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Trans- and *cis*- Cobalt(III), Iron(III), and Chromium(III) Complexes Based on α- and γ-Diimine Schiff Base Ligands: Synthesis and Evaluation of the Complexes as Catalysts for Oxidation of L-Cysteine

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Abstract. The synthesis of a new series of *trans* and racemic *cis* isomers of cobalt(III)-, iron(III)-, and chromium(III)-based complexes with the α- and γ-diimine Schiff base ligands, N,N′-bis(X)-2,3-butandiimine and N,N′-bis(X)-1,2-phenyldiimine (X = cyclohexyl, 2-isopropylphenyl, 1-naphthyl) is described. To confirm the identity of the complexes prepared in the present study, a variety of techniques including elemental analysis, magnetic susceptibility, infrared-, mass- (EI), and UV/Vis- spectroscopy have been utilized. Some of the isolated complexes have been evaluated as catalysts for the oxidation of L-cysteine. Preliminary results showed that the metal atoms, geometry of the complexes, auxiliary substituents, and the backbone of the ligand influenced the rate of oxidation reaction.

Keywords: Cobalt; Iron; Chromium; Diimine ligands; Catalysis; L-cysteine

1 Introduction

Numerous publications describing the coordination chemistry of phosphorus donor ligands and the application of their complexes in homogeneous catalysis have been disclosed [1]. However, few papers have been reported about the organic nitrogen ligands. This may be due to the fact that their complexes have not been used extensively for synthetic organic applications. Recently, some research groups have highlighted the application of nitrogen donors, particularly because they are easily obtained from chiral pool [2, 3] and due to their application in synthesis of optically active organic molecules [4]. Furthermore, transition metal complexes containing the bidentate diimine ligands have been successfully employed in a number of catalytic reactions; including polymerization of alkenes [5], polymerization of polar monomers [3], enantioselective 1,3-dipolar cycloaddition reaction [6], and borylation of vinylarenes [7].

Geometrical isomerisms are common among coordination compounds. They contain the same number of ligands, but arranged differently around the metal atom. Study of isomers provides much of the experimental knowledge used to develop and defend coordination theory. Several investigators have studied the effect of geometrical isomerism on the reactivity of some isomers with various reagents. Using optical rotatory dispersion, IR- and NMR-spectroscopy, *de Vekki* et al. [8] studied the reaction of the optically active geometrical isomers of the platinum(II) complex (-)-[Pt(Me-*p*-TolSO)(Py)Cl_2] with several nucleophilic reagents (Py, Ph_3PS, Ph_3P, Ph_3As, and MeSO).

The effect of geometrical isomerism in platinum complexes, used as antitumor agents, has been studied by *Farrell* et al. [9]. They found that the binuclear platinum complexes [{*trans*-PtCl$(NH_3)_2$}$_2$-μ-{$NH_2(CH_2)_nNH_2$}]$(NO_3)_2$ (n = 4,6) and [{*cis*-PtCl$(NH_3)_2$}$_2$-μ-{$NH_2(CH_2)_nNH_2$}]$(NO_3)_2$ (n = 4,6)] exhibit antitumor activity comparable with cisplatin. Also, they found that at 37 °C, the initial binding and reaction of the *cis* isomer is slower than that for the *trans* isomer. *Toma* et al. [10] reviewed linkage isomerization reactions from the aspect of kinetics and mechanisms involved, with some focusing on selected cases of direct formation. Also, they investigated the electrochemical, photochemical, thermal and pH-induced generation of linkage isomers. The biodegradation kinetics of geometric isomers of model naphthenic acid in water has been studied by *Peru* et al. [11]. The rates of biodegradation of six model naphthenic acids by heterotrophic bacteria were compared. Specifically, they monitored by gas chromatography, the biodegradation of *cis*- and *trans*-isomers of 4-methylcyclohexenylacetic acids, 4-methylcyclohexanylcarboxylic acids, and 3-methylcyclohexenylcarboxylic acids.

In a previous article, we have described the application of some α-diimine-based palladium(II) and nickel(II) complexes as polymerization catalysts [12] and the influence of the terminal substituents (naphthyl, 2-isopropyl, and cyclohexyl) on the catalytic activity of some iron(II) complexes in polymerization reactions [13].

