The high temperature form of MoGe$_2$ is therefore isostructural with MoSi$_2$[8] and ReSi$_2$.[9] Diffraction data for β-MoGe$_2$ are summarized in Table II.

No shift in lattice constants of any of the molybdenum–germanium phases was observed as the compositions of the samples were varied. It therefore appears that all the molybdenum–germanium phases in this system have narrow ranges of homogeneity.

Samples that contained less than 67 atomic % germanium gave no indication of melting when heated to 1350°. All eutectic temperatures for samples containing less than 67 atomic % germanium are therefore believed to lie above that temperature. Samples of composition Mo$_3$Ge did not melt on being heated to 1750°.

The chemical behavior of the molybdenum germanides toward some common reagents was studied. All the phases show similar chemical properties. In general, they do not react quickly with ordinary non-oxidizing acids or with solutions of bases. Sulfuric, hydrochloric and hydrofluoric acids, concentrated or dilute, hot or cold, showed no immediate reaction, though concentrated sulfuric acid, in contact with molybdenum germanides for a week turned blue. Boiling 20% sodium hydroxide or concentrated ammonium hydroxide caused no immediate attack, nor was any reaction observable after the solution had stood for a week in the cold. Oxidizing agents, however, readily attack the molybdenum germanides; a 30% hydrogen peroxide solution or cold nitric acid, either concentrated or dilute, dissolved the germanides readily. Yellow solutions were formed with either oxidizing agent. Mo$_2$Ge$_3$ and MoGe$_2$ yielded white residues, presumably of GeO$_2$, after attack by nitric acid or hydrogen peroxide, but the phases of lower germanium content were dissolved completely. A fused nitrate and carbonate mixture attacked the germanides with almost explosive violence. Fused pyrosulfate dissolved them rapidly to form a clear yellow melt.

The molybdenum germanides resemble the molybdenum silicides in several ways. Mo$_3$Ge, β-MoGe$_2$ and apparently Mo$_3$Ge$_2$, are isostructural with known molybdenum silicides. There is no known molybdenum silicide with a formula corresponding to Mo$_2$Ge$_3$, however. The molybdenum germanides, like the silicides, are high melting compounds. The molybdenum germanides, on the other hand, are not as stable toward oxidizing agents as the corresponding silicides; furthermore, the germanides cannot be expected to show the resistance to high temperature oxidation that some silicides display.

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WEST LAFAYETTE, INDIANA

(8) W. H. Zachariasen, *Z. physik. Chem.*, **128B**, 39 (1927).

(9) H. J. Wallbaum, *Z. Metallkunde*, **33**, 378 (1941).

[CONTRIBUTION FROM AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Stability Constants of Cadmium Chloride Complexes: Variation with Temperature and Ionic Strength[1]

BY CECIL E. VANDERZEE AND HAROLD J. DAWSON, JR.

RECEIVED JUNE 24, 1953

Stability constants for the complex species CdCl$^+$, CdCl$_2$ and CdCl$_3^-$ at constant ionic strengths 0.5, 1, 2 and 3 have been determined by a potentiometric method at 0, 25 and 45°. Extrapolation to zero ionic strength was made using a form of the Hückel equation. All of the complexes are formed endothermally, the values of ΔH becoming more positive for the higher complexes and lower ionic strengths. With increasing ionic strength, ΔS values decrease rapidly at first, then level off and increase slowly at higher ionic strengths.

Complex ion formation in cadmium chloride solutions has been the subject of several investigations. Leden[2] has made a study of the stability constants for various cadmium halide complexes at 25° in solutions at constant ionic strength 3, and gives an extensive summary of references to previous work. Recently King,[3] studying the effect of chloride ion upon the solubility of cadmium ferrocyanide, reported stability constants for the cadmium chloride complexes at ionic strength 3 for temperatures 0, 25 and 47.5°, and evaluated the heats of formation for the complexes CdCl$^+$, CdCl$_2$ and CdCl$_3^-$ as 625, -1100 and 4600 cal. per mole, respectively. The exothermic formation of the uncharged species seemed unusual and worthy of re-examination, especially since the others were formed endothermally.

