localization path as compared to pyrrole rings II–IV. It reduces the σ effect at H12 position to the negligible amount as the mechanism is strongly geometry dependent.[44]

The unpaired spin density is localized on a σ-hybridized N1 orbital, which is not orthogonal to π orbitals of pyrrole ring I. A σ–π overlap within pyrrole ring I will permit the direct transfer of unpaired spin density of the N1 σ pair into the π system without any π M–L bonding.[45]

The 30 ppm difference in the shifts of the H22 and H23 resonances may result from the positive π-spin density delocalized by the porphyrin framework to the C22 carbon but none or relatively small one to the C23 atom. The σ contribution should be similar in both positions. The more detailed theoretical background is lacking in the literature so the semiquantitative analysis of this difference is difficult. A similar shift pattern as this shown by the N-methylated pyrrole ring was proposed for *N*-methylimidazole ligand coordinated by the amine nitrogen (NCH_3), i.e. large downfield shift of NCH_3 and upfield shift of the H4 proton situated in the position corresponding to the pyrrole proton in NCH_3(TPPH).[42] The contribution of the mechanism proposed in the case of meso protons may also be marked in the π delocalization contribution to isotropic shift of pyrrole protons.

The shifts of α-CH_2 of Ni(*N*-CH_3(OEP))Cl are slightly confusing. After the separation of the contact shift, it was found that seven of eight resonances have downfield shifts, which is consistent with both proposed spin delocalization mechanisms. The magnitude of the α-CH_2 shift depends on the pyrrole proton shift in the same position.[15] The group of strongly downfield shifted resonances could be assigned to α-CH_2 of pyrrole rings II–IV. The shifts of α-CH_2 (ring I) are smaller as usually observed in the case when the π-delocalization mechanism is only acting.[14,15] The upfield shift for only one component of the diastereotopic pair (Table III) is probably due to the specific orientation of the ethyl group (preferred in the temperature range studied) as coupling from the α-CH_2 group and pyrrole p_z electron could be accounted by an angular dependence

$$A_{CH_2} = B + B_2 \cos^2 \theta \tag{2}$$

where θ = angle between the p_z orbital and proton, $B < 0$, and $B_2 > 0$.[46,47] Under the condition $\theta \simeq 0$, the B part would dominate the shift, leading to the upfield contact contribution, but only for one proton as a second one has to be shifted downfield ($\theta = 120°$).

Conclusion

The spectroscopic properties of Ni(*N*-CH_3(TPP))Cl and Ni(*N*-CH_3(OEP))Cl complexes are different in many respects from those observed for their nonmethylated counterparts, i.e. Ni(TPP)(nitrogen base)$_2$ and Ni(OEP)(nitrogen base)$_2$.[23] However, in both systems the σ-delocalization mechanism dominates the isotropic shifts. The N-methylation imposes the large asymmetry that results in the characteristic pattern of pyrrole resonances. Such a pattern can be used as a "fingerprint" of *N*-methyl substitution in paramagnetic metalloporphyrins. The isotropic shift in Ni(*N*-CH_3(TPP))Cl is caused by the unpaired electrons on $d_{x^2-y^2}$ and d_{z^2} orbitals, which are responsible mainly for the σ delocalization. Understanding of the spin density distribution mechanism in complexes of *N*-alkylporphyrins will require further studies with metal ions possessing unpaired electrons on orbitals interacting directly via π bonds.

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Registry No. Ni(*N*-CH_3(TPP))Cl, 64813-95-2; Ni(*N*-CH_3(OEP))Cl, 95406-92-1; D_2, 7782-39-0.

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Potentiometric and Raman Spectroscopic Study of the Complex Formation of Gallium(III) in KCl–AlCl$_3$ Melts at 300 °C

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Potentiometric measurements with chlorine–chloride concentration cells and Raman spectroscopic measurements on dilute solutions of $GaCl_3$ in KCl–$AlCl_3$ melts at 300 °C give evidence for the formation of $GaCl_4^-$ in the basic melts ($0.26 < pCl < 3.01$). In the acidic melts ($pCl > 3.01$) the measurements are best explained by assuming the formation of the mixed Ga(III)–Al(III) chloride complex $GaAlCl_7^-$ and $Ga_2Cl_7^-$. The pK values at 300 °C (based on molar concentrations) for the equilibria (i) $GaCl_4^- + AlCl_4^- \rightleftharpoons GaAlCl_7^- + Cl^-$ and (ii) $2GaCl_4^- \rightleftharpoons Ga_2Cl_7^- + Cl^-$ were found to be 6.78 ± 0.04 and 6.56 ± 0.11, respectively.

