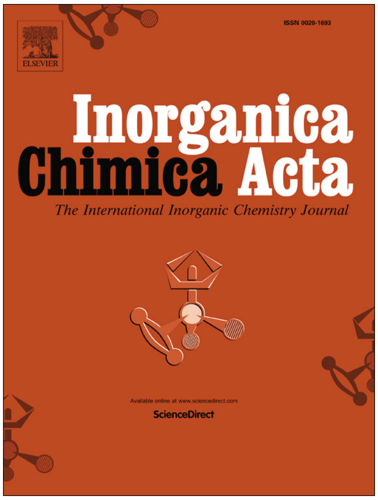

Four Cobalt(III) Schiff base complexes – structural, spectroscopic and electrochemical studies

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Four Cobalt(III) Schiff base complexes – structural, spectroscopic and electrochemical studies

Lukáš Pogány, [a*] Ján Moncol, [a] Miroslav Gál, [a] Ivan Šalitroš, [a] and Roman Boča [a,b]

a) Institute of Inorganic Chemistry, Slovak University of Technology, Bratislava SK-81237, Slovakia, *e-mail: lukas.pogany@stuba.sk
b) Department of Chemistry (FPV), University of SS Cyril and Methodius, 91701 Trnava, Slovakia

Abstract

Four new complexes of the general formula $[Co(L_n)Cl]$ (where L_n is dianion of pentadentate Schiff base ligand *N*,*N*'-bis(2-hydroxybenzylidene)-1,6-diamino-3-azahexane=H_2L_1, *N*,*N*'-bis(2-hydroxy-3-methoxy-benzylidene)-1,6-diamino-3-azahexane=H_2L_2, *N*,*N*'-bis(3-ethoxy-2-hydroxy-benzylidene)-1,6-diamino-3-azahexane=H_2L_3 or *N*,*N*'-bis(2-hydroxybenzylidene)-1,7-diamino-4-methyl-4-azaheptane=H_2L_4) have been synthesized and characterized by elemental analyses, IR, UV–VIS. The redox properties have been studied by cyclic voltammetry. Moreover, the crystal structures of **1**, **2** and **3** have been determined by X-ray diffraction and ^{1}H NMR spectrum of **4** has been obtained.

Keywords: Schiff base; Cobalt(III) complexes; Crystal structure; Spectral properties; Cyclic voltammetry

1. Introduction

Schiff base ligands with imine groups (–RC=N–) capable to coordinated with metal ions have many advantages and they are very popular up to now. These ligands can be easily prepared by a one-pot condensation reaction of an aldehyde or ketone with primary amines usually in an alcohol as a solvent. Generally, even a small modification of the ligand structure can significantly change properties of the corresponding complexes [1-3]. However, simplicity of preparation of Schiff base ligands allows one a fast and systematic preparation of a wide range of ligands with various substituents and tuning of physical properties can be studied easier. Schiff bases represent a very important class of compounds that are applied in many fields of research [4-10]. However, they are often coordinated to various transition metal ions in order to improve or modify their properties. Cobalt(III) complexes with pentadentate N_3O_2 ligands and their reactivity and structural properties have been extensively investigated for their miscellaneous applications, such as antifungal and antimicrobial agents as well as hypoxia-activated transporter of bioactive small molecules [11-17], production of redox-active sensors [18], ionic ferroelectrics [19], highly efficient catalysts in various fields of synthesis, as a precursor for preparation of Co_3O_4 nanoparticles and other useful reactions [20-25].

In the case when pentadentate N_3O_2 Schiff base is coordinated to cobalt(II) ion there is a tendency of this ion to oxidise and one arrives to cobalt(III) Schiff base complex. In order to prevent this oxidation an inert atmosphere has to be involved in synthesis [26]. In comparison to paramagnetic cobalt(II) Schiff base complexeswhich can exhibits even the single molecule magnetism [27], cobalt(III) complexes are, from magnetochemical point of view, usually low-spin and diamagnetic [28].

However also cobalt(III) core may become interesting if such a moiety forms a building block of Prussian blue analogues where it is linked to iron(II) via CN bridge. In this case a pair of diamagnetic centres $\{Fe^{II}_{LS}(t_{2g}^{6},S=0)-(\mu\text{-}CN)Co^{III}_{LS}(t_{2g}^{6},S=0)\}$ is reversibly converted into paramagnetic $\{Fe^{III}_{LS}(t_{2g}^{5},S=1/2)-(\mu\text{-}CN)Co^{II}_{HS}(t_{2g}^{5}e_{g}^{2},S=3/2)\}$ unit by electron transfer induced either thermally (heating above 150 K) or by light (blue light irradiation). This phenomenon is possible also within compounds with higher nuclearity, e.g. in the octanuclear $\{Fe_4Co_4\}$ species [29-31].

Herein we report the synthesis of four cobalt(III) complexes with general formula $[Co(L_n)Cl]$, where L_n is a dianion of pentadentate Schiff base ligand and n=1-4. These compounds have been characterized by elemental analyses, IR, UV–VIS. The X-ray crystal structures of **1**, **2** and **3** have been determined. The structure of **4** has been confirmed by ^{1}H NMR spectroscopy . The electrochemical behaviour and redox properties of these complexes are also reported and discussed.

