

**COMPLEX NICKEL COMPOUNDS WITH SCHIFF BASES DERIVED FROM DIACETYLMOXIME\***

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Schiff bases derived from diacetylmonoxime and ethylenediamine or diethylenetriamine give  $\text{Ni}(\text{HDEM})\text{ClO}_4$ ,  $\text{Ni}(\text{HDEM})(\text{ClO}_4)\text{Br}$ ,  $\text{Ni}(\text{H}_2\text{DTM})\text{Br}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Ni}(\text{H}_2\text{DTM})\text{Br}_4$  complex compounds.  $\text{H}_2\text{DTM}$  splits in solution in the presence of triethylamine, owing to which  $\text{Ni}(\text{DAO})(\text{dien})\text{Cl}$  complex could be isolated. The possibility of employing the above Schiff bases for the preparation of compounds involving nickel in a higher valency state is discussed.

Ethylenediamine is known<sup>1,2</sup> to be capable of stabilization of higher oxidation states of nickel, in contrast to diethylenetriamine with which no  $\text{Ni}(\text{III})$  or  $\text{Ni}(\text{IV})$  complexes have been obtained. Coordination compounds of nickel in a higher oxidation state have also been prepared by using some oximes<sup>3</sup>. Of interest were therefore the pertinent properties of Schiff bases obtained by condensation of selected polyamines and oximes. For this study, we prepared a Schiff base derived from diacetylmonoxime, for which no complex compounds with higher-valency nickel are known, and ethylenediamine. The similar Schiff base derived from diethylenetriamine was also synthesized; since nickel(II) complexes with this base have not been so far described, these are also examined in this work.

**EXPERIMENTAL**

Diacetylmonoxime (Loba Chemie, Vienna), ethylenediamine (Downs Development) and diethylenetriamine (Loba Chemie, Vienna) were used as received. All the other chemicals, of reagent grade purity, were supplied by Lachema, Brno. Infrared absorption spectra of Nujol mulls were scanned on a Specord IR 75 instrument, electronic absorption spectra were run on a Specord M 40 spectrophotometer (both Carl Zeiss, Jena). Magnetic susceptibility was measured by Gouy's method at 293 K on a homemade magnetic balance. An OK 102 conductivity meter (Radelkis, Budapest) was used for conductivity measurements. Thermal decomposition was examined with

\* Abbreviations used in this paper: HDAO diacetylmonoxime; en ethylenediamine; dien diethylenetriamine;  $\text{H}_2\text{DEM}$  Schiff base derived from diacetylmonoxime and ethylenediamine, composition  $\text{HON}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{NCH}_2\text{CH}_2\text{N}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{NOH}$ ;  $\text{H}_2\text{DTM}$  Schiff base derived from diacetylmonoxime and diethylenetriamine, composition  $[\text{HON}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{NCH}_2\text{CH}_2]_2\text{NH}$ .

a Derivatograph Q 1 500D (MOM, Budapest) on 120–140 mg samples using a temperature gradient of 2.5°C/min.

The Schiff base H<sub>2</sub>DEM as well as the nickel complex Ni(HDEM)ClO<sub>4</sub> was prepared following ref.<sup>4</sup>; H<sub>2</sub>DTM was prepared similarly as H<sub>2</sub>DEM.

#### Synthesis of Ni(HDEM)ClO<sub>4</sub> (I)

To a solution of 0.9 g of ligand in 25 ml of boiling ethanol was added a solution of 1.5 g of Ni(ClO<sub>4</sub>)<sub>2</sub> · 6 H<sub>2</sub>O in 5 ml of acetone. After 0.5 h stirring, 0.5 ml of pyridine was added and stirring was continued for another 1 h. The mixture was cooled to 0°C, the crystals separated were filtered out by suction and washed with diethyl ether on the frit.

#### Synthesis of Ni(HDEM) (ClO<sub>4</sub>)Br (II)

To a suspension of 0.6 g of Ni(HDEM)ClO<sub>4</sub> in 30 ml of chloroform was added solution of 0.03 ml of bromine in 2 ml of chloroform. After 2 h stirring at room temperature, the reaction mixture was filtered by suction and the solid on the frit was washed with chloroform.

#### Synthesis of Ni(H<sub>2</sub>DTM)Br<sub>2</sub> · 2 H<sub>2</sub>O (IV)

1.1 g of the ligand dissolved in 15 ml of hot ethanol was mixed with a solution of 1.1 g of NiBr<sub>2</sub> · 3 H<sub>2</sub>O in 5 ml of hot ethanol. After 2 h stirring, the reaction mixture was cooled to 0°C and the solid was filtered out by suction and washed with diethyl ether. The substance was recrystallized from methanol.

