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# Complexes of N-(2-benzothiazole)-2-pyridinaldimine with Co$^{II}$ and Ni$^{II}$ Salts

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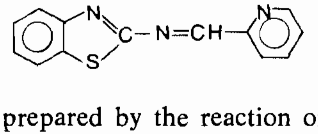
*The following complexes of N-(2-benzothiazole)-2-pyridinaldimine (L) with Co$^{II}$ and Ni$^{II}$ salts have been isolated:*
$Co(L)_2(ClO_4)_2 2H_2O$, $Co(L)_2(NO_3)_2H_2O$, $Co(L)_2SO_4H_2O$, $Ni_2(L)_4Cl_4H_2O$, $Ni(L)_2(CH_3COO)_2H_2O$, $Ni(L)_3(ClO_4)_2 2H_2O$, $Ni(L)_2(NO_3)_2H_2O$. *The ligand acts as a bidentate chelating agent trough both nitrogen atoms of the 2-pyridinaldimine system. The electronic spectra and magnetic properties are consistent with an octahedral coordination for all the complexes. The infrared spectra* (4000-250 $cm^{-1}$) *of the ligand as well as those of Co$^{II}$ and Ni$^{II}$ complexes are also discussed.*

## Introduction

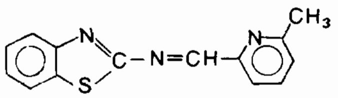
A large number of metal complexes containing the α-diimine grouping $-N=C-C=N-$ in the ligand molecule have been prepared in recent years and their properties were studied using several physical methods.[1,2,3,4] Examples of this type of ligand include expecially 2,2'-bipyridyl and 1,10-phenanthroline. It is also known that heterocyclic nitrogen atoms in five-membered rings, such as benzothiazole, have coordinating properties, although they are less favourably positioned for coordination to a metal ion than are the donor nitrogens in, *e.g.*, 2,2'-bipyridyl. The coordination behaviour of benzothiazole and some 2-substituted benzothiazoles in several complexes has been extensively reviewed in recent publications.[2,3,4,5,6]

We have synthesized the N-(2-benzothiazole)-2-pyridinaldimine,



which was prepared by the reaction of 2-aminobenzothiazole with 2-pyridinaldehyde. This molecule has several potential sites for coordination. Foremost is the methine linkage $-N=C-C=N-$ associated with the pyridinaldimine moiety; there is, in addition, the sulphur or nitrogen atom of the benzothiazole ring.

The present investigation concerns the synthesis and characterisation of some Co$^{II}$ and Ni$^{II}$ complexes formed by N-(2-benzothiazole)-2-pyridinaldimine whose spectral and magnetic properties have also been determined. In addition, it is our intent to extend this investigation to coordinating properties of N-(2-benzothiazole)-6-methyl-2-pyridinaldimine



in metal chelates in order to examine the effect of a methyl group in the α-position of the pyridyl ring; this substituent should alter the steric requirements and the donor properties of the ligand.

## Experimental Section

*Analyses.* Carbon, hydrogen, and nitrogen analyses were carried out by the Laboratorio di Microanalisi dell'Istituto di Chimica Farmaceutica dell'Università di Parma. Metals were determined gravimetrically using standard methods. The water determination was carried out by Karl Fischer method for all the complexes, except $Ni_2(L)_4Cl_4H_2O$.

*Physical Measurements.* The infrared spectra were determined using the KBr discs technique, in the 4000-250 cm$^{-1}$ region, using a Perkin-Elmer Mod. 457 double-beam instrument. The electronic spectra were recorded in methanol solutions from 400 to 1100 mμ using a DK–2 Beckman spectrophotometer. The magnetic susceptibility data were obtained at 25° C on solid powdered samples by a Gouy balance (Newport Instruments).

*N-(2-benzothiazole)-2-pyridinaldimine.* This compound was prepared by adding 2-pyridinaldehyde (10.7g) to 2-aminobenzothiazole (15g), dissolved in methanol. The solution was refluxed for two hours, after which the solvent was removed by vacuum evaporation. The crude solid remaining was washed several times with benzene and recrystallized from this solvent. The cream coloured crystalline product (m.p. 159-160°C) is soluble in chloroform, dimethyl sulphoxide, methanol, and benzene.

