



Synthesis, spectral elucidation, electrochemistry and DFT interpretation of manganese(II)-thioalkyl-arylazoimidazole complex



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ABSTRACT

One new Mn(II) thioalkyl-arylazoimidazole complex (**1**), $[\text{Mn}(\text{SRaaiNR}^l)_2(\text{SCN})_2]$ ($\text{SRaaiNR}^l = 1\text{-alkyl-2-}\{(o\text{-thioalkyl)phenylazo}\}\text{imidazole}$ and $\text{R} = \text{Me}$, $\text{R}^l = \text{Et}$) is afforded and systematically characterized by FT-IR, UV–Vis and EPR spectroscopy. The single crystal X-ray diffraction technique reveals that in complex **1**, the central Mn atom possesses a tetrahedral environment of MnN_4 sphere; coordinated by a pair of monodentate orientation of $\text{N}_{\text{imidazolyl}}$ and N_{SCN} atoms. Variable temperature magnetic moment confirms that in complex **1**, there exists an antiferromagnetic coupling in tetrahedral symmetry. Cyclic voltammogram study of complex **1** evidenced the presence of a Mn(III)/Mn(II) redox response at 1.25 V alongwith azo reductions at -0.8 V. DFT computational using optimized geometry clearly explains the electronic and redox properties which is in accordance with the experimental evidence.

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1. Introduction

Manganese, the 12th most abundant metal on the earth's crust and useful metal in the growth of industry and important in human health, forms an extensive range of complex compounds in different stereo chemistry [1]. The d^5 configuration of Mn(II) offers no CFSE in high-spin octahedral or tetrahedral complexes both of which are adopted in a large number of complexes. However, Mn(II) complexes are generally magnetically active [2]. In construction of the coordination complexes, suitable choice of organic ligands is central to determine the structures of the resulting coordination complexes. The imidazole derivative ligands play an important role in the coordination chemistry of various transition metals [3]. The stability and relatively strong bonding to metals and the possibility of adjusting the electronic and steric properties by

introducing sterically demanding substituents at the N atom are important advantages of the imidazole type ligands, especially in catalytic processes [4]. The research in our group has been focused to the exploration of coordination chemistry of transition metals of arylazoimidazoles [5–10], a series of azoimine ($-\text{N}=\text{N}-\text{C}=\text{N}-$) functionalized ligand. Manganese chemistry of arylazoimidazoles has been the subject of our study towards structural characterization and magnetic studies [11–16]. Thiocyanate and azide-containing metal complexes are considered to be the most investigated systems because of their diverse structures, applications in magnetic materials and luminescence properties. Thiocyanato (SCN^-) and azido (N_3^-) binding are important in Mn(II) coordination chemistry to synthesize bridging coordination polymers [5,8]. We have rationally designed and synthesized an imidazole ligand by functional group modifications. Before some of us reported substituted 1-alkyl-2-((o-thioalkyl)phenylazo)imidazole (SRaaiNR^l), a potential tridentate imidazolyl-N, azo-N and thioether-S ligand [17,18] which also serves as monodentate imidazolyl-N [19] and bidentate imidazolyl-N, azo-N chelator [18]. Based upon our previous articles, we report herein one new Mn complex having the formula $[\text{Mn}(\text{SRaaiNR}^l)_2(\text{SCN})_2]$ (where $\text{R} = \text{Me}$ and $\text{R}^l = \text{Et}$) (**1**). Complex **1** is subjected to X-ray diffraction analysis.

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Both the complexes are characterized by different spectroscopic techniques. The cyclic voltammetric study is also carried out. Moreover, in order to better understand the electronic structures in the complexes and to explain the related experimental observations, density functional theory (DFT) calculations have also governed.

2. Experimental

2.1. Materials

MnCl₂·4H₂O, *o*-(amino)thiophenol, MeOH, methyl iodide (MeI), ethyl iodide (EtI), NH₄SCN were purchased from E. Merck, India. Solvents were used after drying [20]. All experiments were carried out under N₂ atmosphere. The syntheses of the ligands were carried out following common procedure [21] by coupling *o*-(thioalkyl)phenyldiazonium ion (obtained by diazotization of *o*-(thioalkyl)aniline) with imidazole at pH 7 followed by N(1)-alkylation using alkyl iodide in presence of NaH in dry THF under dry and inert condition.

2.2. Physical techniques

IR spectra (KBr discs, 4000–400 cm⁻¹) were recorded on a RX-1 Perkin Elmer FTIR spectrophotometer. Elemental (C, H and N) analysis was carried out with a Perkin-Elmer 2400 CHNS/O elemental analyzer. The electronic spectra were recorded at room temperature on Lambda 25 Perkin Elmer spectrophotometer in 200–900 nm range. EPR spectra were recorded on powder samples at X-band frequency with a BRUKER 300E automatic spectrometer at room temperature (295 K) and 77 K. Electrochemical study was carried out with the use of computer controlled CHI 600D Electrochemical Workstation using Pt-disk working electrode and Pt-wire auxiliary electrode at 298 K. The reported results were referenced to Ag/AgCl in acetonitrile and were uncorrected for junction potential. [n-Bu₄N][ClO₄] was used as supporting electrolyte. The magnetic properties were investigated with a Quantum Design MPMS-XL superconducting quantum interference device magnetometer (SQUID) at an applied field 0.5 T in a temperature range 5–300 K. Powder samples were measured in a pharmaceutical cellulose capsule [22]. The diamagnetic corrections were evaluated from Pascal's constants.

