Synthesis of Cobalt(III), Iron(III), and Chromium(III) Complexes with Salicylaldiminato Ligands: Evaluation of the Complexes as Catalysts for Oxidation of L-Cysteine

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A series of new cobalt(III)-, iron(III)-, and chromium(III)-based complexes of the general formula $[M(N\cap O)_2Cl]$ ($N\cap O$: N-salicylidene(X)amine and sodium *N*-(4-sulfonatosalicylidene(X)amine)) (X = cyclohexyl and 1-naphthyl) was prepared and characterized. Some of the isolated complexes have been evaluated as catalysts for the oxidation of L-cysteine. Preliminary results show that the rate of oxidation of L-cysteine is influenced by the nature of the metal center, the geometry of the complex, the auxiliary substituents, and the backbone of the ligand.

Key words: Co(III), Fe(III), Cr(III), Schiff Bases, Catalysis, L-Cysteine

Introduction

Salen-based complexes are a fundamental class of compounds in coordination chemistry, and they have been known since 1933 [1]. Interest in these complexes intensified in 1990 when the groups of Jacobsen [2] and Katsuki [3] discovered the enantioselective epoxidation of unfunctionalized alkenes using chiral Mn(salen) complexes as catalysts. Since then, an extremely wide variety of reactions catalyzed by salen complexes has been investigated. These include epoxidation of alkene [4], hydrolytic kinetic resolution of epoxides [5], intermolecular hydroamination of allenes [6], and vinyl polymerization of norbornene [7].

For many reasons, Schiff bases have been found to be among the most convenient and attractive ligands for transition metal complexes (TMC) for many reasons: First, steric and electronic effects around the TMC core can be finely tuned by an appropriate selection of bulky and / or electron withdrawing or donating substituents that can be incorporated into the Schiff bases. Second, the two donor atoms, N and O, of the chelating Schiff base exert two opposite electronic effects: the phenolate oxygen atom is a hard donor which is known to stabilize the higher oxidation state of the TM atom while the imine nitrogen atom is a softer donor which stabilizes the lower oxidation state of the TM. Third, Schiff bases are easily prepared, in practically quantitative yields, *via* a one-step procedure through condensation of common aldehydes with amines.

Recently, these authors reported results on the reaction rates of the oxidation of L-cysteine by pairs of *trans-* and racemic *cis*-isomers of octahedral Co(III) and Fe(III) complexes bearing the ligands ethylenediamine, 2,2′-bipyridyl, and 1,10-phenanthroline [8]. Rates were found to be one to three orders of magnitude higher for the *trans*-isomers. The differences in rates were attributed to steric factors. The less crowded *trans*-isomers facilitate electron transfer making the oxidation process faster than that for the *cis*-isomers.

As an extension of our studies on both the coordination chemistry of heteroatom containing ligands [9, 10] and on the catalytical application of their metal complexes [11, 12], we report the synthesis of a series of new cobalt(III), iron(III), and chromium(III) complexes containing bidentate salen ligands. The new complexes were characterized by their physical properties, elemental analysis, magnetic susceptibility, IR and UV/Vis spectroscopy, and thermal gravimetric analysis (TGA). The influence of the metal center, the type of the auxiliary groups and the sulfonyl group in the backbone of the ligands on the rate of oxidation of the amino acid L-cysteine are described.

Results and Discussion

Ligand synthesis

The bidentate ligands **4a**, **4b** and **5a**, **5b** were prepared in moderate to high yields by refluxing the sali-

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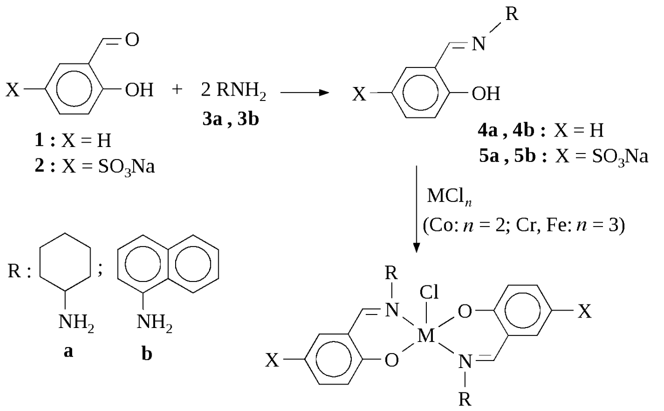


6a, b : M = Co; X = H **9a** : M = Co; X = SO_3Na
7a, b : M = Fe; X = H **10a, b** : M = Fe; X = SO_3Na
8a, b : M = Cr; X = H **11a, b** : M = Cr; X = SO_3Na

Scheme 1. Synthesis and proposed structures of the ligands and the corresponding Co(III)-, Fe(III)-, and Cr(III)-based salen complexes **6**–**11**.

