

CONTRIBUTION NO. 2332 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA 50010

The Electronic Spectrum of the Cadmium(I) Ion Cd_2^{2+} in Cadmium(II) and Sodium Tetrachloroaluminates¹

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Received June 13, 1968

The spectrum of the product of reduction of cadmium(II) by metal has been obtained (1) in NaAlCl_4 and (2) in cadmium(II) solvents ($\text{Cd}(\text{AlCl}_4)_2$ and CdCl_2 and two of their mixtures). In all cases exceptional care must be taken in the synthesis and handling of the salts because of both the sensitivity of the systems to oxidizing impurities and the low concentrations of solute (ca. 10 mM) required by the high absorptivity of the chromophore. The effect of a residual impurity (probably HCl) of about 3 mM on the identification of the reduction product in NaAlCl_4 was eliminated by measurements on $\text{Cd}(\text{AlCl}_4)_2$ solutions in equilibrium with cadmium metal. Two bands are resolved with λ_{max} 289.1 and 218.2 m μ and molar absorptivities of $(3.27 \pm 0.06) \times 10^4$ and $(4.01 \pm 0.05) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, at 350°. These are shown to be consistent with only a Cd_2^{2+} solute, and the equilibrium constant obtained for the reaction $\text{Cd}^{2+} + \text{Cd(l)} = \text{Cd}_2^{2+}$ is 1.71 ± 0.11 . Because of solvent absorption only the lower energy band was resolved in the compositions $\text{Cd}(\text{AlCl}_4)_2$, $\text{Cd}(\text{AlCl}_4)_{1.54}\text{Cl}_{0.46}$, and $\text{Cd}(\text{AlCl}_4)_{0.92}\text{Cl}_{1.08}$ and shown to vary linearly with the concentration of added metal. The similarities of band position (292 m μ) and intensity (4.0×10^4) in $\text{Cd}(\text{AlCl}_4)_2$ at 350° to those in NaAlCl_4 lead to the conclusion that the same transition in Cd_2^{2+} is involved. The molar absorptivities and band energies decrease markedly with increasing chloride content of the cadmium solvents. The more rapid shift of the presumed charge-transfer band edge of the solvent prevents resolution of the solute spectrum in pure CdCl_2 at 600° with 88- μ path lengths ($\lambda_{\text{max}} < 335 \text{ m}\mu$, $\epsilon > 1.2 \times 10^4$). The spectral properties of the Cd_2^{2+} ion in solvents containing AlCl_4^- are inconsistent with interaction absorption or charge-transfer mechanisms. The two bands are assigned to transitions to the $^1\Sigma_u$ (34.59 kK) and $^1\Pi_u$ (45.77 kK) states according to a simple MO scheme for the Cd_2^{2+} ion. The dependence of the spectra on anion composition is interpreted on this basis and compared with the bond properties known for Hg_2^{2+} . Both ions are more stable with a minimum of charge transfer from the anions or solvent.

Introduction

The existence of the cadmium(I) ion Cd_2^{2+} is relatively well established by the isolation of the solid salt $\text{Cd}_2(\text{AlCl}_4)_2$,² by the Raman spectrum of the resultant melt in equilibrium with metal,³ and by emf measurements on the salt in dilute solution in molten NaAlCl_4 .⁴ In the last study the Cd_2^{2+} solute could be distinguished from among the general possibilities ($n\text{Cd}^{2+} + 2e$), *i.e.*, Cd^0 , Cd_2^{2+} , Cd_3^{4+} , etc., by thermodynamic means. On the other hand, this discrimination has usually not been possible by any means for the more frequently studied solutions of metal in pure molten CdCl_2 although the Cd_2^{2+} ion has commonly been assumed to be present therein. The only possible evidence to the contrary is the observation that the freezing point depressions of the dichloride by 4–9.5 mol % metal are better described in terms of Cd_3^{4+} and Cd_4^{6+} solutes if *ideal* solutions are presumed.⁵ However, the same assumption gives a contrary indication of Cd_2^{2+} in studies of the solution equilibria at higher temperatures and over a greater concentration range when the metal is alloyed with copper or gold.^{6,7} To help clarify the situation the work described herein was undertaken, namely, to attempt the observation of the Cd_2^{2+} spec-

trum in the chloride solvent and to compare this with that obtained in the presence of tetrachloroaluminate anions. To date, only two brief and conflicting spectral observations have been reported for the Cd–Cd– Cl_2 system.^{8,9} The inclusion of spectral studies of Cd_2^{2+} in NaAlCl_4 solvent was of considerable aid in unambiguously establishing the identity of the chromophore and in obtaining its spectrum at higher energies. In addition, the investigation gave a test of the suggestions^{2,10} that the intense color of the chloride solutions, dark red even at low metal concentrations, arises from an interaction absorption transition of the sort known in aqueous solutions and in solids containing mixed oxidation states. Consistent with this possibility is the striking change to a pale yellow-green color for even concentrated solutions of Cd_2^{2+} when only tetrachloroaluminate anions are present.

Experimental Section

Preparations and Impurities.—Observation of the intense spectral bands found for Cd_2^{2+} required a combination of short path lengths and fairly low concentrations, such as of the order of 100 μ and 1–10 mM. Impurities which either absorbed or scattered light or oxidized the solute under these conditions constituted a major problem with both $\text{Cd}(\text{AlCl}_4)_2\text{Cl}_{2-x}$ and NaAlCl_4 solvents.

Vacuum sublimation of commercial AlCl_3 from several sources under a few centimeters of inert gas¹¹ readily eliminated any iron impurity. The best purification of CdCl_2 (Baker) was achieved by heating in Cl_2 at 500° for several hours followed by vacuum sublimation at that temperature through a coarse-grade frit. Fusion of the appropriate amounts of these salts yielded dark

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Presented at the Symposium on Characterization and Analysis of Molten Salts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 8–13, 1968.

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melts which deposited a voluminous black mass of mainly carbon on digestion¹¹ at 425–450° for several days, after which a clear, colorless melt was obtained on filtration through a medium-porosity frit. The impurities evidenced appeared to come from both salts and could not be eliminated by treatment with hydrogen or chlorine or by elaborate handling precautions. Even the digested and filtered melt still contained impurities which oxidized the chromophore. This problem was reduced substantially by the use of a "sacrificial" cadmium procedure, *i.e.*, addition of a small amount of metal to the melt followed by heating for several days at 350–450° under 30 cm of argon and then reoxidation of the solute with chlorine. The solvent was stored in small, sealed ampoules.

