Octahedral–Tetrahedral Coordination Equilibria of Nickel(II) and Copper(II) in Concentrated Aqueous Electrolyte Solutions[1]

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Abstract: The coordination states of Ni(II) and Cu(II) in aqueous magnesium chloride solutions have been studied spectrophotometrically at temperatures up to 320° and concentrations up to 8 M in magnesium chloride. For Ni(II), increase in the MgCl$_2$ concentration results in the replacement of H$_2$O in the first coordination sphere of Ni(H$_2$O)$_6^{2+}$ by Cl$^-$ to give NiCl$_6^{4-}$ groups. With increasing temperature, transformation to NiCl$_4^{2-}$ groups occurs through a two-species octahedral–tetrahedral equilibrium. Thermodynamic data are presented for this equilibrium. For Cu(II), at similar temperatures and MgCl$_2$ concentrations, the coordination state is the CuCl$_4^{2-}$ configuration, but in this case the transition from Cu(H$_2$O)$_6^{2+}$ cannot be described in terms of a two-species equilibrium but seems to occur by means of a continuous ligand exchange and distortion mechanism. In the MgCl$_2$–H$_2$O system, H$_2$O coordinates strongly with Mg(II). For compositions near H$_2$O/Mg = 6, the Mg(H$_2$O)$_6^{2+}$ species appears to exist as an independent entity. It is pointed out that changes in the Ni(II) coordination states can serve as indicators for the determination of Mg(II) hydration numbers as well as hydration numbers of other noble gas configuration cations in molten hydrate systems.

The divalent 3d ions in aqueous solutions are generally believed to occur[2] as the well-known hexahydrated ions, M(H$_2$O)$_6^{2+}$. Only in the case of Co(II) is the formation of tetrachlorometalate complexes a well-recognized phenomenon in aqueous solutions.[3] Tetrahedral and octahedral chloro complexes of a number of the other 3d ions have been studied both in fused salt systems[4] and in organic solvent systems.[5,6] Octahedral–tetrahedral equilibria of Ni(II) are particularly convenient to study because the energies of the principal ligand field spectral bands are sufficiently different in the two coordination states so as to make possible the spectroscopic determination of the distribution ratio of Ni(II) between the two states. A detailed study of octahedral–tetrahedral equilibria of Ni(II) in molten KCl–ZnCl$_2$ mixtures has recently been completed.[7]

The possibility that, in addition to the well-known case of Co(II), octahedral–tetrahedral equilibria of several of the other divalent 3d ions, including Ni(II), might be amenable to study in aqueous systems suggested itself on the basis of the following considerations. It appears that in aqueous solutions involving cations with a noble gas electronic core, salt concentrations may be reached at which all the water molecules present are strongly bound to the bulk cation species. Evidence for this view may be derived both from an analysis of the transport behavior of molten hydrates[8] and from measurements of water activity in systems of this type.[9] Thus, in a highly concentrated chloride solution (e.g., of MgCl$_2$, AlCl$_3$), in effect a molten hydrate, in which the bulk cation is sufficiently polarizing to bind all the water molecules, 3d ions might be forced to co-ordinate with the chloride ions. Since the hydrated cations have large ionic radii, the chloro complexes of the 3d ions might be expected to be tetrahedral, by analogy with the situation encountered in molten alkali chlorides where tetrahedral coordination is favored by the large Cs(I) ion.

The prospect of such situations, in a sense intermediate between ordinary molten salts and the more familiar aqueous solutions, and the consequent likelihood of unusual coordination equilibria seemed sufficiently interesting to warrant a systematic study of the behavior of selected 3d ions in a suitable chloride solution as a function of water content and of temperature.

In accordance with the hard and soft acid–base concept,[10] the 3d ions as well as ions such as Zn(II) and Cd(II) have a greater tendency to form halo complexes in aqueous solution than the hard acids Mg(II) and Ca(II) which strongly bind the hard base H$_2$O. Furthermore, various estimates of hydration energies[11] have shown that the stability of hydration sheaths of noble gas configuration cations is proportional to cation charge and inversely proportional to cation size.

For the present study, MgCl$_2$ solutions were chosen since both charge/radius ratio and electronic structure factors strongly favor the Mg(II) ion over the divalent 3d ions in the competition for water molecules. Consequently, it was postulated that under conditions where the water content of the solution is insufficient to satisfy both the tendency of Mg(II) and of 3d ions to form hexahydrated ions, the 3d ions would be forced to ligate exclusively with Cl$^-$. The coordination behavior of Ni(II) and Cu(II) ions in the MgCl$_2$–H$_2$O solvent system forms the subject of the present paper.

Results

Spectra of Ni(II) in MgCl$_2$–H$_2$O Solutions. Complicated changes in the Ni(II) spectrum occur on varying the temperature and composition of the MgCl$_2$–H$_2$O solutions. A selection of spectra is presented here

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.
(2) O. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).
(3) R. Hill and O. R. Howell, *Phil. Mag.*, **48**, 833 (1924).
(4) D. M. Gruen and R. L. McBeth, *Pure Appl. Chem.*, **6**, 23 (1963).
(5) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).
(6) F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **83**, 344 (1961).
(7) C. A. Angell and D. M. Gruen, *J. Phys. Chem.*, **70**, 1601 (1966).
(8) C. A. Angell, *ibid.*, **69**, 2137 (1965); *J. Electrochem. Soc.*, **112**, 1224 (1965).
(9) R. H. Stokes, *Trans Faraday Soc.*, **41**, 642 (1945).

