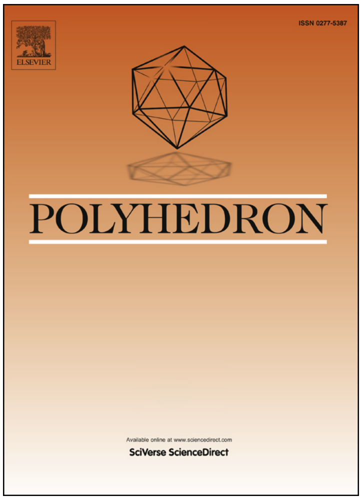

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PII: S0277-5387(13)00334-3
DOI: http://dx.doi.org/10.1016/j.poly.2013.04.047
Reference: POLY 10104

To appear in: *Polyhedron*

Received Date: 6 March 2013
Accepted Date: 24 April 2013

Please cite this article as: S. Öz, J. Titiš, H. Nazır, O. Atakol, R. Boča, I. Svoboda, H. Fuess, Synthesis, Structure And Magnetic Properties Of Ni(Ii)-Co(Ii) Heterodinuclear Complexes With Onno Type Schiff Bases As Ligands, *Polyhedron* (2013), doi: http://dx.doi.org/10.1016/j.poly.2013.04.047

SYNTHESIS, STRUCTURE AND MAGNETIC PROPERTIES OF Ni(II)-Co(II) HETERODINUCLEAR COMPLEXES WITH ONNO TYPE SCHIFF BASES AS LIGANDS

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Abstract

Four new heterodinuclear Ni(II)-Co(II) complexes, NiL.$CoCl_2$.$(DMF)_2$ (**I**), NiL.$CoBr_2$.$(DMF)_2$ (**II**), NiL'.$CoCl_2$.(DMF)2 (**III**) and NiLDM.$CoCl_2$$(DMF)_2$ (**IV**), have been prepared in non-aqueous DMF using the ONNO type Schiff bases N,N'-bis(2-hydroxyphenylidene)-1,3-propanediamine (LH_2), N,N'-bis(2-hydroxyphenylidene)-1,4-butanediamine ($L'H_2$) and N,N'-bis(2-hydroxyphenylidene)-2,2'-dimethyl-1,3-propanediamine ($LDMH_2$), and the inorganic salts $NiCl_2$ and $CoCl_2$. The complexes were characterized by elemental analysis, IR spectroscopy, thermogravimetry and X-ray diffraction. An XRD study revealed that the Ni(II) ion is situated at the center of a distorted octahedral coordination sphere formed by two iminic nitrogen and two phenolic oxygen atoms of the ONNO type Schiff base and two other oxygen atoms belonging to coordinated DMF molecules. On the other hand, the Co(II) ion is situated inside a distorted tetrahedral coordination sphere, members of which being the two halogen atoms and two oxygen atoms, bonded to form a μ-bridge.

The magnetic susceptibility of the complexes was studied using a SQUID magnetometer between 2.0 and 300 K at $B = 0.1$ T, and the magnetization data were taken up to $B = 7$ T at $T = 2.0$ and 4.6 K. The exchange interaction between the metal centers is of a ferromagnetic nature (typically $J_{\text{Co-Ni}}/hc = +2\ \text{cm}^{-1}$) and at low temperature single-ion zero-field splitting applies ($D_{\text{Ni}}/hc = +8\ \text{cm}^{-1}$, $D_{\text{Co}}/hc = +14\ \text{cm}^{-1}$).

Keywords: Heterodinuclear complex, Ni(II)-Co(II), Schiff base ligand, magnetic properties, thermogravimetry

Introduction

It is well known that the Schiff base N,N'-bis(2-hydroxyphenylidene)-1,3-propanediamine (LH_2) readily forms polynuclear complexes. There are numerous reports on trinuclear [1-10], tetranuclear [11-13] and polynuclear [14-15] complexes of this ligand and its derivatives. Being an ONNO type ligand, the molecule is able to coordinate Ni(II) and Cu(II) ions between its donor atoms and the second metal ion by the phenolic oxygen atoms, forming a bridge (Fig 1). Such a dinuclear coordination was first observed in a dinuclear Cu(II)-Cu(II) complex [16]. This class of dinuclear complex possesses interesting magnetic properties due to the magnetic exchange interactions [17-23]. In the mentioned studies, Cu(II)-Cu(II) [17-19], Cu(II)-Mn(II), Cu(II)-Ni(II) [20], Cu(II)-Cu(III) [21] and Cu(II)-In(III) [23] complexes with similar ligands were prepared. Their magnetic properties were also reported. Also, the antimicrobial, antifungal and luminescence properties of a heterodinuclear Mn(II)-Zn(II) complex were investigated [22]. LH_2 and its derivatives readily give NiL and CuL complexes with Ni(II) and Cu(II) ions [24], and these complexes have the tendency to coordinate the salts of the 12-group elements, namely Zn^{2+}, Cd^{2+} and Hg^{2+} [25-28]. The literature also describes similar complexes prepared from Sn^{2+} and Pb^{2+} halides [29-30].

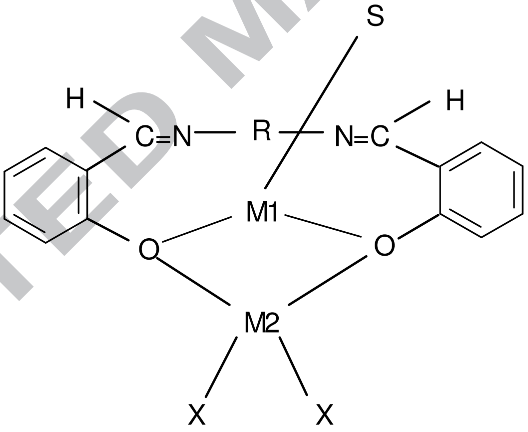

Fig 1 Sketch of the dinuclear complexes prepared via LH_2: M1 = Ni^{2+} or Cu^{2+}; M2 = Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Sn^{2+}; X = Cl^-, Br^-, I^-; S = dioxane or DMF.

The literature is silent about complexes of the above type with M2 = Co(II). This gap is filled by the present communication where four heterodinuclear Ni(II)-Co(II) complexes were synthesized (Fig 2). In parallel with preliminary studies, these complexes were prepared in dry DMF [28]. The complexes were characterized by elemental analysis, X-ray structure analysis and thermogravimetry. Their magnetic properties were investigated by SQUID magnetometry.

