

Synthesis of Two Potentially Heptadentate (N₄O₃) Schiff-base Ligands Derived from Condensation of *Tris*(3-aminopropyl)-amine and Salicylaldehyde or 4-Hydroxysalicylaldehyde. Nickel(II) and Copper(II) Complexes of the Former Ligand.

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Received: 9 December 2000; in revised form: 6 February 2002 / Accepted: 11 February 2002 /

Published: 28 February 2002

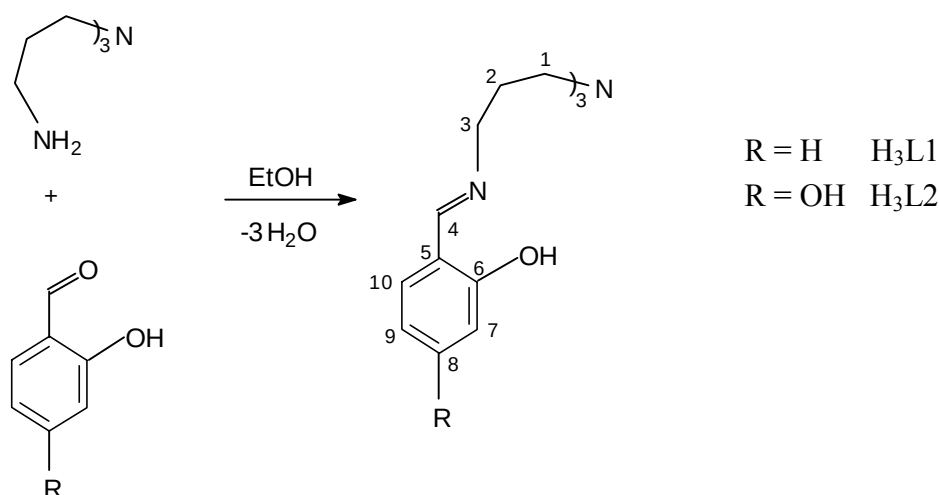
Abstract: Two potentially heptadentate (N₄O₃) tripodal Schiff-base ligands: tris(3-(salicylideneimino)propyl)amine (H₃L1) and tris(3-(4'-hydroxysalicylideneimino)-propyl)amine (H₃L2) have been prepared and characterized by various spectroscopic methods (IR, FAB-MS, NMR). They are derived from the condensation reactions of tris(3-aminopropyl)amine (tpt), with 3 equivalents of either salicylaldehyde or the ring-substituted salicylaldehyde, 4-hydroxysalicylaldehyde. The nickel(II) and copper(II) complexes of H₃L1 were obtained from the its reactions Ni(II) and Cu(II) salts in absolute methanol. These complexes were studied by IR and FAB-Mass spectrometry.

Keywords: Schiff-base, tripodal ligands, potentially heptadentate complexes

Introduction

Potentially heptadentate (N_4O_3) Schiff-base ligands, derived from condensation reactions of tris(2-aminoethyl)amine (tren) with various ring substituted salicylaldehydes, have been prepared, and their coordination chemistry with a number of metal ions has been extensively investigated [1-5]. The amine phenol ligands, which have been prepared from the reduction of the corresponding Schiff-base ligands, have been also reported [6]. We and other workers have prepared complexes of fully condensed potentially heptadentate (N_7) Schiff-base ligands derived from the condensation of tripodal tetraamines with either 2-acetylpyridine or 2-pyridinecarboxaldehyde [7-10]. However, herein we report the synthesis of the two potentially heptadentate (N_4O_3) Schiff-base ligands, H_3L1 and H_3L2 (Figure1) together with the synthesis of nickel(II) and copper(II) complexes of H_3L1 .

Figure 1. The procedure of ligand synthesis, along with NMR numbering



Results and discussion

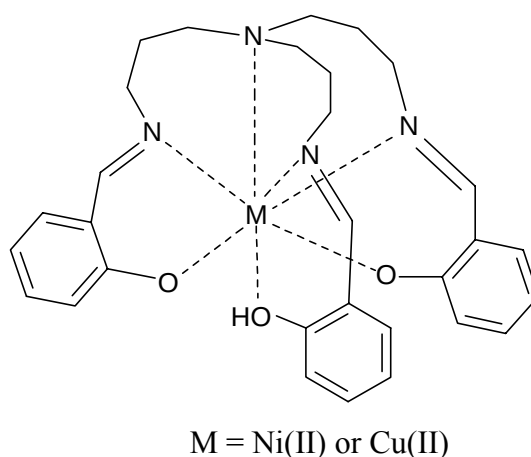
Ligands

Two potentially heptadentate Schiff-base ligands were easily prepared by reaction of tris(3-amino-1-propyl)amine with 3 equivalent of salicylaldehyde or its 4-substituted derivative, as shown in Figure1. They are both sensitive to moisture and must be kept under vacuum. Complete condensation of all primary amino groups is confirmed by the lack of N-H stretching bands in the IR 3150-3450 cm^{-1} region and the presence of strong C=N stretching bands for both H_3L1 and H_3L2 ligands. This conclusion is also supported by the ^1H -NMR data which shows not only the absence of N-H hydrogen resonances but also the presence of CH=N Hydrogen resonances at about 8 ppm. ^1H - and ^{13}C -NMR spectra, mass spectral and infrared data for both ligands are completely consistent with the formulations indicated in Figure 1.