#### Synthesis of Ni(DAO) (dien)Cl (V)

To a solution of 0.55 g of the Schiff base in 10 ml of hot ethanol was added a solution of 0.5 g of NiCl<sub>2</sub> · 6 H<sub>2</sub>O in 5 ml of hot ethanol. After 0.5 h stirring, 0.7 ml of triethylamine was added, the reaction mixture was boiled shortly and allowed to cool slowly for 5 h with stirring; the substance then was precipitated with a double volume of diethyl ether.

#### Bromination of Complex V

a) A solution of 0.55 g of H<sub>2</sub>DTM in 10 ml of ethanol was mixed with 0.55 g of NiBr<sub>2</sub> · 3 H<sub>2</sub>O in 5 ml of ethanol. After cooling the mixture to 0°C, 0.05 ml of bromine was added and the whole was stirred for 0.5 h. The precipitate was filtered out by suction and washed with diethyl ether.

b) To a suspension of 0.5 g of V in 20 ml of chloroform was added 0.05 ml of bromine in 1 ml of chloroform. After 15 min stirring at ambient temperature, the undissolved substance was filtered out by suction and washed on the frit with chloroform.

## RESULTS AND DISCUSSION

The chemical composition of the substances obtained is given in Table I. Ni(HDEM).ClO<sub>4</sub> (I) is a diamagnetic crystalline substance, red in colour. Its molar conductivity (Table II) as well as the positions of the absorption maxima of the ClO<sub>4</sub><sup>-</sup> ion (620 and 1 090 cm<sup>-1</sup>) confirm, in agreement with ref.<sup>4</sup>, planar geometry of the complex. Its oxidation was performed by stirring its chloroform suspension with bromine in the molar ratio 1 : 1 at room temperature. The substance obtained, of the composi-

tion Ni(HDEM) (ClO<sub>4</sub>)Br (*II*), is paramagnetic and its magnetic moment (2.08 BM) corresponds to the data reported for nickel(III) compounds. The complex is thermally unstable, decomposing explosively at 75°C, in contrast to the starting Ni(II) complex

TABLE I  
Chemical composition of substances prepared

| Compound  | Formula<br>(M. W.)   | Found/calculated |       |      |       |                  |
|---|--|------------------|-------|------|-------|------------------|
|   |  | % Ni             | % C   | % H  | % N   | % X <sup>a</sup> |
| Ni(HDEM) (ClO <sub>4</sub> ) ( <i>I</i> )                               | C <sub>10</sub> H <sub>17</sub> ClN <sub>4</sub> NiO <sub>6</sub><br>(383.4)               | 15.70            | 31.99 | 4.06 | 14.90 | 9.45             |
|   |  | 15.33            | 31.32 | 4.47 | 14.61 | 9.25             |
| Ni(HDEM) (ClO <sub>4</sub> )Br ( <i>II</i> )                            | C <sub>10</sub> H <sub>17</sub> BrClN <sub>4</sub> NiO <sub>6</sub><br>(463.3)             | 12.92            | 26.00 | 3.52 | 11.59 | 17.16            |
|   |  | 12.69            | 25.92 | 3.70 | 12.09 | 17.25            |
| H <sub>2</sub> DTM ( <i>III</i> )                                       | C <sub>12</sub> H <sub>23</sub> N <sub>5</sub> O <sub>2</sub><br>(269.3)                   | —                | 53.36 | 8.42 | 26.05 | —                |
|   |  | —                | 53.51 | 8.58 | 26.00 | —                |
| Ni(H <sub>2</sub> DTM)Br <sub>2</sub> .2 H <sub>2</sub> O ( <i>IV</i> ) | C <sub>12</sub> H <sub>27</sub> Br <sub>2</sub> N <sub>5</sub> NiO <sub>4</sub><br>(523.9) | 11.17            | 27.38 | 5.31 | 12.86 | 30.12            |
|   |  | 11.21            | 27.51 | 5.19 | 13.37 | 30.51            |
| Ni(dien) (DAO)Cl ( <i>V</i> )   | C <sub>8</sub> H <sub>20</sub> ClN <sub>4</sub> NiO <sub>2</sub><br>(297.4)                | 19.11            | 31.90 | 5.88 | 18.40 | 11.40            |
|   |  | 19.74            | 32.30 | 6.44 | 18.84 | 11.92            |
| Ni(H <sub>2</sub> DTM)Br <sub>4</sub> .3 H <sub>2</sub> O ( <i>VI</i> ) | C <sub>12</sub> H <sub>29</sub> Br <sub>4</sub> N <sub>5</sub> NiO <sub>5</sub><br>(701.7) | 8.80             | 20.18 | 4.38 | 9.63  | 45.09            |
|   |  | 8.37             | 20.54 | 4.17 | 9.98  | 45.55            |
| Ni(H <sub>2</sub> DTM)Br <sub>4</sub> ( <i>VII</i> )                    | C <sub>12</sub> H <sub>23</sub> Br <sub>4</sub> N <sub>5</sub> NiO <sub>2</sub><br>(647.7) | 9.57             | 21.84 | 3.47 | 10.04 | 49.48            |
|   |  | 9.06             | 22.25 | 3.54 | 10.81 | 49.35            |

