

Preparation and Characterization of Co(II), Ni(II) and Zn(II) Complexes Containing Diazine Ligands

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Preparation and characterization of some of Co(II), Ni(II) and Zn(II) complexes with diazine ligands including phthalazine, pyridazine and naphthyridines are reported. The complexes $[(\text{NH}_3)_4\text{CoL}_2](\text{ClO}_4)_3$ (L = phthalazine, pyridazine) were prepared by reaction of triflate complex $[\text{Co}(\text{NH}_3)_5\text{OSO}_2\text{CF}_3](\text{CF}_3\text{SO}_3)_2$ with the appropriate ligand in sulfolane. Also some complexes of naphthyridines with Co(II), Ni(II), Zn(II) were prepared by reaction of ML_2 salt (L = Cl) and the appropriate naphthyridine ligand. However, preparation of $[(\text{NH}_3)_4\text{CoL}_2](\text{ClO}_4)_3$ with L = naphthyridines was unsuccessful.

Key Words: Preparation, Characterization, Co(II), Ni(II), Zn(II), Complexes, Diazine ligands.

INTRODUCTION

Coordination of diazine ligands to transition metals has been the subject of several researches.^{1–8} While diazine ligands such as pyrazine and 1,5-naphthyridine can form complexes with transition metals in which they may behave either in mono or bidentate ligands^{1,2}, phthalazine, pyridazine and mono-substituted naphthyridines almost display as monodentate ligand. Robert and coworkers¹ have reported some complexes of Co(II), Ni(II), Zn(II) and Cu(II) with diazine ligands in which the ligand reacts as mono or bidentate depending on the nature of the metal, other ligands and reaction conditions. In this work we report the preparation and characterization of some complexes of diazine ligands including phthalazine, pyridazine and 1,5-naphthyridines coordinated to some transition metals.

EXPERIMENTAL

All chemicals were used as received. ¹H and ¹³C NMR spectra were recorded in D₂O on a Gemini 200 (MHz) spectrometer at 25.0 ± 0.5°C. Spectra are reported according to the convention: chemical shift (multiplicity, number of protons, s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Chemical shifts (ppm) are referenced to the internal standards 3-(trimethylsilyl)-2,2,3,3-tetra-deuteropropanoic acid, sodium salt (TSP-d₄) (¹H, 0.00 ppm) or dioxane (¹³C, 67.8 ppm). The IR spectra were recorded using Galaxy FTIR spectrometer.

$[(\text{NH}_3)_4\text{Co}(\text{Phtz})_2](\text{ClO}_4)_3$: A solution of $[(\text{NH}_3)_5\text{OSO}_2\text{CF}_3](\text{CF}_3\text{SO}_3)_2$ (**1g**) and phthalazine (0.5 g) in dry sulfolane was stirred for 40 min at 70°C. The solution was then cooled, diluted to 0.5 L with water and loaded onto Sephadex

SP C-25 cation-exchange resin. Elution with aqueous NaClO_4 (0.1 and 0.2 M) removed low-charged impurities and the orange band was removed using NaClO_4 (0.4–0.8 M). The first band (orange) was eluted, concentrated on a rotary evaporator and then cooled to give orange microcrystals which were collected, recrystallized from warm water by addition of NaClO_4 , washed with ethanol and ether, and dried in air (0.89 g). Microanalysis and NMR data (Signals integration) suggested this to be the bis-phthalazine complex, *cis*- $[(\text{NH}_3)_4\text{Co}(\text{Phtz})_2](\text{ClO}_4)_3$. Analysis: Calcd. for $\text{C}_{16}\text{H}_{24}\text{N}_8\text{CoCl}_3\text{O}_{12}$: C, 28.02; H, 3.53; N, 16.34; Cl, 15.51%. Found: C, 27.73; H, 3.50; N, 16.50; Cl, 15.44%. ^1H NMR (D_2O): $\delta = 9.89$ (s, 2H), 9.62 (s, 2H), 8.46–8.07 (m, 8H). ^{13}C NMR (D_2O): $\delta = 161.9, 156.0, 138.8, 136.6, 129.89, 128.7, 128.6, 128.1$.

