NICKEL (II) MONOTHIOCARBAMATES

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In addition to our work at dithiocarbamato complexes (1) we started some time ago in synthesizing monothiocarbamato complexes.

The publication of Krankovits et al. (2) of the synthesis of nickel (II) bis(pyrrolidine monothiocarbamate) \([\text{Ni(pyrrolmtc)}_2]\), prompts us to report our investigations of nickel (II) bis(di-n-propyl monothiocarbamate) \([\text{Ni(n-pr}_2\text{mtc)}_2]\).

This compound has a much better solubility in organic solvents than the pyrrolidine derivative, so purification by recrystallization is possible and spectroscopic and osmometric studies of solutions can be accomplished. Our results agree with those of Krankovits indicating a polymeric nature of the compounds, however a more detailed picture can now be given for the di-n-propyl compound.

PREPARATION

\(\text{Ni(n-pr}_2\text{mtc)}_2: 0.15 \text{ mole di-n-propylamine in 200 ml acetone and 0.15 mole KOH in 10 ml water were mixed and cooled to 5°C. COS gas was passed through this solution till saturation.}\)
The reaction mixture was dropped to a saturated aqueous solution of 0.075 mole nickel acetate. The precipitate was filtered and washed with acetone, a further purification was possible by dissolving the product in chloroform and reprecipitation with acetone yielding dark green-yellow crystals.

Analysis C: 44.34%; H: 7.41%; N: 7.39%; O: 8.58%; S: 16.67%; Ni: 15.60%. Calc. for Ni(OSCN$_6$H$_{14}$)$_2$: C: 44.34%; H: 7.44%; N: 7.39%; O: 8.44%; S: 16.91%; Ni: 15.48%.

Ni(n-pr$_2$mtc)$_2$py$_2$: A bispyridine adduct could be obtained by dissolving Ni(n-pr$_2$mtc)$_2$ in chloroform, adding pyridine and precipitating the compound with ethanol.

Analysis C: 53.57%; H: 7.12%; N: 10.49%. Calc. for Ni(OSCN$_6$H$_{14}$)$_2$(C$_5$H$_5$N)$_2$: C: 53.64%; H: 7.13%; N: 10.43%.

**DISCUSSION**

In contrast with the observations of Krankovits for Ni(et$_2$mtc)$_2$ our analysis and IR data clearly indicate that there is no water present in Ni(n-pr$_2$mtc)$_2$. The Ni-S vibration frequency for Nickel bis(dialkyldithiocarbamate) is found at 387 cm$^{-1}$ (3). The Ni-O stretching frequency in nickel (II) acetylacetonate is found at 452 cm$^{-1}$ (4).

In the infrared spectra of nickel(II) bis(di-n-propylmonothiocarbamate) absorption bands are found at 385 and 450 cm$^{-1}$ so the conclusion is drawn that the ligand is coordinated to the metal through sulphur as well as oxygen.

Table I gives a comparison between some frequencies found for our species and the various pyrrolidine compounds (2):
### TABLE I

Some infrared absorption frequencies, positions are given in cm⁻¹

<table>
<thead>
<tr>
<th></th>
<th>Ni(n-pr₂mtc)₂</th>
<th>Ni(n-pr₂mtc)₂py₂</th>
<th>Ni(pyrrolmtc)₂*</th>
<th>Ni(pyrrolmtc)₂·dipyrrl*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^\circ)C-O</td>
<td>1545</td>
<td>1540</td>
<td>1610</td>
<td>1618</td>
</tr>
<tr>
<td>(^\circ)C-N</td>
<td>1525</td>
<td>1520</td>
<td>1540</td>
<td>1500</td>
</tr>
<tr>
<td>(^\circ)C-S</td>
<td>668</td>
<td>672</td>
<td>671</td>
<td>670</td>
</tr>
</tbody>
</table>

*Data from Krankovits et al. (2)*
We did not find any band in the 1600 cm\(^{-1}\) region so we described the 1545 cm\(^{-1}\) band to the C-O frequency which is appreciable lower than Krankovits et. al. found for the pyrrolidine monothiocarbamate. There is no explanation at hand for this large difference.

