As part of a study of macrocyclic tetrameric compounds, a new open chain tetradeinate ligand was synthesized possessing two amide groups: N,N'-dipicolyl-1,8-naphthylenediamine (I).

Analogous types of ligands possessing the picolinic acid moiety combined with aliphatic polyamines acting as quinquedentate or terdentate ligands were synthesized by Nonoyama [1] as well as by Ojima and coworkers [2], giving complexes with Cu(II) and Ni(II). Complexes of picolinic acid amide with the above metals have been prepared [3, 4]. Furthermore, 1,8-naphthylenediamine has been shown to give stable complexes with Cu(II) and Ni(II) [5, 6]. It is, therefore, interesting to examine the case in which a compound acquiring both the above mentioned groups acts as a tetradeinate ligand. In the present paper the synthesis and some properties of Cu(II) and Ni(II) complexes of N,N'-dipicolyl-1,8-naphthylenediamine (DPNAP) are reported.

For the synthesis of the ligand the method of active anhydrides was used.

Experimental

All materials used were purchased from Fluka Co. N,N'-dipicolyl-1,8-naphthylenediamine

6.65 g (0.054 mole) of picolinic acid were suspended with a partial dissolution in anhydrous tetrahydrofuran (~40 ml) and then 5.05 g (0.05 mole) of triethylamine added. The solution became clear. It was cooled to ~5 °C and 7 ml ethyl chloroformate was added. After 10 min at the same temperature to the reaction mixture 3.95 g (0.025 mole) of 1,8-naphthylenediamine, dissolved in 10 ml of anhydrous tetrahydrofuran were added. The mixture was kept at room temperature in a well stoppered spherical flask for 12 h. The solvent was evaporated in vacuum and the solid obtained was dissolved in dichloromethane and carefully washed twice with the same volume of 5% sodium bicarbonate. The dichloromethane solution was dried and then evaporated leaving a paste which, immediately treated with alcohol (96%), gave a dark brown solid. The solid was recrystallized several times from a mixture of alcohol and acetone. The substance finally obtained was washed with ether and dried in vacuum over P₂O₅. The substance has a brownish white colour, m.p. 204-205 °C, and gives one spot on the TLC plate, using for developing the system butanol : acetic acid : water (4:1:1). Yield: 5.2 g (52%).

Analysis for C₂₂H₂₆N₄O₂

Calcd C 71.33 H 4.34 N 15.21, Found C 71.20 H 4.40 N 15.84.

The mass spectrum of the substance indicates a molecular ion at m/e 368, while the calculated formula weight is 368.402. The NMR spectrum of the substance was taken in deuterated DMSO solution exhibiting the following peaks (TMS): 7.90, 7.85, 7.90, 3.25, 2.48, 2.03 ppm (δ). The IR absorption spectra of the prepared compounds are given in Table I. The bands at 3290, 1668 (amide IV) are characteristic amide absorptions.

Bi(N,N'-dipicolyl)-1,8-naphthylenediamidato-Cu(II)

2 g (0.0054 mole) of DPNAP were suspended in absolute methanol (~90 ml), then 0.728 g (0.0054 mole) of CuCl₂, dissolved in 20 ml of DMSO, were added to the suspension and the resulting solution was vigorously stirred and refluxed for 1 h. The solution then was cooled to 15 °C and a
methanolic solution of KOH (0.005 g or 0.0108 mole in absolute methanol) was added dropwise with vigorous stirring. The resulting pH was 7.2. The mixture was kept for 12 h in the refrigerator and an olive-green fine crystalline precipitate was obtained, which was washed with alcohol (95%) and ether. Dried in vacuum over P₂O₅ gave 1.4 g (60% yield). The complex is stable up to 260 °C. At this temperature vapours are evolved and the complex finally decomposes at 300 °C. The complex is only soluble in DMSO and slightly soluble in ethyl alcohol. The solution of the complex in DMSO is not conducting.

Analysis for C₂₂H₁₄N₄O₂Cu

Calcd C 61.46  H 3.28  Ni 13.03  Cu 14.78,
Found C 61.30  H 3.71  Ni 12.86  Cu 15.01.

The IR spectrum of the complex is given in Table I.

