

TABLE I
 PREPARATIVE DATA ON THE NEW COMPOUNDS

Anion	Mp, °C	Yield, %	Calcd				Analyses, %			
			C	H	Mn	Cl	C	H	Mn	Cl
$C_5H_5Mn(CO)_2SnCl_3^-$	163-164	30	47.4	3.2	7.0	13.6	47.2	3.3	6.5	13.7
$C_5H_5Mn(CO)_2GeCl_3^-$	141-142	18	50.4	3.4	7.5	14.4	50.6	3.2	7.9	14.0
$CH_3C_5H_4Mn(CO)_2SnCl_3^-$	149-150	27	48.1	3.4	6.9	13.3	48.3	3.5	6.2	13.0
$CH_3C_5H_4Mn(CO)_2GeCl_3^-$	133-135	25	51.1	3.6	7.3	14.2	50.8	3.8	7.6	14.6
$Mn_2(CO)_9SnCl_3^-$	117-119	27	40.8	2.1	11.3	11.0	40.5	2.4	10.8	11.5
$Mn_2(CO)_9GeCl_3^-$	107-109	22	42.9	2.2	11.9	11.5	43.3	1.9	12.3	11.8

samples of $C_5H_5Mn(CO)_3$ and $CH_3C_5H_4Mn(CO)_3$ were generously donated by Ethyl Corp. Dimanganese decacarbonyl was obtained from Strem Chemical Co.

Preparation of $(C_5H_5)_4AsC_5H_5Mn(CO)_2MCl_3$.—Since both the tin and germanium derivatives were prepared in the same manner, only one preparation will be described. A 0.70-g sample of $\pi-C_5H_5Mn(CO)_3$ dissolved in 100 ml of THF was irradiated under an inert atmosphere for 2 hr with a GE AH4 floodlamp. To the red solution a 0.6-g sample of $(C_5H_5)_4AsSnCl_3$ was added. The mixture was stirred for 15 min and the solvent was removed under vacuum. The residue was extracted with a mixture containing 20 ml of CH_2Cl_2 and 100 ml of diethyl ether. The extract was filtered and pentane was slowly added to the filtrate. An orange-yellow solid, 0.21 g, was obtained.

This same procedure was used to prepare the corresponding methyl- π -cyclopentadienyl derivatives. See Table I for details.

Preparation of $(C_5H_5)_4AsMn_2(CO)_9MCl_3$.—Since the preparations of both the tin and the germanium compounds were identical, only one will be described. A mixture containing 0.63 g of $(C_5H_5)_4AsSnCl_3$ and 0.69 g of $Mn_2(CO)_{10}$ in 50 ml of CH_2Cl_2 was irradiated under an inert atmosphere with the same lamp described above. After approximately 0.5 hr some solid had formed in the reactor. This was removed by filtration and the irradiation continued for 1 hr more. The solvent was removed under vacuum and the residue was dissolved in 10 ml of CH_2Cl_2 . Diethyl ether, 60 ml, was added and the mixture was filtered. Pentane was added slowly to the filtrate (too rapid addition results in oiling) and a 0.28-g sample of product was obtained. See Table I for details.

Infrared Spectra.—The infrared spectra were taken on CH_2Cl_2 solutions (concentrations about 10 mg/ml) using a Perkin-Elmer Model 621 spectrometer which had been calibrated with indene. See Table II.

 TABLE II
 INFRARED STRETCHING FREQUENCIES FOR THE NEW COMPOUNDS

Anion	Freq, cm^{-1}
$C_5H_5Mn(CO)_2SnCl_3^-$	1926 s, 1863 s
$C_5H_5Mn(CO)_2GeCl_3^-$	1924 s, 1858 s
$CH_3C_5H_4Mn(CO)_2SnCl_3^-$	1924 s, 1859 s
$CH_3C_5H_4Mn(CO)_2BeCl_3^-$	1922 s, 1855 s
$Mn_2(CO)_9SnCl_3^-$	2102 m, 2062 m, 2016 s, 1974 sh, 1934 m
$Mn_2(CO)_9GeCl_3^-$	2091 mw, 1062 m, 2015 s, 1982 sh, 1932 m