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*Preparation of the complexes.* All the complexes were prepared by the same general method: a methanol solution of the ligand was added slowly to a solution of the transition metal salt, in the same solvent. The reaction mixture was then heated on a water-bath (70-80° C) for an hour and allowed to stand at room temperature until complete precipitation of the product, which was then filtered and washed with cold methanol and ether and dried in air. The following complexes with the ligand (L = N-(2-benzothiazole)-2-pyridinaldimine) have been isolated: $Co(L)_2(ClO_4)_2 2H_2O$; $Co(L)_2(NO_3)_2H_2O$; $Co(L)_2SO_4H_2O$; $Ni_2(L)_4Cl_4 H_2O$; $Ni(L)_2(CH_3COO)_2H_2O$; $Ni(L)_3(ClO_4)_2 2H_2O$; $Ni(L)_2(NO_3)_2H_2O$.

The complexes can also be isolated from a methanol solution in which the formation of the ligand from 2-pyridinaldehyde and 2-aminobenzothiazole occurs in the presence of the transition metal salt. The analytical data are as follows:

*Bis[-(2-benzothiazole)-2-pyridinaldimine]cobalt(II) Perchlorate Dihydrate. Anal.* Calcd for $C_{26}H_{22}Cl_2CoN_6O_{10}S_2$: C, 40.4; H, 2.9; Co, 7.6: N, 10.9; $H_2O$, 4.7. Found: C, 40.5; H, 2.8; Co, 7.6; N, 11.3; $H_2O$, 4.4.

*Bis[N-(2-benzothiazole)-2-pyridinaldimine]cobalt(II) Nitrate Monohydrate. Anal.* Calcd for $C_{26}H_{20}CoN_8O_7S_2$: C, 46.0; H, 3.0; Co, 8.7; N, 16.5; $H_2O$, 2.6. Found: C, 46.4; H, 3.3; Co, 8.5; N, 16.8; $H_2O$, 2.9.

*Bis[-(2-benzothiazole)-2-pyridinaldimine]cobalt(II) Sulphate Monohydrate. Anal.* Calcd for $C_{26}H_{20}CoN_6O_5S_3$: C, 47.9; H, 3.1; Co, 9.0; N, 12.9; $H_2O$, 2.8. Found: C, 47.6; H, 3.3; Co, 8.8; N, 13.2; $H_2O$, 3.0.

Diacetatobis[N-(2-benzothiazole)-2-pyridinaldimine]*nickel(II) Monohydrate. Anal.* Calcd for $C_{30}H_{26}N_6NiO_5S_2$: C, 53,5; H, 4.0; N, 12.5; Ni, 8.7; $H_2O$, 2.7. Found: C, 52.8; H, 3.7; N, 12.6; Ni, 8.4; $H_2O$, 3.1.

*Tris[N-(2-benzothiazole)-2-pyridinaldimine]nickel(II) Perchlorate Dihydrate. Anal.* Calcd for $C_{39}H_{31}Cl_2N_9NiO_{10}S_3$: C, 46.3; H, 3.1; N, 12.5; Ni, 5.8; $H_2O$, 3.6. Found: C, 45.7; H, 2.9; N, 12.9; Ni, 5.2; $H_2O$, 3.7.

*Bis[N-(2-benzothiazole)-2-pyridinaldimine]nickel(II) Nitrate Monohydrate. Anal.* Calcd for $C_{26}H_{20}N_8NiO_7S_2$: C, 46.0; H, 3.0; N, 16.5; Ni, 8.6; $H_2O$, 2.7. Found: C, 46.4; H, 3.2; N, 16.8; Ni, 8.4; $H_2O$, 2.2.