(10) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
(11) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Academic Press Inc., New York, N. Y., 1959, pp 49–72.
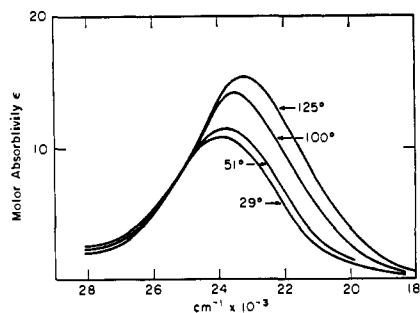
Figure 1. Effect of temperature on the Ni(II) spectrum in an $R = 9.2$ aqueous $MgCl_2$ solution (6 m $MgCl_2$).
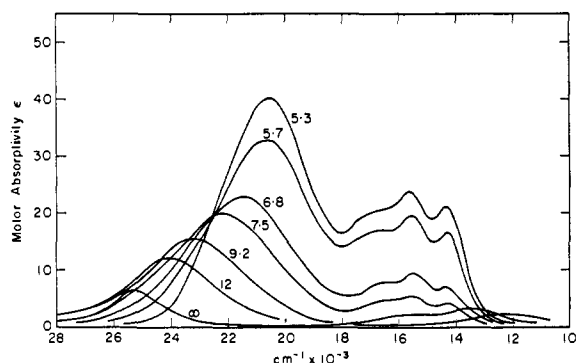

Figure 2. Effect of $MgCl_2$ concentration on the Ni(II) spectrum at 125° in aqueous $MgCl_2$ solutions. Concentrations are marked in R units.
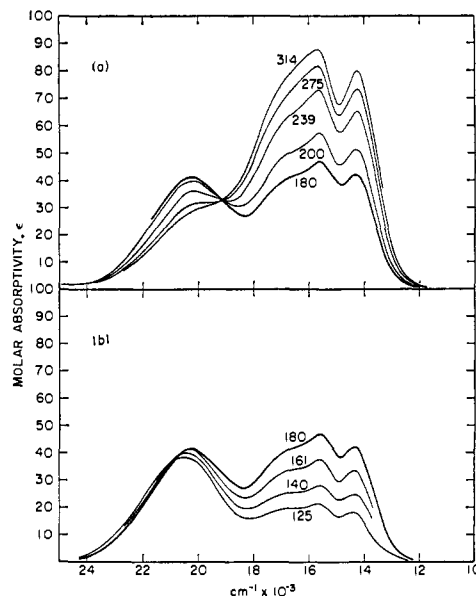

Figure 3. Effect of temperature on the Ni(II) spectrum in an $R = 5$ aqueous $MgCl_2$ solution (11 m $MgCl_2$).
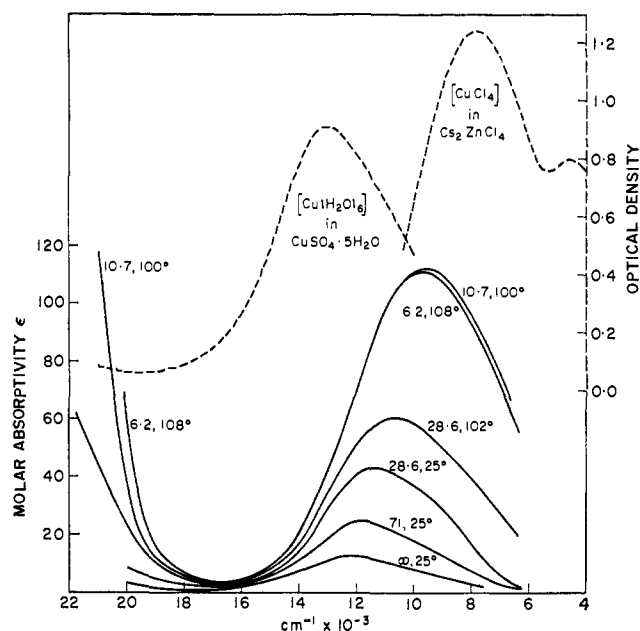

Figure 4. Effect of $MgCl_2$ concentration and temperature on Cu(II) spectra in D_2O solutions; comparison with crystal spectra. The solution curves are marked in R units. The temperature of measurement is also given.

which best illustrate these effects. The commonly used molal, molar, or mole per cent concentration units are not used for the discussion of behavior in the high $MgCl_2$ concentration regions investigated in this work. For various reasons, a more suitable choice is in units of the molar ratio $H_2O:MgCl_2$, designated as R. Thus an $R = 12$ solution contains 12 moles of H_2O per mole of $MgCl_2$ while its concentration is 4.1 M at 25°. The relation of R units to molal and mole per cent units, however, can be seen by reference to the abscissas of Figure 6, discussed later.

The Ni(II) spectra shown in Figure 1 are seen to vary as a function of temperature from 29 to 125° in an $R = 9.2$ solution. The temperature dependence of these spectra will subsequently be shown to be due to changes in octahedrally coordinated Ni(II) species. The set of spectra shown in Figure 2 illustrate the changes which occur on varying R at the fixed temperature, 125°. In the range $R = \infty$ (no $MgCl_2$ present) to $R = 7.5$, the principal spectral changes are a shift of the octahedral peak to lower energies accompanied by an increased absorption intensity. At higher $MgCl_2$ concentrations ($R < 7.5$), a new absorption band in the region 14,000–17,000 cm^{-1} appears.