2. Experimental

2.1. Materials and physical measurements

All solvents and chemicals were purchased from commercial sources and used without further purification. Elemental analyses were performed by using Eager 300 (Carlo Erba) elemental analyser. UV–VIS spectra were obtained on a Specord 250 plus (nujol technique), Analytical Jena spectrophotometer. Infrared spectra (ATR technique) were measured on a Magna FT- IR 750, Nicolet spectrophotometer. ^{1}H NMR spectrum was recorded with a Unity Inova spectrometer (300 MHz). Proton chemical shifts are reported in ppm relative to CD_3OD as an internal standard. The redox properties of the complexes were studied by cyclic voltammetry. LiCl (anhydrous) and absolute ethanol (≥99.8%) were supplied by Sigma–Aldrich. The indifferent electrolyte $TBAPF_6$ was dried under vacuum. Ethanol was dried over activated molecular sieves. Electrochemical measurements were performed using AUTOLAB instrument PGSTAT 302N (Metrohm). An electrochemical data from cyclic voltammetry were analyzed using AUTOLAB software. A three-electrode electrochemical cell was used. The reference electrode (RE), Ag|AgCl|1 M LiCl, was separated from the test solution by a salt bridge. The working electrode (WE) was Pt disk (d=0.8 mm). Prior to each experiment the surface of the WE was polished by 1 μm alumina and subsequently by 0.3 μm alumina. The auxiliary electrode was platinum net. The scan rate for the cyclic voltammetry was in the range 16-1024 mV s^{-1}. Oxygen was prior to each experiment removed from the solution by passing a stream of argon saturated with vapours of the solvent.

2.2. Synthesis and spectral properties

Herein reported Schiff base ligands have been synthesized without isolation, purification or characterisation. „In situ“ prepared ligands have been coordinated with cobalt(II) chloride in the presence of air, which allowed spontaneous oxidation to cobalt(III) complexes (Fig. 1). Complex **3** has already been prepared previously by slightly different procedure [32,33]. However, it has not been isolated and thus studied, characterised and described in details.

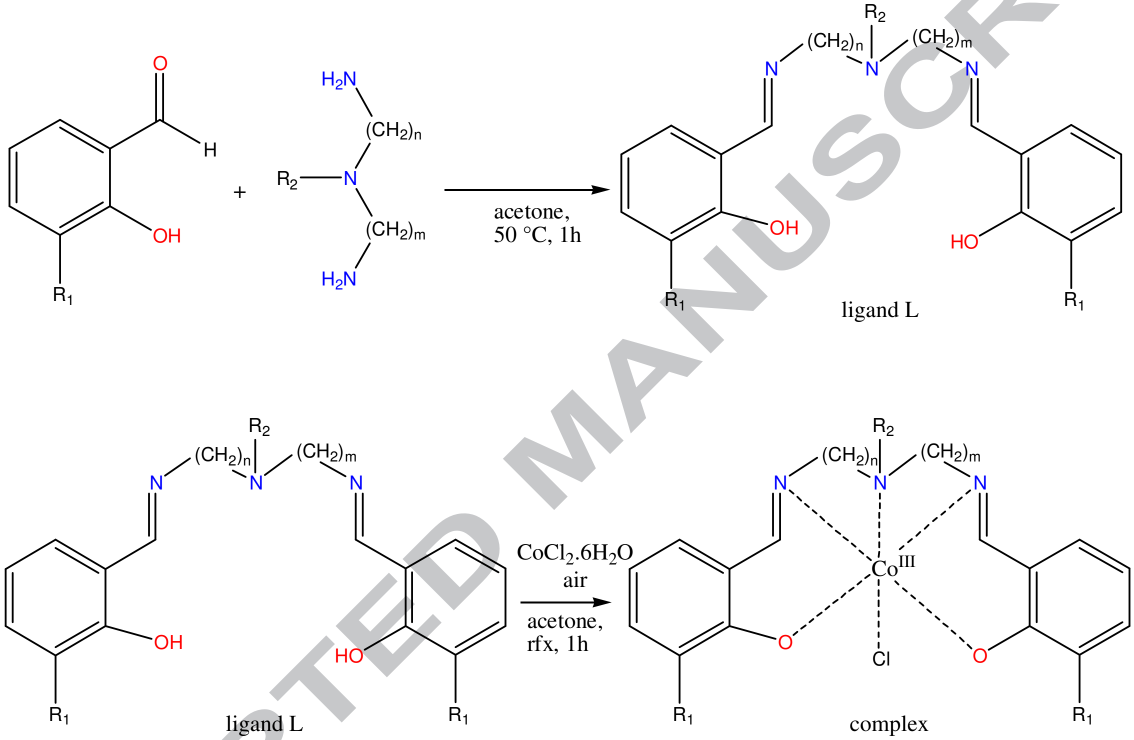

Fig. 1 Scheme of syntheses of ligands (upper) and complexes (bottom). For **1** (and corresponding ligand H_2L_1) $R_1 = R_2 = H$, n=2, m=3. For **2** (and corresponding ligand H_2L_2) R_1=OCH_3, R_2=H, n=2, m=3. For **3** (and corresponding ligand H_2L_3) R_1=OCH_2CH_3, R_2=H, n=2, m=3. For **4** (and corresponding ligand H_2L_4) R_1=H, R_2=CH3, n=m=3.