Conductivity Measurements.—The conductivities of the salts were determined in nitromethane solutions using a Yellow Springs Instrument Co. Ind. Model 31 conductivity bridge. The cell constant of the cell employed was 0.1792 and the specific conductivity of the nitromethane was $5.70 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$. The anion, concentration (M), and equivalent conductance ($cm^2/\text{ohm equiv}$) for the material prepared are as follows: $C_5H_5Mn(CO)_2SnCl_3^-$, 1.052×10^{-3} , 70.2; $C_5H_5Mn(CO)_2GeCl_3^-$, 1.117×10^{-3} , 73.1; $CH_3C_5H_4Mn(CO)_2SnCl_3^-$, 0.989×10^{-3} , 65.8; $CH_3C_5H_4Mn(CO)_2GeCl_3^-$, 1.20×10^{-3} , 75.7; $Mn_2(CO)_9SnCl_3^-$, 1.002×10^{-3} , 67.1; $Mn_2(CO)_9GeCl_3^-$, 1.071×10^{-3} , 71.0.

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Magnetochemical Investigation of Stereochemical Change for the Cobalt(II) Ion in Solution

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In the crystalline state or in solution, the cobalt(II) ion is found most frequently in one of two ligand environments: four-coordinate tetrahedral or six-coordinate octahedral. In the former, the ion possesses an orbitally nondegenerate electronic ground state, 4A_2 , while in the latter (weak-field limit), it possesses a threefold degenerate ground state, $^4T_{1g}$. The magnetic moment would therefore be expected to contain a larger orbital contribution for the ion in the octahedral field than in the tetrahedral field. A considerable amount of work has verified this correlation of the magnetic moment with the geometrical structure for crystalline cobalt(II) compounds.³⁻⁶ However, with the exception of some early work, prior to the development of the ligand field theory and a few recent measurements in single solvents, the authors are unaware of any systematic magnetochemical study of stereochemical change for the cobalt(II) ion in solution. In the present investigation, the magnetic moment of this ion has been determined in water as a function of added chloride or thiocyanate ion and in water-dimethylformamide solutions as a function of solvent composition.

Experimental Section

The magnetic moments, determined by the Gouy method at $25.0 \pm 0.5^\circ$ in a Pyrex tube (25.00 ml) calibrated with nickel chloride solutions,⁷ are reproducible to better than ± 0.02 BM. The diamagnetic gram-susceptibilities of methanol and dimethylformamide (DMF) were determined to be -0.640×10^{-6}

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(-0.65×10^{-6}) and -0.552×10^{-6} , while literature values were used for the ions⁹ and water.¹⁰ No correction was made for temperature-independent paramagnetism, and the magnetic moment, μ_{eff} , was calculated¹¹ from

$$\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2} \text{ BM} \quad (1)$$

Analytical reagent grade $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, methanol, and DMF were used as received. Aqueous stock solutions of HCl (36.60% Cl^-), LiCl (37.17% Cl^-), and KSCN (38.27% SCN^-) were prepared. All solutions were prepared by weight, approximately 1 M in Co(II), except for the thiocyanate study where solubility limited the Co(II) concentration to about 0.5 M. Gravimetric analyses for cobalt, chloride, and thiocyanate were made on the solutions containing them. The results are given in Tables I and II.

TABLE I
MAGNETIC MOMENTS OF Co(II) IN AQUEOUS SOLUTION AT 25°

a		b		c	
Wt fraction Cl^-	μ_{eff} , BM	Wt fraction Cl^-	μ_{eff} , BM	Wt fraction SCN^-	μ_{eff} , BM
0.0638 ^d	4.995	0.1363	4.992	0.0	4.937
0.0650 ^d	4.994	0.2037	4.999	0.0	4.940
0.1023	4.994	0.2635	4.932	0.04697	4.938
0.1373	5.004	0.2730	4.892	0.05093	4.942
0.1800	4.995	0.3270	4.789	0.1050	4.950
0.2082	5.003	0.3477	4.766	0.1312	4.954
0.2394	4.962	0.3583	4.769	0.1732	4.978
0.2730	4.880			0.1818	4.968
0.3041	4.814			0.2101	4.975
0.3362	4.739			0.2810	4.978
0.3511	4.730			0.3080	4.986
0.3520	4.741			0.3433	5.002
0.3750 ^e	4.732			0.3704	4.995

