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Complexes of Cobalt(II). II.[1] An Investigation of Intraligand Steric Hindrance in α-Dihydrazone Complexes of Cobalt(II), Iron(II), and Nickel(II)

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Twelve new α-dihydrazone complexes of iron(II), cobalt(II), and nickel(II) have been prepared and characterized by solid-state magnetic and electronic and vibrational (C=N stretching region) spectral measurements. The data obtained are, in the main, consistent with a decreasing intraligand repulsion (in the complexes) in the order biacetyldihydrazone > benzildihydrazone > pyruvaldihydrazone > glyoxaldihydrazone. The relatively small increase in ligand field strength gained by decreasing intraligand repulsions (in proceeding from biacetyldihydrazone to the ligand pyruvaldihydrazone) apparently is sufficient to cause the 3:1 cobalt(II) complexes to lie near the crossover point between high-spin and low-spin complexes and to exhibit characteristic anomalous Curie–Weiss behavior. Two 2:1 complexes of iron(II) with the ligands pyruvaldihydrazone and glyoxaldihydrazone exhibit normal Curie–Weiss behavior and magnetic moments characteristic of the few complexes presumed to be low-spin and "essentially planar." The nickel complexes are regular.

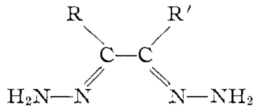
Introduction

It has been demonstrated that ligand stereochemistry can be of major importance in determining the relative ability of ligands to coordinate with transition metal ions;[2-5] however, these investigations have been concerned principally with *interligand* repulsions; *i.e.*, relatively little attention has been directed toward *intraligand* repulsions.

The ligand biacetyldihydrazone (BdH) (structure I) has been reported to produce a rather large ligand field about nickel(II),[6] although examination of a Stuart–Briegleb model of BdH in the *cis* (coordinating) conformation leads one to conclude that there probably exists a repulsive interaction between the methyl groups. The existence of such an interaction has been suggested previously.[7]

The present investigation was undertaken to determine whether there exists a trend in the magnetic and spectral properties, characterizing a series of complexes containing closely related ligand molecules, consistent with the probable change of intraligand repulsions.

The ligands selected for this investigation are glyoxaldihydrazone (GdH), pyruvaldihydrazone (PvdH), and benzildihydrazone (BzdH), structures II, III, and IV, respectively. By using these ligands, twelve new complexes of dipositive iron, cobalt, and nickel have been prepared and characterized.



I, R = R′ = CH_3
II, R = R′ = H
III, R = CH_3; R′ = H
IV, R = R′ = C_6H_5

Experimental Section

Glyoxaldihydrazone, GdH.—Aqueous glyoxal (36 ml of 40%, 0.33 mole) was added dropwise with constant stirring to an excess of hydrazine (approximately 75 ml) cooled by means of an ice bath. The white crystalline product which formed was filtered on a sintered glass filter, washed with a few milliliters of cold 95% ethanol, and dried over P_4O_{10} *in vacuo*. The product, recrystallized from absolute ethanol, gave a melting point of 97–99°; yield, approximately 60%. *Anal.* Calcd for $C_2H_6N_4$: C, 27.90; H, 7.02; N, 65.08. Found: C, 28.13; H, 7.19; N, 64.86.

Tris(glyoxaldihydrazone)iron(II) Chloride, $[Fe(GdH)_3]Cl_2$.—A solution of iron(II) chloride tetrahydrate (1.99 g, 0.0100 mole) in warm absolute ethanol (approximately 20 ml) was added slowly with constant agitation to a solution of glyoxaldihydrazone (2.58 g, 0.0300 mole) in warm absolute ethanol (approximately 25 ml). The microcrystalline product which formed immediately was filtered on a sintered glass filter under an abundant flow of nitrogen, washed with a few milliliters of cold absolute ethanol and a few milliliters of ether, and dried over P_4O_{10} *in vacuo;* yield, approximately 85%; mp 160° dec. *Anal.* Calcd for $FeC_6H_{18}N_{12}Cl_2$: C, 18.72; H, 4.71; N, 43.65. Found: C, 18.48; H, 4.58; N, 43.37.

Tris(glyoxaldihydrazone)cobalt(II) Bromide, $[Co(GdH)_3]Br_2$.—This product was prepared by a method analogous to that used for $[Fe(GdH)_3]Cl_2$ except that anhydrous cobalt bromide was used. The entire preparation was carried out in a glove box filled with dry nitrogen; yield, approximately 95%; mp 140° dec. *Anal.* Calcd for $CoC_6H_{18}N_{12}Br_2$: C, 15.11; H, 3.80; N, 35.23. Found: C, 15.35; H, 3.71; N, 35.08.

