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Chelating behavior of 2-hydroxyacetophenone *N*(4)-disubstituted thiosemicarbazones: Facile formation of Mn(IV) complexes – X-ray structure, EPR and cyclic voltammetric studies

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Abstract

Reaction of tridentate ONS donor ligands H_2L^1, H_2L^2 and H_2L^3 (H_2L^1 = 2-hydroxyacetophenone hexamethyleneimine-3-thiosemicarbazone; H_2L^2 = 2-hydroxyacetophenone morpholine-3-thiosemicarbazone; H_2L^3 = 2-hydroxyacetophenone *N*(4)-methyl, phenyl thiosemicarbazone) with $Mn(OAc)_2 \cdot 4H_2O$ afforded manganese(IV) complexes of the type [MnL_2] in an ethanol–methanol mixture under air. The crystal structure of $Mn(L^2)_2 \cdot 0.25H_2O$ reveals an octahedral geometry with the ligand coordinated in a meridional fashion. The molecule is packed in the crystal lattice with extended hydrogen bonding networks. EPR spectra of the complexes in frozen solution at 77 K show a weak signal at $g \approx 4$ and a strong sextet at $g \approx 2$ consistent with manganese(IV) in an octahedral environment. Cyclic voltammetry in DMSO/ dichloromethane show quasi-reversible peaks corresponding to the Mn(IV)/ Mn(III) redox couple.

Keywords: Manganese(IV); Thiosemicarbazone; X-rays; ESR; Cyclic voltammetry

1. Introduction

The coordination chemistry of manganese has continued to attract attention in recent years due to its presence in several biological systems [1]. A mononuclear Mn(III) centre was found in the active site of some enzymes that display superoxide dismutase activity [2]. In addition, manganese plays an important role in the oxygen-evolving complex (OEC) of photosystem-II [3]. Detailed investigations indicate that the photosystem II (PS II) has an oxo-bridged tetramanganese cluster (Mn_4) as its key structural feature [4]. However the possibility of a mononuclear manganese(IV) center in the S_2 state of PS II cannot be ruled out [5]. Since the manganese is believed to be in its +2 to +4 oxidation state a number of different OEC model complexes were synthesized and their properties investigated [6]. Besides, the use of mononuclear manganese(IV) complexes in catalytic oxidation of organic compounds [7] makes the investigation of mononuclear manganese(IV) complexes more important. Synthetic monomanganese(IV) species in

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biomimetic O, N coordination are also of vital importance in the above perspective. Over the past two decades quite a few manganese(IV) complexes have been isolated and characterised [8,9].

Manganese(IV) is considered as an enigmatic oxidation state; it is usually attained in oxidizing conditions or in the presence of strong bases, except in cases where the presence of phenolato or alcoholato groups in the ligands may bring about the oxidation of Mn(II) into the Mn(III) or even the Mn(IV) oxidation state in aerobic conditions [10]. However the reaction conditions, nature of the ligands or the ligand donor set that yield a stable manganese complex in its +2, +3 or +4 state are yet not clear [11,12]. While a monoprotic ligand with an NNS donor set is likely to give a manganese(II) complex [13], a diprotic ligand with an ONS donor set is most likely to give a manganese(III) or (IV) complex under aerobic condition. It has been reported previously that manganese(II) compounds react with primary hydroxamic acids in aerobic condition, producing Mn(IV) hydroximato complexes with a conjugated metal–ligand ring [14]. In contrast, secondary hydroxamic acids that cannot form conjugated ring systems yield only Mn(II) complexes, while bidentate thiohydroxamic acids yield Mn(IV) complexes from Mn(III) precursors in the presence of oxidizing species [15]. It has also been observed that diprotic ONS donor ligands derived from salicylaldehyde derivatives – (o-OH)RC_6H_3CH=N–NHC(=S)-R′ – that can form conjugated metal–ligand ring systems yield manganese(IV) complexes when R′ is NH_2 or NHPh [16]. As part of our efforts to optimise the factors that determine the spontaneous oxidation of manganese(II) to manganese(IV) in the presence of air, we prepared three manganese complexes of 2-hydroxyacetophenone N(4) disubstituted thiosemicarbazones (H_2L) (Fig. 1). While Mukhopadhyay et al. [12] have reported formation and characterization of manganese(IV) complexes of N(4)-monosubstituted salicylaldehyde thiosemicarbazones, it was not supported by X-ray crystal structure data. Very recently, an optically active manganese(IV) complex was reported whose structure was confirmed by X-ray crystallography [17]. Herein, we report the serendipitous formation of three Mn(IV) complexes of 2-hydroxyacetophenone N(4)-disubstituted thiosemicarbazones, discuss their spectral properties, redox behavior and the X-ray crystal structure of one of them (compound **2**).