The work reported in this paper is part of a program underway in this Laboratory, concerned with the factors influencing the stability of complex ions and particularly with the heats of formation as they relate to differences between ligands and between various metal ions. Since heats of formation obtained from the variation of concentration stability constants with temperature will depend somewhat on the particular ionic strength used, it is important to determine the extent and direction of that dependence.

Stability constants were determined from observations of the e.m.f. of concentration cells of the type

(1) In part from the M.S. thesis of Harold J. Dawson, Jr., May, 1952.

(2) I. Leden, *Z. physik. Chem.*, **A188**, 160 (1941).

(3) E. L. King, THIS JOURNAL, **71**, 319 (1949).

$$\text{Cd(Hg)}\left|\begin{array}{ll}\text{Cd(ClO}_4)_2 & (x)\\ \text{HClO}_4 & (y)\\ \text{NaClO}_4 & (T\text{-}x\text{-}y\text{-}z)\\ \text{NaCl} & (z)\end{array}\right\|\left.\begin{array}{ll}\text{Cd(ClO}_4)_2 & (x)\\ \text{HClO}_4 & (y)\\ \text{NaClO}_4 & (T\text{-}x\text{-}y)\\ & \end{array}\right|\text{(Hg)Cd}$$

in which x, y and z represent concentrations in gram-equivalents per liter, and T represents the ionic strength. Since the total $Cd(ClO_4)_2$ concentration was kept small (0.01 M throughout), the ionic strength was taken equal to the total normality. The $HClO_4$ was kept at 0.01 M. As usual in determining stability constants by this[4] and other methods, it is necessary to assume that substitution of the chloride ion for the perchlorate ion will not appreciably affect the activity coefficients involved in the equilibria.

Experimental

The apparatus and general technique followed essentially the same procedures used in previous work.[4] The cadmium amalgam electrodes were approximately 15% cadmium, prepared by warming clean pieces of reagent grade cadmium metal with triply-distilled mercury under a stream of nitrogen. The molten amalgam was transferred to the bell-shaped cup of the electrode with a previously warmed medicine dropper. Replicate electrodes agreed to better than 0.1 mv. and showed no drift with aging.

Temperature was maintained constant to 0.05° by a well-stirred constant temperature bath. The experimental temperatures are correct to 0.1° as checked against a NBS certified thermometer.

All solutions were prepared with freshly distilled water of conductivity grade. Reagent grade chemicals were used in all cases. All volumetric ware was calibrated before use.

A standard cadmium perchlorate stock solution was prepared by dissolving cadmium carbonate in a measured volume of standard perchloric acid; when no more of the cadmium carbonate would dissolve, the solution was boiled to destroy bicarbonate, filtered and transferred quantitatively to a volumetric flask and diluted to known volume. The resulting solution contained no free acid or bicarbonate.

The cadmium carbonate was prepared by treating cadmium chloride solution with excess sodium carbonate, washing the resulting precipitate several times by decantation, then dissolving it in perchloric acid and reprecipitating the cadmium carbonate, which was then washed repeatedly until samples gave no tests for chloride or sodium ions.

Sodium perchlorate was prepared by treating reagent grade sodium carbonate and perchloric acid, filtering as a slightly alkaline solution, to remove any traces of iron, then acidifying slightly with perchloric acid and evaporating carefully until crystallization began. After cooling to 55° the anhydrous crystals were recovered by filtration through a warm fritted glass filter. They were dried 4 hours at 125° and stored in a desiccator.

To remove traces of oxygen, all solutions were "degassed" for an hour with Matheson "prepurified" nitrogen, appropriately presaturated with water vapor. A slow stream of nitrogen was passed through the titration cell at all times except when e.m.f. readings were being taken.