Fusion of such sublimed AlCl_3 with NaCl which had been dried under vacuum at 450° likewise yielded a brown-gray melt which deposited carbon on digestion. An oxidizing impurity that was substantial at the necessary cadmium(I) levels still remained and was not eliminated by the above "sacrificial" metal technique. The fact that the black precipitate at first reappeared on transfer and redigestion was traced to nonvolatile residues from the de-ionized water which had been used for rinsing the apparatus. The remainder of the carbon impurity was associated with commercial AlCl_3 . A reasonable conjecture^{11,12} is that this contained a chlorinated hydrocarbon of about the same volatility which was cracked at the higher temperatures achieved with these melts. Therefore all of the AlCl_3 used in the preparation of NaAlCl_4 solvent was obtained by the reaction of high-purity metal and "transistor grade" hydrogen chloride (<99.99%, Precision Gas Products). The quality of the product and of the sodium melt improved with a decrease in carbon content of the aluminum used, and the best result was obtained with metal from Cominco Products (Grade 69, 1.6 ppm of C). The majority of the solvent NaAlCl_4 used was prepared using aluminum containing 9 ppm of carbon (United Mineral and Chemical, 99.999%). Another sample ("99.99%") containing 125 ppm of carbon gave a definitely inferior solvent.

The NaAlCl_4 solvent was prepared in a one-piece, fused-silica apparatus which was first baked out under vacuum at 450° overnight and at 850° for 2–3 hr before being loaded with metal and NaCl in the drybox. Helium which first passed over hot copper and through a Linde Molecular Sieve was mixed with the HCl . The AlCl_3 was formed at 340°, sublimed through a coarse-grade Vycor frit, and sealed off from the gas train after completion of the reaction. After evacuation the portion containing the AlCl_3 as well as the NaCl previously loaded in an adjacent side arm was sealed off and heated to 200° to cause the salts to react. The NaCl used was trimmings from optical-grade crystals (Harshaw Chemical Co.) which had been dried at 300° under vacuum and transferred only in the drybox. However, this component of the solvent is not believed to be a source of a significant amount of the carbon or oxidizing impurities encountered earlier. The actual solvent used and referred to elsewhere as NaAlCl_4 contained 52.0 mol % AlCl_3 or 7.69 mol % AlCl_3 in NaAlCl_4 .

The sodium solvent so prepared produced only a very small amount of the black material on digestion at 450° and could be used without such treatment at 350°. The CdCl_2 solute here was likewise prepared from metal (Cominco Products, 59 Grade) and the same HCl at 650°. The molten product was filtered *in situ* and then vacuum sublimed through a second frit at 580°. Stock solutions in NaAlCl_4 were obtained by addition of CdCl_2 to the NaCl in the solvent preparation first described, the weight of the former (10–40 mg) in small sealed ampoules being determined by weight difference. Excess AlCl_3 in the solvent was presumed to convert the solute chloride to $\text{Cd}(\text{AlCl}_4)_2$.

The cadmium(II)-based solvents as well as NaAlCl_4 and its solutions of cadmium(II) slowly attacked Pyrex glass at about 400° and above. This was evidenced by frosting of the glass, particularly above the melt level, and, in extreme cases, by the production of SiCl_4 , as identified by its ir spectrum, vapor pres-

sure, and melting point. At the same time the levels of both silicon and boron in the melts increased as shown by emission spectrographic results. The impurities from this reaction did not interfere at the wavelengths of principal interest with the cadmium solvent (>290 $\text{m}\mu$) but did so seriously in NaAlCl_4 . In addition, a nominal 0.5 *M* solution of cadmium(II) showed a greatly reduced charge-transfer band for the solute after digestion in Pyrex, suggesting a substantial fraction had been lost. Pure NaAlCl_4 so treated developed a significant absorbance below about 250 $\text{m}\mu$, presumably because of silicate and borate impurities, whereas the solvent contribution at the path lengths used was ordinarily negligible to 210 $\text{m}\mu$. These effects appeared to be completely absent if the NaAlCl_4 solvent and solutions were prepared and handled only in fused-silica apparatus suitably baked out under vacuum.

The cadmium solvents were analyzed after preparation. Cadmium was determined by EDTA titration at pH 6.5 using NAS as the indicator¹³ and fluoride to mask aluminum. Total aluminum and cadmium amounts were determined by back-titration with copper(II) under the same conditions after the solution had stood for several hours at pH 1.5 with excess EDTA. Chloride was determined gravimetrically.

Spectral Measurements.—A Cary Model 12 recording spectrophotometer was modified by the direct replacement of the standard sample holder by an integral furnace block and cell holder. The block was constructed of 304 stainless steel after the design of Sundheim and Greenberg¹⁴ with openings for the light paths, cells, thermocouples, and six Chromalox cartridge heaters. Only two of the heaters were under off-on control, and the sample had an estimated temperature variation of $\pm 0.5^\circ$. An additional, serpentine heater of chromel A was placed below the block to reduce the vertical gradient at the cell. All but the top of the block was surrounded by two sheets of asbestos with an intervening heat reflector¹⁵ of 3-mil platinum foil, a 6 mm thick sheet of zirconia insulator, and a water-cooled jacket with silica plates covering the light path holes. The top of the assembly was covered by a 9 mm thick Lavite cap with appropriate openings.

The 1-cm square cells were equipped with cylindrical extensions to hold spacers necessary to reduce the light paths to 73–100 μ . Both were obtained from Pyrocell Manufacturing Co. The dimensions of the spacers were obtained with a pressure-indicating micrometer accurate to 0.1 μ . The inside dimensions of the cells as measured with an indicating hole gauge gave path lengths known to about ± 5 –10% for a given cell and spacer combination. When comparison of data from different cell combinations required a greater precision, the inside dimension was determined to about 2 μ with gauge blocks (Ultra Chex, A accuracy, Scherr Tumico). Corrections of up to 5 μ were necessary with some cells because of the lack of parallelism and planarity of windows. Aqueous K_2CrO_4 gave much poorer results at these path lengths.