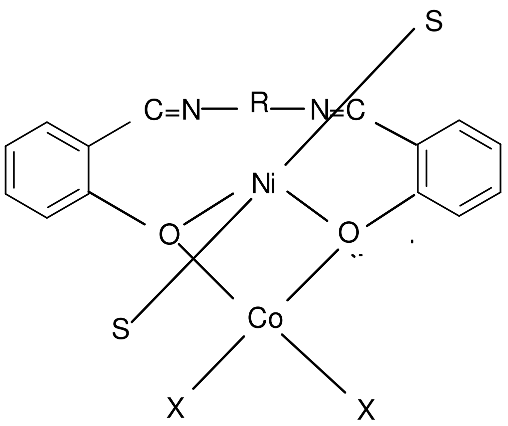

Fig 2 Sketch of heterodinuclear complexes: R = -$(CH_2)_3$-, X = Cl^-, S = DMF (**I**); R = -$(CH_2)_3$-, X = Br^- , S = DMF (**II**); R = -$(CH_2)_4$-, X = Cl^-, S = DMF (**III**); R = -CH_2-$C(CH_3)_2$-CH_2-, X = Cl^-, S = DMF (**IV**).

Experimental

Apparatus

An FTIR-spectrometer (Shimadzu) equipped with three reflection ATR units was used in taking the IR spectra. The C, H and N analyses were performed using an Elemantal Vario Micro Cube instrument. Metal analyses were recorded on a GBC Avanta PM Model atomic absorption spectrometer using the FAAS mode. The mass spectra were obtained by a Shimadzu, 2010 plus with a DI unit with an electron impact ionizer. The DI temperature was varied between 40 and 140 ^{o}C and the ionization was carried out with electrons of 70 eV energy. The NMR spectra were recorded on a Varian Mercury 400 MHz FT-NMR spectrometer using d_6-DMSO as the solvent.

The thermogravimetric analyses were performed by a Shimadzu DTG-60H. In the thermogravimetric analyses, the emperature was varied between 30 and 600 ^{o}C. These analyses were performed at 10 ^{o}C/min scan rate and under a N_2 atmosphere in Pt pans. Calibration of the instrument was done with metallic In, Pb or Zn. The stoichiometry of the complexes was estimated with the help of the mass loss data of the coordinatively bonded DMF molecules and the thermal decomposition properties of the complexes were determined.

The magnetic data were taken with a SQUID apparatus (MPMS-XL7, Quantum Design) using the RSO mode of detection. The temperature dependence of the magnetic susceptibility taken at B = 0.1 T has been corrected for the underlying diamagnetism and converted to the effective magnetic moment. The field dependence of the magnetization has been measured at two temperatures: $T = 2.0$ and $T = 4.6$ K.

X-ray analysis

Single crystals of **I**, **II**, **III** and **IV** were mounted on an Xcalibur (TM) single crystal X-ray diffractometer (Oxford Diffraction) with a sapphire CCD detector using MoK_{α} radiation (λ = 0.71073 Å) operating in the $\omega/2\theta$ scan mode. The unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the $2.79 \leq \theta \leq 26.36$ range for complex **I**, $2.81 \leq \theta \leq 27.82$ range for complex **II**, $2.62 \leq \theta \leq 27.97$ range for complex **III** and $3.07 \leq \theta \leq 27.93$ range for complex **IV**. The data of complexes **I**, **II** and **III** were collected at $T = 293(2)$ K and the data of complex **IV** was collected at 105(2) K. The empirical absorption corrections were applied by the semi-empirical method via the CrysAlis CCD software [31]. Models were obtained from the results of the cell refinement and the data reductions were carried out using the solution software SHELXL97 [32]. The structures of all the complexes were solved by direct methods using the SHELXS97 software implemented in the WinGX package [33].

Synthesis

The used reagents were from Merck or Fluka, and they were used without further purification.

Preparation of N,N'-bis(2-hydroxyphenylidene)-1,3-propanediamine (LH_2)

This Schiff base was prepared via a condensation reaction in EtOH under hydrothermal conditions using 2-hydroxy-benzaldehyde and 1,3-diaminopropane. 2-Hydroxy-benzaldehyde (0.02 mol, 2.44 g) was dissolved in 40 cm^3 of warm EtOH, then 0.01 mol (0.74 g) of 1,3-diaminopropane was added to this solution and heated up to the boiling point. After cooling, yellow crystals were filtered and air-dried. Yield: 92-95 %, mp 58 °C (determined by TG). Elemental analysis for $C_{17}H_{18}N_2O_2$: theoretical C 72.3, H 6.43, N 9.92 %; found C 71.9, H 6.45, N 10.47 %. λ_{max} = 243 nm, ε = 7045 $dm^3\ mol^{-1}\ cm^{-1}$ in DMSO, λ_{max} = 242 nm, ε = 7865 $dm^3\ mol^{-1}\ cm^{-1}$ in MeOH. IR (cm^{-1}): ν_{O-H} 2627, $\nu_{C-H(Ar)}$ 3021-3019, $\nu_{C-H(aliph)}$ 2929-2862, $\nu_{C=N}$ 1629, $\nu_{C=C(ring)}$ 1608, $\nu_{C-O(phenol)}$ 1274-1151, $\delta_{C-H(Ar)}$ 762. ^{1}H-NMR in d_6-DMSO: 13.51 (s) (O-H), 8.60 (s) (-CH=), 7.43 (d) (H_{Ar}), 7.32 (t) (H_{Ar}), 6.88 (t) (H_{Ar}), 3.68 (t) (N-CH_2-), 2.01 (p) (-CH_2-). ^{13}C-NMR in d_6-DMSO: 166.6, 161.1, 132.7, 132.1, 119.1, 118.9 (C_{Ar}), 116.9 (-C=N), 58.5 (N-CH_2-), 31.9 (-CH_2-). *m*/*z*: 282 $[M]^+$, 161 $[HO\text{-}C_6H_4\text{-}CH{=}N\text{-}CH_2\text{-}CH_2\text{-}CH_2]^+$, 148 $[HO\text{-}C_6H_4\text{-}CH{=}N\text{-}CH_2\text{-}CH_2]^+$ (BP), 134 $[HO\text{-}C_6H_4\text{-}CH{=}N\text{-}CH_2]^+$, 120 $[HO\text{-}C_6H_4\text{-}CH{=}N]^+$, 107 $[HO\text{-}C_6H_4\text{-}CH_2]^+$, 77 $[C_6H_5]^+$.