$[(\text{NH}_3)_4\text{Co}(\text{Pydz})_2](\text{ClO}_4)_3$: A solution of pyridazine (1.50 g) and $[(\text{NH}_3)_5\text{CoOSO}_2\text{CF}_3](\text{CF}_3\text{SO}_3)_2$ (3 g) in dry sulfolane (30 mL) was stirred for 1 h at 70–80°C, then overnight at room temperature. The resulting orange solution was diluted with water to 1 L and sorbed on to a Sephadex SP C-25 cation-exchange column. A red band containing low-charged impurities was removed with NaClO_4 (0.1–0.3 M), and the desired orange band was then removed with NaClO_4 (0.5 M). The orange solution was concentrated until crystals began to form. It was then cooled and the orange microcrystals were collected, washed with ethanol and ether and air dried (0.80 g, 28%). Analysis: Calcd for $\text{C}_8\text{H}_{20}\text{N}_8\text{CoCl}_3\text{O}_{12}$: C, 16.41; H, 3.45; N, 19.14; Cl, 18.16%. Found: C, 15.76; H, 3.12; N, 19.09; Cl, 18.60%. ^1H NMR (D_2O): $\delta = 9.52$ (q, 2H), 9.03 (d, 2H), 8.20–8.10 (m, 4H). ^{13}C NMR (D_2O): $\delta = 160.4, 156.3, 134.7, 133.5$.

Preparation of naphthyridines: 2-Chloro- and 2-bromo-1,5-naphthyridine (abbreviated 2-Cl-Naph and 2-Br-Naph respectively) were prepared respectively by Skraup reaction of 2-chloro-5-aminopyridine and 2-bromo-5-aminopyridine with glycerol. The Hamada procedure⁹ with some variation was found to be more convenient than other methods.^{10–12} All compounds were recrystallized in chloroform and kept in a desiccator.

Preparation of Co(II), Ni(II), Zn(II) complexes: 1 mmol of metal chloride was dissolved in 25 mL of $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$ (1 : 1) with stirring. The appropriate ligand (excess equimolar) was added and the mixture stirred at 40–50°C for 10 min and then at room temperature until the colour changed. The product precipitated out of the solution as the reaction proceeded. It was filtered and washed with ether. Yields 40–50%.

$\text{CoCl}_2(6\text{-Cl-NaPh})_2$: Analysis: Calcd. for $\text{C}_{16}\text{H}_{10}\text{N}_4\text{CoCl}_4$: C, 41.84; H, 2.18; N, 12.20; Cl, 30.94%. Found: C, 41.75; H, 2.10; N, 12.01; Cl, 30.75%. IR (KBr): $\nu_{\text{max}} = 2700, 1631, 1404, 1116, 680, 569, 335 \text{ cm}^{-1}$.

$\text{CoCl}_2(6\text{-Br-NaPh})_2$: Analysis: Calcd. for $\text{C}_{16}\text{H}_{10}\text{N}_4\text{CoCl}_2\text{Br}_2$: C, 35.04; H, 1.83; N, 10.22; Cl, 12.96; Br, 29.20%. Found: C, 34.85; H, 1.70; N, 10.11; Cl, 12.81; Br, 29.10%. IR (KBr): $\nu_{\text{max}} = 1685, 1452, 1190, 848, 599, 266 \text{ cm}^{-1}$.

$\text{ZnCl}_2(6\text{-Cl-Naph})_2$: Analysis: Calcd. for $\text{C}_{16}\text{H}_{10}\text{N}_4\text{ZnCl}_4$: C, 41.29; H, 2.15; N, 12.04; Cl, 30.54%. Found: C, 41.11; H, 2.01; N, 11.91; Cl, 30.32%. IR (KBr): $\nu_{\text{max}} = 2350, 1647, 1404, 601, 270 \text{ cm}^{-1}$.