The cell and spacer were baked out under vacuum for at least 6 hr at 450°, loaded with 4–7 g (± 10 mg) of solvent or solution, and, when appropriate, with cadmium weighed to ± 10 μg (cadmium solvents) or ± 50 μg (NaAlCl_4), and then evacuated and sealed off. An additional initial bake-out at 850° for 2 hr was employed with the NaAlCl_4 studies. In some experiments with the latter solvent a subsequent addition of CdCl_2 was made after cracking off an extension on the cell extension in the drybox; the cell was then reevacuated through the use of a second standard taper sealed into the extension below the break-off point.

Densities (g/cm^3) of the cadmium solvent were determined by volume measurements on weighed quantities at temperature and are as follows, with the temperatures and AlCl_3 : CdCl_2 ratios in parentheses: 1.81 (300–400°, 1.99), 1.88, (350°, 1.54),

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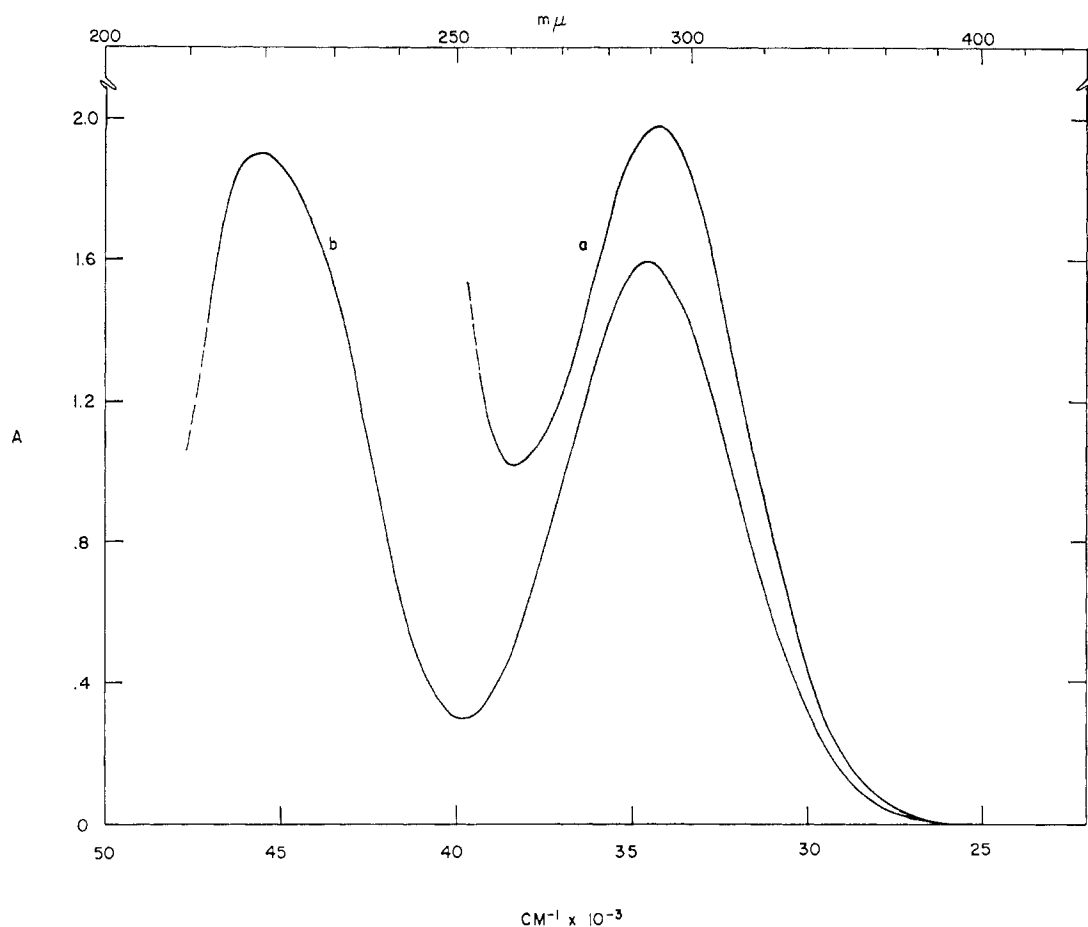


Figure 1.—Spectra of reduced cadmium systems in (a) $\text{Cd}(\text{AlCl}_4)_{1.54}\text{Cl}_{0.46}$ and (b) NaAlCl_4 . (a) $[\text{Cd}^0] = 8.68 \text{ mM}$, $b = 75 \mu$, temperature 300° . (b) $[\text{Cd}^{2+}]^0 = 8.08 \text{ mM}$, $[\text{Cd}^0] = 7.65 \text{ mM}$, $b = 73.7 \mu$, temperature 350° .

2.12 (550° , 0.92). The density of NaAlCl_4 (52 mol % AlCl_3) was taken from Boston.¹⁶

All solution spectra were run *vs.* air and were manually corrected for the absorbance of the cell and the same batch of solvent. Temperatures chosen for the cadmium solvent were based on melting point considerations. An ir filter (Corning 7-60) was used between the sample block and the detector at 550 and 600° . Operation at 350° for the sodium solvent with excess metal present was based on the rate of equilibration. This is extremely slow at 200° , while at 300° recrystallization of the metal (mp 319°) made recovery for a weight change determination nearly impossible. Equilibration for 30 min appears sufficient at 350° according to observations made with more concentrated solutions where the equilibrium is visibly temperature dependent. The spectra utilized throughout were time independent over periods of several hours.

Results

Cadmium(II) Solvent.—Spectral measurements were made with solvents with $\text{AlCl}_3:\text{CdCl}_2$ ratios of 1.99, 1.54, 0.92, and 0, which correspond to 33.4, 39.4, 52.1, and 100 mol % CdCl_2 , respectively. The ratios (R) conveniently define the solvent as $\text{Cd}(\text{AlCl}_4)_R\text{Cl}_{2-R}$ since they are twice the mole fraction of AlCl_4^- —presuming AlCl_4^- and Cl^- are the only important anions. Spectrally the solvents show only the steeply rising edge of what is presumed to be a charge-transfer band, and this edge apparently moves rapidly to lower energies with decreasing AlCl_3 content ($R < 1.5$) so that

pure $\text{Cd}(\text{AlCl}_4)_2$ is colorless while CdCl_2 is yellow. The absorption edge is relatively temperature sensitive, with a red shift of somewhat more than $0.1 \text{ m}\mu \text{ deg}^{-1}$. Wavelengths for an absorbance of 2.0 at 10^{-2} -cm path length are given in Table I.

