpphenH}_2$ : N, N'-*p*-phenylene-bis(3,5-di-*tert*-butylsalicylidene)] and their complexes of Cu(II), Mo(IV) and adduct of Sn(IV) were synthesized and characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and IR spectroscopic methods, mp, elemental analysis, and magnetic susceptibility. According to these data probable structures were assigned to these complexes and adduct. These are of the formula  $[\text{Cu}(\text{}^t\text{Bu}\text{salpphen})]_2$  and  $[\text{MoCl}_2(\text{salpphen})]_2$ , and  $\text{Sn}_2\text{Cl}_8(\text{}^t\text{Bu}\text{salpphen}).2\text{HNEt}_3$ .  $[\text{Cu}(\text{}^t\text{Bu}\text{salpphen})]_2$  was prepared by the reaction of the metal salt with the  ${}^t\text{Bu}\text{salpphenH}_2$  Schiff base ligand in EtOH.  $[\text{MoCl}_2(\text{salpphen})]_2$  was synthesized by reactions of  $[\text{MoCl}_4(\text{CH}_3\text{CN})_2]$  with the salpphenH<sub>2</sub> Schiff base ligand in THF. The Schiff base adduct  $\text{Sn}_2\text{Cl}_8(\text{}^t\text{Bu}\text{salpphen}).2\text{HNEt}_3$  was synthesized by the reaction of SnCl<sub>4</sub> with the  ${}^t\text{Bu}\text{SalpphenH}_2$  Schiff base ligand in the presence of NEt<sub>3</sub> in toluene.

**Key Words:** Copper(II) complex, molybdenum(IV) complex, Schiff base complexes, tin(IV) adduct, tetradentate Schiff base ligands.

## Introduction

Salen-type complexes have been known since 1933 and are now the most important stereochemical models in main group and transition metal coordination chemistry.<sup>1-4</sup> Metal complexes of salen derivatives have become increasingly valuable as reagents and catalysts of many reactions, including electrochemical reduction, hydroxylation, and Diels-Alder transformations.<sup>5-8</sup> More recent applications include use as metal containing liquid-crystalline polymers, as antiviral agents, and as key intermediates in vitamin B<sub>12</sub> enzymatic

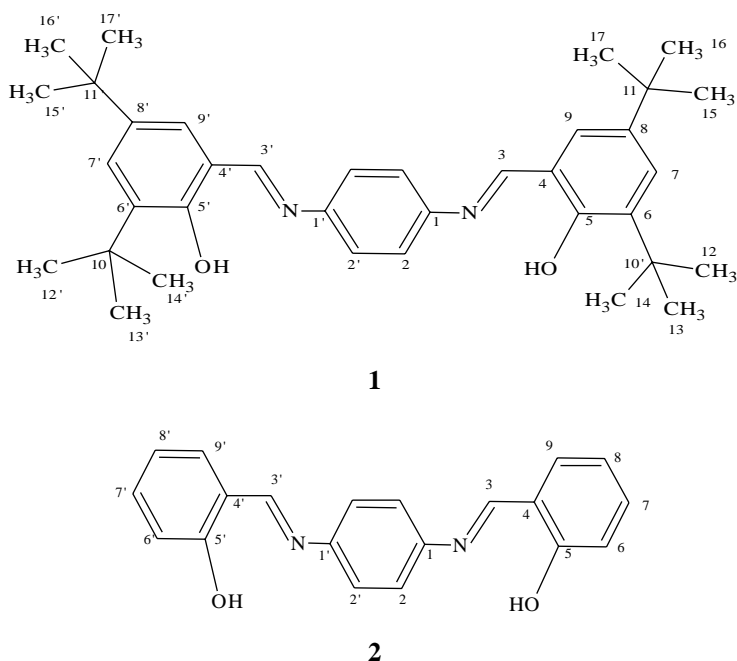
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reactions.<sup>3,9,10</sup> Moreover, Schiff base metal complexes provide a new and interesting environment for M-C functionalities.<sup>11–14</sup> In metal complexes of salen derivatives, the environment at the coordination center can be modified by attaching different substituents to the ligand, which provides a useful range of steric and electronic properties essential for the fine-tuning of structure and reactivity. The ligands feature 2 covalent and 2 coordinate covalent sites situated in a planar array. This makes the ligands ideal for the equatorial coordination of transition metals, leaving the 2 axial sites open for ancillary ligands. By incorporating additional groups around the phenol portion of the ligand, such as *tert*-butyl, the ligands can be made highly soluble in common organic solvents.<sup>3</sup> Incorporation of hydrophilic groups may also lead to ligands that are soluble in water and alcohols. This form of salen-type ligands has been used to great effect in Mn derivatives for enantioselective olefin epoxidation.<sup>15,16</sup>