Synthesis of complex 1[Co(L_1)Cl]:Solution of salicylaldehyde (0.520 g, 4.26 mmol, 2 eq.) in acetone (30 mL) was heated to 50 °C and combined with a solution of N-(2-aminoethyl)-propane-1,3-diamine (0.249 g, 2.13 mmol, 1 eq.) in acetone (25 mL) subsequently. The reaction mixture was stirred at 50 °C for 1 hour, then combined with solution of cobalt(II) chloride hexahydrate $CoCl_2.6H_2O$ (0.507 g, 2.13 mmol, 1 eq.) in acetone (30 mL) and reaction mixture was refluxed for another 1 hour. One spoon of decolourising charcoal was then added to the reaction mixture, reflux continued for another 10-15 minutes and solution was filtered into the beaker with small amount of acetone (5 mL). Solution was set for crystallisation at 5°C and after few days were selected single crystals or polycrystalline powder. Yield 45 %. Elemental analysis for $C_{19}H_{21}ClCoN_3O_2.H_2O$: Found % (Calc %): C 52.46 (52.37); H 5.36 (5.32); N 9.05 (9.64). FT-IR (ATR, cm^{-1}) ν_{max}: 3599 (m, H_2O), 3421 (m, H_2O), 3201 (m, N–H), 1645 (s, C=N). Solid state UV–VIS: λ_{max}(nm) =697, 663, 620, 501, 402, 271.

Synthesis of complex 2 ([Co(L_2)Cl]): Complex **2** has been prepared via procedure similar to that of complex **1**, however salicylaldehyde has been substituted with 3-methoxysalicylaldehyde (0.498 g, 3.27 mmol, 2 eq.). Further procedure continued in the same manner as in the synthesis of complex **1**. Yield 55 %. Elemental analysis for $C_{21}H_{25}ClCoN_3O_4.C_3H_6O$: Found % (Calc %): C 53.46 (53.79); H 5.92 (5.83); N 7.84 (7.84). FT-IR (ATR, cm^{-1}) ν_{max}: 3203 (m, N–H), 1690 (s, C=O; acetone), 1644 (s, C=N). Solid state UV–VIS: λ_{max}(nm)=834, 705, 509, 390, 251.

Synthesis of complex 3([Co(L_3)Cl]): Synthesis of complex **3** has started with 3-ethoxysalicylaldehyde (0.502 g, 3.02 mmol, 2. eq.) instead of salicylaldehyde. Further procedure continued in the same manner as in the synthesis of complex **1**. Yield 53 %. Elemental analysis for $C_{23}H_{29}ClCoN_3O_4.H_2O$: Found %(Calc %): C 52.08 (52.73); H 5.91 (5.96); N 7.88 (8.02). FT-IR (ATR, cm^{-1}) ν_{max}: 3462 (m, H_2O), 3163 (m, N-H), 1718 (s, C=O; acetone), 1650 (s, C=N). Solid state UV–VIS: λ_{max}(nm)=695, 664, 629, 510, 400, 261.

Synthesis of complex 4([Co(L_4)Cl]): Complex **4** has been prepared via procedure similar to that of complex **1**, but in this case a solution of N-methyl-N,N-bis(3-aminopropyl)amine (0.305 g, 2.10 mmol, 1 eq.) instead of N-(2-aminoethyl)-propane-1,3-diamine was used. Further procedure continued in the same manner as in the synthesis of complex **1**. Yield 50 %. Elemental analysis for $C_{21}H_{25}ClCoN_3O_2$.acetone: Found % (Calc %): C 56.93 (57.20); H 6.33 (6.20); N 8.52 (8.34). FT-IR (ATR, cm^{-1}) ν_{max}: 1712 (s, C=O; acetone), 1628 (s, C=N). Solid state UV–VIS: λ_{max}(nm)=773, 594, 500, 393, 262. ^{1}H NMR (300 MHz, CD_3OD, 25 °C, δ/ppm):8.26 (s, 1H, CH=N), 8.06 (s, 1H, CH=N), 7.36-7.33 (d, 2H, H_{ar}), 7.24-7.15 (m, 4H, H_{ar}), 6.65-6.54 (m, 2H, H_{ar}), 6.11-6,04 (m, 2H, H_{ar}), 3.81-3.74 (t, 1H, H_{alif}), 3.65-3.59 (m, 1H, H_{alif}), 3.65-3.59 (m, 1H, H_{alif}), 3.12-3.02 (m, 1H, H_{alif}) 2.37-2.13 (m, 6H, H_{alif}), 1.54 (s, 3H, N-CH_3), 1.37-1.16 (m, 3H, H_{alif}).

