Coordination of Schiff bases derived from pyrrole-2-carboxaldehyde and triamines to copper(II) and nickel(II) ions. Crystal structures of [Cu(C_{15}H_{20}N_{5})]NO_3 and [Ni(C_{15}H_{20}N_{5})]ClO_4

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The Schiff bases 1,9-bis(2-pyrrolyl)-2,5,8-triazaandeca-1,8-diene (H_2L_1), 1,10-bis(2-pyrrolyl)-2,5,9-triazaundeca-1,9-diene (H_2L_2), and 1,11-bis(2-pyrrolyl)-6-methyl-2,6,10-triazaundeca-1,10-diene (H_2L_3) react with copper(II) nitrate or nickel(II) perchlorate in the presence of triethylamine to give new complexes [Cu(HL_2)]NO_3 and [Ni(HL_2)]ClO_4. The crystal structures of [Cu(HL_2)]NO_3 and [Ni(HL_2)]ClO_4 have been determined from single crystal diffractometer data and refined to final R factors of 5.09 and 5.3 %, respectively. Crystallographic data: [Cu(HL_2)]NO_3: monoclinic, P2_1/c, a = 10.036(2), b = 14.500(2), c = 13.317(2) Å, β = 108.14(1)°, Z = 4, and d_c = 1.1427 Mg m^{-3}; [Ni(HL_2)]ClO_4: monoclinic, P2_1/c, a = 10.578(3), b = 13.953(3), c = 12.394(4) Å, β = 93.78(2)°, Z = 4, and d_c = 1.549 Mg m^{-3}. In both the structures the potentially pentadentate ligand (HL_2)- acts as a tetradentate one leaving one pyrrole group uncoordinated. Interesting is the metal dependent sequence of the three chelate rings. While the Ni(II) ion coordinates the (HL_2)- ligand to form a 5-5-6-membered ring system, the ring arrangement in the copper complex is of the 5-6-5 type.

Introduction

In spite of a large number of publications devoted to the syntheses, physicochemical studies and biochemical properties of metal Schiff base complexes, very litttle work has been done on metal complexes incorporating ligands derived from pyrrole-2-carboxaldehyde and triamines. In the reports describing the preparation, magnetic and spectroscopic properties of [Ni(HL_3)]X, where H_2L_3 is the Schiff base ligand presented in Scheme 1 and X = Br, ClO_4, PF_6, and BPh_4 (Heyman et al., 1973; Cheney et al., 1975) it has been suggested that there is incomplete (four- in the solid, three- in the solution) coordination of the potentially pentadentate ligand to the nickel(II) ion. It has been shown that cop-

Scheme 1

\begin{align*}
\text{H}_2\text{L}_1: & \quad R = H, \quad m = n = 2, \quad a = 1 \\
\text{H}_2\text{L}_2: & \quad R = H, \quad m = 2, \quad n = 3, \quad a = 1 \\
\text{H}_2\text{L}_3: & \quad R = H, \quad m = n = 3, \quad a = 1 \\
\text{H}_2\text{L}_4: & \quad R = \text{CH}_3, \quad m = n = 3, \quad a = 1 \\
\text{H}_2\text{L}_5: & \quad R = \text{C}_6\text{H}_5\text{CH}_2-, \quad m = n = 3, \quad a = 1 \\
\text{H}_2\text{L}_6: & \quad R = \text{-CH}_2-(1,3\text{-C}_6\text{H}_4\text{-CH}_2)-, \quad m = n = 3, \quad a = 2
\end{align*}
per(II) coordinates the doubly deprotonated and neutral forms of the aforementioned ligand as well as of its 5-substituted derivatives $\text{H}_2L^{5,6}$ (Scheme 1) (Casella et al., 1986). Physicochemical data on $\text{CuL}^{3,5}$, $\text{Cu}_2L^6$, $[\text{Cu} \,(\text{H}_2L^{3,5})]_2(\text{ClO}_4)_2$, and $[\text{Cu}_2(\text{H}_4L^6)](\text{ClO}_4)_4$ were consistent with the involvement of all the nitrogen atoms of ligands in coordination. A very recent X-ray diffraction study on the $[\text{ReO} \,(\text{OCH}_3)(\text{HL}^4)]PF_6$ compound (Banberry et al., 1990) ($\text{H}_2L^4$ is defined in Scheme 1) revealed that the deprotonated ligand is bound asymmetrically to the metal through four nitrogen atoms leaving one pyrrole group dangling. This mode of coordination of ($\text{HL}^4$)$^-$ contrasts with that of the ($\text{L}^{1,2}$)$^-$ ligand (Scheme 1) in $[\text{ReO} \,(\text{NCS})(\text{L}^1)]$ which is believed (on the basis of $^1\text{H}$ nmr data) to coordinate through both pyrrolyl and imine groups, leaving the central $-\text{NH}-$ group uncoordinated (Banberry et al., 1990).