*Tetrachlorotetrakis[N-(2-benzothiazole)-2-pyridinaldimine]dinickel(II) Monohydrate. Anal.* Calcd for $C_{52}H_{38}Cl_4N_{12}Ni_2OS_4$: C, 50.6; H, 3.1; N, 13.6; Ni, 9.5. Found: C, 50.2; H, 3.7; N, 13.5; Ni, 8.8.*

## Results and Discussion

All the complexes are insoluble in water, as well as in all common organic solvents except for hot methanol, from which they recrystallized. The $Co^{II}$ complexes are orange or pink, while the $Ni^{II}$ compounds are blue or mauve. Attempts to obtain cupric complexes of N-(2-benzothiazole)-2-pyridinaldimine have not met with success. The complex with $Co^{II}$ chloride also has not yet been isolated; the corresponding complex of the 2-aminobenzothiazole, which is formed from the hydrolysis of the Schiff base, has always precipitated from the reaction of the ligand with $CoCl_2 6H_2O$.

*Infrared Spectra.* Table I and II list the infrared spectra (in the 4000-250 cm$^{-1}$ region) of the N-(2-benzothiazole)-2-pyridinaldimine as well as those of $Co^{II}$ and $Ni^{II}$ complexes. All the spectra are complicated by the presence in the ligand molecule of two six-membered aromatic rings in different environments and of a thiazole system. This is particularly evident in the frequency range 1600-1400 cm$^{-1}$ where the vibrations of pyridine and benzene rings occur.

The infrared spectrum of the ligand confirms that the Schiff base condensation has occurred, since the spectrum contains no bands in the region above 3080 cm$^{-1}$.

The vibrations of interest are the $\nu(C=C)$, $\nu(C=N)$ bands observed between 1450 and 1600 cm$^{-1}$ (1600, 1590, 1560, 1550, 1520, 1470, 1450 cm$^{-1}$); the ring-breathing mode near 1000 cm$^{-1}$; the Hydrogen deformation modes at 750-740 cm$^{-1}$ and 720-715 cm$^{-1}$ for phenyl and pyridyl rings; an out-of-plane C–C deformation at 400 cm$^{-1}$. The strong broad band between 1540 and 1505 cm$^{-1}$ (with maximum at 1520 cm$^{-1}$) can be assigned to different vibrational stretching modes ($\nu(C=N)$ of the thiazole ring; a vibrational mode of the $\alpha$-monosubstituted pyridine; $\nu(C=N)$ of the Schiff base). A similar, but less intense band does appear at 1520 cm$^{-1}$, in the spectrum of 2-aminobenzothiazole, which was assigned to the C=N stretching vibration of the thiazole ring.

The infrared spectra of all the complexes are closely similar except for the presence in the spectrum of bands which have been attributed to anions; the only significant differences concern the pyridine ring vibrational bands with respect to the values found for the ligand and a decrease of 1520 cm$^{-1}$ band intensity. In particular, a strong broad band is observed at 1620-1590 cm$^{-1}$, which can be assigned to the pyridine ring. This increase in frequency from the free-ligand is indicative of the coordination of pyridine nitrogen to a metal atom, as well as the other bands: 1570, 1530, 1470, 1450, 1020, 750, 640, 420 cm$^{-1}$.

The decreased C=N stretching intensity (at 1520 cm$^{-1}$) is probably due to a coordination effect of the ligand, which decreases the electron delocalisation of the conjugated system.

All the complexes exhibit two broad bands, at 3400 cm$^{-1}$ and ~3160 cm$^{-1}$, which can be assigned to the OH stretching of the water molecules.

Below 600 cm$^{-1}$ it is not possible to positively assign bands to metal-nitrogen stretching vibration.

Concerning the anions (Table II), the following assumptions can be made: the infrared spectrum of $Co(L)_2SO_4H_2O$ displays $\nu_3$ of the sulphate group as a single broad band at about 11120 cm$^{-1}$ and $\nu_4$ at about 615 cm$^{-1}$. No definite absorptions attributable

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* The direct determination of water was impossible as the quantity of the compound, remained after the other determinations, was too small. The corresponding per cent was deduced indirectly from the other data; the presence of water is supported also by the infrared spectrum.

