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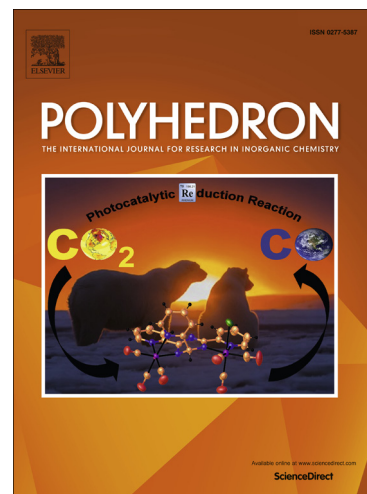
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Terminal Ni^{II}-OH/-OH₂ complexes in trigonal bipyramidal geometries derived from H₂O

Nathanael Lau, Yohei Sano, Joseph W. Ziller, A.S. Borovik*

Department of Chemistry, University of California – Irvine, 1102 Natural Sciences II, Irvine, CA 92697-2025, United States

ABSTRACT

The preparation and characterization of two Ni^{II} complexes are described, a terminal Ni^{II}-OH complex with the tripodal ligand tris[(N)-tertbutylureaylato)-N-ethyl]aminato ([H₃buea]³⁻) and a terminal Ni^{II}-OH₂ complex with the tripodal ligand *N,N',N''*-[2,2',2''-nitriлотris(ethane-2,1-diyl)]tris(2,4,6-trimethylbenzenesulfonamido) ([MST]³⁻). For both complexes, the source of the -OH and -OH₂ ligand is water. The salts K₂[Ni^{II}H₃buea(OH)] and NMe₄[Ni^{II}MST(OH₂)] were characterized using perpendicular-mode X-band electronic paramagnetic resonance, Fourier transform infrared, UV-visible spectroscopies, and its electrochemical properties were evaluated using cyclic voltammetry. The solid state structures of these complexes determined by X-ray diffraction methods reveal that they adopt a distorted trigonal bipyramidal geometry, an unusual structure for 5-coordinate Ni^{II} complexes. Moreover, the Ni^{II}-OH and Ni^{II}-OH₂ units form intramolecular hydrogen bonding networks with the [H₃buea]³⁻ and [MST]³⁻ ligands. The oxidation chemistry of these complexes was explored by treating the high-spin Ni^{II} compounds with one-electron oxidants. Species were formed with S = 1/2 spin ground states that are consistent with formation of monomeric Ni^{III} species. While the formation of Ni^{III}-OH complexes cannot be ruled out, the lack of observable O-H vibrations from the putative Ni-OH units suggest the possibility that other high valent Ni species are formed.

Keywords: Nickel-hydroxido complexes, Nickel-aqua complexes

1. Introduction

Monomeric metal complexes of first-row transition metal ions with terminal hydroxido and aqua ligands are often difficult to prepare because of the strong tendency of these ligands to bridge between metal centers [1–10]. However, hydroxido and aqua bridging may be prevented by using steric effects, as evidenced by the ubiquity of terminal metal hydroxido and aqua units in biology [11–15]. Using steric effects in this manner is also effective in synthetic systems, as most synthetic terminal nickel hydroxido and aqua complexes use sterically encumbered ligand frameworks around the metal center to prevent bridging. Cámpora prepared the earliest examples of monomeric square planar terminal Ni^{II}-OH moieties [16,17], and a number of similar 4-coordinate terminal Ni^{II}-OH complexes have been developed for catalysis [18–21]. To the best of our knowledge, there are only two examples of crystallographically characterized monometallic 5-coordinate Ni^{II}-OH complexes. Riordan has prepared a square pyramidal complex with a 1,4,8,11-tetramethyl-1,4,8,11-tetraazadodecane ligand in which the exogenous hydroxido ligand is derived from dioxygen [22], and Levy has prepared a trigonal bipyramidal complex with a bulky Schiff base ligand where the exogenous hydroxido ligand is derived from adventitious water [23]. The earliest structurally characterized 5-coordinate terminal Ni^{II}-OH₂ complex was reported by

Stuky in 1969 [24], and since then many other structurally characterized terminal Ni^{II}-OH₂ complexes have been prepared [25–27].

Our group has also successfully used this approach to prepare many terminal metal hydroxido and aqua complexes, including a pair of terminal Ni^{II}-OH complexes using sterically bulky tridentate ligands [28]. The ligands used in that work were derived from the urea based tripodal ligand tris[(N)-tertbutylureaylato)-N-ethyl]aminato ([H₃buea]³⁻), shown in Fig. 1A [29]. Various monometallic terminal metal hydroxido and oxido complexes have been stabilized with [H₃buea]³⁻, as the three *tert*-butyl groups of [H₃buea]³⁻ protects the hydroxido or oxido ligand by hindering access [30–32]. An additional feature of [H₃buea]³⁻ is its ability to promote the formation of intramolecular hydrogen bonds (H-bonds). For instance, in our previously prepared M-OH complexes the terminal hydroxido ligand was further stabilized through intramolecular H-bonding networks that are formed between the urea N-H groups of [H₃buea]³⁻ and the oxygen atom of the hydroxido ligand.

Our group has also designed systems that are capable of accepting H-bonds from an apical exogenous ligand. For example, the ligand *N,N',N''*-[2,2',2''-nitriлотris(ethane-2,1-diyl)]tris(2,4,6-trimethylbenzenesulfonamido) ([MST]³⁻) (Fig. 1B) is a sulfonamide-based tripodal ligand that can stabilize hydroxido or aqua ligands through intramolecular H-

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