#### Inorganica Chimica Acta 394 (2013) 237-246

Contents lists available at SciVerse ScienceDirect

### Inorganica Chimica Acta

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

# Inorganica Chimica Acta

### Redox chemistry of copper complexes with various salen type ligands

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#### ARTICLE INFO

Article history: Received 17 April 2012 Received in revised form 11 July 2012 Accepted 20 August 2012 Available online 29 August 2012

Keywords: Salen ligands Copper(II) Electrochemistry EPR Spectroelectrochemistry Alcohol oxidation

#### ABSTRACT

The two essential redox processes in Cu(II) salen (and salan) complexes Cu(II)/Cu(I) and [PhO]-/[PhO[-]] were studied by electrochemical and spectroelectrochemical (UV–Vis-absorption or EPR) techniques on a series of complexes in which the salen (salan) type ligands bear various substituents R = H, F, Ph, *t*Bu or CH<sub>3</sub> on the linker C- or N-atoms or on the phenol core. The substitution pattern can be related to the stability of the phenoxy radicals. The geometry of the complexes (especially around the Cu atom) could be established by XRD for the new complex [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu] {H<sub>2</sub>(Me<sub>2</sub>salhexF<sub>4</sub>) = (1R,2R)-*N*,*N*-bis(2-hydroxy-3,5-di-fluoro-acetophenonylidene)-cyclohexane-1,2-diamine} in the solid and for all other derivatives by EPR in fluid solution. Also, the application of the complexes in oxidation catalysis was tested using the oxidation of benzyl alcohol.

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#### 1. Introduction

Salen (2,2'-Ethylenebis(nitrilomethylidene)diphenol) (Scheme 1) and salen type ligands are known to form stable complexes with various transition metals [1-7]. Many of them have been studied with regard to their catalytic properties, especially in oxidation catalysis [5,8–11]. An example of such a reaction is the two electron oxidation of primary alcohols to the corresponding aldehydes [1,8,12–16], which is e.g. known in nature from the metalloenzyme Galactose Oxidase (GO) which occurs in the fungus Polyporus circinatus [17]. The dehydrogenation of alcohols comprises the transfer of two electrons, in GO they are provided by two cooperating redox pairs Cu(II)/Cu(I) and tyrosyl/tyrosinate ([Tyr]·/[Tyr<sup>-</sup>]) [18] with the tyrosyl radical [Tyr]<sup>•</sup> directly coordinated to the copper ion. The alcohol oxidation is coupled to the formation of H<sub>2</sub>O<sub>2</sub> using aerial oxygen for reoxidation of the enzyme [19]. The electrochemical potentials of both redox couples in GO are very low (0.16 V vs. NHE [20] or -0.24 V vs. FeCp<sub>2</sub>/FeCp<sub>2</sub><sup>+</sup> [21] for the Cu(II)/Cu(I) redox couple and 0.41 V vs. NHE [20] or 0.01 V vs. FeCp<sub>2</sub>/FeCp<sub>2</sub><sup>+</sup> [21] for the [Tyr]<sup>·</sup>/[Tyr<sup>-</sup>] redox couple) and the thermodynamic gap between both processes is small with only 0.25 V. GO owes these low redox potentials to its peculiar molecular structure, showing a distorted

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square pyramidal Cu(II) coordination geometry (at pH 7) [22] and the coordinated tyrosyl group covalently bound to a thioether group. The latter is thought to have a stabilising effect on the radical. However, the exact way of stabilisation remains still under debate [23]. In contrast to this, there is far less doubt that the coordination geometry and (low) coordination number around the Cu(II) ion facilitates the reduction of Cu(II) to Cu(I) [18,24].

Salen type ligands play an important role in developing functional models of GO [10,12,15,25]. They provide an  $N_2O_2$  donor set, similar to that found in GO, with two phenolate O donor functions which are capable of forming (meta)stable ligand radicals. Additionally, the rigidity of the linker determines the coordination behaviour towards transition metals, e.g. a rigid linker forces a square planar binding of the  $N_2O_2$  donor set.

A large number of Cu salen complexes have been successfully applied in alcohol oxidation [1,8,12,26–28]. However, not all of them catalyse alcohol oxidation in a GO like way. Homoleptic complexes of *ortho*-aminophenols form biradical species, with both radicals taking part in the reaction and leaving the coordinated metal ion redox inactive,[1] while Cu-salen complexes with strongly  $\sigma$ -donating ligands containing amide [29] or imine functions in the linker exhibit a comparably stable Cu(III) state instead of a ligand centred radical (at least at low temperatures) [30]. In contrast to this, "reduced" Cu salen complexes (containing amino-functions in the linker; also called "salan") reliably form a [Cu(II)-sal·]<sup>+</sup> species with a redox active metal ion and a ligandcentred radical.



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**Scheme 1.** Salen (2,2'-Ethylenebis(nitrilomethylidene)diphenol).

Depending on the flexibility of the linker group, the coordination geometry of complexes with salen type ligands varies from square planar to tetrahedrally distorted [12]. Generally, a tetrahedral distortion of the complexes makes the complexes more GO-like in that the distortion has a strong impact on the redox potential of the copper ion (i.e. stabilising the Cu(I) state) and supports overlapping of the molecular orbitals of the phenol ring with the singly occupied Cu  $d_{x2-y2}$  orbital. Such overlap results in an anti-ferromagnetic coupling of the odd electrons [31], such as in GO [27,32]. In contrast, Cu salen complexes with rigid linker groups exhibit ferromagnetic coupling (*S* = 1), in line with the Goodenough-Kanamori-Anderson rules [33]. In previous investigations it was found that anti-ferromagnetic spin coupling and catalytic activity of Cu salen complexes go hand in hand [12].

It is well established, that the stability of the salen type phenoxyl radicals depends on the presence of stabilising substituents in *ortho-* and *para*-position to the phenol OH group [25,34]. Very often these substituents were bulky groups such as *t*Bu, *Si*Pr or SPh [12,27]. Non-stabilised radical species have been reported to lack any activity in alcohol oxidation [12]. However, under basic condition catalytic alcohol oxidation has been observed for Cu complexes with un-substituted salen ligands [16] and is has been recognised that also the stabilisation of the Cu(I) species might be crucial for the catalytic activity [28]. Substitution of the salenlinker may have an impact on the stability of the phenoxyl radicals and on the catalytic activity, since the rigidity and bulkiness of the linker groups determine the geometry (and flexibility) around the Cu atom [1,12,25,27,34a,35,36].

In this work, copper complexes of various chiral (R,R)-cyclohexyl salen type ligands were examined (Scheme 2). They are characterised by different *ortho* and *para* positioned substituents and different linker groups, containing imine functions as well as *sec* and *tert* amino functions. Some linker groups are further substituted using small (-CH<sub>3</sub>) or bulky (-Ph) groups. Each linker contains a cyclohexane ring, thus all salen ligands are relatively rigid, with all above mentioned consequences.

The phenol groups of the ligands carry phenyl, fluorine or *t*Bu substituents. Fluorine and alkyl substituents are expected to support phenoxyl radical formation by their electron donation ability (F possesses a +M and a –I effect), while the stabilising ability of Ph groups is unequivocal, since a +I and a –M effect is attributed to this group. Furthermore, the substituents exert different sterical demand (*t*Bu > Ph > F > H). These ligands were used to prepare Cu(II) complexes. Their synthesis, analysis, spectroscopic and electrochemical characterisation will be reported in detail and the results of catalytic test reactions (oxidation of benzyl alcohol) will be discussed in view of these properties.

