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Reactions of Coordinated Ligands. XII. The Synthesis of *o*-Benzylene-2,1-benzimidazole in the Presence of Nickel(II) Ions, and a Study of Some of Its Metal Complexes

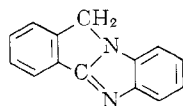
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The condensation of *o*-phenylenediamine and *o*-phthalicdicarboxaldehyde in the presence of nickel(II) ions has been shown to produce *o*-benzylene-2,1-benzimidazole. Several metal complexes containing this ligand have been isolated and shown to be of general formula ML_2X_2 , where $M = Ni(II)$, $X = Cl, Br, I, NO_3, SCN$; $M = Co(II)$, $X = Cl, Br, NO_3$; $M = Cu(II)$ and $Zn(II)$, $X = Cl$. These complexes have been characterized by elemental analysis, infrared spectra, magnetic moments, visible reflectance spectra, and X-ray powder patterns. The compounds when $M = Ni(II)$, $X = Cl, Br, I$; $M = Co(II)$, $X = Cl, Br$; and $M = Zn(II)$, $X = Cl$ are shown to have tetrahedral structures. When $M = Ni(II)$, $X = NO_3, SCN$; $M = Co(II)$, $X = NO_3$; and $M = Cu(II)$, $X = Cl$ octahedral structures are produced. It is suggested in these complexes that the nitrate group is behaving as a bidentate ligand and the thiocyanate group as a bridging ligand.

Introduction

Thiele and Falk² in 1906 investigated the condensation reaction of *o*-phenylenediamine and *o*-phthalicdicarboxaldehyde and assigned the structure below to the



isolated product. Since this first investigation, considerable effort has led to the proof that the condensation product is *o*-benzylene-2,1-benzimidazole (I) (alternatively named benzimidazo[1,2-*b*]1H-isindole).³⁻⁵

Several workers have studied metal complexes containing benzimidazole and substituted benzimidazoles.⁶⁻⁸ From stability constant measurements of copper(II) complexes of benzimidazole, 2-methylbenzimidazole, and 2-ethylbenzimidazole, Lane and Quinlan⁹ deduced that coordination to the metal ion takes place through the unsaturated nitrogen of the imidazole ring. Infrared studies of some metal complexes with 2-substituted benzimidazoles capable of chelation suggested that coordination also takes place through the unsaturated nitrogen in these chelates.^{10,11} Goodgame and Cotton prepared some cobalt(II) complexes of benzimidazole and studied their magnetic and spectral properties.¹² The complexes contained benzimidazole (HBZD) coordinated to the cobalt ion both as HBZD and as $(BZD)^-$, giving rise to tetrahedral struc-

tures. Recently Goodgame and Goodgame¹³ have reported electronic reflectance spectra for some pseudotetrahedral complexes of nickel(II) and cobalt(II) of the types ML_2X_2 and MLX_3^- , where $L =$ benzimidazole.

The following discussion describes a synthesis of *o*-benzylene-2,1-benzimidazole (BBI) from *o*-phenylenediamine and *o*-phthalicdicarboxaldehyde, in the presence of nickel(II) ions, and the preparation and properties of some metal complexes containing this ligand.

Experimental Section

Materials.—*o*-Phenylenediamine (Aldrich Practical Grade) was recrystallized from absolute ethanol. This was converted to the dihydrochloride by the addition of concentrated hydrochloric acid to an alcoholic solution of the recrystallized amine. The precipitated hydrochloride was removed by filtration, washed with absolute ethanol, and dried *in vacuo* over $Mg(ClO_4)_2$.

o-Phthalicdicarboxaldehyde (Aldrich) was used without further purification. *o*-Benzylene-2,1-benzimidazole (BBI) was prepared by the method of Thiele and Falk² from *o*-phenylenediamine hydrochloride and *o*-phthalicdicarboxaldehyde. Nickel thiocyanate was prepared by the addition of potassium thiocyanate to a solution of nickel nitrate 6-hydrate in ethanol. The precipitated potassium nitrate was removed by filtration. The alcoholic filtrate was concentrated on a rotary evaporator, and the precipitated nickel thiocyanate removed by filtration. Nickel iodide was prepared by a similar procedure from potassium iodide and nickel nitrate 6-hydrate.

All other chemicals used were obtained commercially and were of reagent grade or equivalent.