<sup>a</sup> X = Cl, Br.

TABLE II

Properties of substances prepared: molar conductivity in 5 · 10<sup>-4</sup> M-CH<sub>3</sub>OH at 25°C λ (S cm<sup>2</sup> · mol<sup>-1</sup>), magnetic moment μ (BM), and beginning of thermal decomposition in GTA (°C)

| Substance | λ    | μ    | GTA             |
|-----------|------|------|-----------------|
| <i>I</i>  | 91.1 | dia  | 150             |
| <i>II</i> | —    | 2.08 | 75 <sup>a</sup> |
| <i>IV</i> | 108  | 3.00 | 80 <sup>b</sup> |
| <i>V</i>  | 73   | 2.77 | 90              |
| <i>VI</i> | 196  | 2.98 | 70              |

<sup>a</sup> Explosive decomposition; <sup>b</sup> total dehydration up to 130°C.

whose thermal decomposition only starts at 150°C. Its infrared spectrum displays bands at 620 cm<sup>-1</sup> (m) and 1 070–1 110 cm<sup>-1</sup> (s, sh), indicating that ClO<sub>4</sub><sup>-</sup> is bonded by an ionic bond<sup>5</sup>. The substance decomposes in solution, a redox reaction taking place. The positions of the absorption maxima characterizing the organic ligand agree well with the data by Uhlig and Friedrich<sup>4</sup>.

Since no data were found in the literature for complex nickel compounds with H<sub>2</sub>DTM, their synthesis and characterization were attempted by us. A substance of the composition Ni(H<sub>2</sub>DTM)Br<sub>2</sub>·2 H<sub>2</sub>O (IV) was obtained by reacting nickel bromide with H<sub>2</sub>DTM. This substance is paramagnetic, and its magnetic moment (Table II) indicates an octahedral arrangement; this is consistent with the molar conductivity, corresponding<sup>6</sup> to a binary electrolyte, and also with the positions of the absorption bands belonging to the <sup>3</sup>A<sub>2g</sub>–<sup>3</sup>T<sub>2g</sub> and <sup>3</sup>A<sub>2g</sub>–<sup>3</sup>T<sub>1g</sub>(P) transitions. Dehydration of the substance sets in at 80°C and ceases at 130°C; at higher temperatures, decomposition of the anhydrous complex takes place. The infrared spectra exhibit bands of the ν<sub>NH</sub> and ν<sub>OH</sub> vibrations at 3 120 cm<sup>-1</sup> (s) and 3 000 cm<sup>-1</sup> (s), respectively, and bands<sup>7,8</sup> of ν<sub>CN</sub> vibrations at 1 500 cm<sup>-1</sup> (m) and 1 605 cm<sup>-1</sup> (m) and of ν<sub>NO</sub> vibrations at 1 100 cm<sup>-1</sup> (m) and 1 250 cm<sup>-1</sup> (m). Attempted isolation of the analogous chloride or perchlorate resulted in pasty products. In order to force

