
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

(Registered in U. S. Patent Office) (© Copyright, 1961, by the American Chemical Society)

VOLUME 83

DECEMBER 15 1961

NUMBER 23

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASSACHUSETTS]

Studies on Nickel(II) Complexes. II. On the Solution Magnetism of Bis-(N-methylsalicylaldimine)-nickel(II) and Related Complexes

By R. H. HOLM

RECEIVED MAY 22, 1961

The factors affecting the restriction of partial paramagnetism of bis-(R-N-salicylaldimine)-nickel(II) complexes in solutions of non-coordinating solvents to the case in which $R = CH_3$ were investigated. The strong concentration dependence of the magnetic moment of the N-methyl complex in chloroform and benzene and the non-obeyance of Beer's law by a near infrared transition to an excited triplet state lead to the conclusion that axial perturbations caused by solute association are predominantly, if not wholly, responsible for the solution paramagnetism. Molecular weight data indicate association of this complex in benzene whereas the N-n-alkyl complexes, essentially diamagnetic in solution, are monomeric. Examination of the solution magnetism of a number of ring-substituted N-methylsalicylaldimine-Ni(II) complexes indicates the association of the unsubstituted N-methyl complex is sterically controlled. The effects of axial perturbations on the spectral and magnetic properties of the N-methyl complex by pyridine, methanol and solute are compared. Spectral and magnetic data are presented for a number of ring- and N-substituted complexes. Substitution at the donor nitrogen of medium to strong inductively electron-withdrawing groups does not introduce any paramagnetic behavior at room temperature.

Introduction

It is now clearly recognized that there exists a group of complexes of bivalent nickel which may be termed "magnetically anomalous" in the sense that their magnetic moments do not always correspond to an integral number of unpaired electrons per nickel ion, *i.e.*, $0 < \mu_{\text{eff}} \lesssim 3.2$ B.M. Such partial paramagnetism has nearly always been found in solutions prepared by dissolving diamagnetic solid complexes in either coordinating or ostensibly non-coordinating solvents. Examples of this behavior are now well documented.¹⁻⁵

Except for a rather unique class of four-coordinate Ni(II) complexes of aminotroponimines,⁶ nearly all of the magnetically anomalous behavior at this time has been found in the Schiff base complexes of nickel with various substituted salicylaldimines.

Bis-(N-methylsalicylaldimine)-nickel(II) is the outstanding example of these anomalous nickel

complexes. Diamagnetic, monomeric and essentially planar in the solid,⁷ it becomes partially paramagnetic in coordinating and non-coordinating solvents. In inert media magnetic moments in the range 1.7-2.4 B.M. have been reported.^{2-4,8}

Two explanations have been proposed to account for the anomalous magnetism. The first involves a temperature and solvent dependent equilibrium between planar (diamagnetic) and tetrahedral (paramagnetic) forms. This description may now be safely discarded in view of the fact that the N-methyl complex has a very small dipole moment in benzene⁴ and exhibits no spectral features characteristic of tetrahedral species. The most pertinent spectral comparisons are made with those complexes which are known or may logically be assumed to have gross tetrahedral symmetry but in which the ligand field symmetry cannot be fully tetrahedral.⁹ Spectra of the anomalous Ni(II) complexes show no convincing resemblance either in band position or intensity to these pseudo-tetrahedral species.

The second explanation, based on either the strong¹⁰ or weak¹¹ ligand field model, assumes in-

(1) F. Basolo and W. R. Matoush, *J. Am. Chem. Soc.*, **75**, 5663 (1953).

(2) J. B. Willis and D. P. Mellor, *ibid.*, **69**, 1237 (1947).

(3) H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 3431 (1955).

(4) L. Sacconi, P. Paoletti and G. Del Re, *J. Am. Chem. Soc.*, **79**, 4062 (1957).

(5) L. Sacconi, R. Cini, M. Ciampolini and F. Maggio, *ibid.*, **82**, 3487 (1960).

(6) W. R. Brasen, H. E. Holmquist, R. E. Benson, *ibid.*, **82**, 995 (1960); W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **33**, 607 (1960).

(7) E. Frasson, C. Panattoni and L. Sacconi, *J. Phys. Chem.*, **63**, 1908 (1959).

(8) S. Fujii and M. Sumitani, *Sci. Repts. Tohoku Univ. 1st Ser.*, **37**, 49 (1953).

(9) F. A. Cotton, O. D. Faut and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **83**, 344 (1961).

TABLE I
 CHARACTERIZATION OF SUBSTITUTED Ni(II) SALICYLALDIMINE COMPLEXES

Ligand	R	X	M.p. (uncorr.)	Analyses			
				Calcd.		Found	
				Ni	N	Ni	N
3-Methyl-N-methylsalicylaldimine	CH ₃	3-CH ₃	210-211°	16.53	7.89	16.5	7.85
5-Methyl-N-methylsalicylaldimine	CH ₃	5-CH ₃	226-227°	16.53	7.89	16.6	7.84
3-Isopropyl-N-methylsalicylaldimine	CH ₃	3- <i>i</i> Pr	193-194°	14.27	6.82	14.4	6.70
5-Isopropyl-N-methylsalicylaldimine	CH ₃	5- <i>i</i> Pr	14.27	6.82	14.4	6.84
3- <i>t</i> -Butyl-N-methylsalicylaldimine	CH ₃	3- <i>t</i> Bu	214-215°	<i>f</i>	6.38	<i>f</i>	6.54
3-Methyl-N- <i>n</i> -propylsalicylaldimine	<i>n</i> -Pr	3-CH ₃	145-146°	14.27	6.82	14.4	6.96
5-Methyl-N- <i>n</i> -propylsalicylaldimine	<i>n</i> -Pr	5-CH ₃	166-167°	14.27	6.82	14.4	6.89
3-Isopropyl-N- <i>n</i> -propylsalicylaldimine ^a	<i>n</i> -Pr	3- <i>i</i> Pr	87-88°	12.56	6.00	12.6	6.20
5-Isopropyl-N- <i>n</i> -propylsalicylaldimine ^b	<i>n</i> -Pr	5- <i>i</i> Pr	121-123°	12.56	6.00	12.6	5.91
3-Isopropylsalicylaldimine ^c	H	3- <i>i</i> Pr	15.32	7.31	15.3	7.10
N-Allylsalicylaldimine	CH ₂ CH=CH ₂	H	157-158°	15.48	7.39	15.6	7.40
N-Benzylsalicylaldimine ^d	CH ₂ C ₆ H ₅	H	227-228°	12.25	5.85	12.2	5.80
5-Isopropyl-N-benzylsalicylaldimine	CH ₂ C ₆ H ₅	5- <i>i</i> Pr	211-213°	10.42	^e	10.5	^e
5-Nitro-N- <i>n</i> -propylsalicylaldimine ^{d,e}	<i>n</i> -Pr	5-NO ₂	12.40	11.84	12.3	11.76
N-Diphenylmethylsalicylaldimine ^e	CH(C ₆ H ₅) ₂	H	249-252°	9.30	^h	9.22	^h
N-Trifluoroethylsalicylaldimine ^e	CH ₂ CF ₃	H	12.68	6.05	12.7	6.18
5-Isopropyl-N-trifluoroethylsalicylaldimine ^e	CH ₂ CF ₃	5- <i>i</i> Pr	245-246°	...	ⁱ	..	ⁱ