In our previous work, we described the synthesis of a series of Cu(II), Cd(II), Co(II), and Sn(IV) with sal-*p*-pdaH<sub>2</sub> (N, N'-*p*-phenylene-bis(salicylideneimine)) Schiff base complexes, which did not contain *tert*-butyl groups. These complexes are insoluble in common organic solvents, except Sn(IV).<sup>17</sup> In this paper, we report the synthesis and characterization of salen-type metal complexes, Mo(IV) with N, N'-*p*-phenylene-bis(salicylideneimine), Cu(II) complex, and Sn(IV) adduct with N, N'-*p*-phenylene-bis(3,5-di-*tert*-butylsalicylidene).

The ligands used in this study are of the type shown in Figure 1.



**Figure 1.** Structure of <sup>*t*Bu</sup>SalpphenH<sub>2</sub> **1** and SalpphenH<sub>2</sub> **2**.

## Experimental

All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. All solvents were rigorously dried prior to use. MoCl<sub>5</sub>, SnCl<sub>4</sub>, Cu(OAc)<sub>2</sub>·2H<sub>2</sub>O, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, salicylaldehyde, *p*-phenylenediamine, and NEt<sub>3</sub> were purchased from Merck and used without further purification. [MoCl<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>] was prepared from the reaction of molybdenum pentachloride with acetonitrile,

according to the published procedure.<sup>18</sup> IR data were recorded as KBr pellets on a Perkin Elmer Spectrum BX FT-IR System and are reported in  $\text{cm}^{-1}$ . Mass spectra of **1**, **4** and **5** were recorded with a NERMAG R 10-10 mass spectrometer. Elemental analyses were performed on a Leco CHNS 932 elemental analyzer at the Microanalysis Laboratory of TÜBİTAK (The Scientific and Technological Research Council of Turkey).  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  were recorded on a Varian ASW-400 spectrometer. Magnetic susceptibility measurements were obtained using a Sherwood Scientific magnetic susceptibility balance.

### Synthesis of $^t\text{Bu}$ salpphenH<sub>2</sub> **1**

The  $^t\text{Bu}$ SalpphenH<sub>2</sub> Schiff base ligand was prepared by the condensation reaction of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.66 g, 2.8 mmol) with p-phenylenediamine (0.151 g, 1.4 mmol) in a 2:1 ratio in ethanol (20 mL). The mixture was refluxed for 3 h. The orange precipitate was filtered and dried under vacuum.<sup>19,20</sup> Orange product, yield 64% (0.48 g, 0.8 mmol), mp 292 °C, Anal. Calcd (%) for C<sub>36</sub>H<sub>48</sub>N<sub>2</sub>O<sub>2</sub> (540): C, 80.18; H, 8.91; N, 5.23. Found: C, 79.95; H, 8.94; N, 5.10. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2956\text{s}$ ,  $2870\text{s}$ ,  $1612\text{vs}$ , and  $1171\text{vs}$ , FAB MS (DMSO):  $m/z$  540 (C<sub>36</sub>H<sub>46</sub>O<sub>2</sub>N<sub>2</sub>, 100), 525 ([C<sub>36</sub>H<sub>46</sub>ON<sub>2</sub>]<sup>+</sup>, 92.686), 509 ([C<sub>36</sub>H<sub>46</sub>N<sub>2</sub>]<sup>+</sup>, 29.729).

