

calculated from the ν_7 frequencies is 1.72 mdyne/Å and from the ν_3 frequencies is 1.58 mdyne/Å. The disagreement between these values is a measure of the approximations inherent in this approach. The values are intermediate in the range of the metal–nitrogen stretching force constants, $f(M-N)$, reported for numerous other metal–ammine complexes.^{20,23,24} The magnitude of these force constants decreases in the order Hg(II) > Pt(II) > Pd(II) > Co(III) > Ag(I) > Zn(II) > Cr(III) > Cu(II) > Ni(II) > Co(II) > Fe(II),²⁵ and the covalent character of the metal–nitrogen bonds is expected to show the same general trend. Although the uncertainties in the assignments and in the various force constant calculations somewhat limit the reliability of this approach in obtaining relative covalent character, it is interesting to note that Bjerrum's stability constant data²⁶ offer considerable

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(25) The Fe(II)–N force constant is estimated to be about 0.65 mdyne/Å from the reported stretching frequency: L. Sacconi, A. Sabatini, and P. Gans, *Inorg. Chem.*, **3**, 1772 (1964).

support for the indicated ordering of covalency (see Figure 5).

The bands in the region below 120 cm^{-1} are attributable to lattice vibrations. The low-temperature spectra show typical band sharpening and displacement to higher frequencies. The lattice bands observed appear to be of translational origin, since no significant frequency displacements result from deuteration of the ammine groups. From reduced mass considerations, deuteration would be expected to induce measurable frequency changes in the librational modes of the cations but not in the translational modes of the crystal lattice. The two bands at 161 and 139 cm^{-1} in the low-temperature spectrum of $[\text{Ag}(\text{ND}_3)_2]_2\text{SO}_4$ are tentatively assigned to the combination of L_1 (112 cm^{-1}) + L_5 (46 cm^{-1}) and to the overtone of L_4 (69 cm^{-1}), respectively. The weak bands consistently found near the ν_7 fundamentals are ascribed to a combination band of the type $\nu_{11} + \nu_4$.

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Transition Metal Complexes of 1,5-Diazanaphthalene¹

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Coordination compounds have been formed between 1,5-diazanaphthalene and CoCl_2 , $\text{Co}(\text{NCS})_2$, NiCl_2 , CuCl_2 , ZnCl_2 , and AgNO_3 . The complexes have been characterized by means of infrared spectra, visible spectra, and magnetic susceptibilities. 1,5-Diazanaphthalene behaves either as a bridging bidentate ligand or as a nonbridging monodentate ligand depending upon the metal and the reaction conditions.

Introduction

Complexes of aromatic, heterocyclic amines, especially pyridine, 1,10-*o*-phenanthroline, and dipyriddy, have been widely synthesized and characterized. Considerably less attention has been given to systems containing two or more nitrogen atoms and having a configuration which requires bridging if both nitrogens are involved in coordination. Lever and coworkers² have reported complexes of Co(II), Ni(II), and Cu(I) with pyrazine and methyl-substituted pyrazines. They found that some of the compounds were polymeric in nature owing to bridging pyrazine groups. Quinoxaline (1,4-diazanaphthalene) forms stable complexes with Cu(II) salts³ in contrast to Cu(II) com-

plexes of pyrazine which have a strong tendency to be reduced to Cu(I) compounds. The copper(II) quinoxaline adducts have been found to be analogous to the cobalt(II) and nickel(II) pyrazine complexes. Chelates of 4-hydroxy-1,5-diazanaphthalene have been reported^{4,5} but not characterized.

The similar nature of 1,5-diazanaphthalene (1,5-naphthyridine) compared to that of pyrazine led us to believe that complexes of the former should easily be prepared. Since the two nitrogens are in different rings, it was expected that 1,5-diazanaphthalene would be a somewhat stronger base than pyrazine (pyridine is a stronger base than pyrazine⁶) and would form bridged coordination compounds more readily. We wish to report the preparation of complexes of Co(II), Ni(II),

(1) Presented in part at the 18th Southeastern Regional Meeting of the American Chemical Society, Louisville, Ky., 1968.