^a Recrystallized from ligroin; ^b from methanol-water; ^c rust-red solid; ^d violet solid; ^e too insoluble for magnetic measurements; ^f calcd. C, 65.63, H, 7.34, found, 65.96, 7.29; ^g calcd. C, 72.49, H, 6.44; found, 72.79, 6.58; ^h calcd. C, 76.09, H, 5.11; found, 75.52, 5.16; ⁱ calcd. C, 52.68, H, 4.79; found, 52.73, 4.90.

dividual planar molecules and proposes a thermally regulated singlet-triplet distribution of molecules wherein the singlet-triplet energy separation Δ is a sensitive function of phase,¹⁰ and in the solution phase, of the solvent itself.¹¹ The susceptibility of the system is then described by the equation¹⁰

$$X^M = \frac{2g^2\beta^2N}{3kT} \left[1 + \frac{1}{2} \exp\left(\frac{\Delta}{kT}\right) \right]^{-1} + N\alpha \quad (1)$$

where the symbols have their usual meanings.¹⁰ Although it is generally agreed^{5,10,11} that anomalous solution magnetism arises from a singlet-triplet distribution, the correctness of all features of the above model is questioned on at least two counts: (a) the temperature dependent magnetic data for the N-methyl complex in inert solvents^{3,8} cannot be satisfactorily fit by equation 1 assuming temperature-independent Δ values; (b) calculation of Δ values from the experimental susceptibilities reveals unexpectedly large isothermal variations in different inert solvents and very marked temperature dependence in the same inert solvent. While temperature and solvent effects on Δ are perhaps expected, the very large effects reflected in the calculated values are thought to be more apparent than real. Hence, it was felt that a process substantially different from those previously postulated^{10,11} is responsible for the partial paramagnetism of the N-methyl complex in inert solvents. As a result, the magnetic and spectral properties of this complex were re-investigated. Additionally, a number of new derivatives were prepared and similarly investigated in an attempt to learn why in bis-(N-alkyl-salicylaldimine)-Ni(II) complexes, solution paramagnetism is restricted to the case in which the N-substituent is methyl.

Experimental

Preparation of Substituted Salicylaldehydes and their Cu(II) and Ni(II) Complexes.—The alkyl substituted sali-

cyaldehydes were prepared according to the general procedure of the Duff reaction.¹² All of the products except 5-methylsalicylaldehyde were oils and were isolated by extracting the steam distillate with ether, removing the ether and distilling the resultant light yellow oils *in vacuo*.

The bis-(alkylsalicylaldehyde)-Ni(II) complexes were obtained as green hydrated solids by treating aqueous ethanol solutions of the sodium salt of the salicylaldehyde with an excess of a saturated aqueous solution of nickel acetate, added slowly with good stirring to permit the formation of a green microcrystalline product. Too rapid an addition resulted in the formation of a sticky green product not easily isolated. The crude complexes were filtered, washed with water and sparingly with cold ethanol. After drying they were used directly in the reactions described below and not further characterized.

The bis-(alkylsalicylaldehyde)-Cu(II) complexes were prepared by direct reaction of saturated aqueous cupric acetate with an ethanol solution of the salicylaldehyde. The crystalline products were purified by recrystallization.

3-Methylsalicylaldehyde.—Boiling point, 82-85° (16 mm.); phenylhydrazone, m.p. 97°, lit., 97°.¹³

Bis-(3-methylsalicylaldehyde)-Cu(II) was recrystallized from chloroform-petroleum ether to yield olive green matty needles.

Anal. Calcd. for CuC₁₆H₁₄O₄: Cu, 19.03; C, 57.57; H, 4.23. Found: Cu, 19.0; C, 57.22; H, 4.08.

5-Methylsalicylaldehyde.—Melting point 53-54°; lit. 53°.¹⁴

Bis-(5-methylsalicylaldehyde)-Cu(II).—The crude product was only slightly soluble in chloroform, benzene or dioxane. It was recrystallized from 50% pyridine-ethanol and dried *in vacuo* over sulfuric acid to give a brownish-green microcrystalline product.

Anal. Found: Cu, 18.7; C, 57.32; H, 4.58.

3-Isopropylsalicylaldehyde.—Boiling point 86-94° (7 mm.); lit. 88-94° (6 mm.).¹⁵

Bis-(3-isopropylsalicylaldehyde)-Cu(II).—The initial product was recrystallized from ligroin to yield golden brown flaky crystals.

Anal. Calcd. for CuC₂₀H₂₂O₄: Cu, 16.29; C, 61.60; H, 5.69. Found: Cu, 16.4; C, 62.03; H, 5.55.

5-Isopropylsalicylaldehyde.—Boiling point 104-106° (13 mm.); semicarbazone, m.p. 197-198°; lit., 203°.¹⁶

(12) J. C. Duff, *J. Chem. Soc.*, 547 (1941).

(13) O. Anselmino, *Ber.*, **35**, 4099 (1902).

(14) F. Tiemann and C. Schotten, *Ber.*, **11**, 767 (1878).