The synthesis and properties of all three salan ligands  $(NH)_2$ salhex [37],  $(NH)_2$ salhexPh<sub>2</sub>, [9c,38] and  $(NMe)_2$ salhextBu<sub>4</sub> [39] have been reported before. In contrast to this, from the three salen ligands only salhexPh2 [5,37b,38,40] and has been synthesised and characterised in depths, while Ph<sub>2</sub>salhex was only mentioned in a brief report without giving details on the synthesis or analysis [41], and Me<sub>2</sub>salhexF<sub>4</sub> has not been reported so far.

Cu(II) complexes of the salan ligand (NMe)<sub>2</sub>salhextBu<sub>4</sub> have not been reported so far, but its derivatives (NH)<sub>2</sub>salhextBu<sub>4</sub> [12b,28,30,42,43], (NH)<sub>2</sub>salentBu<sub>4</sub> and (NMe)<sub>2</sub>salentBu<sub>4</sub> (ethyl instead of cyclohexyl as spacer) [25,44,45] have been synthesised and investigated in detail in view of their electrochemical or catalytic properties (oxygenation). For the salan ligand (NH)<sub>2</sub>salhex Cu complexes have been only proposed so far, based on catalytic behaviour of solutions of the ligand and Cu(OAc)<sub>2</sub> [37a]. For the ligand (NH)<sub>2</sub>salhexPh<sub>2</sub> Ti complexes have been reported with application in epoxidation catalysis, but no Cu derivatives [9c,38]. For the salen ligand salhexPh<sub>2</sub> Ti complexes are considered as active catalysts in epoxidation reactions, however, no complexes have been isolated so far [5,38,40]. Thus, in this contribution we report for the first time the Cu(II) complexes of the salen and salan ligands depicted in Scheme 2. All complexes have been characterised thoroughly by EPR spectroscopy, electrochemical and spectroelectrochemical methods. Also preliminary catalytic test reactions



Scheme 2. Salen type ligands used in this study and their abbreviations.

are reported. The spectroscopic and electrochemical properties are compared to those of Cu(II) complexes of related salen or salan ligands such as [(salen)Cu] [46–50], [(salhex)Cu] [16,51], [(salhextBu<sub>4</sub>)Cu], [12b,28,30,42,45,51,52] [(salentBu<sub>4</sub>)Cu], [45,48] [((NMe)<sub>2</sub>salentBu<sub>4</sub>)Cu], [44] [((NH)<sub>2</sub>salhextBu<sub>4</sub>)Cu] [28,30,42,43], [((NH)<sub>2</sub>salentBu<sub>4</sub>)Cu] [45] or [((NH)<sub>2</sub>salhexOEt)Cu] [9b] which have been previously investigated in view of their structures, electrochemistry, spectroscopy and catalytic properties.

#### 2. Experimental

#### 2.1. Instrumentation

NMR spectra were recorded on a Bruker Avance II 300 MHz or a Bruker DPX300 spectrometer, using a triple resonance <sup>1</sup>H, <sup>n</sup>BB inverse probe. Unambiguous assignments of <sup>1</sup>H and <sup>13</sup>C resonances was obtained from <sup>1</sup>H NOESY, <sup>1</sup>H COSY, gradient selected <sup>1</sup>H, <sup>13</sup>C HSQC and HMBC experiments. All 2D NMR experiments were performed using standard pulse sequences from the Bruker pulse program library. Chemical shifts are stated relative to TMS. Infrared (IR) spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer with ATR technique. Data are reported as: wavenumber of absorption (cm<sup>-1</sup>), intensity of absorption (s = strong, m = medium, w = weak). HRMS data ( $\Delta u = 0.002 u$ ) and ESI-MS analyses were recorded on a Finnigan MAT 900S instrument. UV– Vis/NIR absorption spectra were measured on Varian Cary50 Scan or Shimadzu UV-3600 photo spectrometers.

Elemental analyses were carried out using a HEKAtech CHNS EuroEA 3000 Analyzer. EPR spectra were recorded in the X-band on a Bruker System ELEXSYS 500E equipped with a Bruker Variable Temperature Unit ER 4131VT (500–100 K or an Oxford Instruments helium-cryostat (300–4 K); the g values were calibrated using a dpph sample. Simulation of the EPR spectra were performed using the Bruker SimFonia. Electrochemical experiments were carried out in 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub> solutions using a three-electrode configuration (glassy carbon working electrode, Pt counter electrode, Ag/ AgCl pseudo reference) and an Autolab PGSTAT30 potentiostat and function generator. The ferrocene/ferrocenium couple (FeCp<sub>2</sub>/ FeCp<sub>2</sub><sup>+</sup>) served as internal reference. UV–Vis spectroelectrochemical measurements were performed with an optically transparent thin-layer electrochemical (OTTLE) cell [53].

#### 2.2. Crystal structure determination

The measurements were performed at 293(2) K using graphitemonochromatised Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) on IPDS II (STOE and Cie.). The structures were solved by direct methods using shelx-97 and WinGX (shelxs-97) [54] and refined by full-matrix least-squares techniques against  $F^2$  (shelxl-97) [55]. The numerical absorption corrections (X-RED V1.22; Stoe & Cie, 2001) were performed after optimising the crystal shapes using X-SHAPE V1.06 (Stoe & Cie, 1999) [56]. The non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were included by using appropriate riding models.

#### 2.3. Catalytic test reactions

A solution of 116 mg (0.23 mmol, 0.5 eq)  $[(Cu(OTf))_2(\mu$ -toluene)] with 0.9 mmol (2.0 eq) ligand in 0.5 mL pure MeCN was prepared. 0.5 g benzyl alcohol was mixed with 180 mg powdered NaOH. Both mixtures were combined and vigorously stirred at 298 K. Samples of the reaction mixtures were taken, mixed with CD<sub>2</sub>Cl<sub>2</sub> upon which a green-brown precipitate was formed. The remaining solution was isolated and submitted to NMR spectroscopic analysis. <sup>1</sup>H NMR spectra (300 MHz) were recorded and product yields were determined by integration of the aldehyde proton.

#### 2.4. Materials and procedures

2-Hydroxybiphenyl-3-carbaldehyde [57] and the ligands  $H_2$ -(salhexPh<sub>2</sub>) [37b],  $H_2((NMe)_2salhextBu_4)$  [39a,b] and  $H_2((NH)_2salhex)$  [37b] were synthesised following published methods. All reactions were carried out in oven-dried or flame-dried round bottom flasks and the reactions were conducted under a positive pressure of argon, unless otherwise stated. Stainless steel syringes or cannulae were used to transfer air- and/or moisture-sensitive liquids.