Preparation of N,N'-bis(2-hydroxyphenylidene)-1,4-butanediamine (L'H_2):

This Schiff base was prepared following the same procedure as for LH_2 from 0.02 mol (2.44 g) 2-hydroxy-benzaldehyde and 0.01 mol (0.88 g) 1,4-diaminobutane. Yield: 89-92 %, mp: 92 °C (determined by TG). Elemental analysis for $C_{18}H_{20}N_2O_2$: theoretical C 72.9, H 6.80, N 9.44 %; found C 72.5, H 6.14, N 9.33 %. λ_{max} = 242 nm, ε = 8055 $dm^3\ mol^{-1}\ cm^{-1}$ in DMSO, λ_{max} = 241 nm, ε = 6005 $dm^3\ mol^{-1}\ cm^{-1}$ in MeOH. IR (cm^{-1}): $\nu_{O\text{-}H}$ 2635, $\nu_{C\text{-}H(Ar)}$ 3021-3019, $\nu_{C\text{-}H(aliph)}$ 2929-2862, $\nu_{C=N}$ 1629, $\nu_{C=C(ring)}$ 1608, $\nu_{C\text{-}O(phenol)}$ 1274-1151, $\delta_{C\text{-}H(Ar)}$ 762. ^{1}H-NMR in d_6-DMSO: 13.51 (s) (O-H), 8.38 (s) (-CH=), 7.29 (d,t) (H_{Ar}), 7.24 (d,d) (H_{Ar}), 6.95 (d) (H_{Ar}), 6.86 (d,t) (H_{Ar}), 3.63 (t) (N-CH_2-), 1.79 (t) (-CH_2-CH_2-). ^{13}C-NMR in d_6-DMSO: 165.16, 161.44, 132.38, 131.43, 118.98, 118.75 (C_{Ar}), 117.22 (-C=N), 59.48 (N-CH_2-), 28.75 (-CH_2-CH_2-). *m/z*: 296 $[M]^+$, 175 $[HO\text{-}C_6H_4\text{-}CH=N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2]^+$, 148 $[HO\text{-}C_6H_4\text{-}CH=N\text{-}CH_2\text{-}CH_2\text{-}CH_2]^+$ (BP), 134 $[HO\text{-}C_6H_4\text{-}CH=N\text{-}CH_2]^+$, 120 $[HO\text{-}C_6H_4\text{-}CH=N]^+$, 107 $[HO\text{-}C_6H_4\text{-}CH_2]^+$, 77 $[C_6H_5]^+$.

Preparation of N,N'-bis(2-hydroxyphenylidene)-2,2'-dimethyl-1,3-propanediamine ($LDMH_2$)

This Schiff base was also prepared accordingly to the LH_2 procedure from 0.02 mol (2.44 g) 2-hydroxy-benzaldehyde and 0.01 mol (1.02 g) 2,2'-dimethyl-1,3-diaminopropane. Yield: 87-90 %, mp: 98 °C (determined by TG). Elemental analysis for $C_{19}H_{22}N_2O_2$: theoretical C 73.5, H 7.14, N 9.02 %; found C 73.4, H 6.35, N 8.72 %. λ_{max} = 243 nm, ε = 7860 $dm^3\ mol^{-1}\ cm^{-1}$ in DMSO, λ_{max} = 243 nm, ε = 7825 $dm^3\ mol^{-1}\ cm^{-1}$ in MeOH. IR (cm^{-1}): $\nu_{O\text{-}H}$ 2578, $\nu_{C\text{-}H(Ar)}$ 3021-3019, $\nu_{C\text{-}H(aliph)}$ 2929-2862, $\nu_{C=N}$ 1629, $\nu_{C=C(ring)}$1608, $\nu_{C\text{-}O(phenol)}$ 1274-1151, $\delta_{C\text{-}H(Ar)}$ 762. ^{1}H-NMR in d_6-DMSO: 13.58 (s) (O-H), 8.36 (s) (-CH=N), 7.30 (t) (H_{Ar}), 7.25 (d,t) (H_{Ar}), 6.97 (d), 6.84 (dt) (H_{Ar}), 3.49 (s) (N-CH_2-), 1.04 (s) (-$C(CH_3)_2$-). ^{13}C-NMR in d_6-DMSO: 166.99, 161.45, 132.57, 131.61, 118.95, 118.87 (C_{Ar}), 117.20(-C=N), 68.36(N-CH_2-), 34.48 (-$C(CH_3)_2$-), 24.61 (-$C(CH_3)_2$-). *m/z*: 310 $[M]^+$, 176 $[HO\text{-}C_6H_4\text{-}CH=N\text{-}CH_2\text{-}C(CH_3)_2]^+$, (BP), 134 $[HO\text{-}C_6H_4\text{-}CH=N\text{-}CH_2]^+$, 120 $[HO\text{-}C_6H_4\text{-}CH=N]^+$, 107 $[HO\text{-}C_6H_4\text{-}CH_2]^+$, 77 $[C_6H_5]^+$.

Preparation of the Ni(II)-Co(II) complexes

All the complexes were prepared using the Schiff bases and metal salts in anhydrous DMF [28]. 0.02 mol of a Schiff base was dissolved in 40 cm^3 of warm, anhydrous DMF, then a solution of 0.002 mol (0.237 g) of $NiCl_2.6H_2O$ in 10 cm^3 of DMF, 0.2 cm^3 Et_3N and a solution of 0.085 g (0.001 mol) of CoX_2 (X= Cl^- or Br^-) salt in 10 cm^3 of hot anhydrous DMF was added. The temperature was raised to 110 °C. The final solution was allowed to stand for 48 hours. The formed blue crystals were separated by vacuum filtration and air dried.

Complex I: $NiL.CoCl_2.DMF_2$ was prepared using 0.565 g LH, 0.475 g $NiCl_2.6H_2O$ and 0.238 g $CoCl_2.6H_2O$ as described above. Elemental analysis for $C_{17}H_{16}N_2O_2Ni.CoCl_2.(C_3H_7NO)_2$: theoretical C 44.9, H 4.92, N 9.10, Cl 11.53, Ni 9.54, Co 9.58 %; found C 44.4, H 4.87, N 9.32, Cl 10.91±0.71, Ni 9.68±0.18, Co 9.35±0.15 %. IR (cm^{-1}): $\nu_{C\text{-}H(Ar)}$ 3033-3017, $\nu_{C\text{-}H(aliph)}$ 2937-2864, $\nu_{C=O(DMF)}$ 1644, $\nu_{C=N}$ 1624, $\nu_{C=C(ring)}$ 1596, $\nu_{C\text{-}O(phenol)}$ 1278-1148, $\delta_{C\text{-}H(Ar)}$ 758. Determination of DMF by TG: found 22.81±0.74, calculated 23.75 %.