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(b) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1235 (1962);

(c) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *ibid.*, 3156 (1963); (d) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *ibid.*, 5042 (1963).

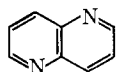
(3) A. E. Underhill, *ibid.*, 4336 (1965).

(4) A. Albert and A. Hampton, *ibid.*, 505 (1954).

(5) T. D. Eck, E. L. Wehry, Jr., and D. M. Hercules, *J. Inorg. Nucl. Chem.*, **28**, 2439 (1966).

(6) D. A. Keyworth, *J. Org. Chem.*, **24**, 1355 (1959).

Zn(II), and Ag(I) with 1,5-diazanaphthalene (designated Dnp).



1,5-diazanaphthalene



pyrazine

Experimental Section

1,5-Diazanaphthalene.—The ligand was prepared according to the method of Albert.⁷ It was purified by recrystallization from petroleum ether (bp 60–70°) followed by vacuum sublimation at 60°; mp 73.5–75°; lit.⁸ mp 74–75°. The ultraviolet and infrared spectra agreed with those of Rapoport⁹ and Armarego.⁹ *Anal.* Calcd for C₈H₆N₂: C, 73.82; H, 4.65. Found: C, 74.07; H, 5.32.

CoCl₂ · Dnp.—One gram of anhydrous CoCl₂ (prepared by dehydration of CoCl₂ · 6H₂O) was dissolved in 175 ml of acetone with heating. The residue was removed by filtration. Addition of 2 g of 1,5-diazanaphthalene to the solution gave an immediate light blue precipitate. The product was suction filtered and air dried. It is slightly soluble in 95% ethanol; dec pt >360°. *Anal.* Calcd for CoCl₂ · C₈H₆N₂: C, 37.0; H, 2.3; Co, 22.66. Found: C, 36.6; H, 1.7; Co, 22.01.

CoCl₂ · Dnp · 2HCl.—One gram of 1,5-diazanaphthalene (7.5 mmol) and 2.0 ml of concentrated HCl were added to a solution of 1.8 g of CoCl₂ · 6H₂O (8 mmol) in 75 ml of water. The solution was evaporated on a hot plate. When approximately 15 ml of solution remained, the color changed from violet to blue and at a volume of 10 ml or less a green precipitate formed. Evaporation was continued almost to dryness. The product was filtered, washed with absolute ethanol until the filtrate was nearly colorless, then washed with ether, and dried in an oven at 95° for 1 hr; dec pt 200°. *Anal.* Calcd for CoCl₂ · C₈H₆N₂ · 2HCl: C, 28.8; H, 2.4; N, 8.41; Co, 17.70; Cl, 42.58. Found: C, 28.7; H, 2.8; N, 8.63; Co, 17.92; Cl, 38.49.

Co(NCS)₂ · 2Dnp.—Co(NCS)₂ · 3H₂O (1.8 g, 8 mmol) was dissolved in 100 ml of water, and 1.1 g (8.5 mmol) of 1,5-diazanaphthalene was added to the solution. It was evaporated almost to dryness on a hot plate and the violet-pink precipitate was collected on a sintered-glass filter and washed with several portions of ice water. Drying in a desiccator caused the compound to turn blue. It is slightly soluble in ethanol and acetone; mp 308° dec. *Anal.* Calcd for Co(NCS)₂ · 2C₈H₆N₂: C, 49.7; H, 2.77; N, 19.3. Found: C, 47.7; H, 2.11; N, 17.7.

NiCl₂ · Dnp.—Two grams of NiCl₂ · 6H₂O (8 mmol) was dissolved in 75 ml of 95% ethanol. One gram of 1,5-diazanaphthalene (8 mmol) was dissolved in 25 ml of 95% ethanol and added to the nickel chloride solution. A pale yellow precipitate formed upon evaporation. It was suction filtered and air dried. It is insoluble in organic solvents; dec pt ~325°. *Anal.* Calcd for NiCl₂ · C₈H₆N₂: C, 36.98; H, 2.33; Ni, 22.60. Found: C, 38.97; H, 2.98; Ni, 22.29.