Tris(glyoxaldihydrazone)nickel(II) Chloride, $[Ni(GdH)_3]Cl_2$.—This product was prepared by a method analogous to that used for $[Fe(GdH)_3]Cl_2$ except that nickel(II) chloride hexahydrate was used; yield, approximately 90%; mp 174° dec. *Anal.* Calcd for $NiC_6H_{18}N_{12}Cl_2$: C, 18.58; H, 4.68; N, 43.33. Found: C, 18.48; H, 4.49; N, 43.19.

Dichlorobis(glyoxaldihydrazone)iron(II), $Fe(GdH)_2Cl_2$.—A solution of glyoxaldihydrazone (2.58 g, 0.0300 mole) in hot absolute ethanol (approximately 20 ml) was added slowly with constant agitation to a solution of iron(II) chloride tetrahydrate (2.98 g, 0.0150 mole) in hot absolute ethanol (approximately 25 ml). The microcrystalline product which formed immediately was filtered on a sintered glass filter under an abundant flow of nitrogen, washed with a few milliliters of cold absolute ethanol, and dried over P_4O_{10} *in vacuo;* yield, approximately 75%; mp 140° dec. *Anal.* Calcd for $FeC_4H_{12}N_8Cl_2$: C, 16.07; H, 4.05; N, 37.48. Found: C, 15.85; H, 4.00; N, 37.12.

Dichlorobis(glyoxaldihydrazone)nickel(II), $[Ni(GdH)_2Cl_2]$.—This product was prepared by a method analogous to that used

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[1] Paper I: R. C. Stoufer, D. W. Smith, E. A. Clevenger, and T. E. Norris, *Inorg. Chem.*, **5**, 1167 (1966).

[2] H. Irving, E. J. Butler, and M. F. Ring, *J. Chem. Soc.*, 1489 (1949).

[3] H. M. Irving and R. J. P. Williams, *Analyst*, **77**, 813 (1952).

[4] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).

[5] M. A. Robinson and D. H. Busch, *Inorg. Chem.*, **2**, 1171 (1963).

[6] M. A. Robinson, J. D. Curry, and D. H. Busch, *ibid.*, **2**, 1178 (1963).

[7] R. C. Stoufer and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 3491 (1960).

for $Fe(GdH)_2Cl_2$ except that nickel(II) chloride hexahydrate was used. The entire preparation was carried out in a glove box filled with dry nitrogen; yield, approximately 50%; mp 150° dec. *Anal.* Calcd for $NiC_4H_{12}N_8Cl_2$: C, 15.92; H, 4.01; N, 37.13. Found: C, 15.52; H, 4.48; N, 32.89.

Pyruvaldihydrazone, PvdH.—This product was prepared by a method analogous to that used for the preparation of GdH using 30% aqueous pyruvaldehyde; yield, approximately 85%; mp 95–96°. *Anal.* Calcd for $C_3H_8N_4$: C, 35.99; H, 8.05; N, 55.96. Found: C, 35.86; H, 8.07; N, 56.09.

Tris(pyruvaldihydrazone)iron(II) Chloride, $[Fe(PvdH)_3]Cl_2$.—This product was prepared by a method analogous to that used for $[Fe(GdH)_3]Cl_2$ except that PvdH was used; yield, approximately 75%; mp 172° dec. *Anal.* Calcd for $FeC_9H_{24}N_{12}Cl_2$: C, 25.29; H, 5.66; N, 39.35. Found: C, 25.81; H, 5.97; N, 35.17.

Tris(pyruvaldihydrazone)cobalt(II) Bromide, $[Co(PvdH)_3]Br_2$.—This product was prepared by a method analogous to that used for $[Co(GdH)_3]Br_2$ except that PvdH was used; yield, approximately 75%; mp 160° dec. *Anal.* Calcd for $CoC_9H_{24}N_{12}Br_2$: C, 20.82; H, 4.66; N, 32.38. Found: C, 21.02; H, 4.52; N, 32.53.

Tris(pyruvaldihydrazone)nickel(II) Chloride, $[Ni(PvdH)_3]Cl_2$.—This product was prepared by a method analogous to that used for $[Ni(GdH)_3]Cl_2$ except that PvdH was used; yield, approximately 85%; mp 178° dec. *Anal.* Calcd for $NiC_9H_{24}N_{12}Cl_2$: C, 25.14; H, 5.63; N, 39.09. Found: C, 24.92; H, 5.76; N, 37.20.

Dichlorobis(pyruvaldihydrazone)iron(II), $Fe(PvdH)_2Cl_2$.—This product was prepared by a method analogous to that used for $Fe(GdH)_2Cl_2$ except that PvdH was used. The product was rust-brown in color, but the filtrate was green; yield, approximately 65%; mp 160° dec. *Anal.* Calcd for $FeC_6H_{16}N_8Cl_2$: C, 22.04; H, 4.93; N, 34.27. Found: C, 22.30; H, 5.22; N, 30.18.

