ON THE EXISTENCE OF A PARAMAGNETIC ADDUCT OF Ni(II)-BIS-(DI-n-BUTYL-DISELENOCARBAMATE). AN EPR STUDY

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Paramagnetic adduct formation of pyridine with nickel(II)-bis(di-n-butyl-diselenocarbamate) is observed by means of EPR at 27°K. The low value of the zero field splitting and the g-factor are explained by strong spin-orbit interactions and by high covalency typical of the Se₄-coordination sphere.

1. Introduction

Planar Ni(II)-chelates are frequently found to expand their coordination number by interaction with a Lewis base forming paramagnetic high-spin adduct complexes:

$$NiL_4 + 2L' \rightleftharpoons trans - NiL_4L_2'$$
 (1)

In contrast to the complexes of the coordination type NiO_4 which are known to create readily quasi-octahedral adducts, NiS_4 -complexes vary substantially in their ability to interact with Lewis bases. To our knowledge there is until now no direct evidence for the existence of a paramagnetic adduct complex of Ni(II)-N,N-dialkyl-dithio- and diselenocarbamates [1-3]. Using EPR we have found that $[Ni(dbsc)_2]$ (dbsc = di-n-butyl-diselenocarbamate) forms a quasi-octahedral high-spin complex (I) in pyridine solution at 27° K.

$$\begin{array}{c|c}
C_{+}H_{g} & & \\
C_{+}H_{g} & & \\
C_{+}H_{g} & & \\
\end{array}$$

$$\begin{array}{c|c}
S_{e} & & \\
N_{i} & & \\
S_{e} & & \\
\end{array}$$

$$C_{+}H_{g} & & \\
C_{+}H_{g} & & \\
\end{array}$$

$$(I)$$

2. Experimental and results

 $[Ni(dbsc)_2]$ was prepared as described earlier [3]. 0.01--0.02 M solutions of $[Ni(dbsc)_2]$ in chloroform containing about 30 vol-% pyridine were used. Attempts to isolate $[Ni(dbsc)_2(pyr)_2]$ brought no success. The EPR studies were carried out at X-band.

In the liquid solution of (1) no EPR spectrum could be detected. The adduct formation is found to be remarkable at temperatures lower than 100°K. In the temperature range 120–77°K we could observe an EPR signal with low intensity. The intensity of the spectrum increases as the temperatures decreases.

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