Introduction

In many respects $GaCl_3$ behaves like $AlCl_3$. They are both Lewis acids having a strong affinity for chloride ions. Phase diagrams[1] of the MCl–$GaCl_3$ systems (M = Li, Na, K, Cs) show the existence of the compounds $MGaCl_4$ and MGa_2Cl_7 (except in the LiCl–$GaCl_3$ system). Raman spectral[2] and crystal structure[3] studies indicate that solid KGa_2Cl_7 has the constitution $K^+Ga_2Cl_7^-$. Raman spectroscopic measurements by Øye and Bues[4,5] on CsCl–$GaCl_3$ melts and by Mascherpa-Corral and Potier[6] on KCl–$GaCl_3$ melts were explained in terms of $GaCl_4^-$, $Ga_2Cl_7^-$, and higher polymers of the type $Ga_nCl_{3n+1}^-$.

Recently Dioum, Vedel, and Trêmillon[7] interpreted voltammetric measurements on the KCl–$GaCl_3$ molten system by the equilibrium

$$2GaCl_4^- \rightleftharpoons Ga_2Cl_7^- + Cl^- \tag{1}$$

with an autodissociation constant $(Ga_2Cl_7^-)(Cl^-)$ of 4.25 mol^2 kg^{-2} at 300 °C.

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Andreasen and Bjerrum[8] investigated dilute solutions of the Lewis acid FeCl$_3$ dissolved in KCl–AlCl$_3$. By spectrophotometric and potentiometric measurements they showed that the most likely reactions in the melt were $AlCl_4^- + FeCl_4^- \rightleftharpoons FeAlCl_7^- + Cl^-$ and $FeAlCl_7^- \rightleftharpoons FeAlCl_6 + Cl^-$.

A mixed chloro complex of similar type, GaAlCl$_7^-$, is believed to exist in melts with the composition CsGaAlCl$_7$.[5] So far no known investigations have been performed on the dilute solutions of GaCl$_3$ in chloroaluminate melts. Therefore, it was considered to be an interesting problem to investigate whether or not Ga(III) forms mixed chloro complexes with Al(III) in dilute solutions of GaCl$_3$ in KCl–AlCl$_3$ melts.

Experimental Section

AlCl$_3$ was made by reaction of molten aluminum (99.999% from Atomergic Chemetals) and HCl gas generated from concentrated sulfuric acid (BDH, analytical grade) and concentrated hydrochloric acid (BDH, analytical grade). The aluminum chloride was further purified by sublimation.[9] KCl (Riedel-de Haën, analytical grade) was heated beyond the melting point while HCl gas (Matheson, 99.999%) was bubbled through. Excess HCl was removed by bubbling dry N$_2$ through the melt for 15 min; finally the melt was filtered, solidified, and sealed off under vacuum.

GaCl$_3$ was synthesized by reaction of gallium metal (99.9% from Fluka) with chlorine (99.9% from Fluka). Since GaCl$_3$ is extremely hygroscopic, the reaction was performed in the potentiometric cell described below by adding gallium metal to the KCl–AlCl$_3$ melt in the working compartment. In order to make sure that all gallium metal had reacted, chlorine was added to the cell several times until the potential of the cell did not change.

The experimental technique was with few exceptions similar to the one used before.[10,11] All weighings and additions to the cells were performed in a nitrogen-filled glovebox with measured contents of water and oxygen of approximately 5 and 50 ppm, respectively. The chemical cells were chlorine–chloride concentration cells of a type similar to those previously used.[10] They were made of Pyrex with electrodes of glassy-carbon rods (Carbone Lorraine, V10, quality) sealed vacuum tight into the bottom of the cell. The reference and measuring chamber were separated by a sintered ceramic pin (Radiometer, diameter approximately 1 mm and length 7–9 mm). After addition of the chemicals the cells were sealed off under pressure of 0.5 atm of chlorine (99.9% from Fluka). In order to avoid distillation of AlCl$_3$ and GaCl$_3$, the connection tube between the two chambers was sealed off before the cells were placed in the furnace. Before the measurements were performed, the cells were equilibrated by rocking them in the furnace described below at 300 °C for at least 12 h.