Complexes

Both complexes were investigated by elemental analysis, IR and FAB mass spectrometry. The lack of N-H stretching bands in the IR 3150-3450 cm^{-1} region and the presence of very strong C=N (Schiff-base) stretching bands at about 1630 cm^{-1} for both compounds show that the expected complexes were synthesized. The mass spectral data for complexes **1** and **2** are consistent with deprotonation of two of the three hydroxyl groups of the ligand, giving neutral complexes (Figure 2). The latter conclusion is also supported by the insolubility of these complexes in water. In both complexes the bridgehead nitrogen atom may be coordinated to the metal ions, as we have observed for the corresponding complexes derived from 2-acetylpyridine [7, 10].

Figure 2. The proposed chemical structure for the complexes **1** and **2**.



Experimental

General

Salicylaldehyde and 4-hydroxysalicylaldehyde were obtained from Aldrich and were used without further purification. The tripodal tetraamine ligand tpt was synthesized according to the literature method [11]. IR and NMR spectra were measured on Shimadzu IR-435 and Bruker DPX 300 spectrometers respectively.

Ligand synthesis

Tris(3-(salicylideneimino)propyl)amine (H₃L1): To a solution of salicylaldehyde (1.46 g, 12mmol) in diethyl ether (12mL) was added tpt (0.75g, 4mmol) in absolute ethanol (12mL). After the addition of additional diethyl ether (20 mL) and cooling in an ice bath for 30 min, the yellow precipitate formed was filtered off, washed with diethylether and dried *in vacuo*. Yield, 1.7g (85%); mp 100-102

°C; Found: C, 64.0%; H, 7.6%; N, 10.1%. $C_{30}H_{36}N_4O_3 \cdot 3H_2O$ requires: C, 65.0%; H, 7.6%; N, 10.1%; 1H -NMR ($CDCl_3$, ppm, 300 MHz, Ar = Aromatic ring): δ 2.17 (m, 6H, 2-H), 3.06 (t, 6H, 1-H), 3.66 (t, 6H, 3-H), 6.85 (m, 6H, Ar H), 7.24 (m, 6H, Ar H), 8.33 (s, 3H, 4-H), 12.80 (bs, 3H, OH); ^{13}C -NMR ($CDCl_3$, ppm, 300 MHz): δ 25.92 (C-2), 51.82 (C-1), 56.33 (C-3), 119.64 (C-5), 117.67, 119.30, 132.94, 133.67 (C-7 to C-10), 162.36 (C-6), 167.96 (C-4); IR (Nujol mull) cm^{-1} : 3000-2300 (b, ν_{O-H}), 1633.6, 1614.2 (sh), 1580, 1496.6 (s, $\nu_{C=N}$ and $\nu_{C=C}$); FAB MS (positive FAB in nitrobenzyl alcohol): m/z 501 (MH^+ , $[C_{30}H_{37}N_4O_3]^+$, 80%).

Tris(3-((4'-hydroxysalicylidene)imino)propyl)amine (H_3L2): This compound was prepared analogously using 4-hydroxysalicylaldehyde. Yield, 1.75g (80%); mp >170 °C (decom.); 1H -NMR (DMSO, ppm, 300MHz, Ar = Aromatic ring) δ : 1.05 (t, CH_3-CH_2OH), 1.69 (m, 6H, 2-H), 2.43 (t, 6H, 1-H), 3.4 (q, CH_3-CH_2OH), 3.5 (t, 6H, 3-H), 6.13 (m, 3H, Ar H), 6.21 (m, 3H, Ar H), 7.13 (m, 3H, Ar H), 8.30 (s, 3H, 4-H), 12.80 (bs, 6H, OH); ^{13}C -NMR (DMSO, ppm, 300 MHz) δ : 28.41 (C-2), 51.08 (C-1), 54.97 (C-3), 111.43 (C-5), 103.02, 106.98, 133.62 (C-7, C-9, C-10), 162.11, 165.76 (C-6, C-8), 164.95 (C-4); IR (Nujol mull) cm^{-1} : 3500-2500 (broad weak band, ν_{O-H}), 1636.8, 1607 sh (vs, $\nu_{C=N}$); FAB MS (positive FAB in nitrobenzyl alcohol): m/z 549 (MH^+ , $[C_{30}H_{37}N_4O_6]^+$, 20%).

Complex Synthesis

Both complexes were readily prepared by addition of H_3L1 (0.5mmol in 50mL methanol) to a solution of the appropriate metal nitrate (0.5 mmol in the same solvent). After the addition of NaOH (3mmol in 10 mL methanol-water), the reaction mixture was heated for 30 min. Evaporation of the solvent yielded the product as a green powder.

Ni(HL1)·2H₂O (1). Yield (0.18gr, 65%); Found: C, 60.5%; H, 5.6%; N, 9.1%. $C_{30}H_{38}N_4O_5Ni$ requires: C, 60.7%; H, 6.4%; N, 9.4%; FAB MS (positive FAB in nitrobenzyl alcohol): m/z 557 (MH^+ , $[C_{30}H_{35}N_4O_3Ni]^+$, 62%). IR (Nujol mull) cm^{-1} : 3345 (w, ν_{O-H}), 1629.5 s, 1610, 1590, 1533 ($\nu_{C=N}$ and $\nu_{C=C}$).

Cu(HL1) (2). Yield (0.17gr, 60%); FAB MS (positive FAB in nitrobenzyl alcohol): m/z 562 (MH^+ , $[C_{30}H_{35}N_4O_3Cu]^+$, 55%). IR (Nujol mull) cm^{-1} : 3300 (w, ν_{O-H}), 1619, 1599, 1536.5 ($\nu_{C=N}$ and $\nu_{C=C}$).

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Sample Availability: Available from the authors.