Recently, we have reported that the rates of oxidation of L-cysteine by pairs of *trans*- and racemic *cis*-isomers of Co^{III}- and Fe^{III}- complexes bearing the ligands, ethylenedi-

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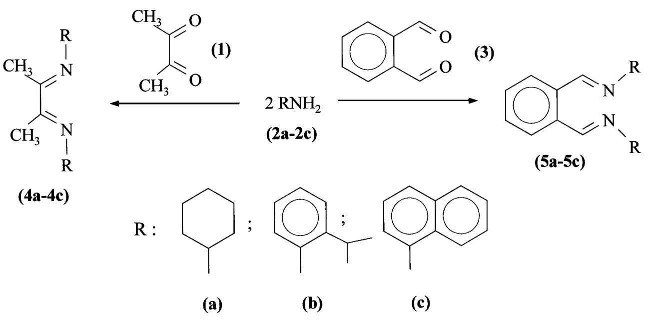
amine, 2,2′-bipyridyl, and 1,10-phenanthroline [14]. Rates were found to be one to three orders of magnitudes higher for the *trans*-isomer. The differences in rates are attributed to the steric factor. The less crowded *trans*-isomers facilitate electron transfer making the oxidation process faster than that for the *cis*-isomers.

As an extension of our studies on both the coordination chemistry of heteroatom containing ligands [15−17] and on the catalytical application of their metal complexes [18−20], we report the synthesis and characterization of new pairs of *trans*- and racemic *cis*-isomers of cobalt(III), iron(III), and chromium(III) complexes containing α-diimine and γ-diimine bidentate nitrogen ligands. The new complexes were characterized by their physical properties, elemental analysis, magnetic susceptibility, IR-, MS (EI), and UV-Vis spectroscopy. The influence of the metal center, the geometry around the metal atom, the type of the auxiliary groups of the ligands and the backbone structures on the rate of oxidation of L-cysteine are described.

2 Results and Discussion

2.1 Ligand synthesis

The bidentate α-diimine ligands **(4a-4c)** and γ-diimine ligands **(5a-5c)** were prepared in moderate to high yields by the condensation reaction of 2,3-butanedione **(1)** or 1,2-phenylendicarboxyldehyde **(3)** with stoichiometric amounts of the desired amine **(2a-2c)** in the presence of a catalytical amount of formic acid (Scheme 1). The isolated diimine ligands were characterized by their physical properties, elemental analysis, IR- and UV-Vis spectroscopy.



Scheme 1 Synthesis of α-(**4a−4c**) and γ-diimine (**5a−5c**) ligands

The condensation reactions were followed by IR spectroscopy. The total vanishing of the carbonyl band (due to the ketone group at about 1700 cm^{-1}) and the appearance of a new band between 1618-1642 cm^{-1}, which is assigned to the imine band (ν C=N), indicates the formation of the diimine ligands.

2.2 Complex synthesis

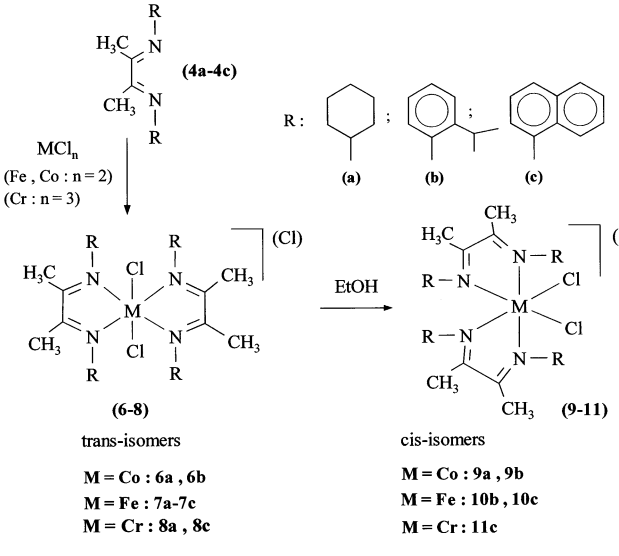
The *trans*-dichloro Fe^{III}- and Co^{III}-based complexes **6a**, **6b**, and **7a-7c**, **12a-12c**, and **13a-13c** were synthesized by the treatment of $MCl_2 \cdot 6H_2O$ (M = Co, Fe) with two molar ratio of the corresponding bidentate ligand in EtOH, followed by oxidation with H_2O_2. The cationic species were formed by the addition of excess HCl (Scheme **2** and **3**). Heating the solution in ethanol and with slow evaporation of the solvent led to the formation of the corresponding *cis*-isomers, **9a**, **9b**, **10b**, **10c**, **15a-15c**, and **16a-16c**.

The *trans* dichloro Cr^{III}-based complexes (**8a, 8c, 14a, 14b, and 14c**) were synthesized by the treatment of $CrCl_3 \cdot 6H_2O$ with two equivalents of the corresponding bidentate ligand in methanol. The cationic *trans*-species were formed by the addition of a small amount of HCl. Crystallization of the *trans* isomer in hot ethanol afforded the corresponding *cis* isomers (**11c** and **17c**) [21]. The isolated complexes are microcrystalline or powder-like and they are stable at atmospheric conditions. Attempts to isolate the rest of the complexes were unsuccessful (Scheme **2** and **3**).

