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Structural, magnetic and electronic characterization of an isostructural series of dinuclear complexes of 3d metal ions bridged by tpbd

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Dedicated to Alfred Werner on the 100th Anniversary of his Nobel prize in Chemistry in 1913.

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ABSTRACT

Dinuclear complexes of the type $[\{M(H_2O)(phen)\}_2(\mu\text{-tpbd})](ClO_4)_4$ with N,N,N′,N′-Tetrakis-(2-pyridylmethyl)-benzene-1,4-diamine (tpbd) as bridging ligand and M = Mn(II) (**1**), Fe(II) (**2**), Co(II) (**3**), Ni(II) (**4**), Cu(II) (**5**), Zn(II) (**6**) were synthesized, structurally analyzed and their magnetic as well as their electrochemical properties are determined. A ligand-centered one-electron oxidation leads to radical complexes for which the lifetimes are strongly dependent on the coordinated metal ion as followed from time-resolved UV–Vis absorption spectroscopy. In addition to the six homometallic dinuclear complexes, one analog heterometallic Mn(II)/Ni(II) compound (**7**) of the same constitution was structurally and magnetically investigated, confirming an high spin ground state.

1. Introduction

The field of molecular magnetism has gained a lot of attention during the last decades [1–5]. Exchange interactions of multiple spin carrying centers in a single molecule possibly result in magnetic properties usually ascribed to extended 3D bulk magnets as a remanent magnetization is observed over a long period at low temperatures [6–8]. The molecular character of such sub-nanometer systems offer a manifold of new features. Beside the miniaturization of magnetic units for utilization as Ångstrom-scale building blocks, the combinations of magnetic properties with other advantageous features, such as solubility, optical activity or transparency, are achievable by these multifunctional materials making molecular sensors possible [9]. Taking advantage of the enormous diversity and flexibility of organic ligands to coordinate spin-carrying metal ions allows for a great diversity to form molecular magnetic materials.

In our present work, we built dinuclear complexes of divalent 3d transition metal ions bridged by the bis-trisdentate ligand N,N,N′,N′-Tetrakis-(2-pyridylmethyl)-benzene-1,4-diamine (tpbd). The ligand was first synthesized by Buchen et al. in 1997 and introduced to build up defined polynuclear coordination-systems [10]. Beside some mononuclear complexes of 3d transition metals and one polynuclear Pd-containing complex, only four multinuclear complexes have been reported by McKenzie and co-workers [11,12,13] magnetic properties were analyzed for only one of them by Li et al. [14] However, this bridging ligand offers formation of a manifold of interesting systems in electronic as well as in magnetic aspects. The free tpbd can be oxidized to its semiquinoid radical species, similar to the related N,N,N′,N′-Tetramethylphenylene-1,4-diamine (*TMPD*), known in its oxidized form Wurster's blue [15] that possesses an extraordinarily high persistence of the radical state. In general paramagnetic ligands that bridge two metal ions reveal complexes with interesting new magnetic and electronic properties, in which we are interested. Thus, one task of the present work was the investigation of the structural and magnetic properties of a series of 3d transition metal ion containing dimers. To gain insight into the metal–ligand–metal interaction, we used first principles of coordination chemistry in order to avoid higher nuclearities, necessary to reduce the interaction parameters to a minimum. On coordination of a tpbd molecule to a metal ion in octahedral geometry, three coordination sites remain uncoordinated. Coordination of a second tpbd would cause oligomerisation of the system. We therefore offered additional the strongly coordinating bidentate 1,10-phenanthroline to the system and finally water completes the coordination sphere of the metal ions as a third ligand. We applied this concept successfully to synthesize dimeric transition metal complexes with divalent ions of manganese,

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iron, cobalt, nickel, copper and zinc. Finally we synthesized a mixed metal species with Mn(II) and Ni(II). For all the complexes we investigated the redox and magnetic properties, moreover, we studied the radical life time dependence for all one electron oxidized species.

2. Experimental

2.1. Materials

The reagents and solvents used were of commercially available reagent-grade quality.

