in a displacement reaction. The central carbon atom is somewhat positive, but not greatly so. The orbitals surrounding carbon are all filled, but the electrons in them are somewhat removed from the critical region by bonding to other atoms or groups. The general situation is clearly intermediate between that of a proton as the substrate and an oxygen atom of a peroxide as a substrate, but rather closer to the oxygen atom case. As one goes from tetrahedral carbon compounds, R_3CX, across the periodic table to R_2NX, ROX and finally FX, one expects polarizability to become more important and basicity less important, as found. The fact that tetrahedral boron compounds, R_3BX, depend more on basicity than does R_3CX, is also expected.

It might also be predicted that as the groups surrounding carbon in R_3CX promote a mechanism with more carbonium ion-like character, the dependence on basicity should increase. This would follow from the increased positive charge on carbon in the transition state. It must be remembered, however, that groups that favor an SN1 mechanism do so by processes which remove positive charge from the central carbon atom. This greatly reduces the expected effect, as was pointed out by Swain and Scott.[2a] The experimental facts are not quite enough at present to make the situation clear.

Acknowledgments. The authors are grateful to their colleagues, especially Myron L. Bender, John F. Neumer, William T. King and William P. Jencks, for their suggestions and comments. J.O.E. wishes to thank Brown University for sabbatical leave and Northwestern University for kind hospitality during the leave.

[Contribution from the Department of Chemistry, University of California, Berkeley, California]

Molecular Association of Nickel(II) Chelates. III. The Reaction of Nickel(II) Acetylacetonate with Pyridine

By J. P. Fackler, Jr.

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The visible spectrum of anhydrous nickel(II) acetylacetonate in benzene containing pyridine is described. The data support the premise that the spectral and magnetic behavior of nickel(II) acetylacetonate is due to molecular association in solvents of low coördinating power. Furthermore, the data indicate that polymerization occurs in a fashion similar to that existing in the solid, namely, trimeric units of $Ni(AA)_2$ with six oxygens surrounding each Ni(II). The spectra show the formation of a species containing two $Ni(AA)_2$ units per pyridine and that the bis-pyridine product is formed only after the pyridine to nickel ratio exceeds 0.5. The preparation and characterization of the heretofore unknown compound $[Ni(AA)_2]_2 \cdot py$ is described. The equilibrium constant for the reaction $[Ni(AA)_2]_2 \cdot py + 3py = 2Ni(AA)_2 \cdot py_2$ has been determined from the spectra. An estimate is made for the equilibrium constant of the initial reaction, $2[Ni(AA)_2]_3 + 3py = 3[Ni(AA)_2]_2 \cdot py$.

Introduction

Molecular association of solute molecules in solvents of low coördinating power[1-4] and in the solid state has been invoked recently to explain the paramagnetism of some "quadricoördinate" Ni(II) chelates. In particular rather strong evidence has been presented[2,3] to suggest that the paramagnetism of Ni(II) acetylacetonate, $Ni(AA)_2$, is due to molecular association. In the solid state, X-ray crystal structure analysis has shown a trimeric arrangement of $Ni(AA)_2$ units with each Ni(II) atom surrounded by a distorted octahedron of oxygens.[5]

Diamagnetic molecules can be obtained if the methyl groups in acetylacetone are replaced by bulky residues which tend to prevent polymerization of the nickel(II) β-diketonate units. Some of the diamagnetic solids such as nickel(II) dibenzoylmethane and nickel(II) phenylacetylacetonate become partially paramagnetic in non-coördinating-solvents.[2,3] Nickel(II) diisobutyrylmethane, which is paramagnetic in the solid state, becomes less paramagnetic in solvents of low coördinating power as the temperature is increased and the concentration is decreased.[2] Polymerization in solution similar to that of the $Ni(AA)_2$ in the solid state apparently causes these peculiar magnetic effects. Molecular weight determinations in benzene[2] for the $Ni(AA)_2$ have suggested a trimer for the anhydrous material in this solvent. The association factor of 2.96 ± 0.2 is quite significant considering the difficulty in obtaining perfectly dry samples and solvent.