**Table I.** Infrared Absorption Bands in the 4000-250 cm$^{-1}$ Region of Pyridine and Benzothiazole Rings.

| L | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| 3060w | 3060m | 3060m | 3060m | 3060m | 3060m | 3060m | 3060m |
| 3030vw | — | — | — | — | — | — | — |
| 2970br | 2980m | 2950br | 2960m | 2970m | 2960m | 2960m | 2960m |
| — | 2960sh | — | — | — | — | — | — |
| 1600s | 1620vs | 1610vs | 1610vs | 1610sh | 1605vs | 1605vs | 1605s |
| 1590s | 1590sh | 1585sh | 1585sh | 1585vs | 1585sh | 1585sh | 1585sh |
| 1560s | 1570s | 1570s | 1570s | 1560s | 1570vs | 1570s | 1570s |
| 1550s | 1560sh | 1560sh | 1560sh | — | 1560sh | — | — |
| 1520vs | 1530s | 1530s | 1530s | 1530s | 1530s | 1530s | 1530s |
| — | — | — | 1505sh | — | 1505sh | 1505sh | 1505sh |
| 1470s | 1470s | 1470s | 1470s | 1470m | 1470s | 1470s | 1470s |
| 1450s | 1453s | 1450s | 1450s | 1445s | 1450s | 1450s | 1450s |
| 1440vs | — | — | — | — | — | — | — |
| 1320m | 1320m | 1320m | 1330m | 1320m | 1325m | 1320m | 1320m |
| 1285m | 1280m | 1280m | 1280m | 1280m | 1280m | 1280m | 1280m |
| 1220m | 1225m | 1225m | 1225m | 1225m | 1225m | 1225sh | 1225sh |
| 1000m | 1020m | 1020m | 1020s | 1020m | 1020m | 1020m | 1020m |
| 880m | 875m | 870m | 870m | 870m | 870m | 870m | 870m |
| 750s | 750vs | 750s | 750s | 750s | 750s | 750s | 750s |
| 740s | — | — | — | 740s | — | — | — |
| 720m | 720m | 725w | 730w | 720m | 725w | 720w | 720w |
| 715s | — | — | — | — | — | — | — |
| 620w | 640m | — | 630w | 640m | — | 630w | 655m |
| 400w | 420m | 420w | 420w | 420w | 420w | 420w | 420w |

L = N-(2-benzothiazole)-2-pyridinaldimine; A = $Ni_2(L)_4Cl_4H_2O$; B = $Ni(L)_3(ClO_4)_2 2H_2O$; C = $Ni(L)_2(NO_3)_2H_2O$; D = $Ni(L)_2(CH_3COO)_2H_2O$; E = $Co(L)_2(ClO_4)_2 2H_2O$; F = $Co(L)_2(NO_3)_2H_2O$; G = $Co(L)_2SO_4H_2O$; w = weak; vw = very weak; m = medium; br = broad; sh = shoulder; s = strong; vs = very strong.

**Table II.** Selected Infrared Assignments for Ni$^{II}$ and Co$^{II}$ Complexes of N-(2-benzothiazole)-2-pyridinaldimine(L).

| complex | band (cm$^{-1}$) | assignment |
|---|---|---|
| $Co(L)_2(ClO_4)_2 2H_2O$ | 1140sh, 1110vs, 1085sh | ν(Cl—O) |
| | 940w | ν(Cl—O) |
| | 630-620s | δ(O—Cl—O) |
| $Co(L)_2(NO_3)_2H_2O$ | 1380vs | ν(N—O) |
| | 820w | δ($NO_3$) |
| $Co(L)_2SO_4H_2O$ | 1115s | ν(S—O) |
| | 615s | δ(O—S—O) |
| $Ni(L)_3(ClO_4)_2 2H_2O$ | 1140sh, 1110vs, 1085sh | ν(Cl—O) |
| | 940w | ν(Cl—O) |
| | 630-620s | δ(O—Cl—O) |
| $Ni(L)_2(CH_3COO)_2H_2O$ | 1620vs | $\nu_{as}$(C—O) |
| | 1410s | $\nu_s$(C—O) |
| $Ni(L)_2(NO_3)_2H_2O$ | 1380vs | ν(N—O) |
| | 825w | δ($NO_3$) |

s = strong; vs = very strong; m = medium; w = weak; sh = shoulder.