Caution!

Although no problems were encountered in this work, transition metal perchlorate salts are potentially explosive and should thus be prepared in small quantities and handled with care!

2.2. Preparations

2.2.1. Synthesis of the ligand

N,N,N′,N′-Tetrakis-(2-pyridylmethyl)-benzene-1,4-diamine (tpbd) was synthesized according to the procedure of Buchen [10].

2.2.2. Synthesis of the homometallic complexes

*2.2.2.1. [{M(phen)H_2O}$_2$(μ-tpbd)](ClO_4)$_4$·x MeOH·y EtOH, M = Mn(II) (**1**), Fe(II) (**2**), Co(II) (**3**), Ni(II) (**4**), Cu(II) (**5**), Zn(II) (**6**).* A solution of the metal perchlorate salt (0.5 mmol) in MeCN (10 ml) was added dropwise to a refluxing suspension of tpbd (0.25 mmol) and phen (0.5 mmol) in MeCN (25 ml). After the addition is completed, the solution becomes transparent and brown or, in the case of (**2**), dark red. After a few minutes of stirring under reflux, a microcrystalline powder precipitated whose formation was completed by 1 h of further heating and cooling to room temperature. The precipitate (Cu: green, Ni: slightly purple, Mn, Fe, Co, and Zn: orange) was filtered according to the yields, (**1**): 70%, (**2**): 59%, (**3**): 82%, (**4**): 49%, (**5**): 35%, (**6**): 80%. For each recrystallisation, 0.1 g of the crude sample was suspended in a refluxing MeOH/EtOH solution (10:10 ml). Water was added dropwise until the microcrystalline products had been completely solved. Single crystals were obtained after filtration and cooling the solution to room temperature.

Elemental analysis (1): Anal. Calc. for $C_{54}H_{54}Cl_4Mn_2N_{10}O_{21}$ (1428.10): C, 45.33; H, 3.80; N, 9.79. Found: C, 45.95; H, 3.38; N, 9.95%. (2): *Anal.* Calc. for $C_{54}H_{54}Cl_4Fe_2N_{10}O_{21}$ (1432.56): C, 52.47; H, 2.34; N, 10.68. Found: C, 52.85; H, 2.36; N, 10.45%. (3): *Anal.* Calc. for $C_{54}H_{54}Cl_4Co_2N_{10}O_{21}$ (1438.74): C, 45.08; H, 3.78; N, 9.74. Found: C, 44.88; H, 3.66; N, 9.56%. (4): *Anal.* Calc. for $C_{56}H_{58}Cl_4N_{10}Ni_2O_{21}$ (1466.32): C, 45.87; H, 3.99; N, 9.55. Found: C, 45.99; H, 4.00; N, 9.71%. (5): *Anal.* Calc. for $C_{54}H_{52}Cl_4Cu_2N_{10}O_{20}$ (1429.95): C, 45.36; H, 3.67; N, 9.80. Found: C, 45.63; H, 3.82; N, 9.63% (6): *Anal.* Calc. for $C_{54}H_{52}Cl_4N_{10}O_{20}Zn_2$ (1433.64): C, 45.24; H, 3.66; N, 9.77. Found: C, 45.07; H, 3.45; N, 9.54%.

IR (KBr, ν/cm^{-1}) (1): 1605, 1518, 1426, 1206, 1145, 1104, 1092, 852, 775, 728, 626; (2): 1606, 1524, 1423, 1354, 1244, 1143, 1113, 1089, 849, 772, 723, 626; (3): 1606, 1518, 1427, 1227, 1205, 1144, 1114, 1090, 852, 777, 728, 626; (4): 1607, 1518, 1427, 1226, 1202 1146, 1113, 1089, 852, 779, 728, 627; (5): 1607, 1519, 1429, 1334, 1214, 1145, 1110, 1087, 856, 778, 723, 626; (6): 1607, 1518, 1427, 1226, 1202, 1146, 1113, 1089, 852, 779, 728, 627