(15) M. Crawford and J. W. Rasburn, *J. Chem. Soc.*, 2155 (1956).

(16) A. J. Birch and P. Elliott, *Australian J. Chem.*, **6**, 360 (1953).

(10) C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **81**, 538 (1959).

(11) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958); *ibid.*, **29**, 1129 (1959).

Bis-(5-isopropylsalicylaldehyde)-Cu(II).—The crude complex was purified by recrystallization from aqueous ethanol to give brilliant green crystals which turned brown upon drying over phosphorus pentoxide.

Anal. Found: Cu, 16.5; C, 61.50; H, 5.39.

3-*t*-Butylsalicylaldehyde.—Boiling point 108–114° (6 mm.).

Bis-(3-*t*-butylsalicylaldehyde)-Cu(II).—The initial product was recrystallized from chloroform-ligroin to yield brown needles.

Anal. Calcd. for $\text{CuC}_{22}\text{H}_{26}\text{O}_4$: Cu, 15.20; C, 63.22; H, 6.27. Found: Cu, 15.4; C, 62.88; H, 6.17.

Preparation of Ni(II) Salicylaldimine Complexes.—The bis-(*R-N*-salicylaldimine)-Ni(II) complexes in which R = Et, *n*-Pr, *n*-Bu were prepared by the method of Sacconi, *et al.*,⁴ and were characterized by melting points.^{4,17} The *N*-methyl complex was prepared by the same method and twice recrystallized from chloroform; m.p. 195–198°; reported, 192–202°, 206.2°–207.2°.¹⁷

Anal. Calcd. for $\text{NiC}_{16}\text{H}_{16}\text{O}_2\text{N}_2$: Ni, 17.97; N, 8.57. Found: Ni, 17.7; N, 8.58.

The new substituted salicylaldimine complexes, set out in Table I, were prepared by the same general method⁴ in yields in excess of 80%. All of the complexes were recrystallized from chloroform or chloroform-ligroin, unless otherwise noted, and were obtained as dark green crystalline solids.

TABLE II
MAGNETIC DATA FOR BIS-(*N*-METHYLSALICYLALDIMINE)-
Ni(II) IN CHLOROFORM AT 297°K.

g./g.	Concentration		$\chi^M_{\text{corr.}}$	$\mu_{\text{eff}}(\text{B.M.})$
	Mmolal	<i>M</i>		
0.008219	25.13	0.03668	541	1.14
.008629	26.39	.03850	583	1.18
.01087	33.23	.04839	717	1.31
.01392	42.58	.06178	846	1.42
.01658	50.71	.07343	1060	1.59
.01974	60.38	.08724	1244	1.73
.02094	64.04	.09236	1304	1.77
.02181	66.70	.09624	1348	1.80
.02332	71.31	.1025	1423	1.85
.02520	77.05	.1107	1443	1.86
.02650	81.02	.1163	1441	1.86
.02977	91.04	.1303	1441	1.86

1,1,1-Trifluoroethylamine was prepared by reduction of trifluoroacetamide according to the procedure of McKay and Vavasour.¹⁸ After isolation of the hydrochloride, the free amine was liberated using Gilman and Jones¹⁹ procedure.

Magnetic Measurements.—Magnetic susceptibilities were measured using a sensitive Gouy balance. Solution measurements were made in split sample tubes calibrated with distilled and freshly boiled water. The susceptibility of the standard was interpolated from the data of Auer.²⁰ The following solvent susceptibilities ($\times 10^6$) were determined and compare favorably with the usually accepted values:²¹ chloroform (alcohol-free), -0.4920 ; benzene (air-saturated), -0.6982 ; pyridine (distilled from barium oxide), -0.6190 ; chloroform-methanol ($\sim 50\%$ v./v.), -0.5640 . Measurements were made four times at each of four field strengths and the average deflection ratios used in the calculations. Sufficiently precise measurements ($\leq 15\%$) on the *N*-methyl complex could not be made below 0.02–0.03 *M* in benzene and chloroform. To obtain the largest possible fields by minimizing the pole gap, the solutions of Table II and III were not thermostated during measurement. These solutions were equilibrated in a constant temperature bath operating at room temperature ($297 \pm 1^\circ\text{K.}$) before use. In Table III susceptibilities $\leq 200 \times 10^{-6}$ could not be

(17) R. G. Charles, *J. Org. Chem.*, **22**, 677 (1957).

(18) A. F. McKay and G. R. Vavasour, *Can. J. Chem.*, **32**, 639 (1954).

(19) H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **65**, 1458 (1943).

(20) H. Auer, *Ann. Physik*, **18**, 893 (1933).

(21) G. Foex, "Constantes Selectiones diamagnetisme et paramagnetisme," Masson and Cie, Paris, 1957.

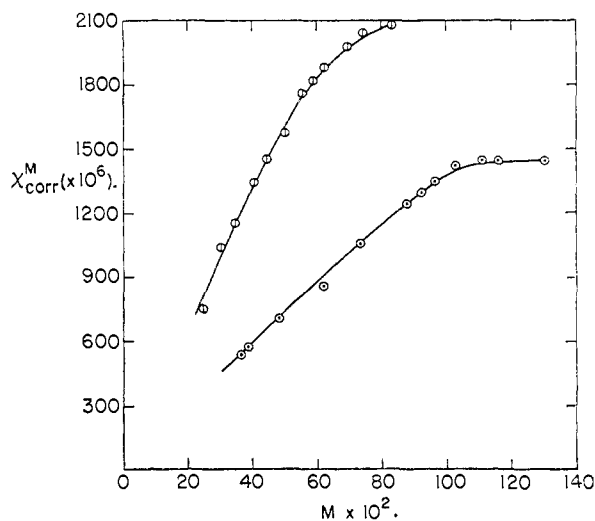


Fig. 1.—Concentration dependence of molar susceptibility of bis-(*N*-methylsalicylaldimine)-Ni(II) in CHCl_3 (O) and benzene (\odot).

measured with precision of less than 25% at the available concentrations. The accuracy of such measurements is of course questionable. Duplicate determinations were made for each entry in Tables II–IV at concentrations $\pm 2\%$ of those shown. Solutions were measured 1 to 2 hr. after preparation; the susceptibilities of solutions of Tables II and III were unchanged after aging for 2–4 weeks.