### Synthesis of salpphenH<sub>2</sub> **2**

To a solution of p-phenylenediamine (1.35 g, 0.125 mmol) in absolute ethanol (25 mL) was added salicylaldehyde (3.05 g, 0.125 mmol) and the mixture was refluxed for 2 h. After ethanol was evaporated, the crude product was purified by recrystallization from toluene.<sup>17,20,21</sup> Orange product, mp 216 °C, yield 83% (3.25 g, 0.1028 mmol), Anal. Calcd (%) for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> (316): C, 76.13; H, 5.06; N, 8.42. Found: C, 75.94; H, 5.06; N, 8.86. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3050\text{w}$ ,  $2900\text{w}$ ,  $1608\text{vs}$ , and  $1279\text{s}$ .

### Synthesis of Sn<sub>2</sub>Cl<sub>8</sub>( $^t\text{Bu}$ salpphen).2HNEt<sub>3</sub> adduct **3**

To a stirring solution of  $^t\text{Bu}$ salpphenH<sub>2</sub> (0.25 g, 0.46 mmol) in toluene (20 mL) was added NEt<sub>3</sub> (0.13 mL, 0.93 mmol). This was allowed to stir for 30 min and SnCl<sub>4</sub> (0.055 mL, 0.46 mmol) was then added. The resulting mixture was refluxed for 12 h. The yellow precipitate was filtered and washed with hexane. The compound was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane. Yellow product, yield 43% (0.14 g, 0.11 mmol), mp 243 °C. Anal. Calcd (%) for Sn<sub>2</sub>Cl<sub>8</sub>C<sub>48</sub>H<sub>78</sub>O<sub>2</sub>N<sub>4</sub> (1262): C, 44.93; H, 6.16; N, 4.43. Found: C, 45.6; H, 6.02; N, 4.44. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2959\text{s}$ ,  $2840\text{s}$ ,  $1608\text{s}$ ,  $1177\text{s}$ , and  $534\text{w}$ .

### Synthesis of [Cu $^t\text{Bu}$ salpphen]<sub>2</sub> complex **4**

To a stirred solution of the  $^t\text{Bu}$ salpphenH<sub>2</sub> Schiff base ligand (0.54 g, 1 mmol) in ethanol (5 mL), a solution of Cu(OAc)<sub>2</sub>.2H<sub>2</sub>O (0.25 g, 1 mmol) in 5 mL of ethanol was added. The brown precipitate was filtered and washed with ethanol and dried under vacuum. Brown product, yield 83% (0.49 g, 0.83 mmol), mp > 300 °C. Anal. Calcd (%) for Cu<sub>2</sub>C<sub>72</sub>H<sub>92</sub>O<sub>4</sub>N<sub>4</sub> (1204.634): C, 69.77; H, 7.80; N, 4.57. Found: C, 71.70; H, 7.69; N, 4.65,  $\mu_{\text{eff.}} = 2.03\mu_B$  at 300 K, IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2958\text{s}$ ,  $2869\text{s}$ ,  $1591\text{vs}$ ,  $1168\text{s}$ ,  $529\text{w}$ .

The reactions of metal salts (Cu(OAc)<sub>2</sub>·2H<sub>2</sub>O, Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O, MnCl<sub>2</sub>·H<sub>2</sub>O, Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O, NiCl<sub>2</sub>·H<sub>2</sub>O, Co(OAc)<sub>2</sub>·2H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O, Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O), and [MoCl<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>] with <sup>t</sup>Bu<sub>3</sub>salpphenH<sub>2</sub> were carried out, but all trials, except Cu(II), failed.

