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∩O)₂Cl] (N∩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 alkenes [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-
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 CoCl₂·6H₂O with two molar equivalents of the corresponding bidentate ligand in MeOH, followed by oxidation with H₂O₂ (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 CrCl₃·6H₂O or anhydrous FeCl₃ 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 H₂O molecules, respectively. This is in agreement with the results obtained by elemental analysis.

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 (μₑff, BM) measurements have shown that the cobalt(III) complexes are low-spin state species with a magnetic moment μₑff 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 × 10⁻¹; 7a: k = 3.25 × 10⁻³ dm³ 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\(_3\)Na, which reduces the \( \sigma \)-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\(_2\)·6H\(_2\)O and CrCl\(_3\)·6H\(_2\)O 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-salicylidencyclohexylamine (4a) and N-salicylidene1-naphthylamine (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 or 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): \( \lambda_{\text{max}} = 326, 416 \text{ nm} \). – IR: \( \nu = 1630 \text{ cm}^{-1} \) (m, C=N). – C\(_{13}\)H\(_{12}\)N\(_2\)O\(_2\): calcd. C 79.98, H 5.97, N 6.11; found C 79.94, H 6.02, N 6.11.

4b: Yield: 2.7 g (98 %). Color: dark-yellow. – UV/Vis (EtOH): \( \lambda_{\text{max}} = 407, 488 \text{ nm} \). – IR: \( \nu = 1622 \text{ cm}^{-1} \) (m, C=N). – C\(_{17}\)H\(_{13}\)NO\(_2\): calcd. C 71.98, H 5.97, N 4.36; found C 71.93, H 5.94, N 4.34.

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 reflushed 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): \( \lambda_{\text{max}} = 316, 395 \text{ nm} \). – IR: \( \nu = 1644 \text{ cm}^{-1} \) (m, C=N). – C\(_{13}\)H\(_{12}\)N\(_2\)O\(_2\)·0.5H\(_2\)O: calcd. C 79.98, H 5.97, N 6.11; found C 79.94, H 5.92, N 6.15.

5b: Yield: 0.84 g (45 %). Color: yellow. – M. p. 350 °C (dec.). – UV/Vis (EtOH): \( \lambda_{\text{max}} = 359, 450 \text{ nm} \). – IR: \( \nu = 1617 \text{ cm}^{-1} \) (m, C=N). – C\(_{17}\)H\(_{12}\)N\(_2\)O\(_2\)·2H\(_2\)O: 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-salicylidencyclohexylamine)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\(_2\)·6H\(_2\)O (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): \( \lambda_{\text{max}} (\lg e) = 389 \text{ nm} \). – IR: \( \nu = 1624 \text{ cm}^{-1} \) (m, C=N). – C\(_{26}\)H\(_{22}\)ClCoN\(_2\)O\(_2\): calcd. C 62.59, H 6.46, N 5.61; found C 62.89, H 6.72, N 5.59.

Chloro-bis(N-salicylidencyclohexylamine)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\(_3\)·6H\(_2\)O (0.75 g, 3.30 mmol) in the same solvent (10.0 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).
A solution of 4a (0.50 g, 2.45 mmol) in THF (5.0 mL) was added dropwise to a solution of CrCl$_3 \cdot 6$H$_2$O (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.

Yield: 0.32 g (64 %). Color: green. – M. p. 113 °C (dec.). – IR: $\nu$ = 1624 cm$^{-1}$ (m, C=N). – $C_{26}H_{32}ClCrN$_2$O$_2$: calcd. C 62.98, H 6.51, N 5.65; found C 62.51, H 6.23, N 5.27.

**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 the metal salt (0.65 mmol) in the same solvent (20.0 mL).

Yield: 0.08 g (13 %). Color: brown. – M. p. 205 °C (dec.). – UV/Vis (EtOH): $\lambda_{max}$ (lg$\varepsilon$) = 480 nm (2.61). – IR: $\nu$ = 1624 cm$^{-1}$ (m, C=N). – $C_{34}H_{32}ClCoN$_2$O$_2$ · 4H$_2$O: calcd. C 61.97, H 4.89, N 4.25; found C 61.80, H 4.57, N 3.55.

Yield: 0.20 g (34 %). Color: violet. – M. p. 230 °C (dec.). – UV/Vis (EtOH): $\lambda_{max}$ (lg$\varepsilon$) = 504 nm (3.19). – IR: $\nu$ = 1616 cm$^{-1}$ (m, C=N). – $C_{26}H_{30}ClFeN$_2$O$_2$: calcd. C 69.94, H 4.14, N 4.79; found C 70.64, H 4.21, N 4.52.

Yield: 0.94 g (19 %). Color: light-brown. – M. p. 207 °C (dec.). – UV/Vis (EtOH): $\lambda_{max}$ (lg$\varepsilon$) = 403 nm (1.83). – IR: $\nu$ = 1634 cm$^{-1}$ (m, C=N). – $C_{34}H_{32}ClCrN$_2$O$_2$ · 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$_3 \cdot 6$H$_2$O (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 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 THF and petroleum ether, and dried.

Yield: 0.050 g (33 %). Color: violet. – M. p. 350 °C (dec.). – UV/Vis (EtOH): $\lambda_{max}$ (lg$\varepsilon$) = 488 nm (2.74). – IR: $\nu$ = 1621 cm$^{-1}$ (m, C=N). – $C_{26}H_{30}ClFeN$_2$O$_2$: calcd. C 36.22, H 5.61, N 3.25; found C 35.98, H 5.10, N 3.08. – TGA (30 – 120 °C): mass loss = 19.92 % (calcd. 19.18 % for 9 H$_2$O).

**Chloro-bis(sodium N-(4-sulfonatosalicylidene)cyclohexylamine)chromium(III) (10a)**

A solution of 5a (0.20 g, 0.65 mmol) in MeOH (5.0 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: 0.20 g (95 %). Color: green. – M. p. 350 °C (dec.). – UV/Vis (EtOH): $\lambda_{max}$ (lg$\varepsilon$) = 488 nm (2.74). – IR: $\nu$ = 1621 cm$^{-1}$ (m, C=N). – $C_{26}H_{30}ClFeN$_2$O$_2$: calcd. C 36.22, H 5.61, N 3.25; found C 35.98, H 5.10, N 3.08. – TGA (30 – 120 °C): mass loss = 19.92 % (calcd. 19.18 % for 9 H$_2$O).

**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$_3 \cdot 6$H$_2$O (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): $\lambda_{max}$ (lg$\varepsilon$) = 387 nm (3.55). – IR: $\nu$ = 1653 cm$^{-1}$ (m, C=N). – $C_{26}H_{30}ClCrN$_2$O$_2$: calcd. C 37.98, H 5.39, N 3.41; found C 37.80, H 4.94, N 3.16. – TGA (30 – 120 °C): mass loss = 18.92 % (calcd. 19.18 % for 9 H$_2$O).

**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): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 511 nm (3.49). – IR: $\nu = 1627$ cm$^{-1}$ (m, C=N). – C$_{34}$H$_{22}$ClFeN$_2$Na$_2$O$_8$S$_2$·H$_2$O: 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): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 395 nm (3.26). – IR: $\nu = 1615$ cm$^{-1}$ (m, C=N). – C$_{34}$H$_{22}$ClCrN$_2$Na$_2$O$_8$S$_2$·9H$_2$O: 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$_2$O).

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