TABLE III
MAGNETIC DATA FOR BIS-(*N*-METHYLSALICYLALDIMINE)-
Ni(II) IN BENZENE AT 297°K.

g./g.	Concentration		$\chi^M_{\text{corr.}}$	$\mu_{\text{eff}}(\text{B.M.})$
	Mmolal	<i>M</i>		
0.009356	28.61	0.02471	755	1.34
.01136	34.74	.03022	1038	1.58
.01299	39.72	.03445	1162	1.67
.01527	46.60	.04041	1345	1.80
.01679	51.34	.04443	1422	1.85
.01891	57.83	.04992	1570	1.94
.02106	64.40	.05558	1753	2.05
.02233	68.28	.05887	1822	2.09
.02361	72.19	.06219	1885	2.12
.02646	80.91	.06953	1974	2.17
.02842	86.91	.07478	2040	2.21
.03165	96.79	.08299	2073	2.23

The concentration dependence of the susceptibility of the *N*-methyl complex in chloroform was further checked using a nuclear resonance method.²² Measurements were made at $28 \pm 2^\circ$ in accurately coaxial sample tubes (Wilma Glass Co., Landisville, N. J.) using the solvent absorption as the external reference. Shifts (± 0.2 cycle) were measured at 60 Mc. by the usual side-band technique using an audio oscillator. The following susceptibility values ($\times 10^6$) were obtained at the indicated millimolarities: 942 (49.77), 1025 (60.19), 1216 (69.99), 1271 (81.12), 1339 (90.43).

Diamagnetic corrections were calculated using Pascal's constant as given by Selwood.²³

Spectral Measurements.—All spectra were obtained at room temperature in quartz cells on a Cary Model 11 spectrophotometer in the visible region and on a Cary Model 14 in the near infrared. The author is grateful to Professor R. B. Woodward for use of the latter instrument.

Results

In this work investigations and discussion are confined to complexes of the general type I. The

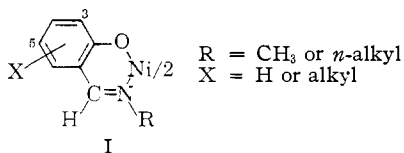
(22) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(23) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 78.

TABLE IV
 SOLUTION MAGNETIC DATA FOR SUBSTITUTED Ni(II) SALICYLALDIMINE COMPLEXES

R	X	Solvent	Conc. (mmolal)	$\chi^{M_{corr.}}$	Dia. corr.	Temp., °K.	μ_{eff} (B.M.)
H	H	Py	25.17	1329	-132	298	1.79
H	3- <i>i</i> -Pr	CHCl ₃	27.11	..	-212	298	0
		CHCl ₃ -MeOH	30.99	..	-212	297	0
		Py	29.74	1097	-212	297	1.62
CH ₃	H	CHCl ₃ -MeOH	29.57	3549	-156	297	2.92
		CHCl ₃ -MeOH	36.98	3642	-156	297	2.95
CH ₃	3-CH ₃	CHCl ₃	23.88	..	-180	296	0
		CHCl ₃	90.75	..	-180	298	0
CH ₃	3- <i>i</i> -Pr	CHCl ₃	25.09	..	-227	298	0
		CHCl ₃	90.00	..	-227	298	0
CH ₃	5-CH ₃	CHCl ₃	27.98	261	-180	297	0.79
		CHCl ₃	54.14	634	-180	298	1.23
CH ₃	5- <i>i</i> -Pr	CHCl ₃	24.92	..	-227	298	0
		CHCl ₃	48.91	319	-227	297	0.87
Et	H	CHCl ₃	90.10	107	-180	300	.51
		C ₆ H ₆	93.28	22	-180	300	.23
		CHCl ₃ -MeOH	27.29	1618	-180	297	1.97
<i>n</i> -Pr	H	CHCl ₃	99.12	74	-212	298	0.42
		C ₆ H ₆	91.80	35	-212	300	0.29
		CHCl ₃ -MeOH	27.23	1436	-212	298	1.86
<i>n</i> -Pr	3-CH ₃	CHCl ₃	91.14	..	-227	298	0
		CHCl ₃ -MeOH	29.90	154	-227	297	0.61
		Py	30.48	3949	-227	298	3.08
<i>n</i> -Pr	3- <i>i</i> -Pr	CHCl ₃	91.41	..	-283	298	0
		CHCl ₃ -MeOH	29.23	..	-283	298	0
		Py	31.02	3955	-283	298	3.08
<i>n</i> -Pr	5-CH ₃	CHCl ₃	90.50	..	-227	298	0
		CHCl ₃ -MeOH	30.17	1334	-227	297	1.79
<i>n</i> -Pr	5- <i>i</i> -Pr	CHCl ₃	93.00	..	-283	298	0
		CHCl ₃ -MeOH	29.75	1324	-283	297	1.78
<i>n</i> -Bu	H	CHCl ₃	97.73	115	-227	297	0.52
		C ₆ H ₆	89.06	83	-227	299	0.45
		CHCl ₃ -MeOH	29.56	1582	-227	296	1.94
CH ₂ CH=CH ₂	H	CHCl ₃	32.08	144	-182	297	0.59
		CHCl ₃	50.67	180	-182	298	.66
		CHCl ₃	97.69	318	-182	298	.87
		C ₆ H ₆	34.96	181	-182	297	.66
		C ₆ H ₆	66.87	190	-182	296	.67
		C ₆ H ₆	99.41	255	-182	297	.78
CH ₂ (C ₆ H ₅)	5- <i>i</i> -Pr	CHCl ₃	35.00	72	-367	298	.42
		C ₆ H ₆	32.13	..	-367	297	0

spectra and magnetism of the analogous tricyclic *sizs* complexes have been discussed recently.²⁴



Complexes in which R = aryl or branched alkyl will be discussed in forthcoming papers.

All Ni(II) complexes studied here are diamagnetic solids. Accurate diamagnetic susceptibilities were not measured.