The trimeric units of Ni(II) acetylacetonate are broken by coördinating solvents. The dihydrate[6] and bis-pyridine[7] compounds are well known and easily obtainable. Changes in the ligand field surrounding the Ni(II) atom occur when the trimer is broken and the solvated material is formed. This field change produces a shift in the visible absorption spectrum of the material.[6] Since pyridine readily coördinates with $Ni(AA)_2$ in hydrocarbon solutions, producing a measurable spectral shift, it was hoped that additional information concerning the polymeric $Ni(AA)_2$ might be obtained by a spectrophotometric titration of the acetylacetonate in benzene with pyridine. Further interest in this

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[1] J. P. Fackler, Jr., and F. A. Cotton, *J. Am. Chem. Soc.*, **82**, 5005 (1960).

[2] F. A. Cotton and J. P. Fackler, Jr., *ibid.*, **83**, 2818 (1961).

[3] J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **83**, 3775 (1961).

[4] R. H. Holm and T. M. McKinney, *ibid.*, **82**, 5506 (1960).

[5] G. J. Bullen, R. Mason and P. Pauling, *Nature*, **189**, 291 (1961).

[6] G. Maki, *J. Chem. Phys.*, **29**, 162 (1958).

[7] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952.

system stems from the possibility of forming a five-coördinate mixed complex before the bis-pyridine product appears. Graddon[8] has shown that copper(II) acetylacetonate appears to form a mono-pyridine adduct. No spectrophotometric evidence was obtained for a bis-pyridine derivative in a titration of the acetylacetonate with pyridine.

In this paper the spectrum of Ni(II) acetylacetonate in benzene is described as pyridine is added to the solution. The data obtained are analyzed for equilibria involving the anhydrous trimer and species containing pyridine. Two pyridine containing compounds are found to be stable under the experimental conditions. The expected bis-pyridine derivative forms only after an intermediate containing one pyridine per two Ni(II) atoms becomes the major constituent of the solution. The isolation and characterization of this intermediate is described.

Experimental

Nickel(II) acetylacetonate was prepared as cited in earlier communications.[2] The material was triply sublimed and kept under vacuum until used. Solutions of $Ni(AA)_2$ in benzene were prepared by diluting 15 ml. aliquots of a benzene solution of known concentration. Known amounts of pyridine were added to the samples by titration from a stock solution of pyridine in benzene. The stock solution of pyridine in benzene was prepared by accurately weighing a known volume of pure pyridine into the benzene. Fifty ml. solutions were prepared and the visible spectra from 800–400 mμ were observed in a 10-cm. quartz cell using a Cary Model 11 spectrophotometer.

Benzene used in this study was distilled from phosphoric anhydride or Linde Molecular Sieves in a 30-cm. Vigreux column, excluding moist air, immediately prior to use. The pyridine (Brothers reagent grade) was used as obtained in the preliminary samples 1–12. In samples 13–31 particular care was taken to purify the pyridine by distillation of the commercial material from barium oxide immediately prior to use. Moist air was excluded from the column and only the center-cut, b.p. 115°, was retained.

Pyridine-tetrakis-(2,4-pentanedionato)-dinickel(II).—In a small dish, 16.3 ml. of 0.1248 *M* solution of purified pyridine in dry benzene was mixed with 1.0568 g. of Ni(II) acetylacetonate until the complex completely dissolved. Upon evaporation in a vacuum desiccator, the crude pyridine-containing complex was formed. After all the solvent was removed, pumping was continued at room temperature for 24 hr. Analysis showed the crude material contained approximately one pyridine for each two Ni(II) atoms (found: N, 2.29). The crude material was redissolved in anhydrous benzene, approximately 10 ml. for a gram of material, and 30 ml. of anhydrous 2,2,4-trimethylpentane was added. The solution was filtered, sealed from the air and stored at 0° for four days. Light green crystals were formed on the walls of the flask. These were removed and dried thoroughly in a vacuum desiccator.

Anal. Calcd. for $C_{25}H_{33}O_8NNi_2$: C, 50.64; H, 5.6; N, 2.36. Found: C, 50.3; H, 5.4; N, 2.40.

Magnetic susceptibility measurements on the new compound and X-ray powder patterns on $Ni(AA)_2$, $Ni(AA)_2 \cdot py_2$ and the new compound were obtained through the courtesy of Professor Burris Cunningham and Mrs. Helena Ruben of the Lawrence Radiation Laboratory. A Faraday balance was used to determine the magnetic susceptibility of the compound.