The furnaces for the potentiometric measurements were constructed at our laboratory.[10,12,13] The temperature could be controlled within 0.1 °C, and the temperature variation was less than 1 °C in the central 20 cm of the furnace. The temperatures were measured with chromel–alumel thermocouples calibrated at the freezing points of Pb and Sn (99.999% from Atomergic Chemetals).

The cells used for the Raman spectroscopic measurements was square 5 × 5 mm Pyrex tubes with a length of approximately 1 cm. They were equipped with a neck of Pyrex tubing (5-mm diameter and 10-cm length), which made further additions possible. The cells were sealed off under 1 atm of chlorine pressure, to prevent reduction of Ga(III). The Raman spectra were obtained by excitation with filtered plane-polarized light (approximately 500 mW at 5145 Å) from a CR argon ion laser and recorded with a JEOL JRS-400D spectrometer with an extended S-20 photomultiplier. The scanning rate was 25 cm^{-1}/min, and the slit width of the spectrograph was around 3 cm^{-1}. The furnace used for the Raman measurements was of a type similar to the one used by Berg, von Winbush, and Bjerrum.[11]

Results and Discussion

General Considerations. The formality C' is defined as the initial molar amount of one of the added substances (KCl, AlCl$_3$, and GaCl$_3$) in 1 L of the melt. The densities of the melt are calculated with the assumption of ideal mixing of KCl–AlCl$_3$ and GaCl$_3$. This assumption is reasonable since the amounts of GaCl$_3$ are less than 0.7 mol% of the amounts of KCl–AlCl$_3$ in the melts investigated by the potentiometric method. The densities of GaCl$_3$ and KCl–AlCl$_3$ were obtained from the work of Greenwood and Wade[14] and Morrey and Carter,[15] respectively.

The acid–base properties of the melt are quantitatively expressed by the pCl here defined as the negative logarithm of the chloride concentration:

$$\mathrm{pCl} = -\log\,[\mathrm{Cl}^-] \tag{2}$$

In this work measurements have been carried out in both the acidic and the basic range. The melts are called acidic if pCl is greater than 3.01 and basic if the opposite is the case. This pCl value of 3.01 corresponds to the pCl of an equimolar KCl–AlCl$_3$ melt ($[Cl^-] = [Al_2Cl_7^-]$).[16]

The potentiometric cell used in this work can be written as

$$\mathrm{Cl_2,\ glassy\ carbon|Cl^-{}_I(KCl\text{–}AlCl_3\text{–}GaCl_3)|ceramic\ pin|Cl^-{}_{II}(KCl_{sat}\text{–}AlCl_3)|glassy\ carbon,\ Cl_2}$$

where index I refers to the working compartment and index II to the reference compartment. As reference a melt of KCl–AlCl$_3$ saturated with KCl is used. The pCl of this melt has been determined to be 0.255 at 300 °C.[16]

For dilute systems (up to 0.3 M) in KCl–AlCl$_3$ melts it has previously been shown[10] that at compositions near 50 mol % KCl the pCl in the working compartment is given by

$$\mathrm{pCl_I} = \mathrm{pCl_{II}} - (F/(RT \ln 10))\Delta E \tag{3}$$

where pCl$_{II}$ is the pCl in the KCl–AlCl$_3$ melt saturated with KCl and ΔE the measured potential of the cell.

It has recently been shown[16] that the solvent properties of the KCl–AlCl$_3$ melts at 300 °C can be mathematically described by assuming the existence of the species K$^+$, Cl$^-$, AlCl$_4^-$, Al$_2$Cl$_7^-$, and Al$_2$Cl$_6$. The experimental average coordination number $\bar{n}$ defined as the average number of moles of chloride bound to 1 mol of Ga(III) can then be calculated by using

$$\bar{n} = (C'_{\mathrm{KCl}} + 3C'_{\mathrm{AlCl_3}} + 3C'_{\mathrm{GaCl_3}} - 4[\mathrm{AlCl_4^-}] - 7[\mathrm{Al_2Cl_7^-}] - 6[\mathrm{Al_2Cl_6}] - [\mathrm{Cl^-}])/C'_{\mathrm{GaCl_3}} \tag{4}$$

In all calculations the variation in the activity coefficients has been neglected. This assumption can be justified by the fact that the concentration of the solute species is small compared to the concentration of K$^+$ and AlCl$_4^-$ in the measured range.