Dichlorobis(pyruvaldihydrazone)nickel(II) Monohydrate, $[Ni(PvdH)_2Cl_2]\cdot H_2O$.—This product was prepared by a method analogous to that used for $[Ni(GdH)_2Cl_2]$ except that PvdH was used; yield, approximately 75%; mp 190° dec. *Anal.* Calcd for $NiC_6H_{18}N_8Cl_2O$: C, 20.71; H, 5.22; N, 32.21. Found: C, 20.09, 19.95; H, 5.44, 5.42; N, 30.12, 31.35.

Tris(benzildihydrazone)cobalt(II) Chloride, $[Co(BzdH)_3]Cl_2$.—A mixture of cobalt chloride hexahydrate (1.19 g, 0.0050 mole) and benzildihydrazone (3.57 g, 0.0150 mole) in 50 ml of absolute ethanol was stirred and heated to approximately 70° for about 10 min. The finely-divided product which formed was filtered on a sintered glass filter, washed with a few milliliters of absolute ethanol, and dried over P_4O_{10} *in vacuo;* yield, approximately 50%; mp 150° dec. *Anal.* Calcd for $CoC_{42}H_{42}N_{12}Cl_2$: C, 59.72; H, 5.01; N, 19.90. Found: C, 59.61; H, 5.20; N, 19.86.

Dichlorobis(benzildihydrazone)nickel(II), $[Ni(BzdH)_2Cl_2]$.—A solution of nickel(II) chloride hexahydrate (1.19 g, 0.0050 mole) in absolute ethanol (approximately 30 ml) was added slowly with constant stirring to a warm solution of benzildihydrazone (3.57 g, 0.0150 mole) in 75 ml of ethanol and 75 ml of ether. A chartreuse product formed immediately. The mixture was allowed to cool overnight, after which time it was filtered on a sintered glass filter, washed with a few milliliters of absolute ethanol, and dried over P_4O_{10} *in vacuo;* yield, approximately 90%; mp 200° dec. *Anal.* Calcd for $NiC_{28}H_{28}N_8Cl_2$: C, 55.48; H, 4.66; N, 18.49. Found: C, 55.16, 55.54; H, 4.70, 4.88; N, 17.85.

All analytical measurements were made by Galbraith Microanalytical Laboratories, Knoxville, Tenn. In a few instances the nitrogen values are low although the carbon and hydrogen analyses compare favorably with the theoretical values, a rather common occurrence with compounds containing N–N bonds.

With the exception of $[Ni(BzdH)_2Cl_2]$, all of the above compounds decomposed in air, some more rapidly than others; thus, all compounds were stored in an atmosphere of dry nitrogen.

TABLE I

ROOM-TEMPERATURE MAGNETIC MOMENTS AND POSITIONS OF THE C=N STRETCHING VIBRATION

Complex	μ_{eff}	T, °K	$\tilde{\nu}_{C=N}$, cm^{-1}
$[Fe(GdH)_3]Cl_2$	1.11	296.9	1565 1555 [b]
$Fe(GdH)_2Cl_2$	3.32	296.1	1565
$[Fe(PvdH)_3]Cl_2$	1.29	297.7	1586
$Fe(PvdH)_2Cl_2$	2.90	296.4	1590
$[Co(GdH)_3]Br_2$	3.18	300.0	1597 1584 1571 [c]
$[Co(PvdH)_3]Br_2$	4.23	295.7	...
$[Co(BzdH)_3]Cl_2$	4.93	296.9	1584
$[Ni(GdH)_3]Cl_2$	3.05	297.2	1583
$[Ni(GdH)_2Cl_2]$	3.07	296.9	1585
$[Ni(PvdH)_3]Cl_2$	2.97	297.2	...
$[Ni(PvdH)_2Cl_2]\cdot H_2O$	3.04	297.2	...
$[Ni(BzdH)_2Cl_2]$	3.08	298.5	1588
$[Fe(BdH)_3]I_2$ [a]	...	...	1595
$[Co(BdH)_2Cl_2]$ [a]	...	...	1623
$[Co(BdH)_3]I_2$ [a]	...	...	1613
$[Ni(BdH)_2Cl_2]$ [a]	...	...	1613
$[Ni(BdH)_3]Cl_2$ [a]	...	...	1613
GdH	...	...	1583
PvdH	...	...	1584
BdH [a]	...	...	1582
BzdH	...	...	1582

[a] Reference 7. [b] Unresolved doublet. [c] Unresolved triplet.

Apparatus.—The magnetic susceptibilities were determined at two different field strengths by the Gouy method using equipment described previously.[1] Water, solid nickel ammonium sulfate hexahydrate, and tris(ethylenediamine)nickel(II) thiosulfate[8] were used as field strength calibrants.

A Cary Model 14 recording spectrophotometer with a Cary Model 1411 diffuse reflectance accessory was used to obtain the solid-state spectra in the visible, ultraviolet, and near-infrared regions. Pharmaceutical grade magnesium carbonate was used as a reference.

The infrared data were obtained by using a Perkin-Elmer Model 21 recording spectrophotometer equipped with sodium chloride optics and calibrated with polystyrene. The pressed potassium bromide pellet technique was used.