The higher C-N and C-S frequencies as compared with Ni(n-pr\(_2\)dtc)\(_2\) (1505 and 616 cm\(^{-1}\)) indicate that the canonical forms b and c with double bond character of the C-N and C-S bond are more important than in the dithiocarbamate.

\[ \text{R} \overset{\text{N}}{\text{=}} \text{C} \overset{\text{O}}{\text{S}} \quad \text{a} \quad \text{R} \overset{\text{N}}{\text{=}} \text{C} \overset{\text{S}}{\text{O}} \quad \text{b} \quad \text{R} \overset{\text{N}}{\text{=}} \text{C} \overset{\text{O}}{\text{S}} \quad \text{c} \]

The data from the visible spectra of the compounds are given in table II. They show a good agreement and can be interpreted assuming pseudo-octahedral symmetry.

The magnetic susceptibility of Ni(n-pr\(_2\)mtc)\(_2\) was measured between 93 and 293 K, the Curie-Weiss law was closely followed with a Weiss temperature of 5 K and a magnetic moment of 3.31 BM, which is just in the range normally found for octahedral Ni(II) compounds. The bispyridine adduct showed a room temperature magnetic moment of 3.25 BM.

Molecular weights of Ni(n-pr\(_2\)mtc)\(_2\) and Ni(n-pr\(_2\)mtc)\(_2\)Py\(_2\) were determined osmometrically in CCl\(_4\) solutions. 1900 and 520 were found respectively, which correspond to \([\text{Ni(n-pr}_2\text{mtc)}_2]_5\) (calc. mol. weight 1896) and a monomolecular
TABLE II

Visible absorption spectra of some monothiocarbamato complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>3T1g (F)</th>
<th>3A2g</th>
<th>3T1g (P)</th>
<th>3A2g</th>
<th>3T1g</th>
<th>3A2g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(n-pr$_2$mtc)$_2$</td>
<td></td>
<td></td>
<td></td>
<td>8.4</td>
<td></td>
<td>13.9</td>
</tr>
<tr>
<td>Ni(n-pr$_2$mtc)$_2$py$_2$</td>
<td></td>
<td>9.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(pyrrolmtc)$_2$</td>
<td>8.7</td>
<td></td>
<td></td>
<td>10.2</td>
<td>14.4</td>
<td>20.5</td>
</tr>
<tr>
<td>Ni(pyrrolmtc)$_2$</td>
<td></td>
<td>8.8</td>
<td></td>
<td>14.1</td>
<td></td>
<td>22.8</td>
</tr>
<tr>
<td>Ni(pyrrolmtc)$_2$</td>
<td></td>
<td></td>
<td></td>
<td>15.0</td>
<td>24.7</td>
<td></td>
</tr>
</tbody>
</table>

Transitions are given in kK. Dq is the ligand field parameter in cm$^{-1}$. B is the Racah parameter in cm$^{-1}$ and $\beta$ the nephelauxetic ratio calculated with B is 1041 cm$^{-1}$ for the gaseous Ni$^{2+}$ ion.

*Data from Krankovits et al. (2).*
bispyridine adduct (calc. mol. weight 537). The mass spectrum of \( \text{Ni(n-pr}_2\text{mtc)}_2 \) showed the highest m/e value at 758 corresponding with a dimer. As the IR and UV-Vis spectra of crystalline and \( \text{CCl}_4 \) solutions of the compound were much alike, a similar polymer structure in both phases is suggested.

Structural studies of the compound are in progress.