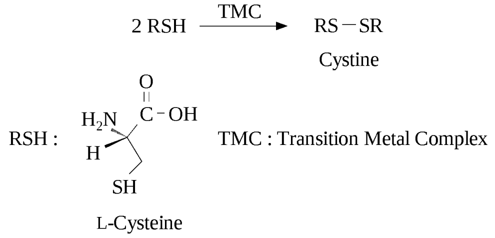
cylaldehyde **1** or **2** with an equivalent amount of the desired amine (**3a**, **b**) in MeOH (Scheme 1). The isolated ligands were characterized by their physical properties, elemental analysis, and IR and UV/Vis spectroscopy.

Complex synthesis

The Co(III)-based complexes **6a**, **6b** and **9a** were synthesized by treating $CoCl_2 \cdot 6H_2O$ with two molar equivalents of the corresponding bidentate ligand in MeOH, followed by oxidation with H_2O_2 (Scheme 1).

The Fe(III)- (**7a**, **7b**, **10a** and **10b**) and Cr(III)-based complexes (**8a**, **8b**, **11a**, and **11b**) were synthesized by the treatment of $CrCl_3 \cdot 6H_2O$ or anhydrous $FeCl_3$ with two equivalents of the corresponding bidentate ligand in methanol (Scheme 1). The isolated cobalt(III) and iron(III) complexes are microcrystalline or powder-like, and they are stable at atmospheric conditions, while the corresponding chromium(III) complexes are moisture sensitive.

IR analyses of the complexes confirm the presence of the ligands. A slight shift of the peak due to the imine bond (ν(C=N)) was observed indicating complexation. Also elemental analyses showed that the metal to ligand ratio in the chloro complexes is 1 : 2. Therefore, a *penta*-coordinate arrangement around the metal center can be assumed, but hexacoordination in a dinuclear aggregate cannot be ruled out. The complexes **10a**, **11a**, and **11b** were also characterized by thermal gravimetric analysis (TGA). The results have shown that the complexes are hydrates with 9, 7, and 9 H_2O molecules, respectively. This is in agreement with the results obtained by elemental analysis.



Scheme 2. Oxidation of cysteine by the complexes prepared in the present study.

The coordination reactions were also followed by UV/Vis spectroscopy. A sharp peak in the visible region due to the coordinated ligands was observed. The complexes **6a**, **7a**, and **8a** show peaks at 389, 487, and 406 nm, respectively, to be compared with the corresponding ligand (**4a**) which shows an absorption peak at 326 nm. Magnetic susceptibility (μ_{eff}, BM) measurements have shown that the cobalt(III) complexes are low-spin state species with a magnetic moment μ_{eff} of 0.0 BM.

Some of the isolated Co(III) and Fe(III) complexes were utilized as catalysts for the oxidation of L-cysteine in aqueous solution at 25 °C and at constant pH in air (Scheme 2). Preliminary investigations showed that the cobalt(III) complexes induce faster catalytical oxidation compared with the corresponding iron(III) complexes (**6a**: $k = 1.0 \times 10^{-1}$; **7a**: $k = 3.25 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}). The complexes containing N-naphthyl substituents were non-reactive. The rates of oxidation reactions by the complexes containing sulfonate groups at the *para* position of the aromatic ring are much lower compared to those of the unsubstituted ligands (**6a**: $k = 1.0 \times 10^{-1}$; **9a**: $k = 7.73 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}). This behavior may be due to the drop of the reduction potential of the metal center caused by the presence of the moderately deactivating group, -SO_3Na, which reduces the σ-donor properties of the ligand [13].

In summary, new families of Co(III)-, Fe(III)-, and Cr(III)-based transition metal complexes bearing salen ligands have been synthesized and characterized. The reactivity of some of the isolated complexes towards the oxidation reaction of L-cysteine has been investigated. Results have shown that the rate of oxidation depends on the metal center, the auxiliary groups, and the substituents on the backbone of the ligand. Further studies on the kinetics of L-cysteine oxidation by these complexes will be reported.

Experimental Section

Materials

$CoCl_2 \cdot 6H_2O$ and $CrCl_3 \cdot 6H_2O$ were purchased from ACROS, naphthylamine and anhydrous $FeCl_3$ were purchased from Aldrich, cyclohexylamine was obtained from Sigma, and L-cysteine (minimum assay 99 %) was purchased from BDH Laboratory Supplies (England). All chemicals were used without further purification.

