

# Structural, Magnetic, and Electrochemical Characterization of Iron(III) and Cobalt Complexes with Penta-N<sub>3</sub>O<sub>2</sub>-dentate Ligands

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Six new mononuclear [Fe<sup>III</sup>(L<sub>Br,Cl</sub>)X]-complexes (L<sub>Br,Cl</sub> is the dianionic penta-N<sub>3</sub>O<sub>2</sub>-dentate Schiff base ligand N,N'-bis(2'-hydroxy-3-bromo-5-chlorobenzylidene)-1,6-diamino-3-azahexane; X: Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>, NCO<sup>-</sup>, NCS<sup>-</sup>, NCSe<sup>-</sup>, CN<sup>-</sup>) were synthesized and their structures, magnetic and electrochemical properties studied. Structure analysis and magnetic measurements showed

that [Fe<sup>III</sup>(L<sub>Br,Cl</sub>)CN] is in the low spin state and the other five complexes are in high spin states. Furthermore, the trinuclear mixed valent cobalt complex {[Co<sup>III</sup>(L<sub>H,H</sub>)CN]<sub>2</sub>[Co<sup>II</sup>(1-methylimidazole)<sub>3</sub>(H<sub>2</sub>O)]} was prepared and its magnetic behavior studied.

## Introduction

The trend of reducing the size of electronic components in technological applications lead to recent developments in the field of intelligent molecular devices. Coordination compounds, showing switching behavior, are promising candidates to be used in applications such as quantum devices, high density data storages and sensors.<sup>[1–5]</sup> Bistable complexes with at least two thermodynamically stable electronic states or phases are

therefore of increasing interest because of their reversible changes of optical, magnetic and electronic properties by external stimuli such as light, temperature, pressure, X-rays or guest absorption/desorption.<sup>[6–11]</sup> These properties can be adjusted by proper molecular design and controlled assemblies of supramolecular networks.<sup>[12–15]</sup>

Complexes with Schiff base ligands have the advantages of mostly simple syntheses and chemical modifications are easily possible.<sup>[16–20]</sup> One example is the series of [M<sup>III</sup>(L<sub>R1,R2</sub>)X] complexes (M: Co or Fe; L: N,N'-bis(2'-hydroxybenzylidene)-1,6-diamino-3-azahexane; X: pseudo halide or organic molecule) which was studied extensively in the past (Figure 1).<sup>[21–27]</sup> The Co(III) complexes are in low spin (LS) states,<sup>[27]</sup> whereas some Fe(III) complexes showed temperature induced reversible conversions between LS and high spin (HS) states, called spin crossover (SCO).<sup>[21–26,28,29]</sup> The spin state and SCO properties of these iron(III) complexes can be changed by introducing substituents to the Schiff base ligand and by exchanging the monodentate ligand. Especially the complexes [Fe<sup>III</sup>(L<sub>H,Cl</sub>)X],<sup>[22]</sup> [Fe<sup>III</sup>(L<sub>H,Br</sub>)X]<sup>[24]</sup> and [Fe<sup>III</sup>(L<sub>Cl,Cl</sub>)X]<sup>[29]</sup> (X=N<sub>3</sub>, NCS, NCSe) should be

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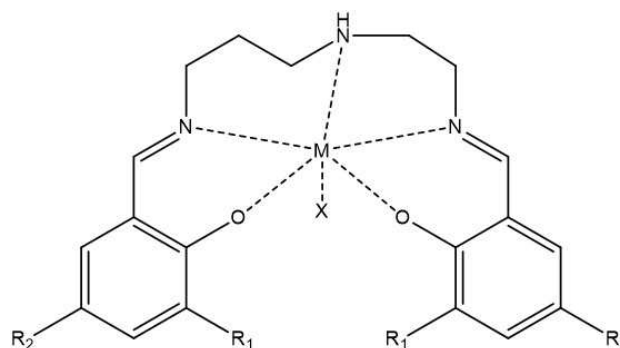
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**Figure 1.** Mononuclear complex [M(L<sub>R1,R2</sub>)X] with M for Co(III) or Fe(III), R<sub>1</sub>, R<sub>2</sub> for different substituents (e.g. R<sub>1</sub>: Br, R<sub>2</sub>: Cl) and X for pseudo halides or organic molecules.

mentioned, which show a temperature induced SCO, whereas the compounds  $[\text{Fe}^{\text{III}}(\text{L}_{\text{Br,Br}})\text{X}]^{[29]}$  are only in the HS state. Complexes with  $\text{X}=\text{CN}^-$  are always in the LS state,<sup>[21,22,30]</sup> but some cyanide bridged multinuclear complexes such as  $[\text{Fe}^{\text{II}}(\text{CN})_6(\text{Fe}(\text{L}_{\text{H,H}}))_6]\text{Cl}_2$  were reported to show SCO.<sup>[30–33]</sup> Moreover, these compounds belong to the class of Prussian blue analogues and are not only interesting because of their SCO properties but they may show an electron transfer-coupled spin transition (ETCST)<sup>[34–36]</sup>. The electron transfer occurs between two metal sites within a cyanide bridged redox pair such as  $[\text{Co}^{\text{II}}_{\text{HS}}\text{Fe}^{\text{III}}_{\text{LS}}]$  and  $[\text{Co}^{\text{III}}_{\text{LS}}\text{Fe}^{\text{II}}_{\text{LS}}]$ .<sup>[35,37–40]</sup> Occurrence of the ETCST needs proper matching of the redox properties, which can be controlled by modifying the precursors, such as substituents of the capping ligands,<sup>[39–41]</sup> which is described in detail by M. Nihei for known building blocks.<sup>[42]</sup> However, so far no complex with a  $[\text{M}(\text{L}_{\text{R1R2}})]^+$ -building block have been proven to show the ETCST behavior. Furthermore, the redox properties of only a few complexes with  $\text{L}_{\text{R1R2}}$  have been reported yet.<sup>[27,30–33,43,44]</sup>