Procedure for the Preparation of Metal Complexes of *o*-Benzylene-2,1-benzimidazole (BBI). **Preparation of Dinitratobis(*o*-benzylene-2,1-benzimidazole)nickel(II).**—A solution of 0.34 g. of nickel nitrate 6-hydrate (1.17×10^{-3} mole) in 15 ml. of absolute ethanol is added to a solution of 0.60 g. of BBI (2.91×10^{-3} mole) in 15 ml. of absolute ethanol at room temperature. An immediate pale green precipitate is produced. The precipitate and solution are stirred for approximately 15 min. and then filtered by suction. The residue is washed with ethanol and ether and dried *in vacuo* over $Mg(ClO_4)_2$; yield of $Ni(BBI)_2(NO_3)_2$, 0.80 g. All other compounds were obtained using a similar procedure and employing a ratio of 2.5 moles of *o*-benzylene-2,1-benzimidazole to 1 mole of metal salt. For the nickel

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TABLE I
 ANALYTICAL DATA FOR THE BBI COMPLEXES

Compound	% calculated					% found				
	C	H	N	Halogen	S	C	H	N	Halogen	S
BBI	81.53	4.89	13.69	81.43	4.90	13.40
Ni(BBI) ₂ Cl ₂	62.04	3.72	10.33	13.08	...	62.15	3.53	10.07	12.86	...
Ni(BBI) ₂ Br ₂	53.25	3.16	8.87	25.37	...	52.75	3.27	9.12	24.96	...
Ni(BBI) ₂ I ₂	46.34	2.76	7.72	35.03	...	46.54	2.79	7.64	35.25	...
Ni(BBI) ₂ (NO ₃) ₂	56.50	3.39	14.12	56.10	3.37	13.95
Ni(BBI) ₂ (NCS) ₂	61.35	3.43	14.31	...	10.92	61.13	3.15	14.21	...	10.75
Co(BBI) ₂ Cl ₂	62.01	3.72	10.33	13.07	...	62.19	3.67	10.16	12.90	...
Co(BBI) ₂ Br ₂	53.20	3.16	8.86	25.35	...	52.41	3.44	9.48	24.53	...
Co(BBI) ₂ (NO ₃) ₂	56.47	3.36	14.11	56.77	3.41	14.25
Cu(BBI) ₂ Cl ₂	61.49	3.68	10.24	12.96	...	61.36	3.92	9.94	12.68	...
Zn(BBI) ₂ Cl ₂	61.28	3.67	10.21	...	Zn, 11.91	61.26	3.71	9.98	...	Zn, 12.12

iodide and nickel thiocyanate derivatives, it is necessary to heat the solution at approximately 65° for 30 min. before precipitation occurs.

Alternative Preparation of Dichlorobis(*o*-benzylene-2,1-benzimidazole)nickel(II).—A solution of 4.0 g. of *o*-phthalaldehyde (3.00 × 10⁻² mole) and 1.19 g. of nickel chloride 6-hydrate (5.00 × 10⁻³ mole) in 50 ml. of absolute ethanol is heated and stirred. When refluxing, a solution of 2.16 g. of recrystallized *o*-phenylenediamine (5.00 × 10⁻³ mole) in absolute ethanol is added. A precipitate forms and the solution appears green in color. The solution is stirred and refluxed for 1.5 hr. During this time, the solution turns dark brown and the precipitate appears to change from green to dark blue. After cooling, the solution is filtered and the dark blue solid residue washed with ethanol and ether and dried *in vacuo* over Mg(ClO₄)₂; yield of Ni(BBI)₂Cl₂, 1.80 g.

Magnetic Measurements.—Magnetic measurements were made by the Gouy method. The susceptibilities of ligands and anions were calculated from Pascal's constants.¹⁴ The standard used was HgCo(NCS)₄.

Infrared Spectra.—Infrared absorption spectra were obtained using a Perkin-Elmer Model 337 recording spectrophotometer. Nujol mull and potassium bromide pellet techniques were employed. Polystyrene was used for calibration.

Reflectance Spectra.—Reflectance spectra were obtained with a Cary Model 14 recording spectrophotometer and reflectance attachment. A potassium bromide pellet technique was employed.

X-Ray Powder Photographs. X-Ray powder photographs were obtained using a Unicam 9-cm. camera and Cu Kα radiation.

Analyses.—Analyses were performed by Schwarzkopf Micro-analytical Laboratories.

