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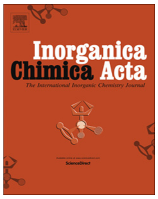

Research paper

Pseudoclathrochelate *n*-hexadecylboron-capped metal(II) tris-pyrazoloximates: synthesis, X-ray structure, spectral and magnetic characteristics

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ABSTRACT

Self-assembly of monohexadecylboron-capped zinc, cobalt, iron and manganese(II) tris-pyrazoloximate pseudoclathrochelates was performed using *one-pot* template condensation of 2-acetylpyrazole oxime with *n*-hexadecylboronic acid as a capping Lewis-acidic agent on the corresponding metal ion as a matrix. Hydrogen atoms of three terminal pyrazolyl NH groups of three pyrazoloxime synthons form a pseudomacrobicyclic ligand through their hydrogen bonding with a chloride counterion $Cl^- \ldots (HN)_3$, thus allowing an encapsulation of the corresponding metal ion. The complexes obtained were characterized using elemental analysis, MALDI-TOF mass spectrometry, IR, UV-Vis-NIR, ^{57}Fe Mössbauer (for the iron complex), ^{1}H and ^{13}C NMR spectroscopy, as well as by SQUID magnetometry. The structure of the complexes synthesized was also confirmed by single crystal X-ray diffraction analysis of the zinc(II) pseudoclathrochelate. Its pseudocaged zinc(II) ion is located almost in the center of ZnN_6-coordination polyhedron, which adopts a trigonal prismatic geometry with a very low distortion angle. As follows from variable-temperature magnetometry data, the χT values for manganese and iron(II) pseudoclathrochelates in the temperature range 50–300 K are close to theoretical pure high-spin values without of orbital contribution. ^{1}H and ^{13}C NMR chemical shifts of their pyrazoloximate nuclei reach to some hundreds of ppm, while those chemical shifts of the normal hexadecyl chain's nuclei, on the distance of more than five chemical bonds from the pseudoencapsulated paramagnetic metal ion, are close to those for the diamagnetic zinc(II) pseudoclathrochelate. This is indicative of the contact nature of thus induced paramagnetic shifts, as well as a weak pseudocontact contribution.

1. Introduction

For the first time, chloride ion-aided self-assembly of pseudoclathrochelate zinc, cobalt, iron, and manganese(II) tris-pyrazoloximates shown in Scheme 1, a has been performed [1] using template cross-linking of three pyrazoloxime ligand synthones with phenylboronic acid as a Lewis acid on a corresponding metal (II) ion as a matrix. The presence of a pseudocross-linking H-bonded chloride ion is reported to be a critical for their formation: all complexes are capped with a chloride ion through three N—H···Cl hydrogen bonds that stabilize their pseudomacrobicyclic frameworks. So, this ion completes the formation of their pseudocapping apical fragment through strong hydrogen bonding with HN groups of three pyrazoloximate chelate moieties. Cobalt(II) pseudoclathrochelates of this type and their hexahalogenoclathrochelate analogs have one of the largest (among *3d*-transition metal complexes) axial anisotropy of magnetic susceptibility [2–6], resulting from an unusual trigonal prismatic (TP) geometry of these complexes. This remarkable anisotropy, translating into large negative value of the zero-field splitting energy, is high enough to promote reliable paramagnetic pseudocontact shifts at the distance beyond 2 nm. This finding paves the way towards the applications of such chemically robust, high-spin boron-capped cobalt(II) pseudo- and clathrochelates as prospective paramagnetic probes for structural biological testings, as well as NMR and MRI applications [7]. Moreover, the phenylboron-capped cobalt(II) tris-pyrazoloximate

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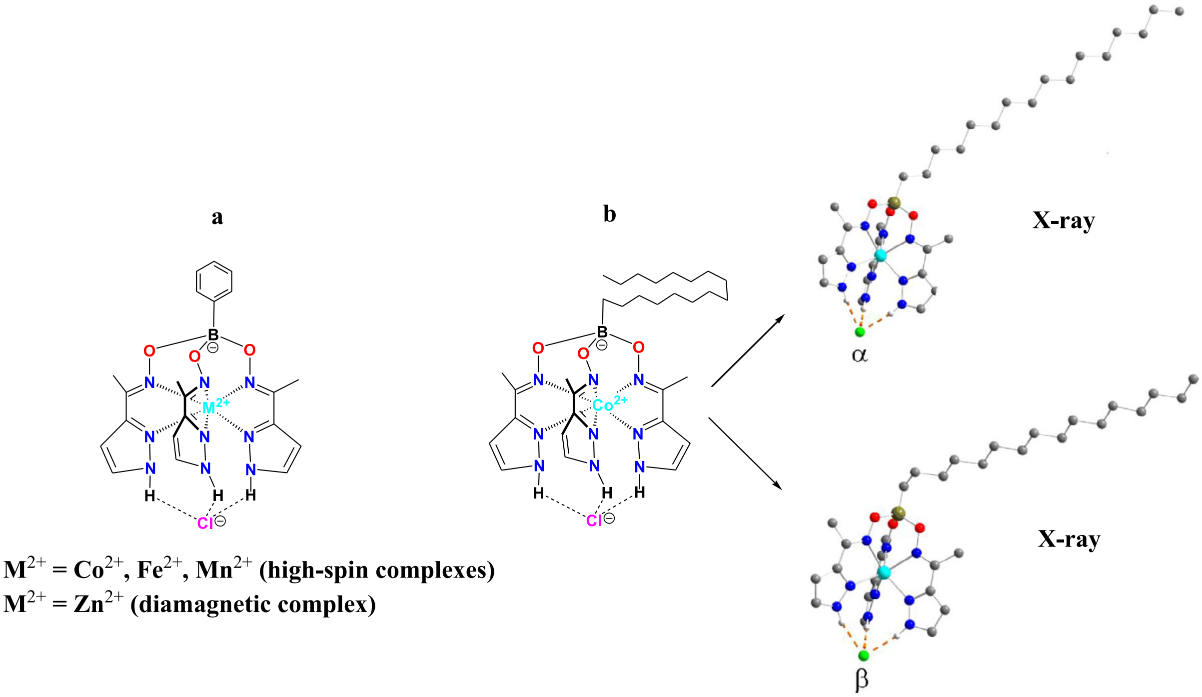