Herein we report a series of six new  $[\text{Fe}(\text{L}_{\text{Br,C}})\text{X}]$  ( $\text{X}: \text{Cl}^-, \text{N}_3^-, \text{NCO}^-, \text{NCS}^-, \text{NCSe}^-, \text{NC}^-$ ) complexes. In extension to the previously reported complexes  $[\text{Fe}^{\text{III}}(\text{L}_{\text{Cl,C}})\text{X}]$  and  $[\text{Fe}^{\text{III}}(\text{L}_{\text{Br,Br}})\text{X}]$ ,<sup>[29]</sup> which show SCO and HS behavior, respectively, the temperature depending magnetic behavior of the six new complexes was analyzed. In order to use  $[\text{M}^{\text{III}}(\text{L}_{\text{R1,R2}})\text{X}]$  building blocks for designing ETCST complexes, we analyzed the redox properties of the  $[\text{Fe}(\text{L}_{\text{Br,C}})\text{X}]$  complexes and of different derivatives.<sup>[22,24,25,30]</sup> Thereby we determined a range of redox potentials that can be accessed by exchanging the substituents  $\text{R}_1$  and  $\text{R}_2$  with hydrogen and  $\text{NO}_2$ . The hydrogen is neutral, while  $\text{NO}_2$  is expected to show strong -M (mesomeric) and -I (inductive) effects resulting in a decreased electron density at the Fe ion. Furthermore, we prepared the trinuclear mixed valence compound  $[\text{Co}^{\text{II}}(\text{L}_{\text{H,H}})\text{CN}]_2[\text{Co}^{\text{I}}(1\text{-methylimidazole})_3] \cdot 1.5 \text{H}_2\text{O}$  ( $[\text{Co}_2\text{Co}]$ )

from the mononuclear precursor complex  $[\text{Co}(\text{L}_{\text{H,H}})\text{CN}]$  and analyzed its structure and magnetic behavior.

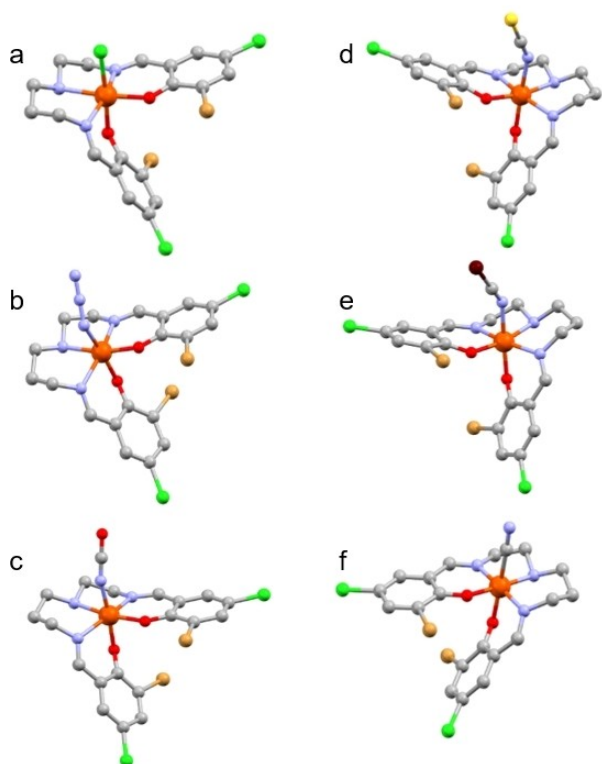
## Results and Discussion

### Structural Data

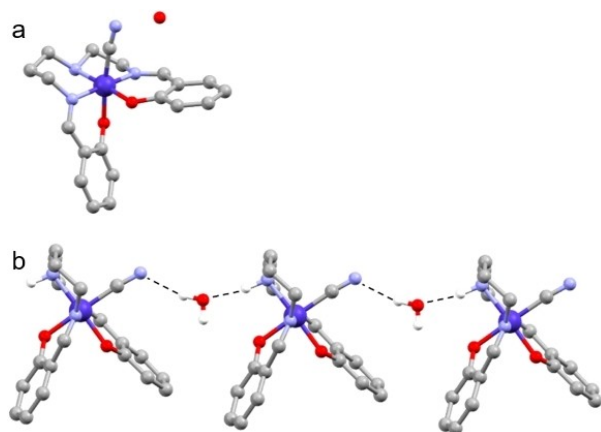
The crystallographic and structural data are summarized in Table 1. Metal ions in the six  $[\text{Fe}(\text{L}_{\text{Br,C}})\text{X}]$  (Figure 2) and the  $[\text{Co}(\text{L}_{\text{H,H}})\text{CN}]$  (Figure 3) complexes are octahedrally coordinated and the compounds  $[\text{Fe}(\text{L}_{\text{Br,C}})\text{NCS}]$  and  $[\text{Fe}(\text{L}_{\text{Br,C}})\text{NCSe}]$  are isostructural to each other. This six coordination sites of the Fe(III)/Co(III) ions are occupied by three nitrogen and two oxygen atoms and a monodentate halogen or pseudo halogen ligand. The three nitrogen atoms are coordinated in *fac* and the two oxygen in *cis* position. The mononuclear complex is overall neutral due to the two deprotonated hydroxyl groups at  $\text{L}_{\text{R1,R2}}$  and the negatively charged monodentate ligand. While the complexes can exist in two different enantiomers, all the samples crystallized as racemic mixture in the monoclinic non chiral space group  $P2_1/c$ . Furthermore, the six structures are showing slightly offset  $\pi$ - $\pi$  stacking with centroid-centroid distances between 3.58 Å and 4.43 Å of the phenyl rings (Table S1). Most distances are comparable to those described for similar complexes,<sup>[22,24]</sup> except for  $[\text{Fe}(\text{L}_{\text{Br,C}})\text{NCO}]$  whose stacking distance is unusual small with 3.58 Å. The structure of  $[\text{Co}(\text{L}_{\text{H,H}})\text{CN}]$  is similar to its precursor  $[\text{Co}(\text{L}_{\text{H,H}})\text{Cl}]$ <sup>[27]</sup> and both form a chain structure with hydrogen bonded water molecules (Figure 3). Crystals of the trinuclear complex  $[\text{Co}_2\text{Co}]$  (Figure 4a) grow in the  $P2_1/n$  space group. In the trinuclear complex the two  $[\text{Co}(\text{L}_{\text{H,H}})\text{CN}]$  and the central  $[\text{Co}^{\text{I}}(1\text{-methylimidazole})_3]^{2+}$  form a cyanide bridged linear structure. Note that three