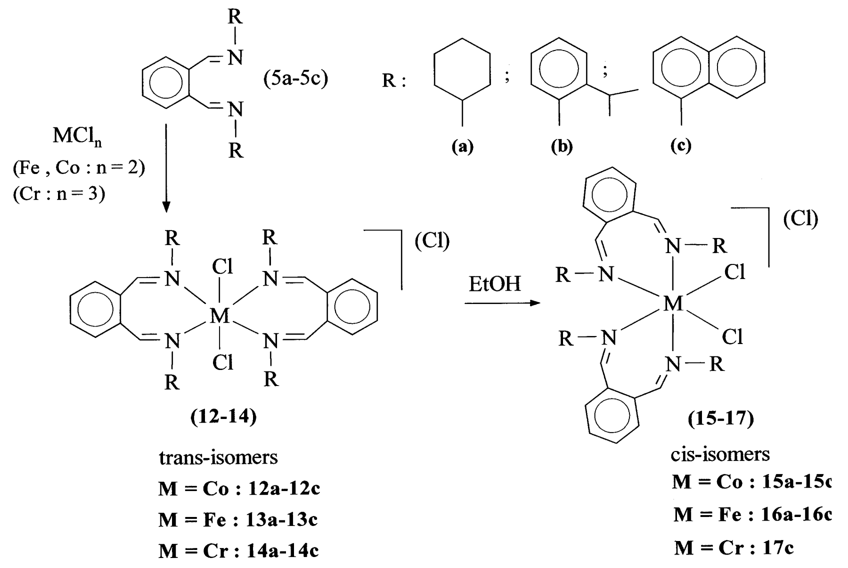
The complexes prepared in the present study were characterized by their physical properties, magnetic susceptibility (μ_{eff}, BM), infrared-, mass- (EI), and UV/Vis spectroscopy. All the *trans*-isomers and most of their corresponding *cis*-isomers were also identified by elemental analysis. Based on these results, the isomerization process did not led to any degradation for the complexes.

IR-analyses of the complexes indicate the presence of the ligands. A slight shift of the imine band (νC=N) was observed due to complexation. Also elemental analyses showed that the metal to ligand ratio in the dichloro complexes is 2:1. Therefore, an octahedral arrangement around the metal atom is formed. Moreover, precipitation with silver nitrate indicates the formation of the mono cationic complexes.

The coordination reactions were also followed by UV/Vis spectroscopy. A sharp peak in the visible region due to the coordination of ligand was observed. The complexes **12a** and **13a** showed peaks at 402 and 368 nm, respectively, compared to the corresponding ligand (**5a**) which showed an absorption peak at 329 nm.



Scheme 2 Synthesis and suggested structures of Co(III)-, Fe(III)-, and Cr(III)-based α-diimine complexes (**6**−**11**)

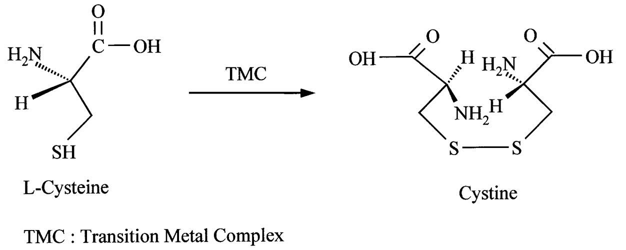


Scheme 3 Synthesis and suggested structures of Co(III)-, Fe(III)-, and Cr(III)-based γ-diimine complexes (**12**−**17**)

The *cis*-, and the *trans*-isomers were distinguished by their distinct absorption spectra in the UV/Vis region and also by their melting points (*trans*-[Co(BIPBD)Cl_2]Cl (**6b**), m.p (dec) = 232 °C, the corresponding *cis*-isomer (**9b**) decomposes at 200 °C). Some of the isolated *cis*-isomers were converted to the more stable *trans*-isomers upon heating (complexes **11c** and **15b** convert to **8c** and **12b**, respectively, at about 150 °C).