### Synthesis of [MoCl<sub>2</sub>(salpphen)]<sub>2</sub> complex **5**

Tributylamine (0.19 mL, 0.79 mmol) was added to the orange solution of salpphenH<sub>2</sub> (0.113 g, 0.36 mmol) in THF (10 mL). The complex [MoCl<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (0.115 g, 0.36 mmol) was then added. The resulting green-black suspension was refluxed for a day. The black product was filtered and washed with THF and CH<sub>2</sub>Cl<sub>2</sub>, and then dried in a vacuum. Black product, yield 62% (0.12 g, 0.24 mmol), mp > 400 °C. Anal. Calcd (%) for Mo<sub>2</sub>Cl<sub>4</sub>C<sub>40</sub>H<sub>28</sub>O<sub>4</sub>N<sub>4</sub> (962): C, 51.93; H, 4.07; N, 4.75. Found: C, 52.10; H, 4.01; N, 5.06,  $\mu_{eff.} = 2.22\mu_B$  at 300 K, IR (KBr, cm<sup>-1</sup>):  $\nu = 3048w, 2862w, 1595s, 1278m, 924w, \text{ and } 866w.$

## Results and Discussion

The reaction of SnCl<sub>4</sub> with <sup>t</sup>Bu<sub>3</sub>salpphenH<sub>2</sub> **1** (Figure 1) in the presence of NEt<sub>3</sub> resulted in the formation of Sn<sub>2</sub>Cl<sub>8</sub>(<sup>t</sup>Bu<sub>3</sub>salpphen).2HNEt<sub>3</sub> adduct **3**. Sn(IV) adduct is air-stable and soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, THF, and acetone, and insoluble in hexane and Et<sub>2</sub>O solvents. Sn<sub>2</sub>Cl<sub>8</sub>(<sup>t</sup>Bu<sub>3</sub>salpphen).2HNEt<sub>3</sub> **3** contains dimeric tin centers surrounded by 4 chlorine atoms and the coordination around the tin is octahedral. The Schiff base is coordinated to the Sn atom from O and N atoms. The Et<sub>3</sub>NH<sup>+</sup> cation is hydrogen-bonded to the coordinated phenolate oxygen.

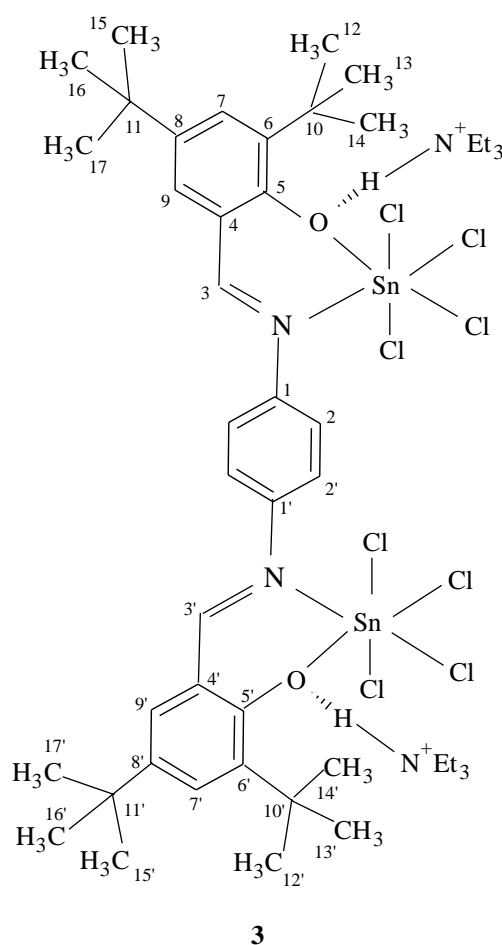
The bands in the region 2956-2870 cm<sup>-1</sup> in <sup>t</sup>Bu<sub>3</sub>salpphenH<sub>2</sub> **1** are assigned to the aromatic C-H stretching vibrations. In compound **3**, bands were observed in the IR spectra at 2959-2850 cm<sup>-1</sup>.<sup>17,22</sup> The IR spectra of <sup>t</sup>Bu<sub>3</sub>salpphenH<sub>2</sub> **1** showed a strong absorption band at 1613 cm<sup>-1</sup>, which can be attributed to the  $\nu_{C=N}$  stretching frequency as compared to the Sn(VI) complex at the band around 1608 cm<sup>-1</sup>, indicating the participation of N atoms in the coordination to the Sn atom.<sup>20</sup> The shift to lower frequencies indicates donation of the nitrogen lone pair of imine group to the Sn atom.<sup>23-25,27</sup> The spectra of the Sn(IV) adduct exhibited broad bands in the region of 3430-3107 cm<sup>-1</sup>, which could originate from the  $\nu_{N-H}$  stretching of a tertiary ammonium cation. The same observations have been made in the case of adduct compounds for the intramolecular N-H...O hydrogen bonding.<sup>20,26-29</sup> In the Sn(IV) adduct, new bands were observed in the infrared spectra at 534 cm<sup>-1</sup> and assigned to the stretching mode of M-O.<sup>23-25</sup>