The results of a re-examination of the magnetic moment of the N-methyl complex in chloroform and benzene are given in Tables II and III and Fig. 1. Contrary to previous reports^{2,3} the solution magnetism as measured by the Gouy method and

nuclear resonance²² (see Experimental) is a function of concentration, reaching at limiting solubility values of 1.86 and 2.23 B.M. in chloroform and benzene, respectively. These values are in fair to good agreement with those usually reported in these solvents^{2-4,8} but differ significantly from those at lower concentrations in the same media. Previously, no concentration dependence was found in chloroform,^{2,3} but there appears to be a small dependence in dioxane.³

The magnetic and spectral properties of a new series of ring-substituted salicylaldehyde complexes in solution were investigated and the data, together with those of several simple N-*n*-alkyl complexes, are shown in Tables IV and VI. The molecular weights of certain of these complexes are set out in Table V. Upon comparison of Tables II-IV with V, it is immediately obvious that there exists correlation between solution paramagnetism and association in the N-methyl complex and the monomeric and essentially diamagnetic behavior

(24) R. H. Holm, *J. Am. Chem. Soc.*, **82**, 5632 (1960). Part I of this series.

of the N-*n*-alkyl complexes.²⁵ Further, in the N-methyl series substitution of the three or five-positions of the aromatic ring by alkyl groups results in diminution or complete loss of paramagnetism. As will be seen, these effects are reasonably ascribed to steric inhibition of association.

TABLE V
MOLECULAR WEIGHT DATA ON BIS-(R-N-SALICYLALDIMINE)-
Ni(II) COMPLEXES^a

R	Solvent	Concn. mmolal	Mol. wt.		Ref.
			Calcd.	Found	
CH ₃	Benzene	~15(0.5%)	327	370 ± 20	26
	Benzene	~23(0.75%)	327	500 ± 25	26
	Benzene	~34(1%)	327	700 ± 30	26
	Benzene	~18(0.6%)	327	358	34
	Benzene	~34(1%)	327	305 ^d	34
	Benzene	~47(1.5%)	327	293 ^d	34
Et	Benzene	32.95	355	348	This work ^b
	Benzene	39.55	355	366	
<i>n</i> -Pr	Benzene	60.60	383	383	This work ^b
	Benzene	61.07	383	401	
<i>n</i> -Bu ^c	Dioxane	57.25	411	425	This work ^b
	Benzene	65.20	411	432	
	Dioxane	~0.1 molar	411	417	17 ^b
<i>n</i> -Amyl	Dioxane	~0.1 molar	440	473	17 ^b
<i>n</i> -Octyl	Dioxane	~0.1 molar	523	567	17 ^b

^a All measurements were made cryoscopically unless otherwise noted. ^b Accuracy ± 5% in molecular weight. ^c $\mu_{\text{eff}} = 0.45$ B.M. in dioxane (~0.05 M, ref. 4). ^d Ebullioscopic measurements.

Dissolution of the complexes in the mixed solvent chloroform-methanol (50% v./v.) results in most cases in the formation of what are probably monomeric six-coördinate weakly tetragonal species. The observed large increases in the magnetic moments are then due to reductions in Δ by weak coördination of alcohol molecules. Similar effects have not been observed in pure dioxane.⁴ Ring-substituted N-methyl complexes were too insoluble to be accurately measured in the mixed solvent. The diamagnetic behavior of the two 3-substituted N-*n*-propyl complexes might be due to a steric effect. The size of the N-*n*-alkyl groups up to *n*-butyl does not create a barrier to solvent interaction.

Discussion

Having discarded the possibility of a conformational equilibrium, an explanation for the solution paramagnetism of certain diamagnetic quadri-coördinate Ni(II) complexes may be sought in any mechanism which decreases the singlet-triplet separation Δ . This could occur by (1) a change in the intrinsic in-plane ligand field strength produced by the donor atom set in the limit of strong tetragonality; (2) an axial perturbation of the ligand field by some agency, generally supposed to be the solvent,¹¹ so as to decrease the tetragonality of the field; (3) a combination of the effects (1) and (2). The first effect has been supposed responsible¹⁰ for partial paramagnetism in melts⁵ and in solutions of inert solvents. The second effect is surely responsible for the partial or full paramagnetism of Ni(II) complexes dissolved in coördinating solvents and of many dihydrates and dipyrindates of complexes which when desolvated are diamagnetic solids. The proposal of Maki¹¹ that even ostensibly inert solvents such

(25) In agreement with Sacconi, *et al.*,⁴ small positive values of the corrected susceptibilities, larger in chloroform than in benzene, were consistently found but are obviously of questionable significance.

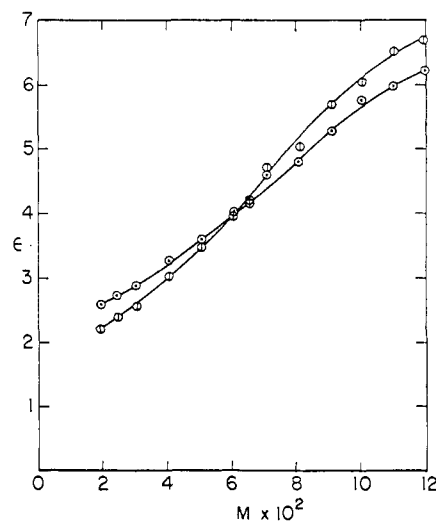


Fig. 2.—Concentration dependence of near infrared absorption intensities of bis-(N-methylsalicylaldimine)-Ni(II) at several wave lengths in chloroform (2 cm. cell): O, 1100 m μ , □, 1200 m μ .

as chloroform and benzene decrease Δ by interaction with the nickel cannot be satisfactorily tested in the case of the N-methyl complex because its low solubility in hydrocarbon solvents precludes magnetic measurements in such media.

If in the N-methyl complex the situation is one involving a singlet-triplet population of nickel ions in individual molecules with or without a solvent perturbation of Δ , then at a fixed temperature, magnetic moments and spectral intensities should be concentration independent. Reference to Tables II and III and Fig. 1 shows clearly the definite concentration dependence of the molar susceptibility and the apparent magnetic moment.

The foregoing results are strongly indicative of solute association which is inferred from the magnetic data to be somewhat greater in benzene than in chloroform. Ferguson²⁶ very recently has found the N-methyl complex to be associated in freezing benzene in a concentration range within and above which partial paramagnetism is found. Relevant molecular weight data are collected in Table V. The higher N-*n*-alkyl complexes all are monomeric and essentially diamagnetic.

