NICKEL (II) MONOTHIOCARBAMATES

J. Willemse

Department of Inorganic Chemistry, University of Nijmegen,
Nijmegen, The Netherlands

(Received 1 June 1971)

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

The publication of Krankovits et.al. (2) of the synthesis of nickel (II) bis(pyrrolidine monothiocarbamate)

$[\text{Ni}(\text{pyrrolmtc})_2]$, prompts us to report our investigations of nickel (II) bis(di-n-propyl monothiocarbamate)

$[\text{Ni}(\text{n-pr}_2\text{mtc})_2]$.

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

$\text{Ni}(\text{n-pr}_2\text{mtc})_2$: 0.15 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 nickelacetate. 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 $\text{Ni}(\text{OSCNC}_6\text{H}_{14})_2$:
C: 44.34%; H: 7.44%; N: 7.39%; O: 8.44%; S: 16.91%;
Ni: 15.48%.

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

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

DISCUSSION

In contrast with the observations of Krankovits for $\text{Ni}(\text{et}_2\text{mtc})_2$ our analysis and IR data clearly indicate that there is no water present in $\text{Ni}(\text{n-pr}_2\text{mtc})_2$. 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}

	$\text{Ni}(\text{n-pr}_2\text{mtc})_2$	$\text{Ni}(\text{n-pr}_2\text{mtc})_2\text{py}_2$	$\text{Ni}(\text{pyrrolmtc})_2^*$	$\text{Ni}(\text{pyrrolmtc})_2\cdot\text{dipyrrol}^*$
$\nu \text{C-O}$	1545	1540	1610	1618
$\nu \text{C-N}$	1525	1520	1540	1500
$\nu \text{C-S}$	668	672	671	670

*Data from Krankovits et. al. (2)

We did not find any band in the 1600 cm^{-1} regio 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 $\text{Ni}(\text{n-pr}_2\text{dtc})_2$ (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.

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 $\text{Ni}(\text{n-pr}_2\text{mtc})_2$ 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 $\text{Ni}(\text{II})$ compounds. The bispyridine adduct showed a room temperature magnetic moment of 3.25 BM . Molecular weights of $\text{Ni}(\text{n-pr}_2\text{mtc})_2$ and $\text{Ni}(\text{n-pr}_2\text{mtc})_2\text{py}_2$ were determined osmotically in CCl_4 solutions. 1900 and 520 were found respectively, which correspond to $[\text{Ni}(\text{n-pr}_2\text{mtc})_2]_5$ (calc. mol. weight 1896) and a monomolecular

TABLE II

Visible absorption spectra of some monothiocarbamate complexes

$\text{Ni}(\text{n-pr}_2\text{mtc})_2$	$\text{Ni}(\text{n-pr}_2\text{mtc})_2\text{py}_2$	$\text{Ni}(\text{pyrrolmtc})_2^*$	$\text{Ni}(\text{pyrrolmtc})_2\text{dipyrrol}^*$	
8.4	9.2	8.7	8.8	${}^3\text{T}_{1g} \leftarrow {}^3\text{A}_{2g}$
10.2				${}^1\text{E}_g \leftarrow {}^3\text{A}_{2g}$
13.9	14.4	14.1	15.0	${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}$
	20.5			${}^1\text{T}_{1g} \leftarrow {}^3\text{A}_{2g}$
23.5	23.8	22.8	24.7	${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}$
840	920	870	880	Dq
810	705	790	779	B
0.78	0.68	0.75	0.75	β

Transitions are given in kK. Dq is the ligand field parameter in cm^{-1} . B is the Racah parameter in cm^{-1} and β 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 $\text{Ni}(\text{n-pr}_2\text{mtc})_2$ showed the highest m/e value at 758 corresponding with a dimer. As the IR and UV-Vis spectra of crystalline and 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

The author wishes to thank Prof. J.J. Steggerda for his continued interest, Mr. E.H.M. Vroemen for his contribution in the experimental work and Mr. J. Diersmann for performing the analyses.

The investigations were supported in part by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organisation for the Advancement of Pure Research.

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NICKEL BIS(N,N DI-n-BUTYLDITHIOCARBAMATO)IODIDE.

A NEW COMPOUND WITH NICKEL IN A FORMAL OXIDATION
STATE III

(Received 13 January 1972)

By J. Willemsse, P.H.F.M. Krouwette, J.A. Cras

Department of Inorganic Chemistry

University of Nijmegen, Nijmegen, The Netherlands

Introduction

During the investigations on the oxidation of palladium and platinum bis(N,N dialkyldithiocarbamate) we found compounds with stoichiometry $M(R_2dtc)_2X_2$ ($X = Cl, Br$ and $R_2dtc = N,N$ dialkyldithiocarbamate group)¹⁾. 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°. Attempts to prepare nickel complexes with the same stoichiometry failed until now. $Ni(IV)(R_2dtc)_3X$ was obtained when the oxidation was carried out at room temperature, on cooling of a reaction mixture to -30° however, a new $Ni(III)$ compound $-Ni(III)(bu_2dtc)_2 I-$ resulted.

Experimental part

To a solution of 1 mole I_2 in diethylether, cooled to -30°, 2 moles of $Ni(bu_2dtc)_2$ were added. The reaction mixture was stirred for several hours at -30° and $Ni(bu_2dtc)_2$ 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° (decomposition)

Analyses :

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

Calc. for $\text{NiC}_{18}\text{H}_{36}\text{N}_2\text{S}_4\text{I}$: 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 $\text{Ni}(\text{bu}_2\text{dtc})_2\text{I}$. Because of decomposition in solvents as chloroform and benzene no molecular weight determinations could be performed. UVV solution spectra yielded evidence that in chloroform the decomposition proceeded slowly to $\text{Ni}(\text{bu}_2\text{dtc})_2$ and iodine. In ethylalcohol $\text{Ni}(\text{bu}_2\text{dtc})_2\text{I}$ solution disproportionated to $\text{Ni}(\text{bu}_2\text{dtc})_3\text{I}_3$ and $\text{Ni}(\text{bu}_2\text{dtc})_2$.

From infrared spectra recorded in CsI on a Perkin Elmer 257 spectrophotometer in the region $4000 - 700 \text{ cm}^{-1}$ the C - N stretching frequency was found to increase with increasing formal oxidation number as expected ($\text{Ni}(\text{bu}_2\text{dtc})_2$, 1502 cm^{-1} ; $\text{Ni}(\text{bu}_2\text{dtc})_2\text{I}$, 1518 cm^{-1} ; $\text{Ni}(\text{bu}_2\text{dtc})_3\text{I}_3$ ^{2,3}, 1538 cm^{-1}).

The spectrum in the region $700 - 200 \text{ cm}^{-1}$ 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°K , with a Weiss temperature $\theta = -28^{\circ}\text{K}$.

For μ_{eff} a value of 1.33 was found. This value ruled out either a d^7 tetrahedral or a octahedral high spin configuration but is low for a five coordination or an octahedral low spin where one unpaired electron and thus μ_{eff} of 1.73 is expected.

Probably a remainder of antiferromagnetic coupling is present. This is supported by the negative value of θ 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 an 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.

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