Results and Discussion

The reaction of *o*-phenylenediamine and *o*-phthalaldehyde in the presence of nickel chloride in ethanol yields a dark blue complex containing two moles of *o*-benzylene-2,1-benzimidazole bound to the nickel ion. If this dark blue complex is treated with water, the color is destroyed and a white solid is produced. The white solid may be removed, either by filtration or ether extraction. On recrystallization from acetone, white crystals are obtained which have a melting point of 210–212° (reported 210°) and an infrared spectrum identical with that of *o*-benzylene-2,1-benzimidazole produced by the method of Thiele and Falk.² On dissolving these white crystals in ethanol and adding to an ethanolic solution of nickel chloride 6-

hydrate, a dark blue precipitate is produced. This has an infrared spectrum and elemental analysis identical with those of the product of the original condensation of *o*-phenylenediamine and *o*-phthalaldehyde in the presence of nickel chloride. If the condensation reaction is performed under identical conditions except that the nickel chloride is omitted, a dark brown solution and an orange solid are produced. The infrared absorption spectrum of the solid is not the same as that of *o*-benzylene-2,1-benzimidazole. The addition of an ethanolic solution of nickel chloride 6-hydrate to the orange solid or to the dark brown solution did not produce the dark blue solid obtained with *o*-benzylene-2,1-benzimidazole. The presence of the metal ion is obviously of great importance in the condensation of *o*-phenylenediamine and *o*-phthalaldehyde. Whether the metal ion is merely functioning as an acid or is acting in a more profound manner remains undetermined.

The reaction between *o*-benzylene-2,1-benzimidazole (BBI) and various metal salts in alcoholic solution yields in all cases complexes containing two moles of the ligand attached to the metal ion. The compounds have been characterized by elemental analyses, infrared spectra, magnetic moments, electronic reflectance spectra, and X-ray powder patterns. The analytical data are reported in Table I.

The infrared absorption bands for the ligand, BBI, and the Ni(BBI)₂Cl₂ complex are shown in Table II (the other metal complexes exhibit very similar spectra to that of Ni(BBI)₂Cl₂). The absence of the stretching and deformation frequencies expected for the NH₂ groups and observed in *o*-phenylenediamine and the absence of an absorption similar to that of the C=O stretching frequency observed in *o*-phthalaldehyde at 1690 cm.⁻¹ is apparent. The presence of a very strong band at 1545 cm.⁻¹ in the ligand and 1535 cm.⁻¹ in the metal complexes assigned to the C=N group suggests the presence of a Schiff base linkage. The infrared spectra of the ligand and metal complexes are very similar, the most significant difference being shown in this shift of the C=N stretching frequency. This suggests that the ligand is attached to the metal atom through the unsaturated nitrogen as suggested for benzimidazole complexes.⁹ The thiocyanate ion in the Ni(BBI)₂(NCS)₂ complex exhibits

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TABLE II

INFRARED SPECTRA OF LIGAND AND TYPICAL COMPLEX

BBI	Assignment	Ni(BBI) ₂ Cl ₂
3060 m	C-H str.	3060 m
2940 w	C-H str.	2940 w
1622 m	C ₆ ring I	1620 m
1590 m	C ₆ ring II	1590 m
1545 vs	C≡N	1535 vs
1478 vs	C ₆ ring III	1478 vs
1455 s	C ₆ ring IV	1455 vs
1442 m		1440 vs
1392 m		...
1380 m		1380 m
1335 s		1339 m
1320 m		1320 m
1235 m		1240 m
1210 m		1210 m
1170 m		1170 m
1070 w		1070 w
1020 w		1020 w
1010 w		...
947 w		946 m
815 m		820 s
785 m		794 m
778 m		771 m
766 s	C-H def.	765 s
...	C-H def.	752 vs
734 s	C-H def.	734 s

two very strong C≡N absorption bands, at 2130 and 2070 cm.⁻¹. This suggests that the thiocyanate ion is acting as a bridging group.¹⁵ No absorption due to the C—S stretching mode could be assigned, but two bands of medium intensity at 478 and 470 cm.⁻¹ are assigned to N—C—S bending modes. The nitrate ion in the Ni(BBI)₂(NO₃)₂ complex, as a Nujol mull or KBr disk, shows very strong bands at 1510 (NO₂ asymmetric stretch) and 1268 cm.⁻¹ (NO₂ symmetric stretch) and strong bands at 1028 (NO stretch) and 810 cm.⁻¹ (out-of-plane deformation) suggesting coordination of the nitrate ion.¹⁶ From the stoichiometry and the fact that the nickel ion is in a roughly octahedral environment (see later), the nitrate ion must be acting as a bidentate ligand or as a bridging group.