Results and Discussion

Infrared Spectra.—The positions of the C=N stretching vibrations are presented in Table I. This absorption occurs at 1584 ± 1 cm^{-1} for each of the free ligand molecules. The relatively low energy position of this absorption is attributed to the existence of an extended π-electron system in the molecules which presumably exist in the *trans* planar conformation. The *trans* planar conformation does not cause any steric interaction between the well-separated R and R′ groups (structures I–IV); thus, the best overlap of π symmetry orbitals occurs. Clearly, the substituents R and R′ produce no perturbation of the ligand π system of sufficient magnitude to alter the position of the C=N stretching vibration.

In contrast to the constant position of the C=N stretching vibration in the spectra of the free ligands, that of the coordinated ligand molecules is observed to vary from 1560 cm^{-1} ($[Fe(GdH)_3]Cl_2$) to 1613 cm^{-1} ($[Co(BdH)_3]I_2$ and $[Ni(BdH)_3]Cl_2$).

Inspection of the infrared absorptions listed in Table

(8) N. F. Curtis, *J. Chem. Soc.*, 3147 (1963).

I reveals that for the complexes of iron(II), the position of the C=N stretching vibration is observed at increasingly higher energies in the order GdH < PvdH < BdH. For those of cobalt(II) the order is GdH < BzdH < BdH and for nickel(II), GdH < BzdH < BdH. Unfortunately, the complexes $[Ni(PvdH)_3]Cl_2$, $[Ni(PvdH)_2Cl_2]\cdot H_2O$, and $[Co(PvdH)_3]Br_2$ exhibit no absorption which can readily be assigned to the C=N stretching vibration. It is unlikely that this absorption has merged with the absorption due to the NH_2 deformation vibration which ordinarily occurs at slightly higher positions (approximately 1620 cm^{-1}). The greatest observed shifts of the C=N stretching vibration to higher energy relative to the free ligand occur with the complexes of BdH in which the NH_2 deformations of the C=N stretching vibrations remain distinct.[7] It is not without precedent that this stretching vibration is not observed, however. Nakamoto[9,10] has reported, for example, that tris[glyoxalbis(methylimine)]iron(II) exhibits a C=N stretching vibration. The analogous biacetyl complex does not.

Within the series of complexes formed by one ligand with several metals, and within a series of complexes formed by the same metal ion with different ligands, the order of shifting of the C=N stretching vibration can be rationalized in terms of two factors, *viz.*, ligand geometry and metal–ligand π bonding.

Whereas the *free* ligand molecule may assume a *trans* planar conformation,[7] the *bonding* ligand molecule must become *cis*, in which conformation the groups R and R′ lie at the closest distance of approach. In this *cis* conformation, moreover, differences in the steric repulsions between the R and R′ (as they represent H, CH_3, and C_6H_5 in turn) which may now occur should be manifest as shifts of the C=N stretching vibration. That is, the greater the interaction between the R and R′ tending to remove the planarity of the ligand molecule (with the concomitant decrease in π bonding within the ligand), the farther will the characteristic absorption be shifted to higher energies. Thus, within a series of complexes involving the same metal atom but in which R and R′ vary, the shift in position of the C=N stretching vibration reflects the relative tendency of the R and R′ interaction to remove the planarity of the chelate ring. The 1600 cm^{-1} regions of representative spectra are shown in Figure 1.

Operating in a direction opposed to that noted above is the π bonding between the metal atom and ligand molecule. As the tendency for metal electrons to be delocalized toward the ligand molecules increases by interaction of the π symmetry metal orbitals (formerly nonbonding t_{2g} orbitals under O_h) with those ligand orbitals of appropriate symmetry (formerly antibonding), the C=N bond order will decrease accordingly. Thus, the greater the extent of π bonding between the metal atom and ligand molecules, the lower will be the wavenumber position of the C=N stretching vibration.

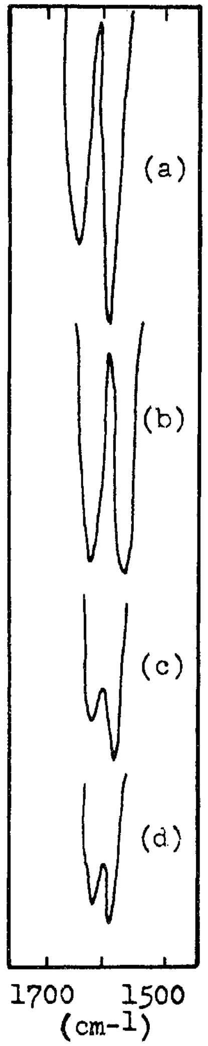

Figure 1.—The NH_2 defomation and C=N stretching vibration region of the infrared spectra of (a) PvdH, (b) $[Fe(GdH)_3]Cl_2$, (c) $[Fe(PvdH)_3]Cl_2$, and (d) $[Fe(BdH)_3]I_2$.