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopic data of <sup>t</sup>Bu<sub>3</sub>SalpphenH<sub>2</sub> **1** and the Sn(IV) adduct **3** are given in Table 1. <sup>1</sup>H-NMR spectra of the free ligand **1** showed a singlet at 13.81 ppm originating from the phenolic O-H.<sup>21</sup> The resonance signals corresponding to CH<sub>3</sub> protons of the *tert*-butyl groups were found in the region of 1.49-1.33 ppm as a singlet. The other signals due to aromatic protons were observed at 7.51-7.50 ppm (*d*, *J* = 2.4 Hz, H7, H7') and 7.53-7.52 ppm (*d*, *J* = 2.4 Hz, H9, H9'); 7.56 ppm (*s*, H2, H2'), and imine proton N=CH were observed at 8.99 ppm as a singlet.<sup>20,23,27,30</sup>

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound **3** indicated a different chemical shift compared to the free ligand **1**. <sup>1</sup>H-NMR of **3** indicated that for the free ligand **1** the low-field signal that appears at 13.81 ppm due to extensive hydroxyl formation disappeared in the tin(IV) adduct. The imine proton (*s*, H3, H3') appeared in the 8.34 ppm for compound **3** and was shifted high-field with respect to the corresponding signal in the free

ligand **1** at 8.99 ppm (*s*).<sup>27</sup> For the  $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$ , the triplet and quartet of the 3 equivalent ethyl groups were found at 1.44 (*t*,  $J = 7.6$  Hz,  $\text{CH}_3$ ) and 3.46 (*m*,  $\text{CH}_2$ ) ppm, which were moved downfield compared to their position in the free tri-ethyl amine (0.96 ppm, *t*,  $\text{CH}_3$  and 2.45 ppm, *q*,  $\text{CH}_2$  in  $(\text{CD}_3)_2\text{CO}$ ).<sup>26,39</sup> The corresponding  $^{13}\text{C}$  signal appeared at 8.81 and 47.38 ppm. This suggested that the broad singlet at 8.14 ppm in the  $^1\text{H}$ -NMR spectrum may have originated from the  $\text{Et}_3\text{NH}^+$  acidic proton involved in hydrogen bonding.<sup>27,28</sup> The  $\text{CH}_3$  protons of the *tert*-butyl groups appeared as a singlet at 1.52-1.31 ppm.<sup>19,31</sup> The signal of the ring H7, H7' was shifted high-field by 0.14 ppm and H9, H9' was shifted downfield by 0.05 ppm, respectively.