The dramatic effect of temperature on the Ni(II) spectrum in an $R = 5$ solution is shown in Figure 3 (a and b).

Spectra of Cu(II) in $MgCl_2–D_2O$ Solutions. A series of spectra obtained on varying temperature and composition are presented in Figure 4. Included for comparison are the spectra of Cu(II) in crystalline $Cu(SO_4)\cdot 5H_2O$, and in Cu(II)-doped crystalline Cs_2ZnCl_4. In the case of Cu(II) one observes only a progressive shift

in the band maximum, with no suggestion of an isosbestic point.

Discussion

The behavior of Ni(II) in the $MgCl_2$ solutions is more interesting and informative than that of Cu(II) and accordingly will be discussed first. Anticipating the detailed discussion to follow, the essential steps appear to be: (i) a replacement of the H_2O ligands in the Ni(II) first coordination shell by six chloride ions with increasing $MgCl_2$ concentration and (ii) a temperature-dependent octahedral–tetrahedral coordination equilibrium between nickel chloro complexes.
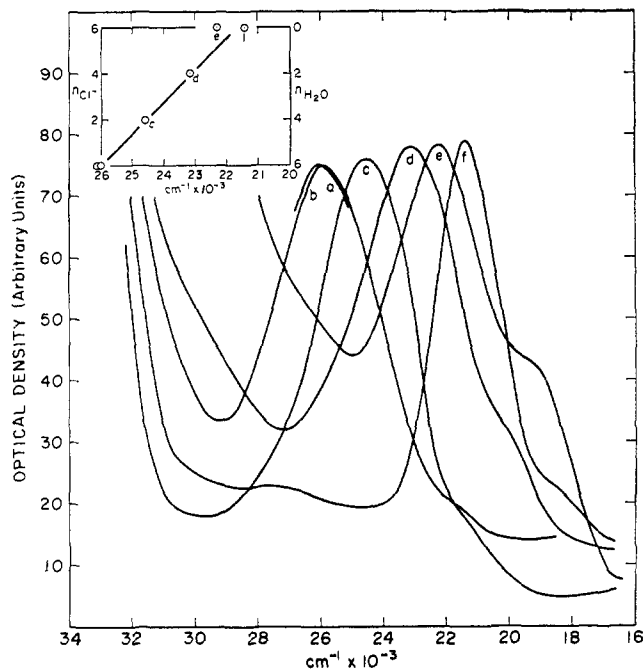
Figure 5. Effect of replacing H_2O ligands with Cl^- ligands in the first coordination shell on the Ni(II) octahedral spectrum in crystals. Inset: dependence of Ni(II) octahedral E_{max} on the number of H_2O ligands replaced by Cl^- ligands.

In order to interpret the solution spectral changes in the $28,000-20,000$-cm^{-1} region for an $R = 9.2$ solution with changing temperature (Figure 1) and with changing $MgCl_2$ concentration, at the fixed temperature, $125°$ (Figure 2), the crystal spectra of various nickel salts containing chloride ions and/or water molecules in known configuration about the Ni(II) ions were studied. For instance, in crystalline $Ni(NO_3)_2 \cdot 6H_2O$ and $NiSO_4 \cdot 6H_2O$, Ni(II) ions are surrounded by six water molecules at a distance of 2.03 A in a regular octahedral arrangement.[12] The $28,000-20,000$-cm^{-1} spectral region of these two compounds (which are both light blue in color) is dominated by a single absorption band with a maximum at $26,000$ cm^{-1} (Figure 5a,b).[13] The close correspondence of the band maxima demonstrates the important fact that the energy of the absorption is little affected by the charge or arrangement of ions beyond the first coordination sheath. These observations are in agreement with the usual assignment of the band at $26,000$ cm^{-1}, observed also in dilute aqueous solutions of Ni(II), to the species $Ni(H_2O)_6{}^{2+}$.

In crystalline $NiCl_2 \cdot 6H_2O$, on the other hand, X-ray studies[12] have shown that the first Ni(II) coordination sphere contains only four water molecules, the octahedron being completed by two chloride ions. The $Ni-H_2O$ distance is 2.10 A and the $Ni-Cl$ distance is 2.38 A. The spectrum of this green compound is characterized by a single band similar in appearance to that due to $Ni(H_2O)_6{}^{2+}$. However, the replacement of two H_2O molecules by Cl^- ions results in a decrease in the energy of the absorption maximum to $24,600$

(12) R. W. G. Wykoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1948.
(13) It should be pointed out that the color of the crystals is influenced by a second less intense octahedral absorption band which overlaps the low-energy region of the visible spectrum (Figure 2) $R = \infty$. This band shows changes in energy with structure which parallel those described here for the principal band.
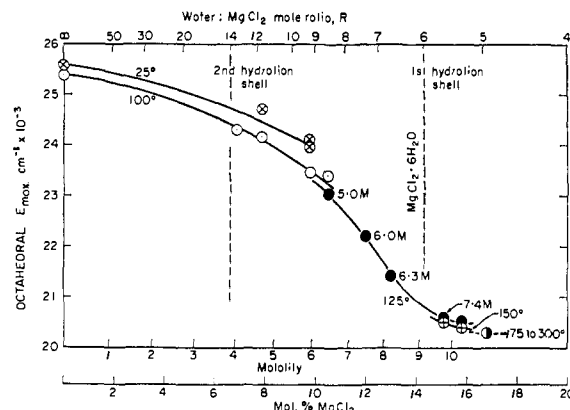
Figure 6. Dependence of Ni(II) octahedral E_{max} on $MgCl_2$ concentration in aqueous $MgCl_2$ solutions. Abscissas show relations among mole %, molal, and R composition units. Molarities (M) at 125° are indicated in the diagram.

cm^{-1} (Figure 5c). No attempts were made in our measurements of the crystal spectra to obtain information on changes in band intensity.