**Table 1.** Crystallographic and structural data.

	$[\text{Fe}(\text{L}_{\text{Br,C}})\text{Cl}]$ $\text{C}_{19}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{FeN}_3\text{O}_2$	$[\text{Fe}(\text{L}_{\text{Br,C}})\text{N}_3]$ $\text{C}_{19}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{FeN}_6\text{O}_2$	$[\text{Fe}(\text{L}_{\text{Br,C}})\text{NCO}]$ $\text{C}_{20}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{FeN}_4\text{O}_3$	$[\text{Fe}(\text{L}_{\text{Br,C}})\text{NCS}]$ $\text{C}_{20}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{FeN}_4\text{O}_2\text{S}$
<i>T</i> in K	100	100	233	233
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
<i>a</i> in Å	9.410(2)	12.1339(12)	9.5265(1)	8.4762(1)
<i>b</i> in Å	9.496(2)	12.4927(13)	15.0275(1)	24.0299(2)
<i>c</i> in Å	25.951(5)	15.2751(16)	16.5494(1)	12.2342(1)
$\alpha/\gamma$ in °	90	90	90	90
$\beta$ in °	93.51(3)	104.735(1)	106.15	106.26
<i>V</i> in Å <sup>3</sup>	2314.7(8)	2239.3(4)	2275.71(3)	2392.25(4)
<i>Z</i>	4	4	4	4
$R_1/wR_2$ ( $I > 2\sigma$ )	0.0416/0.1175	0.0210/0.0529	0.0373/0.0988	0.0346/0.0946
	$[\text{Fe}(\text{L}_{\text{Br,C}})\text{NCSe}]$ $\text{C}_{20}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{FeN}_4\text{O}_2\text{Se}$	$[\text{Fe}(\text{L}_{\text{Br,C}})\text{CN}]$ $\text{C}_{20}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{FeN}_4\text{O}_2$	$[\text{Co}(\text{L}_{\text{H,H}})\text{CN}]$ $\text{C}_{20}\text{H}_{23}\text{CoN}_4\text{O}_3$	$[\text{Co}_2\text{Co}]$ $\text{C}_{52}\text{H}_{63}\text{Co}_3\text{N}_{14}\text{O}_{5.5}\text{B}_2\text{F}_8$
<i>T</i> in K	100	100	100	100
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
<i>a</i> in Å	8.3923(5)	8.1885(11)	9.2557(11)	17.701(3)
<i>b</i> in Å	24.2183(16)	11.1909(15)	12.2576(15)	13.489(2)
<i>c</i> in Å	12.2306(8)	24.353(3)	17.361(2)	24.558(4)
$\alpha/\gamma$ in °	90	90	90	90
$\beta$ in °	106.571(1)	95.835(2)	101.523(2)	101.564(2)
<i>V</i> in Å <sup>3</sup>	2382.6(3)	2220.1(5)	1929.9(4)	5744.7(17)
<i>Z</i>	4	4	4	4
$R_1/wR_2$ ( $I > 2\sigma$ )	0.0289/0.0742	0.0485/0.1089	0.0331/0.0824	0.0806/0.2228

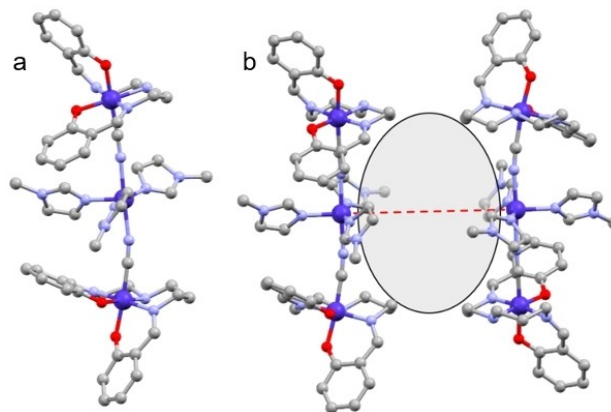


**Figure 2.** Molecular structure of (a)  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{Cl}]$ ; (b)  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{N}_3]$ ; (c)  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{NCO}]$ ; (d)  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{NCS}]$ ; (e)  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{NCSe}]$ ; (f)  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{CN}]$ . Hydrogen atoms have been omitted for clarity. Color code: C, gray; N, light blue; O, red; Fe, orange; Cl, green; Br, light brown; S, yellow; Se, brown red.