Results and Discussion

Treatment of Experimental Data.—In the solution containing cadmium and chloride ions there will be the several simultaneous equilibria

$$\text{Cd}^{++} + n\text{Cl}^- \rightleftarrows \text{CdCl}_n^{+2-n} \qquad (1)$$
$$n = 1, 2, 3, 4$$

The appropriate concentration stability constants are given by

$$K_n = \frac{(\text{CdCl}_n^{+2-n})}{(\text{Cd}^{++})(\text{Cl}^-)^n} \qquad (2)$$

in which the terms in parentheses represent concentrations in gram ions per liter, and K_n is the product of the true equilibrium constant and the appropriate activity coefficient factor which is assumed to remain constant under these experimental conditions.[4] The stability constants are related to the e.m.f. of the cell by the expression

$$f^\circ = \exp(2FE/RT) = 1 + K_1(\text{Cl}^-) + K_2(\text{Cl}^-)^2 + K_3(\text{Cl}^-)^3 + K_4(\text{Cl}^-)^4 \qquad (3)$$

in which (Cl^-) is the uncomplexed chloride ion concentration, computed as described in reference 4, and corrected to the temperature of the experiment.

The junction between the two half cells was made through a fine fritted glass disk. At the higher ionic strengths, substitution of chloride for perchlorate ion up to a chloride concentration of 0.5 M will produce only a negligible junction potential; however, at the lower ionic strengths a small junction potential might be expected. To ascertain the magnitude of this effect, use was made of the Henderson equation for the liquid junction potential.[5] In the calculations, the equivalent conductances of the several ions at infinite dilution were used; this assumes that the variation of conductance with concentration is the same for all ions. Since the major contribution is made by univalent ions, chloride, perchlorate and sodium, all of which exhibit fairly similar conductance behavior, this assumption is reasonable, and is frequently made in using the Henderson equation. For the various cadmium species an average value of 60 was used for the equivalent conductance; values for the other species were taken from reference 5. Concentrations of cadmium species were obtained from approximate values of the stability constants.

Use of the Henderson equation makes it possible to calculate a correction factor f_c^0 by which f_{obs}^0 could be multiplied to give a corrected f^0. (By definition $f_{\text{obs}}^0 = \exp(2FE/RT)$ where E is the observed e.m.f. of the cell.) Since it is assumed that the temperature coefficient of conductance is the same for the ions involved, these factors will be essentially independent of temperature. It is evident from examination of the factors in Table I that the effect of junction potential becomes significant only at low ionic strengths and high chloride concentrations. For example, at ionic strength 0.5 and $(Cl^-)_t$ equal to 0.3 M, the factor corresponds to a junction potential of −0.7 mv., which leads to an error of about 6 in K_2 and about 15 in K_3. Because of the necessary assumptions involved in arriving at these factors, they must naturally be regarded as

TABLE I

CORRECTION FACTORS FOR LIQUID JUNCTION POTENTIAL

	IONIC STRENGTH			
$(Cl^-)_t$, eq./l.	3.0	2.0	1.0	0.5
0.00	1.000	1.000	1.000	1.000
.01	0.999	0.999	0.999	0.998
.02	0.999	0.999	0.999	0.998
.04	1.000	1.000	1.000	0.999
.10	1.001	1.002	1.005	1.010
.20	1.006	1.008	1.017	1.033
.30	1.010	1.015	1.030	1.060
.50	1.019	1.028	1.057	1.109

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(4) C. E. Vanderzee and D. E. Rhodes, *ibid.*, **74**, 3552 (1952); C. E. Vanderzee, *ibid.*, **74**, 4806 (1952).

(5) S. Glasstone, "Introduction of Electrochemistry," D. van Nostrand Co., Inc., New York, N. Y., 1942, p. 212.