Raman Spectra of KCl–AlCl$_3$–GaCl$_3$ Melts at 300 °C. In Figure 1 polarized and depolarized Raman spectra of dilute solutions of GaCl$_3$ in basic (A) and acidic (B) KCl–AlCl$_3$ melts are shown. For comparison the Raman spectrum of an equimolar KCl–AlCl$_3$ melt is shown in Figure 1C. This spectrum consists of four bands at 122, 182, 350, and 487 cm^{-1} characteristic for the tetrahedral complex AlCl$_4^-$. The frequencies are in complete agreement with the ones measured by Øye et al.[17]

The same bands are seen in the spectrum of an 1.31 F solution of GaCl$_3$ in a basic (pCl = 0.631) KCl–AlCl$_3$ melt shown in Figure 1A. In addition to these bands a new depolarized band appears at 152 cm^{-1}. This band is assigned to the GaCl$_4^-$ complex since the ν_4 vibration of this complex is observed at 155 cm^{-1} by Mascherpa-Corral and Potier[6] in an equimolar KCl–GaCl$_3$ melt and at 153 cm^{-1} by Øye and Bues[4,5] in CsCl–GaCl$_3$ melts. It is not surprising that only one band due to GaCl$_4^-$ can be seen since the frequencies of the two other strong bands (122 and 346 cm^{-1})

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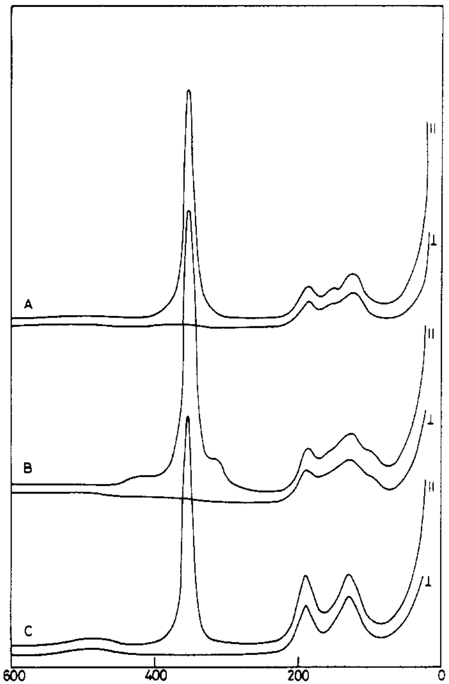

Figure 1. Series of Raman spectra (parallel and perpendicular polarizations) of $GaCl_3$ dissolved in molten KCl-$AlCl_3$ at 300 °C. The mole fractions of KCl and $AlCl_3$, the formal concentration of $GaCl_3$, $\bar{n}$, and pCl were as follows: (A) 0.5075, 0.4084, 1.31, 4.00, 0.631; (B) 0.4555, 0.4555, 1.33, 3.49, 6.04; (C) 0.5000, 0.5000, 0.000, 0.000, 3.01.

Table I. Values of Cell Potentials and Composition of 0.1 M $GaCl_3$ in KCl-$AlCl_3$ Melts at 300 °C

	mole fraction			mole fraction	
$-\Delta E$, mV	KCl	$AlCl_3$	$-\Delta E$, mV	KCl	$AlCl_3$
35.05	0.5090_7	0.4842_3	615.3	0.4855_8	0.5077_0
50.65	0.5065_7	0.4866_9	617.8	0.4851_6	0.5086_7
122.45	0.5014_4	0.4918_2	629.6	0.4814_9	0.5118_5
124.71	0.5014_1	0.4917_7	638.4	0.4779_1	0.5154_7
400.3	0.4970_8	0.4453_8	640.7	0.4771_6	0.5166_3
563.9	0.4946_0	0.4995_4	653.5	0.4714_5	0.5224_2
598.6	0.4894_2	0.5038_1			

are nearly coincidental with the frequencies of the corresponding vibrations of $AlCl_4^-$.