In the  $^{13}\text{C}$ -NMR of compound **3**, the signal of imine carbons C3, C3' were observed at 172.87 ppm and were shifted downfield by about 8 ppm compared to the carbon signal in the free ligand **1** (164.73 ppm). The signals of C5, C5' carbon atoms were observed at 165.49 ppm and were shifted downfield by about 7 ppm because of the presence of the negative charge at the O atom (Figure 2).<sup>19,23</sup> This effect was also apparent, although weaker, on the other ring carbons (Table 1). From the above discussion and on the basis of the elemental analyses,  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, and IR spectroscopic data, the suggested structure of the Sn (IV) adduct is shown in Figure 2.



**Figure 2.** Structure of the  $\text{Sn}_2\text{Cl}_8(\text{}^t\text{Bu salpphen})\cdot 2\text{HNEt}_3$  adduct **3**.

**Table 1.**  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR data of  ${}^{t\text{Bu}}\text{SalpphenH}_2$  **1** and  $\text{Sn}_2\text{Cl}_8({}^{t\text{Bu}}\text{salpphen}).2\text{HNEt}_3$  **3** (100 and 400 MHz, d-acetone).

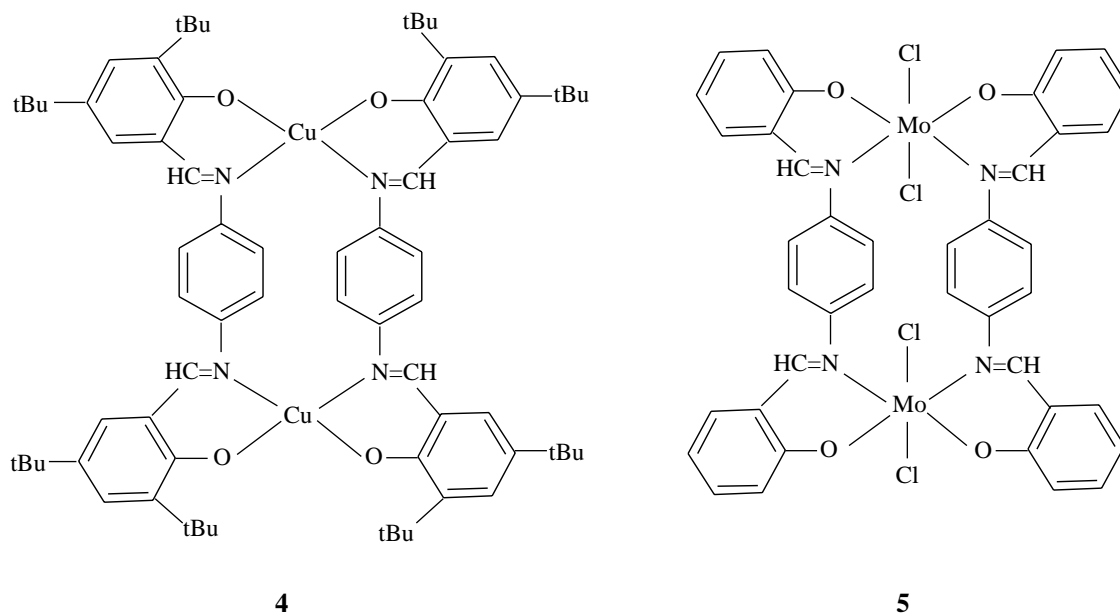
C/H	$\text{Sn}_2\text{Cl}_8({}^{t\text{Bu}}\text{salpphen}).2\text{HNEt}_3$ <b>3</b>		${}^{t\text{Bu}}\text{SalpphenH}_2$ <b>1</b>	
	$\delta_{\text{C}}$	$\delta_{\text{H}}$	$\delta_{\text{C}}$	$\delta_{\text{H}}$
5, 5'	165.49		158.43	
OH				13.81, s
3, 3'	172.87	8.34, s	164.73	8.99, s
1, 1'	148.64		147.30	
8, 8'	141.13		140.85	
6, 6'	138.51		136.62	
9, 9'	131.37	7.58, 7.57, d, $J = 2.4$ Hz	128.05	7.53-7.52, d, $J = 2.4$ Hz
2, 2'	125.35	7.56, s	122.64	7.56, s
7, 7'	130.69	7.37-7.36, d, $J = 2.4$ Hz	127.77	7.51-7.50, d, $J = 2.4$ Hz
4, 4'	117.99		118.98	
$\text{HN}(\underline{\text{CH}_2\text{CH}_3})_3$	47.38	3.46-3.41, m		
$\text{HN}(\text{CH}_2\underline{\text{CH}_3})_3$	8.81	1.44-1.40, t, $J = 7.6$		
15, 16, 17, 15', 16', 17'	31.15	1.52, s	31.08	1.49, s
12, 13, 14, 12', 13', 14'	29.83	1.31, s	29.71	1.33, s
10, 10'	33.99		34.15	
11, 11'	35.30		35.02	