The presence of the 1510 and 1268 cm.⁻¹ bands provides strong support for this conclusion, for these absorptions fall in the regions identified with bidentate chelation of nitrate.¹⁷ The Co(BBI)₂(NO₃)₂ complex absorbs in similar positions to the nickel complex, suggesting a similar structure. In a potassium bromide disk, interaction takes place to produce the bromide derivative, with a corresponding increasing absorption at 1390 cm.⁻¹, indicating the presence of the nitrate ion.¹⁸

The room temperature magnetic properties of the BBI complexes are shown in Table III. The values of μ_{eff} for the nickel(II) complexes Ni(BBI)₂X₂, X = Cl, Br, I, are consistent with those expected for nickel(II) in a ligand field of tetrahedral symmetry.¹⁸ It is interesting to note that for the iodide derivative, the

TABLE III

ROOM TEMPERATURE MAGNETIC PROPERTIES OF THE BBI COMPLEXES

Compound	T, °K.	$\chi_M \times 10^6$	μ_{eff} , B.M.
Ni(BBI) ₂ Cl ₂	301	4910	3.52
Ni(BBI) ₂ Br ₂	300	4880	3.52
Ni(BBI) ₂ I ₂	301	6550	4.04
Ni(BBI) ₂ (NO ₃) ₂	301	4200	3.24
Ni(BBI) ₂ (SCN) ₂	304	4290	3.24
Co(BBI) ₂ Cl ₂	300	8460	4.56
Co(BBI) ₂ Br ₂	300	8940	4.70
Co(BBI) ₂ (NO ₃) ₂	304	9750	4.92
Cu(BBI) ₂ Cl ₂	300	1265	1.87
Zn(BBI) ₂ Cl ₂	300	-190	Diamag.

TABLE IV

REFLECTANCE SPECTRA OF THE BBI COMPLEXES^a

Ni(BBI) ₂ Cl ₂ (dark blue)	9700, 12,080 (w), 15,300, 17,400, 28,200
Ni(BBI) ₂ Br ₂ (dark blue)	9750, 11,500 (w), 14,700, 17,150, 27,800
Ni(BBI) ₂ I ₂ (brown)	9750, 10,150 (w), 13,800, 16,280, 20,600, 24,400
Ni(BBI) ₂ (NO ₃) ₂ (green)	8940, 13,200 (w), 15,500, 25,600
Ni(BBI) ₂ (SCN) ₂ (yellow)	10,400, 13,610 (w), 19,600 (sh), 25,000
Co(BBI) ₂ Cl ₂ (pale blue)	8760, 15,500, 16,000 (sh), 16,950, 25,000
Co(BBI) ₂ Br ₂ (pale blue)	8510, 14,950, 15,650 (sh), 16,800, 25,000
Co(BBI) ₂ (NO ₃) ₂ (violet)	~8700 (br), 18,100, 20,850, 25,000
Cu(BBI) ₂ Cl ₂ (yellow-green)	~13,500 (br), 24,800
Zn(BBI) ₂ Cl ₂ (white)	~24,500

^a All bands in cm.⁻¹; w, weak; sh, shoulder; br, broad.

μ_{eff} value is much higher than for the chloride and bromide. Presumably the iodide ion is similar in size and donor strength to the BBI ligand, so that the ligand field around the nickel(II) ion is closer to T_d symmetry than in the chloride and bromide derivatives. For the nitrate and thiocyanate derivatives, the observed magnetic moments are consistent with the nickel(II) ion in a pseudo-octahedral environment resulting in a triplet ground state. These values are in good agreement with the prediction that the nitrate is a bidentate group and the thiocyanate a bridging group, as both will give rise to octahedral environments around the central metal ion.

For the cobalt(II) complexes, Co(BBI)₂X₂, X = Cl and Br, the magnetic moments are consistent with a tetrahedral environment around the cobalt(II) ion¹⁸ and of similar magnitude to those observed for benzimidazole complexes.¹² When X = NO₃, the magnetic moment observed suggests a pseudo-octahedral environment around the cobalt(II) atom, with a quartet ground state. The values for the copper and zinc compounds are those expected if the metals are in their divalent states.