**Table III.** Magnetic Data of Metal Complexes of N-(2-benzothiazole)-2-pyridinaldimine (L).

| Compound | Color | Molar magnetic susceptibility $10^6\chi'_M$* | Magnetic moment μ(B.M.) |
|---|---|---|---|
| $Co(L)_2(ClO_4)_2 2H_2O$ | orange | 8267.5 | 4.46 |
| $Co(L)_2(NO_3)_2H_2O$ | pink | 6101.0 | 3.83 |
| $Co(L)_2SO_4H_2O$ | pink | 11242.9 | 5.19 |
| $Ni(L)_3(ClO_4)_2 2H_2O$ | mauve | 4047.3 | 3.12 |
| $Ni_2(L)_4Cl_4H_2O$ | blue | 4279.7 | 3.20 |
| $Ni(L)_2(CH_3COO)_2H_2O$ | mauve | 4802.1 | 3.39 |
| $Ni(L)_2(NO_3)_2H_2O$ | mauve | 3193.6 | 2.77 |

* Corrected for diamagnetism[7].

to $\nu_1$ and $\nu_2$ appear. This data indicates that the sulphate group is ionic. The complex $Ni(L)_2(CH_3COO)_2$-$H_2O$ exhibits bands at 1620 and 1410 cm$^{-1}$ attributed to the antisymmetric and symmetric carboxyl stretching frequencies, respectively. The difference of 210 cm$^{-1}$ between the positions of these two bands is consistent with monodentate acetate groups. The infrared spectra of Co$^{II}$ and Ni$^{II}$ perchlorates consist of a strong broad band with a poorly defined maximum at 1110 cm$^{-1}$, a very weak absorption at 940 cm$^{-1}$, and a double peak at 630-620 cm$^{-1}$; this suggest that the perchlorate group in these complexes is

**Table IV.** Electronic Absorption Bands of $Co^{II}$ and $Ni^{II}$ Complexes.

| Compnud | λ(mμ) | |
|---|---|---|
| | $^4T_{1g} \leftarrow {}^4T_{1g}(F)$ | $^4T_{2g} \leftarrow {}^4T_{1g}(F)$ |
| $Co(L)_2(ClO_4)_2 2H_2O$ | 490 | 950 |
| $Co(L)_2(NO_3)_2H_2O$ | 485 | 940 |
| $Co(L)_2SO_4H_2O$ | 480 | 930 |
| | $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ | $^3T_{2g}(F) \leftarrow {}^3A_{2g}$ |
| $Ni(L)_3(ClO_4)_2 2H_2O$ | 540 | 900 |
| $Ni_2(L)_4Cl_4H_2O$ | 540 | 870 |
| $Ni(L)_2(CH_3COO)_2H_2O$ | 580 | 950 |
| $Ni(L)_2(NO_3)_2H_2O$ | 540 | 930 |

L = N-(2-benzothiazole)-2-pyridinaldimine.

present as an ionic species.

The $Ni(L)_2(NO_3)_2H_2O$ and $Co(L)_2(NO_3)_2H_2O$ complexes, which have infrared spectra characteristic of ionic nitrate, show two bands: $\nu_2$ (out-of-plane deformation) and $\nu_3$ (doubly degenerate stretch) at 825 and 1380 $cm^{-1}$ respectively. For the chloride compound, no conclusive evidence for Ni—Cl vibrations could be found.

*Magnetic Properties.* The magnetic moments (see Table III) were calculated from the expression $\mu_{eff} = 2.84\sqrt{\chi'_M T}$ B.M. where $\chi'_M$ is the molar susceptibility corrected using Pascal's constants.[7]

All the nickel complexes are paramagnetic and exhibit magnetic moments near 3 B.M., which are within the range expected for high-spin octahedral $Ni^{II}$. The cobalt complexes also are paramagnetic, their magnetic moments ranging from 3.8 to 5.2 B.M. The lower values are probably related to the distorsion of the octahedral environment or to an equilibrium between a high-spin octahedral state and a low-spin state; diamagnetic impurities would not be present, because several determinations were made on the samples after successive purifications. On the other hand, anomalously low values are sometimes observed in $Co^{II}$ and $Ni^{II}$ six-coordinated complexes: *e.g.*: $Ni(en)_3SO_4$[8] = 2.82 B.M.; $Ni(en)_3SO_3H_2O$[8] = 2.82 B.M.; $Co(bipy)_2(CN)_2$[1] = 3.65 B.M.; $Co(terpy)_2I_2$[9] = 3.97 B.M.; $Co(PMH)_3I_2$ = 4.21[10] B.M.