Physical measurements

Elemental analyses were performed using a EURO EA 3000 instrument. Infrared spectra (KBr pellets) were measured on a Nicolet Magna-IR 560 spectrophotometer. Magnetic susceptibility measurements were carried out using a magnetic susceptibility balance from Alfa Johnson Mathey. Thermal gravimetric analysis (TGA) was carried out on a Netzsch STA 409 PC LUXX instrument at a heating rate of 10 K/min. Kinetic measurements were performed using a diode array spectrophotometer model 8453E from HP Agilent. Melting points were measured with a Stuart Scientific melting apparatus (uncorrected, ±0.1 °C).

Synthesis of ligands

*N-salicylidenecyclohexylamine (**4a**) and N-salicylidenenaphthylamine (**4b**)*

A solution of salicylaldehyde (**1**) (2.0 g, 0.016 mol) in ethanol (10.0 mL) was added dropwise to a solution of the desired amine (**3a** and **3b**) (0.022 mol) in the same solvent (10.0 mL). The mixture was stirred at r. t. for 3 h, during which time the color changed from colorless to yellow. After evaporation of the solvent, an oily residue was left, which was extracted with ethanol and dried.

4a: Yield: 3.29 g (98 %). Color: yellow. – UV/Vis (EtOH): λ_{max} = 326, 416 nm. – IR: ν = 1630 cm^{-1} (m, C=N). – $C_{13}H_{17}NO$: calcd. C 76.81, H 8.43, N 6.89; found C 76.40, H 8.75, N 6.60.

4b: Yield: 2.7 g (98 %). Color: dark-yellow. – UV/Vis (EtOH): λ_{max} = 407, 488 nm. – IR: ν = 1622 cm^{-1} (m, C=N). – $C_{17}H_{13}NO \cdot 0.5EtOH$: calcd. C 79.98, H 5.97, N 5.18; found C 80.43, H 5.80, N 5.30.

*Sodium N-(4-sulfonatosalicylidene)cyclohexylamine (**5a**) and sodium N-(4-sulfonatosalicylidene)-1-naphthylamine (**5b**)*

A solution of sodium *p*-sulfonatosalicylaldehyde (**2**) (0.75 g, 3.30 mmol) in a methanol : water mixture (1 : 1) was added dropwise to a solution of the amine (**3a** or **3b**) (0.33 g, 3.30 mmol) in ethanol (10.0 mL). The mixture was stirred at r. t. for 3 h, then refluxed for 30 min. Upon cooling, a yellow precipitate was formed. The product was filtered, washed with methanol, and dried.

5a: Yield: 0.67 g (66 %). Color: yellow. – M. p. 350 °C (dec.). – UV/Vis (EtOH): λ_{max} = 316, 395 nm. – IR: ν = 1644 cm^{-1} (m, C=N). – $C_{13}H_{16}NNaO_4S \cdot 0.5H_2O$: calcd. C 49.7, H 5.45, N 4.46; found C 49.9, H 5.86, N 4.16.

5b: Yield: 0.84 g (45 %). Color: yellow. – M. p. 350 °C (dec.). – UV/Vis (EtOH): λ_{max} = 359, 450 nm. – IR: ν = 1617 cm^{-1} (m, C=N). – $C_{17}H_{12}NNaO_4S \cdot 2H_2O$: calcd. C 52.98, H 4.18, N 3.64; found C 52.90, H 3.92, N, 3.65.

Synthesis of complexes

*Chloro-bis(N-salicylidenecyclohexylamine)cobalt(III) (**6a**)*

A solution of **4a** (0.50 g, 2.45 mmol) in MeOH (5.0 mL) was added dropwise to a solution of $CoCl_2 \cdot 6H_2O$ (0.24 g, 1.025 mmol) in MeOH (20.0 mL) with continuous stirring. The mixture was heated at 150 °C for 30 min, then stirred at r. t. for 2 h. After that, hydrogen peroxide (30 %, 3.0 mL) was added dropwise. During addition, a dark green precipitate was formed. The mixture was stirred for another hour, then the precipitate was filtered, washed with EtOH (5.0 mL), and dried.

6a: Yield: 0.12 g (24 %). Color: green. – M. p. 198 °C (dec.). – UV/Vis (EtOH): λ_{max} (lgε) = 389 nm (3.78). – IR: ν = 1624 cm^{-1} (m, C=N). – $C_{26}H_{32}ClCoN_2O_2$: calcd. C 62.59, H 6.46, N 5.61; found C 62.89; H 6.72; N 5.59.

