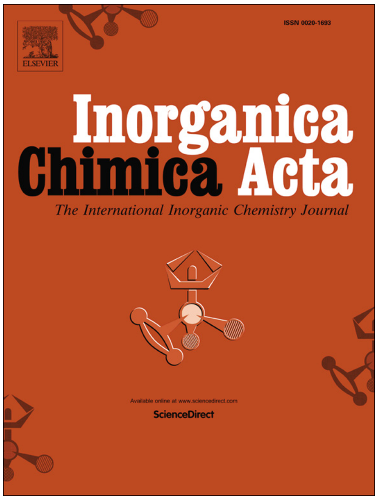

Research paper

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Synthesis, Characterization and Catalytic Studies of two Ni(II) Complexes of Pentane-2,4-dionate

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ABSTRACT

Two nickel(II) complexes, $[Ni(acac)_2(dmpeO_2)]_n{\cdot}2CHCl_3$ (**1**) and $[(Ni(acac)(MeO)(MeOH)]_4$ (**2**) (acac$^-$ = pentane-2,4-dionato) have been synthesized and characterized by elemental analysis, FT-IR spectroscopy, and single crystal X-ray diffraction. The geometries around the central nickel(II) ion are distorted octahedral in both complexes. The equatorial plane includes four oxygen donor atoms of two acetylacetonato ligands and the axial positions are occupied by two oxygen atoms of two $dmpeO_2$ ligands. Complex **1** has a polymeric chain structure in the solid state, while complex **2** has a tetranuclear cubane structure. These complexes are the first reported examples of polymeric and tetranuclear structures of Ni((II) containing acac$^-$ ligand. Neither complex is catalytically active for the hydrogenation of CO_2 to formamide, even though a mixture of $Ni(acac)_2$ and dmpe form a very active *in situ* catalyst together.

Keywords: $Ni(acac)_2$ complexes; dmpe ligand; X-ray structures; CO_2 conversion

1. Introduction

The chemistry of polynuclear transition metal complexes of 3*d*-metals has attracted attention from many research groups around the world, owing to their potential applications as biomimetic models [1], target molecules in supramolecular chemistry [2], medicine [3], and catalysts [4]. Multinuclear coordination complexes of nickel have also been receiving increasing attention in the field of molecular magnetism [5]. This $3d^8$ metal ion has shown promise in the synthesis of single molecule magnets (SMMs) [6] and spin-phonon traps [7]. Bis(acetylacetonato)nickel(II) was used as a precursor in the synthesis of water-dispersible hydrogen phosphate stabilized nickel(0) nanoclusters [8]. Our interest in Ni complexes arises from their high activity, amongst catalysts containing base metals, for the hydrogenation of CO_2 [9].

In the development of new synthetic routes to polynuclear coordination complexes, the choice of organic ligands, such as alkoxides, carboxylates and β-diketonates is always a key issue. Metal complexes with pentanedionato ligands were widely studied as starting materials in the early days of metallocene chemistry [10]. Complexes containing the pentanedionato ligand have also been the focus of much investigation as electroluminescent materials [11], presumably due to their ease of preparation, high stability and high volatility in comparison to other chelate complexes [12, 13]. The pentanedionato ligand possesses a rather complicated coordination behavior toward redox active and inactive transition metal ions because it can exist in various protonated forms [14]. A literature survey revealed very few existing reports on the crystal structure of bis(acetylacetonato) nickel(II), $[Ni(acac)_2]$, *trans*-$[Ni(acac)_2(PMe_2Ph)_2]$, and $[Ni(acac)_2(dppp)]$ (dppp = 1,3-bis(diphenylphosphino)propane) [15-18]. Two different crystal structures have been reported for the former complex. Shibata [15] reported a square planar arrangement for the mononuclear complex, $[Ni(acac)_2]$, while another study determined the existence of a trinuclear complex $[Ni_3(acac)_6]$ [19]. In 2015, Sui et al. [18] studied polymerization of fluorene monomers with an *in situ* formed $Ni(acac)_2$/dppp complex as a catalyst. This complex served as a promising catalyst for the controlled synthesis of polyfluorenes with molecular weights (M_ns) in the range 2.8-62.2 kDa *via* Kumada catalyst transfer polycondensation (KCTP). A trinuclear platinum nickel complex was synthesized and characterized as $[\{(acac)Pt[P(C_2F_5)_2O]_2\}_2Ni]$ in good yield by reacting $[(acac)Pt\{[P(C_2F_5)_2O]_2H\}]$ and $[Ni(Cp)_2]$ in a diethyl ether /n-hexane mixture [20]. Given the number of emerging applications for these acetylacetonato complexes, their design, synthesis, and structural characterization are of great interest to chemists and biochemists [21].

An added complexity in the study of Ni(acac) complexes with phosphines is the ability of such complexes to oxidize phosphines in the presence of small amounts of water [17]. Thus incomplete removal of water from all reagents and solvents can cause the conversion of phosphine to phosphine oxide, which could result in either failure of the ligand to bind at all or the coordination of the ligand as an oxide. The coordination chemistry of phosphine oxides has not been studied nearly as extensively as the coordination chemistry of phosphines [22]. Most relevant to the current study is Brisdon's report of the preparation and spectral properties of divalent cobalt, nickel, and copper complexes of ethylenebis(diphenylphosphine oxide) (dpeo) [23].

In our continuing efforts to identify base metal complexes that are effective catalyst precursors for the hydrogenation of CO_2, we identified *in situ* catalysts made from $Ni(acac)_2$ and dmpe (1,2-bis(dimethylphosphino)ethane) are particularly active for the hydrogenation of CO_2 to formamide [24]. In order to understand their activity, we attempted to isolate and structurally characterize complexes produced from the reaction of those two species. While we did not isolate any complex containing both acetylacetonate and a phosphine ligand, and were therefore little further ahead in our mechanistic understanding on the catalysis, we did isolate and characterize two Ni complexes that illustrated unexpected reactivity in this system. These complexes are the first structurally characterized nickel-acac complex containing ethylenebis(dimethylphosphine oxide), $dmpeO_2$, MeO$^-$, and MeOH as ligands.

2. Experimental Section

2.1. General