

PREPARATION AND CHARACTERIZATION OF [Ni (MAP)₂]₂; H- MAP = 2- (METHYLAMINO) PYRIDINE

H. Aghabozorg* and H. H. Monfared

*Department of Chemistry, Teacher Training University, Tehran, Islamic Republic of Iran

Abstract

We have recently synthesized [Ni (MAP)₂]₂ complex [H-MAP = 2- (methylamino) pyridine]. 2- (Methylamino)pyridine reacts with MeLi in THF and generates the lithium salt (Li-MAP). Further reaction of NiCl₂ with two equivalent of this ligand in THF leads to the formation of a dark red solution. Analytical data, molecular weight, and magnetic susceptibility of this complex confirm the formula [Ni (MAP)₂]₂.

Introduction

The coordination chemistry of nickel(II) has been studied extensively. Nickel(II) complexes show a variety of coordination environments ranging in coordination number from two to six in monomeric species. Recent results from a number of laboratories have shown that it is possible to achieve a two-coordination geometry in some transition-metal complexes [1-8].

Anionic organic amides obtained by deprotonation of secondary amines may act as versatile ligands in the preparation and stabilization of early transition metals in low oxidation states [9]. The synthesis of Ti(NPh)₂, the first transition metal amide, was reported in 1935 [10]. Surprisingly the reaction of NiCl₂(Pφ)₂ (1 mol) with LiN(Si(CH₃)₃)₂ (2 mol) gave as the product {Ni(Pφ)₂[N(Si(CH₃)₃)₂]}₂. The presence of univalent nickel (d⁹ system) was confirmed by its paramagnetism (μ = 1.91 B.M.) and its EPR spectrum.

Determination of crystal and molecular structure by X-ray diffraction proved that nickel complexes exhibit a discrete mononuclear unit containing three-coordinated nickel [11]. In [Li(THF)₄][Ni(NPh)₂]₂·0.5 PhMe and [{Ni(NPh)₂}]₂ complexes, Ni(II) has trigonal-planar geometry. The Ni-Ni distance of 2.327(2) Å in [{Ni(NPh)₂}]₂ complex is extremely short and implies a

significant Ni-Ni interaction [12]. Short Ni-Ni distances have also been seen in a few nickel complexes [13-16]. In this research project, complex of MAP [H- MAP = 2 - (methylamino)pyridine] with NiCl₂ has been prepared and investigated.

Experimental Section

All the operations were performed under dry nitrogen using standard Schlenk techniques or in a nitrogen-filled dry-box. THF, toluene, and 2-(methylamino)pyridine were dried and distilled by standard methods before using. Infrared spectrum was recorded on a Perkin Elmer 393 instrument from Nujol mull prepared in a dry-box. Elemental analyses were performed with an Elemental Analyzer CHN-O-RAPID, Heraeus and an Atomic Absorption, 2830, Perkin Elmer. Samples for magnetic susceptibility measurements were sealed in a calibrated tube inside a dry-box. Measurements were carried out at room temperature using a Guoy balance (Johnson-Mathey). Magnetic moments were calculated by following standard methods [17], and corrections for underlying diamagnetism were applied to the data [18]. MeLi was used in diethylether (5%).

Preparation of [Ni (MAP)₂]₂ Complex

To a stirred 150 mL THF solution of dry 2- (methylamino)pyridine (4.00g, 36.98 mmol) was added one equivalent of MeLi (0.812 g, 21.7 mL 1.7 M, 36.96

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mmol) at $\approx -40^\circ\text{C}$. After the mixture was warmed to room temperature, NiCl_2 (2.40 g, 18.50 mmol) was added. The light yellow clear solution changed to a deep red-brown color. The mixture was stirred for about 24 hours. The resulting deep red-brown suspension was filtered to reveal a deep red-brown clear solution. This solution was evaporated *in vacuo* and the residual solid dissolved in toluene.

After filtration and concentration, the deep red crystals separated upon standing overnight at -40°C . The solid was dried and stored under nitrogen in sealed ampoules (yield $\approx 65\%$). Analytical data, molecular weight, and magnetic susceptibility measurements confirm the formula $[\text{Ni}(\text{MAP})_2]_2$. M.W. Calcd., (found): 545.94 (540.2) [cryoscopy in cyclohexane].

Anal. Calcd., (found) for $\text{C}_{24}\text{H}_{28}\text{N}_8\text{Ni}_2$: C, 52.80 (52.91); H, 5.18 (5.10);

N, 20.53 (20.40); Ni, 21.51 (21.63).

Magnetic measurement: $\mu_{\text{eff}} = 0$

IR (Nujol mull, KBr, cm^{-1}):

[Nujol: 3000-2860(vs), 1455(s), 1375(s), 1345(w, sh)].

$[\text{Ni}(\text{MAP})_2]_2$: 1630(vs), 1555(vs), 1525(s), 1435(vs), 1316(vs), 1293(s), 1200(s), 1175(w), 1155(s), 1105(s), 1045(s), 955(w), 860(s), 835(s), 800(w), 770(vs), 750(vs), 678(w), 600(w), 545(w), 485(w), 460(w), 420(w).

Results and Discussion

Planar four-coordinated nickel(II) complexes are diamagnetic, the $3d_{x^2-y^2}$ orbital being involved in accepting electrons from the ligands. Nickel forms a moderately large and very heterogeneous group of compounds in oxidation states of 2, 1.5 and 1, in which there are Ni-Ni bonds varying in length from 2.32 to 2.79 Å [13-16]. Unlike the M-M bonds formed by some of the early transition elements such as Cr, Mo, W, Re, and Ru, many of these Ni-Ni bonds have received little theoretical discussion and are not well understood.

In $[\text{Ni}(\text{DPT})_2]_2$ (HDPT = 1,3-diphenyltriazene), Ni-Ni distance is 2.40 Å [15]. Very short metal-metal bonds have also been found in the chemistry of divalent transition metals in the presence of two or more anionic bridging ligands which have the characteristic three-center chelating geometry and the four pi electron configuration of an allylic system. 2-(Methylamino)pyridine (H-MAP) reacts with MeLi in THF and generates lithium salt (Li-MAP). Further reaction of NiCl_2 with two equivalent of Li-MAP in toluene leads to the formation of deep red-brown crystals,

$[\text{Ni}(\text{MAP})_2]_2$. Analytical data, molecular weight, and magnetic susceptibility measurements, confirm the dimer or dinuclear nickel complex and probably the geometry of each Ni atom is square planar. Finally, infrared spectrum does not show any NH stretching vibration, which is not surprising.

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