*Chloro-bis(N-salicylidenecyclohexylamine)iron(III) (**7a**)*

A solution of **4a** (0.50 g, 2.46 mmol) in MeOH (5.0 mL) was added dropwise to a solution of $FeCl_3$ (0.34 g, 2.24 mmol) in the same solvent (20.0 mL). Upon addition, a dark violet solution was formed. The solution was heated at 150 °C for 30 min, then stirred at r. t. for 2 h. A violet precipitate was formed which was extracted with a petroleum ether/diethyl ether mixture (1 : 1).

7a: Yield: 0.075 g (13 %). Color: green. – M. p. 187 °C (dec.). – UV/Vis (EtOH): λ_{max} (lgε) = 487 nm (3.45). – IR: ν = 1624 cm^{-1} (m, C=N). – $C_{26}H_{32}ClFeN_2O_2$: calcd. C 62.98, H 6.51, N 5.65; found C 62.51, H 6.23, N 5.27.

*Chloro-bis(N-salicylidenecyclohexylamine)chromium(III) (**8a**)*

A solution of **4a** (0.50 g, 2.45 mmol) in THF (5.0 mL) was added dropwise to a solution of $CrCl_3 \cdot 6H_2O$ (0.27 g, 1.02 mmol) in the same solvent (3.0 mL) with continuous stirring. Upon addition, the pink color of the solution changed to dark green. The mixture was stirred at r. t. for 24 h, then the solution was concentrated at 150 °C until an olive green precipitate was formed. The product was filtered, washed thoroughly with petroleum ether, and dried.

8a: Yield: 0.32 g (64 %). Color: green. – M. p. 113 °C (dec.). – UV/Vis (EtOH): λ_{max} (lgε) = 406 nm (3.16). – IR: ν = 1618 cm^{-1} (m, C=N). – $C_{26}H_{32}ClCrN_2O_2 \cdot 8H_2O$: calcd. C 49.09, H 7.61, N 4.40; found C 49.33, H 7.81, N 4.67. – TGA (30 – 120 °C): mass loss = 22.3 % (calcd. 22.7 % for 8 H_2O).

*Chloro-bis(N-salicylidene-1-naphthylamine)cobalt(III) (**6b**), chloro-bis(N-salicylidene-1-naphthylamine)iron(III) (**7b**), and chloro-bis(N-salicylidene-1-naphthylamine)chromium(III) (**8b**)*

The complexes were prepared following the procedures described for the synthesis of the corresponding complexes **6a**, **7a**, and **8a**, respectively. A solution of **4b** (0.50 g, 2.02 mmol) in MeOH (5.0 mL) was reacted with a solution of the metal salt (1.81 mmol) in the same solvent (20.0 mL).

6b: Yield: 0.08 g (13 %). Color: brown. – M. p. 205 °C (dec.). – UV/Vis (EtOH): λ_{max} (lgε) = 480 nm (2.61). – IR: ν = 1624 cm^{-1} (m, C=N). – $C_{34}H_{24}ClCoN_2O_2 \cdot 4H_2O$: calcd. C 61.97, H 4.89, N 4.25; found C 61.80, H 4.57, N 5.35.

7b: Yield: 0.20 g (34 %). Color: violet. – M. p. 230 °C (dec.). – UV/Vis (EtOH): λ_{max} (lgε) = 504 nm (3.19). – IR: ν = 1616 cm^{-1} (m, C=N). – $C_{34}H_{24}ClFeN_2O_2$: calcd. C 69.94, H 4.14, N 4.79; found C 70.64, H 4.21, N 4.52.

8b: Yield: 0.94 g (19 %). Color: light-brown. – M. p. 207 °C (dec.). – UV/Vis (EtOH): λ_{max} (lgε) = 403 nm (1.83). – IR: ν = 1634 cm^{-1} (m, C=N). – $C_{34}H_{24}ClCrN_2O_2 \cdot 2MeOH$: calcd. C 67.13, H 5.01, N 4.35; found C 67.25, H 5.25, N 4.64.

