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Formation of Ionic Liquids of Divalent Metal Complexes Comprising *N*-alkylethylenediamines and the Solvation of the Nickel(II) Complexes

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Abstract

A series of divalent *N*-alkylethylenediamine (alkyl-en) metal(II) (alkyl = hexyl, 2-ethylhexyl, octyl, dodecyl; metal = Ni, Cu, and Zn) complexes was prepared and their phase behavior was studied using differential scanning calorimetry. This kind of metal complexes is very useful for systematically investigating the relationship between phase behavior and molecular structures. It was found that several of the zinc(II) and nickel(II) complexes form room-temperature ionic liquids (RTILs), despite the divalent cation.

Although the solid-to-liquid transition temperatures of metal(II) complex-based ILs are typically higher than those of the more common monovalent ionic liquids (ILs), they are dependent on the nature and combination of the metal(II) ions, alkyl chains, and counter anions. The zinc(II) complexes coupled with weakly coordinating bis(fluorosulfonyl)amide (FSA) or bis(trifluoromethanesulfonyl)amide (Tf_2N) anions have significantly lower melting points, which is attributable to the longer distance between the zinc(II) ions and the counter anions upon the formation of tetrahedral bis(alkyl-en)zinc(II) complexes as compared to the corresponding distances in NO₃ and trifluoroacetate (TFA) complexes. The correlation of melting points with the molecular structures of the zinc(II) complexes is similar to that for the silver(I) alkyl-en complexes. The tris(alkyl-en)nickel(II) complexes coupled with Tf_2N counter ions do not readily solidify and have glass transition temperatures below 0 °C, whereas the corresponding bis complexes have much higher melting points despite the counter-ions residing in the outer-spheres of the nickel(II) ions. The interactions of NO₃, TFA, FSA, and Tf_2N anions with the nickel(II) ions of the bis(alkyl-en) complexes and their solvation behaviors were also studied in organic solvents using visible absorption spectroscopy based on the structures of the neat states. The characteristic solvation behaviors of the nickel(II) complexes were rationalized in terms of the counter anions and solvents.

Key words: ionic liquids; divalent metal complexes; phase behavior; chelate amines; solvation of alkylethylenediamine nickel(II) complexes

1. Introduction

Ionic liquids (ILs) and ionic liquid crystals containing transition-metal ions show a variety of specific properties that are not exhibited by conventional organic compounds. [1-10] It is of particular note that the ILs of metal complexes (met-ILs) are regarded as soft materials in which the metal ions are highly condensed in nano-sized regions. Therefore, met-ILs are expected to become increasingly utilized as functional soft materials in fields such as nanochemistry, electrochemistry, and magnetochemistry.[11-23] It is important for the rational molecular design of met-ILs to be able to relate their phase behavior to the molecular structures of the ligands and the nature of the central metal ions, and counter ions, as well as the relationships between them. However, systematic studies on these relationships have not been performed. From this viewpoint, a suitable series of alkylethylenediamine (alkyl-en) metal complexes would be a model upon which to perform intensive studies on the above relationship based on the different molecular moieties and structures within the series. In previous studies, our research group has prepared several alkyl-en silver(I) complexes related to the formation of silver(0) nanoparticles (AgNPs) revealing the close correlation between their molecular structures and phase behavior. [24-26] Silver(I) complexes as well as alkyl-en monoprotic ILs (PILs) form ILs more easily than multivalent compounds owing to their smaller inter-ionic interactions. For divalent metal complexes, although the melting points are generally higher, several structural factors, e.g., molecular sizes and geometries are expected to act more synergistically on the formation of ILs compared to those for monopositive silver(I) complexes and monoprotonated PILs.

In the present study, several divalent metal (Ni(II), Cu(II), and Zn(II)) alky-en complexes coupled with the counter anions of NO_3^- , TFA⁻, FSA⁻, and Tf₂N⁻ were prepared and their phase behaviors were studied using differential scanning calorimetry (DSC). The preparation of the [Zn(NO₃)₂(octen)₂] complex and its X-ray crystallographic analysis has been previously reported in a short communication by us [27], revealing that the NO₃ anions directly coordinate to the zinc(II) ion to form an octahedral complex. However, the phase behavior of most divalent metal complexes comprising alkyl-en moieties in the neat states has not been studied, although it is

expected to be dependent on various molecular structures. ILs are generally defined as normal salts with melting points below 100 °C, with room temperature ionic liquids (RTILs) being attractive as functional soft materials. The melting points of the metal alkyl-en complexes studied herein cover a wide range, from below 0 °C to ≈ 200 ° C. Therefore, a series of these complexes is a suitable system for studying the relationship between molecular structures and melting points.

The structures of nickel(II) complexes can be mainly categorized into two types, i.e., those with octahedral and those with square-planar geometry. These two structure types can be clearly discriminated by their visible absorption spectra and can be expected to exhibit distinct phase behaviors. Based on their neat states, the structures of the bis(alkyl-en) nickel(II) complexes are also studied in terms of their solvation behaviors in different organic solvents, with particular attention being given to the differences between the complexes with strongly coordinating anions and those with weakly coordinating anions.

