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Encapsulation of $[Mn(bpy)_3]^{2+}$ cations in 2D $[Mn(dca)_3]^-$ sheet: Synthesis, X-ray structure and EPR study

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Abstract

The reaction of $Mn(NO_3)_2 \cdot 4H_2O$, 2,2′-bipyridine (bpy) and sodium dicyanamide (dca) in aqueous medium yielded the $\{[Mn(bpy)_3][Mn(dca)_3]_2\}_n$ (**1**). The single-crystal X-ray analysis of **1** revealed that the anionic part of the complex, $[Mn(dca)_3]^-$, features infinite 2D sheets with a honeycomb-like porous structure having a void space of ca. 12 Å in which $[Mn(bpy)_3]^{2+}$ cations are encapsulated to yield a fascinating molecular assembly. Mn^{II} ions possess an octahedral geometry both in the anionic and cationic components of complex **1**. In the anionic component, each Mn^{II} ion is bridged by three pairs of dicyanamide anions in an end-to-end fashion with two other Mn^{II} ions from adjacent $[Mn(dca)_3]^-$ moieties. This type of linking propagates parallel to the *bc* crystallographic plane to form 2D sheets. $[Mn(bpy)_3]^{2+}$ is found to have somewhat "squeezed" upon encapsulation. No measurable magnetic interaction was evidenced through variable temperature magnetic susceptibility measurements. However, in addition to the broad $g \approx 2$ resonance typical of magnetically diluted $[Mn(bpy)_3]^{2+}$ cations, EPR spectroscopy evidenced exchange narrowing of the $[Mn(dca)_3]^-$ resonance at $g \approx 2$ thus indicating operation of weak magnetic interactions extended over the whole 2D network through the dca^- bridges.

Keywords: Manganese(II) dca complex; Crystal structure; EPR spectroscopy; Two-dimensional structure

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1. Introduction

The design of synthetic pathways to chemical system of desired properties continues to be a challenge for chemists. The recent surge in research devoted to coordination polymers was generated by a fundamental interest in the development of new approaches that can afford an impressive array of new network architectures, many of which do not exist in natural solids. This surge has subsequently been fueled by the practical opportunities that are offered by new classes of functional materials. In this context, a great deal of interest has been devoted to the development of rational synthetic route to novel 1D, 2D and 3D polymeric coordination compounds that have applications as molecule based materials [1]. The coordination polymers of pseudohalide ligands such as cyanide, azide and thiocyanate have long been studied for their interesting magnetic properties [2]. Of late, however, the larger pseudohalide ligand dicyanamide $[N(CN)_2]^-$ (dca) has attracted a lot of attention due to the discovery of long magnetic ordering in rutile-like 3D systems, $M(dca)_2$, M = Cr, Mn, Fe, Co, Ni, Cu [3–7]. These systems showed a variety of magnetic behaviors like ferromagnetism, antiferromagnetism and paramagnetism depending on the metal ion (M). For example, $Ni(dca)_2$ is ferromagnetic [4,5] and $Mn(dca)_2$ is antiferromagnetic [8] below the corresponding transition temperature whereas $Cu(dca)_2$ is paramagnetic [7]. Besides, dca is a close congener of the chemical entities that are believed to have a role in chemical evolution since prebiotic times [9]. The particular feature of the dca ligand is its

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variability in coordination modes [6]. It behaves as a monodentate, bidentate, tri- or tetradentate, or even pentadentate ligand involving either nitrile or amide or both groups in coordination. The coordination properties of dca thus allow for the preparation of compounds with various kinds of architectures: mononuclear, polynuclear as well as 1D, 2D and three-dimensional networks [6]. The magnetic coupling through a dca bridge is generally weak but the ferromagnetic or antiferromagnetic nature of interactions could not be easily predicted due to the need for successful theoretical models to analyze the magneto-structural correlations of these systems. As a result studies on dca bridged compounds received intense attention in recent years [6,10–13]. In this context, the structural varieties exhibited by $[Mn(dca)_3]^-$ is particularly fascinating. A one-dimensional ladder type arrangement with doubly bridging dca ligands (rails) and disordered dca (rungs) feature the structure of $(Ph_4As)_2[\{M(dca)_3\}_2(H_2O)] \cdot H_2O \cdot CH_3OH$ (M = Co and Ni) salts [14], while the structure of their congeners $(Ph_4E)_2[Mn(dca)_3]$ (E = P or As) and $(Ph_4P)_2[Co(dca)_3]$ include 2D anionic sheets consisting of metal atoms bridged by two dca in one direction and by a single disordered dca bridge in another direction [15,16]. Cation templating in anionic 2D or 3D networks involving dca has been a subject of great attention in synthetic coordination polymers. The cation $(MePh_3P)$ is templated in all 3D networks of $[Mn(dca)_3]^-$ [15]. A hexagonal cavity that has been created by doubly bridging dca anions in $[Mn(dca)_3]^-$ is able to entrap cations like $[M(bpy)_3]^{2+}$, M = Ni^{II} or Fe^{II} [17]. These structures have been of interest in order to gain a deeper insight into the basics of magnetic interaction between metal ions as well as for the development of porous structure consisting of pores and channels like the naturally occurring zeolites and clays for storage of volatile molecules and catalytic and nano-technological applications [18].