Consideration of the position of the C=N stretching vibration in the infrared spectra of the dipositive zinc ion complexes formed by these ligands provides a means of inferring the effect of intraligand repulsions without the added complexity of metal–ligand π bonding. The ligands forming the zinc complexes and the positions of the C=N stretching vibrations are: BdH, 1620 cm^{-1}; PvdH, 1615 cm^{-1}; GdH, 1605 cm^{-1}. These data manifest the same trends as the analogous data for the dipositive iron, cobalt, and nickel complexes.

Provided the rationale presented above be correct, several conclusions may now be drawn which will be compared subsequently with those drawn from other data obtained during these investigations.

The ligand which is least sterically hindered when bonded to the metal ion is glyoxaldihydrazone. The ligand pyruvaldihydrazone is but slightly more hindered. Contrary to our *a priori* predictions, however, benzildihydrazone, although more hindered than either of the first two ligands, is not as hindered in the complexes it forms as is biacetyldihydrazone.

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[9] S. Kirschner, Ed., "Advances in the Chemistry of the Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p 437.

[10] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 189.

The order of decrease of metal–ligand π bonding is Fe > Co = Ni. Support for this conclusion is found in the reports of several investigators. Nakamoto[9,10] reported that the C═N and C—C stretching force constants in tris[glyoxalbis(methylimine)]iron(II) are much smaller than those of pure double bonds, whereas the N—Fe stretching force constant is much larger than those of other coordinate bonds. Busch, *et al.*, have concluded from considerations of the infrared spectra of iron, cobalt, and nickel complexes of biacetylbis(methylimine), pyridinalmethylimines, and pyridinalhydrazones that the order of decreasing π interaction between metal and ligand is Fe > Co > Ni.[5,11]

Electronic Spectral Measurements.—The free ligands have no absorption maxima in the region which is of primary interest in the case of the complexes, *viz.*, 3000–13,000 A. A summary of the absorption maxima observed in the diffuse reflectance spectra of the complexes together with transition assignments and values of the ligand field splitting parameter Δ is given in Table II.

TABLE II

SPECTRAL ABSORPTIONS AND TRANSITION ASSIGNMENTS

Complex	Absorption maxima, cm^{-1} × 10^2	Transition assignment	Δ, cm^{-1}
[Fe(GdH)$_3$]Cl$_2$	271	. . .	. . .
	220	. . .	. . .
[Fe(GdH)$_2$Cl$_2$]	278	. . .	. . .
	217	. . .	. . .
[Fe(PvdH)$_3$]Cl$_2$	286	. . .	. . .
	227	. . .	. . .
[Fe(PvdH)$_2$Cl$_2$]	294	. . .	. . .
	220	. . .	. . .
[Co(GdH)$_3$]Br$_2$	256	. . .	. . .
[Co(PvdH)$_3$]Br$_2$	307 sh	. . .	. . .
	247 sh	${}^4T_1 \rightarrow {}^4A_2$	. . .
	161	. . .	. . .
	110	${}^4T_1 \rightarrow {}^4T_2$	13,800
[Co(BzdH)$_3$]Cl$_2$	256 sh	. . .	. . .
	188	${}^4T_1 \rightarrow {}^4A_2$	. . .
	145	. . .	. . .
	87.7	${}^4T_1 \rightarrow {}^4T_2$	11,000
[Ni(GdH)$_3$]Cl$_2$	257	. . .	. . .
	196 sh	${}^3A_2 \rightarrow {}^3T_1$	. . .
	132 sh	${}^3A_2 \rightarrow {}^3T_2$	13,200
	113 sh	${}^3A_2 \rightarrow {}^1E(D)$	. . .
[Ni(GdH)$_2$Cl$_2$]	308	. . .	. . .
	108	${}^3A_2 \rightarrow {}^3T_2$	10,800
[Ni(PvdH)$_3$]Cl$_2$	267	. . .	. . .
	198	${}^3A_2 \rightarrow {}^3T_1$	. . .
	129	${}^3A_2 \rightarrow {}^3T_2$	12,900
	115	${}^3A_2 \rightarrow {}^1E(D)$	. . .
[Ni(PvdH)$_2$Cl$_2$]·H$_2$O	182	${}^3A_2 \rightarrow {}^3T_2$	. . .
	117	${}^3A_2 \rightarrow {}^3T_2$	11,700
[Ni(BzdH)$_2$Cl$_2$]	257	. . .	. . .
	154	${}^3A_2 \rightarrow {}^1E(D)$ or ${}^3A_2 \rightarrow {}^3T_1$	. . .
	88.5	${}^3A_2 \rightarrow {}^3T_2$	8,850

The solution spectra of the complexes are not reported for two reasons. It can be misleading to correlate *solution* electronic spectra with *solid-state* infrared spectra and magnetic moments. Furthermore, either the complexes do not exhibit sufficiently large solubilities to permit observation of the d–d transition or the solution process occurs with displacement of ligand (from the 2:1 complexes) as evidenced by a change in visual color of the complex upon solution and by the conductances exhibited by the resulting solutions, which behavior has been noted previously for related complexes.[5]

