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Electronic and magnetic properties of the binuclear $[Mn_2\{(OPPh_2)_2N\}_4]$ complex, as revealed by magnetometry, EPR and density functional broken-symmetry studies

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ABSTRACT

In this work, magnetometry and EPR spectroscopy studies on the binuclear Mn(II) complex $[Mn_2\{(OPPh_2)_2N\}_4]$ (**1**) established antiferromagnetic interactions between the two $S = 5/2$ Mn(II) centers being at 3.378 Å from each other. The magnitude of the J_{AB} coupling constant, in the framework of the $\hat{H}_{HDvV} = -2J_{AB}\hat{S}_A\hat{S}_B$ formalism, was determined to be $-4.5 \pm 0.5\ cm^{-1}$, by the temperature dependence of the magnetic susceptibility of **1**. This value is comparable with the one of the previously studied $[Mn_2\{(OPPh_2)[OP(OEt)_2]N\}_4(H_2O)_2]$ complex ($-3.5\ cm^{-1}$), which bears similar type of ligands. The antiferromagnetic nature of the coupling within the binuclear Mn_2O_4 core of **1** was unequivocally confirmed also by EPR studies on frozen CH_2Cl_2 solutions at various temperatures. Density functional broken-symmetry calculations confirmed the above experimental findings and provided J_{AB} values in close agreement with the experiment. Comparisons with literature binuclear Co(II) or Mn(II) complexes were made.

1. Introduction

The existence of binuclear manganese centers in the active sites of various enzymes such as arginases, catalases, ribonucleotide reductases, dinitrogenase reductase-activating glycohydrolases, etc., has been well established by X-ray crystallography [1–3] (and references therein). In particular, binuclear Mn(II) active sites have been recently documented by EPR spectroscopy, owing to the close proximity of two high-spin (HS) $S = 5/2$ centers, for instance in sulfate thiohydrolase [4], phosphotriesterase [5], the manganese transport regulator MntR [6], and a Mn(II)-reconstituted purple acid phosphatase [7].

EPR spectroscopy provides significant insight to the electronic structure of a paramagnetic metalloenzyme active site, which is considered to be crucial for its catalytic reactivity [8]. It should be stressed that, as in other types of metalloenzymes [9], invaluable information has been obtained by studies on appropriate synthetic analogues of binuclear Mn(II) biological sites, in this case mainly by magnetometry and EPR investigations [10–14].

Most of the binuclear synthetic analogues already investigated, contain Mn(II) centers bridged by μ-oxo (aquo, hydroxo, phenoxo, carboxylato) or $\mu_{1,3}$-carboxylato moieties. Also, a search in the Cambridge Structural Database reveals that most of the Mn(II) centers in such analogues are six-coordinate, whereas coordination numbers 5 and 7 are more rare [15]. It would be desirable to extend this set of analogues by studying Mn(II) binuclear centers of different first and second coordination spheres. A case in point is the $[Mn_2\{(OPPh_2)_2N\}_4]$ complex (**1**) bearing deprotonated tetraphenylimidodiphosphinic acid $[(OPPh_2)_2N]^-$ as ligands, synthesized and structurally characterized by Silvestru and co-workers [16,17].

In order to put this complex into perspective, a brief introductory survey of similar complexes is included below. Bis-chalcogenated imidodiphosphinate type of ligands, $R_2P(E)NHP(E')PR'_2$, E, E′ = O, S, Se, Te; R, R′ = alkyl or aryl groups, have been extensively studied with respect to their coordination to both main group and transitional metal ions [18–20]. These acids are readily deprotonated to anionic $[R_2P(E)NP(E')PR'_2]^-$ (Scheme 1), denoted in the following as (E, E′), which are usually coordinated in a chelating fashion [21]. The structural, stereochemical or electronic properties in this type of ligands, or their corresponding metal complexes, can be readily affected by the nature of the E, E′ donor atoms, or the R, R′ peripheral groups bonded to the P atoms of the P–N–P ligand backbone. A

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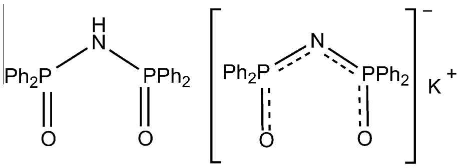

Scheme 1. The $Ph_2P(O)NHP(O)Ph_2$ ligand and its deprotonated form employed in this work.

representative example of first coordination sphere effects is the structural preference of the $[Ni\{(EP^{i}Pr_2)_2N\}_2]$ complexes, E = S (tetrahedral), Se (square planar/tetrahedral), Te (square planar) [22,23]. On the other hand, the EPR properties of $S = 3/2$ tetrahedral $Co^{II}S_4$-containing complexes are profoundly affected when half of the – second coordination sphere – Ph peripheral groups in $[Co\{Ph_2P(S)NP(S)PPh_2\}_2]$ (axial EPR system) are replaced by ^{i}Pr groups in $[Co\{Ph_2P(S)NP(S)P^{i}Pr_2\}_2]$ (rhombic EPR system) [24].

Manganese complexes bearing bis-chalcogenated imidodiphosphinate ligands have been reported for Mn(I), Mn(II) and Mn(III) ions. As expected, Mn(I) is stabilized by its additional coordination to π-acceptor CO ligands, which complement the coordination sphere [25–28]. The Mn(I)/Mn(I) and the mixed valence Mn(I)/Mn(II) binuclear complexes, $[Mn_2(CO)_6\{Me_2P(S)NP(S)Me_2\}_2]$ [27] and $[Mn_2(CO)_3\{Ph_2P(O)NP(O)Ph_2\}_3]$ [29], respectively, have also been structurally characterized. Most of the reported manganese complexes bearing (E, E′) ligands are homoleptic Mn(II) tetrahedral complexes containing MnS_4 [30–32], $MnSe_4$ [31], or MnO_2S_2 [17,33] first coordination spheres. Moreover, the $[(OPPh_2)_2N]^-$ ligand has been shown to afford crystals of tris-chelated $[Mn^{III}\{(OPPh_2)_2N\}_3]$ [34].