Figure 1B is the Raman spectrum of a 1.33 F solution of $GaCl_3$ in an acidic KCl-$AlCl_3$ melt (pCl = 6.04). In this spectrum the bands at 122, 184, and 352 cm^{-1} can be assigned to $AlCl_4^-$, and the shoulder at 155 cm^{-1} is probably the ν_4 vibration of $GaCl_4^-$. The polarized band at 311 cm^{-1} has the same frequency as the strongest band in the spectrum of $Al_2Cl_7^-$ published by Øye et al.;[17] consequently this band is assigned to $Al_2Cl_7^-$. The shoulder at ~95 cm^{-1} can be due to the 99-cm^{-1} vibration[17] of $Al_2Cl_7^-$, the 90-cm^{-1} vibration[6] of $Ga_2Cl_7^-$, or a combination of these. The polarized band at 405 cm^{-1} has been observed neither in MCl-$GaCl_3$ (M = K, Cs) melts[4-6] nor in MCl-$AlCl_3$ (M = Li, Na, K, Cs) melts.[17-19] However, if Ga_2Cl_6 was present, one would expect that the strong band at 340 cm^{-1} typical for this species[4,5] would be observed in Figure 1B. Since no such band is seen in the spectrum, it seems reasonable to assume that the 405-cm^{-1} band is not caused by a Ga_2Cl_6 vibration but must be due to a mixed Ga(III)-Al(III) chloro complex. Support for this view can be found in the spectrum of a melt with the composition $CsGaAlCl_7$, where a polarized band appears at the same frequency.[5] Further, a Raman spectrum of a 1:1:1 KCl-$AlCl_3$-$GaCl_3$ melt showed a band at 402 cm^{-1} besides bands due to $Ga_2Cl_7^-$ (366, 138, and 92 cm^{-1}), $Al_2Cl_7^-$ (312 cm^{-1}), and $GaCl_4^-/AlCl_4^-$ (348 cm^{-1}); no bands from Ga_2Cl_6 were observed in this spectrum.

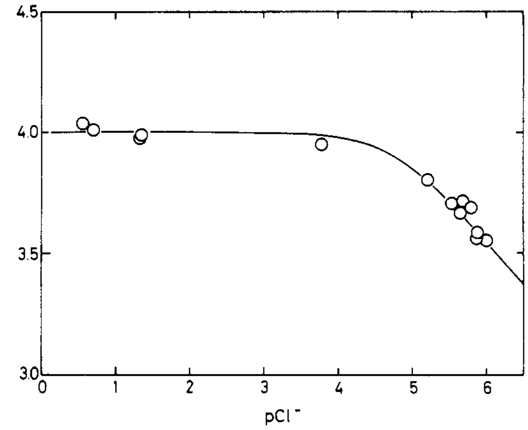

Figure 2. Experimental average coordination number for Ga(III) in solutions of $GaCl_3$ in KCl-$AlCl_3$ as a function of pCl at 300 °C. The curve is drawn with the assumption of the equilibrium $GaCl_4^- + AlCl_4^- \rightleftharpoons GaAlCl_7^- + Cl^-$ with a p*K* value of 6.78. ($GaAlCl_7^-$ is for computational reasons considered as $GaCl_3$ solvated with $AlCl_4^-$, i.e. having $\bar{n}$ = 3.)

Measurements and Calculations on Cell Potentials in KCl-$AlCl_3$-$GaCl_3$ Melts. In Table I the measured values of $-\Delta E$ and the corresponding mole fractions of KCl and $AlCl_3$ for 0.1 F solutions of $GaCl_3$ are given. The potentiometric measurements could not be performed at higher pCl values than approximately 6.0 since the vapor pressure of $AlCl_3$ and $GaCl_3$ will cause mass transport from the working to the reference compartment through the filter beyond this pCl.

The values from Table I are used for calculating the plot of the experimental average coordination number of Ga(III) as a function of pCl shown in Figure 2. From this figure it can be seen that the average coordination number in the basic range (pCl < 3.01) is equal to 4. This together with the Raman spectra of Ga(III) in basic KCl-$AlCl_3$ solutions strongly indicates the formation of the complex $GaCl_4^-$ in these melts.

In the acidic melts (pCl > 3.01) the average coordination number is decreasing with increasing pCl. This suggests the formation of other Ga(III)-chloride complexes with less chloride relative to Ga(III) than in $GaCl_4^-$.

The measurements in the basic range (the first five measurements in Table I), where the average coordination number is 4, are used for calculating the experimental standard error on the KCl formality. The result of this calculation is a standard error of 3.01×10^{-3} corresponding to a variance of 0.907×10^{-5}.