Additional evidence for the effect of association on the paramagnetism is afforded by the behavior of the very broad near infrared band at 1160 m μ , which has been assigned as an excitation to the ³B_{1g} state.^{11,27} In the solid this band is spin-forbidden and very weak,¹¹ but in solution its intensity is enhanced with increasing concentration as Fig. 2 shows. This effect is due to the increased population of the low-lying triplet state and the attendant increase of spin-allowed transitions. A similar band was not observed in the other essentially diamagnetic complexes.

The singlet-singlet absorption in the visible at 610 m μ (assigned as ¹A_g - ¹B_{3g}¹¹ or ¹B_{1g}²⁸) in the

(26) J. Ferguson, *Spectrochim. Acta.*, **17**, 316 (1961).

(27) The intensity at 1160 m μ could not be followed accurately due to solvent interference.

(28) J. Ferguson, *J. Chem. Phys.*, **34**, 611 (1960).

TABLE VI
 SPECTRAL DATA FOR SUBSTITUTED Ni(II) SALICYLALDIMINE COMPLEXES

R	X	Solvent ^a	Concn. (M)	λ_{\max}	ϵ
H	H	CHCl ₃	Satd.	550	...
H	3- <i>i</i> -Pr	CHCl ₃	0.0203	560	104
		Py	.0205	555	78
CH ₃	H	CHCl ₃	.0207	(~500), 610, 1160	—, 67, 2.7
		CHCl ₃ -MeOH ^c	.0329 ^b	(~500), 610, 1050	—, 25, 16
CH ₃	3-CH ₃	CHCl ₃	.0205	614	73
CH ₃	3- <i>i</i> -Pr	CHCl ₃	.0206	625	89
		CHCl ₃ -MeOH	.00969	620	85
CH ₃	3- <i>t</i> -Bu	CHCl ₃	.0199	(~525), 640	—, 155
CH ₃	5-CH ₃	CHCl ₃	.0205	619	83
CH ₃	5- <i>i</i> -Pr	CHCl ₃	.0207	618	87
Et	H	CHCl ₃	.0203	615	70
		CHCl ₃ -MeOH	.0306 ^b	612, 1090	47, 8.2
<i>n</i> -Pr	H	CHCl ₃	.0198	615	70
		CHCl ₃ -MeOH	.0305 ^b	613, 1100	49, 7.2
		Py	.0503	580	26
<i>n</i> -Pr	3-CH ₃	CHCl ₃	.0189	630	74
<i>n</i> -Pr	3- <i>i</i> -Pr	CHCl ₃	.0199	629	97
		CHCl ₃ -MeOH	.0323 ^b	626	96
<i>n</i> -Pr	5-CH ₃	CHCl ₃	.0209	625	82
		CHCl ₃ -MeOH	.0335 ^b	620	61
<i>n</i> -Pr	5- <i>i</i> -Pr	CHCl ₃	.0197	622	84
		CHCl ₃ -MeOH	.0329	620	65
<i>n</i> -Pr	5-NO ₂	CHCl ₃	Satd.	(490), 590	..
<i>n</i> -Bu	H	CHCl ₃	0.0198	615	70
		CHCl ₃ -MeOH	.0328 ^b	615, 1100	47, 7.5
CH ₂ CH=CH ₂	H	CHCl ₃	.0203	615	74
CH ₂ (C ₆ H ₅)	H	CHCl ₃	.00749	615	73
	5- <i>i</i> -Pr	CHCl ₃	.0194	625	94
CH(C ₆ H ₅) ₂	H	CHCl ₃	.0145	615	88
CH ₂ CF ₃	H	CHCl ₃	Satd.	630	..
CH ₂ CF ₃	5- <i>i</i> -Pr	CHCl ₃	0.00333	640	93

^a CHCl₃-MeOH ~50% v./v.; ^b solutions used in magnetic measurements; ^c same as 0.01 M.

N-methyl complex was found to be only slightly concentration dependent ($\epsilon = 70.0-67.3$, $0.0023-0.023$ M) in chloroform. Ferguson²⁸ inferred from a non-obeyance of Beer's law in the ultraviolet that association was occurring at concentrations as low as 0.0012 M. In dioxane the monomeric *n*-Bu complex strictly obeyed Beer's law at 615 m μ ($\epsilon = 72.5$, $0.0017-0.021$ M). The increase in intensity of the 610 m μ band of the N-methyl complex^{4,8,29} and its 5-chloro and 5-bromo analogs²⁹ and the decrease in paramagnetism^{3,8} with increasing temperature in inert solvents now can be interpreted as due to increasing thermal dissociation of the associated species to produce the strongly tetragonal diamagnetic monomer.

It may now be concluded that the partial paramagnetism of bis-(N-methylsalicylaldehyde)-nickel (II) in inert solvents is predominantly, if not completely, a consequence of solute association and is not a result of changes in the in-plane ligand field strength upon dissolving. A correlation between solution paramagnetism and solute association in certain Ni(II) complexes is now well established. Holm and McKinney³⁰ previously had found the paramagnetism of bis-(N-sec-alkyl-salicylaldehyde) Ni(II) complexes to be roughly parallel to their degree of association. Fackler and Cotton,³¹

(29) H. C. Clark and R. J. O'Brien, *Can. J. Chem.*, **37**, 436 (1959).
 (30) R. H. Holm and T. M. McKinney, *J. Am. Chem. Soc.*, **82**, 5506 (1960).

in an important proof, have shown that the solution paramagnetism of certain β -diketone complexes is a result of molecular association. Graddon and Watton³² have shown the fully paramagnetic acetylacetonate³¹ to be trimeric in benzene as it is in the solid.³³

It is reasonably assumed that monomers interact to form the associated species in such a fashion so as to produce effective five- or six-coordination of some or all of the nickels in the aggregate. In this respect the structure proposed by Harris, Lenzer and Martin³⁴ for the fully paramagnetic buff-colored modification of the N-methyl complex is in degree an acceptable model and is shown in II for a dimer. The weak Ni...O interactions produce a z-component to the ligand field thereby lessening the tetragonality and decreasing Δ to a point at which the triplet state becomes thermally accessible to some or all of the nickels in the aggregate. There is now some precedent for the structure set out in II. Bis-(salicylaldehyde)-ethylenediimine-Cu(II) has been found to be dimeric in the solid,^{35,36} the association occurring

(31) J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **82**, 5005 (1960); *ibid.*, **83**, 2818 (1961).