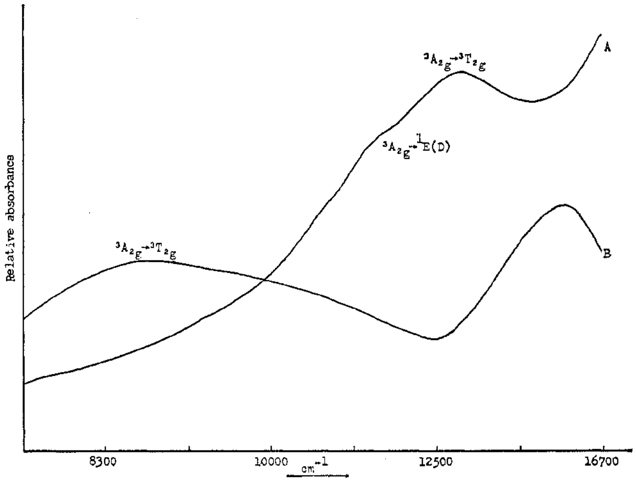

Figure 2.—Near-infrared spectra of (A) [Ni(PvdH)$_3$]Cl$_2$ and (B) [Ni(BzdH)$_2$Cl$_2$].

The electronic spectra of iron(II) complexes in general are not well understood and very few assignments of d–d transitions have been made. The iron–dimethine chromophore has been studied in some detail by Krumholtz[12] and by Busch and Bailar.[13] Spectral investigations of several complexes of iron(II) with ligands containing the α-dimethine group revealed that all those studies exhibit strong *charge-transfer* absorptions in the visible region of the spectrum; therefore, it is likely that the absorptions of the iron(II) complexes reported herein are of the charge-transfer variety. The transitions of this type are presumably associated with the extensive double bond formation which must occur between metal ion and ligand.[14] These conclusions find support in the relatively low energy position of the C═N stretching vibrations (1555–1595 cm^{-1}) of the iron(II) complexes (Table I). No attempt has been made, therefore, to assign Δ values to these complexes.

The transitions observed for the nickel(II) complexes prepared during the course of this investigation are listed in Table II. The ligand field strength Δ is evaluated from the ${}^3A_2 \rightarrow {}^3T_2$ transition energy to which it corresponds for the nickel(II) ion in an octahedral environment. In the case of the 2:1 complexes, however, the value of Δ is considered to arise from an averaging of the ligand field strengths of the two bidentate ligands and from the two chloride ions. Two representative spectra containing the ${}^3A_2 \rightarrow {}^3T_2$ absorption are illustrated in Figure 2.

The assignment of nickel(II) transitions listed in

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[11] P. E. Figgins and D. H. Busch, *J. Phys. Chem.*, **65**, 2236 (1961).

[12] P. Krumholtz, *J. Am. Chem. Soc.*, **75**, 2163 (1953); P. Krumholtz, *Inorg. Chem.*, **4**, 612 (1965).

[13] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **78**, 1137 (1956).

[14] L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1953).

Table II is in keeping with the criteria discussed in ref 6, *viz.*, the $^3A_{2g} \rightarrow {}^3T_{2g}$ band should exhibit considerable breadth because of spin–orbit coupling effects, the $^3A_{2g} \rightarrow {}^1E(D)$ transition should be of lower intensity than the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition, the $^3A_{2g} \rightarrow {}^1E(D)$ transition should be that of lowest energy when Δ exceeds 12,000 cm^{-1}, and the Δ value for complexes containing unsaturated nitrogen atoms should be of similar magnitude to that exhibited by 2,2′-bipyridine, 1,10-phenanthroline, etc., all of which exhibit Δ values near 12,700 cm^{-1}. In the list of transitions for related compounds tabulated by Busch, *et al.*,[6] the largest Δ value reported (12,800 cm^{-1}) is that of $[Ni(BdH)_3]^{2+}$. The analogous complexes of PvdH and GdH have values in excess of that exhibited by the BdH analog, *viz.*, 12,900 cm^{-1} for $[Ni(PvdH)_3]Cl_2$ and 13,200 cm^{-1} for $[Ni(GdH)_3]Cl_2$. It is observed that the ligand field strength relative to nickel(II) increases in the order BdH < PvdH < GdH, consistent with the conclusions drawn from the infrared data.

Interpretations of electronic spectra of cobalt(II) complexes in terms of the ligand field theory have been less common than interpretations of nickel(II) spectra; however, transitions which have been assigned generally give values of between 1.0 and 1.1 times the values for analogous nickel(II) complexes. The value of Δ for $[Co(PvdH)_3]Br_2$ is 1.06 times the value for the analogous nickel(II) complexes, in excellent agreement with previous observations of this type. Unfortunately, the complex $[Co(GdH)_3]Br_2$ does not exhibit a spectrum which is sufficiently resolved to locate more than the one absorption noted in Table II despite several attempts to obtain a more clearly resolved spectrum. Assignment of Δ values is based on the $^4T_1 \rightarrow {}^4T_2$ transition.