^a CoCl_2 in aqueous HCl (1 M Co(II)). ^b CoCl_2 in aqueous LiCl (1 M Co(II)). ^c $\text{Co}(\text{NO}_3)_2$ in aqueous KSCN (0.5 M Co(II)). ^d No acid added. ^e Prepared from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ dried under vacuum at 110°.

TABLE II
MAGNETIC MOMENTS OF Co(II) IN SOLUTION AT 25°

a			b		
Wt fraction H_2O	Wt fraction DMF	μ_{eff} , BM	Wt fraction H_2O	Wt fraction CH_3OH	μ_{eff} , BM
0.8816	0.0	4.978	0.8411	0.0	4.945
0.7864	0.0928	4.972	0.6745	0.1710	4.959
0.7110	0.1702	4.976	0.4952	0.3431	4.967
0.6198	0.2633	4.987	0.3233	0.5150	4.985
0.5076	0.3719	4.989	0.1529	0.6873	5.018
0.4196	0.4686	4.991	0.0938	0.7329	5.011
0.3379	0.5394	4.990			
0.2745	0.6021	4.932			
0.1787	0.7006	4.872			
0.0992	0.7816	4.827			
0.0	0.9243 ^{c,d}	4.801			
0.0	0.9697 ^e	4.806			
0.0	0.9868 ^{c,f}	4.793			

^a CoCl_2 in water-DMF mixtures (1 M Co(II)). ^b $\text{Co}(\text{NO}_3)_2$ in water-DMF mixtures (1 M Co(II)). ^c Used anhydrous CoCl_2 ; prepared under vacuum at 110°. ^d Approximately 0.5 M Co(II). ^e Approximately 0.12 M Co(II). ^f Approximately 0.08 M Co(II).

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Results

A survey of the literature on μ_{eff} for the Co(II) ion in solution reveals that the work could be divided into three categories: (1) aqueous solutions containing a single cobalt salt at different concentrations, (2) aqueous solutions containing a cobalt salt at a fixed concentration with varying concentration of a second solute, and (3) nonaqueous solutions of a cobalt salt.

In the first category, Brant¹² reported that the magnetic susceptibility of aqueous solutions of CoCl_2 was constant ($\mu_{\text{eff}} = 4.94$ BM at 20°) over the concentration range 0.001-2.035 M. In contrast, Cabrera,^{13,14} Trumpler,¹⁵ and Chatillon¹⁶ found that the susceptibility of aqueous solutions of CoSO_4 exhibited a pronounced maximum, although the quantitative agreement was only fair. More recently, Lin¹⁷ found the susceptibility of aqueous solutions of CoSO_4 to be practically independent of concentrations and also independent of added H_2SO_4 . In a study of aqueous solutions of cobalt(II)-amino acid complexes, White¹⁸ reported a value of 5.02 BM for CoCl_2 and $\text{Co}(\text{NO}_3)_2$ (0.057 M, room temperature).

Cabrera,^{13,14} Trumpler,¹⁵ Chatillon,¹⁶ and, more recently, Varadi¹⁹ have reported a dependence of μ_{eff} for Co(II) in aqueous solution on added HCl, but the lack of mutual agreement suggested that a thorough and systematic investigation was necessary. Matura²⁰ has reported a slight dependence of μ_{eff} on pH.

