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Tetraanionic N₂O₂-coordinating ligands as potential building blocks for supramolecular magnetic networks†

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A bisoxamate ligand containing three different types of coordination sites was designed and synthesized. The developed synthetic strategy was adopted to prepare a related 1,2-bis-(2-hydroxybenzamido)benzene-derived ligand. Nickel(II) complexes of both the novel ligands were obtained and characterized by X-ray crystallography, NMR, electronic absorption spectroscopy, and theoretical calculations.

o-Phenylene-bisoxamates coordinated by a metal ion M^1 at the central position represent versatile building blocks for constructing multidimensional magnetic materials (Scheme 1). This is due to the ability of metal bisoxamates to coordinate additional metal ions M^2 through the four carbonyl groups, thus forming multimetallic complexes, chain structures, as well as two- and three-dimensional networks of interacting paramagnetic metal ions that find applications as single-molecule magnets, single-chain magnets, and high-dimensional molecule-based magnets.^{1–3} Metal ions (M^2) coordinated to the periphery of the ligand act as bridges being actively involved in the formation of metallosupramolecular chains and multidimensional networks, whereby the intrinsic magnetic properties of a monomer $M^2M^1M^2$ -bisoxamate are perturbed.

Another approach to creating molecular magnetic materials with novel and enhanced physical properties consists of the controlled synthesis of metallosupramolecular assemblies *via* a rational ligand design.⁴ In this context, modifications at the *o*-phenylene-bisoxamate backbone that could assist the formation of supramolecular structures are very scarce.^{5–8} The only example of a successful ligand modification leading to a multimetallic structure was reported by Aukauloo *et al.*, who

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prepared a tetranuclear species $[Fe(L^{Phen}Cu)_3]^{4-}$ (Scheme 1) by reacting a preformed $[Fe(L^{Phen})_3]^{2+}$ with a copper(II) source.⁶ Since both phenanthrolines and bisoxamates bind strongly to most transition metal ions, competitive metal binding to the different coordination sites of L^{Phen} is expected, rendering the controlled synthesis of such heterometallic architectures a challenging task.

Targeting the synthesis of multidimensional magnetic materials, our approach to the design of o-phenylene-bisoxamate ligands employs the creation of auxiliary weakly binding "soft" coordination sites at the phenylene unit that are not competing with the central "hard" N₂O₂ and the two side "intermediate" O=C-C=O oxamate coordination sites. Appropriate metal ions added to a preformed M²M¹M²-bisoxamate and capable of coordinating to the auxiliary sites can consequently act as bridges offering the possibility to control the formation of metallosupramolecular structures. Thus, we decided to introduce two "soft" thiophene groups to o-phenylene-bisoxamate (Scheme 2), since thiophenes are known to be weakly coordinating ligands with diverse coordination modes including $\eta^1(S)$ and $\eta^2 - \eta^5$ that form supramolecular architectures when coordinated to Ag(1) or Rh(11) ions.⁹⁻¹¹ Here, we report the synthesis of the *o*-phenylene-bisoxamate ligand¹² H_4L^1 bearing two thiophene groups at the phenylene unit and our first results on the coordination chemistry of this novel ligand, where a monometallic complex (TBA)₂[NiL¹]



Scheme 1 o-Phenylene-bisoxamates: general structure (left) and ligand modification by Aukauloo et al.⁶ (right).

(TBA = tetra-*n*-butyl-ammonium) has been obtained and characterized (Scheme 2). Moreover, the established synthetic route towards H_4L^1 can be easily transferred to other related ligand systems as we demonstrated by preparing the 1,2-bis-(2-hydroxybenzamido)benzene derived ligand H_4L^2 and its nickel complex (TBA)₂[NiL²] (Scheme 2). Note that similarly to metal bisoxamates, metal complexes of 1,2-bis(2-hydroxybenzamido)-benzenes are known to form multimetallic spin coupled species with high potential for molecular magnetism.^{13,14}

 H_4L^1 in its protected doubly ethylated form $H_2L^1_{Et}$ can be prepared *via* a multistep synthetic route that includes one C–C cross-coupling reaction (Scheme 3). After commercially available 2,5-dimethylthiophene is doubly brominated,¹⁵ one bromine atom is replaced with a hydrogen *via* lithiation and subsequent hydrolysis.¹⁶ A corresponding boronic acid **1** is then obtained *via* a boronate ester in a one-pot reaction.¹⁷ The second component for the cross-coupling reaction, aryl

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 H_4L^2

Scheme 2 Protonated ligands of this work.