Magnetic Measurements.—The room-temperature magnetic moments of the complexes prepared during the course of this investigation are listed in Table I. The magnetic susceptibilities, all of which are independent of field strength, were corrected for the diamagnetic contribution of the ligands, the anions, and the metal ions, using Pascal's constant.[15]

The effective magnetic moments of the nickel(II) complexes lie between 2.97 and 3.09 BM, reflecting a small orbital contribution to the spin-only value from the $^3T_{2g}$ state.

The two tris-bidentate complexes of iron(II) are of the low-spin variety, as expected, exhibiting "residual" paramagnetic moments[16] somewhat larger than those customarily reported.[17] The other two iron(II) complexes, $Fe(GdH)_2Cl_2$ and $Fe(PvdH)_2Cl_2$, exhibit unexpected magnetic moments, *viz.*, 3.32 and 2.90 BM, respectively. Normally, iron(II) complexes of this type are of the high-spin variety, exhibiting magnetic moments near 5.6 BM.[17] The existence of a complex of the type $[FeL_3][FeLCl_4]$ where L = GdH or PvdH (which retains the same empirical composition) containing a diamagnetic cation and a paramagnetic anion is inconsistent with the data because such a compound should manifest a magnetic moment between 3.7 and 4.1 BM.[18]

In order to characterize more completely these two complexes, the magnetic susceptibility of each was measured as a function of temperature. Both $Fe(GdH)_2Cl_2$ and $Fe(PvdH)_2Cl_2$ display normal Curie–Weiss behavior exhibiting Weiss constants of 8 and 4°, respectively. Therefore, it is highly unlikely that the magnetic moments can be explained either in terms of an antiferromagnetic interaction or a Boltzmann distribution over states characterized by different spin multiplicities.

We suggest that the magnetic properties of these two complexes are consistent with the coordination of the two bidentate ligands in a plane about the metal ion, the chloride ions lying above and below this plane. As a consequence of the greater ligand field strength of the bidentate ligands relative to that of the chloride ions, a significant tetragonal distortion may result, the configurational limit of which is the square plane. Clearly the magnetic moments of 2.90 BM for $Fe(PvdH)_2Cl_2$ and 3.32 BM for $Fe(GdH)_2Cl_2$ correspond rather closely to the spin-only value of two unpaired electrons (2.83 BM) expected for a low-spin, planar iron(II) complex. Unfortunately, few square-planar iron(II) complexes have been reported with which comparisons can be made. The planar phthalocyanine complex of iron(II) is reported to have a magnetic moment of 3.95 BM,[19] reflecting a sizable orbital contribution to the magnetic moment arising from two unpaired electrons. Iron(II) complexes exhibiting similar magnetic moments have been reported by Dwyer, *et al.*,[20] and by Petrofsky;[21] however, no structural data are available for these compounds.

The effective magnetic moment of 4.93 BM for $[Co(BzdH)_3]Cl_2$ is within the range expected for a normal octahedral cobalt(II) complex.[22] The magnetic moments for the other two cobalt(II) complexes, *viz.*, $[Co(PvdH)_3]Br_2$ and $[Co(GdH)_3]Br_2$, are 4.22 and 3.18 BM, respectively, lower than values normally encountered. Both of these complexes exhibit anomalous Curie–Weiss behavior, which we believe indicates an equilibrium mixture of high- and low-spin species.[1] Further, it is significant that the complex presumed to have the greater low-spin character, $[Co(GdH)_3]Br_2$, contains the ligand with the smallest intraligand repulsion as inferred from both infrared and crystal field splitting data.

Conclusion

It has been demonstrated that the ligand field splitting of the d orbitals of cobalt(II) and nickel(II)

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[15] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1956, pp 78, 92, 93.

[16] J. Gavis and M. J. Sienko, *J. Am. Chem. Soc.*, **77**, 1973 (1955).

[17] W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, **54**, 980 (1954).

[18] These values are obtained recognizing that the molar magnetic susceptibilities, not the magnetic moments, are additive.

[19] J. C. Bailar, Jr., "The Chemistry of the Coordination Compounds," Reinhold Publishing Corp., New York, N. Y., 1956, p 243.

[20] F. P. Dwyer, F. Lions, and D. P. Mellor, *J. Am. Chem. Soc.*, **72**, 5037 (1950).

[21] J. L. Petrofsky, Thesis, The University of Florida, 1962.