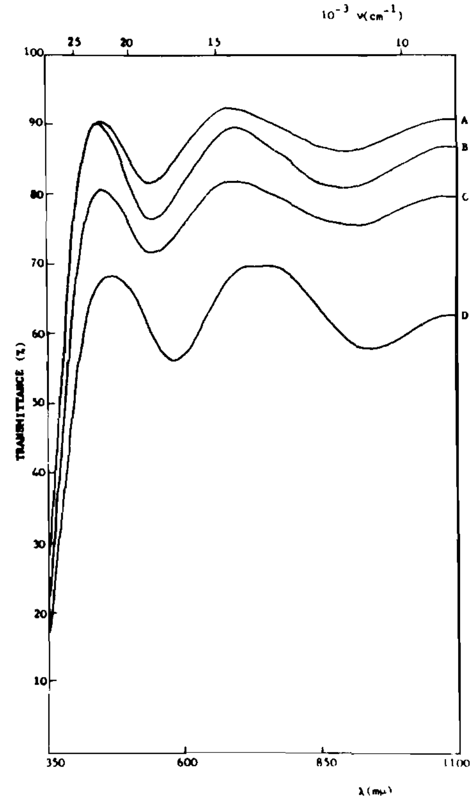

Figure 1. Electronic spectra of nickel complexes. A, $Ni(L)_3(ClO_4)_2 2H_2O$; B, $Ni_2(L)_4Cl_4H_2O$; C, $Ni(L)_2(NO_3)_2H_2O$; D, $Ni(L)_2(CH_3COO)_2H_2O$.

*Electronic Spectra.* The absorption spectra )350-1100 mμ) of the $Ni^{II}$ compounds, in methanol, are given in Figure 1; they show two absorption bands with maxima at about 500 mμ and 900 mμ, which are typical of high-spin octahedrally coordinated nickel. Table IV lists the absorption values with their relative assignments. The band observed near 900 mμ in each complex can safely be attributed to the $^3T_{2g} \leftarrow {}^3A_{2g}$ transition of an octahedral nicekl ion.[9]

The electronic spectra of the $Co^{II}$ complexes (Table IV) display bands of very weak intensity. The band near 940 $cm^{-1}$ is assigned to the $^4T_{2g} \leftarrow {}^4T_{1g}$ transition of a six-coordinate cobalt atom.[9]

The diffuse reflectance spectra, which exhibit absorption bands at essentially the same positions, confirm the assignment of octahedral structure for the whole series.

## Conclusions

As a result of the investigations described in this paper, the following conclusions may be drawn: the N-(2-benzothiazole)-2-pyridinaldimine forms complexes with some $Co^{II}$ and $Ni^{II}$ salts. The ligand acts probably as a bidentate chelating agent through the

—N=CH— system (trichelation to the same

metal would impose a considerable angular strain on the ligand); the possibility that the thiazole nitro-

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gen coordinate to a metal atom of a neighboring molecule, giving a polymeric structure, must be considered. This latter structure might explain the lack of solubility of the complexes in all solvents except methanol; in this solvent the complexes could break down to monomeric species with cordinated $CH_3OH$ molecules. But this hypothesis is not supported by any shift of the $C=N$ stretching to higher frequencies as must be expected.[12,13]

In the infrared spectra of all the complexes a shift of the pyridine ring vibrations to higher frequencies is observed, which is indicative of the coordination of the pyridine nitrogen to a metal ion. The anions are all ionic, except for the acetate group, which is monodentate.

The electronic spectra and magnetic moments, determined at room temperature, agree with an octahedral coordination for all the $Co^{II}$ and $Ni^{II}$ complexes.

Complexes of the same series with other transition metals are being prepared at present in our laboratory.

*Acknowledgments.* The authors are indebted to Professor M. Nardelli for help and advice and to the Laboratorio di Microanalisi dell'Istituto di Chimica Farmaceutica dell'Università di Parma for C, H, N analyses.

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