$\text{AlCl}_3:\text{CdCl}_2$	λ (for $A = 2$, $b = 10^{-2} \text{ cm}$),		Temp, $^\circ\text{C}$
	$\text{m}\mu$		
1.99	252		300
	264		400
1.54	254		300
	264		400
0.92	299		550
0.0	336		600

Reduction of the solvents containing AlCl_3 with cadmium metal gives rise to a new band, partially overlapped by the solvent edge. The example of the solute spectrum given in Figure 1, curve a, also shows evidence for a second band at higher energies before the solvent cutoff is reached. No other absorption is observed to 1.0μ . Typical data for reduced melts in the three solvents containing AlCl_3 are listed in Table II. The solute band exhibits a red shift both with increasing CdCl_2 (or Cl^-) content of the solvent and with increasing temperature, but both effects are substantially less than those found for the solvents

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TABLE II
SPECTRAL DATA IN CADMIUM-BASED SOLVENTS

Solvent	[Cd ²⁺], mM	Temp, °C	λ_{max} , m μ	$10^{-2}A_{\text{max}}/b$, ^a cm ⁻¹	$10^{-3}\epsilon/2$, cm ⁻¹
AlCl ₃ : CdCl ₂	1.99	300	291.4	1.20	2.83
		400	293.0	1.10	3.19
	6.39	300	290.9	2.06	2.77
		400	293.7	1.70	3.18
	8.26	300	291.2	3.15	2.79
		400	293.6	2.74	3.05
1.54	4.47	300	291.5	0.91	2.87
		400	293.0	0.79	3.27
	8.68	300	292.0	2.64	2.80
		400	294.5	2.40	3.09
	450	296.0	2.32	3.29	
		11.78	300	291.8	3.40
400	294.2	3.08	3.14		
	450	295.7	2.95	3.24	
0.92	6.68	550	312.5	0.89	3.22
	9.43	550	312.5	1.12	3.06
	16.00	550	310.6	2.34	3.17

^a Each composition was measured with the same cell and spacer combination.

(Table I). The anticipated solute band in CdCl₂ could not be resolved at 5 mM metal, 88- μ path length, and 600°. This appears to be a simple consequence of the more rapid red shift of the solvent absorption edge with increasing chloride content, so that its proximity substantially overwhelms the solute feature. An upper limit of 335 m μ is then about all that can be established for the band maximum in the chloride.

Changes in the character of the band with either concentration or temperature suggest that it results from a single transition. The half-width δ (measured to the low-energy side only because of the lack of resolution on the other side) remains reasonably constant on increasing reduction at constant temperature and solvent (Table II). The product $\delta\epsilon_{\text{max}}/2$ as a function of temperature at constant composition shows only random variation within a 5% range, as is appropriate for a band which has a Gaussian distribution in energy. Such an analysis fits the spectrum shown within experimental error when contributions of a second band are included below 280 m μ . At this point it appears that a single band contributes to the observed maximum and that this shifts with change in solvent composition instead of a new band growing in.

The Beer's law test of the data at λ_{max} for each solvent composition, Figure 2, shows adherence to within about 10% with no regular trend in deviations. Note should be made of the fact that the intensity of the transition severely limits the composition range which can be covered for the AlCl₃-rich solvents. The finite intercept is taken to indicate that a small amount of oxidizing impurity is still present in the solvent as prepared [1.4–2.0 mM or (2.9–3.6) $\times 10^{-4}$ mol fraction]. This residual is far greater without the use of "sacrificial" cadmium (see Experimental Section). The probable source of this and of the scatter of the data will be evident from work to be discussed later.

Within the above limitations the results indicate that only a single solute species is present in these melts and that its concentration varies linearly with added metal. The decrease in molar absorptivity

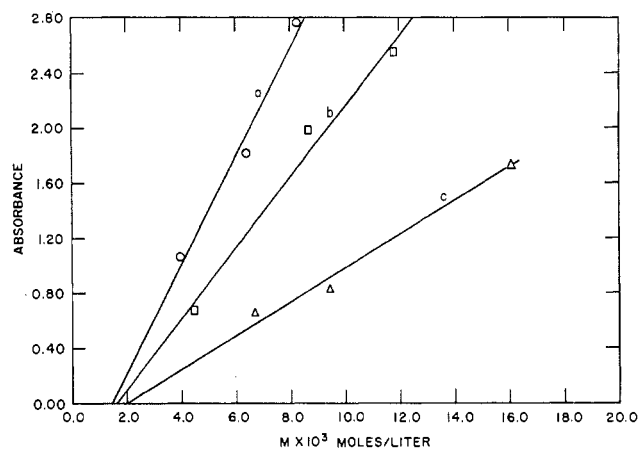


Figure 2.—Absorbance vs. metal concentration in cadmium-based solvents: (a) in Cd(AlCl₃)₂ at 291.2 m μ , 300°, and 88 μ ; (b) in Cd(AlCl₃)_{1.54}Cl_{0.46} at 291.8 m μ , 300°, and 75 μ ; (c) in Cd(AlCl₃)_{0.92}Cl_{1.08} at 312.5 m μ , 550°, and 73 μ .

ϵ at λ_{max} with decreasing AlCl₃ content is particularly striking: $(4.42 \pm 0.39) \times 10^4 M^{-1} \text{cm}^{-1}$ with an AlCl₃:CdCl₂ ratio of 1.99 at 300°; $(3.45 \pm 0.36) \times 10^4 M^{-1} \text{cm}^{-1}$ with a ratio of 1.54 at 300°; and $(1.67 \pm 0.15) \times 10^4 M^{-1} \text{cm}^{-1}$ with a ratio of 0.92 at 550° for the data in Figure 2. A lower limit of about $1.2 \times 10^4 M^{-1} \text{cm}^{-1}$ is obtained from the band edge in pure CdCl₂ at 340 m μ and 600°. The above changes in molar absorptivity with composition substantially exceed those which may be attributed to the temperature dependencies, which are about -0.17 and -0.09% deg⁻¹ in the first two solvents.