#### 2.4.1. (1R,2R)-N,N'-bis(2-hydroxybenzophenonylidene)cyclohexane-1,2-diamine $H_2(Ph_2salhex)$

To a solution of (1R,2R)-(-)-trans-cyclohexane-1,2-diamine (257 mg, 2.25 mmol, 1 eq) in anhydrous ethanol (8 mL) was added 2-hydroxybenzophenone (892 mg, 4.50 mmol, 2 eq). The resulting yellow solution was refluxed for 48 h at 80 °C. After cooling to ambient temperature, water (16 mL) was added whereupon a yellow precipitate was formed. The reaction mixture was stirred for 1 h and the precipitate was collected by suction filtration, washed with small portions of cold ethanol and dried in vacuo to yield a yellow powder (928 mg, 1.95 mmol, yield 87%). Mp = 86 °C; *v*<sub>max</sub>(ATR)/cm<sup>-1</sup> 2929, 2856, 2160, 2029, 1977, 1604, 1571, 1492, 1442, 1300, 1253, 1147, 964, 827, 752, 719, 693, 646;  $\delta_{\rm H}$ (300 MHz; CDCl<sub>3</sub>) 1.12-1.18 (2 H, m), 1.43-1.46 (2 H, m), 1.63-1.71 (4 H, m), 3.49-3.52 (2 H, m), 6.59-6.64 (2 H, m), 6.70-6.73 (2 H, m), 6.98-7.01 (2 H, m), 7.13-7.15 (2 H, m), 7.23-7.28 (2 H, m), 7.32-7.35 (2 H, m), 7.48-7.52 (4 H, m), 7.61-7.65 (2 H, m), 15.29 (2 H, s(br)); δ<sub>C</sub>(75 MHz; CDCl<sub>3</sub>) 23.7 (t, CH<sub>2</sub>), 32.4 (t, CH<sub>2</sub>), 64.7 (d, CH), 117.3 (d, CH), 117.7 (d, CH), 119.9 (s, Cq), 126.7 (d, CH), 128.1 (d, CH), 128.3 (d, CH), 128.8 (d, CH), 129.1 (d, CH), 131.8 (d, CH), 132.2 (d, CH), 133.8 (s, Cq), 162.8 (s, Cq), 173.6 (s, Cq); m/z (ESI-MS) 475 ([M+H]<sup>+</sup>. C<sub>32</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub> requires 475), 497 ([M+Na]<sup>+</sup>) and 475 ([M+K]<sup>+</sup>); (HR–MS, ESI) 475.235 ([M+H]<sup>+</sup> C<sub>32</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub> requires 475.235).

#### 2.4.2. (1R,2R)-N,N'-Bis(2-hydroxy-3,5-di-fluoro-acetophenonylidene)cyclohexane-1,2-diamine $H_2(Me_2salhexF_4)$

To a solution of (1R,2R)-(-)-trans-cyclohexane-1,2-diamine (299 mg, 2.62 mmol, 1 eq) in anhydrous ethanol (15 mL) was added 1-(3,5-difluoro-2-hydroxy-phenyl)-ethan-1-one (900 mg, 5.23 mmol, 2 eq). The resulting yellow solution was refluxed for 18 h. After cooling to ambient temperature, water (8 mL) was added whereupon a yellow precipitate was formed. The reaction mixture was stirred for 1 h at 298 K and the precipitate was collected by suction filtration, washed with water and small portions of cold ethanol and dried in vacuo to yield a yellow powder (874 mg, 2.07 mmol, yield 79%). Mp = 154 °C;  $v_{max}(ATR)/cm^{-1}$ 3043, 2939, 2160, 1595, 1479, 1448, 1350, 1269, 1116, 844, 800, 584; δ<sub>H</sub>(300 MHz; CDCl<sub>3</sub>) 1.46–1.53 (2 H, m), 1.67–1.53 (2 H, m), 1.91-1.99 (4 H, m), 2.29 (6 H, s), 3.88-3.91 (2 H, m), 6.86-6.92 (4 H, m);  $\delta_{C}(75 \text{ MHz}; \text{ CDCl}_{3})$  14.8 (q, CH<sub>3</sub>), 24.0 (t, CH<sub>2</sub>), 32.1 (t, CH<sub>2</sub>), 62.9 (d, CH), 107.5 (d, CH), 108.6 (d, CH), 118.7 (s, C<sub>q</sub>), 150.4 (s C<sub>q</sub>), 153.6 (s, C<sub>q</sub>), 153.7 (s, C<sub>q</sub>); 170.9 (s, C<sub>q</sub>); m/z (ESI-MS) 423 ( $[M+H]^+ C_{22}H_{22}F_4N_2O_2$  requires 423), 445 ( $[M+Na]^+$ ) and 461 ( $[M+K]^+$ ); (HR-MS, ESI) 423.169 ( $[M+H]^+$  C<sub>22</sub>H<sub>22</sub>F<sub>4</sub>N<sub>2</sub>O<sub>2</sub> requires 423.169).

## 2.4.3. (1R,2R)-N,N'-Bis(3-phenylsalicyl)cyclohexane-1,2-diamine H<sub>2</sub>((NH)<sub>2</sub>salhexPh<sub>2</sub>)

To a solution of (1R,2R)-N,N'-bis(3-phenylsalicylidene)cyclohexane-1,2-diamine (2.0 g, 4.22 mmol, 1 eq) in methanol was added sodium borohydride (479 mg, 12.7 mmol, 3 eq) in small portions. The colourless solution was stirred for 3 h at 298 K. Water (20 mL) was added and the mixture was extracted three times using ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous magnesium sulphate. The solvent was evaporated under reduced pressure to yield a colourless powder (1.53 g, 3.11 mmol, yield 74%). Mp = 78 °C;  $v_{max}(ATR)/$ cm<sup>-1</sup> 3298, 2927, 2854, 2360, 1591, 1498, 1460, 1427, 1230, 1087, 1028, 918, 827, 754, 696;  $\delta_{\rm H}(300 \text{ MHz}; \text{CDCl}_3)$  1.22–1.26 (4 H, m), 1.69-1.71 (2 H, m), 2.14-2.18 (2 H, m), 2.45-2.47 (2 H, m), 3.95 (2 H, d, J 14.0), 4.07 (2 H, d, J 14.0), 6.86 (2 H, t, J 7.6), 6.95 (2 H, d, J 7.6), 7.26-7.33 (4 H, m), 7.40 (4 H, t, J 7.6), 7.58 (4 H, d, J 7.6); δ<sub>C</sub>(75 MHz; CDCl<sub>3</sub>) 24.1 (t, CH<sub>2</sub>), 30.3 (t, CH<sub>2</sub>), 49.6 (t, CH2-N), 59.5 (d, CH), 119.2 (d, CH), 123.3 (s, Cq), 126.7 (d, CH), 127.6 (d, CH), 128.0 (d, CH), 129.0 (s, Cq), 129.3 (d, CH), 129.8 (d, CH), 138.3 (s, C<sub>q</sub>), 154.9 (s, C<sub>q</sub>); m/z (ESI-MS) 479 ([M+H]<sup>+</sup> C<sub>32</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub> requires 478.62) and 501 ([M+Na]<sup>+</sup>); (HR-MS, ESI) 479.269 ([M+H]<sup>+</sup> C<sub>32</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub> requires 479.269).

#### 2.4.4. General Procedure for the synthesis of salen type complexes

1 eq ligand and 1 eq  $Cu(OAC)_2 \cdot H_2O$  (or  $Zn(OAC)_2 \cdot 2H_2O$ ) were dissolved in methanol and both solutions were mixed at 298 K. The mixture was stirred at 298 K for 16 h. While [((NH<sub>2</sub>)salhexPh<sub>2</sub>)Cu] and [(salhexPh<sub>2</sub>)Cu] precipitated and were filtered off and washed with small portions of methanol, all other complexes were isolated by removing the solvent under vacuum and recrystallisation from acetone solution.

2.4.4.1. [(( $NMe_2$ )salhext $Bu_4$ )Cu]. Fifty eight milligram (0.1 mmol)  $H_2((NMe_2)$ salhext $Bu_4$ ) and 20 mg (0.1 mmol)  $Cu(OAc)_2$ · $H_2O$  were reacted to yield dark green needle shaped crystals (24 mg, 0.04 mmol, yield 40%). Anal. Calc. for  $C_{38}H_{60}CuO_2N_2$ : C, 71.26; H, 9.44; N, 4.37%. Found: C, 71.25; H, 9.45; N, 4.34%.

2.4.4.2. [((NH)<sub>2</sub>salhex)Cu]. Thirty ove milligran (0.1 mmol) H<sub>2</sub>-((NH)<sub>2</sub>salhex) and 20 mg (0.1 mmol) Cu(OAc)<sub>2</sub>·H<sub>2</sub>O were reacted to yield reddish-brown crystalline needles (26 mg, 0.07 mmol, yield 70%). Anal. Calc. for C<sub>20</sub>H<sub>24</sub>CuO<sub>2</sub>N<sub>2</sub>: C, 61.92; H, 6.24; N, 7.22%. Found: C, 62.01; H, 6.28; N, 7.22%.