**Figure 3.** (a) Molecular structure of  $[\text{Co}(\text{L}_{\text{H,H}})\text{CN}]$ . (b) Hydrogen bonding network of  $[\text{Co}(\text{L}_{\text{H,H}})\text{CN}]$ . Most hydrogen atoms have been omitted for clarity. Color code: C, gray; N, light blue; O, red; Co, dark blue.

coordination sites of the centered Co(II) are coordinated by 1-methylimidazole. The fourth ligand is considered to be a strongly disordered water molecule which could not be modeled correctly. Therefore, its electron density was treated by the Olex 2 solvent mask<sup>[45]</sup> (BYPASS<sup>[46]</sup>). The void (Figure 4b) is considered to be filled with 1.5 water molecules per asymmetric unit which correspond to 15 electrons with 14



**Figure 4.** (a) Molecular structure of  $[\text{Co}_2\text{Co}]$ . (b) Void between two  $[\text{Co}_2\text{Co}]$ . Hydrogen atoms and counter anions have been omitted for clarity. Color code: C, gray; N, light blue; O, red; Co, dark blue.

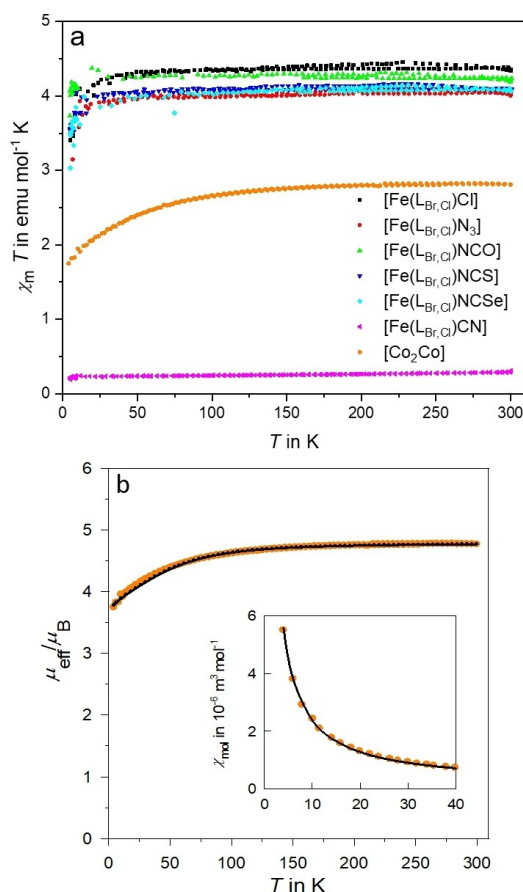
found and is supported by the elemental analysis. Therefore, three water molecules are located between two neighboring complexes with a Co(II)–Co(II) distance of 9.191(2) Å, which suits the distance for a Co–H<sub>2</sub>O–H<sub>2</sub>O–H<sub>2</sub>O–Co bridge (Figure S3). The angles between the Co(II) ligands match with a distorted octahedral coordination sphere (Table S2) as expected by the VSEPR concept.<sup>[47,48]</sup> Additionally, the two charge balancing  $[\text{BF}_4]^-$  anions do not occupy this coordination site (Figure S4).

Bond lengths (Table S3) of  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{CN}]$  are characteristic for a Fe(III) in the LS state, while the bond length of the other five Fe(III) complexes are indicating a HS state.<sup>[22,24,30]</sup> The Co(III) ions bond lengths in  $[\text{Co}(\text{L}_{\text{H,H}})\text{CN}]$  and  $[\text{Co}_2\text{Co}]$  are typically for the LS state. Moreover, the bond lengths of the Co(II) ion are typically for a octahedral coordinated Co(II) in the HS state.<sup>[37,40]</sup>

### Magnetic Data

Temperature dependences of magnetic data were measured for all compounds except  $[\text{Co}(\text{L}_{\text{H,H}})\text{CN}]$  in the range of 5–300 K (Figure 5a).

The  $\chi_m T$  values for the six Fe(III) show similar behavior as expected for HS and LS states. For the low temperature range magnetic anisotropy might be the origin, as expected for zero-field splitting (ZFS).  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{CN}]$  shows a  $\chi_m T$  value of 0.28 emu mol<sup>-1</sup> K which is typically for a Fe(III) in the LS state<sup>[22,30]</sup> with a slightly reduced g factor. The other five Fe(III) complexes showed  $\chi_m T$  values of 4.0–4.4 emu mol<sup>-1</sup> K which are characteristic for Fe(III) complexes in HS state<sup>[21,22,24,25,30]</sup> and the results agree with the coordination bond length. Moreover,  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{NCO}]$  showed weak intermolecular ferromagnetic interactions below 20 K which might be caused through a stronger  $\pi$ – $\pi$  stacking compared to the other five complexes. Unlike the compound  $[\text{Fe}^{\text{III}}(\text{L}_{\text{Cl,Cl}})\text{NCSe}]$ , which shows SCO with a broad thermal hysteresis, this series of complexes only shows one spin state. The  $\chi_m T$  value for  $[\text{Co}_2\text{Co}]$  is at 300 K 2.81 emu mol<sup>-1</sup> K which is consistent with an insulated  $S = 3/2$  spin system with enlarged  $g_{\text{av}} > g_e$  of the two LS–Co(III) and HS–Co(II).<sup>[49–52]</sup> These



**Figure 5.** (a)  $\chi_m T - T$  plots of  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{X}]$  and  $[\text{Co}_2\text{Co}]$ . (b)  $\mu_{\text{eff}}/\mu_B - T$  and  $\chi_m - T$  plot and fit of  $[\text{Co}_2\text{Co}]$ .

values are slightly decreasing as the temperature lowers until  $\sim 100$  K, followed by a gradual decrease of  $\chi_m T$  which is typical for Co(II) systems with large ZFS. Details of the fitted magnetic data of  $[\text{Co}_2\text{Co}]$  (Figure 5b) are summarized in the supporting information (Table S4).