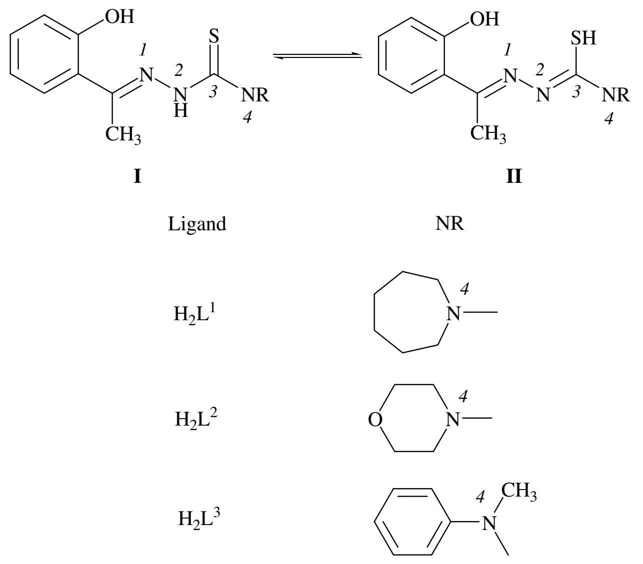

Fig. 1. Schematic diagram of the ligands used for preparation of the complexes.

2. Experimental

2.1. Materials and methods

The thiosemicarbazones H_2L^1, H_2L^2 and H_2L^3 were prepared as reported previously [18]. All the ligands were purified by recrystallisation, manganese(II) acetate tetrahydrate (Reagent grade, E. Merck) was purified by standard methods and solvents were purified by standard procedures before use.

2.2. Preparation of the complexes

2.2.1. $[Mn(L^1)_2]$ (**1**)

To a hot ethanol solution (25 mL) of the thiosemicarbazone, H_2L^1 (0.291 g, 1.0 mmol), was added 10 mL of a methanolic solution of manganese(II) acetate tetrahydrate (0.122 g, 0.5 mmol) with stirring. The yellow solution changed slowly into a coffee brown color on continued stirring. A deep brown residue appeared within 10 min. Stirring was continued for another 20 min. The deep brown precipitate was washed with ethanol followed by ether. It was then dried over P_4O_{10} in vacuo: Yield 0.21 g (67%). *Anal.* Calc. for $C_{30}H_{38}MnN_6O_2S_2$ (633.73): C, 56.77; H, 6.19; N, 13.24; Mn, 8.66. Found: C, 57.26; H, 6.09; N, 13.42; Mn, 8.82%.

2.2.2. $[Mn(L^2)_2] \cdot H_2O$ (**2**)

To a hot ethanol solution (20 mL) of the thiosemicarbazone, H_2L^2 (0.28 g, 1.0 mmol), was added 10 mL of a methanolic solution of manganese(II) acetate tetrahydrate (0.122 g, 0.5 mmol) with stirring. The yellow solution changed into a deep greenish black color in barely a minute. Black powdery material began to form within 3 min. Stirring was continued for an hour, the product formed was allowed to settle, it was filtered, washed with ethanol and ether in succession and then dried over