



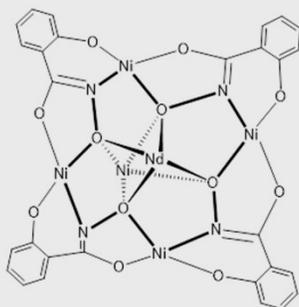
Heterotrimetallic Coordination: Incorporating Neodymium into the Nickel 12-Metallacrown-4 Framework



Charles Wood and Jessica M. Fautch
Department of Chemistry, York College of Pennsylvania, York, PA 17403

Introduction

Heterotrimetallic coordination complexes are studied due to their exciting applications of molecular magnetism, luminescence, and catalysis.¹ Metallacrowns are the inorganic complement of crown ethers; they traditionally have a repeat unit of [M-N-O] and can bind a wide range of cations including alkali and 4f cations (i.e. neodymium) in the central cavity.¹ A variety of heterotrimetallic coordination complexes can be synthesized with variations in the following components: lanthanides, alkali metal cations, 12-MC-4 inducing hydroxamates and bridging monoanion carboxylates.² This work focuses on one such complex, $\text{Nd}^{\text{III}}\text{Ni}(\text{OAc})_4[12\text{-MC}_{\text{Ni}}\text{III}(\text{N}_{\text{shi}})_4] \cdot \text{DMF}$ (**Compound 2**, Scheme 1) as well as the intermediate complexes giving rise to this Nd-complex. The intermediate complexes included, $\text{Ni}(\text{OAc})_2[12\text{-MC}_{\text{Ni}}\text{III}(\text{N}_{\text{shi}})_4] \cdot \text{DMF}$ (**Compound 1**), $\text{Na}_2(\text{OAc})_2[12\text{-MC}_{\text{Ni}}\text{III}(\text{N}_{\text{shi}})_4] \cdot (\text{DMF})_6 \cdot 2\text{DMF}$ (**Compound 3**), and $\text{Ni}(\text{OAc})_2[12\text{-MC}_{\text{Ni}}\text{III}(\text{shi})_4] \cdot 12\text{H}_2\text{O}$ (**Compound 4**).



Scheme 1. Proposed structure of Compound 2. $\text{Nd}^{\text{III}}\text{Ni}(\text{OAc})_4[12\text{-MC}_{\text{Ni}}\text{III}(\text{N}_{\text{shi}})_4] \cdot \text{DMF}$

In **Compound 2**, neodymium is the lanthanide used in the central cavity of the complex and sodium is the alkali metal cation in the central cavity. The 12-MC-4 inducing hydroxamate used is salicylhydroxamic acid ("shi") and acetate is the bridging monoanion carboxylate for **Compound 2**. The intermediate complexes leading to **Compound 2** have variations of the cations in the central cavity, as well as the solvent used in crystal formation.

Experimental Methods

Preparation of Compound 1 (Intermediate):

1. In 6.25 mL dimethylformamide (DMF), 4 mmol of $\text{Ni}(\text{OAc})_2$ was dissolved.
2. In 6.5 mL DMF, 4 mmol salicylhydroxamic acid (H_3shi) and 4 mmol of $\text{Ni}(\text{OAc})_2$ were dissolved.
3. The contents of both beakers were combined and stirred overnight
4. The mixture was filtered by vacuum and the filtrate was allowed to evaporate slowly.
5. The solution was checked periodically for several weeks for crystal growth (4 weeks).

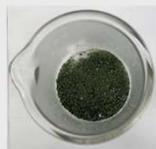


Figure 1. **Compound 1** after 4 weeks of drying, appearance was noted to be dark green and shiny.

Preparation of Compound 2:

1. In 10.0 mL DMF, 0.125 mmol $\text{Nd}(\text{NO}_3)_3$, 4 mmol $\text{Ni}(\text{OAc})_2$, and 2 mmol H_3shi , were dissolved.
2. In 10.0 mL DMF, 2 mmol $\text{Ni}(\text{OAc})_2$ was dissolved.
3. The contents of both beakers were combined and stirred overnight
4. The mixture was filtered by vacuum and the filtrate was allowed to evaporate slowly.
5. The solution was checked periodically for several weeks for crystal growth (4 weeks).