2.3. X-Ray Crystallography for 1, 2 and 3

Data collection and cell refinement of **1-2** were carried out using a κ-axis diffractometer Xcalibur SCCD (Oxford Diffraction) with graphite monochromated MoKα radiation. The diffraction intensities were corrected for Lorentz and polarization factors. The data collection for **3** at 100 K was made by StoeStadiVari diffractometer using Pilatus 300K HPAD detector and microfocus source Xenocs FOX3D with CuKα. The structures were solved by direct methods using SHELXT [34] or SUPERFLIP [35] and refined by the full-matrix least-squares procedure with SHELXL (version 2016/4) [36]. The absorption corrections were made by using SCALE3 ABSPACK in CRYSALIS-RED. Geometrical analyses were performed with SHELXL. The structures were drawn using the OLEX2 package [37]. Crystal data and conditions of data collection and refinement are reported in Table 1.

Tab. 1 Crystallographic data for the reported compounds

Compound	**1**	**2**	**3**
Empirical formula	$C_{19}H_{23}ClCoN_3O_3$	$C_{24}H_{31}ClCoN_3O_5$	$C_{23}H_{29}ClCoN_3O_4$
Formula weight	435.78	535.91	505.87
Temperature (K)	293(1)	293(1)	100(1)
Wavelength (Å)	0.71073	0.71073	1.54186
Crystal system	monoclinic	monoclinic	trigonal
Space group	$P2_1/n$	$P2_1/c$	R–3
a (Å)	8.7080(4)	8.9154(4)	27.0224(7)
b (Å)	12.5195(6)	19.7800(10)	27.0224(7)
c (Å)	17.7401(9)	13.7207(6)	16.7206(4)
α (°)	90	90	90
β (°)	100.338(5)	92.081(4)	90
γ (°)	90	90	120
V (Å^3)	1902.63(16)	2418.00(19)	10573.8(6)
Z, ρ_{calc} g.cm^{-3}	4, 1.521	4, 1.472	18, 1.430
Radiation type	Mo-K_α	Mo-K_α	Cu-K_α
μ (mm^{-1})	1.067	0.861	7.058
F (0 0 0)	904	1120	4752
Crystal size (mm)	0.06x0.20x0.40	0.08x0.16x0.50	0.09x0.11x0.50
2θ Ranges (°)	8.154 to 52.744	8.184 to 52.744	6.496 to 142.554
Final R indices [I > 2σ(I)]	R_1=0.0519	R_1=0.0673	R_1=0.0327
	wR_2=0.0694	wR_2=0.0988	wR_2=0.0691
R indices (all data)	R_1=0.0927	R_1=0.1139	R_1=0.0481
	wR_2=0.0795	wR_2=0.1147	wR_2=0.0725
S	1.100	1.182	0.903
CCDC number	1507220	1507221	1510657

3. Results and discussion

3.1. Syntheses and spectral characterisation

Schiff base ligands H_2L_1 – H_2L_4 were prepared by the literature method [38] via the condensation of salicylaldehyde (H_2L_1, H_2L_4), 3-metoxysalicyladehyde (H_2L_2) or 3-etoxysalicyladehyde (H_2L_3) with 1,6-diamino-3-azahexane (H_2L_1, H_2L_2 and H_2L_3) or 1,7-diamino-4-methyl-4-azaheptane (H_2L_4) in acetone The yellow solutions of ligands were prepared „in situ“ and used for the further complexation without any purification and characterisation. The new complexes (**1**–**4**) were prepared through the oxidation of corresponding Co(II) intermediates by stirring in aerobic conditions. In case of **1**, **2** and **3** dark brown crystals suitable for the diffraction analysis were obtained after several days of controlled evaporation of solution at lowered temperature (45 - 55 % yields). The crystallisation of compound **4** failed therefore the polycrystalline powder has been used for the spectral and electrochemical investigation. Its structure was confirmed by ^{1}H NMR spectroscopy.

In the infrared spectroscopy (see supporting information Fig. S1) one can observe vibrational bands of secondary amino group –N – H at 3201, 3203 and 3163 cm^{-1} in **1** – **3**, respectively. This band is missing in the spectrum of **4** because aliphatic part of related Schiff base ligand contains tertiary amino group. In case of imino group –C=N bands located at 1645, 1644 and 1650 cm^{-1} are observed in IR spectra of complexes **1** – **3**, respectively. It reaches maximum at 1628 cm^{-1} in case of complex **4**. However, it is combined with a band of skeletal vibrations of aromatic rings IR spectrum of **1** exhibits bands 3599 and 3421 cm^{-1} that can be assigned to those of symmetric and antisymmetric vibration bands of crystal water molecules. Similarly, also in the IR spectrum of **3** a band at 3462 cm^{-1} of crystal water was found. On the other hand bands of acetone were found at 1690 and 1712 cm^{-1} in **2** and **4**, respectively.