CuCl₂ · Dnp.—One gram of CuCl₂ · 2H₂O (6 mmol) was dissolved in 75 ml of 95% ethanol. Addition of 1.0 g of 1,5-diazanaphthalene (8 mmol) resulted in the formation of a green precipitate. The product was suction filtered, washed with ethanol, and air dried. It is insoluble in organic solvents; dec pt 285–295°. *Anal.* Calcd for CuCl₂ · C₈H₆N₂: C, 36.3; H, 2.3; Cu, 24.04. Found: C, 36.8; H, 2.2; Cu, 23.66.

2AgNO₃ · Dnp.—AgNO₃ (7.42 g, 43.7 mmol) was dissolved in 130 ml of a 77% methanol–water solution. Dropwise addition, with stirring, of 0.563 g (4.3 mmol) of 1,5-diazanaphthalene in 25 ml of methanol gave an immediate white precipitate. The

mixture was stirred for 1 hr, then suction filtered, and washed with 80% methanol–water; mp 293–294° dec. *Anal.* Calcd for 2AgNO₃ · C₈H₆N₂: C, 20.4; H, 1.28; N, 11.92. Found: C, 20.2; H, 1.18; N, 11.2.

AgNO₃ · Dnp.—AgNO₃ (0.726 g, 4.3 mmol) was dissolved in 10 ml of distilled H₂O. 1,5-Diazanaphthalene (0.556 g, 4.3 mmol) was dissolved in 10 ml of methanol. The AgNO₃ solution was added slowly to the Dnp solution with vigorous stirring. A white precipitate formed immediately. The mixture, after standing for 15 min with occasional stirring, was suction filtered and washed with 50% methanol–water, methanol, and ether; mp 295–296° dec. *Anal.* Calcd for AgNO₃ · C₈H₆N₂: C, 32.0; H, 2.01; N, 14.0. Found: C, 31.7; H, 2.79; N, 14.0.

ZnCl₂ · Dnp.—The compound was prepared in the same manner as CuCl₂ · Dnp. The cream-colored product melts with decomposition at 350–360°. *Anal.* Calcd for ZnCl₂ · C₈H₆N₂: C, 36.1; H, 2.3; Zn, 24.55. Found: C, 35.8; H, 2.6; Zn, 24.48.

C₈H₆N₂ · HClO₄.—The salt was isolated from an attempt to prepare a complex of a metal perchlorate. It is a white crystalline compound readily soluble in H₂O; mp 216–218° (detonates at a slightly higher temperature). *Anal.* Calcd for C₈H₆N₂ · HClO₄: HClO₄, 43.55. Found: HClO₄, 43.44 (by titration with standard NaOH).

Spectra.—Infrared spectra were obtained over the region 4000–300 cm⁻¹ as KBr pellets on a Perkin-Elmer Model 621 recording spectrophotometer. Visible spectra were obtained as mineral oil mulls on a Cary Model 14 recording spectrophotometer as described by Lee.¹⁰

Magnetic Moments.—Magnetic susceptibilities were obtained by the Gouy method using a permanent magnet developing approximately 5200 G. Hg[Co(NCS)₄] was used as a standard.

Results and Discussion

The infrared spectra of CoCl₂ · Dnp, NiCl₂ · Dnp, ZnCl₂ · Dnp, AgNO₃ · Dnp, and 2AgNO₃ · Dnp are all very similar to each other. Changes in frequency upon coordination are similar to those reported for complexes of pyridine.¹¹ The remaining compounds have additional absorptions in the region 900–1300 cm⁻¹; also Dnp · HClO₄ and CoCl₂ · Dnp · 2HCl have additional absorptions in the region 900–1100 cm⁻¹. Some selected absorptions are listed in Table I.