Results and Discussion

Figure 1 presents selected spectra of Ni(II) acetylacetonate in benzene with different amounts of pyridine. The pyridine varies from a concentration of approximately four times that of the Ni(II), in sample 25, to zero in sample 13. The exact concentrations for each sample are listed in Tables I and II. The molar extinction coefficient, $\epsilon_0 = (\log I_0/I)/lc$ cm.$^{-1}$ M^{-1}, is based on the total Ni(II) concentration.

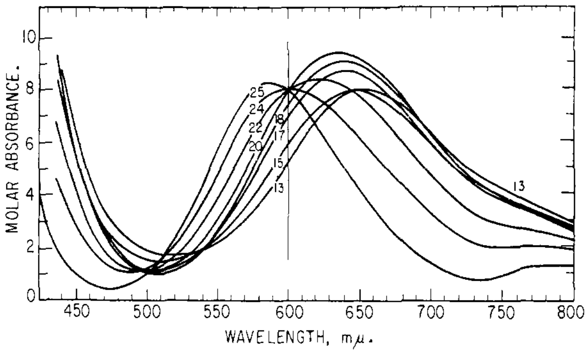

Fig. 1.—Visible spectra of Ni(II) acetylacetonate in benzene and in benzene-pyridine mixtures. Pyridine increases from 15–25.

At approximately 600 mμ an isosbestic point is observed for solutions 20–25. Over the indicated range of pyridine concentrations only two species are present in appreciable concentrations. One species has its maximum absorption at ~645 mμ while the other has its peak at ~590 mμ. The latter band appears at the position observed by Maki for nickel(II) acetylacetonate dihydrate dissolved in pyridine, and with comparable intensity.

TABLE I

SUMMARY OF SPECTRAL DATA AT 600 mμ FOR THE REACTION OF PYRIDINE WITH NICKEL(II) ACETYLACETONATE

Solution No.	Solution Concn. $Ni(AA)_2$, *M*	Ratio of pyridine to Ni(II), C_{py}/C_T	Molar absorbance (liter/mole cm), ϵ_0	Mole fraction species $Ni(AA)_2$
1	5.38×10^{-3}	0.00	4.93[a]	1.00
2		.0923	5.93	0.803
3		.184	6.23	.632
4		.369	7.62	.236
5		.563	8.00	.126
6		.738	8.45	. . .
13	1.153×10^{-2}	0.00	5.07[a]	1.00 > 1.00
26		.00	4.86[a]	1.00
14		.0650	5.46	0.856 > 0.85
27		.0650	5.33	.836
15		.1298	5.73	.752 > .74
28		.1298	5.63	.733
16		.2162	6.01	.649 > .62
29		.2162	6.06	.584
17		.3241	6.75	.372 > .34
30		.3241	6.84	.312
18		.4325	7.22	.194 > .18
31		.4325	7.28	.159
19		.4975	7.39	0.13
20		.649	7.74	

[a] Molar absorbance of anhydrous $Ni(AA)_2$.

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(8) D. P. Graddon, *Nature*, **183**, 1610 (1959). See also W. R. Walker, *Australian J. Chem.*, **14**, 161 (1961), and references therein.

For purposes of discussion we shall label the material producing this band species 3, the bis-pyridine derivative,[7] $Ni(AA)_2 \cdot py_2$. The material in equilibrium with the bis-pyridine derivative over the above range of pyridine concentrations we shall label species 2. Anhydrous $Ni(AA)_2$, species 1, produces an absorption maximum at ~660 mμ which is in agreement with other work.[2,9]

TABLE II

SUMMARY OF THE SPECTRAL DATA FOR THE REACTION OF PYRIDINE WITH NICKEL(II) ACETYLACETONATE

Sample[a]	Ratio of pyridine to Ni(II), C_{py}/C_T	Molar absorbance[b] (liter/mole cm.) $\epsilon_0(\lambda_1)$	$\epsilon_0(\lambda_2)$	Average for mole fraction species (2)	$K \times 10^{-8}$ (mole^{-2} liter^2)
6	0.739	4.28	8.50	0.958	..
7	1.10	4.65	7.88	.755	4.1
8	1.47	5.30	7.05	.638	1.8
9	1.84	5.89	6.45	.484	2.1
10	2.74	6.94	5.61	.237	1.3
11	3.68	7.66	4.84	.043	2.9
12	7.37	7.86	4.73	.003	..
20	0.649	5.34	4.54	.962	2.8
21	1.084	5.94	3.69	.729	2.7
22	1.295	6.16	3.35	.632	2.2
23	1.515	6.36	2.84	.510	3.1
24	1.952	7.01	2.20	.303	3.6
25	4.32	7.67	1.82	.025	..