2.4.4.3. [(( $NH_2$ )salhexPh<sub>2</sub>)Cu]. Hundred milligram (0.2 mmol) H<sub>2</sub>-(( $NH_2$ )salhexPh<sub>2</sub>) and 40 mg (0.2 mmol) Cu(OAc)<sub>2</sub>·H<sub>2</sub>O were reacted to yield a blue-green powder (45 mg, 0.08 mmol, yield 40%). Anal.Calc. for C<sub>32</sub>H<sub>32</sub>CuO<sub>2</sub>N<sub>2</sub>: C, 71.15; H, 5.97; N, 5.19%. Found: C, 71.22; H, 5.99; N, 5.22%.

2.4.4.4. [( $Me_2salhexF_4$ )Cu]. Fourty milligram (0.1 mmol) H<sub>2</sub>(Me<sub>2</sub>salhexF<sub>4</sub>) and 20 mg (0.1 mmol) Cu(OAc)<sub>2</sub>·H<sub>2</sub>O were reacted to yield dark green crystals (36 mg, 0.075 mmol, yield 75%). Anal. Calc. for C<sub>22</sub>H<sub>20</sub>CuO<sub>2</sub>N<sub>2</sub>F<sub>4</sub>: C, 54.60; H, 4.17; N, 5.79%. Found: C, 54.62; H, 4.14; N, 5.77%.

2.4.4.5. [( $Ph_2salhex$ )Cu]. Fifty five milligram (0.12 mmol, 1 eq)  $H_2$ -( $Ph_2salhex$ ) and 24 mg (0.12 mmol, 1 eq)  $Cu(OAc)_2 \cdot H_2O$  were reacted to yield a brown powder (20 mg, 0.04 mmol, yield 33%). *Anal.* Calc. for  $C_{32}H_{28}CuO_2N_2$ : C, 71.69; H, 5.26; N, 5.23%. Found: C, 71.75; H, 5.24; N, 5.24%.

2.4.4.6. [(salhexPh<sub>2</sub>)Cu]. Hundred milligram (0.21 mmol) H<sub>2</sub>(salhexPh<sub>2</sub>) and 42 mg (0.21 mmol) Cu(OAc)<sub>2</sub>·H<sub>2</sub>O were reacted to yield a light brown powder (86 mg, 0.16 mmol, yield 76%). Anal. Calc. for  $C_{32}H_{28}CuO_2N_2$ : C, 71.69; H, 5.26; N, 5.23%. Found: C, 71.62; H, 5.28; N, 5.28%.

2.4.4.7. [(( $NH_2$ )salhexPh<sub>2</sub>)Zn]. Hundred milligram (0.2 mmol) H<sub>2</sub>-(( $NH_2$ )salhexPh<sub>2</sub>) and 44 mg (0.2 mmol) Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O were reacted to yield an off-white powder (74 mg, 0.14 mmol, yield

70%). Anal. Calc. for  $C_{32}H_{32}ZnO_2N_2$ : C, 70.23; H, 5.99; N, 5.24%Found: C, 70.43; H, 5.95; N, 5.27%.  $\delta_H(300 \text{ MHz}; C_3D_6O)$  1.00 (4 H, m), 1.74 (4 H, m), 2.51 (2 H, m), 3.37 (2 H, s(br)), 3.98 (2 H, s(br)), 6.46 (2 H, s(br)), 6.81 (2 H, s(br)), 7.07 (4 H, s(br)), 7.41 (4 H, m), 7.57 (2 H, s(br)) 7.66 (2 H, s(br)).

#### 3. Results and discussion

# 3.1. Synthesis and structure of the salen ligands and their copper complexes

While the ligands  $H_2((NH)_2 \text{salhex})$  [37],  $H_2((NH)_2 \text{salhexPh}_2)$ [9c,38], H<sub>2</sub>((NMe)<sub>2</sub>salhextBu<sub>4</sub>), [39] and H<sub>2</sub>(salhexPh<sub>2</sub>) [5,37b,38, 40], have been reported before, for  $H_2(Ph_2salhex)$  [41] only a titanium complex is described in the literature (thus the synthesis of  $H_2(Ph_2salhex)$  is reported herein).  $H_2(Me_2salhexF_4)$  is a new salen ligand and its synthesis is outlined in the Experimental part as well as the synthesis of  $H_2((NH)_2 \text{salhexPh}_2)$  which was obtained through a modified synthesis. All ligands were characterised by elemental analysis, NMR, UV/Vis absorption spectroscopy, and cyclic voltammetry (CV). The ligands H<sub>2</sub>((NH)<sub>2</sub>salhex) and H<sub>2</sub>(Me<sub>2</sub>salhexF<sub>4</sub>) were obtained as single crystals by recrystallisation from methanol and were analysed by XRD. Both ligands crystallise in the orthorhombic space group  $P2_12_12_1$  and both molecules (Fig. 1 and Supplementary material) do not provide the O,N,N,O binding pocket; one phenol ring lies above and one beneath the cyclohexane ring plane. Details on the crystal structure solution and refinement as well as graphics of the crystal packing can be found in the Supplementary material.

The Cu complexes were prepared by reacting the ligands and  $Cu(OAc)_2$  in 1:1 stoichiometry in methanol solution. The complexes [((NMe)\_2salhextBu\_4)Cu] (green), [((NH)\_2salhex)Cu] (dark green), [((NH)\_2salhexPh\_2)Cu] (green), [(Me\_2salhexF\_4)Cu] (green), [(Ph\_2salhex)Cu] (brown) and [(salhexPh\_2)Cu] (brown) were obtained in moderate to high yields (79–33%) and in high purity as inferred from elemental analyses. For comparison, also the zinc complex [((NH)\_2salhexPh\_2)Zn] was prepared and included into our studies.

The complex [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu] could be crystallised from methanol and single crystals suitable for XRD were obtained. The crystal structure was solved and refined in the monoclinic space group C2 (Fig. 1, and Supplementary material). In the crystal, the copper complex molecules are stacked along the *c* axis with large Cu $\cdots$ Cu distances of 3.820(1) Å and 3.865(1) Å. No intermolecular interaction such as hydrogen bridges were found in the crystal structure. The stacked molecules leave tunnels in the structure along the c axis. The tunnels have ellipsoid cross-sections and were "coated" with fluorine atoms. The observed residual electron density found in these tunnels was assigned to small amounts of solvent molecules and the solvent correction tool of Platon (SWAT) was used during refinement. Assignment and refinement of the solvent molecules was impossible due to statistic distribution of these molecules. In the two independent molecules, the geometry around the Cu atoms is square planar ( $\Sigma$  of angles around Cu = 363.9(3) or  $360.1(3)^\circ$ , respectively) and also with negligible distortion in the linker group. The Cu–O distances are 1.859(6) (molecule 1) Å 1.834(7) and 1.855(5) Å (molecule 2) respectively which is common for copper coordinated to phenolate groups [9b,45,47,51,58,59].

#### 3.2. EPR spectroscopy

The (parent) Cu<sup>II</sup> complexes were analysed by EPR spectroscopy from solid samples (microcrystalline powder) or MeCN solutions at 298 K or from glassy frozen Me-THF solutions at 115 K. Fig. 2 shows representative spectra and Table 1 lists the obtained data.



Fig. 1. ORTEP representation (50% probability level) of the molecular structure of H<sub>2</sub>(Me<sub>2</sub>salhexF<sub>4</sub>) (left) and [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu] (one of the two independent molecules; right); except for OH all H atoms were omitted for clarity.



Fig. 2. X-band EPR spectra of  $[(Me_2salhexF_4)Cu]$  and recorded in glassy frozen DMF solution at 110 K with simulation below.