Scheme 1. Chemical drawings of the boron-capped metal(II) tris-pyrazoloximates.

pseudoclathrochelate (Scheme 1, a) is reported [2] to show a SMM behavior with very high Orbach relaxation barrier of 152 cm^{-1}, a high magnetic anisotropy, caused by a TP geometry of CoN_6-coordination polyhedron with orbitally – degenerated ground state. Its hexadecylboron-capped analog is described [3] to form two polymorphs (α and β) also shown in Scheme 1(b) and having substantially different SMM behavior with effective barriers of 109 and of 180 cm^{-1}, respectively, the latter value was the largest one reported at the moment for cobalt-based mononuclear SMMs. So, even such small structural differences caused the change an effective relaxation barrier by approximately 70 cm^{-1}. This result is explained [3] by high orbital contribution to the orbital moment that is not quenched by the crystal field of a TP pseudocaging hexadentate ligand. Here we report the detailed synthetic procedures, magnetometry and spectral data for the paramagnetic hexadecylboron-capped iron and manganese(II) tris-pyrazoloximates, and the preparation and the single crystal X-ray structure of their diamagnetic zinc(II)-pseudoencapsulating analog, the derivatives of the same ligand synthon, 2-acetylpyrazol oxime (*PzOxH*), as well as the detailed synthetic procedure and optical spectral characteristics of the above cobalt(II) pseudoclathrochelate, compared with those for other metal(II) pseudocage complexes of this type.

2. Experimental

2.1. Materials and methods

The reagents used $FeCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$ and anhydrous $ZnCl_2$, sorbents, organic bases, and solvents were obtained commercially (SAF). Pyrazoloxime *PzOxH* and hexadecylboronic acid ($HdB(OH)_2$) were prepared as described elsewhere [8,9],.

Analytical data (C, H, N contents) were obtained with a Carlo Erba model 1106 microanalyzer.

HR-ESI mass-spectra were measured in CKP FMI IPCE RAS on a Bruker maXis impact mass spectrometer. The acetonitrile solutions of the complexes under study were injected using Agilent 1260 autosampler.

UV-Vis spectra of their solutions in dichloromethane were recorded in the range 230–1100 nm with a Lambda 9 Perkin Elmer spectrophotometer. Vis-NIR spectra in the range 700–2500 nm were recorded with a Tensor 37 Bruker FT-spectrophotometer. The individual Gaussian components of these spectra were calculated using the Fityk program [10].

IR spectra of the solid samples (KBr tablets and the suspensions in fluoroluble) in the range 400–4000 cm^{-1} were recorded with a Perkin Elmer FT-IR Spectrum BX II spectrometer.

^1H and ^{13}C NMR spectra were recorded from CD_2Cl_2 solutions with a Bruker Avance 600 spectrometer. The measurements were done using the residual signals of CD_2Cl_2: ^1H 5.32 ppm, ^{13}C 54.00 ppm.

^{57}Fe Mössbauer absorption spectrum of the iron complex was recorded at 298 K using a NP-255 spectrometer (Hungary) with a constant acceleration mode and a symmetrical triangular change in the velocity of a γ-quantum source (^{57}Co in a rhodium matrix with an activity equal to 5 mCu and with a line emission width equal to 0.11 mm s^{-1}). The spectrum was collected with a 511-multichannel analyzer. The speed scale of the spectrometer was calibrated using the spectrum of sodium nitroprusside as a standard. The isomeric shift (IS) value was obtained relative to the center of this spectrum.

The magnetic susceptibility of the polycrystalline samples was measured with a Quantum Design MPMSXL SQUID magnetometer in the temperature range 2–300 K with magnetic field of up to 5 kOe. None of complexes exhibited any field dependence of molar magnetization at low temperatures. The diamagnetic corrections were made using the Pascal constants [11,12],. The effective magnetic moment was calculated as $\mu_{eff}(T) = [(3k/N_A\mu_B^2)\chi T]^{1/2}{}^{13}C \approx (8\chi T)^{1/2}$.

2.2. Synthesis

2.2.1. [Co(PzOx)$_3$(BHd)]Cl [3]

Pyrazoloxime *PzOxH* (2.5 g, 20 mmol) and hexadecylboronic acid (1.97 g, 7.3 mmol) were dissolved in dry ethanol (20 ml) with intensive stirring under argon, and $CoCl_2 \cdot 6H_2O$ (1.58 g, 6.7 mmol)