[a] In samples 6–12, the total concentration is 5.38×10^{-3} *M* and in samples 20–25 the concentration is 1.153×10^{-2} *M*. [b] In samples 6–12, λ_1 is 560 mμ, $\epsilon_2 = 4.15$, $\epsilon_3 = 7.87$; λ_2 is 660 mμ, $\epsilon_2 = 8.70$, $\epsilon_3 = 4.72$. In samples 20–25, λ_1 is 575 mμ, $\epsilon_2 = 5.22$, $\epsilon_3 = 7.72$; λ_2 is 725 mμ, $\epsilon_2 = 4.64$, $\epsilon_3 = 1.78$.

At low pyridine concentrations, species 2 apparently is in equilibrium with the anhydrous trimer $Ni(AA)_2$. This is evident from the isosbestic point appearing at ~537 mμ. The spectra of the anhydrous material (13) and solution 14 (not shown) also cross curves 15–20 at wave lengths above 650 mμ. Since samples 1–6 and 26–31 displayed no similar inconsistency in their spectra, it is suspected that either solutions 13 and 14 had not reached equilibrium with the small amount of water persistent in the solvents or that these solutions absorbed less water from the air than the solutions with higher pyridine concentrations. Samples 26 and 27 show the largest deviations (decrease) in molar absorbancies from the same solutions (13 and 14) run 24 hours earlier (see below). Since the molar absorbance of the hydrated species, $Ni(AA)_2 \cdot 2H_2O$, never exceeds ~ 3.2 in the 500–800 mμ region,[6] small amounts of water would be expected to produce a general decrease in the molar absorbances of the spectra. The most sensitive region of the spectrum will be where the difference between the molar absorbancy of the anhydrous material and the hydrated species is the greatest. This appears to be the 630–750 mμ region of the spectrum for the anhydrous species. Beer's law was found to be obeyed at 600 mμ for three freshly prepared samples of the anhydrous $Ni(AA)_2$ while deviations occurred in the direction of increasing molar absorbancy with increasing concentration at 660 mμ.

On the premise that only three Ni(II) species are present in substantial amounts in benzene solutions of $Ni(AA)_2$ containing pyridine, the observed molar absorbance at any wave length is expressed by the relationship

$$\epsilon_0 = f_1\epsilon_1 + f_2\epsilon_2 + f_3\epsilon_3$$

The f_i's are ratios of Ni(II) in species i to the total Ni(II) and the ϵ_i's are the extinction coefficients per mole Ni(II) for these species. At the isosbestic point for species 2 and 3, ~600 mμ, $f_1 = (\epsilon_0 - \epsilon_2)/(\epsilon_1 - \epsilon_2)$, since $\epsilon_2 = \epsilon_3$. Species 3 does not contribute to the spectrum until the pyridine concentration approaches $^1/_2$ the Ni(II) concentration and has been neglected in analyzing the data listed in Table I. Similarly the trimer, species 1, apparently does not contribute to the spectrum after the isosbestic point at ~600 mμ is observed. It has been neglected from the analysis of the data in Table II.

In Table I are found the data obtained from two concentrations of $Ni(AA)_2$ over the pyridine range showing dominance of species 1 and 2. Two sets of spectra are shown for the 1.153×10^{-2} *M* Ni(II) concentration. The second set, samples 26–31, was obtained 24 hr. after observing the spectra initially, samples 13–20. The small changes observed are due to the presence of water from the air introduced in filling the cells. Since water was not entirely avoided in making the solutions and filling the cells, the molar extinction coefficient for each species was determined by graphical extrapolation in each set of spectra. The reliability of the data at the lower concentration is not as good as that obtained for the higher concentration due to the low absorbances and uncertain purity of the pyridine. However, the results are entirely consistent with subsequent work at the higher concentration.