Sodium Tetrachloroaluminate Solvent.—The foregoing studies do not allow a distinction to be made among possible solute formulas, Cd₂²⁺, Cd₃⁴⁺, etc., because of the invariability of the cadmium(II) concentration. For this reason a study of the system in dilute solution in NaAlCl₄ was desirable, whereby a substantial gain in resolution also occurred because of greatly reduced solvent absorption. A typical spectrum was shown as curve b in Figure 1, where a band very similar to that already seen is well resolved at λ_{max} 289.1 \pm 0.3 m μ (350°). In addition the second, higher energy band only suggested in the above solvents is now clearly resolved, as shown, with λ_{max} 218.5 \pm 0.5 m μ . The latter feature appears somewhat skewed although it should be noted that the resolution on the high-energy side of the band becomes increasingly poor as the total absorbance measured approaches the practical limit of the instrument, which is 210 m μ even with pure NaAlCl₄. It will be shown later that this band at least above 215 m μ arises solely from the Cd₂²⁺ chromophore. Corrections for absorption by Cd²⁺ are needed only for the second band and are entirely negligible above 255 m μ at the highest concentrations employed. Both maxima show what is considered to be a normal ($10^{-2}\%$ deg⁻¹) shift to lower energies with increasing temperature.

Unfortunately, melts freed of carbon by digestion as before still gave extreme scatter and Beer's law intercepts 3–5 times as great as those found with the

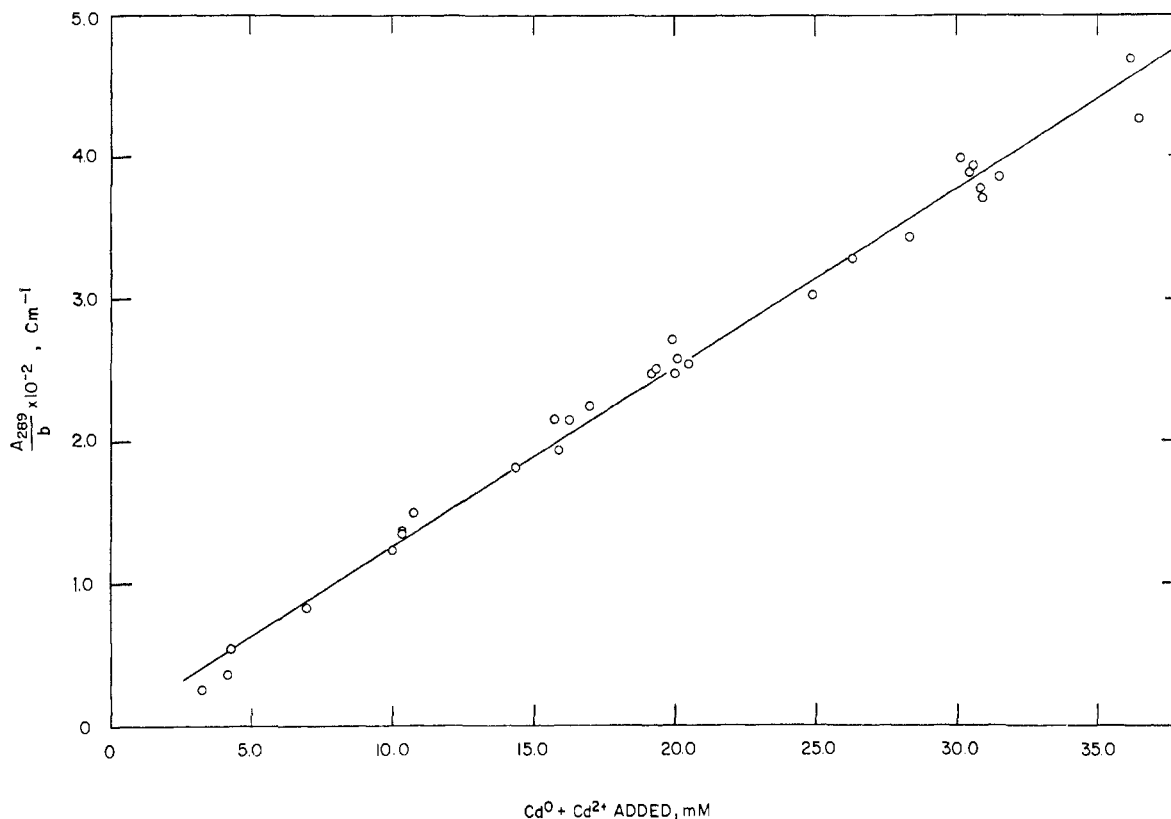
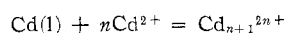


Figure 3.— A/b vs. C_T , the concentration of total cadmium in solution in NaAlCl_4 , according to eq 1 (350° , $289.1 \text{ m}\mu$).

cadmium-based solvents. This trouble still remained to a small extent even when the problem of carbonaceous impurities was eliminated by direct synthesis and careful handling of the salts. The sacrificial metal treatment was also of no avail. The residual impurity is now suspected to originate largely with HCl both retained by the NaAlCl_4 solvent and solutions in the synthetic method used and formed after exposure in the drybox. The same probably pertains to the above studies with cadmium solvents.

The solution to the impurity problem in the sodium-based solvent is to use only solutions containing known initial amounts of $\text{Cd}(\text{AlCl}_4)_2$ (or just the initial impurity) and also to measure the weight loss of excess, added metal at equilibrium. These quantities will be denoted hereafter by the molar concentrations C_2^0 and C_0^0 , respectively, and the chromophore as C_1 , the subscripts following the oxidation states. Since the 1:1 correspondence between cadmium dissolved and solute formed has been demonstrated in many studies, the inquiry will be limited to the amount of cadmium-(II) participation in the general reaction



although the results make it clear that the assumption of unit coefficients for the other two species is correct. For dilute solutions in equilibrium with metal, an expression can easily be derived which does not depend on a constancy of the oxidizing impurities but only on the spectral data and the total cadmium in solution, *i.e.*, $C_T = (n + 1)C_1 + C_2 = C_2^0 + C_0^0$. For the simplest case, $n = 1$, substitution in $K = C_1/C_2$ gives

$$A/b = (\epsilon K/2K + 1)C_T \quad (1)$$

A wide variety of data, some of which are known to involve greater than 2.5-fold variation in the impurity, are so plotted in Figure 3 using the absorbance data at the $289.1\text{-m}\mu$ maximum. The result is taken to be a confirmation of the assumption of $n = 1$; higher integral values result in complex, nonlinear relationships which will not describe the data with constant K and ϵ . The slope of the line in the figure yields the relationship $K^{-1} = (7.94 \pm 0.075) \times 10^{-5}\epsilon - 2$.