X-band EPR spectra recorded at 298 K on microcrystalline samples showed broad, largely featureless resonances, while spectra in MeCN solution (at 298 K) showed the four line pattern corresponding to the hyper fine ( $A_{cu}$ ) coupling of the unpaired electron with the nuclear spin of the  $^{63/65}$ Cu isotopes (I = 3/2, 69 and 31% nat. abundance). The values for  $A_{cu}$  were simulated and range from 82 to 90 G, which is typical for Cu(II) complexes of salen type ligands [28,45,49,58], the smallest value was observed for the fluorine substituted complex [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu] in line with previous findings [49]. The axial spectra recorded in glassy frozen Me-THF or DMF solutions show large  $A_{Cu}$  for the  $g_{\parallel}$  component, while the  $g_{\perp}$  component reveals far smaller  $A_{Cu}$  but frequently resolved  $A_{N}$ .

X-band EPR data of the salen Cu complexes	X-band	EPR	data	of	the	salen	Cu	complexe
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Again, the  $A_{\text{Cu}\parallel}$  is smallest for the fluorine substituted complex, while the  $A_{\text{N}\perp}$  is comparably large. Also, we find slightly larger  $A_{\text{Cu}\parallel}$  values for the salan vs. the salen derivatives and slightly smaller values in DMF compared to Me-THF solutions, both in line with earlier investigation [45,49]. Generally however, the obtained *g* and *A* parameters do not vary markedly within the investigated series and the values largely agree with those of related salen or salan Cu(II) complexes [28,45,49,58]. Importantly, for the behaviour of the complexes in solution we can state that regardless of the solvent, the complexes retain largely their square planar geometry observed in the solid state, which can be inferred from the  $g_{\parallel}/A_{\parallel}$  ratio which all lie around 100 cm for the salan and around 95 cm for the salen complexes (largely distorted systems exhibit values up to 250 cm) [45,60]. Also, the solvents do not seem to coordinate (in the axial position).

#### 3.3. Electrochemical properties

Electrochemical investigations were carried out on the free ligands and on the copper complexes. Fig. 3 shows representative examples and Table 2 lists the collected data (complete data in the Supplementary material).

The free ligands exhibit irreversible oxidations in the range of +0.27 V-+0.84 V, except for  $(\text{NMe})_2$ salhextBu<sub>4</sub> (partly reversible with a peak current ratio of 0.37). On cathodic scans irreversible reductions at potentials lower than -2.2 V were observed.

On first view, the Cu complexes exhibit similar oxidation behaviour as the corresponding ligands. However, the oxidation waves were markedly shifted to lower potentials and exhibit a far higher

Salen ligand	$g_{iso}$ or $_{av.}$	$g_{\parallel}$ or $g_3$	$g_{\perp}$ or $g_{1,2}$	⊿g	$A_{\rm Cu} A_{\rm H}/A_{\perp}$	$A_{ m N\perp}$	Conditions
(NMe) <sub>2</sub> salhextBu <sub>4</sub>	2.107	_	-	_	87	-	MeCN/298 K
(NH)salhexPh <sub>2</sub>	2.093	-	-	-	87	-	MeCN/298 K
(NH) <sub>2</sub> salhex	2.090	-	-	-	85	-	MeCN/298 K
Ph <sub>2</sub> salhex	2.106	-	-	-	87	-	MeCN/298 K
Me <sub>2</sub> salhexF <sub>4</sub>	2.105	-	-	-	82	-	MeCN/298 K
salhexph <sub>2</sub>	2.107	-	-	-	88	-	MeCN/298 K
(NMe) <sub>2</sub> salhextBu <sub>4</sub>	2.102	2.221	2.048	0.173	194/31	11	Me-THF/115 K
(NH) <sub>2</sub> salhex	2.096	2.211	2.038	0.173	195/34	15	Me-THF/115 K
Ph <sub>2</sub> salhex	2.108	2.223	2.051	0.185	186/33	16	Me-THF/115 K
Me <sub>2</sub> salhexF <sub>4</sub>	2.102	2.228	2.039	0.189	181/22	15	Me-THF/115 K
(NMe) <sub>2</sub> salhextBu <sub>4</sub>	2.115	2.236	2.055	0.181	184/22	11	DMF/110 K
(NH) <sub>2</sub> salhexPh <sub>2</sub>	2.109	2.231	2.048	0.183	182/33	12	DMF/110 K
(NH) <sub>2</sub> salhex	2.101	2.227	2.038	0.189	183/31	13	DMF/110 K
Me <sub>2</sub> salhexF <sub>4</sub>	2.107	2.236	2.043	0.193	177/25	15	DMF/110 K
salhexph <sub>2</sub>	2.103	2.213	2.048	0.165	194/24	15	DMF/110 K

<sup>a</sup> Measured either in MeCN solution at 298 K or in glassy frozen Me-THF or DMF solution at 115 or 110 K.  $g_{av}$  = averaged g value =  $(g_1 + g_2 + g_3)/3$  or  $(g_{||} + 2g_{\perp})/3$ ;  $\Delta g = g_3 - g_1$  or  $g_{||} - g_{\perp}$ .



Fig. 3. Cyclic voltammogramms of [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu] (left) and [((NMe)<sub>2</sub>salhextBu<sub>4</sub>)Cu] (right) in MeCN/nBu<sub>4</sub>NPF<sub>6</sub> solution at 298 K at 100 mV/s scan rate.

#### Table 2

Electrochemical data of salen Cu complexes [(ligand)Cul.<sup>4</sup>

Ligand	$E_{\rm ox2}$ (ligand)	E <sub>ox1</sub> (ligand)	$\Delta E_{ox2-ox1}$	$E_{\rm red1}$ Cu(II)/Cu(I)	Solvent (ref.)
(NMe) <sub>2</sub> salhex <i>t</i> Bu <sub>4</sub>	0.35 (rev)	0.15 (rev)	0.20	-1.76 (rev)	MeCN/this work
(NH) <sub>2</sub> salhextBu <sub>4</sub>	0.21 (rev)	0.08 (rev)	0.13	<-1.5	CH <sub>2</sub> Cl <sub>2</sub> /ref. [28]
salhex <i>t</i> bu <sub>4</sub>	0.65 (rev)	0.45 (rev)	0.20	<-1.5	CH <sub>2</sub> Cl <sub>2</sub> /ref. [28]
salen <i>t</i> bu <sub>4</sub>	-	0.42 (rev)	_	-1.63 (rev)	DMF/ref. [48]
Salen	-	0.57 (irr)	_	-1.63 (rev)	DMF/ref. [48]
(NH) <sub>2</sub> salhex	0.91 (irr)	0.38 (irr)	_	-1.71 (rev)	MeCN/this work
(NH) <sub>2</sub> salhexPh <sub>2</sub>	0.53 (irr)	0.26 (irr)	-	-1.67 (rev)	MeCN/this work
$Me_2salhexF_4$	$0.88 (p.rev)^{b}$	0.60 (rev)	_	-1.26 (rev)	MeCN/this work
Ph <sub>2</sub> salhex	0.84 (irr)	$0.44 (p.rev)^{b}$	_	-1.58 (rev)	MeCN/this work
salhexph <sub>2</sub> <sup>c</sup>	0.81 (irr)	0.46 (irr)	-	-1.40 (rev)	DMF/this work

<sup>a</sup> From cyclic voltammetry measured in MeCN/nBu<sub>4</sub>NPF<sub>6</sub> at 298 K at 100 mV/s scan rate; Half-wave potentials E<sub>1/2</sub> for reversible waves (rev), cathodic peak potentials E<sub>pc</sub> for irreversible reductions (irr) in V vs. FeCp<sub>2</sub>/FeCp<sub>2</sub><sup>+</sup>.