In the present study, μ_{eff} has been determined for CoCl_2 over a range of chloride concentration, 2-13 M, using added HCl or LiCl (Figure 1). The results are

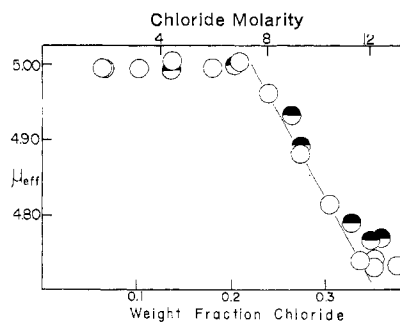


Figure 1.—Magnetic moment of Co(II) (1 M CoCl_2) in aqueous solution at 25°C: O, as a function of added HCl; ●, added LiCl.

interesting both as a magnetochemical study and as a satisfactory corroboration with spectrophotometric,^{21,22}

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ion-exchange,²³ and magnetic resonance^{24,25} studies on Co(II) in chloride solutions. The μ_{eff} is constant, within experimental error, over the range of 2–7 *M* chloride ion, at which point a pronounced decrease begins. It should be noted that, for the HCl solutions, the decrease is a linear function of the chloride ion concentration over the range 8–12 *M*. The LiCl solutions show a similar but slightly more scattered decrease. For chloride concentrations greater than 12 *M*, μ_{eff} appears to be constant at 4.73 ± 0.01 BM in the HCl studies. It is interesting to note that μ_{eff} values for three crystalline quaternary ammonium salts of the CoCl_4^{2-} anion have been reported²⁶ as 4.72^{5,6} and 4.67²⁷ BM.

The μ_{eff} results indicate that below 7 *M* chloride the Co(II) is predominantly in an octahedral ligand field, while above 12 *M* the equilibrium has been shifted completely to Co(II) in a tetrahedral field. However, it would be unwise to attempt on the basis of μ_{eff} values an interpretation of the $\text{H}_2\text{O}-\text{Cl}^-$ composition of the octahedral complexes below 7 *M* ($\text{Co}(\text{H}_2\text{O})_6^{2+}$, $\text{Co}(\text{H}_2\text{O})_5\text{Cl}^+$, or $\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2$) or of the tetrahedral complexes above 12 *M* (CoCl_4^{2-} or $\text{Co}(\text{H}_2\text{O})\text{Cl}_3^-$).

From a spectrophotometric analysis of this system, Howell²¹ concluded that up to about 5 *M* chloride, two chloride ions were replacing two water molecules, preserving the octahedral ligand field. The extinction coefficient at 690 nm (one of the λ_{max} characteristic of Co(II) in a tetrahedral environment) was negligible up to 7 *M* and then increased as a linear function of chloride concentration (7–9 *M*), at which point he concluded the Co(II) was present entirely as $\text{Co}(\text{H}_2\text{O})\text{Cl}_3^-$. Further increase in the chloride ion concentration converted the trichlorocobalt(II) complex to the tetrachloro complex.

In a study of the behavior of the Co(II) ion on an anionic exchange resin, Kraus²³ found that the elution constant was high and independent of chloride concentration up to about 3 *M*, while at higher concentrations the Co(II) began to be adsorbed, suggesting the conversion of the positive or neutral complexes to anionic complexes by further substitution of Cl^- into the coordination shell.

Finally, Chmelnick²⁴ has found confirmation from magnetic resonance studies of the existence of $\text{Co}(\text{H}_2\text{O})_6^{2+}$ in water, while Zeltmann²⁵ has studied the oxygen and chlorine nmr of chloride solutions of Co(II). In the latter study, it was found that in the 0–6 *M* chloride region the hexaaquo complex was converted into the monochloropentaaquo complex, the latter reaching a maximum concentration at 6 *M*. With further increase in the chloride concentration, small amounts of $\text{CoCl}_2(\text{H}_2\text{O})_2$ and $\text{CoCl}_3\text{H}_2\text{O}^-$ appear, reaching maxima at 9 and 10 *M*, respectively, and then from 11 to 16 *M* the CoCl_4^{2-} complex is the predominant species in solution.