TABLE II

SUMMARY OF EXPERIMENTAL DATA[a,c]

Temp., °C.	0	0	0	0	25	25	25	25	45	45	45	45
Ionic strength	0.5	1.0	2.0	3.0	0.5	1.0	2.0	3.0	0.5	1.0	2.0	3.0
$Cl^-)_t$, eq./l.	E.m.f. millivolts											
0.000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00[b]	0.00[b]	0.00[b]	0.00[b]	0.00
.025	4.94	4.86	5.52	6.85	5.44	5.22	5.97	7.32	6.21	6.00	6.52	7.67
.050	9.00	8.88	10.06	12.23	9.85	9.53	10.88	13.12	11.01	10.82	11.77	14.12
.075	12.27	12.17	13.74	16.44	13.50	13.14	14.90	17.80	15.00	14.72	16.18	19.37
.100	15.00	14.98	16.80	20.00	16.54	16.20	18.28	21.75	18.50	18.16	20.00	23.81
.15	19.65	19.70	22.00	26.05	21.67	21.34	24.11	28.40	24.05	23.82	26.32	31.23
.20	23.45	23.50	26.20	31.00	25.75	25.64	28.82	33.85	28.60	28.55	31.50	37.27
.25	26.67	26.73	29.84	35.15	29.26	29.28	32.84	38.55	32.45	32.60	36.00	42.48
.30	29.37	29.59	32.98	38.80	32.14	32.47	36.38	42.72	35.60	36.15	40.00	47.10
.35	...	32.16	35.73	42.05	...	35.34	39.62	46.43	....	39.25	43.65	51.25
.40	...	34.45	38.25	45.05	...	37.90	42.51	49.65	....	42.15	47.00	54.95
.50	...	38.65	42.80	50.20	...	42.35	47.57	55.55	....	47.00	52.65	61.50

[a] All cells contained 0.01011 *M* $Cd(ClO_4)_2$ and 0.01 *M* $HClO_4$. [b] Mean of two runs. [c] Chloride concentrations refer to temperature of run.

approximate, rather than exact or absolute, corrections to be applied in evaluating the constants from the experimental data.

The calculation of uncomplexed (Cl^-) from total $(Cl^-)_t$ and the evaluation of the stability constants from the data were carried out by methods previously described[4], based on Leden's method.[2] It is worth noting that when the data were evaluated without applying junction corrections, apparent negative values were obtained for K_4, and also for K_3 at ionic strength 0.5; on evaluation after applying the corrections, these spurious results practically disappeared and the data behaved in the same manner at ionic strength 0.5 as at 3.

Interpretation of the Data.—In Table II are presented experimental data for rounded values of chloride concentrations, taken from large scale graphs of E against total chloride concentration. These tabulated values of E represent the experimental data to about 2 parts per thousand; the reproducibility of the data is of the order of 5 parts per thousand.

Values of K_n were determined with correction for the junction potential and also without the correction in order to show its magnitude, with the results shown in Table III. At the two higher ionic strengths, the correction was found to be less than the uncertainty in determining the constants. As would be expected, the correction affects K_3 more than K_2, and K_1 hardly at all.

Within the range of chloride concentration employed, three constants are all that can be determined; at the lowest ionic strength, (0.5), only two constants could be determined, and the value of K_3 lay between 0 and 10. To obtain K_4, runs would need to be carried to higher chloride concentrations; there, however, the effects of the several necessary assumptions become so considerable that, unless K_4 is larger than K_3, the value obtained cannot be treated with much confidence. In agreement with Leden[2] and King,[3] it appears that K_4 is considerably less than K_3 for this system.

Comparison of our values at 25° and ionic strength 3 with those of Leden,[2] who used the same method, shows good agreement. King's[3] values, obtained from solubility measurements, are in fair agreement, except for the variation of K_2 with temperature. Only in a few cases are the differences greater than the range of the estimated uncertainties of measurement.

TABLE III

SUMMARY OF STABILITY CONSTANTS[a,b]

Temp., °C. Ionic strength	0	25	45
	Values of K_1		
0.5	23.0	23.5	24.8
1.0	23.0	22.3	24.2
2.0	27.1	26.5	26.8
3.0	35.4	34.8	34.9
	Values of K_2		
0.5	62 (56)	63 (57)	69 (61)
1.0	58 (55)	60 (58)	65 (61)
2.0	83 (79)	89 (86)	99 (96)
3.0	151	160	182
	Values of K_3		
1.0	19 (12)	26 (14)	40 (34)
2.0	46 (42)	61 (59)	98 (92)
3.0	150 (145)	195 (190)	255 (245)

[a] Whenever different, values calculated without correcting for liquid junction potential are reported in parentheses. [b] Estimated uncertainties in the reported values: K_1, 1%; K_2, 3%; K_3, 8%.