Neglecting species 3 over the pyridine to Ni(II) ratio (C_{py}/C_T) of 0 to 0.5, the fraction of species 1 present is given by the expression $f_1 = -\alpha C_{py}/C_T + 1$, in the limit of no non-coördinated pyridine. The constant α is the Ni(II) to pyridine ratio in species 2 and is expected to be one-half for $Ni(AA)_2 \cdot py_2$, one for $Ni(AA)_2 \cdot py$, and two for $[Ni(AA)_2]_2 \cdot py$, etc. In Fig. 2, f_1 is plotted against the ratio C_{py}/C_T. The dashed line of minus 2 slope in the plot corresponds to the formation of a species containing two $Ni(AA)_2$ to each pyridine. The extent of the linearity of the plot indicates that little "free" pyridine is present until the C_{py}/C_T ratio approaches 0.5. This indicates a large equilibrium constant for the reaction of anhydrous $Ni(AA)_2$ with pyridine and suggests that species 2 might be isolated. An equilibrium constant for the reaction $2[Ni(AA)_2]_3 + 3py = 3[Ni[AA)_2]_2 \cdot py$ is estimated to be approximately 10^{10}. The curve drawn in Fig. 2 corresponds to the deviation from linearity expected for solutions with $C_T = 1.153 \times 10^{-2}$ *M* and $K = 10^{10}$ liter^{+2} mole^{-2}.

By dissolving nickel(II) acetylacetonate in benzene which contained an appropriate quantity of pyridine, species 2 was isolated as described. An X-ray diffraction pattern confirmed the visual observation that the pure material was crystalline.

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[9] C. K. Jorgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

Furthermore, the powder pattern was significantly different from the powder patterns of the trimeric anhydrous material and the bis-pyridine product. New lines, not present in either known species, excluded the possibility that species 2 was a mixture of species 1 and 3. The magnetic moment of the material, $\mu_{\text{eff.}} = 3.31$ B.M. ($\chi_g = 16.2 \times 10^{-4}$ c.g.s. units $\pm$ 3% at 20°) confirmed the existence of a triplet ground state.[2]

Spectral data for solutions with a pyridine to nickel ratio greater than 0.5 are presented in Table II. Assuming an equilibrium between species 2 and 3, the data were treated in the usual manner. The wave lengths used for obtaining absorbances are those which gave the greatest change in intensity for the smallest change in the pyridine concentration. Molar extinction coefficients for each species at each wave length were obtained by extrapolation. An equilibrium constant for the reaction $[Ni(AA)_2]_2 \cdot py + 3py = 2Ni(AA)_2 \cdot py_2$ was computed at each pyridine concentration. An average value of 2.7×10^5 mole^{-2} liter^{+2} was obtained with a standard deviation of $\pm$ 0.3. The constancy of this equilibrium quotient with respect to total Ni(II) indicates that species 2 is not a polymeric multiple of $[Ni(AA)_2]_2 \cdot py$.

The results show quite conclusively that the nickel(II) acetylacetonate readily bonds to two donor molecules. The apparent stability of these pyridine adducts is to be compared with the equilibrium constant of 3.2 obtained by Graddon[8] for the reaction of pyridine with copper(II) acetylacetonate in $CHCl_3$. One does not expect distortions in the spin-free nickel(II) systems to weaken axial bonds, as in copper(II) complexes.

The spectral evidence presented here directly supports the postulate that intermolecular association is responsible for the paramagnetism of Ni$(AA)_2$. Furthermore the existence of a stable $[Ni(AA)_2]_2 \cdot py$ molecule coincides well with the premise that the structure of the acetylacetonate in solution is similar to the structure in the solid. Only one coördination position is available on the dimer if a $Ni(AA)_2$ is broken from the trimer leaving the remaining two $Ni(AA)_2$ units associated by means of shared octahedral faces. A structure whereby the pyridine is involved in bridging fits the stoichiometry but requires the unlikely situation of two Ni(II) atoms coördinated to one pyridine. In a previous communication,[2] it was stated that planar molecules could come together with their planes parallel so that each nickel atom could be coördinated by an oxygen atom of the other molecule. If the trimer were of this form in solution, one would not expect to find a pyridine intermediate with the stoichiometry of species 2 without observing a species involving a single pyridine for each Ni(II) atom. If one maintains octahedral coördination of the Ni(II) by means of shared faces, species 2 is the only one to be expected in going from the trimer to the bis-pyridine monomer. Other species are possible only if the premise of shared octahedral faces is rejected. All other species apparently are less stable thermodynamically than species 1, 2 or 3.[10]

Having obtained an understanding of the structure of the anhydrous nickel(II) acetylacetonate, it seems appropriate to ask why the visible spectrum of the dihydrate is so similar to the spectrum of the anhydrous species.[6] Maki previously has concluded that the spectra of the anhydrous and hydrated species may be explained by the assumption that in both cases the axial perturbation is small compared to the effect of the chelate oxygen atoms. The distorted octahedral configuration[2] of the anhydrous trimeric material discounts the possibility that this explanation is correct.