H₄L¹

OH HO

ΝН

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bromide 2, is easily prepared from *o*-phenylenediamine in a three-step procedure¹⁸ including protection by tosylation, subsequent bromination, followed by deprotection of the product. The boronic acid 1 and the aryl bromide 2 are subsequently fused *via* a double Suzuki cross-coupling reaction using [PdCl₂(dppf)] (dppf = 1,1'-bis(diphenylphosphino)ferrocene) as a catalyst. After purification *via* column chromatography the product 3 can be isolated with yields up to 84%. In the final step ethyl oxalyl chloride is allowed to react with 3 and the protected ligand $H_2L_{Et}^1$ is obtained with yields up to 77%. The total yield of the 8-step synthesis of $H_2L_{Et}^1$ is 40%.

A related ligand H_4L^2 in its protected doubly acylated form $H_2L^2{}_{Ac}$ can be prepared by adopting the synthetic protocol established for $H_2L^1{}_{Et}$, except the last step (Scheme 3): acetyl-salicylic acid chloride, generated *in situ* from acetylsalicylic acid and oxalyl chloride, reacts with 3 to give the target compound $H_2L^2{}_{Ac}$ with a yield of 45%. The total yield of the 8-step synthesis of $H_2L^2{}_{Ac}$ is 23%. The obtained $H_2L^2{}_{Ac}$ can be deprotected, if necessary, by the action of 6 M NaOH to give H_4L^2 in a quantitative yield on a small scale (50 mg). However, scaling up of this procedure is tedious due to difficulties in controlling precisely the pH value during the work-up on larger scales.

Crystals of the protected ligand $H_2L_{Et}^1$ suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into an acetonitrile solution. The ligand crystallizes in the $P2_1/n$ space group (Fig. 1). Five-membered thiophene rings make dihedral angles of 61° and 62° with the six-membered phenylene ring, thus the three π -systems are essentially electronically uncoupled. The two thiophenes are rotated in the same direction, thus forming an anti-parallel conformation in the



Scheme 3 Multistep synthesis of protected ligands $H_2L_{Et}^1$ and $H_2L_{Ac}^2$



Fig. 1 Molecular structure of $H_2L_{Et}^1$ thermal ellipsoids are drawn at the 50% probability level.



Fig. 2 Molecular structure of H_4L^2 , thermal ellipsoids are drawn at the 50% probability level.

crystal.¹⁹ The tetradentate metal coordination site in $H_2L_{Et}^1$ is non-planar: the two planes of the OOC–CON oxamic acid backbones have dihedral angles of 44° and 47° with the six-membered phenylene ring. Rotation of oxamic acid backbones in opposite directions results in the appearance of an O6…H2– N2 intramolecular hydrogen bond in the crystal structure. Additionally an intermolecular O2*…H1–N1 hydrogen bond was found in the crystal lattice (see ESI†).

The crystals of H_4L^2 suitable for X-ray structure determination were obtained by recrystallization from $CHCl_3$. The compound crystallizes in the $P\bar{1}$ space group (Fig. 2). Two fivemembered thiophene rings form dihedral angles of 43° and 86° with the central phenylene plane that indicates a weak electronic coupling between the π -systems of one thiophene and the phenylene moiety. The tetradentate metal coordination site of the metal-free ligand is non-planar: two nearly planar salicylamide groups show dihedral angles of 45° and 50° with the plane of the phenylene, thereby an intramolecular hydrogen bond O3…H1^A–N1 is built. Two additional intramolecular hydrogen bonds and one intermolecular hydrogen bond are formed *via* –NH and –OH groups (see ESI†).



Fig. 3 Molecular structure of $(TBA)_2[NiL^1]$, thermal ellipsoids are drawn at the 50% probability level, TBA⁺ cations and water molecules are omitted.

All three ligands $H_2L_{Et}^1$, $H_2L_{Ac}^2$, and H_4L^2 are colorless compounds as confirmed by their electronic absorption spectra (see ESI[†]) featuring high intensity absorption bands exclusively in the UV region (200–340 nm). These bands are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ intraligand transitions.

After $H_2L_{Et}^1$ and $H_2L_{Ac}^2$ are deprotected and deprotonated by the action of aqueous NaOH, addition of a Ni(II) salt and (TBA)Br results in the formation and precipitation of target complexes (TBA)₂[NiL¹] and (TBA)₂[NiL²], respectively. Sharp signals in ¹H NMR spectra and the X-ray structures of the complexes confirm the presence of a diamagnetic Ni^{II} ion in both compounds.