ACKNOWLEDGEMENT

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REFERENCES

NICKEL BIS(N,N DI-n-BUTYLDITHIOCARBAMATO)IODIDE.
A NEW COMPOUND WITH NICKEL IN A FORMAL OXIDATION STATE III

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Introduction

During the investigations on the oxidation of palladium and platinum bis(N,N dialkyldithiocarboxamato) we found compounds with stoichiometry

\[ \text{M}(R_2\text{dtc})_2X_2 \quad (X = \text{Cl}, \text{Br} \text{ and } R_2\text{dtc} = N,N \text{ dialkyldithiocarboxamato group}) \]

The platinum complexes could be synthesized at room temperature, whereas the palladium compounds could only be obtained by lowering the temperature of the reaction mixture to 0°C. Attempts to prepare nickel complexes with the same stoichiometry failed until now. Ni(IV)(R_2\text{dtc})_3X was obtained when the oxidation was carried out at room temperature, on cooling of a reaction mixture to -30°C however, a new Ni(III) compound -Ni(III)(bu_2\text{dtc})_2 I- resulted.

Experimental part

To a solution of 1 mole I_2 in diethylether, cooled to -30°C, 2 moles of Ni(bu_2\text{dtc})_2 were added. The reaction mixture was stirred for several hours at -30°C and Ni(bu_2\text{dtc})_2 slowly dissolved whereas a black precipitate appeared. After filtration the compound was washed with water and with cold diethylether and dried at room temperature.
Melting point: 88°C (decomposition)

Analyses:

Found: C, 36.41; H, 6.10; N, 4.71; S, 21.58; I, 21.57; Ni, 9.96%

Calc. for NiC_{18}H_{36}N_{2}S_{4}I: C, 36.37; H, 6.02; N, 4.80; S, 21.60; I, 21.35; Ni, 9.88%

Discussion

Analytical data showed the stoichiometry to be Ni(bu₂dtc)₂I. Because of decomposition in solvents as chloroform and benzene no molecular weight determinations could be performed. UV-V solution spectra yielded evidence that in chloroform the decomposition proceeded slowly to Ni(bu₂dtc)₂ and iodine. In ethylalcohol Ni(bu₂dtc)₂I solution disproportionated to Ni(bu₂dtc)₃I and Ni(bu₂dtc)₂²⁻.

From infrared spectra recorded in CsI on a Perkin Elmer 257 spectrophotometer in the region 4000 - 700 cm⁻¹ the C - N stretching frequency was found to increase with increasing formal oxidation number as expected (Ni(bu₂dtc)₂, 1502 cm⁻¹; Ni(bu₂dtc)₂I, 1518 cm⁻¹; Ni(bu₂dtc)₃I²⁻, 1538 cm⁻¹).

The spectrum in the region 700 - 200 cm⁻¹ recorded in CsI on a Hitachi EPI-L apparatus showed an absorption band at 377 cm⁻¹ which we ascribed to one of the M-S stretching frequencies and at 275 cm⁻¹ which could be due to a Ni-I stretching frequency.

Magnetic measurements on a Gouy balance showed that the Curie - Weiss law was followed in the range from 103 till 295°C, with a Weiss temperature θ = - 28°C.

For μᵥₑᶠ the value of 1.33 was found. This value ruled out either a d⁷ tetrahedral or an octahedral high spin configuration but is low for a five coordination or an octahedral low spin where one unpaired electron and thus μᵥₑᶠ of 1.73 is expected.
Probably a remainder of antiferromagnetic coupling is present. This is supported by the negative value of $\Theta$ indicating antiferromagnetism at very low temperatures.

An esr spectrum of a powdered sample revealed three absorption lines from which the three principal $g$-values could be calculated to be 2.260, 2.215 and 2.027 respectively. Because the values $g_1$ and $g_2$ are nearly the same, there is almost and axial symmetry around the direction of $g_3$. These data could be ascribed to a square pyramidal coordination of the Ni atom in which we should expect $g_1 = g_2 \neq g_3$.

Acknowledgment

Thanks are due to Mr. E.W.J.M. van der Drift for the recording of the esr spectra and to Professor J.J. Steggerda for his interest in the work.

References

1) J.A. Cras, J. Willemse, to be published.