The solid state electronic absorption spectra of **1** – **4** exhibit very similar features (see supporting information Fig. S2). One can observe bands at 251 – 271 nm that belong to $\pi \rightarrow \pi^*$ transitions of Schiff base ligands. The charge transfer transitions appear in 390–402 nm region. Bands in the visible region at 500-510 nm and 594-620 nm correspond to d-d transitions ($^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$). Compound **4** was purified by column chromatography (silica, 1% methanol in CH_2Cl_2) prior to ^{1}H NMR experiments. In the ^{1}H NMR spectrum of **4** (see supporting information Fig. S3) two imine protons of the ligand appear as two separate singlet peaks at 8.26 and 8.06 ppm. This is in agreement with thenon-similarity of the imine protons environment in octahedral coordination sphere of complex **4**. The aromatic protons of benzene rings are except doublet between 7.36 and 7.33 ppm found as complex multiplets appearing between 6.92 and 8.01 ppm. Signals of the aliphatic protons of the ethylene and propylene linkages in ligands appear except triplet in range 3.81-3.74 ppm as multiplets in the ranges 6.11-6.04, 3.65-3.59, 3.12-3.02, 2.37-2.13, 1.37-1.16 ppm. Aliphatic methyl group attached to the tertiary amino nitrogen atom was found as singlet at 1.54 ppm.

3.2. Description of crystal structures

Complexes **1** and **2** crystallize in centrosymmetric monoclinic space groups $P2_1/n$ and $P2_1/c$ for **1** and **2**, respectively. On the other hand, complex **3** crystallizes in centrosymmetric trigonal space group R–3. Selected crystallographic parameters are listed in the Table 1. Asymmetric unit contains in both monoclinic crystal structures one molecule of complex and either one molecule of water (**1**) or acetone (**2**) and four of them can be found in the unit cell (Fig. 2). The independent part of cell in crystal structure of **3** contains one complex molecule and undefined disordered solvent molecules of water around special positions. Coordination polyhedra can be expressed as deformed tetragonal bipyramid (for selected bond angles see Tab. S1) and distortion parameters acquire comparable values (Σ ≈ 28°, 29°and 23° for **1**, **2** and **3** [39] with similar iron(III) low-spin analogues [40,41], thus one can predict the same spin state for **1**, **2** and **3** as well. The low-spin state is evident also from values of Co1–N2(imino), Co1–N1(amino) and Co1–N3(amino) bond distances which vary in the ranges 1.97–1.98Å, 1.92–1.94 and 1.88–1.89Å, respectively (Tab. 2).The Co1–O1 and Co1–O2 distances are the shortest within the coordination core and in the compound **1** are the same 1.88Å, on the other hand in both cases **2** and **3** they reach the bonds values 1.88 and 1.89Å. The axial Co-Cl distances are the longest and weakest with distances 2.30, 2.27 and 2.29Å for **1**, **2** and **3,** respectively.

The equatorial planes are in both complexes formed by one phenolate oxygen donor atom, two imino and one amino nitrogen donor atoms. The second phenolate oxygen atom and chlorido terminal ligand anion occupy axial positions. Two oxygen atoms are mutually arranged in *cis* position; on the other hand the three nitrogen atoms form a meridional conformation (Fig. 2-Fig. 4).

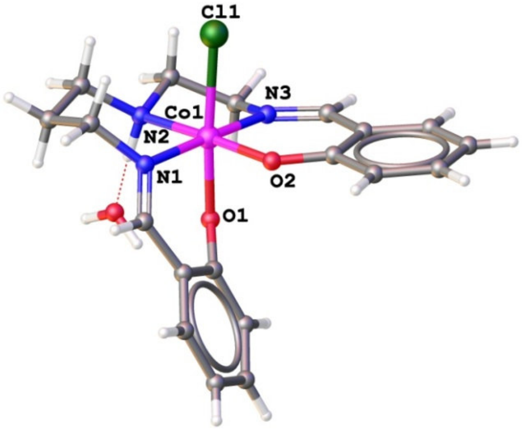

Fig. 2 Asymmetric unit of **1**

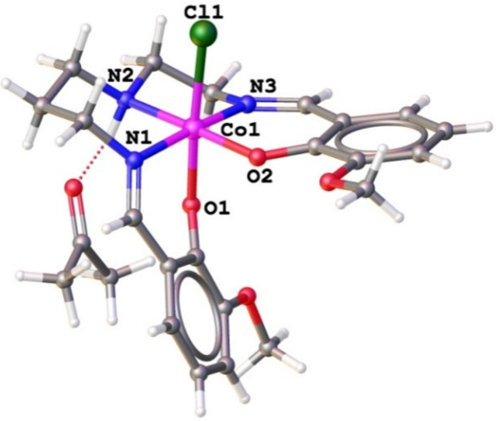

Fig. 3 Asymmetric unit of **2**

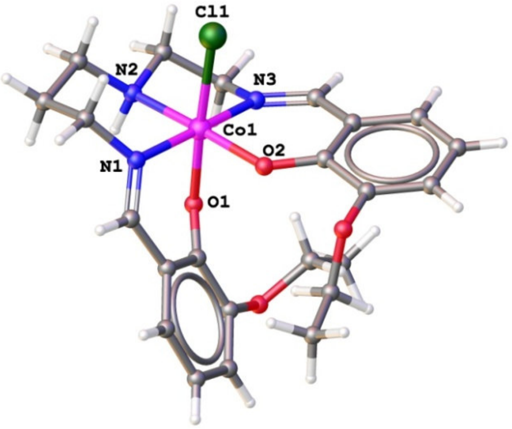

Fig. 4 Asymmetric unit of **3**

Tab. 2 Selected bond lengths of **1**, **2** and **3**

bond lengths	**1**	**2**	**3**
Co1-O1	1.884(2)	1.898(3)	1.8994(14)
Co1-O2	1.884(2)	1.881(3)	1.8969(14)
Co1-N1	1.928(3)	1.942(3)	1.9392(17)