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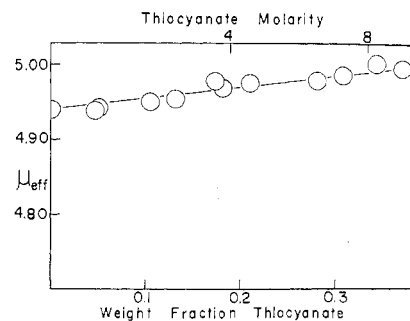


Figure 2.—Magnetic moment of Co(II) (0.5 *M* $\text{Co}(\text{NO}_3)_2$) in aqueous solution at 25° as a function of added KSCN.

Figure 2 shows the effect of added thiocyanate ion (0–9 *M*) on μ_{eff} for aqueous 0.5 *M* $\text{Co}(\text{NO}_3)_2$ solutions. Over the entire concentration range, μ_{eff} shows a gradual increase from 4.94 to 5.00 BM, values characteristic of the octahedrally coordinated Co(II) ion. This is in sharp contrast to the effect of added chloride ion. Considering that the μ_{eff} values for the tetrahedrally coordinated Co(II) salts, $((\text{C}_2\text{H}_5)_4\text{N})_2\text{Co}(\text{SCN})_4$ and $((\text{C}_6\text{H}_5)_4\text{As})_2\text{Co}(\text{SCN})_4$, are 4.56^{6,26} and 4.48 BM,^{26,28} respectively, the present results would suggest that a $\text{SCN}^-:\text{Co}(\text{II})$ ratio of about 18 is insufficient for this ligand to bring about tetrahedral coordination of Co(II) in aqueous media.

Csokán and Kiss²⁹ and Lehné³⁰ have investigated the effect of added thiocyanate on the spectrum of the aqueous Co(II) ion. The latter author reported the stepwise formation of the complexes $\text{Co}(\text{SCN})_n^{2-n}$ where $n = 1-4$, the value of n depending on the thiocyanate concentration. In the complexes where $n = 1-3$, the Co(II) coordination number was brought up to 6 with water molecules, while for $n = 4$, the coordination number was 4. Lehné, working at 0.01 *M* Co(II), found that at 8.6 *M* SCN^- the Co(II) was present entirely as $\text{Co}(\text{SCN})_4^{2-}$. The much higher Co(II) concentration in the present study may explain the apparent absence of the four-coordinate complex.

Horrocks³¹ has interpreted shifts of the water proton magnetic resonance in 0.1 *M* Co(II) solutions, up to a $\text{SCN}^-:\text{Co}(\text{II})$ ratio of about 7, in terms of the four octahedral complexes: $\text{Co}(\text{H}_2\text{O})_{6-n}(\text{SCN})_n^{2-n}$ where $n = 0-3$.

Bhatnagar,³² Fahlenbrach,³³ and Haberditzl³⁴ have investigated the magnetic susceptibility of various Co(II) salts in a number of nonaqueous solvents. The results of the present study provide a logical extension of Haberditzl's work, where values of 5.05 and 4.96 BM were reported for CoCl_2 in water and DMF.

Figure 3 shows the μ_{eff} for CoCl_2 and $\text{Co}(\text{NO}_3)_2$ in water–DMF mixtures. The chloride shows a constant value, characteristic of octahedral coordination, to a

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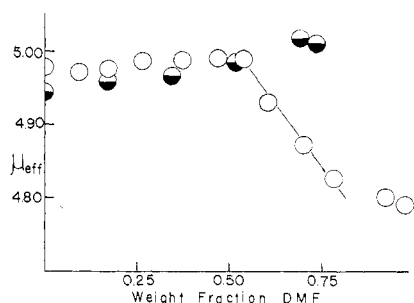


Figure 3.—Magnetic moment of Co(II) in water-DMF mixtures at 25°: O, 1 M CoCl₂; ●, 1 M Co(NO₃)₂.

weight fraction DMF of about 0.5 and then decreases approximately linearly to 0.80 weight fraction, becoming constant again at about 4.80 BM. Bull³⁵ has reported a value of 4.71 BM²⁶ for the solid CoCl₂DMF₂, suggesting that in the present study, even in the DMF-rich mixtures, some of the Co(II) is still in an octahedral field. In contrast to the chloride, the nitrate salt shows a slight increase in μ_{eff} over this solvent composition range, the value being consistent with octahedral coordination.