2. Experimental

2.1 *Materials*. The *N*-hexyl-, *N*-2-ethylhexyl-, *N*-octyl-, and *N*-dodecyl-ethylenediamines (C6, C2C6, C8, and C12, respectively) were prepared by reacting the corresponding alkyl bromides (purchased from Tokyo Chemical Industry) with ethylenediamine (guaranteed reagent, purchased from Wako Pure Chemical Industry) 1:5 molar ratio according to the literature, [28] followed by distillation at 1 kPa. The MX₂ salts (M = Ni(II) Cu(II), or Zn(II), and X = Tf₂N or TFA) were isolated as follows. 5×10^{-3} mol NiCO₃ (594 mg) CuO (398mg), or ZnO (407mg) was dispersed in 10 mL water, and 10^{-2} mol HTf₂N or HTFA (acidic form) dissolved in 10 mL water was gradually added, and then the mixture was stirred until the solid was almost dissolved. After the solution was passed through #5C filter paper, the filtrate was condensed by an evaporator at 40 °C until a small amount of solid was precipitated. The solution with precipitates was then cooled in a refrigerator; the solids were collected and dried *in vacuo*. The dehydration was performed with Hitachi VR-16 high-vacuum pump over 48 h. Ni(TFA)₂ was obtained as a trihydrate and the other MX₂ salts were as an

anhydride. The purities of the isolated salts were confirmed by CHN elemental analyses.

The NO₃ complexes of $[MX_2(alkyl-en)_2]$ (or $[M(alkyl-en)_2]X_2$) for Ni(II), Zn(II), and Cu(II) were prepared following previously reported procedures and obtained as solids.[27] The FSA salts were obtained from the nitrate (for Ni(II), Zn(II), and Cu(II)) of each complex by the counter ion exchange using potassium bis(fluorosulfonyl)amide (KFSA) (purchased from Mitsubishi Materials Electronic Chemicals Co.) following the way for the Ag(I) complexes [26], whereas the solids of FSA salts were obtained as described below as for the other solids. The alkyl-en complexes were prepared by the reaction of the MX₂ (X = Tf₂N or TFA) salt with alky-en in 1:2.05 molar ratio for the $[M(alkyl-en)_2]X_2$ salt or 1:3.05 molar ratio for the $[Ni(alkyl-en)_3]X_2$ salt following the previously reported procedure [24-27, 29-31]. The solvents used for the syntheses were methanol or methanol/dichloromethane mixtures. To solidify the complexes, dichloromethane or diethyl ether was gradually added to the methanol solutions. For the $[Ni(alkyl-en)_2]X_2$ complexes where X = Tf₂N or FSA, the solids obtained from the solution are purple blue and by dryness under high vacuum they changed to hygroscopic orange solids. We herein used the orange solids, which gradually change to the color of purple blue by an absorption of moisture. In the case of the RTILs of the $[Ni(alkyl-en)_3]X_2$ and of some zinc(II) complexes, the residual liquids of the ligands as well as the organic solvents in the products were completely removed using Hitachi VR-16 high-vacuum pump over a few days.

The organic solvents used for the solvation study of the nickel(II) complexes were dichloromethane (DCM), diethyl ether (Et_2O), acetone, acetonitrile (MeCN), methanol (MeOH), ethanol (EtOH), *N*,*N*-dimethylformamide (DMF), and dimethylsulfoxide (DMSO). All the solvents were purchased from Wako Chemicals, dehydrated by passing over molecular sieves (3A 1/16, Wako Chemicals), and then once distilled before use.

2.2 Measurements.

The purities of the obtained metal complexes were determined using CHN elemental analyses with a Perkin Elmer 2400II Elemental Analyzer (equipped in the division of Instrumental Analysis of Nagasaki University) and ¹³C NMR spectra with a JEOL EX-270 spectrometer for the Zn(II) complexes. The CHN elemental analyses for the alkyl-en metal(II) complexes used in the study of the phase behavior are listed in

Table S1. The concentrations of the nickel(II) complexes in organic solvents are expressed as molality unit (mol kg⁻¹). The solid-liquid transitions for the newly synthesized metal(II) complexes were examined using differential scanning calorimetry with a Shimadzu DSC-50 equipped with an LTC-50 apparatus for low-temperature measurements; the temperature was increased at a constant rate (10 K min⁻¹) from – 80 to 200 or 250 (only for the Ni(II)C2C6(NO₃) complex) °C. The transition behavior was observed only for the temperature-increasing process. The sample (2–3 mg) was placed in an aluminum pan and the measurement was performed under nitrogen at a flow rate of 20 cm³ min⁻¹. Indium metal (purchased from Wako Chemicals) was used as a standard for the transition temperature and enthalpy. The melting point was defined as the minimum point in the endothermic curve and the glass transition point follows the common definition as shown in Fig. 2. [24,25] Several systems showed double melting points on the DSC profiles as described below. In order to confirm the transition temperatures from solid to liquid, we followed the melting processes using polarizing microscope (Olympus BH2).

The TG/DTA measurements were performed to detect the thermal stabilities of the complexes using a Shimadzu DTG-60/60H with the temperature increasing at a constant rate (10 K min⁻¹) from room temperature to 300 $^{\circ}$ C.