The Magnetic susceptibilities (μ_{eff}, BM) of the complexes were measured at room temperature. All complexes were found to have a formal oxidation state of +3. The electronic environment of the complexes was influenced by the backbone of the ligand and the bulkiness of the auxiliary substituents. Both iron(III) complexes **10c** and **16c** are high spin species with magnetic moment values of 3.04 and 5.78 BM, respectively. This indicates that the coordination strength of the α-diimine ligands (**10c**) is higher than that for the γ-diimines (**16c**). The *trans*-cobalt(III) complexes (**12a**, and **12c**) are diamagnetic (low spin state species), while the corresponding complex (**12b**), with isopropyl terminals, is a high spin state species that has a magnetic moment (μ_{eff}) of 4.87 BM. The magnetic moment of the complexes, *trans*-cobalt(III)- (**12c**), *trans*-iron(III)- (**13c**), and *trans*-chromium(III)- (**14c**), which bear the same ligand, depends also on the metal center. Compared to **12c** which is diamagnetic, the complexes **13c** and **14c** are high spin state species with a magnetic moment (μ_{eff}) of 5.48 and 1.89 BM, respectively [22].

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 constant pH (Scheme 4). Preliminary investigation showed that the cobalt complexes are faster oxidation catalysts compared with the corresponding iron(III) complexes (**12a**, $k = 2.10\times10^{-2}$; **13a**, $k = 7.16\times10^{-3}$). The *trans*-isomers were also found to react faster with L-cysteine than the corresponding *cis*-isomers (**12b**, $k = 9.10\times10^{-2}$; **15b**, $k = 4.19\times10^{-2}$). We believe that this is due to the facile ligand substitution reactions on the *trans*-isomer (less hindrance) compared with the *cis*-isomer (crowded) that inhibits the substitution reaction.



Scheme 4 Oxidation of Cysteine by the complexes prepared in the present study.

Moreover, the rates of oxidation reactions by the cobalt complexes bearing the α- or γ-diimine with 2-isopropylphenyl terminals are faster than those bearing the cyclohexyl substituents (**15b**, $k = 4.19\times10^{-2}$; **15a**, $k = 2.10\times10^{-2}$). However, the complexes based on the naphthyl terminals were non-reactive. Such influence of the auxiliary groups on the activity of transition metal complexes towards polymerization reactions has been observed before [13].

In summary, new families of cationic, octahedral, Co^{III}-, Fe^{III}-, and Cr^{III}-based transition metal complexes bearing α- and γ-diimine 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 showed that the rate of oxidation depends on the metal center, geometry of the complexes, and size of the ligand. In addition, it also depends on the auxiliary substituents on the ligand and its backbone. Further studies on the kinetics of L-cysteine oxidation of by these complexes will be reported in details.

3 Experimental Section

3.1 General

$CrCl_3 \cdot 3THF$, $CrCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, and $FeCl_2 \cdot 6H_2O$ were purchased from (ACROS), isopropylaniline, naphthylamine, and anhydrous $FeCl_3$ from Aldrich, cyclohexylamine from Sigma, and *L*-cysteine (minimum assay 99 %) was purchased from BDH Laboratory Supplies (England). All chemicals were used without further purifications.

Elemental analyses were performed using a (EURO EA 3000 instrument). Infrared spectra (KBr pellets) were measured on a Nicolet- Magna-IR 560 Spectrophotometer. Mass spectra (EI) were acquired using a Shimadzu-QP5050A. Magnetic susceptibility measurements were carried out using Magnetic susceptibility balance from Alfa Johnson Mathey Company. Kinetic measurements were performed using Diod Array Spectrophotometer model 8453E from HP Agilent. Melting points were measured by a Stuart Scientific melting Apparatus (uncorrected ±0.1 °C).

3.2 Synthesis of ligands

The ligands were prepared following similar procedures described in literature [15].

3.2.1 N,N′-bis(cyclohexyl)-2,3-butanediimine (BCBD, 4a), N,N′-bis(2-isopropyl-phenyl)-2,3-butanediimine (BIPBD, 4b), and N,N′-bis(1-napthyl)-2,3-butanediimine (BNBD, 4c) [12]:

A solution of 2,3-butanedione (**1**) (1.00 g; 0.012 mol) in methanol (10 ml) was added to a solution of the desired amine (**2a**-**2c**) (0.028 mol) in methanol (20 ml) with continuous stirring. The mixture was stirred at room temperature for 3 hr, during which, a precipitate was formed. After additional 2 hrs stirring, the product formed was filtered, washed with methanol and dried in vacuum.

4a: Yield: 2.45 g (85 %), brown. M.p. 63 °C. UV/Vis (EtOH): λ_{max} = 303 nm (439 nm). IR: ν/cm^{-1} = 1636 m (C=N). Anal. Calcd. for $C_{16}H_{28}N_2$: C, 77.36; H, 11.36; N, 11.28. Found: C, 77.80; H, 11.16; N, 10.78 %. **4b**: Yield: 2.5 g (67 %), yellow. M.p. 83 °C. UV/vis (EtOH): λ_{max} = 382 nm (488 nm). IR: ν/cm^{-1} = 1632 m (C=N). Anal. Calcd. for $C_{22}H_{28}N_2$: C, 82.45; H, 8.81; N, 8.74. Found: C, 82.50; H, 9.13; N, 8.51 %. **4c**: Yield: 1.75 (45 %), dark-yellow. M.p. 141 °C. UV/Vis (EtOH): λ_{max} = 355 nm (491 nm). IR: ν/cm^{-1} =1637 m (C=N). Anal. Calcd. for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 86.02; H, 6.36; N, 8.36 %.