The spectrum of Ni(II) in an octahedral environment of two H_2O and four Cl^- ligands was obtained from the light yellow compound $NiCl_2 \cdot 2H_2O$ (Figure 5d). The structure of this compound involves infinite chains of $[NiCl_4(H_2O)_2]$ octahedra in which the Cl^- ligands serve as bridges.[12] The replacement of an additional two H_2O molecules by chloride ligands produces a further decrease in the energy of the band maximum to $23,200$ cm^{-1} (A). The estimated distances based on data for $CoCl_2 \cdot 2H_2O{}^{12}$ are 1.91 A for the $Ni-H_2O$ distance and 2.48 A for the $Ni-Cl$ distance.

Finally, the spectrum due to $[NiCl_6]$ octahedra was obtained from crystalline $NiCl_2$ (orange-brown in color) and from Ni(II) introduced as a substitutional impurity into the $CdCl_2$ lattice. In $NiCl_2$ itself (Figure 5e) the octahedral band has a maximum at $22,300$ cm^{-1} (A). The shoulder at $19,000$ cm^{-1} is probably a transition to the ^1D state. In $CdCl_2$ (Figure 5f) the band maximum is at a still lower energy, $21,500$ cm^{-1}, presumably because the $Ni-Cl$ distance in the $CdCl_2$ lattice is somewhat larger than in pure $NiCl_2$.

In crystal lattices, therefore, the chief result of pairwise substitution of chloride ions for water molecules in the Ni(II) coordination sheath is to shift the absorption maximum to lower energies. Interestingly enough, the energy of the band maximum seems to be linearly related to the number of H_2O ligands replaced by Cl^- ligands (Figure 5, inset).

On the basis of the results obtained on the crystal spectra, one concludes that the decreasing energy of the Ni(II) octahedral peak position in an $R = 9.2$ solution with increasing temperature (Figure 1), and in the $MgCl_2$ solutions with increasing $MgCl_2$ concentration (Figure 2), is due to a replacement of H_2O ligands by Cl^- ligands in the first coordination sphere of Ni(II). The decrease in the energy of the band maximum with changing $MgCl_2$ concentrations is shown graphically in Figure 6. The band maximum reaches an almost constant energy of $20,500$ cm^{-1}, both with respect to temperature and composition changes in the $R = 5-6$ composition region. The close correspondence of the energy of the octahedral band maximum at $R = 5.3$ with the crystal spectrum due to Ni(II) substituted for
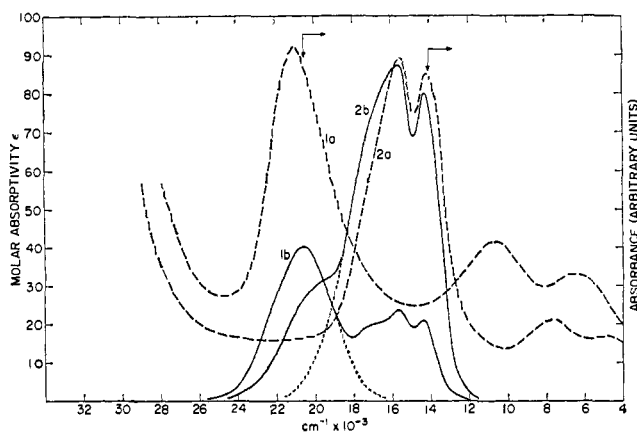
Figure 7. Comparison spectra of Ni(II) in aqueous $MgCl_2$ solutions and in crystals. 1a and 2a are crystal spectra taken at 550° of Ni(II)-doped $CsMgCl_3$ and Cs_2MgCl_4, respectively. 1b is the spectrum in an $R = 5.3$ solution at 125°, and 2b is that in an $R = 5$ solution at 314°. The dotted extensions of the liquid spectra for 1b and 2b show the effect of separating out the tetrahedral and octahedral (respectively) components of the spectra.

Figure 8. Dependence of log $(N_{[NiCl_4]}/N_{[NiCl_6]})$ on $1/T$ in an $R = 5$ aqueous $MgCl_2$ solution.

octahedrally coordinated Mg(II) in the compound Cs-$MgCl_3$ (see Figure 7) strongly suggests that the limiting peak position at 20,500 cm⁻¹ in the $MgCl_2$ solutions is due to the fully complexed species $[NiCl_6]$. The over-all shift from 25,600 to 20,500 cm⁻¹ in going from $[Ni(H_2O)_6]$ to $[NiCl_6]$ is also consistent with a decrease in Dq of about 30% in going from octahedral H_2O to octahedral Cl^- coordination.[14] If the band shift in the solution is proportional to the number of H_2O ligands replaced by Cl^- as appears to be the case for the crystal spectra (Figure 5, inset), then Figure 6 shows that most (~80%) of the H_2O ligand replacement leading to $[NiCl_6]$ occurs in the composition region corresponding, in the simplest view, to the removal of the second Mg(II) hydration shell.