Complex II: $NiL.CoBr_2.DMF_2$ was prepared from 0.565 g LH_2, 0.475 g $NiCl_2.6H_2O$ and 0.219 g $CoBr_2$ by the procedure given above. Elemental analysis for $C_{17}H_{16}N_2O_2Ni.CoBr_2.(C_3H_7NO)_2$: theoretical C 39.2, H 4.30, N 7.95, Br 22.7, Ni 8.34, Co 8.37 %; found C 38.8, H 3.93, N 8.07, Br 21.34±0.52, Ni 7.91±0.27, Co 7.87±0.19 %. IR (cm^{-1}): $\nu_{C\text{-}H(Ar)}$ 3029-3011, $\nu_{C\text{-}H(aliph)}$ 2949-2866, $\nu_{C=O(DMF)}$ 1644, $\nu_{C=N}$ 1625, $\nu_{C=C(ring)}$ 1593, $\nu_{C\text{-}O(phenol)}$ 12734-1155, $\delta_{C\text{-}H(Ar)}$ 756. DMF: found 21.11±1.23, calculated 20.75 %.

Complex III: $NiL'.CoCl_2.DMF_2$ was prepared from 0.592 g $L'H_2$, 0.475 g $NiCl_2.6H_2O$ and 0.238 g $CoCl_2.6H_2O$ as described above. Elemental analysis for $C_{18}H_{18}N_2O_2Ni.CoCl_2.(C_3H_7NO)_2$: theoretical C 45.8, H 5.13, N 8.90, Cl 11.27, Ni 9.33, Co 9.37 %; found C 46.1, H 4.95, N 9.14, Cl 10.88±0.27, Ni 8.94±0.34, Co 8.89±0.47 %. IR (cm^{-1}): $\nu_{C\text{-}H(Ar)}$ 3034-3015, $\nu_{C\text{-}H(aliph)}$ 2991-2866, $\nu_{C=N}$ 1627, $\nu_{C=O(DMF)}$ 1645, $\nu_{C=C(ring)}$ 1601, $\nu_{C\text{-}O(phenol)}$ 1271-1155, $\delta_{C\text{-}H(Ar)}$ 758. DMF: found 23.01±1.13, calculated 23.22 %.

Complex IV: $NiLDM.CoCl_2.DMF_2$ was prepared with 0.620 g $LDMH_2$, 0.475 g $NiCl_2.6H_2O$ and 0.238 g $CoCl_2.6H_2O$ as described above. Elemental analysis for $C_{19}H_{20}N_2O_2Ni.CoCl_2.(C_3H_7NO)_2$: theoretical C 46.7, H 5.32, N 8.70, Cl 11.02, Ni 9.13, Co 9.16 %; found C 46.4, H 4.97, N 8.76, Cl 10.49±0.64, Ni 8.81±0.21, Co 8.95±0.71 %. IR (cm^{-1}): $\nu_{C\text{-}H(Ar)}$ 3031-3017, $\nu_{C\text{-}H(aliph)}$ 2950-2867, $\nu_{C=O(DMF)}$ 1644, $\nu_{C=N}$ 1627, $\nu_{C=C(ring)}$ 1605, $\nu_{C\text{-}O(phenol)}$ 1284-1156, $\delta_{C\text{-}H(Ar)}$ 757. DMF: found 22.49±1.33, calculated 22.70 %.

Results and discussion

X-ray structure

The molecular structures obtained by the X-ray diffraction analysis are shown in Fig. 3. The crystal data, data collection and refinement parameters are given in Table 1. Selected bond lengths and angles are listed in Table 2.

Fig. 3 reveals that the Ni(II) atom lies in plane formed by two phenolic oxygen atoms and two iminic nitrogen atoms. The oxygen atoms of the coordinated DMF molecules are located in axial positions in the NiN_4O_2 coordination sphere, so this coordination sphere is distorted octahedral. The Co(II) atom is coordinated by two phenolic oxygens and two halogen atoms, and the CoO_2Cl_2 coordination sphere is distorted tetrahedral.

The chelate rings in vicinity of the Ni(II) central atom are 6-membered in complexes **I**, **II** and **IV**, whereas it is 7-membered in complex **III**. The expected conformation of the 6-membered ring is the chair conformation, however complexes **I**, **II** and **IV** show almost a half-chair conformation [27]. The angles between the C8C9C10 and N1C8C9N2 planes of the NiN1C8C9C10N2 ring are calculated as 65.37° for complex **I**, 63.85° for complex **II** and 54.34° for complex **IV**. These values for complexes **I** and **II** are close to those expected for an ideal chair conformation. This angle deviates due to the steric effects of the two methyl groups. The unexpected situation seen in the chelate rings is the small angle between the N1NiN2 and C8N1N2C9 planes (1.5, 0.79 and 9.39° for complexes **I**, **II** and **IV**, respectively). Previous studies have reported these angles to be around 10-15°. The Ni atom and the C8N1O1O2N2C9 atoms are situated in the same plane. The angle between the N1O1O2N2Ni atom plane and O1CoO2 plane is also small: 6.26, 6.65 and 1.03° for complexes **I**, **II** and **IV**, respectively.