3.2.2 N,N′-bis(cyclohexyl)-1,2-phenyldiimine (BCPD, 5a), N,N′-bis(2-isopropyl-phenyl)-1,2-phenyldiimine (BIPPD, 5b), and N,N′-bis(1-naphthyl)-1,2-phenyldiimine (BNPD, 5c).

A solution of 1,2-phenylendicarboxyldehyde (**3**) (5.00 g; 0.037 mol) in ethanol (10 ml) was added to a solution of cyclohexylamine (**2a**), isopropylamine (**2b**), or 1-naphtylamine (**2c**) (0.086 mol) in ethanol (20 ml) withcontinuous stirring .The mixture was stirred at room temperature for 3 hrs, during which, a white precipitate was formed. The product was filtered, washed with ethanol (4×15 ml) and dried in vacuum.

5a: Yield: 5.4 g (71 %). M.p. (dec) 236 °C. UV/Vis (EtOH): λ_{max} = 324 nm. IR: ν/cm^{-1} = 1618 m (C=N). Anal. Calcd. for $C_{20}H_{31}N_2O1.5$: C, 74.26; H, 9.66; N 8.66 %. Found: C, 74.20; H, 9.31; N 8.49 %. **5b**: Yield: 3.13 g (21 %). M.p. (dec) 148 °C. UV/Vis (EtOH): λ_{max} = 291 nm. IR: ν/cm^{-1} = 1642 m (C=N). Anal. Calcd. for $C_{26}H_{30}N_2O$: C, 80.79; H, 7.82; N, 7.25. Found: C, 81.16; H, 7.99; N, 7.06 %. **5c**: Yield: 8.10 g (57 %). M.p. (dec) 112 °C. UV/vis (EtOH): λ_{max} = 342 nm (500 nm). IR: ν/cm^{-1} = 1636 m (C=N). MS (EI, 70 eV): m/z (%) = 383.3 [M^+]. Anal. Calcd. for $C_{28}H_{20}N_2 \cdot 0.25H_2O$: C, 86.44; H, 5.31; N, 7.20. Found: C, 86.10; H, 5.19; N, 6.76 %.

3.3 Synthesis of complexes

3.3.1 Trans-[Co(BCBD)$_2$Cl$_2$]Cl (6a) and trans-[Co(BIPBD)$_2$Cl$_2$]Cl (6b):

A solution of the corresponding ligand (**4a** or **4b**) (2.03 mmol) in ethanol (5.0 ml) was added dropwise to a solution of $CoCl_2 \cdot 6H_2O$ (0.198 g; 0.834 mmol) in ethanol (5.0 ml). The mixture was stirred at room temperature for 2 hrs, then H_2O_2 (30 %) (3.0 ml) was added dropwise. Stirring was continued for an additional hour then hydrochloric acid (37 %, 5.00 ml) was added. After stirring for 1 hr at room temperature, the solution was concentrated by heating to 150 °C until a crust was formed. After slow cooling of the system to room temperature the obtained crystals were isolated, rinsed with ethanol (5.0 ml) and diethyl ether (2×5.0 ml) and dried in vacuum.

6a: Yield: 0.24 g (44 %), green. M.p. (dec) 142 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 400 nm (2.23×10^2). IR: ν/cm^{-1} = 1629 m (C=N). Anal. Calcd. for $C_{32}H_{56}N_4CoCl_3$: C, 58.05; H, 8.53; N, 8.46. Found: C, 57.92; H, 8.47; N 8.09 %. **6b**: Yield: 0.34 g (51 %), light-blue. M.p. (dec) 232 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 419 nm (3.47×10^1). IR: ν/cm^{-1} = 1642 m (C=N). Anal. Calcd. for $C_{44}H_{56}N_4CoCl_3$: C, 65.55; H, 7.00; N 6.95. Found: C, 65.86; H, 7.43; N 7.40 %.