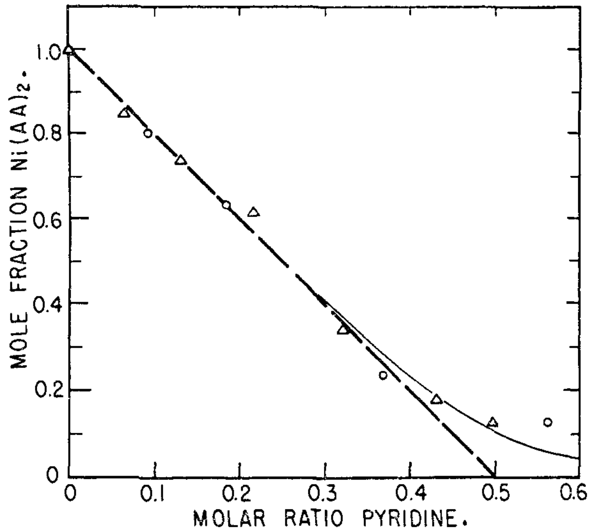

Fig. 2.—Plot of mole fraction $Ni(AA)_2$ *versus* molar ratio pyridine to Ni(II). Circles represent total concentration of 5.38×10^{-3} *M* Ni(II); triangles correspond to concentration of 1.153×10^{-2} *M* Ni(II).

Upon comparing the visible spectrum of Cu(II) acetylacetonate in alcohol with the spectrum of the aqueous copper(II) ion, broad bands are observed at ~15,000 cm.$^{-1}$ and 12,600 cm.$^{-1}$ respectively.[11,12] Belford, Calvin and Belford[11] have performed a Gaussian analysis of the copper(II) acetylacetonate band in 1-pentanol assuming peaks at 17,000, 15,200 and 13,000 cm.$^{-1}$ which they assign to the three expected crystal field transitions from filled d orbitals to the partially filled $d_{x^2-y^2}$ orbital. A similar analysis of the visible spectrum of $CuSO_4 \cdot 5H_2O$ by Holmes and McClure[13] indicates that the three bands occur at 14,500, 13,000 and 10,500 cm.$^{-1}$. The red shift observed for the bands of the aqueous complex compared with the acetylacetonate suggests that the acetylacetonate produces a ligand field splitting somewhat larger than the splitting

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(10) D. P. Graddon and E. C. Watton, *Nature*, **190**, 906 (1961), published a note which appeared during the preparation of this manuscript in which they analyzed the visible spectrum of anhydrous Ni$(AA)_2$ in toluene upon the addition of 4-methylpyridine and 2,6-dimethylpyridine at one concentration of Ni(II). The results are in direct disagreement with this work over the species present upon addition of base. The above authors claim the presence of a 1:1 adduct in contradiction to the isolation of $[Ni(AA)_2]_2 \cdot py$ presented in this paper.

(11) L. Belford, M. Calvin and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).

(12) T. M. Dunn in J. Lewis and R. G. Wilkins, "Modern Coördination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960.

(13) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

produced by water.[14] Comparing the bands of the anhydrous nickel(II) acetylacetonate with the hydrated ion, one observes that the effective ligand field splittings are approximately equal.

$Ni(AA)_2$ (cm.$^{-1}$)[6]	$Ni(AA)_2 \cdot 2H_2O$ in CH_3OH (cm.$^{-1}$)[6]	$Ni(H_2O)_6^{++}$ (cm.$^{-1}$)[15]
8,810	9,217	8,500
12,900	(13,423)	13,500
15,280	15,873	15,400