2.3. Synthesis of [Mn(SMeaiiNEt)₂(NCS)₂] (1)

1-Ethyl-2-[*o*-(thiomethyl)phenylazo]imidazole (SMeaiiNEt) (0.75 g, 3.03 mmol) in methanol (25 ml) was added drop wise to MnCl₂·4H₂O (0.3 g, 1.52 mmol) in the same solvent (20 ml) at 298 K under N₂ environment. To this solution NH₄SCN (0.23 g, 3.03 mmol) was added in small volume of water. Brown solution was stirred for 3 h, then filtered and N₂ gas was bubbled to reduce its volume to 10 ml. The solution was then kept into freeze for 12 h. Dark brown mass was precipitated at bottom of the container and filtered. Residue was then washed with cold water followed by methanol-water (1:1, v/v) and dried in vacuum over CaCl₂. Yield was 0.60 g (60%). Microanalytical data for [Mn(SMeaiiNEt)₂(NCS)₂] (1), C₂₆H₂₈N₁₀S₄Mn: C, 47.01 (47.05); H, 4.31 (4.25); N, 21.17 (21.10); Mass (*m/z*), 663.08.

2.4. X-ray crystallography

A suitable crystal (0.34 × 0.29 × 0.24 mm³) of **1** for X-ray analysis was mounted on the Siemens SMART CCD diffractometer equipped with fine-focus sealed tube monochromator and MoK α radiation ($\lambda = 0.71073$ Å). Data were collected at 293(2) K for the

red coloured blocked crystal. Unit cell parameters were determined from least-squares refinement of setting angles with 2θ range 2.80–49.94°. The *hkl* range were $0 \leq h \leq 12$, $-12 \leq k \leq 13$, $-17 \leq l \leq 18$. Of 5679 collected reflections, 1644 unique reflection ($I > 2\sigma(I)$) were recorded using the ω -scan technique. Data were corrected for Lorentz polarization effects and for linear decay. Semi-empirical absorption correction based on ψ -scans were applied. Bruker SMART and BRUKER SAINT program carried out data refinement and reduction, respectively. The structure was solved by direct method using SHELXS-97 [23] and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using riding model. All calculations were carried out using SHELXL-97 [24], ORTEP-32 [25] and PLATON-99 [26] programs. The crystallographic data are given in Table 1.

2.5. Theoretical calculations

The geometry optimization of complex **1** was carried out using density functional theory (DFT) at the B3LYP level [27]. All calculations were carried out using the Gaussian 03 program package [28] with the aid of the GaussView visualization program [29]. For C, H, N, O the 6-31G (d) basis set were assigned, while for Ni the LANL2DZ basis set with effective core potential was employed [30]. The vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and there are only positive eigen values. Vertical electronic excitations based on B3LYP optimized geometries were computed using the time-dependent density functional theory (TD-DFT) formalism [31–33] in acetonitrile using conductor-like polarizable continuum model (CPCM) [34]. Gauss Sum was used to calculate the fractional contributions of various groups to each molecular orbital [35].

3. Results and discussion

3.1. Synthesis and formulation

The reaction of 1-alkyl-2-[*o*-(thioalkyl)phenylazo]imidazole (SRaiiNR^l) (where R = Me and R^l = Et) and MnCl₂·4H₂O in presence of NH₄SCN in 2:1:2 mol ratio in N₂ environment in dry MeOH generate shining dark brown crystals of complexes of composition

Table 1
Crystallographic data of complex **1**.

Empirical formula	C ₂₆ H ₂₈ N ₁₀ S ₄ Mn
Formula weight	663.80
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	10.667(2)
<i>b</i> (Å)	11.140(3)
<i>c</i> (Å)	15.351(3)
β (°)	71.216(5)
<i>V</i> (Å ³)	1616.1(6)
<i>Z</i>	2
λ (Å)	0.71073
μ (Mo-K α) (mm ⁻¹)	0.701
<i>D</i> _{calc} (mg m ⁻³)	1.3641(5)
Refine parameters	370
Total reflections	5679
Observed data [$I > 2\sigma(I)$]	1644
R_1^a [$I > 2\sigma(I)$]	0.0974
wR_2^b	0.2954
Goodness of fit	0.928

^a $R = \sum |F_o - F_c| / \sum F_o$.

^b $wR_2 = [\sum w(F_o^2 - F_c^2)] / \sum w F_o^2$, $w = 1/[\sigma^2(F_o^2) + (0.1207P)^2]$ (1b); where $P = (Fo^2 + 2Fc^2)/3$.

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