3.3.2 Trans-[Fe(BCBD)$_2$Cl$_2$]Cl (7a), trans-[Fe(BIPBD)$_2$Cl$_2$]Cl (7b), and trans-[Fe(BNBD)$_2$Cl$_2$]Cl (7c):

A solution of the ligand (**4a**, **4b**, or **4c**) (1.56 mmol) in 10.0 ml ethanol was added drop wise to a solution of $FeCl_2 \cdot 6H_2O$ (0.17 g; 0.71 mmol) in the same solvent (20.0 ml). The mixture was stirred at room temperature for 2 hrs, then H_2O_2 (30 %) (3.0 ml) was added drop wise. Stirring was continued for another 1 hr, and then hydrochloric acid (37 %, 5.00 ml) was added. After stirring for 1 hr at room temperature, the solution was concentrated by heating to 150 °C for 1 hr. Slow cooling of the mixture to room temperature resulted in a brown crystals formation which was rinsed with ethanol (5.0 ml) and diethyl ether (2×5.0 ml) then dried under vacuum.

7a: Yield: 0.30 g (58 %). M.p. (dec). 250 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 488 nm (1.97×10^2). − IR: ν/cm^{-1} = 1630 m (C=N). Anal. Calcd. for $C_{32}H_{64}N_4O_4FeCl_3$: C, 52.57; H, 8.82; N, 7.66. Found: C, 52.56; H, 9.17; N, 8.01 %. **7b**: Yield: 0.15 g (26 %). − M.p. (dec.) 250 °C. UV/vis (EtOH): λ_{max} (lg ε) = 490 nm (1.88×10^3). IR: ν/cm^{-1} = 1628 m (C=N). **7c**: Yield: 0.25 g (40 %). M.p. (dec.) 350 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 400 nm (8.55×10^3). IR: ν/cm^{-1} = 1617 m (C=N). Anal. Calcd. for $C_{48}H_{46}N_4O_3FeCl_3$: C, 64.84; H, 5.21; N, 6.30. Found: C, 64.87; H, 5.10; N, 5.97 %.

3.3.3 Trans-[Cr(BCBD)$_2$Cl$_2$]Cl (8a) and trans-[Cr(BNBD)$_2$Cl$_2$]Cl (8c):

A solution of the ligand (**4a** or **4c**) (0.81 mmol) in 10.0 ml methanol was added dropwise to a solution of $CrCl_3 \cdot 6H_2O$ (0.14 g, 0.37 mmol) in the same solvent (5.0 ml). Upon addition, the color of the solution was changed from pink to green. The mixture was stirred at room temperature for 24 h, then hydrochloric acid (1.0 ml) (HCl, 37 %) was added. After stirring for 1 h, the solution was concentrated at 150 °C until a green crust was formed. The mixture was cooled and the complex was separated as a dark yellow precipitate. The product was thoroughly rinsed with THF (5.0 ml) followed by pet.ether (2×5.0 ml), and dried in vacuum.

8a: Yield: 0.18 g (74 %). M.p. (dec.) 250 °C. UV/vis (EtOH): λ_{max} (lg ε) = 432 nm (3.04×10^1). IR: ν/cm^{-1}) = 1617 m (C=N). Anal. Calcd. for $C_{32}H_{56}N_4CrCl_3$: C, 58.90; H, 8.61; N, 8.55. Found: C, 59.54; H, 10.49; N, 7.20 %. **8c**: Yield: 0.14 g (44 %), green. M.p. (dec) 247 °C. UV/vis (EtOH): λ_{max} (lg ε) = 390 nm (1.60×10^3). IR: ν/cm^{-1} = 1628 m (C=N). Anal. Calcd. for $C_{48}H_{44}N_4O_2CrCl_3$: C, 66.75; H, 5.11; N, 6.46. Found: C, 66.24; H, 5.00; N, 5.14 %.

3.3.4 Cis-[Co(BCBD)$_2$Cl$_2$]Cl (9a) and cis-[Co(BIPBD)$_2$Cl$_2$]Cl (9b)

Small portions of the corresponding *trans*-isomers (**6a**, and **6b**) were dissolved in minimum volume of ethanol and gently evaporated until brown crystals were formed. The crystals were isolated and dried under vacuum.

9a: Yield: (31 %). M.p. (dec) 130 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 488 nm (1.07×10^2). IR: ν/cm^{-1} = 1629 m (cm^{-1}). Anal. Calcd. for $C_{32}H_{56}N_4CoCl_3$: C, 57.67; H, 8.82; N, 7.91. Found: C, 57.75; H, 8.69; N 7.92 %. **9b**: Yield: (8.4 %), brown. M.p. (dec) 200 °C. UV/vis (EtOH): λ_{max} (lg ε) = 490 nm (1.92×10^2). IR: ν/cm^{-1} = 1629 m (cm^{-1}).

