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Synthesis, structure and magnetic properties of homotrinuclear Ni(II) complexes with asymmetric Schiff-base ligands

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ABSTRACT

By using 1,3-propanediamine, 2-hydroxyacetophenone and salicylaldehyde an asymmetric ONNO type Schiff base, N(hydroxyphenylidene)-N′(2-hydroxyacetophenylidene)-1,3-propanediamine (H_2metsalpn), has been prepared and isolated. This Schiff base has been reduced yielding N(2-hydroxybenzyl)-N′[1-(2-hydroxyphenyl)ethyl]-1,3-diaminopropane (H_2metsalpn^H) These two ligands were used in preparing three trinuclear Ni(II) complexes with *catena*-[Ni_3] structural motif, where DMF and carboxylato (formato, acetato, benzoato) ligands occur. These complexes were characterized by EA, IR, TG, DTA and MS data. The X-ray diffraction confirms that the Ni(II) central atoms are in a distorted octahedral coordination environment: the terminal centers possess {NiN_2O_4} octahedral coordination sphere whereas the very central atom possesses {NiO_6} chromophore. The coordinated DMF groups are liberated between 140–240 °C. The SQUID magnetometry confirms presence of weak exchange coupling of the antiferromagnetic nature, $J/hc = -2$ to -7 cm^{-1}, with a moderate single-ion anisotropy reflected by the zero-field splitting $D/hc = +4$ to $+7$ cm^{-1}.

1. Introduction

The ONNO type symmetric Schiff base made of 1,3-propanediamine and salicylaldehyde, N,N′(salicylidene)-1,3-propanediamine, finds applications in the coordination chemistry for about 70 years [1]. From 1990 to today, a few trinuclear complexes of the symmetric Schiff base were reported [2–11]. In the last decade also the complexes of the ONNO type asymmetric Schiff bases were prepared [12–19]. The asymmetric Schiff base complexes are usually obtained by a template synthesis; there are only a few studies on the isolated asymmetric Schiff bases. In the amphyprotic solvents, the Schiff bases can easily be reduced by $NaBH_4$ to the secondary amines [20–22].

In this study a preparation of the asymmetric Schiff base is described by combining 1,3-propanediamine and two different aldehydes (salicylaldehyde and 2-hydroxyacetophenone) giving rise to N(2-hydroxyphenylidene)-N′(2-hydroxyacetophenylidene)-1,3-propanediamine (H_2metsalpn). In methanol solution this Schiff base has been reduced by using $NaBH_4$, and N(2-hydroxybenzyl)-N′[(2-hydroxyphenyl)ethyl]-1,3-propanediamine (H_2metsalpn^H) has been isolated. These ligands are sketched in Scheme 1.

Using these ligands, the formate, acetate or benzoate anions in presence of DMF (dimethylformamide), trinuclear Ni(II) complexes have been prepared, namely [{Ni metsalpn^H}$_2$Ni(HCOO)$_2$(DMF)$_2$] (**1**), [{Nimetsalpn}$_2$Ni(AcO)$_2$(DMF)$_2$] (**2**), and [{Ni metsalpn}$_2$Ni(C_6H_5COO)$_2$(DMF)$_2$] (**3**). Single-crystal X-ray diffraction confirms their trinuclear structure of the *catena*-[Ni_3] type. In addition, thermogravimetry and magnetometry have been used in order to characterize thermal and magnetic properties of these species.

2. Experimental

2.1. Materials and instruments

All reagents and solvents were purchased from chemical sources and used directly without purification. Elemental C, H and N analysis was performed using Eurovector 1018 apparatus. Ni analysis was conducted using atomic absorption spectrometer (GBC Avanta PM) using the FAAS mode. The mass spectra were obtained by a Shimadzu, 2010 plus with a DI (direct inlet) unit with an electron impact ionizer. The interface temperature of DI

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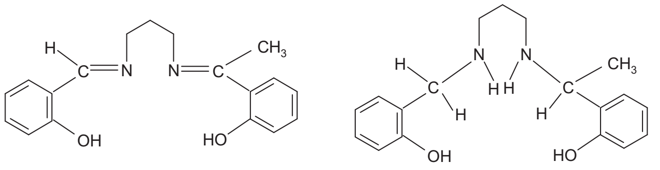

Scheme 1. Sketch of H_2metsalpn (left) and H_2metsalpn^H (right) asymmetric Schiff bases.

unit was varied between 40 and 230 °C and the ionization was carried out with electrons of 70 eV energy.