Co1-N2	1.970(3)	1.973(3)	1.9792(17)
Co1-N3	1.888(3)	1.890(3)	1.8919(17)
Co1-Cl1	2.3029(10)	2.2746(13)	2.2892(5)

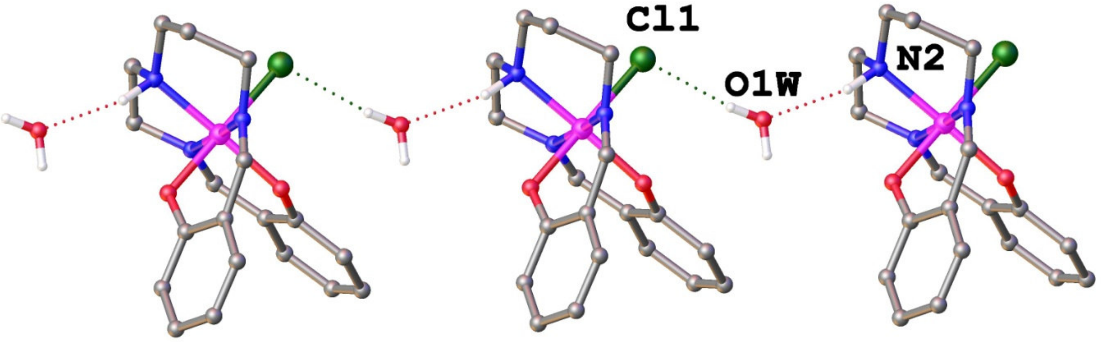

Fig. 5 Formation of 1D supramolecular chain in crystal structure of complexes **1**

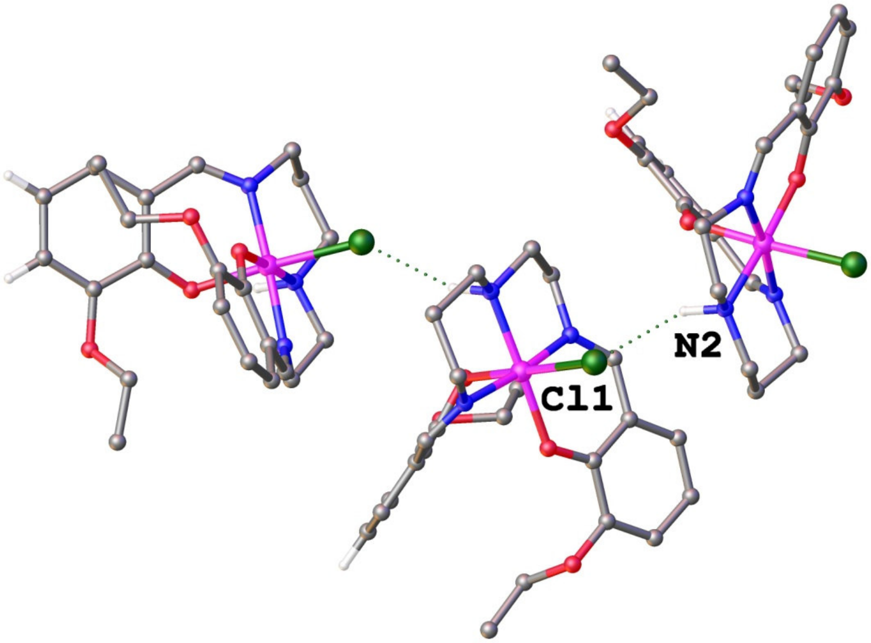

Fig. 6 Formation of 1D supramolecular chain in crystal structure of complexes **3**

Molecules of complex [Co(L_1)Cl] and lattice water form supramolecular hydrogen bounded 1D chain within the crystal structure of **1.** The oxygen atom of water molecule creates non-covalent contacts with amine nitrogen atoms of the first neighbouring [Co(L_1)Cl] molecule (N2···O1W distance of 2.97Å) on the one site and with chlorine atom of the second [Co(L_1)Cl] molecule (O1W-H2W···Cl1 with O1W···Cl1 distance of 3.23Å) on the other site, as is presented inFig. 5. In the crystal structure of **2** (Fig. 6) **,** there is a single hydrogen bond between a hydrogen atom attached to amine nitrogen and oxygen atom of acetone molecule (N3···O5 distance of 3.01 Å). The crystal structure of **3** forms spiral supramolecular chains from connecting complex molecules through hydrogen bonds between imine nitrogen groups and chloride ligands of neighbouring [Co(L_3)Cl] molecule (N2-H2...Cl with N2···Cl1 distance of 3.29Å).