The coordination versatility of (E, E′) ligands towards transition metal ions has also been demonstrated by the formation of the isostructural binuclear complexes $[M_2\{(OPPh_2)_2N\}_4]$, M = Mn [17], Co [35]. These complexes contain two monometallic biconnective $[(OPPh_2)_2N]^-$ ligands (Scheme 1), as well as two additional ones acting as bimetallic triconnective ligands, forming two oxygen atom bridges between the two M(II) ions. In the crystal structure of **1**, the two approximately trigonal bipyramidal Mn(II) ions are at a distance of 3.378 Å (Fig. 1).

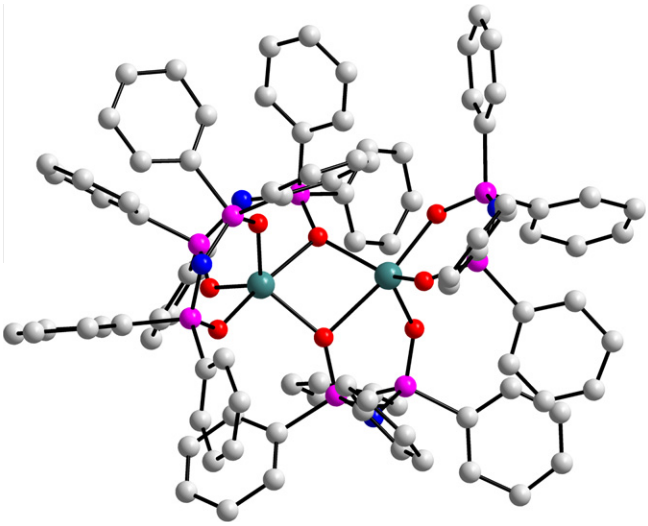

Fig. 1. The X-ray crystal structure of **1** [17] drawn with 30% ellipsoids. The H atoms have been omitted for clarity. Atom color coding: Mn, cyan; O, red; P, magenta; N, blue; C, light gray. (Color online.)

On the other hand, in the binuclear $[Ni_2\{(OPPh_2)_2N\}_4]$ complex, only one (O,O) ligand is monometallic biconnective, whereas three are bimetallic triconnective [36]. Moreover, $[M_2\{(OPPh_2)_2N\}_4(H_2O)]$ complexes have been structurally characterized for M = Cd [37] and Ca [38], in which a H_2O molecule completes the coordination sphere, either as bridging or coordinating the one of the two metal sites, respectively. More recently, the binuclear $[Mn_2\{(OPPh_2)[OP(OEt)_2]N\}_4(H_2O)_2]$ complex has been reported, in which each Mn(II) center is additionally coordinated to a H_2O molecule, thus being six-coordinate [32].

As far as the magnetic properties of binuclear M(II) complexes of the above type are concerned, recent magnetometry studies have established anti- and ferro-magnetic interactions for the $[Mn_2\{(OPPh_2)[OP(OEt)_2]N\}_4(H_2O)_2]$ [32] and $[Co_2\{(OPPh_2)_2N\}_4]$ [35] complexes, respectively. On the other hand, the electronic and magnetic properties of **1** have not been extensively investigated, apart from a brief report on its powder EPR spectrum at room temperature [17]. Therefore, in this work, the electronic and magnetic properties of the latter complex were investigated by magnetometry and EPR studies.

It should also be noted that significant effort has been recently devoted to translate experimental data obtained on paramagnetic systems into electronic structure properties. Among several approaches, *ab initio* multireference electronic structure calculations [39–41], as well as Density Functional Theory (DFT) methods [39,42–49], combined with the broken-symmetry (BS) approach, have shown great success in providing reliable magnetostructural correlations. The latter approach has provided a rigorous way to study magnetic coupling phenomena in numerous transition metal complexes or metalloprotein active sites. Based on the above, theoretical calculations were performed on **1**, in order to further elucidate its electronic structure.

The analysis of both the magnetic and EPR properties of this binuclear Mn(II) complex provides evidence for an antiferromagnetic coupling between the two $S = 5/2$ Mn(II) ions. Comparisons are being made to other similar binuclear complexes.

2. Experimental

2.1. Synthesis

The synthesis of **1** was carried out according to a published procedure [17].

2.2. Physical measurements

Variable-temperature magnetic susceptibility measurements were carried out on powdered samples of **1** in the 2–300 K temperature range using a Quantum Design PPMS SQUID susceptometer. Corrections were based on the diamagnetic contribution of the complex estimated from Pascal's constants and from the sample holder ($-0.011\ cm^3\ mol^{-1}$). X-band EPR spectra at liquid helium temperatures were recorded on a Bruker ER 200D-SRC X-band spectrometer equipped with an Oxford ESR 9 cryostat, an NMR-Gaussmeter, and an Anritsu microwave frequency counter. Parallel mode spectra were recorded with a Bruker dual mode cavity.

2.3. Methodological aspects

The magnetic properties of a system comprised of two interacting magnetic centers with fictitious local spins $\mathbf{S}_A$ and $\mathbf{S}_B$ are typically interpreted in the context of the phenomenological Heisenberg–Dirac–van Vleck spin-Hamiltonian:

$$\hat{H}_{\mathrm{HDvV}} = -2J_{\mathrm{AB}}\hat{S}_{\mathrm{A}}\hat{S}_{\mathrm{B}} \tag{1}$$