### Electrochemical Data

The cyclic voltametric (CV) measurements of the six  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{X}]$  complexes and previously reported five  $[\text{Fe}(\text{L}_{\text{H,R2}})\text{Cl}/\text{CN}]$  complexes showed quasi reversible redox waves of  $[\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}]$  processes. The redox potentials are summarized in Table 2. Note that no redox wave was observed for  $[\text{Co}_2\text{Co}]$ . Moreover, the second reduction wave of  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{NCSe}]$  might be caused by a partial solvent exchange of the monodentate ligand.

The redox potentials of the  $[\text{Fe}(\text{L}_{\text{R1,R2}})\text{Cl}/\text{CN}]$  systems (Figure 6) show a clear trend for varying the phenyl substituents (R1,R2). By introducing electron withdrawing groups,  $-\text{NO}_2$  ( $-I$ ),  $-M$ ),  $-\text{Cl}$  and  $-\text{Br}$  ( $-I$ ),  $E_{1/2}$  is shifted to higher values. The redox potential shift for the chloride compounds  $\Delta E_{1/2}(E_{1/2}[\text{Fe}(\text{L}_{\text{H,H}})\text{Cl}] - E_{1/2}[\text{Fe}(\text{L}_{\text{R1,R2}})\text{Cl}])$  is  $-0.105$  V for  $[\text{Fe}(\text{L}_{\text{H,NO}_2})\text{Cl}]$  and  $-0.075$  V for  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{Cl}]$ . For the cyanide complexes the  $\Delta E_{1/2}$  value of  $E_{1/2}[\text{Fe}(\text{L}_{\text{H,H}})\text{CN}] - E_{1/2}[\text{Fe}(\text{L}_{\text{R1,R2}})\text{CN}]$  is about  $-0.05$  V for  $[\text{Fe}(\text{L}_{\text{H,Cl/Br}})\text{CN}]$ ,

**Table 2.** Redox potentials vs SCE of the mononuclear  $[\text{Fe}(\text{L}_{\text{R1,R2}})\text{X}]$  compounds.

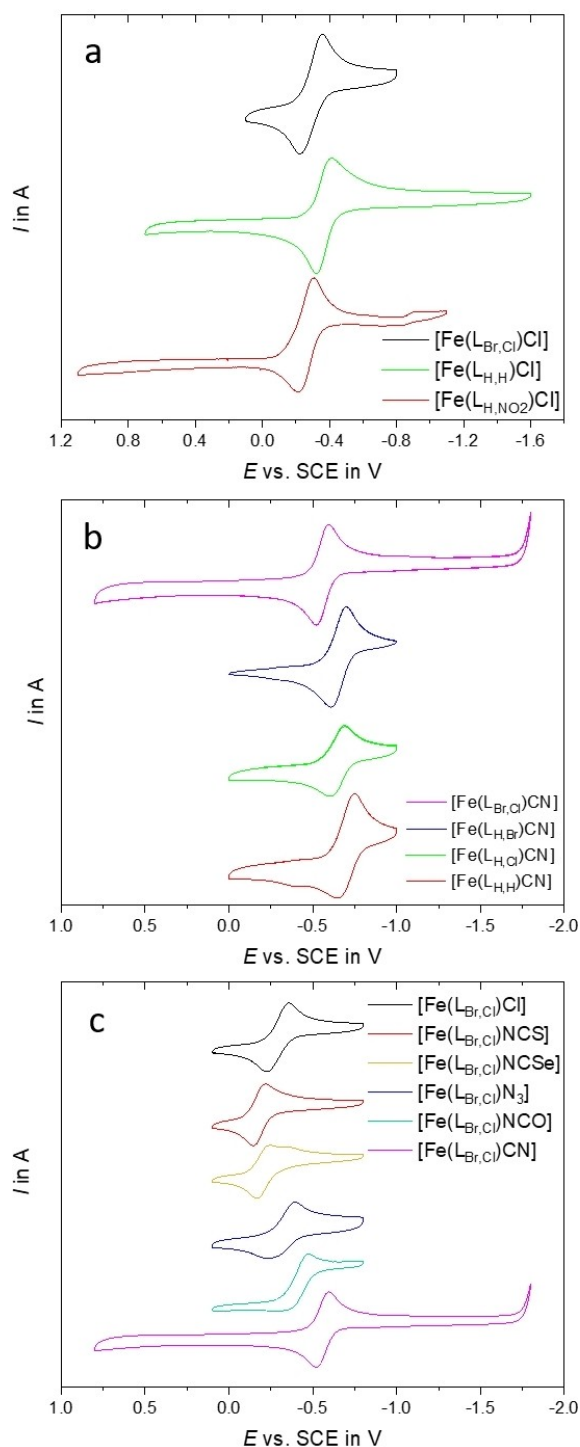
	$E_{\text{red}}$	$E_{\text{ox}}$	$E_{1/2}$
$[\text{Fe}(\text{L}_{\text{H,H}})\text{Cl}]$	$-0.41$ V	$-0.32$ V	$-0.365$ V
$[\text{Fe}(\text{L}_{\text{H,NO}_2})\text{Cl}]$	$-0.31$ V	$-0.21$ V	$-0.26$ V
$[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{Cl}]$	$-0.36$ V	$-0.22$ V	$-0.29$ V
$[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{NCS}]$	$-0.22$ V	$-0.14$ V	$-0.18$ V
$[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{NCSe}]$	$-0.25/-0.35$ V	$-0.17$ V	$-0.21$ V/ $-0.26$ V
$[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{N}_3]$	$-0.4$ V	$-0.24$ V	$-0.32$ V
$[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{NCO}]$	$-0.48$ V	$-0.28$ V	$-0.38$ V
$[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{CN}]$	$-0.59$ V	$-0.52$ V	$-0.555$ V
$[\text{Fe}(\text{L}_{\text{H,H}})\text{CN}]$	$-0.75$ V	$-0.65$ V	$-0.70$ V
$[\text{Fe}(\text{L}_{\text{H,Cl}})\text{CN}]$	$-0.69$ V	$-0.61$ V	$-0.65$ V
$[\text{Fe}(\text{L}_{\text{H,Br}})\text{CN}]$	$-0.70$ V	$-0.61$ V	$-0.655$ V