TABLE I

SELECTED INFRARED AND FAR-INFRARED ABSORPTIONS

Compound	Skeletal stretch	In-plane ring def	Out-of-plane ring def	$\nu(\text{M-Cl})$
Dnp	1494	617	403	
CoCl ₂ · Dnp	1508	639	434	
CoCl ₂ · Dnp · 2HCl	1480	614	387, 410	325
Co(NCS) ₂ · 2Dnp	1497	635	433	321 ^a
NiCl ₂ · Dnp	1511	631	438	
CuCl ₂ · Dnp	1506	640	439	316
ZnCl ₂ · Dnp	1510	653	438	335, 305
2AgNO ₃ · Dnp	1499	637	423	
AgNO ₃ · Dnp	1497	636	414	
Dnp · HClO ₄	1461			

^a $\nu(\text{Co-NCS})$.

The band in 1,5-diazanaphthalene near 1500 cm⁻¹, assigned to a skeletal stretching mode by Armarego,⁹ is increased in frequency upon complexation in all cases except Dnp · HClO₄ and CoCl₂ · Dnp · 2HCl. The ab-

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(10) R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 1278 (1964).

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sorptions near 600 and 400 cm^{-1} also show increases in frequency upon complexation except for $\text{CoCl}_2 \cdot \text{Dnp} \cdot 2\text{HCl}$. Absorptions in these regions have been assigned to in-plane ring deformations in pyridine¹¹ and should be similar in 1,5-diazanaphthalene. Increases in frequency have been noted in these three bands in pyridine upon complexation with metals.^{11,12}

The $\text{Co}(\text{NCS})_2 \cdot 2\text{Dnp}$ complex has absorptions at 2070 and 814 cm^{-1} and a doublet at 741 and 478 cm^{-1} which are in the ranges attributed to nitrogen-bonded NCS groups by Clark and Williams.¹³ Both AgNO_3 complexes have absorptions at 1483 and 833 cm^{-1} which are indicative of ionic NO_3^- ions.¹⁴ A very weak band often present at 720 cm^{-1} was not observed.

The visible and near-infrared spectral data were obtained as mineral oil mulls rather than in solution owing to their insolubility in suitable solvents. Absorptions are given in cm^{-1} and relative absorbance values are listed with the strongest absorption in each case assigned a value of 1.0.

$\text{NiCl}_2 \cdot \text{Dnp}$.—All data indicate that this complex is a polymeric tetragonal compound. This type of structure with one bidentate ligand and two chloride ions per metal requires that the chloride ions serve as bridging ligands in addition to the 1,5-diazanaphthalene. The magnetic moment of 3.32 BM is within the range normally observed for tetragonally distorted octahedral nickel complexes.¹⁵ The visible and near-infrared spectrum obtained at liquid nitrogen temperature is similar to that reported by Rowley and Drago.¹⁶ The bands observed are 6280 (0.69), 7870 (0.31), 10,200 (0.56), 12,900 (0.32), 13,300 (sh), 22,100 (sh), 23,000 (1.0), and 25,400 (sh) cm^{-1} .

The lowest energy transition 6280 cm^{-1} has been assigned to $10Dq^{xy}$.¹⁶ This value for Dq for bridging chloride ions of 628 cm^{-1} compares to a value of 627 cm^{-1} reported for $\text{Ni}(\text{py})_2\text{Cl}_2$.¹⁶ Using the method of Brubaker and Busch,¹⁷ we calculate a value for Dq^z of 946 cm^{-1} . This method neglects off-diagonal elements and has been shown to introduce an error of about 10%,¹⁶ but, for comparison purposes, it is sufficiently accurate. For apical pyridine molecules, Dq^z has been reported as 1200 cm^{-1} . The ligand field strength of 1,5-diazanaphthalene is less than that of pyridine. This is in line with the base strengths of these ligands. However, steric factors^{2d} do influence metal-ligand bond lengths and we cannot estimate the relative differences in interligand repulsions in these cases.