Bis(N,N’-(dipicolyl) 1,8-naphthylenediamidato)-Ni(II)

The same procedure was followed as in the complex of copper. 1.92 g (0.005 mole) of DPNAP were used and 0.67 g (0.0051 mole) of anhydrous NiCl₂ as well as 0.697 g (0.0194 mole) of KOH dissolved in a minimum amount of absolute methanol. The final pH was 6.5. Heating and stirring for 1/2 h is required after the final precipitation of the complex. The complex is a brown-red crystalline powder. The pH was 6.5. Heating and stirring for 1/2 h is required after the final precipitation of the complex. The magnetic moment or the copper complex agrees with the expected value for a magnetically dilute copper(II) complex. The magnetic moment of the nickel(II) complex suggests either octahedral or tetrahedral structure. Planar paramagnetic nickel(II) complexes are rare and their magnetic moments are found low [8]. The visible spectra of the prepared Ni(II) complex either in the solid or in DMSO solution are not

Table II. Visible spectra in DMSO solution, diffuse reflectance spectra of the solids in the UV-visible, and magnetic moments of the Cu(II) and Ni(II) complexes of DPNAP.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solution spectra (KK) (e)</th>
<th>Solid diffuse reflectance spectra (KK)</th>
<th>μ_ett (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPNAP–Cu</td>
<td>22.7 (610)</td>
<td>42.3 sh, 37.0, 25.2</td>
<td>1.98</td>
</tr>
<tr>
<td></td>
<td>17.4 (351)</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16.0 (305) sh</td>
<td>15.2 sh</td>
<td></td>
</tr>
<tr>
<td>DPNAP–Ni</td>
<td>22.7 (10.177)</td>
<td>45.9, 36.8, 21.9</td>
<td>3.41</td>
</tr>
<tr>
<td></td>
<td>15.0 (442)</td>
<td>15.3 sh</td>
<td></td>
</tr>
</tbody>
</table>

Results and Discussion

The copper complex (in the solid or in DMSO solution) exhibits visible absorption spectra which are consistent with a planar structure. The maximum of the observed broad band lies closer to the high energy end of the band which often indicates square planar geometry for the Cu₄ chromophore [7].

Otherwise if the maximum of the band lies closer to the low energy region of the broad band, an octahedral arrangement of the ligand atoms around Cu(II) is expected, provided that such ligands exist to participate in this geometry.

The magnetic moment or the copper complex agrees with the expected value for a magnetically dilute copper(II) complex.

The magnetic moment of the nickel(II) complex suggests either octahedral or tetrahedral structure. Planar paramagnetic nickel(II) complexes are rare and their magnetic moments are found low [8]. The visible spectra of the prepared Ni(II) complex either in the solid or in DMSO solution are not...
adequate in this case to reveal an octahedral structure, because the very intense UV bands of the complex owing to the $\pi \rightarrow \pi^*$ and the charge transfer transitions from 45 to 16 kK mask the three weak characteristic bands for the $O_h$ symmetry d-d transitions for Ni(II). The observed relatively intense band of the complex in DMSO solution at 15.0 kK (shoulder in the diffuse reflectance spectrum) can equally be an absorption due to a planar, tetrahedral or even octahedral ligand field. Since the prepared Ni(II) complex is neutral and definitely not hydrated as indicated by the IR spectrum, the high intensity of the band at 15.0 kK in DMSO solution strongly suggests that the complex is tetrahedral. The IR spectra of both complexes clearly indicate that the hydrogen of the secondary amide is completely ionized. The second NH stretch strong band at 3290 cm$^{-1}$ of DPNAP is missing entirely from the spectra of the complexes. In addition, a strong band appears at 1580 cm$^{-1}$ for the Cu(II) complex and at 1595 cm$^{-1}$ for the Ni(II) complex which is due to the coordinated azomethine group (>$C=N<$).

This investigation was supported by the National Hellenic Research Foundation, to which we are gratefully indebted.

We thank Dr. R. A. W. Johnstone of the University of Liverpool for the above information.

Note added in proof:
Molecular weight determination of Cu and Ni complexes by mass spectrometry using field-desorption method gave molecular ions for the Cu-complex at $m/e$ 429 with another peak at $m/e$ 881 of low intensity, possibly indicating dimers. For the Ni-complex $m/e$ 424 and $m/e$ 850 were observed. The values obtained agree with the calculated molecular weights of the prepared complexes.