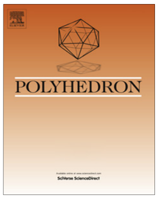
Polyhedron 59 (2013) 1–7

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Synthesis, structure and magnetic properties of Ni(II)–Co(II) heterodinuclear complexes with ONNO type Schiff bases as ligands

Sevi Öz [a,*], Ján Titiš [b], Hasan Nazır [c], Orhan Atakol [c], Roman Boča [b], Ingrid Svoboda [d], Hartmut Fuess [d]

[a] Ahi Evran University, Faculty of Science and Arts, Department of Chemistry, 40100 Kırşehir, Turkey
[b] Department of Chemistry, FPV, University of SS Cyril and Methodius, 91701 Trnava, Slovakia
[c] Ankara University, Faculty of Science, Department of Chemistry, 06100 Ankara, Turkey
[d] Strukturforschung, FB Materialwissenschaft, TU- Darmstadt, Petersenstrasse 23, D-64287 Darmstadt, Germany

ARTICLE INFO

Article history:
Received 6 March 2013
Accepted 24 April 2013
Available online 3 May 2013

Keywords:
Heterodinuclear complex
Ni(II)–Co(II)
Schiff base ligand
Magnetic properties
Thermogravimetry

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 $J_{Co-Ni}/hc = +2\ cm^{-1}$) and at low temperature single-ion zero-field splitting applies ($D_{Ni}/hc = +8\ cm^{-1}$, $D_{Co}/hc = +14\ cm^{-1}$).

1. 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].

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.

2. Experimental

2.1. Apparatus

An FTIR-spectrometer (Shimadzu) equipped with three reflection ATR units was used in taking the IR spectra. The C, H and N

---

* Corresponding author. Tel.: +90 3122126720.
E-mail address: sevioz@hotmail.com (S. Öz).

0277-5387/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.poly.2013.04.047

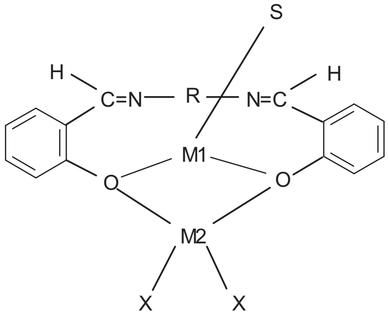


Fig. 1. Sketch of the dinuclear complexes prepared via LH_2: M1 = Ni^{2+} or Cu^{2+}; M2 = Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Sn^{2+}; X = Cl^-, Br^-, I^-; S = dioxane or DMF.

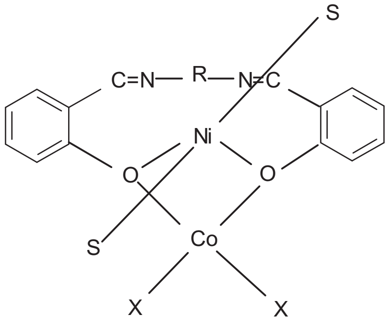


Fig. 2. Sketch of heterodinuclear complexes: R = $-(CH_2)_3-$, X = Cl^-, S = DMF (**I**); R = $-(CH_2)_3-$, X = Br^- , S = DMF (**II**); R = $-(CH_2)_4-$, X = Cl^-, S = DMF (**III**); R = $-CH_2-C(CH_3)_2-CH_2-$, X = Cl^-, S = DMF (**IV**).

analyses were performed using an Elemental 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 °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 temperature was varied between 30 and 600 °C. These analyses were performed at 10 °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.

2.2. 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 Mo Kα radiation ($\lambda = 0.71073$ 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 $2.79 \leqslant \theta \leqslant 26.36$ range for complex **I**, $2.81 \leqslant \theta \leqslant 27.82$ range for complex **II**, $2.62 \leqslant \theta \leqslant 27.97$ range for complex **III** and $3.07 \leqslant \theta \leqslant 27.93$ 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].

2.3. Synthesis

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

2.3.1. 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 *Anal.* Calc. for $C_{17}H_{18}N_2O_2$: C, 72.3; H, 6.43; N, 9.92. Found: C, 71.9; H, 6.45; N, 10.47%. $\lambda_{max} = 243$ nm, $\varepsilon = 7045\ dm^3\ mol^{-1}\ cm^{-1}$ in DMSO, $\lambda_{max} = 242$ nm, $\varepsilon = 7865\ dm^3\ mol^{-1}\ cm^{-1}$ 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. ^1H 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 $[HO-C_6H_4-CH=N-CH_2-CH_2-CH_2]^+$, 148 $[HO-C_6H_4-CH=N-CH_2-CH_2]^+$ (BP), 134 $[HO-C_6H_4-CH=N-CH_2]^+$, 120 $[HO-C_6H_4-CH=N]^+$, 107 $[HO-C_6H_4-CH_2]^+$, 77 $[C_6H_5]^+$.

2.3.2. 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 *Anal.* Calc. for $C_{18}H_{20}N_2O_2$: C, 72.9; H, 6.80; N, 9.44. Found: C, 72.5; H, 6.14; N, 9.33%. $\lambda_{max} = 242$ - nm, $\varepsilon = 8055\ dm^3\ mol^{-1}\ cm^{-1}$ in DMSO, $\lambda_{max} = 241$ nm, $\varepsilon = 6005\ dm^3\ mol^{-1}\ cm^{-1}$ in MeOH. IR (cm^{-1}): ν_{O-H} 2635, $\nu_{C-H(Ar)}$ 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. ^1H 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 $[HO-C_6H_4-CH=N-CH_2-CH_2-CH_2-CH_2]^+$, 148 $[HO-C_6H_4-CH=N-CH_2-CH_2-CH_2]^+$ (BP), 134 $[HO-C_6H_4-CH=N-CH_2]^+$, 120 $[HO-C_6H_4-CH=N]^+$, 107 $[HO-C_6H_4-CH_2]^+$, 77 $[C_6H_5]^+$.

2.3.3. 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 *Anal.* Calc. for $C_{19}H_{22}N_2O_2$: C, 73.5; H, 7.14; N, 9.02. Found: C, 73.4; H, 6.35; N, 8.72%.