3.3.5 Cis-[Fe(BIPBD)$_2$Cl$_2$]Cl (10b), cis-[Fe(BNBD)$_2$Cl$_2$]Cl (10c), and cis-[Cr(BNBD)$_2$Cl$_2$]Cl (11c)

Small portions of the corresponding *trans*-isomers (**7b**, **7c**, and **8c**) were dissolved in minimum volume of ethanol and gently evaporated until violet (**10b** and **10c**) or light brown (**11c**) crystals were formed. The isolated crystals were filtered, washed with THF (5.0 ml), pet. ether (2×5.0 ml), and dried under vacuum.

10b: Yield: (47 %), dark-violet. M.p. (dec) 140 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 545 nm. IR: ν/cm^{-1} = 1624 m (cm^{-1}). μ_{eff}: 3.34 BM. **10c**: Yield: (83 %), violet. M.p. (dec) 350 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 510 nm (2.84×10^3). IR: ν/cm^{-1} = 1630 m (cm^{-1}). Anal. Calcd. for $C_{48}H_{44}N_4O_2FeCl_3$: C, 66.18; H, 5.09; N, 6.43. Found: C, 66.24; H, 5.00; N, 6.24 %. μ_{eff}: 3.04 BM. **11c**: Yield: (89 %), light-brown. M.p. (dec) convert to *trans* at 150 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 437 nm (1.29×10^3). IR: ν/cm^{-1} = 1624 m (cm^{-1}).

3.3.6 Trans-[Co(BCPD)$_2$Cl$_2$]Cl (12a), trans-[Co(BIPPD)$_2$Cl$_2$]Cl (12b), trans-[Co(BNPD)$_2$Cl$_2$]Cl (12c), trans-[Fe(BCPD)$_2$Cl$_2$]Cl (13a), trans-[Fe(BIPPD)$_2$Cl$_2$]Cl (13b), trans-[Fe(BNPD)$_2$Cl$_2$]Cl (13c), trans-[Cr(BCPD)$_2$Cl$_2$]Cl (14a), trans-[Cr(BIPPD)$_2$Cl$_2$]Cl (14b), and trans-[Cr(BNPD)$_2$Cl$_2$]Cl (14c).

All of these *trans*-complexes were prepared according to the procedures described above. Starting from the corresponding metal salt and the desired γ-diimine ligand (**5a**, **5b**, and **5c**, respectively) the complexes were produced.

12a: Yield: (49 %), light-green. M.p. (dec) 238 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 402 nm (2.68×10^1). IR: ν/cm^{-1} = 1619 m (C=N). Anal. Calcd. for $C_{40}H_{56}N_4CoCl_3$: C, 63.37; H, 7.44; N, 7.39. Found: C, 64.13; H, 7.30; N, 7.39 %. μ_{eff}: (0.0) BM. **12b**: Yield: (84 %), green. M.p. (dec) 251 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 400 nm (3.42×10^1). IR: ν/cm^{-1} = 1621 m (C=N). Anal. Calcd. for $C_{52}H_{57}N_4O_{0.5}CoCl_3$: C, 68.53; H, 6.30; N, 6.15. Found: C, 68.35; H, 6.21; N 5.89 %. μ_{eff}: 4.87 BM. **12c**: Yield: (24 %), green. M.p. (dec) 130 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 385 nm (4.77×10^2). IR: ν/cm^{-1} = 1627 m (C=N). MS (EI, 70 eV): m/z (%) = 544.2 [M^+- $C_{28}H_{20}N_2Cl$]. Anal. Calcd. for $C_{56}H_{42}N_4OCoCl_3$: C, 70.63; H, 4.45; N, 5.88. Found: C, 70.32; H, 4.01; N, 5.96 %. − μ_{eff}: (0.0) BM. **13a**: Yield: (54 %), light-green. M.p. (dec) 145 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 368 nm (9.97×10^2). IR: ν/cm^{-1} = 1636 m (C=N). Anal. Calcd. for $C_{40}H_{62}N_4FeCl_9$: C, 49.33; H, 6.43; N, 5.75. Found: C, 49.39; H, 6.40; N, 5.76 %.