The spectral studies strongly suggest that at compositions $R < 6$, the H_2O molecules are predominantly bound to Mg(II). The Ni(II) ions present in low concentrations are forced into chloride environments in the molten magnesium chloride hydrate systems in much the same way as in pure molten chloride systems.

In the composition region where $[NiCl_6]$ becomes the predominant Ni(II) species, a new absorption band in the 19,000–12,000-cm⁻¹ region, to be identified as due to the tetrahedral $[NiCl_4]$ group, simultaneously makes its appearance. In Figure 7(2b) this new band, whose intensity increases with temperature, is compared with the spectrum of Ni(II) substituted for tetrahedrally coordinated Mg(II) in crystalline Cs_2MgCl_4 (Figure 7(2a)). It is apparent from this comparison that the tetrahedral Ni(II) species in these liquids is only slightly distorted from regular symmetry. This observation, of value in understanding the state of the solvent, will be discussed later.

Having identified the coordination states giving rise to the spectra observed at high $MgCl_2$ concentrations ($R < 6$), it is now possible to give a more detailed interpretation of the spectra shown in Figure 3. At high temperatures (Figure 3a) a well-defined isosbestic point is found at 19,150 cm⁻¹. Since an isosbestic point occurs at the wavelength at which two species

which are in equilibrium have equal molar absorptivities, its presence in the temperature range 180–314° is indicative of the equilibrium between octahedral $[NiCl_6]$ and tetrahedral $[NiCl_4]$ species. Treating the chloride ion activity as invariant in this temperature interval, one can obtain the enthalpy of the transformation from the expression

$$\Delta H = R \frac{d \ln K}{d(1/T)} = Rd\left(\ln \frac{N_{tet}}{N_{oct}}\right)/d\left(\frac{1}{T}\right) =$$
$$Rd \ln \left(\frac{N_{tet}}{1 - N_{tet}}\right)/d\left(\frac{1}{T}\right)$$

where N represents a mole fraction and K is an equilibrium quotient without thermodynamic significance.

A plot of log K vs. $1/T$ obtained by analysis of the temperature dependence of the optical density of the 14,300-cm⁻¹ tetrahedral absorption band (which is not overlapped by the octahedral band) is shown in Figure 8. ΔH for the transformation can thus be obtained with good accuracy, and the value found is 8.5 ± 0.3 kcal/mole.[15] The points included on the dashed portion of the Figure 8 plot were obtained from the spectra below 180° shown in Figure 3b.

Equilibria between octahedral and tetrahedral Ni(II) configurations have been observed previously,[7,16] but only in the case of Ni(II) in the LiCl–KCl eutectic[16] is the tetrahedral configuration as little distorted as in the present case. Although the isosbestic point is not well defined in LiCl–KCl solutions, an estimate of ΔH for the transformation may be made. The value obtained is 7.3 ± 2 kcal/mole which agrees with the value derived from Figure 8 within the uncertainty of the estimate. In view of the different nature of the

(14) C. K. Jørgensen, Proc. Tenth Solvay Conf., 355 (1956).

(15) Solution densities, necessary to allow for the effect of expansion on the optical density, are not easy to measure accurately in this temperature range for aqueous liquids. Consequent uncertainties in the densities, and also in the value of ϵ for the $NiCl_4{}^{2-}$ species, determine the uncertainty assigned to ΔH.

(16) C. R. Boston and G. P. Smith, J. Phys. Chem., 62, 409 (1958).

solvents in these two cases, it is somewhat surprising that the enthalpies of the transformation are so similar.

The molar absorptivity at 17,700 cm^{-1} for NiCl$_4{}^{2-}$ in an $R = 5$ solution is 99 at 200–300°. This may be compared with the value of 90 for Ni(II) in molten K$_2$ZnCl$_4$ at 500°,[7] and 170 for Ni(II) in molten pyridinium chloride at 160°.[17] The molar absorptivity of NiCl$_4{}^{2-}$ varies depending on solvent and temperature. No satisfactory explanation of this variation can as yet be attempted.

From the spectra in Figure 3b it can be seen that at temperatures below 180° in the $R = 5$ solution, the behavior can no longer be described in terms of a simple equilibrium between octahedral and tetrahedral chloro complexes. It has already been shown that $E_{\max}$ increases when Cl$^-$ is replaced by H$_2$O in the Ni(II) first coordination sphere. Examination of Figure 3b makes it seem likely that the octahedral species below 180° becomes increasingly hydrated with decreasing temperature. However, the optical density of the tetrahedral component of the spectrum still appears accurately to reflect the concentration of [NiCl$_4$] (see Figure 8, dashed portion) even in the 125–180° temperature range.

It is now of interest to examine in more detail the behavior of the solvent system and other, more general, aspects of the observed Ni(II) coordination equilibrium.