Partly reversible, 0.37 < peak current ratio < 0.92.

<sup>c</sup> Virtually not soluble in MeCN.

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UV–Vis Absorption	data of	the salen	copper	complexes <sup>a</sup> .

Complexes	λ				
[((NMe)2salhextBu4)Cu]	255 (9690), 297	434		623	
	(6570)	(820)		(510)	
[((NH) <sub>2</sub> salhex)Cu]	246 (8940), 278	385		595	
	(7030)	(680)		(190)	
[((NH) <sub>2</sub> salhexPh <sub>2</sub> )Cu]	232 (8320), 318	394		611	
	(9330)	(910)		(450)	
[(Me <sub>2</sub> salhexF <sub>4</sub> )Cu]	264 (50770)		369	613	
			(6270)	(140)	
[(Ph <sub>2</sub> salhex)Cu]	257 (37740)		352	616	
			(1970)	(120)	
[(salhexPh <sub>2</sub> )Cu]	262 (26910)				
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<sup>a</sup> Absorption maxima  $\lambda$  in nm; extinction coefficients  $\epsilon$  in L mol<sup>-1</sup> cm<sup>-1</sup> in parentheses, measured in MeCN.

degree of reversibility. Only for the complexes [((NH)<sub>2</sub>salhex)Cu], [((NH)<sub>2</sub>salhexPh<sub>2</sub>)Cu] and [(salhexPh<sub>2</sub>)Cu] and for the Zn derivative [((NH)<sub>2</sub>salhexPh<sub>2</sub>)Zn] (0.30 and 0.55 V) the oxidations are completely irreversible. On the cathodic scan markedly broadened, but essentially reversible reduction waves were observed for all Cu complexes while the Zn complex [((NH)<sub>2</sub>salhexPh<sub>2</sub>)Zn] does not exhibit any reduction wave up to potentials lower than -2.5 V.

Based on comparison with previous work (Table 2) [12,25,34b,46,48,50] we can assign the oxidations to phenolate-ligand centred processes (PhO<sup>-</sup>/PhO<sup>-</sup>), while the reduction processes correspond to the Cu(II)/Cu(I) couple. The partly irreversible character of the latter and the broadening of the waves are in line with earlier investigations and might be due to ligand exchange in not completely dried solvents (DMF/MeCN vs. H<sub>2</sub>O).[36,45,46,48] The waves at more negative potentials (e.g.  $E_{red2}$  in Fig. 3) are assigned to ligand-centred reduction processes which lead to de-coordination of the ligand.[46] Consequently, at very negative potentials the reduction waves of the uncoordinated salen<sup>2-</sup> can be observed (E < -2.5 V).

Within the series of our complexes the 3,5-tBu substitution stabilises the Cu(II) phenoxy radical complexes as expected, while 3-Ph substitution as in [(salhexPh<sub>2</sub>)Cu] does not provide stability. Also, when comparing our cyclohexyl-bridged systems with ethylenediamine derivatives ("salen" in Table 2) no marked differences were observed, the same is true when imine (salen) and amine (salan) type of systems were compared. More surprising is, that the imine-Ph substituted complex [(Ph<sub>2</sub>salhex)Cu] exhibits a partially reversible first oxidation at rather low potential (for CVs see Supplementary material). Not surprising is the completely reversible system [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu] containing a 3,5-F<sub>4</sub>-substitution pattern, since the stabilising role of the 3,5-tBu groups lies mainly in hampering follow-reactions of phenoxyl radicals [34,52]. The F substituents very probably contribute in the same way to the radical stability, although it cannot be excluded, that the imine CH<sub>3</sub> substituent might play an additional stabilising role. As a consequence for the presence of the electron-demanding F substituents, the oxidation potentials are quite high for this complex.

Finally, it should be noted, that comparison of our results with reported data is delicate in case where different solvents have been employed, since it is obvious that the potentials are markedly depending on the solvent. Our measurements using either MeCN or DMF showed marked differences even between these two seemingly similar solvents (see Supplementary material).

#### 3.4. UV–Vis absorption spectroscopy

Absorption spectra were recorded for all Cu complexes dissolved in MeCN from 200 nm to 800 nm (Table 3). All complexes show two intense absorption bands in the UV range (assigned to  $\pi$ - $\pi^*$  transition) and d-d absorption bands around 600 nm. In the range from 300 to 450 nm, there are further absorption bands of medium intensity.[61] For the complexes with amine linkers, these bands lie at about 400 nm ( $\varepsilon$  < 1000 L mol<sup>-1</sup> cm<sup>-1</sup>) and are attributed to the corresponding  $\pi$ - $\pi^*$  triplet absorptions, while complexes with imine linkers show bands at around 350 nm ( $\varepsilon$  > 1000 Lmol<sup>-1</sup> cm<sup>-1</sup>), which are assigned to metal to ligand charge transfer (MLCT) transitions. The spectrum of the zinc complex [((NH)<sub>2</sub>salhexPh<sub>2</sub>)Zn] showing the long-wavelength absorption band (attributable to  $\pi$ - $\pi^*$  transitions) at 307 nm supports the assignment for the Cu complexes.

#### 3.5. UV-Vis and EPR spectroelectrochemistry

UV/Vis spectroelectrochemical experiments, using an optical transparent thin-layer electrochemical (OTTLE) cell, were carried out on selected samples to support the assignment of the oxidation processes. Representative spectra were shown in Figs. 4 and 5, further spectra and a table summarising the results can be found in the Supplementary material. For the complexes [((NMe)<sub>2</sub>salhextBu<sub>4</sub>)Cu], [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu] and [((NH)<sub>2</sub>salhexPh<sub>2</sub>)Zn] two oxidation processes could be defined from the appearance of isosbestic points and reversibility, which is in line with the results from cyclic voltammetry, while for the other complexes only one oxidation process could be monitored. The spectra recorded upon anodic electrolysis of the complex [((NMe)<sub>2</sub>salhextBu<sub>4</sub>)Cu] at low potentials reveal the growth of bands at 520, 414 and 292 nm, while the 436, 297 and 255 nm bands decrease in intensity. The

absorption bands for the corresponding complex  $[((NH)_{2-} salentBu_4)Cu]^+$  were reported with maxima at 607, 527, and 413 nm in CH<sub>2</sub>Cl<sub>2</sub> solution [28], or at 626 and 384 nm in CH<sub>2</sub>Cl<sub>2</sub>:-DMSO (9:1) solution respectively [45], in line with the corresponding generation of phenoxyl radicals and the expected negative solvatochromism of these bands [25]. The long-wavelength band at 1600 nm reported in the first of the two studies, indicating the mixed-valent state (inter-valence charge transfer) could not be observed by us, due to spectrometer limitations.

Upon further oxidation (second wave) of [((NMe)<sub>2</sub>salhextBu<sub>4</sub>)-Cu] the 520 nm band vanishes, the 414 nm band increases and the 292 nm band shifts to 302 nm, slightly intensifying. Very similar observations have been reported before for the analogous [((NH)<sub>2</sub>salentBu<sub>4</sub>)Cu]<sup>2+</sup> species [28,45]. The latter state very probably represents both phenolate-moieties in the oxidised (phenoxy) state (spectra in the Supplementary material).

Anodic electrolysis of  $[(Me_2salhexF_4)Cu]$  leads to similar new bands at 542, 337 and 313 nm. Upon further oxidation (second wave) both the 542 and 337 nm band vanish, while the 313 nm band increases markedly. Also here, we assign both processes to the oxidation of the phenolate moieties. Interestingly, the characteristic band for the phenoxy state lies markedly higher in energy for the fluorine-substituted derivative than for the other complexes, which can be explained by the electron-withdrawing effect of the F substituents.