2.3 *Electronic spectral measurements.* The VIS absorption spectra of the nickel(II) complexes in solution were acquired in the 400–1200 nm wavelength range at 0.2 nm intervals using a JASCO V-670iRM (single-beam) instrument at ambient temperature. The precision of the wavelength was ± 0.3 nm. The cell length was 0.05, 0.2, or 1.0 cm. The concentrations were 0.05 mol kg⁻¹ unless otherwise stated and the molar extinction coefficient (*e*) is expressed in mol⁻¹kg cm⁻¹ unit. For the solid samples, the spectra were measured by the diffuse reflectance method with a JASCO ISN-723 (integrating sphere) attachment for the typical samples. The rough measurements to decide whether the octahedral or square-planar geometry for the nickel(II) complexes in the solid states were performed by nujol mull method [32] in the 400–800 nm wavelength region.

3. Results and discussion

Characterization of the alkyl-en metal(II) complexes.

As shown in Table S1 the calculated (anhydride) and experimental CHN elemental analysis values for most of the complexes agree within 0.3% with several agreeing within 0.5%. The exceptions are [Ni(doden)₂](FSA)₂ (the differences are 3.34 % and 0.55 % for C and H, respectively) and [Ni(doden)₂](NO₃)₂ (the differences are 1.16 and 0.53 % for C and H, respectively).

The purities of the diamagnetic Zn(II) complexes were also assessed using ¹³C NMR spectra on the basis of previous studies. [24, 25, 33]

Coordination of the counter anions in the neat-state alkyl-en nickel(II) complexes.

The nickel(II) complexes in the neat states typically exhibit one of two colors depending on the counter anions: with the NO₃ and TFA salts being purple-blue and the FSA and Tf₂N complexes being orange. The absorption spectra of the solids were measured using the diffuse reflectance method and those of $[Ni(hexen)_2(TFA)_2]$ and $[Ni(hexen)_2](Tf_2N)_2$ are given as typical examples in Fig. 1. These results clearly indicate that the geometry of the main component of the TFA salt is octahedral and that of the Tf₂N salt is square planar. [34,35] The absorption spectra of the neat nickel(II) complexes were also measured using a nujol mull method in order to classify the complexes into two types depending on whether the counter anion is directly coordinating to the nickel(II) ion or not. These results indicate that the NO₃ and TFA anions directly coordinate to the nickel(II) ion to form octahedral complexes while the FSA and Tf₂N anions do not directly coordinate to the nickel(II) ion, forming instead square- planar complex. These results are also related to the phase behavior, as discussed below.



Fig. 1. Diffuse reflectance AB spectra of solid bis(hexen) nickel(II) complexes of Tf_2N (—) and TFA (---) salts.

Phase behavior

The features of the DSC curves can be classified into the following four types of solid-liquid transitions. 1) a crystal-to-liquid transition above 100 °C. 2) a crystal-to-liquid transition with double melting peaks. 3) a glass transition below 0 °C. 4) a crystal-to-liquid transition below 100 °C. Typical DSC curves for each type of the Zn(II) complexes are shown in Fig. 2. The solid-to-liquid phase transition temperatures (T_{MP}) are listed in Table 1 together with the transition enthalpies (in parentheses). Here, glass transitions are indicated by (*g*) and the other temperatures are melting points or double melting points. The T_{MP} values for the analogous monopositive silver(I) complexes and protic alkyl-en ILs reported previously are also listed for comparison. Double endothermic peaks are observed in many of the NO₃ and TFA metal(II) complexes (Fig. 2b, Table 1). For these complexes, it was confirmed using polarized microscope (PM) that melting occurs at the higher of the two T_{MP} values' while the PM image does not change across the lower transition [36,37]. In the present system, formation of liquid crystals was not clearly detected. However, formation of liquid crystals was well characterized for several of the silver(I) complexes. [38] Herein, for simplicity we take the higher temperature in the double transitions as the melting point.

Before addressing the phase transitions, we obtained the TG profiles of each complex. The TG profiles of the hexyl(C6) and ethylhexyl(C2C6) complexes are presented in Fig. 3 as typical examples. The temperatures at which significant weight losses are observed are higher than the transition temperature (T_{tr}) except for Ni(II)-C2C6(NO₃) (Fig. 3b) and are generally dependent on the counter anions in the order TFA < NO₃ < FSA \approx Tf₂N. The lower thermal stability of the TFA salt has also been reported for the monopositive PILs of the alkyl-en derivatives.[33] In terms of the alkyl chains, the ethylhexyl (C2C6) complex tends to be degraded at a lower temperature compared to the other alkyl derivatives. However, the Ni(II)-C2C6(NO₃) complex is unique, having a particularly-higher melting point (above 200 °C) and a lower decomposition temperature.





Fig. 2. Typical DSC curves for the zinc(II) complexes. (a) bis(hexen)Zn(II) nitrate, (b) bis(ethexen)Zn(II) nitrate, (c) bis(ethexen)Zn(II) Tf₂N salt, and (d) bis(doden)Zn(II) Tf₂N salt.