but for  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{CN}]$  with  $-0.145$  V nearly twice of the shifts expected from Chloride complexes. Therefore, the redox potential of complexes with the general formula  $[\text{Fe}(\text{L}_{\text{R1,R2}})\text{X}]$  cannot simply be calculated by increments suggested by Lever et al. for other coordination compounds.<sup>[53–55]</sup> Furthermore, these redox potentials are in the range of typical Fe(III) precursors for  $[\text{FeCo}]$  ETCST complexes which are between  $-0.45$  V and  $-1.00$  V vs. SCE.<sup>[39–42]</sup>

The  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{X}]$  complexes show the following trend, depending on their monodentate ligands in the order of decreasing redox potentials:  $\text{NCS}^- > \text{NCSe}^- > \text{Cl}^- > \text{N}_3^- > \text{NCO}^- > \text{NC}^-$ . The found order differs from the expected order found in the literature which depends on the  $\pi$ -backbonding abilities of the monodentate ligand:  $\text{N}_3^- > \text{NCO}^- > \text{Cl}^- > \text{NCSe}^- > \text{NCS}^- > \text{NC}^-$ , by the increment method of Lever et al.<sup>[53–55]</sup> These results suggest that Lever's model is inapplicable for  $[\text{Fe}(\text{L}_{\text{R1,R2}})\text{X}]$  complexes, likely because of its high generality,<sup>[55]</sup> ignoring the structural distortions and other inter- and intramolecular interactions. This needs to be further investigated and serves as a hint for an extension of Lever's model.

### Conclusion

A series of six new Fe(III) complexes  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{X}]$  (X:  $\text{Cl}^-$ ,  $\text{N}_3^-$ ,  $\text{NCO}^-$ ,  $\text{NCS}^-$ ,  $\text{NCSe}^-$ ,  $\text{NC}^-$ ) was studied. All mononuclear complexes crystallized in the  $P2_1/c$  space group. Magnetic measurements agreed with the structural data that the monodentate cyanide ligand leads to the LS state while the other five complexes are in the HS state. The electrochemical investigation indicates a one electron redox process with  $E_{1/2}$  values between  $-0.18$  V and  $-0.555$  V. Additionally, the redox properties of previously reported  $[\text{Fe}(\text{L}_{\text{R1,R2}})\text{Cl}/\text{CN}]$  complexes have been investigated as well. The  $E_{1/2}$  values of our reported complexes are in the range of typical ETCST precursors. However, all our attempts to synthesize mixed valance multinuclear complexes, starting from  $[\text{Fe}(\text{L}_{\text{R1,R2}})\text{CN}]$ , did not succeed, nor to the best of our knowledge, such a compound is reported yet. Instead we yielded previously  $\{[\text{Fe}^{\text{III}}(\text{L}_{\text{H,H}})]_2\text{CN}\}$ .<sup>[30–33,43,44]</sup> However, bridging cyanide containing compound e.g.  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  to  $[\text{Fe}(\text{L}_{\text{R1,R2}})\text{Cl}]$  or using  $[\text{Co}(\text{L}_{\text{R1,R2}})\text{CN}]$  can result in multinuclear cyanide bridged



**Figure 6.** Cyclic voltammogram of different  $[\text{Fe}(\text{L}_{\text{R1,R2}})\text{X}]$  complexes. (a) Three  $[\text{Fe}(\text{L}_{\text{R1,R2}})\text{Cl}]$  complexes. (b) Four  $[\text{Fe}(\text{L}_{\text{R1,R2}})\text{CN}]$  complexes. (c) All six  $[\text{Fe}(\text{L}_{\text{Br,Cl}})\text{X}]$  complexes.

complexes<sup>[31–33]</sup> and are promising for tunable switching compounds. Therefore,  $[\text{Co}(\text{L}_{\text{H,H}})\text{CN}]$  instead of  $[\text{Fe}(\text{L}_{\text{R1,R2}})\text{CN}]$  was used with Co(II) and 1-methylimidazole to synthesize the trinuclear mixed valence complex  $[\text{Co}_2\text{Co}]$ . The crystal structure and magnetic data of  $[\text{Co}_2\text{Co}]$  correspond to two LS–Co(III)

species and one HS–Co(II) as only paramagnetic metal ion in this complex.

Previous results showed the tunability of spin states and SCO properties using the  $[\text{M}^{\text{II}}(\text{L}_{\text{R1,R2}})\text{X}]$  system.<sup>[22,24,25,30,31]</sup> This results reveal that also the redox potentials are tunable upon substitution of the Schiff base ligands and that the tuneability might be useful to design switchable molecules.