Based on polarographic data, Strocchi and Hume[6] have reported constants for the cadmium chloride complexes at 25° and ionic strength 2, using sodium nitrate as the inert salt. Their values ran from one-half to one-third as large as ours. This difference is readily shown to be due to the weak complexing between cadmium and nitrate ions to form $CdNO_3^+$ as shown by Leden.[2] Inclusion of the equilibrium in our equilibria, and taking

$$Cd^{++} + NO_3^- \rightleftarrows CdNO_3^+;\ K' = \frac{(CdNO_3^+)}{(Cd^{++})(NO_3^-)} \quad (4)$$

$(NO_3^-) = (NO_3^-)_0 - (Cl^-)$, where $(NO_3^-)_0$ is the initial concentration of nitrate ion in the system, shows that the constants actually measured and reported by Hume are $(K_1 - K')/(1 + 2K')$,

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(6) P. M. Strocchi and D. N. Hume, Paper No. 10, Division of Physical and Inorganic Chemistry, Los Angeles Meeting, March, 1953.

$K_2/(1 + 2K')$ and $K_3/(1 + 2K')$, respectively, where $(NO_3^-)_0$ is equal to 2. Comparison of his constants with our values for K_1, K_2 and K_3 suggests a value of K' equal to 0.7 ± 0.3, which is reasonable agreement with Leden's value of 1.3 at ionic strength 3. It is quite evident that at the nitrate concentrations employed, even a small value for K' leads to a large reduction in the observed constants when using nitrate ion as the inert anion.

The variation of the constants with ionic strength is what would be expected for the variation of the activity coefficient factors. Assuming that a form of the Hückel equation[7] will represent the activity coefficient of each ion, we can write

$$\log K_n - \Delta Z_n^2 A\mu^{1/2}/(1 + aB\mu^{1/2}) = \log K_n^0 + \Delta C_n\mu \quad (5)$$

where

$$\Delta Z_n^2 = Z^2_{\text{CdCl}_n{}^{+2-n}} - Z^2_{\text{Cd}^{+2}} - nZ^2_{\text{Cl}^-}$$

and in which

$$-\Delta C_n = C_{\text{CdCl}_n{}^{+2-n}} - C_{\text{Cd}^{+2}} - nC_{\text{Cl}^-}$$

Here K_n^0 is the value of the constant K_n at zero ionic strength, Z is the charge on the ion, A and B are the usual Debye–Hückel constants for water, a is the "mean distance of closest approach" of the ions, and C is an arbitrary constant for each ion. The ionic strength μ is computed on a molarity basis. No distinction is made between rational and practical activity coefficients, since whatever small distinction exists will be absorbed to a major extent in the constant C.

Then for the proper value of a, a plot of the left hand member of equation 5 against ionic strength should give a straight line of slope ΔC_n and intercept K_n^0. Over this range of ionic strengths, the plots are not especially sensitive to a. However, a test of the equation with several values showed that all of the data, at all temperatures and for all complexes, could be fitted with a value of a equal to 4.3 ± 0.2 Å. Values of a outside of this range gave a poorer fit.

Using the value 4.3 Å. for a, the values presented in Table IV were obtained for K_n^0 and ΔC_n. The variation of ΔC_n with temperature is probably not significant; the data could have been fitted within experimental error by a single value of ΔC_n for each set. The values reported are taken from curves which seemed to give the best fit of the data.

TABLE IV

CONSTANTS FOR EQUATION 5

	0°	25°	45°
K_1^0	93 ± 3	100 ± 3	109 ± 3
K_2^0	440 ± 20	500 ± 20	590 ± 20
K_3^0	82 ± 6	130 ± 10	218 ± 15
ΔC_1	0.190	0.188	0.190 ± 0.003
ΔC_2	.340	.345	.355 ± .007
ΔC_3	.575	.570	.560 ± .010

The uncertainties in the values of K_n^0 were estimated by plotting the data several times and averaging the intercepts obtained, and are within the range consistent with the range of values of a. Another test of fit lay in the mean deviations from equation 5. The mean deviations of the points from the curves were 0.006, 0.006 and 0.020, corresponding to 1.4, 1.4 and 4.5% for K_1, K_2 and K_3, respectively.