The NMR spectra of the ligands were recorded on a 400 MHz FT-NMR (Varian Mercury) spectrometer using d_6-DMSO as a solvent. The IR spectra of the complexes and ligand were recorded using Shimadzu Infinity model FTIR spectrometer equipped three reflections ATR attachment.

The thermogravimetric analysis was performed by a Shimadzu DTG-60H apparatus; temperature varied between 30 and 600 °C and scan rate was 10 °C/min under N_2 atmosphere in Pt pans. Calibration of the instrument was done with metallic In and Zn. The stoichiometry of the complexes was estimated using elemental analysis results and with the help of the mass loss data of the coordinated DMF ligands.

The magnetic data was taken with a SQUID apparatus (MPMSXL7, 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 structure analysis

Single crystals of **1** through **3** were mounted to 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 $2.466 \leqslant \theta \leqslant 27.817$ range for complex **1**, $2.74 \leqslant \theta \leqslant 26.37$ range for complex **2**, $2.615 \leqslant \theta \leqslant 27.705°$ range for complex **3**. The Data of complex **1** and **2** was collected at $T = 293$ K and the data of complex **3** at 105 K. The empirical absorption corrections were applied by the semi empirical method via the CrysAlis CCD software [23]. Models were obtained from the results of the cell refinement and the data reductions were carried out using the solution software SHELXL97 [24]. The structure of all complexes was solved by direct methods using the SHELXS97 software implemented in the WinGX package [25].

2.3. Synthesis of H_2metsalpn

The asymmetric Schiff base N-(2-hydroxyphenylidene)-N′-(2-hydroxyacetophenylidene)-1,3 diaminopropane was prepared in MeCN dehydrated by CaH_2 [26]. 1,3-diaminopropane (3.7 g, 0.05 mol) was dissolved in 50 cm^3 of MeCN and temperature was decreased to −10 °C in a salt-ice bath. 2-hydroxyacetophenone (6.80 g, 0.05 mol) was added under stirring for 5 min. This solution was kept in ice-water mixture for 30 min and the temperature was kept under 1 °C. Afterwards, salicylaldehyde (2-hydroxybenzaldehyde) (6.10 g, 0.05 mol) was added to the solution and again the solution was kept in ice-water mixture for 30 min under stirring. This solution was kept in the deep freeze at -20 °C for 12 h. A yellow crystalline substance was obtained, and filtered by vacuum. The filtrate was rinsed with MeCN and Et_2O and air-dried. This crystalline product is a mixture of H_2metsalpn (67%) and bis-N,N′(2-hydroxyacetophenylidene)-1,3-diaminopropane (33%) [26]. For the purification a silica column was used: Merck silica gel 60, 40–63 μm with 50 cm height and 2.0 cm diameter; EtAcO:n-C_6H_{14} (1:1) was used as a solvent for separation. It was observed that $LACH_2$ moved rapidly within this solvent. In addition, the ratio of the R_f value of $LACH_2$ and R_f value of H_2metsalpn was approximately 1:2 (both substances are yellow). The pure compounds were isolated separately by evaporating the solvent from the eluent. H_2metsalpn was recrystallized from MeCN and its purity was checked by HPLC. Yield: 36–40%, mp 92–93 °C. IR (cm^{-1}): $\nu_{C-H(Ar)}$ 3023–3010, $\nu_{C-H(Aliph)}$ 2941–2854, $\nu_{C=N}$ 1631–1624, $\nu_{C=C(ring)}$ 1610, $\nu_{C-O(Phenol)}$ 1278–1159, $\delta_{C-H(Ar)}$ 752. $\lambda_{max} = 242$ nm, $\varepsilon = 8164$ dm^3 mol^{-1} cm^{-1} in DMSO. ^1H NMR data in d_6-CH_3SOCH_3 (δ, ppm): 16.55 (s), 13.47 (s), 8.58 (s), 7.62 (d), 7.45(d), 7.31 (p), 6.88 (t), 6.77 (t), 3.73 (t), 3.66 (t) 2.40 (s), 2.06 (p). ^{13}C NMR data in d_6-CH_3SOCH_3 (δ, ppm): 167.70, 164.32, 161.13, 132.86, 132.74, 132.09, 129.21, 119.31, 119.11, 118.97, 118.95, 118.62, 117.13, 117.08, 116.91, 56.46, 46, 33, 14.80. MS (m/z): 296 (molecular peak), 175, 162, 148 (base peak), 134, 107, 91, 77. *Anal.* Calc. for $C_{18}H_{20}N_2O_2$: C, 72.94; H, 6.80; N, 9.44. Found: C, 73.07; H, 6.23; N, 9.81%.