Figure 2. **Compound 2** after 9 weeks of drying, appearance was noted to be light green, shiny, and appeared to be crystalline

Characterization using UV-Vis Spectroscopy

- Spectroscopy was used for qualitative determination to conclude the presence or lack of neodymium and nickel in the proposed complexes. The approximate concentration of each complex was 0.0027 M in methanol at room temperature.

Results

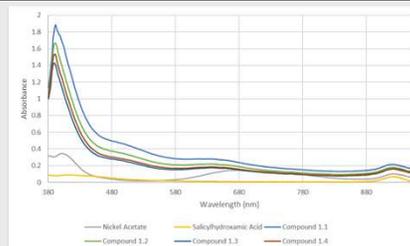


Figure 3. UV-Vis spectra of four separately prepared samples of **Compound 1**. Starting materials are shown in yellow and purple. The approximate concentration of **Compound 1** was 0.0027 M in methanol.

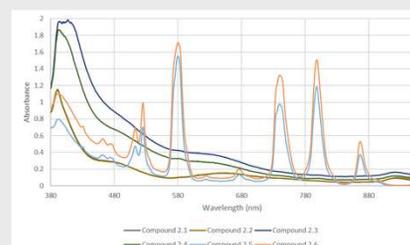


Figure 4. UV-Vis spectra of six separately prepared samples of **Compound 2**, with three varying synthetic preparations. The approximate concentration of **Compound 2** was 0.0027 M in methanol.

Compound ID	Absorbance at 580 nm
1.1	0.284
1.2	0.211
1.3	0.152
1.4	0.170
2.1	0.102
2.2	0.103
2.3	0.425
2.4	0.330
2.5	1.550
2.6	1.707

Table 1. Absorbance values at λ max 580 as referenced to Compound 2.6

- Figure 3 shows that the four samples of **Compound 1** are relatively similar.
- Figure 4 shows that the six samples (prepared in three different methods) of **Compound 2** likely have varying structure. Compounds 2.1 and 2.2 used the same procedure, while 2.3 and 2.4 shared a different procedure and 2.5 and 2.6 shared yet another synthetic approach.
- Table 1 shows these compounds have similar absorbance at 580 nm

Conclusion and Discussion

Qualitative preparation of intermediate **Compound 1** was completed. The qualitative preparation of **Compound 1** provided sufficient evidence to attempt the synthesis of **Compound 2**.

The preparation of **Compound 2** began with three varying synthetic procedures. The three synthetic procedures can be distinguished visually in the spectral analysis. When comparing absorbance values at 580 nm, Compounds 2.1 and 2.2 are relatively similar to **Compound 1** (Table 1). However, compounds 2.3, 2.4, 2.5 and 2.6 display drastically different absorbance values at 580 nm. Additionally, compounds 2.5 and 2.6 have a drastic spectral difference compared to the other compounds (Figure 4).

The next step for this project would be to determine the cause of the λ max at 580 nm in Compounds 2.5 and 2.6, possibly using X-Ray Crystallography.

Literature Cited

1. Azar, Michael R.; Boron, Thaddeus T.; Ill, Lutter, Jacob C.; Daly, Connor I.; Zegalia, Kelcie A.; Nimthong, Ruthairat; Ferrence, Gregory M.; Zeller, Matthias; Kampf, Jeff W.; Pecoraro, Vincent L.; and Zaleski, Curtis M. *Inorganic Chemistry*, **2014**, 53 (3), 1729-1742.
2. Atzeri, Corrado; Marzaroli, Vittoria; Quaretti, Martina; Travis, Jordan R.; Di Bari, Lorenzo; Zaleski, Curtis M.; and Tegoni, Matteo; *Inorganic Chemistry*, **2017**, 56 (14), 8257-8269.

Acknowledgments



Additional thanks for special funding support from
York College of Pennsylvania:
The Department of Chemistry, YCP Alumni, YCP Chemistry Society, YCP Student Senate, and the YCP Center for Academic Innovation; The Huber Foundation of York, PA; and Gaussian, Inc