2.2.3. Synthesis of the heterometallic complex

2.2.3.1. [Mn(phen)H_2O(μ-tpbd)Ni(phen)H_2O](ClO_4)$_4$ ·0.5 MeOH·3.5 EtOH. A solution of Mn(ClO_4)$_2$·6H_2O (0.25 mmol) and Ni(ClO_4)$_2$·6H_2O in MeCN (10 ml) was added dropwise to a refluxing suspension of tpbd (0.25 mmol) and phen (0.5 mmol) in MeCN (25 ml). Upon completion of the addition, the solution becomes transparent and orange. After a few minutes of stirring under reflux, a microcrystalline powder precipitated. After 1 h of further heating and cooling to room temperature the orange precipitate was filtered off (yield: 30%). Recrystallization was performed analogue to the homometallic samples.

Elemental analysis: (Mn(ClO_4)$_2$ as impurity in crude product) *Anal.* Calc. for $C_{54}H_{54}Cl_4MnN_{10}O_{21}$ (1434.50): C, 45.21; H, 3.79; N, 9.89. Found: C, 43.97; H, 2.47; N, 9.13%, corresponding to 96% complex. *IR (KBr, ν/cm^{-1}):* 1607, 1519, 1428, 1206, 1144, 1116, 1087, 853, 778, 727, 630; AAS: 1.1:1 (Mn:Ni).

2.3. Physical measurements

2.3.1. Spectroscopy

The electronic spectra were measured by a Jasco UV–Vis/NIR V570 Spectrometer. The half lifetimes (HLT) were determined as the time between the maximum and the half maximum value. A Bruker DRX 400 MHz spectrometer was used to record ^{1}H-NMR spectra. The infrared spectra were determined as KBr-disks by a JASCO FT/IR 2400 Spectrometer.

2.3.2. Elemental analysis

The elemental analyses for C, H and N were performed at the microanalytical lab at the Johannes Gutenberg University of Mainz by the use of an Elemanta Vario EL 2.

2.3.3. Electrochemistry

The cyclovoltammograms were measured in a three-electrode set-up with a Princeton Applied Research Potentiostat 263 A. A glassy carbon electrode was used as a working electrode. In addition, a Pt counter electrode and an Ag/$AgNO_3$ reference electrode (0.01 mol/l $AgNO_3$) were used. Tetrabutylammoniumperchlorate was used as the conducting electrolyte and ferrocene as the internal standard.

2.3.4. Magnetic susceptibility and magnetization

The magnetic properties were determined on a Quantum Design SQUID Magnetometer MPMS XL-7. Gelatine capsules were filled with the samples which were transferred into plastic straws. The 37 data points for susceptibility measurements were taken in DC mode, each one averaged by three measurements in a range of 4 cm by 24 single points. Experimental susceptibility data were corrected for the underlying diamagnetism using Pascal's constants. The temperature dependent magnetic contribution of the holder was experimentally determined and subtracted from the measured susceptibility data. The measurements were simulated using the JulX programme version 1.4.1 [16].

2.4. X-ray crystallographic data collection and refinement of the structures

The crystals suitable for X-ray diffraction studies were isolated from recrystallization in Ethanol:Methanol:H_2O. Single crystals of (**1**)–(**7**) were coated with perfluoropolyether, picked up with a glass fiber and mounted on a SMART APEX II CCD diffractometer equipped with a nitrogen cold stream operating at 171(2) K. Graphite monochromated Mo Kα radiation (λ = 0.71069 Å) from a fine-focus sealed tube was used throughout. The crystallographic data of the compounds are listed in Tables 1–3. Cell constants were obtained from least-squares refinement using all observed reflections. The data reduction was carried out with APEX2 v2.0, while SIR-97 [17] was used for the structure solution and SHELXL-97 [18] was used for the refinement. No absorption correction was employed.

Crystal data as well as selected bond lengths (Å) and angles (°) for compounds (**1**)–(**7**) are summarized in Tables 1 and 2.