The value of K_1^0 at 25° agrees well with the value 99 reported by Righellato and Davies.[8] Harned and Fitzgerald[9] reported the values 88, 90 and 100 for K_1^0 at 0, 25 and 45°, respectively; their values are slightly low but probably agree within limits of uncertainty, and show about the same variation with temperature.

For each of the sets of constants a plot was made of log K against $1/T$ for each ionic strength; the families of curves so obtained were practically straight lines. In several cases there was a slight tendency for the plots to be concave upward, but the curvature was not beyond the experimental uncertainties in the data. After comparing these curves for internal consistency with plots of equation 5, values of ΔF, ΔH and ΔS were computed for the reactions (1) at each ionic strength[10] (Table V).

TABLE V

VALUES FOR FREE ENERGY, HEAT CONTENT AND ENTROPY CHANGES FOR COMPLEX FORMATION AT 25°

Ionic strength	ΔF, cal./mole	ΔH, cal./mole	ΔS, cal./deg./mole
Process: $Cd^{++} + Cl^- \rightleftarrows CdCl^+$			
0.0	−2740 ± 50	600 ± 50	11.2 ± 0.3
0.5	−1870 ± 10	290	7.2
1.0	−1870	180	6.9
2.0	−1950	0	6.5
3.0	−2100	−45	6.9
Process: $Cd^{++} + 2Cl^- \rightleftarrows CdCl_2$			
0.0	−3680 ± 50	1200 ± 300	16.4 ± 1.0
0.5	−2480 ± 30	780	10.9
1.0	−2435	750	10.7
2.0	−2670	700	11.3
3.0	−3000	650	12.2
Process: $Cd^{++} + 3Cl^- \rightleftarrows CdCl_3^-$			
0.0	−2880 ± 100	3850 ± 600	22.3 ± 2
1.0	−2030	3300	17.9
2.0	−2480	3020	18.4
3.0	−3140	2840	20.1

It was also of interest to combine the data in Table V with values in the literature[11] to obtain the standard free energies and heats of formation as well as the entropies for the three species, with the results shown in Table VI.

The results in Table V are in fair agreement with those obtained by King[3]; comparison of values of ΔH and ΔS is difficult since the uncertainties in his ΔH values are quite large. He reported the $CdCl_2$ species to be formed exothermally; however, the formation of this species should reasonably be several hundred calories more endothermal than the formation of the $CdCl^+$ species because of less electrostatic contribution to the energy of formation.

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(7) Reference 5, p. 147.

(8) E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **23**, 351 (1927).

(9) H. S. Harned and M. E. Fitzgerald, THIS JOURNAL, **58**, 2624 (1936).

(10) These values were calculated using the K's obtained after applying the correction for the liquid junction potential. From the nature of the correction, it will have practically no effect on the values of ΔH.

(11) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

TABLE VI

	ΔH^0_f, kcal./mole	ΔF^0_f, kcal./mole	ΔS^0, cal./mole/deg.
$CdCl^+$	−56.72	−52.67	9.8
$CdCl_2$	−96.3	−84.96	27.6
$CdCl_3^-$	−132.8	−115.5	47.4

The decrease of ΔH with increasing ionic strength is most pronounced in the ionic strength range 0 to 0.5; as the ionic strength increases to the higher range the rate of decrease becomes much less. The values of ΔS likewise decrease rapidly in the low range, but exhibit a minimum and then increase with ionic strength at higher concentrations. Consequently in the low range ΔF will decrease rapidly due to the combined variations in ΔH and ΔS being in the same sense. This is in accord with the observations of Newton and Arcand,[12] who found a small variation of ΔH and larger variations of ΔF and ΔS in the region of lower ionic strengths. In the region where ΔS increases while ΔH decreases, the variation in ΔF will be lessened; whether ΔF eventually passes through a maximum and falls off again will depend on the relative rates of variation of ΔH and $T\Delta S$; in this system a maximum in ΔF is found, followed by a gradual decrease with ionic strength.