*Chloro-bis[sodium N-(4-sulfonatosalicylidene)cyclohexylamine]cobalt(III) (**9a**)*

A solution of **5a** (0.20 g, 0.65 mmol) in MeOH (5.0 mL) was added dropwise to a solution of $CoCl_2 \cdot 6H_2O$ (0.064 g, 0.27 mmol) in the same solvent (20.0 mL) with continuous stirring. The mixture was heated at 150 °C for 30 min, then stirred at r. t. for 2 h. Hydrogen peroxide (30 %, 3.0 mL) was added dropwise. Upon addition, a green precipitate was formed. The mixture was stirred for 1 h, then the precipitate was filtered, washed with THF and petroleum ether, and dried. Yield: 0.090 g (47 %). Color: green. – M. p. 300 °C (dec.). – UV/Vis (EtOH): λ_{max} (lgε) = 383 nm (3.09). – IR: ν = 1614 cm^{-1} (m, C=N). – $C_{26}H_{30}ClCoN_2Na_2O_8S_2$: calcd. C 44.42, H 4.30, N 3.98; found C 44.25, H 4.58, N 3.92.

*Chloro-bis[sodium N-(4-sulfonatosalicylidene)cyclohexylamine]iron(III) (**10a**)*

Schiff base **5a** (0.147 g, 0.48 mmol) in MeOH (10.0 mL) was added dropwise to a solution of $FeCl_3$ (0.035 g, 0.218 mmol) in MeOH (5.0 mL) with continuous stirring. Upon addition, a dark violet solution was formed. The solution was heated at 150 °C for 30 min, then stirred at r. t. for 2 h. A violet precipitate was formed. The product was filtered, washed with petroleum ether, and dried. Yield: 0.050 g (33 %). Color: violet. – M. p. 350 °C (dec.). – UV/Vis (EtOH): λ_{max} (lgε) = 488 nm (2.74). – IR: ν = 1621 cm^{-1} (m, C=N). – $C_{26}H_{30}ClFeN_2Na_2O_8S_2 \cdot 9H_2O$: calcd. C 36.22, H 5.61, N 3.25; found C 35.98, H 5.10, N 3.08. – TGA (30 – 120 °C): mass loss = 18.92 % (calcd. 19.18 % for 9 H_2O).

*Chloro-bis[sodium N-(4-sulfonatosalicylidene)cyclohexylamine]chromium(III) (**11a**)*

A solution of **5a** (0.20 g 0.65 mmol) in MeOH (5.0 mL) was added dropwise to a solution of $CrCl_3 \cdot 6H_2O$ (0.11 g, 0.30 mmol) in MeOH (3.0 mL) with continuous stirring. Upon addition the pink color of the solution changed to dark green. The mixture was stirred at r. t. for 24 h, then the solution was concentrated at 150 °C. After cooling, a light green precipitate was formed. The product was extracted with THF. Yield: 0.20 g (95 %). Color: green. – M. p. 350 °C (dec.). – UV/Vis (EtOH): λ_{max} (lgε) = 387 nm (3.55). – IR: ν = 1653 cm^{-1} (m, C=N). – $C_{26}H_{30}ClCrN_2Na_2O_8S_2 \cdot 7H_2O$: calcd. C 37.98, H 5.39, N 3.41; found C 37.81, H 4.94, N 3.16. – TGA (30 – 120 °C): mass loss = 16.10 % (calcd. 15.17 % for 7 H_2O).

*Chloro-bis[sodium N-(4-sulfonatosalicylidene)naphthylamine]iron(III) (**10b**), and chloro-bis[sodium N-(4-sulfonatosalicylidene)-1-naphthylamine]chromium(III) (**11b**)*

The complexes **10b** and **11b** were prepared following the procedures described above for the synthesis of the complexes **10a** and **11a**, respectively. A solution of **5b** (0.30 g, 0.86 mmol) in MeOH (5.0 mL) was reacted with the metal salt (0.39 mmol) in the same solvent (20.0 mL).

10b: Yield: 0.019 g (11 %). Color: dark green. – M. p. 350 °C (dec.). – UV/Vis (EtOH): λ_{max} (lgε) = 511 nm (3.49). – IR: ν = 1627 cm^{-1} (m, C=N). – $C_{34}H_{22}ClFeN_2Na_2O_8S_2 \cdot H_2O$: calcd. C 50.67, H 3.00, N 3.48; found C 50.33, H 3.31, N 3.71.

11b: Yield: 0.20 g (95 %). Color: light-green. – M. p. 350 °C (dec.). – UV/Vis (EtOH): λ_{max} (lgε) = 395 nm (3.26). – IR: ν = 1615 cm^{-1} (m, C=N). – $C_{34}H_{22}ClCrN_2Na_2O_8S_2 \cdot 9H_2O$: calcd. C 43.16, H 4.26, N 2.69; found C 43.23, H 4.03, N 2.67. – TGA (230 – 120 °C): mass loss = 17.08 % (calcd. 17.13 % for 9 H_2O).

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