Rather surprising was, that the Zn(II) complex [((NH)<sub>2</sub>sal-hexPh<sub>2</sub>)Zn] also allowed to monitor two separate oxidation processes (Fig. 4). Both processes create species which exhibit intense structured bands ranging from around 400 to 600 nm, assignable to transitions within the phenoxyl radical ligands.

Even more surprising was, that the complexes  $[(Ph_2salhex)Cu]$ ,  $[((NH)_2salhex)Cu]$  and  $[((NH)_2salhexPh_2)Cu]$  also revealed the growth of a band attributable to the generation of phenoxyl radical



Fig. 4. Absorption spectra of [((NH)<sub>2</sub>salhexPh<sub>2</sub>)Zn] during anodic electrolysis in MeCN/nBu<sub>4</sub>NPF<sub>6</sub> at 298 K, from 0 to 0.4 V (left) and from 0.4 to 0.8 V (right).



complexes (Fig. 5). For [(Ph<sub>2</sub>salhex)Cu] the partially reversible behaviour allows the observation of the corresponding species for a few minutes, while for [((NH)<sub>2</sub>salhex)Cu] and [((NH)<sub>2</sub>salhexPh<sub>2</sub>)Cu] the signals vanished rapidly. Although both complexes are not able to stabilise phenoxyl radicals (as indicated by irreversible oxidation waves), intense absorption bands around 450 nm (undoubtedly caused by phenoxyl radicals) were observed in both cases.

In previous work, the energy of the absorption bands assigned to a Cu(II)-bound phenoxyl-radical (400–500 nm) was taken as a measure for the radical stabilisation. The fully stabilised systems were expected to show absorption maxima shifted to lower energies, while the non- and partly stabilised complexes were expected to show charge transfer bands shifted to higher energy [25]. For the complexes investigated herein, the energy of the absorption increases for the series Me<sub>2</sub>salhexF<sub>4</sub> < (NMe)<sub>2</sub>salhextBu<sub>4</sub> < (NH)<sub>2</sub>salhexPh<sub>2</sub> < Ph<sub>2</sub>salhex < (NH)<sub>2</sub>salhex, and correlates roughly with the substitution pattern, the low oxidation potential and the reversibility of the oxidation(s). In this sense, the complexes of Me<sub>2</sub>salhexF<sub>4</sub> and (NMe)<sub>2</sub>salhextBu<sub>4</sub> are at the lower end, and the (NH)<sub>2</sub>salhex derivative at higher energy.

In further experiments we tried to record EPR spectra of the oxidised species, generated from the parent Cu(II) complexes (dissolved in MeCN) by chemical oxidation, using NO[BF<sub>4</sub>] as oxidant [27]. The samples were oxidised at ambient temperature and then measured at 110 K (glassy frozen solutions). For none of the complexes reasonable signals were detected, which is in line with recent observations on the related complex [((NH)<sub>2</sub>salentBu<sub>4</sub>)Cu]<sup>+</sup> [27,45]. The ground state of Cu(II) phenoxyl radicals can be either S = 1 if the unpaired electrons on Cu(II) and the phenoxyl radical couple ferromagnetically, or S = 0 if an antiferromagnetic coupling occurs (EPR silent). This can be rationalised from the orbital overlapping becoming ideal if the Cu–O–C angle is approximately 130°, and the angle between the Cu coordination plane and the phenol ring is about 90°.[25,31] In [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu] the Cu-O-C angle is found to be around 127° (XRD), while the plane angle mentioned is 7.6°. Thus, the geometrical requirements for efficient antiferromagnetic coupling are not given, and the oxidised species thus might a triplet ground state (S = 1). However, from our experiments we cannot discriminate between the two cases (S = 0 or S = 1), since also for the S = 1 case our experimental conditions would not allow the detection of the corresponding signal [45].

To support the assignment on the reduction processes the complexes [((NMe)<sub>2</sub>salhextBu<sub>4</sub>)Cu], [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu] and [(NH)<sub>2</sub>salhex)Cu] were submitted to cathodic electrolysis in the OTTLE cell. Reduction leads in all three cases to spectra characterised by a red shift of the MLCT bands, while the  $\pi$ - $\pi$ \* absorption bands are less affected, thus confirming the assignment for the reduction Cu(II) to Cu(I). Unfortunately, the weak d–d absorption bands of



**Fig. 6.** X-band EPR spectra of  $[(Me_2salhexF_4)Cu]$  measured during electrochemical reduction from 0 to -1.3 V (first reduction) in MeCN/*n*Bu<sub>4</sub>NPF<sub>6</sub> at 298 K.

the Cu(II) species could not be observed in the optically transparent thin layer electrochemical (OTTLE) cell. To support our conclusions we thus performed reductive EPR spectroelectrochemistry in the same potential range and beyond. E.g. reducing a MeCN solution of the complex [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu] at potential higher than – 0.8 V lead to the loss of the EPR signal typical for Cu(II) (Fig. 6).

Upon prolonged electrolysis at potential lower than -1.6 V, a narrow unresolved signal evolves at  $g_{iso} = 2.0045$ , which might be assigned to a ligand-centred radical  $[(Me_2salhexF_4)^{-3-})Cu(I)]^{2-}$ . The same experiment was carried out using the zinc complex  $[((NH)_{2-salhexPh_2})Zn]$ , and a similar spectrum was obtained ( $g_{iso} = 2.0046$ ; for spectra see Supplementary material). Both EPR signals do not show any hfs (at a resolution of 3 G) to <sup>14</sup>N (nor to <sup>1</sup>H), thus, the N atoms of the ligands do not contribute markedly to electron density of the radical ligands singly occupied molecular orbital (SOMO).

#### 3.6. Catalytic test reactions

A standard method to generate the catalytically active species is to use a Cu(I) precursor complex in the presence of aerial oxygen, as described in Eq. (1). This method has previously been applied to generate the active enzyme from isolated apo Galactose Oxidase (GO) *in vitro* [62].

$$Cu(I) - [OPh^{-}] + O_2 + 2H^{+} \leftrightharpoons Cu(II) - [OPh] + H_2O_2$$
(1)

For the test reactions, the ligands were mixed with  $[(Cu(OTf))_2 (\mu-toluene)]$  and this catalyst solution was used at  $10\%_{mol}$  concentration. Benzyl alcohol was added and the reaction was performed at room temperature in the presence of solid NaOH (see Section 2). The product benzaldehyde was detected by <sup>1</sup>H NMR spectroscopy using the aldehyde proton to monitor the product concentration. Samples were taken after 1 and 17 h reaction time. Table 4 summarises the results of the catalytic test reactions. Importantly, in control experiments (under the same conditions) neither the free ligands nor Cu(OTf)<sub>2</sub> showed any catalytical activity.

We observed product formation for four of the salen complexes (Table 4), only the complexes containing the salhexPh<sub>2</sub> and the (NH)<sub>2</sub>salhex ligand failed. After one hour the highest activity was observed for the 3,5-tBu-substituted complex [((NMe)<sub>2</sub>salhextBu<sub>4</sub>)Cu] (note that the catalyst concentration was only 3% in this case) in line with earlier reports, concluding that 3,5-substitution on the phenol core stabilises the phenoxyl radicals and thus promotes the catalytic reaction [12,25,27,28]. Also in line with this rule is the behaviour of the fluorine substituted complex [(Me2salhexF<sub>4</sub>)Cu] and to some extent the (NH)<sub>2</sub>salhexPh<sub>2</sub> derivative, having bulky Ph substituents in the three positions. The complex [(Ph<sub>2</sub>salhex)Cu] obviously does not follow this rule but nevertheless shows catalytic activity comparable to the other derivatives. On the other hand this behaviour is in line with the partly reversible CV wave for the first oxidation of this complex and the high rate of phenoxyl radical generation in our spectroelectrochemical experiments (Fig. 5). Furthermore, also the un-substituted salen

Table	4
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Results of the catalytic test reactions for salen Cu complexes.