Dunn,³⁶ in a spectrophotometric study of CoCl₄²⁻ and CoCl₂ in DMF, has suggested that there is strong solute-solvent interaction in these systems leading to both four- and six-coordinate complexes: CoCl₂DMF₂, CoCl₃DMF⁻, Co(DMF)₆²⁺, and Co(DMF)₅Cl⁺. Popov³⁷ has found a pronounced dependence of the Co(II) spectra in DMF on the anion, finding the chloride and nitrate to have different spectra, consistent with the present study.

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Metal Complexes of 4-Methylthiazole

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A recent publication¹ has reported the preparation of a number of complexes of alkyl-substituted thiazoles. We are interested² in the preparation of model compounds for thiazole- and thiamine-metal ion interactions in biological processes and have examined the coordination behavior of 4-methylthiazole (4-MeT) with cobalt(II), nickel(II), copper(II), zinc(II), and palladium(II) salts. Our results with cobalt(II), zinc(II),

and copper(II) halides agree with those of Hambright, *et al.*, but we have prepared several additional complexes with these metals and also with nickel(II). Certain of our conclusions differ from those previously reported.

Results and Discussion

Table I lists the new complexes we have prepared, together with our results for certain of those already reported.¹ Diffuse reflectance electronic spectra and room-temperature magnetic moments are also given. In certain cases we were unable to obtain magnetic moment data. Far-infrared spectra (666–222 cm⁻¹) are listed in Table II, together with $\nu_{\text{M-N}}$ and $\nu_{\text{M-X}}$ assignments where possible.

Nickel Complexes.—We had already prepared a blue complex, Ni(4-MeT)₂Br₂, to which we had assigned a tetrahedral stereochemistry. Hambright, *et al.*, reported the formation of a light blue complex of this stoichiometry and suggested it has an octahedral structure. We have repeated their preparation and have obtained a blue complex identical with the one we had obtained earlier. We have repeated the preparation a number of times under widely varying conditions and have always obtained the same product, with the blue color varying somewhat in intensity from preparation to preparation. The electronic spectrum is slightly different from that quoted earlier.¹ We assign the spectrum in *T_d* symmetry, bands at 9.65 and 17.3 kK corresponding to transitions ⁸T₁(F) → ⁸A₂ and ³T₁(F) → ³T₁(P), respectively. The tetrahedral stereochemistry is supported by the fact that blue Ni(4-MeT)₂Br₂ and tetrahedral Co(4-MeT)₂Br₂ are isomorphous. In acetone solution, in the presence of a slight excess of ligand, this complex retains its tetrahedral structure. Using the method of Ballhausen³ we calculate values of *Dq* = 450 cm⁻¹ and *B* = 772. We have also prepared the tetrahedral complex [(C₂H₅)₄N⁺][Ni(4-MeT)Br₂⁻] which has a spectrum with band positions intermediate between those of Ni(4-MeT)₂Br₂ and NiBr₄²⁻.

We have also obtained a yellow form of the complex Ni(4-MeT)₂Br₂ from ethanol solution. This reverts to the blue isomer at room temperature and rapidly so on heating. We assume that the yellow form corresponds to an octahedral halogen-bridged complex with axial 4-methylthiazole groups. The magnetic moment of 2.98 BM is consistent with such a structure.

The previously reported octahedral complex Ni(4-MeT)₃(NO₃)₂ appears to be stable in solution in the presence of excess ligand or excess metal nitrate, there being no evidence for the formation of the 1:4 or 1:2 species. The infrared spectrum clearly shows that the nitrate group is coordinated; thus the ν_3 band is split into broad bands at 1445 and 1288 cm⁻¹. The complex probably has one monodentate and one bidentate nitrate group as suggested⁴ for Ni(py)₃(NO₃)₂.

We have also prepared Ni(4-MeT)₂I₂ and Ni(4-MeT)Br₂. The former complex is isomorphous with the corresponding cobalt analog, of tetrahedral stereochem-

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