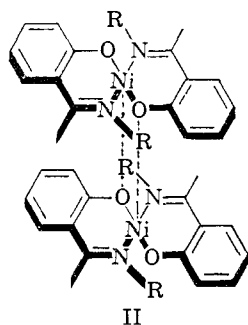
(32) D. P. Graddon and E. C. Watton, *Nature*, **190**, 906 (1961).

(33) G. J. Bullen, R. Mason and P. Pauling, *ibid.*, **189**, 291 (1961).

(34) C. M. Harris, S. L. Lenzer and R. L. Martin, *Austr. J. Chem.*, **11**, 331 (1958).

(35) K. Pachler and M. v. Stackelberg, *Z. anorg. u. allgem. Chem.*, **305**, 286 (1960).

by just such weak bonding (at 2.41 Å.) between copper and the donor oxygen in another molecule.³⁶ Dimeric bis-(dimethylglyoxime)-Cu(II)³⁷ associates in the solid in a rather similar fashion.



II

The partial paramagnetism of the N-*n*-alkyl complexes in chloroform-methanol lends some support to the proposed model of association, which requires that axial interaction by oxygen can substantially reduce Δ . Here the paramagnetism seemingly can only arise from an axial perturbation of the field by one or, more likely, two alcohol molecules. The band at 615 $m\mu$ persists, unchanged or altered only very slightly in energy, but is markedly reduced in intensity, an effect attributable to the reduced population of the singlet ground state. Δ is lowered to 330–390 cm^{-1} and a very broad band appears at 1100 $m\mu$. The N-methyl complex becomes increasingly paramagnetic in this medium and the intensity of the 610 $m\mu$ band is greatly weakened. It is not possible to tell if the association is completely broken down in the mixed solvent as it is in pyridine, but it is evident that methanol interaction represents an intermediate situation between strong axial perturbation in pyridine and similar but quite weak effects in the aggregates. The solvent dipole μ' , in the sense of Maki,¹¹ is deduced as 0.4. Table VII illustrates the results. It is suggested that the μ' value of 0.15 arises from weak solute-solute interactions with possibly some small contribution from solvent, noting that there exists spectral evidence for perturbation of ligand field energies by chloroform³⁸ but that the interaction affects mainly an excited state. Therefore, the principal, if not the only role of inert solvents is one of permitting varying degrees of solute association rather than direct interactions with the complex. Indeed, several complexes now have been prepared,³⁹ *viz.*, those with R = *i*-Pr, X = 3-CH₃ and 3-*i*-Pr, which have moments of 2.19 and 2.47 B.M., respectively, in cyclohexane in which solvent interaction of the above type is impossible.

The specificity of the association and partial paramagnetism to the case in which R = CH₃ is suggestive of a steric effect. When R is larger than methyl Stuart-Breigle metal chelate scale models indicate that rotational motion of the alkyl chains will strongly inhibit association as depicted

(36) D. Hall and T. N. Waters, *J. Chem. Soc.*, 2644 (1960).

(37) E. Frasson, R. Bardi and S. Bezzi, *Acta Cryst.*, **12**, 201 (1959).

(38) R. L. Belford, M. Calvin and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957); T. N. Waters and D. N. Hall, *J. Chem. Soc.*, 1200 (1959); D. P. Graddon, *J. Inorg. Nuclear Chem.*, **14**, 161 (1960).

(39) R. H. Holm, to be published in Part III.

TABLE VII

EFFECT OF AXIAL PERTURBATION ON THE SPECTRA OF THE N-METHYL COMPLEX

Solvent	λ_{max} (ϵ)	Assignment ^e	μ'	μ_{eff}	Δ (cm^{-1})
Pyridine ^a	960 (14.1)	$^3B_{3g}-^3B_{1g}$	0.7	3.16 ^d	-640
	785 (4.2)	$^{-1}B_{3g}$			
	570 (11.5)	$^{-3}B_{2g}$			
CHCl ₃ -MeOH	1050 (16.0)	$^3B_{3g}-^3B_{1g}$.4	2.92	-94 ^e
	610 (25.0)	$^1A_g-^1B_{3g}$			
	(~500) (very weak)	$^1B_{1g}$			
CHCl ₃ ^b	1160 (3-7)	$^1A_g-^1B_{3g}$.15	<i>f</i>
	610 (67.0)	$^{-1}B_{3g}$			
	(~500)	$^{-1}B_{1g}$			

^a Data and assignments from ref. 11. ^b Assignments from ref. 11. ^c See Fig. 9, ref. 11b. ^d Ref. 4. ^e Assuming solvated monomers only. ^f See Table II.

in II or for the alternative mode of association involving dual Ni...O interactions in which the molecules are at approximate right angles to each other. The N-allyl complex (*cf.* Table IV) is apparently a weak exception to this steric effect.

In order to substantiate further the proposed correlation between solution paramagnetism and association and to affirm that the N-CH₃ grouping differs from N-*n*-alkyl groups only in its capacity to allow association, sterically enforced separation of a series of N-CH₃ complexes into monomers was accomplished by substitution of alkyl groups at the 3- and 5-positions of the benzene ring (I). A parallel series of N-*n*-propyl complexes was prepared in order to observe the effect of substitution on the spectra with no complications due to possible association. The data of Table IV show that ring substituents at the 3-position eliminate paramagnetism in the N-methyl series, whereas those at the 5-position are somewhat less effective, in agreement with the models which show the 3-position to be sterically the more critical.