The diversity of coordination modes of ligands derived from pyrrole-2-carboxaldehyde and triamines as well as the catalytic activity of some of their complexes (Casella et al., 1986) encouraged us to look for new complexes of this type. This paper reports the syntheses and properties of new nickel(II) and copper(II) complexes with single deprotonated forms of the ligands $\text{H}_2L^{1,2,4}$ (Scheme 1). The crystal structures of $[\text{Cu}(\text{HL}^2)]\text{NO}_3$ and $[\text{Ni}(\text{HL}^2)]\text{ClO}_4$ have been determined and show $\text{i}$ complete but different coordination of the asymmetric $\text{H}_2L^2$ ligand to the Cu(II) and Ni(II) ions.

**Experimental**

**Materials**

Pyrrole-2-carboxaldehyde was recrystallized from hexane. Bis-(2-aminoethyl)-amine and bis-(3-aminopro-

Ligands

To a stirred solution of pyrrole-2-carboxaldehyde (10 mmol) dissolved in 40 ml of absolute methanol was added an appropriate triamine (5 mmol). The solution was refluxed for 1 h turning from pale yellow to a dull orange. Then the solvent was removed under reduced pressure using a rotary evaporator to give the symmetrical ligands ($\text{H}_2L^1$, $\text{H}_2L^5$) as solids and the unsymmetrical ($\text{H}_2L^2$) as an oily residue. Solid ligands were recrystallized from the methanol-isopropyl ether mixture to give yellowish orange crystals of 1,9-bis-(2-pyrrolyl)-2,5,8-triazanona-1,8-diene $\text{H}_2L^1$, m.p. 114-116°C, Anal. Found: C, 65.5; H, 7.5; N, 27.4; Calcd. for $\text{C}_{14}\text{H}_{18}\text{N}_6$: C, 65.3; H, 7.4; N, 27.2%; molecular ion in the mass spectrum, m/e: Found 257; Calcd. 257. and of 1,11-bis-(2-pyrrolyl)-6-methyl-2,6,10-triazaundeca-1,10-diene $\text{H}_2L^1$, m.p. 63-65°C, Anal. Found: C, 68.0; H, 8.5; N, 23.4; Calcd. for $\text{C}_{17}\text{H}_{25}\text{N}_5$: C, 68.2; H, 8.5; N, 23.4%; molecular ion in the mass spectrum, m/e: Found 299; Calcd. 299. The oily residue shows a mass spectrum with an intense ion at m/e = 271 corresponding to the molecular ion of 1,10-bis-(2-pyrrolyl)-2,5,9-triazadeca-1,9-diene $\text{H}_2L^2$ (Scheme 1).

Copper (II) Complexes

To copper(II) nitrate trihydrate (0.7248 g, 3 mmol) dissolved in methanol (40 ml) was added a solution of the appropriate ligand ($\text{H}_2L^1$, $\text{H}_2L^5$, or $\text{H}_2L^2$) (3 mmol) and triethylamine (0.84 ml, 6 mmol) in methanol (40 ml). The resulting mixture was refluxed for 15 min and then evaporated to a small volume. In each case, dark coloured solids separated, which were filtered off and washed with cold methanol. After recrystallisation from methanol the following crystalline products (yields 35-60%) were obtained:

- dark purple $[\text{Cu}(\text{HL}^2)]\text{NO}_3$, Anal. Found: C, 43.9; H, 4.9; N, 21.9; Calcd. for $\text{C}_{14}\text{CuH}_{18}\text{N}_6\text{O}_3$: C, 44.0; H, 4.8; N, 22.0%;
- dark green $[\text{Cu}(\text{HL}^2)]\text{NO}_3$, Anal. Found: C, 45.6; H, 5.2; N, 21.2; Calcd. for $\text{C}_{15}\text{CuH}_{20}\text{N}_6\text{O}_3$: C, 45.5; H, 5.1; N, 21.2%;
- dark green $[\text{Cu}(\text{HL}^2)]\text{ClO}_4$, Anal. Found: C, 47.8; H, 5.7; N, 20.2; Calcd. for $\text{C}_{17}\text{CuH}_{24}\text{N}_6\text{O}_3$: C, 48.2; H, 5.7; N, 19.8%.

Nickel (II) Complexes

To a stirred solution of nickel(II) perchlorate hexahydrate (1.8285 g, 5 mmol) in methanol (20 ml) was added a solution of an appropriate ligand (5 mmol) and