Although thermodynamic data on MgCl$_2$ solutions are not available at the highest salt concentrations investigated in this work, information on the water activity up to concentrations of about 6 M ($R = 7.5$) are available from vapor pressure[18,19] and isopiestic solution[9] data. These measurements show that the activity coefficient of H$_2$O decreases drastically as the composition $R = 6$ is approached. The activity coefficient data together with the spectral observations, which show that the strongly hydrating Ni(II) ion is completely dehydrated at the $R = 6$ H$_2$O:MgCl$_2$ ratio, suggest that molten Mg(H$_2$O)$_6$Cl$_2$ may be described in terms of Mg(H$_2$O)$_6{}^{2+}$ cations and chloride anions. This description of the structure of the molten hydrate is also consistent with the observation that the [NiCl$_4$] configuration is little distorted in this solvent system. Previous studies[7] have shown that the degree of distortion of [NiCl$_4$] from tetrahedrality depends on the competition between ligand electrostatic repulsion energies, which favor the tetrahedral configuration, and ligand field stabilization energies, which, for four coordination, favor a square-planar configuration. Factors which diminish the charge density on the chloride ligands, such as the presence of cations of high polarizing power, e.g., Zn(II) and Mg(II) in the second coordination sphere, favor distorted [NiCl$_4$] groups. This effect is perhaps seen most clearly in the behavior of Ni(II) spectra in ZnCl$_2$–KCl melts and crystals.[7] The degree of distortion in the MgCl$_2$ solutions appears to be no greater than observed, for example, in molten K(I), Rb(I), or Cs(I) chlorides. The observation implies that on the average there are few, if any, small, highly polarizing Mg(II) ions in the second coordination sheath

(17) D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **63**, 393 (1959).
(18) (a) G. Tammann, *Wiedeman's Ann.*, 24, 523 (1885); (b) I. H. Derby and V. Yngve, *J. Am. Chem. Soc.*, 38, 1439 (1916).
(19) H. Lescouer, *Ann. Chim. Phys.*, [VI] 11, 431 (1894); tabulated in "Physico-Chemical Constants of Binary Systems" Vol. 3, J. Timmermans, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.

of the Ni(II) ions. This fact is, of course, consistent with the idea that Mg(II) ions occur predominantly as the hydrated species Mg(H$_2$O)$_6{}^{2+}$. The ionic potential, z_+/r_+, of Mg(H$_2$O)$_6{}^{2+}$ is almost the same as that of the Cs(I) ion.

While exchange of H$_2$O ligands among Mg(H$_2$O)$_6{}^{2+}$ cations undoubtedly is rapid, both the spectral and thermodynamic data indicate the usefulness of considering the liquid hydrate as a molten salt. Such a picture is also consistent with the interpretation of the transport behavior of Mg(II) in molten nitrate hydrate systems.[8] On this view the observed octahedral–tetrahedral equilibrium of Ni(II) becomes simply another example of a phenomenon which has now been observed in a number of molten chloride systems at low temperatures. The detailed information of this equilibrium, made available by the present study, is an example of the potential usefulness of molten hydrates as analog systems to aiding our understanding of the behavior of other fused salt systems.

The existence of octahedral–tetrahedral equilibria of Ni(II) in molten Mg(H$_2$O)$_6$Cl$_2$ suggests using the phenomenon as a tool to investigate the localization of water molecules around the principal cation in other molten hydrates. Thus the use of the Ni(II) coordination state as a means of determining equivalent hydration states may be investigated and may provide a new approach to the problem of comparative hydration energies and hydration shell stabilities. A paper which is in preparation describes studies of this sort for molten lithium and aluminum chloride hydrates. In that paper it will be shown that states approximately equivalent to those occurring in molten Mg(H$_2$O)$_6$Cl$_2$ are realized at about $R = 4$ for M = Li(I), $9 > R > 6$ for M = Al(III).

Observations on the behavior of Cu(II) in MgCl$_2$ solutions are summarized in Figure 4. In this case only a progressive shift in the octahedral peak position of the dilute aqueous solution is observed. As with Ni(II) an increase in temperature has an effect similar to that caused by an increase in MgCl$_2$ concentration. The final spectrum at $R = 6.2$ and 108° corresponds almost exactly (within 3 % of ϵ at all wavelengths) with the spectrum of Cu(II) in molten LiCl–KCl at 400°,[4] which was shown to be due to a distorted tetrahedral configuration.

An increase in temperature above 108° at $R = 6$ produces a decrease in both $E_{\max}$ and ϵ, an effect similar to that produced by an increase in temperature above 400° in molten LiCl–KCl. One concludes that, as in the case of Ni(II), high concentrations of MgCl$_2$ in aqueous solutions cause replacement of H$_2$O by Cl$^-$ in the Cu(II) coordination shell. Evidently the four-coordinated state is stable to lower temperatures in the case of Cu(II). More interesting, however, is the absence of an isosbestic point at any stage of the transformation. Coordination changes with and without isosbestic points have been discussed previously for the case Ni(II) in ZnCl$_2$–KCl melts.[7] It was pointed out then that the absence of an isosbestic point implies a continuous distortion mechanism for the transformation. This can occur when all configurations intermediate between the high- and low-temperature configurations are also intermediate in energy. Such a condition can evidently be met when the high-tempera-

ture, four-coordinated state is a very distorted tetrahedron. For Cu(II), the distorted state is strongly favored; even in usually symmetrical crystals of the type Cs_2MCl_4, the $[MCl_4]$ tetrahedra are distinctly flattened when M is Cu.[20] The continuous distortion mechanism for Cu(II) observed in this work is therefore not unexpected, and, in fact, its occurrence supports the interpretation given to the phenomenon in the Ni(II) instance. In the transformation from $[Cu(H_2O)_6]$ to $[CuCl_4]$ configurations then, the ligand replacement and distortion processes presumably are concurrent.