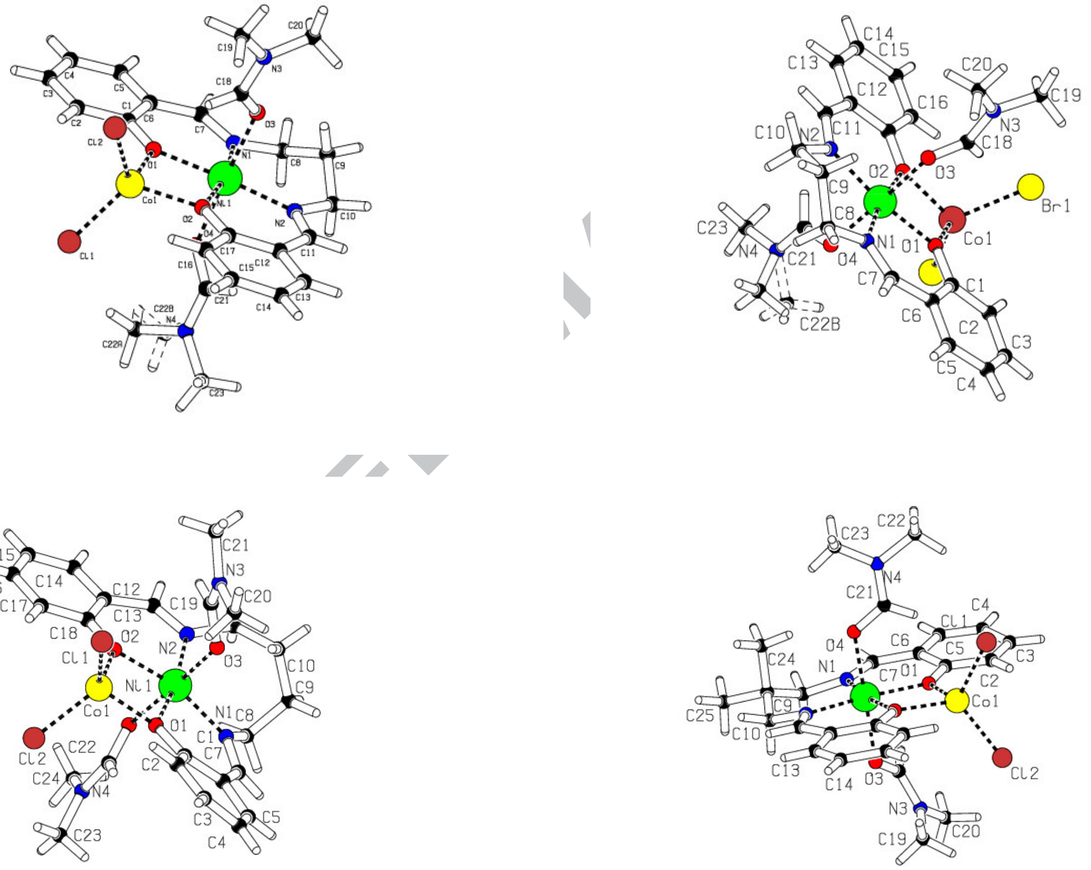

Fig 3 ORTEP drawing of complexes **I** through **IV** (in the reading direction).

The C8N1O1O2N2C9, Co(II) and Ni(II) atoms span the same planar structure. The 7-membered chelate ring in complex **III** does not show analogous behavior, since the C8C11N1N2 atoms do not form an exact plane. In addition, the O1N1N2O2Ni atoms exhibit a deviation from the mean plane. The maximum deviation of the O1N1N2O2Ni atoms from the mean plane is 0.0314 Å for the complexes **I**, **II** and **IV** and between 0.839-0.1229 Å for complex **III**. This can be related to the torsion effect of the C9 and C10 atoms.

Thermogravimetry

TG has been utilized in studying the thermal stability and stoichiometry of the complexes. DMF coordinated to the Ni(II) atoms can be liberated from the crystal structure in a characteristic temperature range. Thus, measurement of the mass loss in this temperature range can help us in determining the stoichiometry of the complexes. Fig. 4 shows comparative TG curves of the four complexes. The thermal mass loss temperature of DMF molecules is between 168 and 195 ºC for the complexes **I** and **II**. This interval is shifted down to 145-152 ºC and 140-155 ºC for complexes **III** and **IV**, respectively. Since the distortion in **I** and **II** is lower (these molecules are more symmetric), the DMF molecules tend to stay within the structure until higher temperatures. Distortion of the structures in complexes **III** and **IV** shifts the DMF decomposition temperature to lower values.

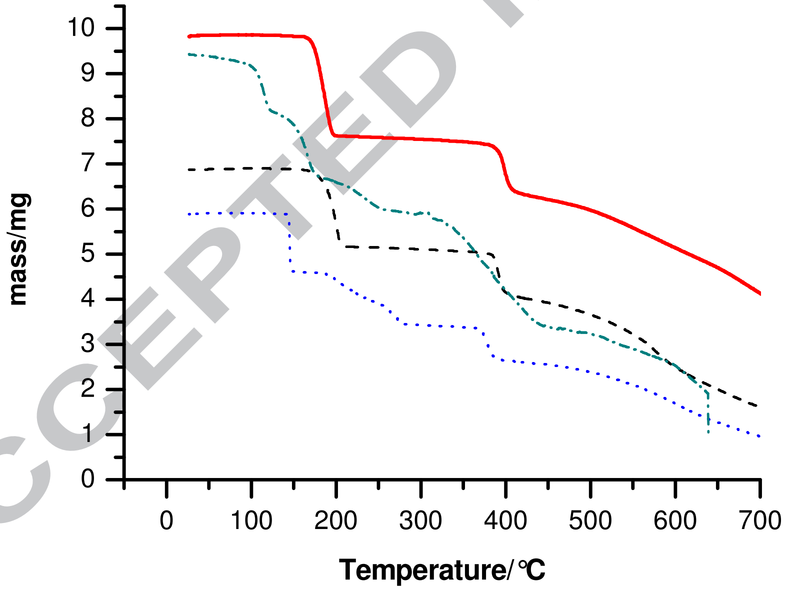

Fig 4 TG records for the Ni(II)-Co(II) complexes: **I** – dashed, **II** – solid, **III** – dotted, **IV** – dot dashed.

The electron density in the Ni-O bond decreases as the Co^{2+} ions withdraw an electron from the phenolic oxygens. Consequently the Ni^{2+} ions tend to accept electrons from other donors, which are the solvent molecules. When the DMF molecules are thermally separated from the structure, the electron of the phenolic oxygens become insufficient to stabilize both ions and the Co-O coordination bond can disintegrate. The thermal degradation of NiL has been reported to occur at 360-380 ºC. Inspection to the TG curves confirms that a degradation of NiL proceeds at 380 ºC. This shows that NiL degradation takes place only after liberation of DMF.

Magnetometry

One Ni(II) and one Co(II) center produce a high-temperature limit for the effective magnetic moment, $\mu_{\mathrm{eff}} = [g_{\mathrm{Co}}^2 s_{\mathrm{Co}}(s_{\mathrm{Co}}+1) + g_{\mathrm{Ni}}^2 s_{\mathrm{Ni}}(s_{\mathrm{Ni}}+1)]^{1/2}\mu_{\mathrm{B}}$, which amounts to 5.27 μ_{B} when all g = 2.2 are applied. On cooling from the room temperature, the effective magnetic moment for complex **I** slightly increases from μ_{eff} = 5.75 μ_{B} until T = 10 K and then it decreases rapidly to a value of 5.15 μ_{B} at T = 2.0 K (Fig 5). This feature indicates a weak ferromagnetic coupling between the magnetic centers and some zero-field splitting that applies at low temperature. Down to 2.0 K the molar magnetic susceptibility only increases, showing no local maximum. The molar magnetization per formula unit possesses the saturation limit $M_1 = M_{\mathrm{mol}} / N_{\mathrm{A}}\mu_{\mathrm{B}} = g_{\mathrm{Co}} s_{\mathrm{Co}} + g_{\mathrm{Ni}} s_{\mathrm{Ni}}$, which yields M_1 = 5.5 for $S_{\max}$ = 5/2 and g = 2.2. The measured magnetization adopts a value of only M_1 = 4.8 at T = 2.0 K and B = 7 T, which confirms some zero-field splitting.