$\text{Co}(\text{NCS})_2 \cdot 2\text{Dnp}$.—The infrared absorption bands due to the thiocyanate group are typical of terminal nitrogen-bonded NCS^- .¹³ The magnetic moment of 4.63 BM is within the range normally observed for tetrahedral cobalt(II) complexes.¹⁸ The stoichiometry

found, combined with this information, requires that the 1,5-diazanaphthalene ligands be bonded to cobalt by one nitrogen only. Lever, *et al.*,^{2b} reported that pyrazine bonded at one end only to a metal atom has one more infrared absorption than corresponding complexes with a metal at both ends. This extra absorption occurs in the region 8–11 μ . We find an extra absorption in this region at 1114 cm^{-1} . Visible and near-infrared absorptions are 8510 (0.16), 9850 (0.16), 16,400 (1.0), 17,900 (0.80), 20,400 (0.08), and 26,700 (sh) cm^{-1} . Absorption in the region of 16,500 cm^{-1} does not disagree with a tetrahedral configuration but the inability to calculate molar extinction coefficients does not aid in interpretation of absorption in this region. Absorptions in the far-infrared spectrum about 320 and 280 cm^{-1} are assigned to metal-NCS stretching frequencies for tetrahedral cobalt(II) compounds.¹³ We observe a medium-strength band at 321 cm^{-1} providing further indication of the tetrahedral configuration of this complex.

$\text{CoCl}_2 \cdot \text{Dnp}$.—The data available for this complex suggest a polymeric octahedral structure. The magnetic moment of 5.29 BM is typical for octahedral structures and a light blue color has been observed for octahedral cobalt(II) complexes.¹⁰ Visible and near-infrared absorptions are 8230 (0.12), 14,600 (0.88), 16,800 (1.0), 18,500 (0.67), and 22,500 (sh) cm^{-1} . The absorption centered around 16,000 cm^{-1} is assigned to the transition ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ and that at 8230 cm^{-1} to ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$.

$\text{CoCl}_2 \cdot \text{Dnp} \cdot 2\text{HCl}$.—The over-all picture presented for this compound leads us to propose that the structure is $[\text{DnpH}_2][\text{CoCl}_4]$. The mull spectrum absorptions are 8000 (0.11), 14,600 (0.71), 15,700 (0.71), 16,300 (0.58), 16,800 (0.45), 18,900 (0.04), and 31,300 (1.0) cm^{-1} . It was possible to dissolve this complex in reagent grade acetone to the extent of 10^{-4} M . The spectrum is identical with that of the mull with approximate molar extinction coefficients for the three principal bands: 14,600 cm^{-1} , ϵ 500; 16,800 cm^{-1} , ϵ 300; 31,300 cm^{-1} , ϵ 1100. The position and general shape of the absorptions in the region 14,000–18,000 cm^{-1} are identical with those for CoCl_4^{2-} .^{19,20} The magnetic moment of 4.63 BM is also close to that reported for CoCl_4^{2-} .¹⁸

Changes in the infrared spectra upon forming $\text{Dnp} \cdot \text{HClO}_4$ and $\text{CoCl}_2 \cdot \text{Dnp} \cdot 2\text{HCl}$ are observed which are similar to changes observed upon forming $\text{C}_5\text{H}_5\text{NH}^+$ salts.^{11,12} The absorption in pyridine at 1578 cm^{-1} decreases in frequency, the absorption in pyridine at 604 cm^{-1} increases very slightly, and the band at 405 cm^{-1} decreases by ~ 16 cm^{-1} with decreased intensity.

We also observe a decrease in the corresponding absorption going from 1,5-diazanaphthalene (1494 cm^{-1}) to the HClO_4 salt (1461 cm^{-1}) and $\text{CoCl}_2 \cdot \text{Dnp} \cdot 2\text{HCl}$ (1480 cm^{-1}). We have noted that the 617- cm^{-1} band in 1,5-diazanaphthalene is essentially unchanged (614 cm^{-1}) in $\text{CoCl}_2 \cdot \text{Dnp} \cdot 2\text{HCl}$. However, in the region of

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the 403-cm^{-1} band we find two bands at 387 and 410 cm^{-1} . The complexity of the spectra of pyridinium salts is greater than that of pyridine in the region $1100\text{--}650\text{ cm}^{-1}$. We have noted this increase in the number of absorptions in both $\text{HClO}_4 \cdot \text{Dnp}$ and $\text{CoCl}_2 \cdot \text{Dnp} \cdot 2\text{HCl}$.