The last eight measurements in Table I have an average coordination number of less than 4. These measurements are used in the calculations of the equilibrium constants of the Ga(III)-chloride complex equilibria. Computations have been made with the assumption of equilibria between $GaCl_4^-$ and one or two other Ga(III)-chloride species. The Ga(III) species taken into consideration are $Ga_2Cl_7^-$, $Ga_3Cl_{10}^-$, Ga_2Cl_6, $GaCl_3$, and the mixed complex $GaAlCl_7^-$. The first three species are known from the binary $GaCl_3$-MCl (M = K, Cs) melts,[4-6] and $GaCl_3$ is a possible candidate since dilute solutions of other chlorides like $ZnCl_2$, $TeCl_4$, and $NbCl_5$ form monomeric species in chloroaluminate melts.[10,20,21]

In the calculations two equilibria, $2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$ and $Al_2Cl_7^- \rightleftharpoons Al_2Cl_6 + Cl^-$, were used to describe the behavior of the solvent. The p*K* values for these two reactions, 7.78 and 6.86 (300 °C), were taken from the work of Brekke, von Barner, and Bjerrum.[16]

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Table II. Comparison between Models for the Chloro Complex Formation of Ga(III) in KCl–AlCl$_3$ Melts at 300 °C[a] (0.1 F GaCl$_3$ Solutions)

model no.	equilibria	p*K*	variance × 10^5
1	$GaCl_4^- \rightleftharpoons GaCl_3 + Cl^-$	6.02 ± 0.03	2.0*
2	$2GaCl_4^- \rightleftharpoons Ga_2Cl_7^- + Cl^-$	4.20 ± 0.10	2.6*
3	$2GaCl_4^- \rightleftharpoons Ga_2Cl_6 + 2Cl^-$	10.88 ± 0.07	5.9
4	$3GaCl_4^- \rightleftharpoons Ga_3Cl_{10}^- + 2Cl^-$	9.17 ± 0.09	1.6*
5	$GaCl_4^- + AlCl_4^- \rightleftharpoons GaAlCl_7^- + Cl^-$	6.74 ± 0.03	1.2*
6	$2GaCl_4^- \rightleftharpoons Ga_2Cl_7^- + Cl^-$	4.97 ± 0.19	
	$Ga_2Cl_7^- \rightleftharpoons 2GaCl_3 + Cl^-$	7.3 ± 0.3	1.3*
7	$2GaCl_4^- \rightleftharpoons Ga_2Cl_7^- + Cl^-$	4.59 ± 0.11	
	$Ga_2Cl_7^- \rightleftharpoons Ga_2Cl_6 + Cl^-$	6.39 ± 0.11	1.2*
8	$2GaCl_4^- \rightleftharpoons Ga_2Cl_7^- + Cl^-$	4.60 ± 0.11	
	$3Ga_2Cl_7^- \rightleftharpoons 2Ga_3Cl_{10}^- + Cl^-$	4.78 ± 0.16	1.6*
9	$3GaCl_4^- \rightleftharpoons Ga_3Cl_{10}^- + 2Cl^-$	13.4 ± 0.03	
	$Ga_3Cl_{10}^- \rightleftharpoons 3GaCl_3 + Cl^-$	4.6 ± 0.3	2.3*
10	$3GaCl_4^- \rightleftharpoons Ga_3Cl_{10}^- + 2Cl^-$	9.21 ± 0.09	
	$2Ga_3Cl_{10}^- \rightleftharpoons 3Ga_2Cl_6 + 2Cl^-$	18.4 ± 1.0	1.9*
11	$2GaCl_4^- \rightleftharpoons Ga_2Cl_7^- + Cl^-$	6.56 ± 0.11	
	$GaCl_4^- + AlCl_4^- \rightleftharpoons GaAlCl_7^- + Cl^-$	6.78 ± 0.04	1.2*

[a] 0.1 M GaCl$_3$ solutions. Asterisks are based on $F_{0.10}(7.4) = 3.98$ (one equilibrium) or $F_{0.10}(6.4) = 4.01$ (two equilibria).

For each model the best p*K* value (i.e. the one that gave the lowest variance) was found by a computer program. The potassium chloride formality was least-squares fitted by means of Marquardt's method for nonlinear regression[22] using the p*K* values as independent variables. By comparison of the so obtained minimum variances for each model with the experimental variance, an *F* test can be used to make distinction between models with more or less probability than 90%.