Table 1. Phase transition temperatures ($T_{\rm MP}$ / °C) and enthalpies ($\Delta H_{\rm MP}$ / kJ mol⁻¹, in parentheses)

Metal(II)		counter anion		
/ alkyl			K	
(a) Zn(II) NO ₃	TFA	FSA	Tf_2N
C6	144.1 (30.4)	61.7 (10.5), <u>122.8 (13.8)</u>	<u>)</u> -48 (g)	-44 (g)
C2C6	141.5 (4.5), <u>168.6 (23.2)</u>	61.8 (1.8), <u>87.3 (17.2)</u>	-45 (g)	-37 (g)
C8	150.4 (35.5)	68.6 (8.7), <u>102.3 (13.2)</u>	64.8 (27.9)) –44 (g)
C12	83.4 (55.9), <u>139.0 (36.1)</u>	71.7 (40.6), <u>118.5 (46.7)</u>) 58.8 (67.0) 52.8 (65.6)
(b) Ni(II) NO ₃	TFA	FSA	Tf_2N
C6	137.1 (39.1)	94.7 (8.1), <u>154.2 (27.9)</u> ^{<i>a</i>}	98.6 (23.5)	85.9 (22.7)
tris(C6)				$-7 (g)^{b}$
C2C6	237.9 (39.4)	93.2 (1.2), <u>124.6 (26.2)</u>	78.1 (17.7)	76.0 (28.4)
C8	123.8 (7.2), <u>143.8 (35.4)</u>	90.0 (8.1), <u>125.5 (20.8)</u>	118.1 (43.3)	90.0 (14.8)
tris(C8)				-37 (g)
C12	93.0 (73.5)	124.3 (53.6)	114.3 (55.0)	101.9 (43.5)
^{<i>a</i>} : glass transition				
(c) Cu(II	() NO ₃	TFA	FSA	Tf_2N
C6	122.7 (5.4), <u>179.0 (44.3)</u>	111.4 (16.8), <u>168.4 (20.5)</u>	118.0 (43.3)	109.3 (48.8)
C2C6	130.9 (18.0)	48.3 (6.9), <u>88.9 (4.5)</u>	86.2 (22.8)	108.2 (53.6)
C8	171.8 (2.8), <u>188.7 (35.0)</u>	85.8 (20.8), <u>151.5 (28.2)</u>	122.8 (43.6)	84.5 (38.1)
C12	98.8 (31.5), <u>170.7 (36.4)</u>	85.5 (43.6), <u>143.8 (39.0)</u>	132.5 (63.6)	44.8(18.0), <u>100.9(31.4)</u>

Ag(I) (ref. 26)	NO ₃	TFA	FSA	Tf_2N
C6	44	11	-87 (g)	-75 (g)
C2C6	-54 (g)	-7 (g)	-78 (g)	-72 (g)
C8	48	30	26	-10 (g)
C12	59	45	37	38
H ⁺ (ref. 25)			A	Tf_2N
C6			Q	16
C2C6			0-	-70 (g)
C8			G	18
C12		0	0	30
^a Underlined temperatures are identified as melting points from solid-to-liquid using PM. (see text)				

^b Glass transition temperatures.



Fig. 3. Thermo-gravimetric curves for the typical systems of the $[Ni(alkyl-en)_2X_2]$ complexes depending on the counter anions (X = NO₃, TFA, FSA, and Tf₂N) for (a) alkyl = hexyl, and (b) alkyl = 2-ethylhexyl.



Fig. 4. Melting points or glass transition temperatures (T_{MP}) vs. counter anions for each bis(alkyl-en) metal(II) complex. alkyl : C6 = hexyl, C2C6 = 2-ethylhexyl, C8 = octyl, C12 = dodecyl.

For the dipositive alkyl-en complexes, the effect of molecular structures on the phase transition is more irregular compared to that for the monopositive alkyl-en silver(I) complexes and PILs, since several intermolecular interactions act on the phase behavior synergistically due to the stronger ionic interactions. We can, however, identify several significant trends based on the principle of intermolecular interactions. The results are interpreted in terms of the two molecular components, i.e., the anion and the alkyl-chain of the cation, for each metal(II) complex. Figures 4 and 5 illustrate the respective effects on the phase transition temperatures (T_{MP}) for each metal complex.

(1) <u>Anion effects</u> (Fig. 4): The abscissa in Fig. 4 is taken as an approximate indicator of the anion size.

(a) Zn(II) complexes. (Fig. 4(a)) Among the three metal(II) complexes, the zinc(II) complexes show the clearest trends concerning the anion effect, i.e., the melting points decreases with an increase in anion size and decrease in T_{MP} is significant for the weakly coordinating FSA and Tf₂N anions. A similar trend is seen in the silver(I) alkyl-en complexes as previously reported (Table 1). It is remarkable that, despite the dipositive charge, the Zn(II)-C6(FSA), C6(Tf₂N), C2C6(FSA), C2C6(Tf₂N), and C8(Tf₂N) complexes form RTILs as also observed in the corresponding Ag(I) complexes. X-ray crystallographic analysis of the Zn(II)-C8(NO₃) complex revealed that the NO₃ anions directly coordinate to the zinc(II) center.[27] Conversely, although X-ray structural study has not been performed for the FSA and Tf₂N complexes, the FSA and Tf₂N anions most likely do not coordinate to the zinc(II) center.