Clark¹² assigned absorption in the range $320\text{--}350\text{ cm}^{-1}$ to Co-Cl stretching for tetrahedral complexes. Octahedral complexes have this vibration at lower frequencies. We observe a band at 325 cm^{-1} which appears to be a Co-Cl frequency.

$\text{CuCl}_2 \cdot \text{Dnp}$.—The observed magnetic moment of 1.77 BM agrees very well with the spin-only value of 1.73 BM for one unpaired electron. The visible absorptions at $13,000$ and $15,200\text{ cm}^{-1}$ are very broad with an over-all band width of about 2000 cm^{-1} . In the far-infrared spectrum Clark and Williams¹² assigned a band at 294 cm^{-1} in $\text{CuCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, a distorted polymeric octahedral compound, to the copper-chlorine stretching vibration. We observe a well-defined, medium-strength band at 316 cm^{-1} which we believe to be the copper-chlorine stretching frequency.

There are no bands in the region $500\text{--}300\text{ cm}^{-1}$ which we can interpret as metal-nitrogen vibrations. Owing to experimental difficulties, we were unable to measure the spectra below 300 cm^{-1} where metal-Dnp vibrations would be expected.¹² The primary factor in determining the metal-ligand vibration appears to be mass, and since metal-pyridine vibrations are in the range $200\text{--}287\text{ cm}^{-1}$, the larger mass of Dnp would place metal-Dnp vibrations below those of pyridine complexes.

$\text{ZnCl}_2 \cdot \text{Dnp}$.—In the absence of chloride bridging, with the stoichiometry found, we expect the geometry of $\text{ZnCl}_2 \cdot \text{Dnp}$ to be tetrahedral. Zinc-chlorine stretching frequencies in tetrahedral $\text{ZnCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ at 329 and 296 cm^{-1} have been reported.¹² We observe strong absorptions at 335 and 305 cm^{-1} which we also interpret to be zinc-chlorine stretching frequencies. The positions of frequencies such as these are often indicative of geometry involved¹² and the similarity between the pyridine and the 1,5-diazanaphthalene complexes lends support to a tetrahedral configuration in $\text{Zn}(\text{Dnp})\text{Cl}_2$.

$\text{AgNO}_3 \cdot \text{Dnp}$ and $2\text{AgNO}_3 \cdot \text{Dnp}$.—From the stoichiometry exhibited, we expect the 2:1 complex to be monomeric with the 1,5-diazanaphthalene bridging between the two silver ions, $[\text{Ag}_2(\text{Dnp})](\text{NO}_3)_2$. The 1:1 complex is expected to be a linear polymer $[\text{Ag}(\text{Dnp})]_n(\text{NO}_3)_n$ also having bridging 1,5-diazanaphthalene molecules. The infrared spectra of the two complexes are very similar, but this would be expected since both contain the ligand in essentially the same environment between two silver ions. The similarities in melting points may be accounted for by the differences in behavior upon heating. The 2:1 complex turns dark gradually beginning at a much lower temperature than the 1:1 complex. At the melting point, the 2:1 complex is very dark while the 1:1 complex is slightly darkened. Perhaps the 2:1 complex decomposes into the 1:1 complex. The solubility behavior is also indicative of structure. The ionic monomer $2\text{AgNO}_3 \cdot \text{Dnp}$ is more soluble in the polar solvent, water, and less soluble in the less polar solvent, absolute ethanol, than is the polymer $\text{AgNO}_3 \cdot \text{Dnp}$. The ethanol solution of $\text{AgNO}_3 \cdot \text{Dnp}$ rapidly darkens.