Now that the correctness of the model is assured the value of ϵ (or K) may be deduced directly from the data if explicit account is taken of a substantially constant oxidizing impurity. The form of the equilibrium constant is such that we can do this incrementally, partitioning the total metal dissolved (C_0^0) between that which was oxidized by added Cd^{2+} (C_0) and that by the impurities (C_0^i). For the former, K takes the form $C_0/(C_2^0 - C_0)$ and for the latter, C_1^i/C_2^i , where by mass conservation $C_0^i = 2C_1^i + (C_1^i/K)$. Then

$$C_1 = C_1^i + C_0 = C_0^0 - C_1^i(K + 1)/K \quad (2)$$

so that the Beer's law test, A/b vs. C_0^0 , has the usual slope of ϵ and an intercept of $C_1^i(K + 1)/K$ at $A = 0$. Such a treatment is shown in Figure 4 for two types of data. The solid line spans data collected in the usual way so that the scatter probably represents mainly the variation in the initial impurity. The slope corresponds to $\epsilon (3.26 \pm 0.09) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, and from Figure 3, K is then 1.70 ± 0.20 . The lower dashed line covers a series of data obtained for a different

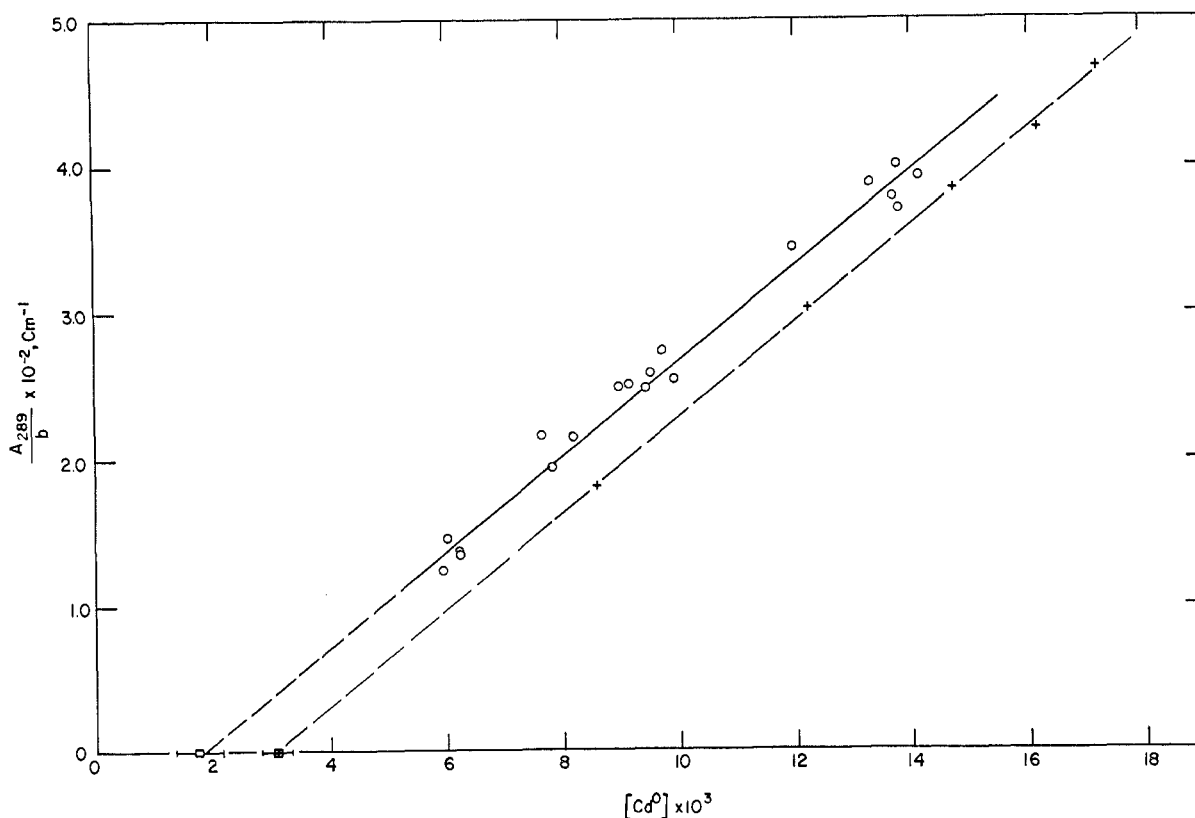


Figure 4.— A/b vs. the concentration of metal dissolved by solutions of $\text{Cd}(\text{AlCl}_4)_2$ in NaAlCl_4 , eq 2 (350° , $289.1 \mu\mu$): solid line, direct measurements; dashed line, measurements after second addition (see text). The points on the abscissa are single- and double-impurity concentrations obtained from other data (see text).

purpose (below) wherein the cell was opened and cadmium(II) was added after equilibration of the solvent with metal alone. The additional exposure in the drybox is evidently responsible then for the higher intercept. The fact that the data were collected in a short period using two solvent batches and at the end of the study is presumably responsible for the lower scatter. For this group ϵ is $(3.28 \pm 0.05) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and K from Figure 3 is 1.66 ± 0.10 . The averages used are $(3.27 \pm 0.06) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and 1.68 ± 0.16 , respectively; the latter depends on a small difference of large numbers and will be improved later.

Absorbance measurements made on eight systems in which only metal had been added to the solvent together with the above data give an alternate, direct estimate of the initial impurity. The average C_1^i thus obtained is 1.078 mM , but with an average deviation of 0.359 mM which reflects the difficulty in obtaining closely reproducible systems. The corresponding quantity for the intercept plotted in Figure 4 is consistent with the extrapolation of the other data. The 63% higher impurity found after only a second, brief opening of the system (dashed line) suggests that this exposure may be the primary source of the impurity trouble.