Here, comparing the Zn(II) system to the Ni(II) system is useful, in that, as described above, FSA and Tf₂N anions do not directly coordinate to the nickel(II) ion while the NO₃ and TFA anions coordinate to the nickel(II) ion to form octahedral complexes in the neat states. Therefore, the large difference in the melting points between the NO₃ and TFA group and the FSA and Tf₂N group for the zinc(II) complexes can be attributed to the counter anions directly coordinating to the zinc(II) ion or not. Such significantly lower melting points for shorter alkyl-chained complexes have also been observed in the Ag(I) complexes coupled with FSA and Tf₂N anions. Thus, the structural bulkiness of the anion seems more effective on reducing melting points when coupled with shorter alkyl-chained cations (Table 1)[26]. Low melting points for tetrahedral and bulky zinc(II) complexes are, furthermore, similarly observed for imidazolium zinc(II) complexes, as reported by Lin *et al.*[3, 4]. In the present study, the significantly low melting points for the zinc(II) complexes are achieved by the combination of bulky tetrahedral alkyl-en ligands and weakly coordinating bulky anions. A similar trend has been reported for imidazolium nickel(II) and cobalt(II) complexes. [20, 23]

A remarkable difference between the Ag(I) and Zn(II) ions is observed for the $C2C6(NO_3)$ complexes, where the zinc(II) complex has a higher melting point than that of the other alkyl(NO₃) complexes while the Ag(I) complex has a remarkably low melting point. For the nickel(II) $C2C6(NO_3)$ complex, a similarly high melting point to that of the zinc(II) complex is observed, as discussed below.

(b) *Ni(II) complex*. Figure 4(b) shows that, except for the two NO₃ complexes (C6 and C12), the melting point decreases with an increase in anion size. As described above, the geometrical structure of the nickel(II) complex in the neat state is clearly dependent on the counter anion, with the NO₃ and TFA salts being octahedral and the FSA and Tf₂N salts being square planar. However, Fig. 4(b) shows that, even for the FSA and Tf₂N complexes, the decrease in melting point is not so large as that observed for the zinc(II) FSA and Tf₂N complexes (Fig. 4(a)). This difference between the nickel(II) and zinc(II) complexes indicates that, although the FSA and Tf₂N counter anions are in the outer-sphere of the nickel(II) complexes as well, these anions should be located on the *z*-axis of the square-planar complex, and that the distance between the nickel(II) ion and the anions should not be as large as those for the non-coordinating anions in the tetrahedral bis(alkyl-en) zinc(II) complexes. From this viewpoint, we can also understand the appreciably lower glass transition points (– 7 and – 37 °C, respectively. See Table 1) of the

tris(C6 and C8) nickel(II) Tf_2N anion complexes. The remarkable difference between the tris and bis complexes is attributable to the significantly larger distance between the nickel(II) ion and the counter anion in the tris complex.

The inverse relationship concerning the anion size between the NO₃ and TFA salts in the C6 and C12 complexes is remarkable and can be explained in terms of the stronger interaction for the nickel(II) ion and the TFA anion rather than that for the NO₃ anion, which is also observed in solution (as discussed in the next section). However, the modes of interaction for the NO₃ and TFA anions with the metal(II) ion seem to be somewhat complicated, as evidenced by the double endothermic peaks that are observed for some complexes (Fig. 2 and Table 1). Furthermore, it is not clear why the inverse relationship occurs in the two unique nickel(II) complexes. Although CHN elemental analysis indicates poorer purities for the C12(NO₃) and C12(FSA) complexes, only the C12(NO₃) complex shows irregularly lower melting points. (Fig. 4b)

Furthermore, it is possible that the higher melting points of the C12 complexes containing the FSA and Tf_2N counter anions than that for the NO₃ salt may be due to the stronger van der Waals interactions of the longer alkyl chain with the larger anion.

The higher melting point of the C2C6(NO₃) complex is also seen for the zinc(II) complex. In the divalent complexes, the bulkiness of the ethyl-branch is not always sufficient to lower the melting point but rather in some cases enhances the intermolecular (van der Waals) interactions. This trend is in contrast to that observed in the mono positive Ag(I) and proton analogs (Table 1) and can be interpreted in terms of the interaction mode, where the van der Waals interactions due to the ethyl branch may become synergistically effective on the interactions in combination with the stronger electrostatic interaction. The Ni(II)C2C6(NO₃) complex is unique: although it has a significantly higher melting point (Fig. 4(b)), it is gradually decomposed at a lower temperature than the other complexes. (Fig. 3(b))

(c) Cu(II) complex. An increase in the anion size tends to decrease in the melting point (except for the C2C6(Tf₂N) complex) as demonstrated in Fig. 4(c). This trend indicates that the electrostatic interaction dominates the anion size effect. The increase in the melting point of the C2C6(Tf₂N) complex can be attributed to the van der Waals interactions between the bulky cation and the bulky anion. It is notable that the C2C6(NO₃) complex shows a different trend to those of the other metal(II) alkyl-chain complexes, i.e., the

ethyl branch lowers the melting point. This trend is similarly observed in the monopositive Ag(I) complex and PIL (Table 1), where it is suggested that the ethyl branch may cause a steric hindrance for the intermolecular interactions. However, it is not clear why there is a difference between the copper(II) complexes and the other divalent metal complexes. The ambivalent factors (steric hindrance and the van der Waals attraction force) of the ethyl branch may affect the melting point in a complex manner in combination with the counter anions and molecular structures.