The reflectance spectra of the compounds were measured over the range from 7400 to 29,000 cm.⁻¹ and are recorded in Table IV. For the Ni(BBI)₂X₂ compounds, when X = Cl, Br, I, the observed absorption

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bands suggest nickel(II) in a tetrahedral environment.¹⁹⁻²¹ The band at approximately 9700 cm^{-1} is assigned in T_d symmetry to the transition ${}^3T_1(F) \rightarrow {}^3A_2$, usually designated ν_2 , while the strong band consisting of two components between 14,000 and 17,000 cm^{-1} is assigned to the transition ${}^3T_1(F) \rightarrow {}^3T_1(P)$, ν_3 , the splitting being caused by spin-orbit coupling lifting the degeneracy of the $T_1(P)$ state.

When $X = \text{NO}_3$ and SCN , four bands are observed, consistent with octahedral nickel(II) species.²² The absorptions are assigned to the following transitions in (pseudo) O_h symmetry: ν_1 , 9000–10,000 cm^{-1} , ${}^3A_{2g} \rightarrow {}^3T_{2g}$; ν_2 , $\sim 13,000 \text{ cm}^{-1}$, ${}^3A_{2g} \rightarrow {}^1E_g$; ν_3 , 15,000–19,000 cm^{-1} , ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$; and ν_4 , 25,000 cm^{-1} , ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ plus charge transfer.

For the $\text{Co}(\text{BBI})_2\text{X}_2$ compounds, when $X = \text{Cl}$ and Br , three main bands are observed. The band at 8500 cm^{-1} is assigned to the transition ν_2 , ${}^4A_2 \rightarrow {}^4T_1(F)$ in T_d symmetry.^{23,24} The second broad multicomponent band between 15,000 and 17,000 cm^{-1} is assigned to the transition ν_3 , ${}^4A_2 \rightarrow {}^4T_1(P)$. Several investigators have also observed the multicomponent nature of this band^{25,26} and have suggested this arises because spin-orbit coupling effects split the ${}^4T_1(P)$ state and also this state is coupled to close lying doublet states such as the 2E and 2T_1 states. Thus the ν_3 transition is actually a combination of transitions from the 4A_2 ground state to several higher states. The band at 25,000 cm^{-1} found in all the compounds including $\text{Zn}(\text{BBI})_2\text{Cl}_2$ may be due to charge transfer.

In the violet nitrate derivative, the observed spec-

trum suggests cobalt(II) in an octahedral environment. The absorption bands have been assigned to the following transitions in O_h symmetry²⁷: ν_1 , $\sim 8700 \text{ cm}^{-1}$, ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$; ν_2 , 18,100 cm^{-1} , ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$; ν_3 , 20,800 cm^{-1} , ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. Thus the electronic absorption spectra of all the nickel(II) and cobalt(II) compounds agree well with the predictions regarding structure made from the magnetic data.

For $\text{Cu}(\text{BBI})_2\text{Cl}_2$, one broad band is observed with a maximum at approximately 13,500 cm^{-1} , in addition to the charge-transfer band at 25,000 cm^{-1} . This broad band is due to Jahn-Teller distortion in octahedrally coordinated copper(II) removing the degeneracies of the 2E and ${}^2T_{2g}$ states, so that the observed absorption band is more correctly a combination of three transitions.²⁸

The X-ray powder patterns for the compounds suggested to have tetrahedral structures from the magnetic and spectral data, *i.e.*, $\text{Ni}(\text{BBI})_2\text{Cl}_2$, $\text{Ni}(\text{BBI})_2\text{Br}_2$, $\text{Ni}(\text{BBI})_2\text{I}_2$, $\text{Co}(\text{BBI})_2\text{Cl}_2$, and $\text{Co}(\text{BBI})_2\text{Br}_2$, were all similar and similar to that of $\text{Zn}(\text{BBI})_2\text{Cl}_2$. Those suggested to have octahedral structures, *i.e.*, $\text{Ni}(\text{BBI})_2(\text{NO}_3)_2$, $\text{Ni}(\text{BBI})_2(\text{SCN})_2$, $\text{Co}(\text{BBI})_2(\text{NO}_3)_2$, and $\text{Cu}(\text{BBI})_2\text{Cl}_2$, all showed similar patterns to one another, but different from those listed as tetrahedral above.

Models seem to indicate that when the ligands are coordinated to the metal ion through the unsaturated nitrogen atom, considerable steric interaction between the benzene rings of two ligands occurs. This may be the reason for the ease of formation of tetrahedral environments when X is a unidentate anion.

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(28) Reference 22, p. 269.