Salen ligand	% product after	% product after	Turn over
	1 h	17 h	number
(NH) <sub>2</sub> salhexPh <sub>2</sub>	25.6	67.6	$7.1 \cdot 10^{-4}$ $2.5 \cdot 10^{-4}$ $1.3 \cdot 10^{-4}$ $-$ $3 \cdot 1.10^{-4}$
Me <sub>2</sub> salhexF <sub>4</sub>	9.1	81.5	
Ph <sub>2</sub> salhex	4.8	70.0	
Salhexph <sub>2</sub>	a,b	<sub>a,b</sub>	
(NH) <sub>2</sub> salhex	b	b	
(NMe) <sub>2</sub> salhextBu	3.3 <sup>c</sup>	38.8 <sup>c</sup>	

Extensive precipitation occurred during the reaction.

' No product was observed.

<sup>c</sup> The reaction was performed with 3%<sub>mol</sub> instead of 10%<sub>mol</sub>.

complex [(salPrOH)Cu] (PrOH =  $-CH_2-CH(OH)-CH_2-$  as linker) has been reported to show considerable activity in the oxidation of primary alcohols und very basic conditions [16]. For this system it was concluded, that also the stabilisation of the Cu(I) species might be crucial for the catalytic activity [28]. In our experiments the unsubstituted complex [((NH)<sub>2</sub>salhex)Cu] gave no benzaldehyde product, while for the complex [(salhexPh<sub>2</sub>)Cu] extensive precipitation probably explains the lack of activity.

Not unexpectedly, the product yield was far higher for all four active complexes after 17 h, which points to a slow formation of the catalytically active species. Previous investigations gave evidence for a substrate-binding equilibrium (second order kinetics), which markedly influences the reaction rate [12b,28]. Very recently, for the complex [(salhextBu<sub>2</sub>OMe<sub>2</sub>)Cu] very rapid decomposition of the complex in the presence of benzyl alcohol, very low substrate affinity and restoration of the complex upon addition of NEt<sub>3</sub> confirmed that the reaction proceeds via Eq. (2) [28,52].

 $2[(salhextBu_2OMe_2)Cu]^+$ 

+ PhCH2OH
$$\Rightarrow$$
2[(HsalhextBu<sub>2</sub>OMe<sub>2</sub>)Cu]<sup>+</sup> + PhCHO (2)

Interestingly, the complex [((NH)<sub>2</sub>salhexPh<sub>2</sub>)Cu] showed rather high product concentration after 1 h reaction time, but markedly dropped in catalytic activity compared to the other derivatives over a longer period of time, which might represent some evidence for different substrate-binding abilities of the investigated Cu complexes. Detailed studies on the reaction kinetics will thus be carried out in the near future.

From the calculated turn over numbers (Table 4), we can conclude that all our complexes catalyse the oxidation reaction at rather low reaction rates compared to systems as 1,1'-binaphtyl linked [(salbntBu<sub>4</sub>)Cu] [12a], but similar to other GO model systems [14]. Frequently, the paramagnetic ground state (S = 1) of such complexes is discussed as one of the reasons for the reluctant reaction [25].

#### 4. Conclusions

A number of salen-Cu complexes bearing different combinations of substituents and linkers were synthesised and investigated in detail. All complexes show two electrochemical oxidation processes at comparably low potentials, the lowest values lie around 0.3 V. The first oxidation of [((NMe)<sub>2</sub>salhextBu<sub>4</sub>)Cu], [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu] occurs fully reversibly, while for the complex [(Ph<sub>2</sub>salhex)Cu] partly reversible behaviour is observed. For all other complexes the oxidation is completely irreversible on the timescale of the CV experiment. For the first two complexes the reversible behaviour can be related to the presence of substituents in the 3,5-position of the phenol-core, stabilising the phenoxyl radical generated by the one-electron oxidation process. Consequently, [((NMe)<sub>2</sub>salhextBu<sub>4</sub>)Cu] and [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu] exhibit a second oxidation process at slightly higher potentials, which is fully reversible for [((NMe)<sub>2</sub>salhextBu<sub>4</sub>)Cu] and partly reversible for [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu], which might be due to the far higher oxidation potential required for the latter. The second oxidation processes for all other complexes were irreversible. Spectroelectrochemical (UV-Vis) investigations clearly showed that these oxidation processes are due to the formation of phenoxyl radical species. The energy of the observed phenoxyl-to-metal charge transfer band correlates roughly with the stability of the radicals as inferred from the reversibility of the redox waves and assumed from the substitution pattern. Corresponding spectroelectrochemical EPR experiments did not show signals for the oxidised complexes [(PhO<sup>•</sup>)Cu(II)]<sup>+</sup>, although a triplet ground state can be assumed from the geometry of the complexes. In both the solid state (from XRD of  $[(Me_2salhexF_4)Cu]$  reported herein, others previously) and in solution (from EPR in glassy frozen solution) the complexes exhibit a relatively rigid square planar geometry for the Cu atom which does not allow antiferromagnetic coupling of the unpaired electron localised in the phenoxyl ligand and the Cu(II) ion. Largely reversible reduction waves for all complexes were assigned to the Cu(II)/Cu(I) couple which could be substantiated by EPR and UV–Vis spectroelectrochemistry.

Very preliminary catalytic test reactions (oxidation of benzyl alcohol by aerial O<sub>2</sub>), [((NMe)<sub>2</sub>salhextBu<sub>4</sub>)Cu], [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu], [(Ph<sub>2</sub>salhex)Cu] and [((NH)<sub>2</sub>salhexPh<sub>2</sub>)Cu] revealed reasonable activities, although compared to established salen Cu catalysts, the overall reaction rates of these complexes are low. Interestingly, amongst the active catalysts in our series, we find imine as well as amine systems, stabilised and non-stabilised phenol cores and the correlation of the activity with the structures is not straightforward. Neither the rigidity of the linker group nor the stabilisation of the phenoxyl radicals by substituents seems to be an exclusion criterion. While the activities of the substituted systems [((NMe)<sub>2-</sub> salhextBu<sub>4</sub>)Cu], [(Me<sub>2</sub>salhexF<sub>4</sub>)Cu] and [((NH)<sub>2</sub>salhexPh<sub>2</sub>)Cu] were not unexpected in terms of the established rules (substituent-stabilised systems are active catalyst), the good catalytic performance of [(Ph<sub>2</sub>salhex)Cu] was unexpected. However, if catalytic activity correlates with radical stability, the activity of [(Ph<sub>2</sub>salhex)Cu] is in line with the partially reversible character of the oxidation observed for this complex. Furthermore, the failure of [((NH)<sub>2</sub>salhex)Cu] and [(salhexPh<sub>2</sub>)Cu] to perform catalysis goes along with the irreversibility of the oxidation of these two complexes. Therefore, electrochemical reversibility seems to be a reliable tool for the estimation of catalytic activity of such complexes, whereas predictions based on the substitution pattern might exclude reasonable candidates for catalysis. Strangely, the behaviour of the system [((NH)<sub>2</sub>salhexPh<sub>2</sub>)Cu] (irreversible oxidation, good catalysis) is not in line with this correlation. However, in this case we have evidence that the catalytic mechanism for this complex is different from the other complexes and future studies will try to allow more comprehensive and unequivocal conclusions.

#### Acknowledgements

We would like to thank Dr. Ingo Pantenburg and Ms. Ingrid Müller, University of Cologne, for the collection of crystal data and the "Studienstiftung des Deutschen Volkes" for financial support (KB).

#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.08.016.

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