The coexistence of tetrahedral $MCl_4{}^{2-}$ complex anions with $Mg(H_2O)_6{}^{2+}$ cations in these solutions, even in the least likely case of $NiCl_4{}^{2-}$, suggested the possible existence of compounds of the type $Mg(H_2O)_6MCl_4$ (M = Zn, Co, Fe, Cu, Ni). Compounds of this type are, in fact, easily prepared in the case of Zn(II) and Co(II). Fe(II) and Cu(II) form compounds of the same stoichiometry but different crystal structure. In the case of Ni(II), a compound of this type does not appear to form. These findings have been reported elsewhere in more detail.[21]

Experimental Section

For measurements at concentrations up to H_2O:Mg = 6:1 (7.2 M at 100°), the experimental arrangement and procedure are relatively simple and are described below. In order to carry out measurements at higher concentrations and temperatures, where the partial pressure of H_2O exceeds 1 atm, sealed pressure cells had to be used. The temperature and concentration ranges of the investigation could be extended by sealing the solution and excess solid in specially constructed thick-walled Pyrex optical cell made by a technique described in the Appendix. Such cells are capable of withstanding internal pressures of the order of 75 atm, and experiments were conducted to temperatures of 350° (ca. 170° above the normal boiling point) before the cell exploded. In view of the hazard of explosion, the cells were housed in a separate brass chamber.

Optical Cell and Heater Assembly. The optical cell and heater assembly employed are shown in Figures 9a and b, respectively. The cell (A) was located in the bore of a 2.5-in. diameter cylindrical aluminum block (B) which was heated by two series-connected 250-w Firerod heaters (C) located on either side of the cell position. The advantages of this method of heating are that uniform temperature distribution is obtained, temperature inhomogeneities due to radiation loss from the windows are reduced, and containment of cell fragments from explosions is achieved. The block also contained holes for a platinum resistance temperature control sensor (D) and measuring thermocouple (E). This assembly was seated on an adjustable-height insulating brick pad (F) inside a protective brass casing (G) from which it was separated by spacer screws, (H). The side arms on the casing contained glass disks to protect the spectrophotometer.

Spectrophotometer. Spectra were recorded using the Cary Model 14 H spectrophotometer described previously.[22]

Preparation of Solutions and Procedure. Concentrations up to R = 6. For both Ni(II) and Cu(II) the less concentrated solutions were contained in a 1-cm path length Pyrex glass optical cell to which a graduated stem had been attached. This allowed densities of the solutions (necessary to obtain molar absorptivities) to be determined to an accuracy comparable to that with which their optical densities were measured.

(a) Ni(II) Study. A dilute solution of $NiCl_2$ was prepared, and the absorption spectrum in the range 3–14,000 A was recorded. An amount of AR crystalline $MgCl_2 \cdot 6H_2O$ to give an R = 14 (~3.3 M) solution was then dissolved, and the spectra were recorded at 25, 50, 75, and 100°, the volume of the solution being noted at each temperature. To change the composition a known mass of water was boiled off. The spectra at each succeeding composition

were taken at temperatures determined by crystallization on the one hand and ebullition on the other.

(b) Cu(II) Study. Because H_2O absorption bands overlap those of Cu(II), the measurements were made in D_2O solutions. In this case, a D_2O solution of Cu(II) was taken as the starting point, and composition changes were made by successive additions of anhydrous $MgCl_2$.

Concentrations > R = 6 (Ni(II) only). Solutions were prepared by adding a calculated amount of anhydrous $MgCl_2$, distilled water, and standard $NiCl_2$ solution (in that order) to the pressure cell before sealing off. In this case, of course, homogeneous solutions were not obtained until the cell had been placed in the heater assembly and agitated at high temperature.

Preparation of Crystalline Samples. The spectra of Ni(II) in different octahedral environments in crystal lattices were obtained using mulls of powdered samples susepended in a silicone fluid. $Ni(NO_3)_2 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$, and $NiCl_2 \cdot 6H_2O$ were reagent grade materials. Crude $NiCl_2 \cdot 2H_2O$ was obtained by crystallizing a concentrated $NiCl_2$ solution at 90°, removing the crystals, and rapidly absorbing the adherent solution between pressed filter papers. Analysis of the product gave $NiCl_2 \cdot 2.1H_2O$. Anhydrous $NiCl_2$ was obtained by heating the hydrated salt in a stream of dry HCl. $NiCl_2$ in the $CdCl_2$ lattice was obtained by quenching the Ni(II)-doped melt to obtain a flat sheet suitable for mounting in the spectrophotometer.

Acknowledgment. We are indebted to Mr. Joseph Hodur for developing the procedure for the construction of the high-pressure Pyrex optical cells.