3.3. Electrochemical studies

The redox behaviour of cobalt(III) complexes was studied by cyclic voltammetry in 0.1 M LiCl solution in dry ethanol. Voltammetric measurements confirmed a reversible one-electron transfer reaction which is in good agreement with previous studies. The expected direct relationship between both the electron-withdrawing and electron-donating character of the individual substituents and its reduction potential was recorded. In the next figure (Fig. 4) cyclic voltammograms are plotted.

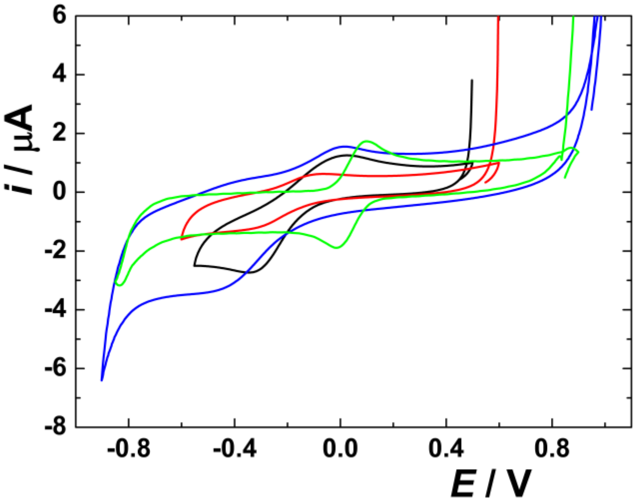

Fig. 4 Cyclic voltammogram of scan rate 128 mV s^{-1}; compound **1**– blue line, **2**– black line, **3 –** red line, **4**– green line.

All curves are characterized by the presence of single oxidation and reduction peak. The position of both oxidation and reduction peak depends on the structure of the respective compounds. Moreover, the broadness and separation of oxidation and respective reduction counter peak also depends on the structure of individual compounds. The lowest and the sharpest reduction potential, E_{red} was observed in case of compound **4**, E_{red} = -0.015 V vs. RE followed by the reduction potential of compounds **2** and **3**, $E_{red} \cong$ -0.330 V vs. RE and compound **1**, where E_{red} = -0.450 V vs. RE was recorded. Furthermore, reduction potential of the compound **1** is much broader compare to the compound **4**. The most positively on the potential axis is situated the oxidation peak of the compound **4**. Compounds **1** and **2** are oxidized at approximately the same potentials, $E_{ox} \cong$ 0.015 V vs. RE. The oxidation of compound **3** occurs at the lowest potential, $E_{ox} \cong$ -0.075 V vs. RE compare to the previous compounds.

In case of compound **4** the smallest separation ca ΔE = 90 mV between oxidation and reduction peaks was detected. This value of the peak separation is slightly higher compare to the potential difference ΔE = 65 mV found for ferrocene/ferrocenium redox couple. In case of the compounds **2** and **3** the separation of the respective oxidation and reduction peaks are almost ΔE = 250 mV. The ratio between the anodic and the cathodic peak (i_{pa}/i_{pc} ratio) is in case of the compound **4**approximately unity, in case of compounds **2** and **3** approximately 0.9. However, if the scan rate is lowered the i_{pc}/i_{pa} ratio reached unity. The position of oxidation and reduction peaks are somewhat dependent of the scan rate for all measured compounds, which indicate slower electron transfer and, therefore, quasi reversible behaviour. Little bit different situation is recorded in case of compound **1**. The peak separation is more than 350 mV (Figure 4) and the peak ration is ca 0.6. The position of respective oxidation and reduction peaks depends on the scan rate similarly as in case of previous compounds **2** – **4**. It seems that the electron transfer rate is for compound **1** slower than for the previous compounds **2** – **4**. One can conclude that even small changes in the structure of individual studied compounds **1** – **4** influence the electrochemical behaviour of all compounds.

The presence of alkoxy groups in case of compounds **2** and **3** shifts both reduction and oxidation potential to the more negative values compare to the compound **4**. More energy is required for the reduction and oxidation of the respective compounds. The differences between voltammograms of compound **1** and **4** are caused by the presence of methyl group and propylene link between nitrogen atoms in the structure of compound **1**.

In the next Fig. 5 the dependence of the height of oxidation and reduction peak of the compound **4** on the scan rate is plotted.

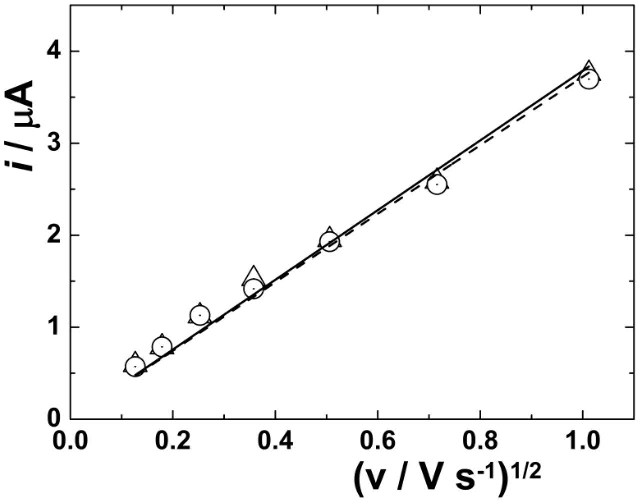

Fig 5 Dependence of the height of the (9) oxidation and (.) reduction peak of the compound **4** on the scan rate.