## Experimental Section

All chemicals were purchased from commercial suppliers and used without further purification. The mononuclear complexes for CV where synthesized according to literature methods.<sup>[22,24,25,27,30]</sup> The synthesis of the other mononuclear complexes was slightly modified.

**$[\text{Fe}^{\text{III}}(\text{L}_{\text{Br,Cl}})\text{Cl}]$ :** A solution of 3-bromo-5-chlorosalicylaldehyde (10.6 mmol) in 60 ml methanol was combined with N-(2-aminoethyl)-1,3-propandiamine (5.3 mmol). The yellow solution was refluxed for 30 min. The precursor complex was synthesized in situ by the addition of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (5.3 mmol) dissolved in 10 mL methanol and triethylamine (10.6 mmol) resulting in a dark red solution. After stirring the solution for 60 min at their boiling temperature, it was cooled to  $-37^\circ\text{C}$  for 24 h. The resulting black crystals were filtered off and washed with cold methanol. Single crystals were obtained by slow evaporation of the solvent.  $\text{C}_{19}\text{H}_{17}\text{Br}_2\text{Cl}_3\text{FeN}_3\text{O}_2$ :  $M = 641.37 \text{ g mol}^{-1}$ ; found % (calcd. %) C 35.73 (35.58), H 2.54 (2.67), N 6.46 (6.55); ESI-MS  $m/z$  calc. for  $\text{C}_{19}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{N}_3\text{O}_2\text{Fe}^+$ : 602.8409, found 602.8420; IR (KBr;  $\text{cm}^{-1}$ ): 3260 (N–H); 3048 (C–H<sub>arom</sub>); 2935 (C–H<sub>alif</sub>); 1637, 1612 (C=N).

**General synthesis of  $[\text{Fe}^{\text{III}}(\text{L}_{\text{Br,Cl}})\text{X}]$  (X:  $\text{N}_3^-$ ,  $\text{NCO}^-$ ,  $\text{NCS}^-$ ,  $\text{NCSe}^-$ ,  $\text{CN}^-$ ):** The mononuclear complex  $[\text{Fe}^{\text{III}}(\text{L}_{\text{Br,Cl}})\text{Cl}]$  (0.3 mmol) was dissolved in 150 ml methanol. The solution was combined with a solution of  $\text{NaN}_3$ ,  $\text{KOCN}$ ,  $\text{KSCN}$ ,  $\text{KSeCN}$  or  $\text{KCN}$  (0.3 mmol) in 2 ml methanol, respectively. After filtration, single crystals were obtained by slow evaporation of the solvent.

**$[\text{Fe}^{\text{III}}(\text{L}_{\text{Br,Cl}})\text{N}_3]$ :**  $\text{C}_{19}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{FeN}_6\text{O}_2$ :  $M = 647.94 \text{ g mol}^{-1}$ ; found % (calcd. %) C 34.96 (35.22), H 2.46 (2.64), N 12.58 (12.97); ESI-MS  $m/z$  calc. for  $\text{C}_{19}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{N}_3\text{O}_2\text{Fe}^+$ : 602.8414, found 602.8414; IR (KBr;  $\text{cm}^{-1}$ ): 3244 (N–H); 3057 (C–H<sub>arom</sub>); 2932 (C–H<sub>alif</sub>); 2083, 2066 (N=N); 1632, 1612 (C=N).

**$[\text{Fe}^{\text{III}}(\text{L}_{\text{Br,Cl}})\text{NCO}]$ :**  $\text{C}_{20}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{FeN}_4\text{O}_3$ :  $M = 647.93 \text{ g mol}^{-1}$ ; found % (calcd. %) C 37.12 (37.07), H 2.35 (2.64), N 8.57 (8.65). ESI-MS  $m/z$  calc. for  $\text{C}_{19}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{N}_3\text{O}_2\text{Fe}^+$ : 602.8414, found 602.8414; IR (KBr;  $\text{cm}^{-1}$ ): 3271 (N–H); 3069 (C–H<sub>arom</sub>); 2934 (C–H<sub>alif</sub>); 2207 (C≡N); 1637, 1612 (C=N).

**$[\text{Fe}^{\text{III}}(\text{L}_{\text{Br,Cl}})\text{NCS}]$ :**  $\text{C}_{20}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{FeN}_4\text{O}_2\text{S}$ :  $M = 664.00 \text{ g mol}^{-1}$ ; found % (calcd. %) C 36.10 (36.18), H 2.35 (2.58), N 8.40 (8.44); ESI-MS  $m/z$  calc. for  $\text{C}_{19}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{N}_3\text{O}_2\text{Fe}^+$ : 602.8414, found 602.8403; IR (KBr;  $\text{cm}^{-1}$ ): 3264 (N–H); 3053 (C–H<sub>arom</sub>); 2934 (C–H<sub>alif</sub>); 2039 (C≡N); 1638, 1619 (C=N).

**$[\text{Fe}^{\text{III}}(\text{L}_{\text{Br,Cl}})\text{NCSe}]$ :**  $\text{C}_{20}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{FeN}_4\text{O}_2\text{Se}$ :  $M = 711.00 \text{ g mol}^{-1}$ ; found % (calcd. %) C 33.94 (33.79), H 2.20 (2.41), N 7.81 (7.88); ESI-MS  $m/z$  calc. for  $\text{C}_{19}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{N}_3\text{O}_2\text{Fe}^+$ : 602.8414, found 602.8422. IR (KBr;  $\text{cm}^{-1}$ ): 3264 (N–H); 3049 (C–H<sub>arom</sub>); 2934 (C–H<sub>alif</sub>); 2043 (C≡N); 1638, 1618 (C=N).