2. Experimental

2.1. General

Manganese(II) nitrate tetrahydrate (Aldrich) and sodium dicyanamide (Aldrich) were used without further purification. All other chemicals used were of AR grade. The EPR spectra were obtained on a Bruker ESP 300 E spectrometer. The microwave frequency was generated with a Bruker ER 04 (≈9–10 GHz). The microwave frequencies were measured with a Racal-Dana frequency-meter and the magnetic field was measured with a Bruker NMR probe gauss-meter. The facilities used for all other physical measurements have been described earlier [20].

2.2. Preparation of complex $\{[Mn(bpy)_3][Mn(dca)_3]_2\}_n$ (**1**)

To prepare complex **1** an ethanol–water (1:1) solution (30 mL) of sodium dicyanamide (300 mg, 3.24 mmol) and $Mn(NO_3)_2 \cdot 4H_2O$ (407 mg, 1.62 mmol) was added to an aqueous solution (25 mL) of 2,2′-bipyridyl (253 mg, 1.62 mmol) and finally few drops of L-ascorbic acid were added to the resulting solution. Pale yellow crystals that formed after two days were collected by filtration [19]. Faintly red colored mother liquor obtained after filtration was allowed for further evaporation. Deep red block type crystals of the desired complex **1** formed in 10 days. The crystals were collected under microscope and recrystallized from water and dried in a desiccator (Yield ca. 10%). *Anal.* Calc. for $C_{42}H_{24}Mn_3N_{24}$: C, 49.0; H, 2.3; N, 32.6. Found: C, 48.5; H, 2.9; N, 32.8%. IR (KBr pellets, cm^{-1}): $\nu_s(C{\equiv}N)$, 2140(vs); $\nu_{as}(C{\equiv}N)$, 2240(m); $\nu_s(C{\equiv}N) + \nu_{as}(C{\equiv}N)$, 2240 and 2300.

2.3. X-ray crystallography

2.3.1. Crystal data

$C_{42}H_{24}Mn_3N_{24}$, $M = 1029.67$, orthorhombic, space group *Fdd2*, $a = 28.899(6)$, $b = 12.5518(16)$, $c = 23.849(3)$ Å, $V = 8651(2)$ Å^3, $Z = 8$, $D_{calc} = 1.581$ g cm^{-3}, $F(000) = 4152$, $\mu = 0.927$ mm^{-1}, $T = 100$ K, crystal size = 0.18 × 0.10 × 0.08 mm, $R_1 = 0.0454$, $wR_2 = 0.1150$.

2.3.2. X-ray single crystal structure determination of **1**

Single crystals of complex **1** suitable for X-ray diffraction study were obtained by slow evaporation of its aqueous solution. Intensity data were collected using a Bruker Smart CCD diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K. The Bruker SAINT software [21] was used for data reduction and empirical absorption corrections SADABS, based on measurements of equivalent reflection used. The structure was solved by direct methods (SHELXS-97) [22] which revealed the positions of the metal atoms. The remaining non-hydrogen atoms were located by successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The structure was refined by full-matrix least-squares on F^2 using SHELXL-97 [22]. Molecular graphics softwares used were ORTEP III [23] and MERCURY [24]. The largest difference in peak and hole were 0.550 and −0.365, respectively.

3. Results and discussion

3.1. Description of structure of the complex **1**

The structure of **1** consists of $[Mn(bpy)_3]^{2+}$ cations and $[Mn(dca)_3]^-$ anions (Fig. 1). Selected bond lengths and bond angles are collated in Table 1. The Mn1 ion is exclusively coordinated by nitrogen atoms (six) from bpy ligands to form tris-(bipyridyl) manganese(II) cation. On the other hand, the anion has a complicated structure. The two Mn^{II} ions, Mn2 and Mn3, are doubly bridged by end-to-end dicyanamido groups. Each of these Mn^{II} ions is again connected to the three symmetry related Mn^{II} ions through two end-to-end dicyanamido groups. Mn2 is connected to a pair of $Mn3^{ii}$ ions (symmetry operation ii = x,