Ideally, the effects of substituents on the solution magnetism of the N-methyl complexes should be observed at a constant in-plane ligand field strength equal to that of the unsubstituted complex. The spectral data of Table VI show that alkyl substitution invariably produces small low energy shifts of the visible band, and the possibility of attendant substantial changes in Δ exists. Since the substituents are electron releasing, their dominant effect must be to increase the ligand oxygen dipole and thus strengthen the field. This is borne out by the spectra of a series of bis-(alkyl-salicylaldehyde)-Cu(II) complexes. The following data show for 3-substitution a pronounced blue shift as is expected for -Cu(II) on increasing the field strength. The *t*-Bu complex is anomalous in this respect. Although the ligand field strengths

X	Concn. (M)	λ_{max}	ϵ
H	0.00343	670	69
3-CH ₃	.00752	645	62
5-CH ₃	Satd.	675	..
3- <i>i</i> Pr	.00716	630	66
5- <i>i</i> Pr	.00691	675	63
3-Bu	.00797	680	100

and Δ are unavoidably altered, the partial paramagnetism exhibited by the 5-substituted com-

plexes of the *n*-Pr series indicates that weak axial effects perturb Δ to an extent comparable to that in the unsubstituted complex. It is concluded that steric inhibition of association is the dominant effect in the diminution or complete loss of solution paramagnetism by the N-methyl complexes.

The small red shifts in the spectra of the alkyl-substituted complexes point out the general situation accounting for the ease in obtaining paramagnetism in the N-alkylsalicylaldimine complexes. In bis-(salicylaldimine)-Ni(II) the spin-allowed visible band (presumably $^1A_g - ^1B_{3g}$) occurs at 555 $m\mu$, and neither this complex^{2,3} nor its 3-isopropyl variant becomes fully paramagnetic in pyridine. Upon replacing the imine hydrogen by the more strongly electron releasing methyl group, the visible band in chloroform is shifted ~ 1700 cm^{-1} to lower energies and Δ becomes negative in pyridine. These results are anticipated by the weak field model¹¹ in D_{2h} symmetry. In the salicylaldimines the in-plane ligand field provided by the O_2N_2 donor set and modified by the nitrogen substituent is such that Δ is more or less perturbed by weak axial effects. It would be of interest to assess the criticality of this range of field strengths by comparison with other ligands providing D_{2h} symmetry, but sufficient data on other systems are not yet available.

It is a general conclusion of symmetry arguments that the d^8 configuration in each of the three common planar symmetries should possess in some range of ligand parameters a triplet ground state. An important point at issue in the study of any series of quadricoördinate Ni(II) complexes is whether

or not a triplet ground state can be stabilized strictly as a result of the in-plane ligand field strengths. This is evidently not possible with the N-alkylsalicylaldimine complexes in solution nor with certain Ni(II) β -diketone complexes³¹ whose paramagnetism is the result of molecular association. Attempts in this work to alter the ligand field strength sufficiently to cause a change in spin state resulted in diamagnetic solids when the medium to strong electron withdrawing groups $CH_2C_6H_5$, $CH(C_6H_5)_2$ and CH_2CF_3 were appended to nitrogen. Only $-CH_2CF_3$ affected the visible spectrum, and the small red shift seems curious if the field retains D_{2h} symmetry. However, it has been found possible to produce extensive population of the triplet state in both the solid and solution when the nitrogen substituent is aromatic.³⁰ These complexes will be the subject of a forthcoming part of this series.

The results of this investigation together with the earlier significant findings on Ni(II) bis-(β -diketone) complexes³¹ emphasize the necessity for the consideration of solute association in solution and specific associative interactions in the solid among those factors which may lessen the tetragonal character of the ligand field and hence promote the relative stability of a triplet state.

Acknowledgments.—This work was supported by the Milton Fund of Harvard University and the National Science Foundation. The author is grateful to Mr. T. M. McKinney for technical assistance and to Professors F. A. Cotton and H. C. Clark for their courtesy in allowing the author examination of their results prior to publication.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

The Electronic Structures of Tetrahedral Cobalt(II) Complexes

BY F. A. COTTON,^{1a} D. M. L. GOODGAME^{1b} AND M. GOODGAME

RECEIVED MAY 27, 1961

Thorough spectral and magnetic studies of the tetrahedral Co(II) species $[CoI_4]^{2-}$, $[CoBr_4]^{2-}$, $[CoCl_4]^{2-}$, are reported. New data on some other tetrahedral species are also given, and from these and previously reported data the following general conclusions, *inter alia*, about tetrahedral Co(II) complexes and their electronic structures are drawn. (1) The order of ligands in the spectrochemical series, as deduced from the Δ values, agrees well with the established order and several additional ligands are now accurately or approximately located in the general order. (2) From the Racah parameters (B'), and from the spin-orbit coupling constants (λ'), we obtain two more or less independent lines of evidence that appreciable overlap of metal and ligand orbitals occurs in these complexes. (3) $[CoX_4]^{2-}$ ions probably are not obtained, or only partially obtained, in aqueous solutions of Co(II), even when saturated with HX or LiX (X = Cl, Br, I). (4) $Co(OH)_2$ dissolves in concentrated alkali metal hydroxide to give one or more tetrahedral species, which probably are $[Co(OH)_4]^{2-}$ and/or $[Co(OH)_3(H_2O)]^-$.

Introduction

Previous papers from this Laboratory have reported spectral and magnetic data concerning the electronic structures of tetrahedral complexes of cobalt(II) and discussed the analysis and interpretation of these data for several groups of compounds.²⁻⁶ There is also a number of papers from

other laboratories containing experimental and theoretical contributions to this subject. Many of these⁷⁻¹⁷ will be discussed later in this paper.

(1) (a) Alfred P. Sloan Foundation Fellow. (b) Now in the Department of Chemistry, Imperial College of Science and Technology, London.

(2) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **31**, 788 (1959).

(3) R. H. Holm and F. A. Cotton, *ibid.*, **32**, 1168 (1960).

(4) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2983 (1960).

(5) F. A. Cotton and M. Goodgame, *ibid.*, **83**, 1777 (1961).

(6) F. A. Cotton, D. M. L. Goodgame, M. Goodgame and A. Sacco, *ibid.*, **83**, 4157 (1961).

(7) L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

(8) C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955).

(9) T. Dreisch and W. Trommer, *Z. physik. Chem.*, **B97**, 37 (1937).

(10) C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectroscopy*, **2**, 342 (1958); **4**, 190 (1960).

(11) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(12) B. N. Figgis and R. S. Nyholm, *ibid.*, 338 (1959).

(13) B. N. Figgis, *Trans. Faraday Soc.*, **56**, 1553 (1960).