The magnetic data were analyzed using the following spin Hamiltonian:

$$\begin{aligned}\hat{H}_a &= -J(\vec{S}_{\mathrm{Ni}} \cdot \vec{S}_{\mathrm{Co1}})\hbar^{-2} + [\hat{H}_a^{(\mathrm{Ni})} + \hat{H}_a^{(\mathrm{Co})}] \\ &\quad + [D_{\mathrm{Ni}}(\hat{S}_{\mathrm{Ni},z}^2 - \hat{S}_{\mathrm{Ni}}^2/3)\hbar^{-2} + D_{\mathrm{Co}}(\hat{S}_{\mathrm{Co},z}^2 - \hat{S}_{\mathrm{Co}}^2/3)\hbar^{-2}]\end{aligned} \tag{1}$$

which accounts for the isotropic exchange (the first term), the Zeeman term (the second contribution) and single-ion zero-field splitting (the remainder); a is the direction of the applied magnetic field. The generated energy levels for a trial set of magnetic parameters were inserted into the partition function, from which the magnetic susceptibility and magnetization were reconstructed using the apparatus of statistical thermodynamics [34]. The Zeeman term was modelled through a uniform distribution of the field orientation in 210 directions in one hemisphere

$$\hat{H}_{kl}^{(A)} = \mu_{\mathrm{B}} B_m (g_{A,x}\hat{S}_{A,x}\sin\vartheta_k\cos\varphi_l + g_{A,y}\hat{S}_{A,y}\sin\vartheta_k\sin\varphi_l + g_{A,z}\hat{S}_{A,z}\cos\vartheta_k)\hbar^{-1} \tag{2}$$

for each centre A = Ni, Co. This procedure properly mimics the powder average.

The susceptibility data were corrected for the molecular-field correction (zj) and eventually the temperature-independent magnetism χ_{TIM} as $\chi_{corr} = \chi_{mol} / [1 - (zj)\chi_{mol}] + \chi_{TIM}$. The latter term accounts for the uncompensated underlying diamagnetism and the temperature-independent paramagnetism, along with the signal of the sample holder. The susceptibility and magnetization data sets have been fitted simultaneously by applying an error functional that multiplies the relative error of susceptibility and magnetization: $F = R(\chi) \times R(M)$.

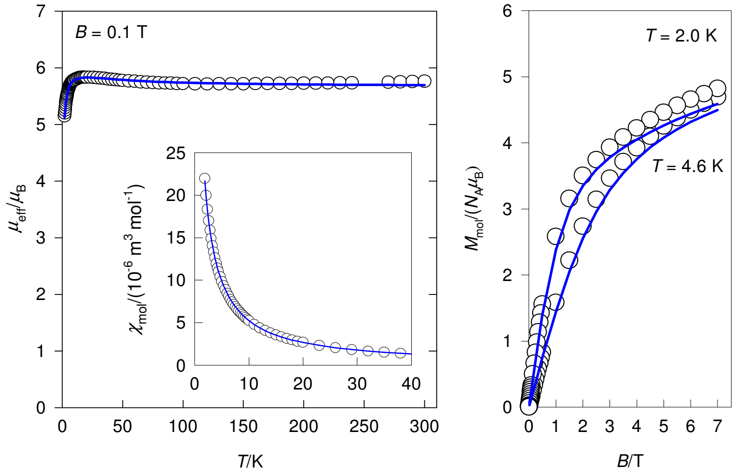

Fig 5 Magnetic functions for complex **I**. Left - effective magnetic moment, right - magnetization per formula unit, inset - molar magnetic susceptibility (SI units). Solid lines - fitted with J/hc = +1.91 cm^{-1}, D_{Ni}/hc = +8.44 cm^{-1}, D_{Co}/hc = +14.1 cm^{-1}, g_{av} = 2.362.

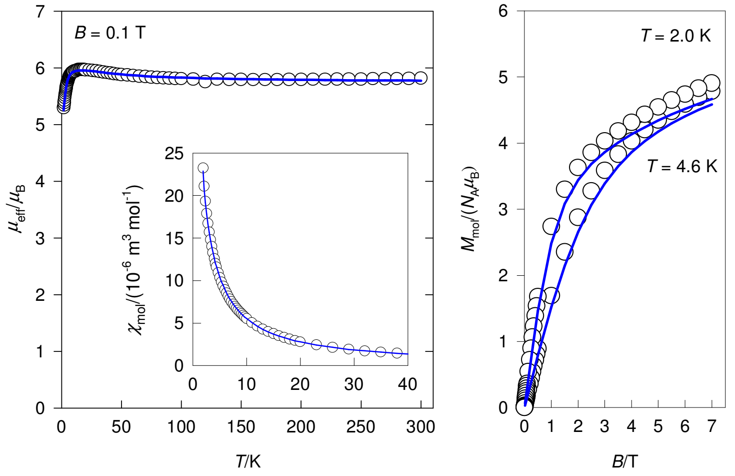

Fig 6 Magnetic functions for complex **II**. Left - effective magnetic moment, right - magnetization per formula unit, inset - molar magnetic susceptibility (SI units). Solid lines - fitted with J/hc = +2.23 cm^{-1}, D_{Ni}/hc = +8.67 cm^{-1}, D_{Co}/hc = +14.1 cm^{-1}, g_{av} = 2.395; $R(\chi)$ = 0.0076, $R(M)$ = 0.051

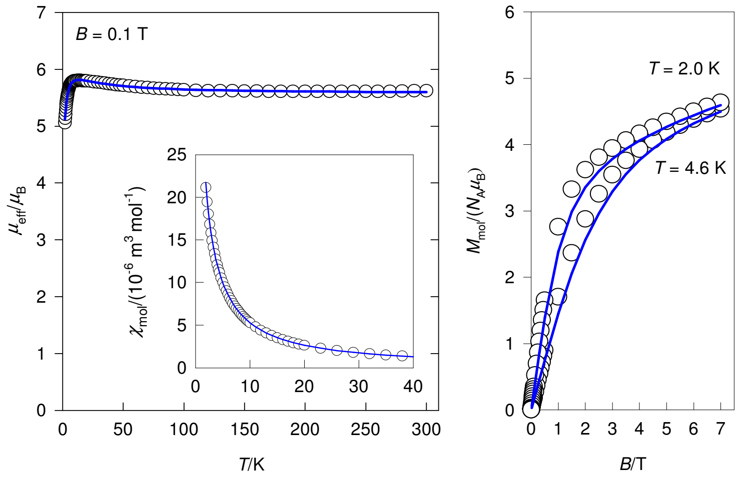

Fig 7 Magnetic functions for complex **III**. Left - effective magnetic moment, right - magnetization per formula unit, inset - molar magnetic susceptibility (SI units). Solid lines - fitted with $J/hc = +2.08$ cm^{-1}, $D_{\rm Ni}/hc = +8.38$ cm^{-1}, $D_{\rm Co}/hc = +11.5$ cm^{-1}, $g_{\rm av} = 2.322$; $R(\chi) = 0.011$, $R(M) = 0.052$.

