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

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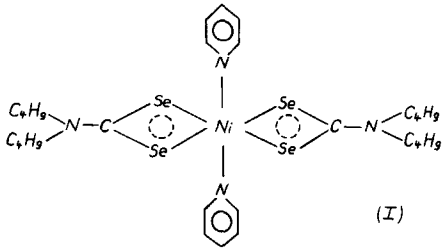
Paramagnetic adduct formation of pyridine with nickel(II)-bis(di-*n*-butyl-diselenocarbamate) is observed by means of EPR at 27°K. The low value of the zero field splitting and the *g*-factor are explained by strong spin–orbit interactions and by high covalency typical of the Se_4-coordination sphere.

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:

$$NiL_4 + 2L' \rightleftharpoons \textit{trans}\text{-}NiL_4L'_2 \,. \qquad (1)$$

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.



(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 (I) 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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