X-ray quality crystals of $(TBA)_2[NiL^1]$ were obtained from an EtOH-H₂O mixture; the complex crystallizes in the $P2_1/c$ space group (Fig. 3). The fourfold deprotonated ligand coordinates to the Ni ion through the two oxygen and two nitrogen donors. The Ni–N (1.819(2) and 1.821(2) Å) and Ni–O (1.8819(19) and 1.890(2) Å) bond distances in $(TBA)_2[NiL^1]$ are similar to those found in other *o*-phenylene-bis(oxamato) low-spin Ni(π) complexes.^{8,20,21} Five-membered thiophene rings form dihedral angles of 53° and 54° with a six-membered phenylene ring that are slightly reduced compared to the respective angles in the metal-free H₂L¹_{Et}. The two thiophene substituents are in parallel conformation in crystalline (TBA)₂[NiL¹].¹⁹ The *o*-phenylene-bis(oxamato)nickel(π) fragment is nearly planar that results in strong electronic coupling between the π -systems of two oxamate moieties and the phenylene ring.

Crystals of $(TBA)_2[NiL^2]$ suitable for X-ray analysis were obtained from a CHCl₃ solution on cooling; the complex crystallizes in the *P*2₁/*n* space group (Fig. 4). The fourfold deprotonated ligand is coordinated to the Ni ion through two oxygen and two nitrogen atoms building a distorted square-planar environment around the central metal ion. Short Ni–N (1.885(3) and 1.870(2) Å) and Ni–O (1.853(2) and 1.852(2) Å) bond distances in (TBA)₂[NiL²] compare well with those observed for a similar low-spin Ni(π) complex without thiophene substituents.²² Two thiophene rings form dihedral angles of 49° and 54° with the central phenylene plane, thus the π-systems of



Fig. 4 Molecular structure of $(TBA)_2[NiL^2]$, thermal ellipsoids are drawn at the 50% probability level, two TBA⁺ cations and a water molecule are omitted.

these three fragments are essentially uncoupled. The metal coordination site N_2O_2 is slightly twisted: the Ni1N1N2 plane shows a dihedral angle of 10° with the Ni1O1O4 plane that is likely due to a too small ligand cavity to accommodate a low-spin Ni(π) ion without being distorted. Consequently, the two salicylamide groups are slightly twisted and not coplanar with the central phenylene fragment: the C₆-rings of the salicyl-amide groups have dihedral angles of 21° and 22° with the six-membered central phenylene ring. Thus, significant electronic coupling is expected between the π -systems of the metal coordination site and the central phenylene unit in (TBA)₂[NiL²], albeit it is weaker than that in the nearly planar (TBA)₂[NiL¹].

Electronic absorption spectra of (TBA)₂[NiL¹] and (TBA)₂[NiL²] reveal absorption bands in the near UV and visible regions that are absent in the spectra of the corresponding metal-free ligands (see ESI⁺). A strong broad band centered at 350 nm (ε = 1.56 × 10⁴ M⁻¹ cm⁻¹) and a strong broad band at 352 nm (ε = 3.14 × 10⁴ M⁻¹ cm⁻¹) accompanied by two shoulders for (TBA)₂[NiL¹] and (TBA)₂[NiL²], respectively, both spread into the visible region that results in red colored complexes. Surprisingly, these absorption bands are not due to MLCT transitions. As determined by time-dependent density functional theory (TD-DFT) calculations at the B3LYP level (see ESI⁺), these are predominantly intraligand $\pi \rightarrow \pi^*$ and *intra*ligand charge transfer transitions with only a small amount of MLCT character. We ascribe the significant bathochromic shift of some intraligand transitions in the complexes to the increased overall planarity of the metal coordinated ligands compared to the metal-free ligands that allows stronger electronic coupling between the individual π -subsystems of the ligands in (TBA)₂[NiL¹] and (TBA)₂[NiL²]. Additionally, very weak ligand field d-d transitions at about 450 nm ($\varepsilon = 4 \times 10^2$ $M^{-1} \text{ cm}^{-1}$) and 510 nm ($\varepsilon = 7 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$) can be detected in the visible for (TBA)₂[NiL¹] and (TBA)₂[NiL²], respectively.

In summary, a synthetic strategy has been developed and consequently utilized to prepare a phenylene-bisoxamate derived ligand featuring three different types of coordination sites $(H_2L_{Et}^1)$. Our synthetic approach can be adopted to modify other related ligand systems as demonstrated by preparing 1,2-bis(2-hydroxybenzamido)benzene derivatives $H_2L_{Ac}^2$ and H_4L^2 . The novel ligands form stable mononuclear Ni(II) complexes that were characterized by X-ray crystallography, NMR and electronic absorption spectroscopy as well as theoretical calculations. The obtained ligands represent attractive building blocks to create multidimensional magnetic materials in a controllable way that is currently under investigation in our laboratory.

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