Fig. 5. Melting point or glass transition temperature (T_{MP}) *vs*. alkyl-chain length of the ligand in each bis(alkyl-en) metal(II) complex with four different counter anions.

<u>Alkyl chain length of the cations</u> Figure 5 shows the dependence of phase transition temperatures (T_{MP}) on alkyl chain length for each metal complex. The effect of the alkyl chain on the molecular interaction and on the melting point becomes more irregular in comparison with those for the alkyl-en monopositive silver(I)-ILs, PILs, and common AILs (Table 1 [25, 26, 39-41]) where an increase in T_{MP} with an increase in the alkyl-chain length (from C6 to C12) is observed, which is basically attributable to an increase in the van der Waals interaction between the cationic units. Conversely, if the electrostatic force between the cation and the anion rather the van der Waals interactions dominates the overall interaction, the phase transition temperatures *vs*. alkyl chain length plot present a negative slope due to a decrease in the Coulombic force [40,41]. This trend can also be interpreted in terms of a decrease in the entropic effect, i.e., as the ordering of molecular assemblies increases with increasing alkyl-chain length, the stability of the molecular assemblies

decreases, leading to a lower melting point [39]. Figure 5 demonstrates that, although the two opposite driving forces affect T_{MP} in a complex manner, there is a rough trend for each metal(II) system, i.e., the lower melting complexes comprising FSA and Tf₂N counter anions tend to have positive slopes while the higher melting complexes comprising the smaller NO₃ and TFA counter anions tend to have a negative slope. From the standpoint of the intermolecular interactions, this trend is reasonable since the former system tends to be van der Waals interaction-driven and the latter system tends to be electrostatic interaction-driven.

The other outstanding feature concerning the alkyl chain effect is observed for the C2C6 derivatives as described above.

Interactions of the NO₃, TFA, FSA, and Tf_2N anions with the nickel(II) ion and the resultant solvation behavior of the nickel(II) complexes in organic solvents

As described above, there are two structures for the neat bis(alkyl-en) nickel(II) complexes depending on the counter anions. They can be unambiguously distinguished by their visible absorption spectra, so we can easily compare the coordination modes between the neat state and the solution state. Solvatochromism of $[Ni(acac)(tmen)]^+$ (acac = acetylacetonato, tmen = tetramethylethylenediamine) with the weakly coordinating counter anions CIO_4^- or BF_4^- has been studied in various solvents, revealing that this nickel(II) complex is useful as a good donor number (*DN*) probe for common molecular solvents.[34,35,42,43] In those studies, in order to focus on the solvation of the nickel(II) complex, the counter anions chosen coordinate weakly to the nickel(II) ion. In the present study, bis(alkyl(C6, C2C6, C8, and C12)-en) nickel(II) complexes with the anions (NO₃, TFA, FSA, and Tf₂N) were dissolved in various organic solvents as listed in the experimental section (or below). Their visible absorption spectra were measured and the results correlate with solvation behavior as well as in terms of the counter-anion binding to the cationic complex except for several poorly soluble complexes. Several of the absorption spectra for the octahedral [Ni(alkyl-en)₂X₂] complexes (where X is the monodentate anion or solvent) have been previously studied [30] on the basis of the established absorption spectra for nickel(II) complexes. [34,35,44-48] These results are useful for this study, whereas the discrimination between the *cis* and *trans* geometries using the first absorption peak (960 nm) is not discussed

here due to ambiguities. However, there is a significant difference in the absorption spectra of $[Ni(alkyl-en)_2X_2]$ for $X = NO_3^-$, TFA⁻, and molecular solvent for the first absorption peak (λ_{max} is around 960 nm) as shown in Fig. 6, which shows the spectrum of the hexyl complex as a typical example. These absorption spectra depend significantly on the counter anions and solvents while being almost independent of the alkyl moieties of the ligands. In the two anion-coordinating systems (NO₃ and TFA) the intensity of the first absorption peak is significantly smaller than that of the solvated systems and also present splitting, as exemplified in Fig. 1 and Figs. 6(a) and 6(b) (in DCM).



Fig. 6. Visible absorption spectra of the $[Ni(hexen)_2]X_2$ complexes in solution for each counter anion (X = Anion) depending on the solvents.