The tetradentate Schiff base **1** reacts with the Cu(II) metal salt and the tetradentate Schiff base **2** reacts with the  $[\text{MoCl}_4(\text{CH}_3\text{CN})_2]$  complex to yield complexes of the general formula  $[\text{M}(\text{L})_2]$  (M:Cu, Mo; L:salpphenH<sub>2</sub>,  ${}^{t\text{Bu}}\text{salpphenH}_2$ ).  $[\text{Cu}^{t\text{Bu}}\text{salpphen}]_2$  **4** and  $[\text{MoCl}_2(\text{salpphen})]_2$  **5** complexes are stable at room temperature, non-hygroscopic, and insoluble in water and many common organic solvents. In the Schiff bases derived from *o*-phenylenediamines, the proximity of nitrogen atoms permits simultaneous coordination to the metal cation and leads mainly to monomer species that are highly soluble in different kinds of solvents. On the other hand, ligands derived from *m*- or *p*-phenylenediamines can only coordinate nitrogen atoms to any one metal cation. Para position of the nitrogen atoms on the aromatic ring facilitates the formation of polymer complexes or bimetallic species.<sup>1</sup> The insolubility of compounds **4** and **5** can be related to the para position of nitrogen atoms. Furthermore, *tert*-butyl groups were used to make more soluble the Cu(II) complex in the common solvent, but the results showed that it was not effective on the solubility of compound **4**. The studied species Cu(II) and Mo(IV), which were found to be formed, as expected, due to the para position of nitrogen atoms in the ligand, facilitate the formation of dimeric species. The bands in the region of 3050-2980  $\text{cm}^{-1}$  in the salpphenH<sub>2</sub> **2** are assigned to the aromatic C-H stretching vibrations.<sup>22</sup> These bands are observed at 3048-2862  $\text{cm}^{-1}$  in the Mo(IV) complex. The IR spectra of salpphenH<sub>2</sub> showed a strong absorption band at 1608  $\text{cm}^{-1}$ , which can be attributed to the  $\nu_{\text{C}=\text{N}}$  stretching frequency. The band around 1595  $\text{cm}^{-1}$  in the compound **5** complex is assigned to the C=N stretching vibrations. The shift to lower frequencies (compared to the free ligand **2**) indicates donation of a nitrogen atom lone pair of the azomethine group to the Mo atom.<sup>14</sup> In compound **5**, bands were observed in the IR spectra at 924-866  $\text{cm}^{-1}$  and assigned to stretching modes of Mo-O. Gomez and co-workers also made similar observations in the case of metal complexes.<sup>32</sup> The vibrations of the azomethine groups of  ${}^{t\text{Bu}}\text{salpphenH}_2$  **1** is observed at 1612  $\text{cm}^{-1}$ . The major shift of  $\nu_{\text{C}=\text{N}}$  is observable in the IR spectrum of  ${}^{t\text{Bu}}\text{salpphenH}_2$  **1** as compared to the