The relatively large variation of ΔS in the range 0 to 0.5 emphasizes that intercomparisons for complexes of different metals and ligands should be limited to comparable ionic strengths. On the other hand, the relatively small variation of ΔH suggests that this quantity is probably fairly characteristic of the complex itself, and that intercomparisons for ΔH values are considerably less limited with respect to ionic strengths.

LINCOLN, NEBRASKA

[12] T. W. Newton and G. M. Arcand, THIS JOURNAL, **75**, 2449 (1953).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Changes in Configuration of Some Nickel(II) Complexes[1]

BY FRED BASOLO AND WILLIAM R. MATOUSH[2]

RECEIVED JUNE 10, 1953

Diamagnetic nickel(II) complexes were allowed to react with anhydrous pyridine. In several instances it was possible to isolate well-defined crystalline compounds of hexacoördinated nickel(II) containing two molecules of pyridine. These solid compounds were paramagnetic and removal of pyridine at reduced pressures yielded the original diamagnetic materials. It is therefore concluded that the paramagnetism of certain pyridine solutions of diamagnetic nickel(II) complexes results from an expansion of coördination to yield hexa-coördinated nickel(II) compounds. It was also observed that no direct correlation exists between the magnetic susceptibility of solutions of bis-(formylcamphor)-ethylenediiminenickel(II) in methyl benzenes and the base strength of these solvents. This would indicate that the paramagnetism of these solutions is due not to solvation but rather to formation of tetrahedral nickel(II) compounds.

The complex compounds of nickel(II) are of particular interest because of the variety of spatial configurations which are encountered. Nickel(II) may have a coördination number of either four or six. If the coördination number is four and the bonds are essentially covalent then the complex has a planar configuration and is diamagnetic (dsp^2) whereas if the bonds are ionic the complex has a tetrahedral configuration and is paramagnetic (sp^3) (Table III). With a coördination number of six the structure of the compound is that of an octahedron. However, if the bonds are primarily covalent the compound is diamagnetic (d^2sp^3)[3] and if ionic it is paramagnetic (sp^3d^2) (Table III).

Lifschitz, Bos and Dijkema[4] have shown that changes in the configuration of some nickel(II) complexes occur with considerable ease. The observation that diamagnetic bis-(formylcamphor)-ethylenediiminenickel(II) was weakly paramagnetic (1.9 B.M.) in methanol solution led French, Magee and Sheffield[5] to postulate a partial conversion of the planar complex to a tetrahedral form. A more extensive investigation of this phenomenon by Willis and Mellor[6] has revealed that a number of diamagnetic nickel(II) complexes exhibit paramagnetic behavior in various organic solvents. The paramagnetism was observed to be especially high in pyridine solutions. They suggested that this may result from the reaction of the diamagnetic complex with two molecules of pyridine to form an octahedral complex but attempts to isolate such compounds were not successful. However, Willis and Mellor[6] postulated that in solvents such as alcohol, benzene and chloroform, any paramagnetism observed must be caused by the formation of some tetrahedral complex. It should perhaps be noted that there is no direct experimental evidence in support of either of these postulates. Hall and Willeford[7] found that in general the nickel(II) complexes which form paramagnetic solutions undergo exchange with radionickel.

This paper reports the isolation of paramagnetic hexacoördinated nickel(II) complexes containing two molecules of pyridine. The suggestion of Willis and Mellor[6] that a solvation reaction takes place in pyridine solutions has therefore been confirmed. Some attempt has also been made to determine what occurs in methylbenzene solutions.

[1] Presented at the Chicago Meeting of the American Chemical Society, September, 1953.

[2] Taken in part from a thesis submitted by William R. Matoush in partial fulfillment of the requirements for the M.S. degree, 1952.

[3] F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

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