Conversely, for the second absorption peak (λ_{max} is around 570 nm, $\varepsilon_{max} = 6-7$ kg cm⁻¹mol⁻¹) the peak intensities for [Ni(solv)₂(alkyl-en)₂]²⁺ and [NiX₂(alkyl-en)₂] are comparable (X = NO₃ or TFA) (Figs. 6(a) and (b), and ref. 30). Therefore, in the following discussion, we focus on the relative intensity and shape of the first absorption peak compared to those for the neat state or in DCM (for the TFA salt) and in DCM (for the NO₃ salt), and use them as a rough indicator for the extent of solvation of the [NiX₂(alkyl-en)₂] complex (where X = NO₃ or TFA), i.e., the [Ni(solv)₂(alkyl-en)₂]²⁺/[NiX₂(alkyl-en)₂] ratio. For the FSA and Tf₂N salts, on the other hand, as the neat state shows no coordination of counter anions to form the square-planar complex (the spectra of the Tf₂N salt for the neat states and in DCM are shown in Fig. 1 and in Fig. 6(c), respectively), the extent of solvation can be easily monitored by using the peak height of the single large peak for $\varepsilon_{max} = 70$ kg cm⁻¹mol⁻¹ at $\lambda_{max} = 460$ nm, where the absorption peak becomes much weaker upon solvation to form an

octahedral complex. (as exemplified in Figs. 6(a)-(c), in comparison with Fig. 6(c) (DCM))

As described in the experimental section, all the measurements except for some systems in DCM, Et₂O, and acetone were performed at 0.05 mol kg⁻¹. The absorption spectra are largely dependent on the relative dielectric constant (ε_r) as well as on the *DN* of the solvents. The two parameters (ε_r and *DN*) for each solvent are as follows (in the order of increasing dielectric constant (ε_r)). Et₂O: $\varepsilon_r = 4.3$, *DN* = 19.2; DCM: $\varepsilon_r = 8.9$, *DN* = 1; acetone: $\varepsilon_r = 20.7$, *DN* = 17; EtOH: $\varepsilon_r = 24.5$, *DN* = 20; MeOH: $\varepsilon_r = 32.7$, *DN* = 19; MeCN: $\varepsilon_r = 36.0$, *DN* = 14.1; DMF: $\varepsilon_r = 36.7$, *DN* = 26.6; DMSO: $\varepsilon_r = 46.7$, *DN* = 29.8. [49, 50] The results allowed the solvents to be categorized into the following five groups (a – e) based on the spectral solvation modes for the nickel(II) complexes.

- (a) DCM: This has the smallest *DN* and the second lowest ε_r among the solvents used here resulting in the lowest solvation. Among the nickel(II) complexes, C6(NO₃) (0.01 mol kg⁻¹), C6(FSA) (2 mmol kg⁻¹), and C8(FSA) (2 mmol kg⁻¹) were measured at lower concentrations due to solubility limitations. The other complexes were measured at 0.05 mol kg⁻¹. For the alkyl-en complexes, the salts show very similar absorption spectra to that in the neat state as shown in Figs. 1 and 6. Therefore, direct solvation of the nickel(II) ion hardly occurs. Thus, the spectra of the nickel(II) complexes in DCM can be taken as representative of zero solvation.
- (b) Et₂O: Although the *DN* of this solvent is larger than those of MeCN and acetone and is comparable to that of MeOH, its ε_r value is the smallest among the solvents used here. Thus, the counter anions (either inner sphere or outer sphere) hardly dissociate from the nickel(II) ion in this solvent. As a result, the NO₃ and FSA salts except for C2C6(FSA) do not dissolve in this solvent, whereas the TFA and Tf₂N salts are slightly soluble ($\approx 1-5$ mmol kg⁻¹). This solubility difference may be due to whether a hydrophobic CF₃ or ethyl branch is present or not. For the TFA salts, the absorption spectra (measured at 1–5 mmol kg⁻¹) indicate coordination of the TFA anion to form the [Ni(TFA)₂(alkyl-en)₂] complex, despite the low concentrations, whereas for all the Tf₂N complexes and the C2C6(FSA) complex the major component has square-planar geometry ($\varepsilon_{max} = 35-40$ kg cm⁻¹mol⁻¹ at $\lambda_{max} = 460$ nm). However, the significantly smaller

 ε_{max} values than those in DCM ($\varepsilon_{\text{max}} = 70-80 \text{ kg cm}^{-1} \text{mol}^{-1}$ at $\lambda_{\text{max}} = 460 \text{ nm}$) suggest that Et₂O may slightly coordinate to the nickel(II) ion and thus the ratio of the square planar complex is less than those for the neat state and in DCM.

(c) acetone : As both the ε_{r} and *DN* values for acetone are intermediate among the solvents used here, the NO₃, FSA, and Tf₂N salts show characteristic behaviors in this solvent. The TFA salt, on the other hand, present a similar absorption spectrum as that in DCM or Et₂O, indicating that most of the TFA anions still coordinate to the nickel(II) ion in solution. The spectrum of the NO₃ complex is different from that in DCM and is like that in MeCN. (Fig. 6a) The first absorption peak is significantly less intense than the second (at around 570 nm). This feature is different from those of the solvated [Ni(solv)₂(alkyl-en)₂]²⁺ in polar solvents (group(e), (Figs. 6(a–c) for DMF)) and of the FSA and Tf₂N salts in this solvent at infinite time, as shown in Fig. 7, where the intensity of the first band is larger than that of the second. This difference in spectral shape indicates that the NO₃ counter anion is partially dissociated from the nickel(II) ion and replaced by acetone.

It is a particularly interesting phenomenon that when the FSA and TF_2N salts are dissolved in this solvent, the color gradually changed from orange to blue. An example of the change in the absorption spectra is shown in Fig. 7.