It is also possible to verify the foregoing results using only the slope of Figure 3 together with the result of the double measurements mentioned above. These yield the initial absorbance (A_1) with only

solvent and metal, a second value (A_2) after the addition of a known amount of cadmium(II) (C_2^0), and the total weight loss of metal (C_0^0) given in Table III. In this case the equation

$$\epsilon(C_2^0 - C_0^0) + (2/b)(A_2 - A_1) - (S\epsilon/b)(A_2 - 2A_1) = C_{12}^i \epsilon (1 - S\epsilon) \quad (3)$$

can be derived, where $S = 7.94 \times 10^{-5}$ from Figure 3 and C_{12}^i is the additional $[\text{Cd}_2^{2+}]$ which results from opening the cell a second time. Graphical solution of eq 3 gives $\epsilon (3.28 \pm 0.13) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $C_{12}^i = 0.77 \pm 0.17 \text{ mM}$. The respective values are in very good agreement with what was just found and the larger intercept for these data in Figure 3 (dashed line) where this impurity result is marked on the abscissa as the increment above the intercept of the solid line. However the results are not as precise as obtained *via* Figure 4 because of the more limited data.

TABLE III
DATA FOR DOUBLE MEASUREMENTS IN NaAlCl_4

$10^{-2}A_1/b$, cm^{-1}	$10^{-2}A_2/b$, cm^{-1}	C_2^0 , mM	C_0^0 , mM
0.0953	4.263	20.32	16.18
0.4105	1.817	5.74	8.61
0.502	4.682	18.97	17.22
0.244	3.026	12.67	12.24

Sufficient information is also available to characterize the higher energy band. A small ($\leq 4.7\%$) correction was applied to the absorbance data at $216 \mu\mu$ (and to

curve b in Figure 1) to allow for the Cd^{2+} present at equilibrium, using its molar absorptivity at this wavelength (3.2×10^3), and the concentration calculated from $A_{289.1}$ with the above values of K and $\epsilon_{289.1}$. The plot of eq 1 (not shown) resembles very much that already given for the lower energy transition (Figure 3) save for the lower concentration range accessible (<26 mM) and yields a slope of $(1.554 \pm 0.033) \times 10^4 M^{-1} \text{cm}^{-1}$. This property at the maximum (as well as for the low-energy side of the band) thus identifies this transition with the Cd_2^{2+} ion as well. The ratio of the molar absorptivities at the two band maxima is given by the ratios either of the slopes of the plots of eq 1 or of the individual absorbances for the two bands, the latter differing only in the absence of a zero intercept requirement. With the previous $\epsilon_{289.1}$ values of $(4.035 \pm 0.045) \times 10^4$ and $(3.976 \pm 0.088) \times 10^4 M^{-1} \text{cm}^{-1}$ are calculated for ϵ_{218} by these two treatments, respectively. The average of $(4.006 \pm 0.049) \times 10^4 M^{-1} \text{cm}^{-1}$, together with the above slope, gives 1.73 ± 0.16 for K . A probably better value of 1.71 ± 0.11 for K is obtained when the last is averaged with the value deduced earlier from the low-energy band. This constant compares with 3 ± 1 estimated at 300° at a higher solute concentration in about the same solvent⁴ and 1.85 ± 0.10 in pure $\text{Cd}(\text{AlCl}_4)_2$ at 335° .²

Discussion

The spectral results for the systems in NaAlCl_4 in equilibrium with metal firmly establish that the solute is Cd_2^{2+} . The agreement found between the spectrum in NaAlCl_4 and in $\text{Cd}(\text{AlCl}_4)_2$ solvent (interpolated to 350°) as to position (289 *vs.* 292 μ) and molar absorptivity (3.3×10^4 *vs.* $4.0 \times 10^4 M^{-1} \text{cm}^{-1}$) of the lower energy band strongly implies that the same internal transition of the same Cd_2^{2+} ion is observed in $\text{Cd}(\text{AlCl}_4)_2$ as well, in agreement with the identity of the reduced species deduced from the less sensitive Raman measurements.³ In any case the only viable alternative is, again, a ground-state aggregate such as Cd_3^{4+} , which is certainly without precedent. The observations also give no support to the possibility that an excited state spanning Cd^{2+} and Cd_2^{2+} (interaction absorption) is important in the accessible spectral region even when these are the only cations present.

The two bands seen in NaAlCl_4 seem to be readily accounted for by a simple MO scheme. This construction is aided by the moderately large separation of the atomic levels in the Cd^+ ion, over 44 kK to $5p^1$ ($^2P_{1/2}$) and 69 kK to the lowest involving a $d \rightarrow s$ promotion ($^2D_{5/2}$),¹⁷ which is taken to mean that the bonding level is derived principally from $5s$. A qualitative ordering of the levels which would be appropriate to such a situation would be σ_u , π_u , σ_g , and σ_u in that order above the $\sigma_g^2(^1\Sigma_g^+)$ ground state. In this situation only three excited states are accessible by electric dipole transitions— $^1\Sigma_u$, $^1\Pi_u$, and, at much higher energies, $^1\Sigma_u$. Therefore the inclination is to

assign the transitions as $^1\Sigma_u \leftarrow ^1\Sigma_g$, 34.59 kK (289.1 μ), and $^1\Pi_u \leftarrow ^1\Sigma_g$, 45.77 kK (218.5 μ), though no experimental fact would disallow their reversal.

The only direct analog for comparison seems to be the gaseous Ag_2 molecule, for which the spectrum has been obtained in absorption by Ruamps.¹⁸ However he found *five* bands between 23 and 40.1 kK, more than expected for the simple species unless excitation from the $4d^{10}$ core is also involved. The latter is not unreasonable since the effect of charge on transition to silver is substantial, the $^2D_{5/2}$ level now being about 30.2 kK above ground rather than the 69.3 kK with Cd^+ . The presence of an anion sheath about Cd_2^{2+} would also be expected to increase the energies of the assigned transitions relative to Ag_2 as both involve an outward transfer of charge.