In Table II the results of the calculations on models involving such complexes are shown. Models with a probability of more than 90% compared with the experimental variance are marked with an asterisk.

When only one equilibrium is taken into account, the potentiometric measurements can be explained by several models. The lowest variance is, however, obtained for the formation of the mixed Ga(III)–Al(III) complex GaAlCl$_7^-$ according to the equation

$$GaCl_4^- + AlCl_4^- \rightleftharpoons GaAlCl_7^- + Cl^- \qquad (5)$$

If three Ga(III)–chloride complexes are supposed to exist, the calculations show that models involving Ga$_2$Cl$_7^-$ (i.e. eq 1 as the first equilibrium) generally have small variances. Two different possibilities for the third Ga(III) species give the minimum variance, namely Ga$_2$Cl$_6$ and GaAlCl$_7^-$. Since the Raman spectroscopic measurements suggested that a mixed Ga(III)–Al(III) chloro complex was present in acidic solutions of GaCl$_3$ in KCl–AlCl$_3$, it seems likely that GaAlCl$_7^-$ is the best choice for the third complex.

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Registry No. AlCl$_3$, 7446-70-0; GaCl$_3$, 13450-90-3; GaAlCl$_7^-$, 95156-16-4; Ga$_2$Cl$_7^-$, 33847-92-6; KCl, 7447-40-7.

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Racemic Adsorption, Antiracemization, and Induction of Optical Activity of Metal Chelates in the Presence of a Colloidal Clay

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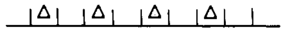
The adsorption of an optically active metal chelate by a colloidal particle of sodium–montmorillonite clay has been studied by means of the electronic spectra and electric dichroism and circular dichroism measurements. An adduct of a clay with Λ-tris(1,10-phenanthroline)ruthenium(II) (Λ-Ru(phen)$_3^{2+}$) accepted the adsorption of Δ-M(phen)$_3^{2+}$ (M = Ru, Fe, Ni) but not Λ-M(phen)$_3^{2+}$ in excess over the cation-exchange capacity. Due to such stereospecific adsorption, the racemic mixture of a labile metal complex such as Co(phen)$_3^{2+}$ and Fe(phen)$_3^{2+}$ antiracemized in the presence of Λ-Ru(phen)$_3^{2+}$–montmorillonite (or Δ-Ni(phen)$_3^{2+}$–montmorillonite). When an achiral molecule such as the acridine orange cation was adsorbed by Δ-Ni(phen)$_3^{2+}$–montmorillonite, the optical activity was induced in the electronic spectrum of the adsorbate.

Introduction

Recently I studied the adsorption of an optically active metal chelate by a colloidally dispersed clay.[1] Certain tris-chelated complexes were found to be adsorbed as a single unit of a racemic pair. For example, tris(1,10-phenanthroline)iron(II) (Fe(phen)$_3^{2+}$) was adsorbed within the cation-exchange capacity (CEC) of a clay when the chelate was added as a pure enantiomer. On the other hand, the same chelate was adsorbed in a 2-fold excess of the CEC from a solution of a racemic mixture. Schematically the states of saturated adsorptions of enantiomeric and racemic Fe(phen)$_3^{2+}$ can be written as (1) and (2), respectively. At a state (2), the closely stacked racemic pairs were distributed over a bidimensional surface of a silicate sheet of a clay. Such highly packed states were, however, impossible for enantiomeric adsorption (1) because of the steric interference between the adjacent molecules.



(1)

(2)

This paper describes the new aspects concerning the above phenomena. One is the study of the competitive adsorption of two different metal chelates on a colloidal clay. The results clarified to what extent the competitive chelates should possess structural similarity for realizing the highly packed state as in (2). The other is the antiracemization and induction of optical activity of a metal chelate when the molecule was adsorbed on an empty site of a clay surface at a state (1). The results revealed that a surface (1) not only recognized the absolute configuration of a new adsorbate but also stabilized the configuration of an adsorbed molecule against racemization. As a result, a labile metal complex, which was added to the system of a clay–optically active chelate adduct, was accumulated as a pure enantiomer.

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[1] (a) Yamagishi, A.; Soma, M. *J. Am. Chem. Soc.* **1981**, *103*, 4640. (b) Yamagishi, A. *J. Phys. Chem.* **1982**, *86*, 2472.