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produced by three α-dihydrazone ligands increases in the order BdH < PvdH < GdH. These data, inferred from the diffuse reflectance spectra of the complexes, demonstrate also that the field strengths produced by PvdH and GdH are greater than any reported previously for α-dimine and α-dihydrazone complexes of nickel(II); however, few Δ values for cobalt(II) complexes are available for comparison. These observations can be interpreted in terms of intraligand repulsion effects augmented by coordination to a central metal atom. Observations on the shifts in the position of the C═N stretching vibrations in the infrared spectra of these complexes provide additional data to support this proposal. Further support is found in the fact that the cobalt(II) complexes of PvdH and GdH exhibit anomalous Curie–Weiss behavior interpreted on the basis of an equilibrium mixture of high- and low-spin complexes; *i.e.*, the two ligands in which intraligand repulsions are least provide a ligand field splitting approximately equal to the electron pairing energy.

It is suggested that the unusual magnetic moments of the two 2:1 iron(II) complexes of GdH and PvdH (exhibiting normal Curie–Weiss behavior) result from a *trans* configuration and the unusually large ligand fields produced by the coplanar bidentate ligands.

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CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY,
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Chemistry of the Cyclopentadienylmetal Carbonyls. II. Cyclopentadienyliron Carbonyl Derivatives[1]

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Cyclopentadienyliron carbonyl triphenylphosphine halides ($C_5H_5Fe(CO)[(C_6H_5)_3P]X$, X = Cl, Br, or I) have been shown to be formed in the direct reaction of triphenylphosphine and the cyclopentadienyliron dicarbonyl halide in refluxing benzene, along with the ionic derivatives $C_5H_5Fe(CO)_2(C_6H_5)_3P^+X^-$ (X = Cl, I, not Br), previously reported to be formed in this reaction. Cyclopentadienyliron dicarbonyl methyl and triphenylphosphine under ultraviolet irradiation at 90–100° give mixtures of the new compounds $C_5H_5Fe(CO)[(C_6H_5)_3P]CH_3$ and $C_5H_5Fe(CO)[(C_6H_5)_3P]COCH_3$. Evidence suggests that the pathway of this reaction involves initial formation of the former compound only and subsequent carbonylation to give the acetyl derivative. The nature of the reactions between $C_5H_5Fe(CO)_2X$ and CH_3CN and pyridine is discussed. In the course of this study several new ionic compounds of the formulas $C_5H_5Fe(CO)_2L^+PF_6^-$ and $C_5H_5Fe(CO)L_2^+PF_6^-$ (L = $(C_6H_5)_3P$, CH_3CN, py) have been prepared and characterized. Carbonyl stretching frequencies and proton nmr spectra of these compounds are reported.

Substitution reactions involving metal carbonyls, or metal carbonyl halides and alkyls, and electron-pair donor ligands have been extensively studied,[2] but little work has yet been done on similar reactions of the cyclopentadienylmetal carbonyl systems, except in the case of cyclopentadienylmanganese tricarbonyl.[3] This work was initiated to determine similarities or differences in behavior between carbonyl derivatives and cyclopentadienylmetal carbonyl derivatives. Work on cyclopentadienyliron carbonyl systems is reported here.

Experimental Section[4]

Cyclopentadienyliron dicarbonyl dimer,[5,6] cyclopentadienyliron dicarbonyl halides,[7] and cyclopentadienyliron dicarbonyl methyl[5,7] were prepared by methods well established in the literature. Merck acid-washed alumina was used without purification in column chromatographic separations.

Infrared spectra of the compounds prepared here were run on a Beckman IR-10 grating spectrometer and are reported in Table I. Proton nmr spectra were recorded on a Varian A-60; these data are tabulated in Table II. All molecular weight determinations were made using a Mechrolab osmometer, on approximately 0.01 *m* solutions in benzene.

Reaction of $C_5H_5Fe(CO)_2I$ and Triphenylphosphine.[8]—Triphenylphosphine (6.0 g, 22.9 mmoles) and $C_5H_5Fe(CO)_2I$ (5.0 g, 16.5 mmoles) were refluxed in benzene under nitrogen for 18 hr. During this time a yellow precipitate formed. The reaction mixture was filtered while hot, giving a yellow solid and a green filtrate. The yellow solid was washed with several portions of hot benzene and finally rinsed with hexane and then dried, giving 4.70 g of $C_5H_5Fe(CO)_2[(C_6H_5)_3P]^+I^-$ (50.2% yield).

Anal. Calcd for $C_{25}H_{20}O_2PIFe$: C, 53.03; H, 3.56; P, 5.47; I, 22.42. Found: C, 52.83; H, 3.68; P, 5.55; I, 22.68.

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[1] Previous paper in this series: P. M. Treichel and G. Werber, *Inorg. Chem.*, **4**, 1098 (1965).

[2] This subject is summarized in an excellent review article. See T. A. Manuel, *Advan. Organometal. Chem.*, **3**, 181 (1966).

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[5] See procedures described in R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press Inc., New York, N. Y., 1965.

[6] We thank the Antara Chemical Co. for their generous gift of iron pentacarbonyl, a precursor to this material.

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