Several interesting changes in the spectra are found in the cadmium-based solvents when the amount of AlCl_3 added to CdCl_2 is decreased so that the anions are presumably converted from AlCl_4^- to Cl^- . The band energy shows a negligible shift to lower energies until more than about one-fourth of the anions have been converted to chloride. This observation tentatively suggests a reciprocal salt effect,¹⁹ the large ion aggregates Cd_2^{2+} and AlCl_4^- persisting at first since the added chloride should have a preference for the smaller, higher field Cd^{2+} cation. The ultimate effect of added chloride in shifting the band to lower energies would appear consistent with the destabilizing effects that basic anions are known to have on Cd_2^{2+} .² In our model this effect would be viewed as the result of anion overlap with the lowest energy, empty orbital σ_u or, alternatively, as a competition between halide and the metal-metal bond for the $5p$ orbitals. Accordingly, the most stable state for Cd_2^{2+} results when charge transfer from the anions is minimal and *not* when covalency reduces the cation charge and coulombic repulsion therein. This property is also very reminiscent of the effect that presumed anion-metal covalency is known to have on the metal-metal distance in the more stable Hg_2^{2+} .³ However, interpretation of this change in terms of the foregoing model seems much preferable to sp hybridization arguments in which the shorter bond is associated with a greater amount of s character.²⁰ The same anion effect should probably also appear if $5d_z$ is important in the Hg_2^{2+} σ system, as has been suggested to account for the predominance of linear coordination with this ion.²¹

The decrease in molar absorptivity of the lower energy Cd_2^{2+} band in the cadmium-based melts as chloride is added would also seem consistent with the simultaneous weakening of the metal-metal bond but not with a mixed-valence, interaction absorption assignment since chloride should doubtlessly function as a better bridge than tetrachloroaluminate. A

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resonant charge transfer here would seem to be precluded by the difficulty of symmetrizing the ionic atmospheres and this is reflected in the absence of a detectable electronic conduction.²²

The inability to resolve more than the low-energy side of the presumed band of Cd_2^{2+} in CdCl_2 solvent results from the proximity of the presumed charge-transfer band of the solvent (see below) which effectively limits observation to 335–340 $m\mu$ at the 88- μ pathlength employed. No other feature appears in the spectrum out to 1.0 μ , and so it is concluded, but by no means assured, that the lower energy transition of the same, albeit weakened, Cd_2^{2+} ion accounts for the pronounced visible color of the solutions. The probable energy of the transition to the $^1\Sigma_u$ state in CdCl_2 is appropriately about twice the dissociation energy estimated for Cd_2Cl_2 in this solution, 40 kcal mol⁻¹.²³

Attempts to verify the previous spectral reports for the chloride system have been unsuccessful. An earlier, qualitative study on a 5% solution in CdCl_2 showed a relatively weak band at 455 $m\mu$ and 575° which split into two bands at 450 and 550 $m\mu$ on heating to 618°. In the present work a poorly resolved band was found in this region only with a dilute solution which had been briefly exposed to air; absorption at about 415 $m\mu$ has also been observed (along with precipitation of the brown oxide) after treatment of Cd-CdCl_2 solutions with oxygen.²⁴ Another study⁹ indicated that a weak ($\epsilon \sim 150$) band at 345 $m\mu$, with a possible shoulder at 325 $m\mu$, was well resolved from the metal-saturated solution (~ 15.5 mol % or 2.6 M) at 575° using 50- μ pathlengths. Anything of this magnitude would be

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very difficult to resolve in the dilute solutions studied here since ϵ_{345} is already about 10^4 ; in fact, if Beer's law were to hold up to saturation, the cutoff would be at substantially lower energies. Nonetheless, Gaussian analyses of solute bands in both $\text{Cd}(\text{AlCl}_4)_2$ and NaAlCl_4 commonly gave small negative deviations from experiment ($\Delta A \leq 0.02$) in the neighborhood of 340 $m\mu$, corresponding to molar absorptivities of a few hundred for a Cd_2^{2+} solute. Although the differences are probably of the order of experimental error, the nominally forbidden transition to the $^3\Sigma_u$ state could be involved instead.

The effect of the anion on the positions of the band edges for the sodium and cadmium(II) solvents is quite consistent with a charge-transfer assignment. However, the only thing that can be safely concluded is that in each case the conversion from chloride to tetrachloroaluminate anion should raise the ionization energy of the donor and probably decrease the coulombic loss; the effect of covalency is more difficult to assess although it is possibly quite important in CdCl_2 .²⁵ In any case substitution of AlCl_4^- yields a far more useful solvent optically; e.g., at 220 $m\mu$ the molar absorptivity of NaAlCl_4 is only 0.034 at 300° and that of the $\text{Cd}(\text{AlCl}_4)_2$ solute is 2.2×10^3 at 350°. On the other hand, a charge-transfer assignment for the Cd_2^{2+} spectrum therein is inconsistent although the same cannot be firmly eliminated for the unresolved spectrum in CdCl_2 .

Acknowledgment.—Considerable assistance was given to phases of this work by Douglas Adolphson and Lynn Holloman, Summer Research Participants.

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A Vibrational Spectroscopic Study of Aqueous Cadmium Nitrate Solutions¹

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Received June 28, 1968

Raman and infrared spectra of aqueous cadmium nitrate solutions indicate the presence of nitratocadmium species. The intensity variation of the Raman bands at 1404 cm^{-1} , originating from solvated nitrate ion, and 1452 cm^{-1} , originating from complexed nitrate, has been used to characterize the species present in solution. The observation of a polarized Raman band at 1324 cm^{-1} indicates that the nitrate ion is acting as a monodentate ligand. A vibrational assignment for the monodentate nitrate group, in terms of the C_{2v} point group, is described. The calculated association constant for the CdNO_3^+ species is 0.38 (± 0.05) at 44°. No evidence for species higher than CdNO_3^+ has been obtained from the molar ratio solutions studied. Nevertheless, this work does not rule out the existence of higher species.

Introduction

Apart from some earlier work which detected no evidence for complexation in solutions of cadmium nitrate,^{2,3} there is evidence from such techniques as con-

ductivity,^{4,5} calorimetry,⁶ emf measurements,^{7,8} and polarography⁹ for a mononitratocadmium species. A

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