

Synthesis of Novel Nickel(II) Macrocylic Complex: A Case of Stabilization of Dicarbinolamine

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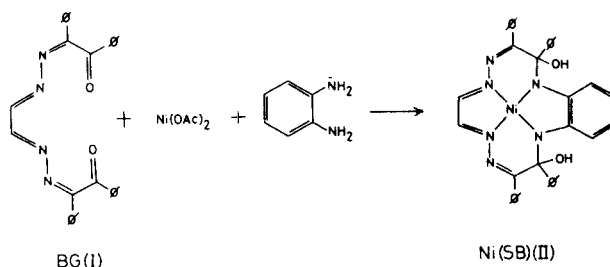
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A neutral macrocylic complex of nickel(II), Ni(SB) has been synthesized by a template condensation of the open chain ligand 1,2,9,10-tetraphenyl-3,4,7,8-tetraazadeca-2,4,6,8-tetraen-1,10-dione (BG) with *o*-phenylenediamine in the presence of nickel(II) acetate. The presence of dicarbinolamine moiety in this complex has been established by NMR spectra.

The synthesis of complexes of planar N_4 macrocylic ligands with the first row transition metal ions is important because of their utility as model compounds in the study of naturally occurring macrocycles. The template synthesis, which affects the steric course of reactions, has helped in the development of a variety of new macrocycles^{1,2}. The condensation of a carbonyl compound with a primary amine, in the presence of metal ions, usually results in the formation of an azomethine ($>C=N$) linkage in the molecule. Very little information is available on the intermediate carbinolamine and its complexes. Barefield *et al.*³ have reported the possibility of the formation of an imine-carbinolamine complex in the nickel(II) ion assisted cyclization of 1,5,8,12-tetraazadodecanes with glyoxal. In the present communication we wish to report the synthesis of a novel nickel(II) complex of a macrocylic ligand wherein the existence of the dicarbinolamine has been proved unequivocally.

The ligand 1,2,9,10-tetraphenyl-3,4,7,8-tetraazadeca-2,4,6,8-tetraen-1,10-dione (BG) (I), was obtained by the condensation of two equivalents of benzilmonohydrazone and one equivalent of glyoxal in benzene medium. The golden yellow coloured ligand (m.p. 182°) was characterized by spectral data and elemental analysis. [Calc. for $C_{30}H_{22}N_4O_2$: C, 76.59; H, 4.68; N, 11.91. Found: C, 76.27; H, 4.39; N, 12.28 %]. The ligand showed a single spot in TLC (3:2, benzene: petrol). The orientation of the keto groups of the ligand BG is well suited for the ring closure reactions with diamines when the metal ion acts as a template. The nickel complex Ni(SB)(II), hitherto unknown, was synthesized by the template condensation of the ligand BG with *o*-phenylenediamine in the presence of nickel(II) acetate in an alcoholic

medium with an overall yield of 50%. [Calc. for $C_{36}H_{28}N_6O_2Ni$: C, 68.06; H, 4.4; N, 13.23; Ni, 9.24. Found: C, 68.21; H, 4.2; N, 14.10; Ni, 9.45 %]. Since the diamine was added in small amounts over a period of time, the formation of any polymeric product in this reaction was prevented. The reaction sequence is given in Scheme 1.



SCHEME 1

BG(I): 1,2,9,10-Tetraphenyl-3,4,7,8-tetraazadeca-2,4,6,8-tetraen-1,10-dione

Ni(SB)(II): {4,9-Dihydroxy-3,4,9,10-tetraphenyl-benzo(*b*)-1,2,5,8,11,12-hexaazacyclotetradeca-2,6,10,12,14-pentaenato}nickel(II), [NiBzo(OH)₂Ph₄[14]pentaenato $N_4(N_2)$]

The nickel(II) complex(II) was found to be diamagnetic at room temperature and a non-electrolyte in DMF solution indicating the presence of low-spin square-planar nickel(II). The infrared spectrum (both in KBr and in dry $CHCl_3$ solution) showed the presence of OH absorption at 3400 cm^{-1} (broad) and that of the azomethine at 1600 cm^{-1} . The characteristic absorptions due to neither the free amino group nor the carbonyl group were observed in the above spectrum indicating the formation of the macrocylic complex. The electronic spectrum of a $CHCl_3$ solution of the complex exhibited a broad band with a maximum at 512 nm ($\log \epsilon 3.36$) and a shoulder at 568 nm ($\log \epsilon 3.36$). The reflectance spectrum of the complex is not too dissimilar from the solution spectrum which confirms the essentially planar geometry of the complex.

The presence of the hydroxyl group has been confirmed by recording the NMR spectrum of the complex in $CDCl_3/TMS$. The following signals were seen in the 90 MHz 1H NMR spectrum: $\delta 5.1$ (2H, *s*), 6.81 (4H, *d*), 7.17-7.33 (20H, *m*) and 7.43 (2H, *s*). Deuterium exchange with D_2O resulted in the disappearance of the signal at $\delta 5.1$ due to the hydroxyl group and a sharp peak corresponding to HOD was observed at $\delta 5.13$. The integration of the $\delta 5.13$ peak and the above D_2O exchange experiment prove the

presence of the dicarbinolamine moiety. The mass spectrum of this complex showed a parent ion peak at 634 (m/z) in accordance with the proposed molecular formula for the macrocyclic complex.

The stabilisation of dicarbinolamine moiety in the complex can be explained in the following way. The condition under which the reaction was carried out was essentially basic^{4,5} and the presence of bulky phenyl groups in the ligands might have influenced the stabilization of the dicarbinolamine. Also, from the studies on the mechanism of oxime and ketimine formation by Williams and Bender⁶, it appears that the difficulty in the relief of steric strain in the molecule must be one of the factors responsible for the stabilization of dicarbinolamine.

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