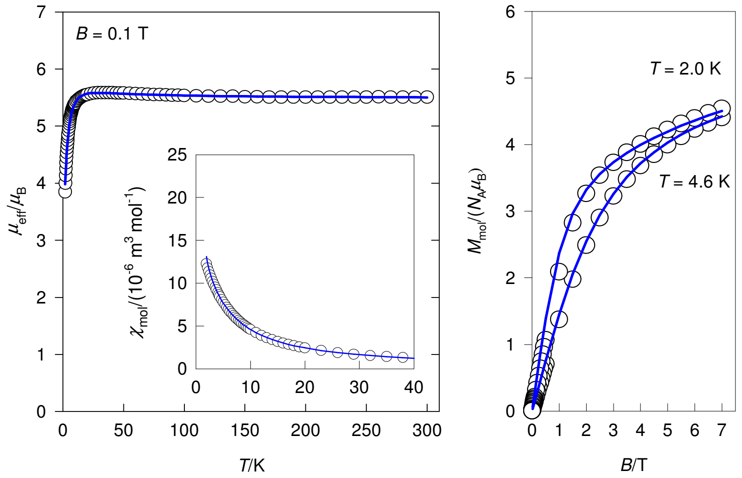

Fig 8 Magnetic functions for complex **IV**. Left - effective magnetic moment, right - magnetization per formula unit, inset - molar magnetic susceptibility (SI units). Solid lines - fitted with $J/hc = +2.58$ cm^{-1}, $D_{\rm Ni}/hc = +8.91$ cm^{-1}, $D_{\rm Co}/hc = +11.3$ cm^{-1}, $g_{\rm av} = 2.286$, $(zj)/hc = -0.099$ cm^{-1}; $R(\chi) = 0.026$, $R(M) = 0.029$.

An advanced fitting procedure using a genetic algorithm has been applied. The final set of magnetic parameters for complex **I** reads: $J/hc = +1.91$ cm^{-1}, $D_{\rm Ni}/hc = +8.44$ cm^{-1}, $D_{\rm Co}/hc = +14.1$ cm^{-1}, $g_{\rm av} = 2.362$, $\chi_{\rm TIM} = 0$, $zj/hc = 0$, discrepancy factors $R(\chi) = 0.0059$ and $R(M) = 0.047$. During the fitting procedure, the g-factors were taken as isotropic and equal each to the other. The remaining complexes exhibit analogous magnetic behavior (Figs. 6-8). Consequently the magnetic parameters obtained by the fitting procedure are very similar. Only in complex **IV** is some molecular field correction essential. The zero-field splitting at the Ni(II) centre ($|D| \sim 8$ cm^{-1}) spans the interval typical for hexacoordinate systems [35]. In tetracoordinate Co(II) complexes the D-values typically range between -15 and $+12$ cm^{-1} [36]. The bond angle along the superexchange path, Ni-O-Co, is $\alpha = 99$-101°. This is a bit higher than the critical angle in copper(II) diads ($\alpha = 97.5$ °), below which the antiferromagnetic coupling switches to a ferromagnetic one [37]. Nevertheless, the observed ferromagnetic coupling in the complexes under study is rather weak.

Conclusion

Four Ni(II)-Co(II) heterodinuclear complexes were prepared from three Schiff bases of the ONNO type. The stoichiometries of the complexes were determined and their molecular structures were determined by means of X-ray diffraction. It was found that the Ni(II) ion lies between the O_2N_2 donor set of the Schiff base and the coordination is completed by two DMF molecules. The Co(II) centre is coordinated by the phenolic oxygen atoms, that bear the function of μ-bridges. Thermal analysis showed that the DMF molecules leave the structure with the expected mass loss values and it was estimated that the complexes decompos at this temperature. Magnetic susceptibility measurements were conducted between 4.6 and 300 K and the temperature dependence of the magnetic susceptibility and field dependence of the magnetization have been fitted simultaneously to a conventional spin Hamiltonian model. The magnetic exchange is of a weak ferromagnetic type and the remaining magnetic parameters adopt the usual values: $J/hc = +1.91$ to $+2.58$ cm^{-1}, $D_{\mathrm{Ni}}/hc = +8.38$ to $+8.91$ cm^{-1}, $D_{\mathrm{Co}}/hc = +11.5$ to $+14.1$ cm^{-1}, $g_{\mathrm{av}} = 2.395 - 2.286$.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 924091, 924092, 924093, 924094. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www://www.ccdc.cam.ac.uk).

Acknowledgements

Slovak Grant Agencies (VEGA 1/0233/12, APVV 0014-11) are acknowledged for the financial support. In addition, financial support of this work by the University of Ankara Scientific

Research Fund under contract no. 12B4240003 and Ahi Evran University Scientific Research Fund under contract no. 4001.12.014 are gratefully acknowledged.

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Table 1 Data collection properties and crystal data

Compound	**I**	**II**	**III**	**IV**
empirical formula	$C_{23}H_{30}O_4N_4Cl_2CoNi$	$C_{23}H_{30}O_4N_4Br_2CoNi$	$C_{24}H_{32}O_4N_4Cl_2CoNi$	$C_{25}H_{34}O_4N_4Cl_2CoNi$
formula weight /g mol^{-1}	615.05	703.97	629.08	643.10
T /K	293(2)	293(2)	293(2)	105(2)
crystal size/mm	0.36x0.35x0.12	0.44x0.36x0.16	0.18x0.18x0.12	0.50x0.22x0.04
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	Cc	Cc	P21/c	Cc
a /Å	10.5261(3)	10.5304(4)	9.9822(5)	8.5673(9)
b /Å	15.1535(5)	15.1790(5)	15.0065(7)	17.611(2)
c /Å	17.2235(5)	17.4479(6)	18.1711(9	19.216(3)
α /°	90.00	90.00	90.00	90.00
β /°	98.949(3)	99.066(3)	94.611(4)	101.800(10)
γ /°	90.00	90.00	90.00	90.00
V /Å^3	2713.83(14)	2754.05(17)	2713.2(2)	2838.0(6)
Z	4	4	4	4
Calc. density /g cm^{-3}	1.505	1.698	1.540	1.505
μ /mm^{-1}	1.537	4.222	1.539	1.473
F (000)	1268	1412	1300	1332
T_{min}-T_{max}	0.6076-0.8370	0.2581- 0.5515	0.7691- 0.8368	0.5262- 0.9434
□ range / °	2.79 - 26.36	2.817 - 27.823	2.622- 27.970	3.078- 27.938
index ranges	-11<=h<=13 , - 17<=k<=18 , -21<=l<=17	-13<=h<=10 , - 17<=k<=18 , -14<=l<=21	-12<=h<=11 , - 12<=k<=18 , -20<=l<=22	-6<=h<=10 , - 17<=k<=22 , -22<=l<=24
reflections collected	5489	5497	12098	5506
reflections unique	3882	3852	5497	3318
*R*1, w*R*2 (2ó)	0.0372 -0.0771	0.0611- 0.1634	0.0823- 0.1049	0.0634-0.1353
*R*1, w*R*2 (all)	0.0321- 0.0728	0.0562- 0.1566	0.0468- 0.0923	0.0884- 0.1523
data / parameters	3882/326	3852/327	5497/325	3318/338
GOOF of F^2	1.096	1.087	1.071	1.042
largest difference peak hole /e Å^{-3}	0.290 / -0.289	0.890/-1.237	0.417/-0.476	0.966/ -0.642
CCDC number	924091	924092	924093	924094