2.4. Preparation of H_2metsalpn^H

3.0 g of asymmetric Schiff base H_2metsalpn was dissolved in 70.0 cm^3 of MeOH by stirring and heating. This solution was heated up to 50 °C and to this solution solid $NaBH_4$ in small portions was added until colorless under strong mixing [26–29]. After 10 min. of stirring, 300 cm^3 of ice water was added. The final mixture was left to stand for 24 h. After filtration the white precipitate was air-dried. The product H_2metsalpn^H was recrystallized from MeOH:H_2O (2:1,v/v). Yield: 54–67 %, mp: 107 °C. IR (cm^{-1}): ν_{N-H} 3307, $\nu_{C-H(Ar)}$ 3041–3014, $\nu_{C-H(Aliph)}$ 2965–2846, $\nu_{C=C(ring)}$ 1610–1588, $\nu_{C-O(Phenol)}$ 1255–1107, $\delta_{C-H(Ar)}$ 752. ^1H NMR data in d_6-CH_3SOCH_3 (δ, ppm): 7.03 (m), 6.68 (m), 6.30(d), 3.84 (q), 3.78 (s), 2.52(t), 2.36 (m), 1.63 (s), 1.28 (d), 1.27 (d), ^{13}C NMR data in d_6-DMSO (δ, ppm): 157.49, 157.15, 157.09, 128.40, 127.91, 127.73, 127.52, 124.02, 118.32, 115.75, 115.31, 57.23, 50.63, 46.27,45.03, 28.98, 22.86. MS (m/z): 300 (molecular peak), 178, 164, 150 (base peak), 135, 107, 91, 77. *Anal.* Calc. for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.05; N, 9.32. Found: C, 72.49; H, 7.58; N, 9.24%.

2.5. Preparation of [{Ni metsalpn^H}$_2$Ni$(HCOO)_2(DMF)_2$] (**1**)

0.300 g (0.001 mol) of the reduced asymmetric Schiff base H_2metsalpn^H was dissolved in 40.0 cm^3 of DMF by heating. The temperature was raised up to 95 to 110 °C. To this solution, added were the solution of 0.237 g (0.0015 mol) $NiCl_2 \cdot 6H_2O$ salt in 10 cm^3 MeOH : DMF (50/50, v/v) and the solution of 0.070 g (0.001 mol) NaHCOO in MeOH : DMF (50/50, v/v), and the solution of 0.28 g Et_3N in 5 cm^3 MeOH. The final mixture was allowed left to stand for 4–5 days. The formed crystalline complex was separated by vacuum filtration and air dried. Yield: 27%, IR (cm^{-1}): ν_{N-H} 3279, 3047–3020, $\nu_{C-H(Aliph)}$ 2966–2849, $\nu_{C=O(DMF)}$ 1648, $\nu_{C=O(formate)}$ 1635, $\nu_{C=C(ring)}$ 1597–1591, $\nu_{C-O(Phenol)}$ 1195, $\delta_{C-H(Ar)}$ 756. MS (m/z): 356 (base peak). *Anal.* Calc. for $C_{44}H_{58}N_6Ni_3O_{10}$: C, 52.36; H, 5.99; N, 8.32; Ni, 17.45. Found: C, 52.83; H, 5.66; N, 7.91; Ni, 18.11%.

2.6. Preparation of [{Ni metsalpn}$_2$Ni$(AcO)_2(DMF)_2$] (**2**)

0.296 g (0.001 mol) of the asymmetric Schiff base, H_2metsalpn was dissolved in 50.0 cm^3 of DMF by heating. This solution was heated up to 110 °C and then the solution of 0.375 g (0.0015 mol) of $Ni(AcO)_2 \cdot 4H_2O$ in 10 cm^3 of MeOH : DMF (50/50, v/v) was added.