$\text{ZnCl}_2(6\text{-Br-Naph})_2$: Analysis: Calcd. for $\text{C}_{16}\text{H}_{10}\text{N}_4\text{ZnCl}_2\text{Br}_2$: C, 34.66; H,

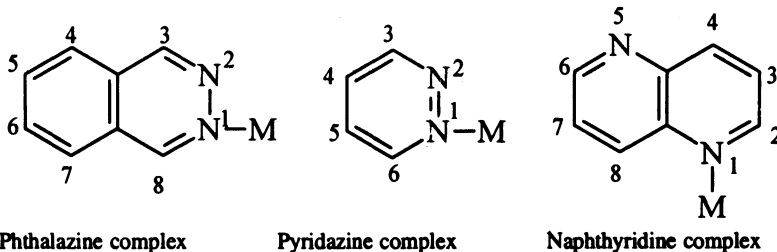
1.81; N, 10.11; Cl, 12.82; Br, 28.88%. Found: C, 34.45; H, 1.54; N, 9.83; Cl, 12.62, Br, 28.52%. IR (KBr): $\nu_{\max} = 2341, 1635, 1384, 572, 275 \text{ cm}^{-1}$.

NiCl₂(6-Cl-Naph)₂: Analysis: Calcd. for C₁₆H₁₀N₂NiCl₄: C, 41.86; H, 2.18; N, 12.21; Cl, 30.96; Found: C, 41.64; H, 1.95; N, 11.97; Cl, 30.71%. IR (KBr): $\nu_{\max} = 2750, 1791, 1645, 1384, 825, 680, 330 \text{ cm}^{-1}$.

NiCl₂(6-Br-Naph)₂: Analysis: Calcd. for C₁₆H₁₀N₂NiCl₂Br₂: C, 35.06; H, 1.83; N, 10.22; Cl, 12.96; Br, 29.21%. Found: C, 34.78; H, 1.63; N, 9.92; Cl, 12.69, Br, 28.94%. $\nu_{\max} = 2740, 1626, 820, 669, 340 \text{ cm}^{-1}$.

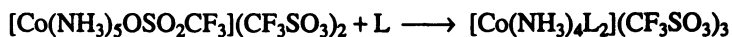
RESULTS AND DISCUSSION

Numbering systems for phthalazine, pyridazine and naphthyridine rings coordinated to metal ion (M) for all complexes are shown as:



in which nitrogen atom coordinated to the metal ion (M) is called N-1. Note that this numbering system differs from those for phthalazine and substituted naphthyridine but this numbering for pyridazine does not depend on whether it is bound to metal ion or not.

Bisphthalazine and bispyridazine, (NH₃)₄Co(Phtz)₂(ClO₄)₃ and [(NH₃)Co(Pydz)₂](ClO₄)₃, complexes were prepared easily by reaction of [(NH₃)₅CoOSO₂CF₃](CF₃SO₃)₂ with excess amount of phthalazine and pyridazine in dry sulfolane. Reactions were usually carried out at 70–80°C for 30 min to 1 h. Yields following isolation by ion exchange chromatography were of the order of 40–60% (Scheme-1).



(Scheme-1)

Reaction of 1,5-naphthyridines with [(NH₃)₅CoOSO₂CF₃](CF₃SO₃)₂ as labile triflate complex in dry acetone, sulfolane and DMSO at 70–80°C gave no reaction, with the purple colour of triflate complex remaining unchanged. Even dissolution of the triflate complex in molten 1,5-naphthyridine gave no reaction. The failure to prepare the naphthyridine complex was probably due to a combination of the low basicity of 1,5-naphthyridine (pK_a = 2.84)¹³ and unfavourable steric interactions between H-8 of the naphthyridine ligand and the (NH₃)₅Co³⁺ moiety. Attention then turned to preparation of naphthyridine complexes of Co(II), Ni(II) and Zn(II).

As the results show, all complexes of naphthyridines with Co(II), Ni(II) and Zn(II) complexes are ML₂X₂ type. This type of complexes has been reported by

Choudhary and coworkers.¹⁴ In ¹H NMR spectra of these compounds signals are very broad due to paramagnetic properties of the metal ions. The infrared spectra of these complexes look relatively similar. The band near 1500 cm⁻¹ in all naphthyridine complexes is assigned to the ring stretching vibrations, which increased its frequency due to complexation with metal ion. An increase in frequency of absorption near 600 cm⁻¹ is also due to coordination of the naphthyridine to metal. These absorptions could be assigned to in-plane ring deformations.^{15, 16} The bond in the range of 340–266 cm⁻¹ is assigned to $\nu(\text{M}-\text{N})$ frequencies.

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