The decrease in the apparent ligand field strength of the acetylacetonate anion relative to water in the Ni(II) complex presumably can be described in part as due to the specific configuration of the anhydrous nickel(II) acetylacetonate. In the trimer, the Ni–Ni distance is ~2.8 Å.,[16] implying metal–metal interaction. Since the t_{2g} orbitals of the nickel atoms give maximum density between the ligand atoms, the presence of filled t_{2g} orbitals from the adjacent nickel atom or atoms in the octahedral faces should lead to decreased stability of the t_{2g} orbitals and increased stability of e_g orbitals. Consequently the ligand field splitting produced by the acetylacetonate in the trimer would be smaller than expected in the absence of nickel–nickel interactions. The approximately equal splittings observed in the trimeric acetylacetonate and the aqueous Ni(II) complex qualitatively coincide with a weakened acetylacetonate field. Nickel–nickel interaction is removed in forming the $Ni(AA)_2 \cdot 2H_2O$. Thus one expects a slightly larger ligand field splitting in this molecule compared with the aqueous Ni(II) species. The observed spectrum[6] of $Ni(AA)_2 \cdot 2H_2O$ does not contradict this conclusion. The spectral shifts are too small to conclusively show the above reasoning to be valid, however. Furthermore the effect of distortion from an octahedral configuration should be considered when quantitatively comparing the spectra of the acetylacetonates with the aqueous Ni(II) species.

Acknowledgments.—Gratitude is expressed to Professors W. B. Schaap and R. E. Connick for their helpful discussion of this work and to Professor F. Albert Cotton for his stimulating thoughts leading to other communications on this subject.

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[14] Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29**, 311 (1956), indicate that both the acetylacetonate anion and water produce stronger fields than the oxalate anion but weaker fields than ammonia. R. H. Holm (Ph.D. Thesis, M.I.T., 1959) has compared spectral data for $M(OX)_3$, $M(H_2O)_6$ and $M(AA)_3$ complexes of V(III), Cr(III), Mn(III), Fe(III), Co(III) and Rh(III). It appears that the fields in $M(H_2O)_6$ are ~5% greater than those in $M(OX)_3$ and ~5% less than in $M(AA)_3$, but there are complications in some of these spectra which raise some doubt about the validity of these crude generalizations.

[15] A. D. Liehr and C. J. Ballhausen, *Ann. phys.*, **6**, 134 (1959).

[16] G. J. Bullen, *Nature*, **177**, 537 (1956).

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

The Equilibrium of α-Silver–Zinc–Cadmium Alloys with Zinc and Cadmium Vapors[1]

BY GEORGE SCATCHARD AND TUNG-PO LIN

RECEIVED MAY 13, 1961

An improved hollow cathode discharge tube has been developed which gives simultaneously the spectra of zinc and cadmium intense enough to be measured with a photomultiplier tube and galvanometer without further amplification, even after the light beam is halved by splitting mirrors and monochromated in a spectrograph. The vapor pressures of both zinc and cadmium in four ternary α-silver–zinc–cadmium alloys have been determined at several temperatures by means of the absorption of their resonance lines. The results are combined with earlier ones for the binary α-silver–zinc and α-silver–cadmium alloys to determine the thermodynamic properties of the ternary alloys.

The method of determining vapor pressures by the measurement of the absorption of the resonance line is particularly adapted to the study of mixed vapors because it determines directly the concentration of each component. The method of Scatchard and Boyd[2] of measuring the absorption photoelectrically has been applied to the vapor pressures of both zinc and cadmium from four ternary α-silver–zinc–cadmium alloys and the results have been combined with those of Scatchard and Westlund[3] for α-silver–zinc and those of Scatchard and Boyd for α-silver–cadmium[2] binary alloys to obtain analytic expressions for the thermodynamic properties of the ternary alloys.

A marked improvement in the hollow cathode discharge tube has permitted several developments which have increased the precision of the measurements.

Light Source.—It was important to have a single light source for both cadmium and zinc to avoid realigning the apparatus after each measurement. Hollow cathode lamps with the two metals electroplated successively were unsatisfactory because they became unsteady and flickering after a short time. The fact that they required at least seven days baking to give a satisfactory small degassing rate indicated that the difficulty was due to contamination from the plating solutions. We made a satisfactory source by reducing the impurities to a very low level. It was essentially the same as the one previously used,[2] but several changes were made.

The first change was to replace the Pyrex window with a quartz window and a graded quartz–Pyrex

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[1] Taken from the Ph.D. Thesis of Tung-Po Lin, M.I.T., 1958; Frank M. Shu Scientific Fellow during 1955–1957. The spectroscopic work was carried out in the Spectroscopy Laboratory of M.I.T. This work received financial support from the United States Atomic Energy Commission.

[2] G. Scatchard and R. H. Boyd, *J. Am. Chem. Soc.*, **78**, 3889 (1956).

[3] G. Scatchard and R. A. Westlund, Jr., *ibid.*, **75**, 4189 (1953).