**$[\text{Fe}^{\text{III}}(\text{L}_{\text{Br,Cl}})\text{CN}]$ :**  $\text{C}_{20}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{FeN}_4\text{O}_2$ :  $M = 631.94 \text{ g mol}^{-1}$ ; found % (calcd. %) C 37.18 (38.01), H 2.50 (2.71), N 8.56 (8.87). ESI-MS  $m/z$  calc. for  $\text{C}_{19}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{N}_3\text{O}_2\text{Fe}^+$ : 602.8414, found 602.8420; IR (KBr;  $\text{cm}^{-1}$ ): 3154 (N–H); 3063 (C–H<sub>arom</sub>); 2932 (C–H<sub>alif</sub>); 2127, 2114 (C≡N); 1626, 1618 (C=N).

[Co(L<sub>H,H</sub>)CN]: [Co(L<sub>H,H</sub>)Cl] was synthesized according to a modified literature method.<sup>[27]</sup> [Co(L<sub>H</sub>)Cl] (2.3 mmol) was dissolved in 70 ml methanol. Remaining undissolved crystals were filtered off and the solution was added dropwise to a solution of KCN (4.15 mmol) in 30 ml methanol and stirred over night at RT. About half of the solvent was removed and the solution stored over night at 4 °C. A dark red-black powder was filtered of and used for the following synthesis without further purification.

{[Co<sup>III</sup>(L<sub>H,H</sub>)CN]<sub>2</sub>[Co<sup>II</sup>(1-methylimidazole)<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>·1.5 (H<sub>2</sub>O)]}: 1-Methylimidazole (0.4 mmol) was added to a solution of Co<sup>II</sup>(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1 mmol) in 10 ml Acetonitrile. Then a second solution containing [Co(L<sub>H,H</sub>)Cl] (0.2 mmol) in 5 ml Acetonitrile was dropwise added to the first solution. The mixture was stirred for 4 h at RT and filtrated. While slow evaporation of the solvent results in single crystals of [Co(L<sub>H,H</sub>)CN], single crystals of the trinuclear compound could be obtained by ether diffusion. C<sub>52</sub>H<sub>63</sub>Co<sub>3</sub>N<sub>14</sub>O<sub>5.5</sub>B<sub>2</sub>F<sub>8</sub>: found % (calcd. %): C 47.55 (47.32), H 4.76 (4.48), N 14.93 (15.02); IR (KBr; cm<sup>-1</sup>): 3213 (N–H), 3127 (C–H<sub>arom</sub>), 2936 (C–H<sub>aliph</sub>), 2149 (C≡N), 1626 (C=N).

**Crystal structure analysis:** Most of the diffraction data were collected with a Bruker SMART APEX II diffractometer with a CCD area detector and graphite-monochromated Mo–K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 100 K. The compounds [Fe<sup>III</sup>(L<sub>Br,C</sub>)NCO] and [Fe<sup>III</sup>(L<sub>Br,C</sub>)NCS] were collected with a KAPPA APEX II diffractometer with a CCD area detector and graphite-monochromated Cu–K $\alpha$  radiation ( $\lambda = 1.54178$  Å) at 233 K. The data frames were integrated using the SAINT program and merged to give a unique data set for structure determination. An absorption correction was performed using SADABS.<sup>[56]</sup> The structure was solved by direct methods and refined on  $F^2$  by the full-matrix least-squares methods using SHELXTL package (Bruker Analytical X-ray systems, Olex2).<sup>[45,57]</sup> Non hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Electron densities of the disordered solvent molecules were flattened using Olex 2 solvent mask<sup>[45]</sup> (BYPASS<sup>[46]</sup>).

**Physical measurements:** Magnetic susceptibility data were collected using a Quantum Design MPMS-5S SQUID magnetometer. The measurements were performed with an applied magnetic field of 1000 Oe in the temperature range of 5–300 K. Magnetic data were corrected for the diamagnetism of the sample holder, and for the diamagnetism of the sample using Pascal's constants. The six [Fe(L<sub>Br,C</sub>)X] compounds were measured at 5.0 K increments in the settle mode with a fixed scan rate of 3.0 K/min and 30 seconds after the temperature had stabilized. [Co<sub>2</sub>Co] was measured with a scan rate of 2 K/min in sweep mode. Infrared absorption spectra were measured on KBr pellet samples using a SHIMADZU IR Affinity-1 spectrometer or a Bruker Tensor 27. Cyclic voltammetry measurements were carried out in a standard one-compartment cell under N<sub>2</sub> at RT equipped with a platinum-wire counter electrode, an SCE reference electrode, and a glassy carbon (GC) working electrode using a BAS 620 A electrochemical analyzer. The measurements were performed in MeCN or DMF with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) as the supporting electrolyte and a scan rate of 0.1 V/s.

Deposition Numbers 2059672 (for [Fe<sup>III</sup>(L<sub>Br,C</sub>)Cl]), 2059673 (for [Fe<sup>III</sup>(L<sub>Br,C</sub>)NCS]), 2059674 (for [Co<sup>III</sup>(L<sub>Br,C</sub>)CN]), 2059675 (for [Fe<sup>III</sup>(L<sub>Br,C</sub>)CN]), 2059676 (for [Fe<sup>III</sup>(L<sub>Br,C</sub>)NCO]), 2059677 (for [Fe<sup>III</sup>(L<sub>Br,C</sub>)N<sub>3</sub>]), 2059678 (for [Fe<sup>III</sup>(L<sub>Br,C</sub>)NCSe]), 2059679 (for [CoCo<sub>2</sub>]) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

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## Conflict of Interest

The authors declare no conflict of interest.

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