Cu(II) complex with a band around  $1591\text{ cm}^{-1}$ , indicating the participation of N atoms in the coordination to the Cu atom.<sup>33–36</sup> The phenolic C-O stretching vibrations of compound **1** are observed at  $1171\text{ cm}^{-1}$ . A comparison between the IR spectra of compound **1** and **4** also shows that a band characteristic of  $\nu_{C-O}$  at  $1171\text{ cm}^{-1}$  is shifted remarkably to  $1168\text{ cm}^{-1}$ , suggesting that the phenolic O atoms participate in the coordination to the metal atom.<sup>34,36</sup> For compound **4**, the new band at  $529\text{ cm}^{-1}$  can be assigned to the M-O band.<sup>33</sup> The magnetic susceptibility values of the complexes show that  $d^9$  compound **4** is paramagnetic with a magnetic moment of 2.03, which corresponds to one unpaired electron. The coordination geometry at the Cu(II) ion is a square-planar structure.<sup>35–38</sup> Compound **5** has the expected  $d^2$  high-spin configuration with a magnetic moment of  $2.22\ \mu_B$  at 300 K, which corresponds to 2 unpaired electrons. The coordination around the molybdenum is octahedral, with 2 chlorine atoms being bonded to  $[\text{MoCl}_2(\text{salpphen})]_2$  **5** moiety in trans arrangement.<sup>14</sup>

The mass spectrum of compound  $[\text{Cu}^{tBu}\text{salpphen}]_2$  **4** (in DMSO) obtained with a computerized data system shows a molecular ion at  $m/z$  100 for which accurate mass measurement gives 1204. The peaks at  $m/z = 602$  and  $m/z = 540$  correspond to the monomer unit ( $\text{CuC}_{36}\text{H}_{46}\text{O}_2\text{N}_2$ ) and ligand unit ( $\text{C}_{36}\text{H}_{48}\text{O}_2\text{N}_2$ ), respectively. One fragment ion at  $m/z = 539$  corresponds to the  $[\text{C}_{36}\text{H}_{47}\text{O}_2\text{N}_2]^+$  unit; loss of 63 mass units from the monomer ion suggests the expulsion of Cu. The peak at  $m/z = 525.3$  corresponds to the  $[\text{C}_{36}\text{H}_{48}\text{ON}_2]^+$  unit; loss of one oxygen atom and the peak at  $m/z = 497$  corresponding to  $[\text{C}_{36}\text{H}_{48}\text{O}]^+$  unit is also observed.

The mass spectrum of  $[\text{MoCl}_2(\text{salpphen})]_2$  **5** (in MeOH) contains the molecular ion peak at  $m/z = 480$  corresponding to the monomer unit, which shows complex formation. The peaks at  $m/z = 466$  and  $m/z = 439$  correspond to  $[\text{C}_{20}\text{H}_{14}\text{Cl}_2\text{MoNO}_2]^+$  and  $[\text{C}_{20}\text{H}_{14}\text{Cl}_2\text{MoN}]^+$ , respectively. The ligand unit  $[\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2]$  is detectable at  $m/z = 315$ . The peak at  $m/z = 97$  corresponds to the Mo atom. Additionally, the peaks at  $m/z = 55$  and  $m/z = 43$  correspond to 2 fragments,  $\text{C}_4\text{H}_7^+$  and  $\text{C}_3\text{H}_7^+$ .



**Figure 3.** Structure of  $[\text{Cu}^{(tBu)\text{salpphen}}]_2$  **4** and  $[\text{Mo}(\text{salpphen})]_2$  **5** complexes.

From the above discussion and on the basis of the elemental analyses, magnetic susceptibility, mass,

and IR data, the suggested structures of the Cu(II) and Mo(IV) complexes are shown in Figure 3. The coordinating agents derived from *p*-phenylenediamines and the special conformation of the ligand with nitrogen atoms in para positions on the aromatic ring facilitate the formation of dimeric Cu(II) and Mo(IV) complexes.

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