13b: Yield: (53 %), green. M.p. (dec) 107 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 390 nm (9.69×10^1). IR: ν/cm^{-1} = 1638 m (C=N). Anal. Calcd. for $C_{52}H_{64}N_4OFeCl_3$: C, 64.30; H, 6.64; N, 5.77. Found: C, 64.77; H, 7.04; N, 5.88 %. **13c**: Yield: (61 %), light-brown. M.p. (dec) 138 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 400 nm (4.59×10^3). IR: ν/cm^{-1} = 1629 m (C=N). MS (EI, 70 eV): m/z (%) = 544.2 [M^+- $C_{28}H_{20}N_2$], 471.3 [M^+- $C_{28}H_{20}N_2Cl_2$], 383.3 [M^+- $C_{28}H_{20}N_2FeCl_3$]. Anal. Calcd. for $C_{56}H_{40}N_4FeCl_3$: C, 72.23; H, 4.33; N, 6.02. Found: C, 72.46; H, 4.27; N 5.62 %. μ_{eff}: 5.48 BM. **14a**: Yield: (70 %), green. M.p. (dec) 164 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 390 nm (9.79×10^1). IR: ν/cm^{-1} = 1637 m (C=N). Anal. Calcd. for $C_{40}H_{68}N_4O_6CrCl_3$: C, 55.91; H, 7.98; N, 6.52. Found: C, 55.65; H, 7.79; N 7.04 %. **14b**: Yield: (65 %), green. M.p. (dec) 122 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 487 nm (3.72×10^2). IR: ν/cm^{-1} = 1625 m (C=N). Anal. Calcd. for $C_{52}H_{70}N_4O_7CrCl_3$: C, 61.14; H, 6.91; N, 5.48. Found: C, 61.24; H, 6.47; N 5.90 %. **14c**: Yield: (59 %), green. M.p. (dec) 132 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 347 nm (1.71×10^3). IR: ν/cm^{-1} = 1628 m (C=N). Anal. Calcd. for $C_{56}H_{46}N_4O_3CrCl_3$: C, 68.82; H, 4.72; N, 5.71. Found: C, 68.61; H, 4.77; N 5.52 %. μ_{eff} : 1.89 BM.

3.3.7 Cis-[Co(BCPD)$_2$Cl$_2$]Cl (15a), cis-[Co(BIPPD)$_2$Cl$_2$]Cl (15b), cis-[Co(BNPD)$_2$Cl$_2$]Cl (15c), cis-[Fe(BCPD)$_2$Cl$_2$]Cl (16a), cis-[Fe(BIPPD)$_2$Cl$_2$]Cl (16b), cis-[Fe(BNPD)$_2$Cl$_2$]Cl (16c), and cis-[Cr(BNPD)$_2$Cl$_2$]Cl (17c).

All of these *cis*-isomers were prepared according to the above mentioned procedures but starting from the corresponding *trans*-isomers.

15a: Yield: (53 %), pink. M.p. (dec) converts to *trans* at 130 °C. UV/vis (EtOH): λ_{max} (lg ε) = 490 nm (1.15×10^3). IR: ν/cm^{-1} = 1618 m (C=N). **15b**: Yield: (10 %), pink. M.p. (dec) converts to *trans* at 150 °C. UV/vis (EtOH): λ_{max} (lg ε) = 459 nm (1.51×10^1). IR: ν/cm^{-1} = 1621 m (C=N). **15c**: Yield: (16 %), brown. M.p. (dec) 120 °C. UV/vis (EtOH): λ_{max} (lg ε) = 500 nm (9.51×10^2). IR: ν/cm^{-1} = 1629 m (C=N). Anal. Calcd. for $C_{56}H_{48}N_4O_4CoCl_3$: C, 66.84; H, 4.81; N, 5.57. Found: C, 67.01; H, 4.52; N, 5.26 %. **16a**: Yield: (22 %), yellow. M.p. (dec) 130 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 400 nm (2.28×10^2). IR: ν/cm^{-1} = 1637 m (C=N). Anal. Calcd. for $C_{40}H_{68}N_4O_6FeCl_3$: C, 55.66; H, 7.94; N, 6.49. Found: C, 55.90; H, 8.20; N, 7.35 %. **16b**: Yield: (15 %), yellow. M.p. (dec) 78 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 432 nm (2.06×10^2). IR: ν/cm^{-1} = 1617 m (C=N). The elemental analysis of the corresponding *trans* isomer (**13b**) was carried out. **16c**: Yield: (94 %), violet. M.p. (dec) 114 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 510 nm (5.49×10^3). IR: ν/cm^{-1} = 1618 m (C=N). Anal. Calcd. for $C_{56}H_{40}N_4FeCl_3$: C, 72.23; H, 4.33; N, 6.02. Found: C, 72.05; H, 4.48; N, 5.79 %. μ_{eff}: 5.78 BM. **17c**: Yield: (79 %), red. M.p. (dec) 215 °C. UV/Vis (EtOH): λ_{max} (lg ε) = 501 nm (1.76×10^3). IR: ν/cm^{-1} = 1617 m (C=N). Anal. Calcd. for $C_{56}H_{40}N_4CrCl_3\cdot5\,H_2O$: C, 66.38; H, 4.95; N, 5.51. Found: C, 66.29; H, 5.24; N, 5.36 %. μ_{eff}: 3.75 BM.

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