TABLE III  
Electronic absorption spectra of nickel complexes

| Complex | $\tilde{\nu}$ , cm <sup>-1</sup> (ε <sup>a</sup> ) | Electronic transition   |
|---------|--|---|
| I       | 29 000 (270)                                       | CT  |
|         | 24 200 (50)  | <sup>1</sup> A <sub>1</sub> – <sup>1</sup> B <sub>1</sub>     |
|         | 19 440 (33)  | <sup>1</sup> A <sub>1</sub> – <sup>1</sup> A <sub>2</sub>     |
| II      | 30 000 (320)                                       | CT  |
|         | 24 900 (78)  | <sup>1</sup> A <sub>1</sub> – <sup>1</sup> B <sub>1</sub>     |
|         | 20 000 (30)  | <sup>1</sup> A <sub>1</sub> – <sup>1</sup> A <sub>2</sub>     |
| IV      | 29 000 (360)                                       | CT  |
|         | 24 960 (15)  | <sup>3</sup> A <sub>2</sub> – <sup>3</sup> T <sub>1</sub> (P) |
|         | 11 500 (6)   | <sup>3</sup> A <sub>2</sub> – <sup>3</sup> T <sub>2</sub>     |
| V       | 30 000 (350)                                       | CT  |
|         | 27 600 (36)  | <sup>3</sup> A <sub>2</sub> – <sup>3</sup> T <sub>1</sub> (P) |
|         | 12 000 (18)  | <sup>3</sup> A <sub>2</sub> – <sup>3</sup> T <sub>2</sub>     |
| VI      | 31 000 (112)                                       | CT  |
|         | 14 700 (5)   | <sup>3</sup> A <sub>2</sub> – <sup>3</sup> T <sub>1</sub> (F) |
|         | 11 800 (8)   | <sup>3</sup> A <sub>2</sub> – <sup>3</sup> T <sub>2</sub>     |

<sup>a</sup> In m<sup>2</sup> mol<sup>-1</sup>.

deprotonation of the ligand, its reaction with nickel chloride was conducted in 96% ethanol with an addition of triethylamine. However, hydrolysis of the Schiff base took place and a substance of Ni(dien) (DAO)Cl composition was isolated instead. This complex is paramagnetic (Table II) and again, both the magnetic moment and the electronic absorption spectra (Table III) indicate an octahedral coordination. Although lower than as corresponds to a binary electrolyte, the molar conductivity indicates a rather high degree of dissociation of the substance in methanol.

Addition of bromine to an ethanolic solution of hydrated nickel bromide mixed with H<sub>2</sub>DTM results in the separation of a substance of Ni(H<sub>2</sub>DTM)Br<sub>4</sub>·3 H<sub>2</sub>O composition (IV) (Table I). This compound is paramagnetic, its magnetic moment is 2.98 BM and it is thermally low stable, its decomposition starting at 70°C. Its molar conductivity in methanol corresponds to a ternary electrolyte. The infrared absorption spectrum shows bands of the  $\nu_{\text{NH}}$  vibrations at 2 820 cm<sup>-1</sup> (s),  $\nu_{\text{CN}}$  vibrations at 1 580 cm<sup>-1</sup> (s, sh) and 1 500 cm<sup>-1</sup> (m), and  $\nu_{\text{NO}}$  vibrations at 1 250 cm<sup>-1</sup> (m). It can be inferred that the substance is a nickel(II) complex, not very stable in the solid phase or in methanolic solution. In view of the fact that the infrared spectrum of this substance does not differ markedly from that of the complex of Ni(H<sub>2</sub>DTM)·Br<sub>2</sub>·2 H<sub>2</sub>O composition (IV), the presence of the Br<sub>3</sub><sup>-</sup> anion bonded to the nickel(II) complex is conceivable. Stirring of a suspension of complex IV in chloroform with bromine at ambient temperature also results in a substance of Ni(H<sub>2</sub>DTM)Br<sub>4</sub> composition, whose magnetic moment is 3.25 BM. Attempted oxidation of the H<sub>2</sub>DTM-Ni(II) complex with nitric acid or (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> failed.

The following conclusions can be drawn from the results. Ethylenediamine is able to stabilize nickel in a higher oxidation state; the formation of the corresponding compounds, however, is actually promoted by their low solubility. Diacetylmonoxime alone does not form complex compounds with nickel in a higher oxidation state. The Schiff base obtained by their condensation is a tetradentate ligand which in the complex compounds acts as an anion-ligand forming a closed ring with a H-bridge between the oxime groups. Consequently, there is an enhanced electron density at these nitrogen atoms, and this has a favourable effect on their  $\sigma$ -donor ability, thereby enabling this ligand to be used for stabilization of trivalent nickel. Another Schiff base was prepared by condensation of diethylenetriamine and diacetylmonoxime, hence, components from which no compounds involving nickel in a higher valency have been obtained. Unlike the above-mentioned base, this substance does not include a ring because the N—O—H groups are not ionized. Attempted deprotonation with triethylamine resulted in hydrolytic splitting of the base. Thus, although it is a pentadentate ligand, it acts in the complexes studied as a molecular ligand, which is a less powerful  $\sigma$ -donor. The results obtained do not allow us to conclude unambiguously whether bromine reacts with this ligand or it is located, similarly as in nickel(II)-diphenylglyoximate complexes<sup>9</sup>, in cavities of the solid separated, or whether it is bonded as the Br<sub>3</sub><sup>-</sup> anion.

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