Appendix

Preparation of Pressure Cells. The tubing employed in the preparation of the cells was 8 mm i.d. and 25 mm o.d., and was available in short lengths (3 in.). Extension tubes were attached for mounting in a lathe. A 0.25-in. square graphite mandrel was inserted into the bore, one end of the extension tube was closed, and a vacuum was applied to the other. Using a glass temperature slightly above the annealing range, the thick-walled section was then allowed to collapse slowly onto the mandrel. When the collapse was complete, one extension tube was removed and the mandrel chipped and bored out. The slightly uneven internal surfaces were flame polished, and one end of the cell was sealed off to give an approximately flat internal base. The other end was then drawn down to leave a 1.5-in. capillary section of approximately 1-mm bore
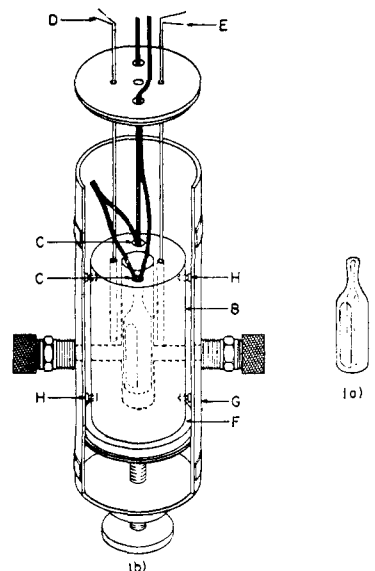

Figure 9. Apparatus for optical studies of aqueous systems to 320°: (A) pressure cell, (B) aluminum block furnace, (G) protective casing. For details see text.

(20) A. F. Wells, "Inorganic Structural Chemistry," 3rd ed, Clarendon Press, Oxford, 1962, p 877.

(21) D. M. Gruen and C. A. Angell, *Inorg. Nucl. Chem. Letters*, 2, 75 (1966).

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through which the sample could be introduced. Finally, two external flats were ground and polished parallel to internal surfaces. After filling, the cell could be sealed very simply at a point well removed from the sample. The ability of the capillary section to withstand internal pressure could be made to exceed that of the main section of the cell. The cell after filling and sealing is illustrated in Figure 9a.

The cells were calibrated by comparing the optical density of a suitable solution in the cell with that of the same solution in a standard 1-cm cell. Within the calibration error, the path length corresponded to the mandrel dimension (0.25-in.).

Barring explosions from excessive pressure buildup, the cells can be reused many times, as no etching by the high-pressure liquids has been evident.

Diethyldipyridylnickel. Preparation, Characterization, and Reactions

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Abstract: Diethyldipyridylnickel, $Et_2Ni(dipy)$, was synthesized by the reaction of $Ni(acac)_2$, α,α'-dipyridyl, and Et_2AlOEt in ether. The dark green, air-sensitive, crystalline complex was characterized by means of elemental analysis, thermal decomposition, alcoholysis, hydrolysis, visible light absorption spectra, infrared spectra, and nmr spectra. The nmr spectra of the complex show a quartet and a triplet near τ 9 which are assigned to the ethyl protons σ-bonded to nickel, and a quartet and two doublets in the region τ 0.9–2.6 of the coordinated dipyridyl ligand. These data are interpreted in connection with the structure of the complex. The complex has the catalytic activity for the cyclooligomerization of butadiene to cyclododecatriene as the main product.

W ilke and his co-workers have prepared a variety of zero-valent nickel complexes relevant to the catalytic oligomerization of butadiene.[2] The main synthetic method to prepare these complexes is the reaction of nickel compounds with organoaluminum compounds in the presence of electron donors. In the preparation, organonickel complexes have been postulated as unstable intermediates which are then reduced to zero-valent nickel complexes by homolytic fission of nickel–carbon bonds. However, no such complexes have been isolated from the mixed catalyst system. In one case the formation of an ethylene–nickel π complex via the postulated ethyl–nickel intermediates has been described in a system of nickel acetylacetonate, diethylaluminum monoethoxide, and triphenylphosphine.[3]

The thermal instability of the nickel–ethyl σ bond makes the isolation of ethyl–nickel complexes considerably difficult.[4] It is known that the coordination of an appropriate ligand to a transition metal stabilizes the metal–alkyl bond. With a cyclopentadienyl group and triphenylphosphine as the stabilizing ligands such an ethyl–nickel complex was prepared as the first example.[5] We found that α,α'-dipyridyl is an excellent stabilizer and isolated by the reaction of metal acetylacetonates, α,α'-dipyridyl, and diethylaluminum monoethoxide, the crystalline nickel, iron,[6] and cobalt[7]
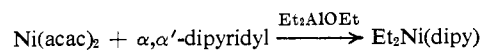
complexes which have σ-ethyl groups and dipyridyl ligands.

In the present paper, we wish to report the preparation, characterization, and reactions of the nickel complex in detail.[7a]

Experimental Section

Reagents. Nickel acetylacetonate[8] and α,α'-dipyridyl were prepared with the methods in the literature.[9] Diethylaluminum monoethoxide was prepared by the reaction of triethylaluminum with ethyl alcohol in hexane followed by vacuum distillation. Solvents were purified by usual methods and distilled under purified nitrogen.

Syntheses. Every operation was carried out under vacuum or in an atmosphere of nitrogen or argon purified by an activated copper column. The reactor was a two-necked round-bottom flask with a tail stopcock as a nitrogen inlet. As a typical example, 4 g of nickel acetylacetonate and 6 g of dipyridyl were suspended in 50 ml of ether, and 7 ml of diethylaluminum monoethoxide was added to this mixture by use of a pipet at $-20°$. The mixture was agitated with a magnetic stirrer at -20 to $\sim-10°$ until the reagents were completely dissolved in ether, and then it was kept standing at room temperature. Dark green crystals which precipitated were separated by filtration and washed repeatedly with ether and hexane. The yield of the crystals was 80% based on the nickel acetylacetonate.

$$Ni(acac)_2 + \alpha,\alpha'\text{-dipyridyl} \xrightarrow{Et_2AlOEt} Et_2Ni(dipy)$$

(1) (a) University of Tokyo; (b) Tokyo Institute of Technology.

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