Table2 Selected bond lengths and angles around the coordination spheres of the complexes

Complex	Bond lengths (Å)	Bond angles (°)
I	N1 Ni1 2.019(4)	N1 Ni1 O1 90.10(13)
	N2 Ni1 2.027(4)	N1 Ni1 N2 100.23(16)
	O1 Co1 1.980(3)	O1 Ni1 N2 169.55(14)
	O1 Ni1 2.023(3)	N1 Ni1 O2 168.87(13)
	O2 Co1 1.988(3)	O1 Ni1 O2 78.77(11)
	O2 Ni1 2.028(3)	N2 Ni1 O2 90.90(14)
	O3 Ni1 2.135(3)	N1 Ni1 O3 88.76(13)
	O4 Ni1 2.136(3)	O1 Ni1 O3 92.01(12)
	Co1 Cl1 2.2277(14)	N2 Ni1 O3 86.64(14)
	Co1 Cl2 2.2524(14)	O2 Ni1 O3 91.66(12)
		N1 Ni1 O4 90.44(13)
		O1 Ni1 O4 90.24(12)
		N2 Ni1 O4 91.29(13)
		O2 Ni1 O4 89.55(12)
		O3 Ni1 O4 177.62(14)
		O1 Co1 O2 80.77(11)
		O1 Co1 Cl1 112.65(10)
		O2 Co1 Cl1 118.03(9)
		O1 Co1 Cl2 112.51(9)
		O2 Co1 Cl2 111.98(9)
		Cl1 Co1 Cl2 115.95(6)
II	N1 Ni1 2.005(7)	N1 Ni1 O1 91.2(3)
	N2 Ni1 2.023(7)	N1 Ni1 N2 100.4(3)
	O1 Co1 1.955(6)	O1 Ni1 N2 168.2(3)
	O1 Ni1 2.017(6)	N1 Ni1 O2 169.5(3)
	O2 Co1 1.988(5)	O1 Ni1 O2 78.4(2)
	O2 Ni1 2.033(6)	N2 Ni1 O2 90.1(3)
	O3 Ni1 2.138(6)	N1 Ni1 O4 90.2(3)
	O4 Ni1 2.127(5)	O1 Ni1 O4 90.7(2)
	Br2 Co1 2.3230(19)	N2 Ni1 O4 91.2(3)
	Br1 Co1 2.3439(16)	O2 Ni1 O4 88.6(2)
		N1 Ni1 O3 89.1(3)
		O1 Ni1 O3 90.8(2)
		N2 Ni1 O3 87.5(3)
		O2 Ni1 O3 92.3(2)
		O4 Ni1 O3 178.3(3)
		O1 Co1 O2 80.9(2)
		O1 Co1 Br2 112.00(18)
		O2 Co1 Br2 117.13(18)
		O1 Co1 Br1 113.48(17)
		O2 Co1 Br1 112.78(16)
		Br2 Co1 Br1 115.74(7)
III	N1 Ni1 2.030(3)	N1 Ni1 O1 89.11(11)
	N2 Ni1 2.054(3)	N1 Ni1 O2 164.83(11)
	O1 Co1 1.977(2)	O1 Ni1 O2 78.55(9)
	O1 Ni1 2.033(2)	N1 Ni1 N2 101.94(12)
	O2 Co1 1.990(2)	O1 Ni1 N2 168.59(11)
	O2 Ni1 2.034(2)	O2 Ni1 N2 90.93(11)
	O3 Ni1 2.089(2)	N1 Ni1 O3 96.91(11)
	O4 Ni1 2.139(2)	O1 Ni1 O3 82.85(10)
	Co1 Cl1 2.2197(12)	O2 Ni1 O3 90.33(10)
	Co1 Cl2 2.2552(12)	N2 Ni1 O3 92.91(11)
		N1 Ni1 O4 85.21(11)
		O1 Ni1 O4 94.19(10)
		O2 Ni1 O4 86.91(10)
		N2 Ni1 O4 89.59(11)
		O3 Ni1 O4 176.31(10)
		O1 Co1 O2 80.91(9)
		O1 Co1 Cl1 122.16(8)
		O2 Co1 Cl1 111.96(8)
		O1 Co1 Cl2 107.89(8)
		O2 Co1 Cl2 120.25(8)
		Cl1 Co1 Cl2 111.24(5)

IV	N1 Ni1 1.981(9) N2 Ni1 2.015(8) O1 Co1 1.948(7) O1 Ni1 2.020(6) O2 Co1 1.983(6) O2 Ni1 2.041(7) O3 Ni1 2.065(9) O4 Ni1 2.129(9) Co1 Cl2 2.214(4) Co1 Cl1 2.260(5)	N1 Ni1 N2 99.0(4) N1 Ni1 O1 91.7(3) N2 Ni1 O1 169.3(3) N1 Ni1 O2 169.7(3) N2 Ni1 O2 91.2(3) O1 Ni1 O2 78.1(2) N1 Ni1 O3 94.2(5) N2 Ni1 O3 89.1(4) O1 Ni1 O3 89.9(3) O2 Ni1 O3 87.5(3) N1 Ni1 O4 90.8(5) N2 Ni1 O4 88.4(4) O1 Ni1 O4 91.7(3) O2 Ni1 O4 87.8(3) O3 Ni1 O4 174.7(3) O1 Co1 O2 81.2(3) O1 Co1 Cl2 115.2(3) O2 Co1 Cl2 119.7(2) O1 Co1 Cl1 111.4(3) O2 Co1 Cl1 111.8(3) Cl2 Co1 Cl1 113.53(17)

Gaphical Abstract ()

Four heterodinuclear Ni^{II}-Co^{II} complexes were prepared using N,N’-bis(salicylidene)-1,3-propanediamine and its derivatives. These complexes were characterized and their molecular structures determined by the X-ray diffraction method. It was found that the Ni(II) ion lies in a O_4N_2 distorted octahedral coordination sphere, in contrast the Co(II) ion is in a distorted tetrahedral coordination sphere. The magnetic susceptibilities of the complexes were measured between 2 and 300 K and the μ_{eff} values were determined.

Graphical Abstract