The reaction is controlled by the diffusion, which is demonstrated by the linear dependence of the peaks height, i_{pa} and i_{pc} on the square root of the scan rate, $v^{1/2}$. Moreover, the dependence of logarithm of anodic peak current vs. logarithm of scan rate gave a straight line with a slope of 0.45, which is close to the theoretical value of 0.5 for a purely diffusion controlled process. The current peak analysis of several voltammograms recorded at different scan rates gave, according to the Randles-Sevcik equation, the number of electrons exchanged during redox reaction, $n = 0.9\pm0.1$. This means that during negative scan direction Co(III) is reduced to Co(II) and, *vice versa*, during reversal scan direction, Co(II) is quasi reversibly reoxidized to Co(III).

4. Conclusion

Spectroscopic (IR and UV-VIS) and redox properties (cyclic voltammetry) of four new complexes of the type [Co(L_n)Cl], where L_n is dianion of pentadentate Schiff base ligand and n=1-4, crystal structure of **1**-**3** and ^{1}H NMR of **4** have been investigated. IR and UV-VIS spectra follow very similar features for all of them and all differences are fully in agreement with expectations based on the variation of structure. The crystal structures of complexes **1**-**3** are similar: low-spin diamagnetic cobalt(III) atom is surrounded by pentadentate Schiff base ligand and chlorido anion that form deformed tetragonal bipyramid environment. However, from supramolecular point of view one can found 1D infinite chain of alternating and H-bound water and complex molecules in **1**, a single H-bond between complex molecule and acetone molecule in **2** and spiral supramolecular chains from H-bond connected complex molecules in **3**. Structure of **4** was confirmed by ^{1}H NMR. A reversible one-electron transfer reaction was confirmed by voltammetric measurements. In case of compound **4** was observed the lowest and the sharpest reduction potential $E_{\mathrm{red}} = -0.015$ V vs. RE, followed by the compounds **2** and **3** with reduction potential $E_{\mathrm{red}} \cong -0.330$ V vs. RE and finally was recorded compound **1**, where $E_{\mathrm{red}} = -0.450$ V vs. RE. One can thus conclude that even small changes in the structure of individual studied compounds **1** – **4** influenced the electrochemical behaviour of all compounds. Slower electron transfer and thus quasi reversible behaviour was indicated by observation that the positions of oxidation and reduction peaks were somewhat dependent of the scan rate for all measured compounds. The dependence of the height of oxidation and reduction peak of the compound **4** on the scan rate was also studied. It was found that reaction is controlled by the diffusion and according to the Randles-Sevcik equation, the number of electrons exchanged during redox reaction is $n = 0.9\pm0.1$. The change between cobalt (II) and cobalt(III) thus took place.

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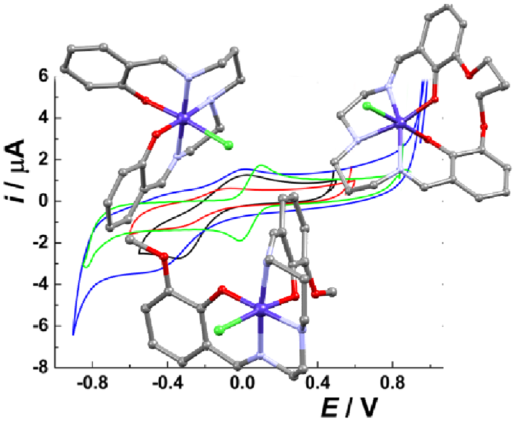
Graphical Abstract

Four Cobalt(III) Schiff base complexes – structural, spectroscopic and electrochemical studies

Lukáš Pogány,[a*] Ján Moncol,[a] Miroslav Gál,[a] Ivan Šalitroš,[a] and Roman Boča[a,b]

c) Institute of Inorganic Chemistry, Slovak University of Technology, Bratislava SK-81237, Slovakia, ***e-mail:** lukas.pogany@stuba.sk*

d) Department of Chemistry (FPV), University of SS Cyril and Methodius, 91701 Trnava, Slovakia



Four new mononuclear Co(III) complexes with pentadentate Schiff base ligands have been synthesized, spectrally and structurally characterised. In addition, electrochemical study revealed significant dependence of redox properties on the subtitle modification of Schiff base ligand structure.

Highlights

- **Four mononuclear Co(III) complexes with Schiff base ligands have been prepared-**
- **Structural investigation confirmed miscellaneous intermolecular interactions-**
- **Redox properties are strongly dependent on the Schiff base ligand skeleton.**