Fig. 7. Typical spectral change of the square planar $[Ni(octen)_2]^{2+}$ complex in acetone, where counter anion = FSA⁻. The concentration is ca. 0.03 mol kg⁻¹ and at 20 °C.

The spectrum at 15h (approximating infinite time) is similar to that of $[Ni(solv)_2(alkyl-en)_2]^{2+}$ (where solv is MeOH, EtOH [30], or DMF(Fig. 6)). (Only the C6(Tf₂N) complex exhibits the presence of slight amount of the residual square planar complex whose absorption appears at 460 nm.) This change clearly indicates that the square planar bis(alkyl-en) complex is gradually solvated to form the octahedral $[Ni(solv)_2(alkyl-en)_2]^{2+}$. The absorbance at 460 nm was monitored at 20 °C and the $-ln(A_t - A_{\infty})/(A_0 - A_{\infty})$ vs. *t* plot, where A_t , A_{∞} , and A_0 are the absorbances at time *t*, an infinite time, and time zero, respectively, presents a straight line for each system as illustrated in Fig. S-1. The linearity indicates that the reaction is nearly first-order. Accordingly, the first-order rate constant *k* [h⁻¹] was determined for each system and the results are listed in Table 2. Note that the (dod)(FSA)₂ system was not included here due to its poor elemental analysis result.

Table 2. First-order rate constants (*k*) for the acetone solvation of the square planar bis (alkyl-en)Ni(II) complexes.

	k/h^{-1}	
alkyl / anion =	FSA ⁻	$\mathrm{Tf}_2\mathrm{N}^-$
C6	0.37	1.31
C2C6	0.33	1.29
C8	0.29	1.22
C12	n/a	1.38

Table 2 reveals a trend concerning the anion effect, i.e., the higher reaction rate for the Tf_2N anion system than that for the FSA system. As both the FSA and Tf_2N anions do not coordinate to the nickel(II) ion in the inner sphere, these anions may have an obstructing effect on the solvation reaction for the $[Ni(alkyl-en)_2]^{2+}A^-$ outer-sphere complex. This is consistent with the melting point result, because the larger anion experiences a smaller electrostatic interaction with the nickel(II) ion and may thus obstruct

solvation of the nickel(II) ion less. On the other hand, the alkyl chain moiety appears to have no effect on the kinetic stability of the ion-pair.

(d) MeCN : As this solvent has a larger ε_r value than acetone, the counter anion is more easily dissociated from the nickel(II) ion, whereas the solvation will be weaker than that by acetone due to the smaller *DN*. Typical spectra for the hexyl complex in this solvent are shown in Fig. 6(a–c), demonstrating that the spectra are largely independent of the alkyl moiety.

For the nitrate (Fig. 6a), the first absorption peak is significantly larger than that in DCM and does not double. This feature is not observed for the TFA system (Fig. 6b), where the spectra in MeCN and in DCM are similar. The difference between the NO₃ and TFA systems indicates that the TFA anion may more strongly coordinate to the nickel(II) ion than the NO₃ anion does. This is consistent with the results observed for acetone.

For the FSA and Tf₂N salts, no time dependency of the spectra is observed and their shapes (Fig. 6c, Fig. S2) are close to that at infinite time (15h) in acctone or in solvents having larger *DN* values, such as MeOH, EtOH, DMF (Fig. 6(c)) and DMSO. The nickel(II) complex is kinetically more easily solvated by MeCN to form [Ni(solv)₂(alkyl-en)₂]²⁺ than in the less polar acctone (smaller c_i). However, we can see that the second absorption peak (at around 520 nm) is broader and shows a blue shift in this solvent compared to those for the five polar solvents above having larger *DN* values (exemplified for the DMF system in Fig. 6(c)). This difference indicates that solvation by MeCN of the nickel(II) ion may be weaker than those in the solvents having larger *DN* values at equilibrium and that the spectrum contains a contribution by the square-planar complex. As shown in Fig. S2, the shape of the spectrum somewhat depends on the alkyl-chain and the hexyl complex (also shown in Fig. 6(c)) exhibits the largest blue shift of the second absorption peak. Here, it should be noted that although acetone coordinates to the nickel(II) ion through the nitrogen atom, whether the coordination atom is nitrogen or oxygen does not significantly affect the spectral shape. For example, [Ni(alkyl-en)₃]²⁺ presents a very similar spectrum to that of the [Ni(solv)₂(alkyl-en)₂]²⁺ complex where 'solv' is the (e) group solvent, as previous reported [30].

(e) EtOH, MeOH, DMF, DMSO: These solvents with larger ε_r and *DN* values all present similar nickel(II) ion solvation modes. Spectra typical of this group are shown in Fig. 6(a–c) for the hexyl complex in DMF. A significant difference between the (e) group and the (a)–(d) groups is observed for the first absorption peak (980 nm) of the TFA salt. (Fig. 6(b)) The intensity of this peak for the (e) group solvents is comparable to (EtOH) or higher (other solvents) than that of the second peak (570 nm). This result indicates that, in these solutions, the TFA anion is largely dissociated from the nickel(II) ion and replaced by the solvents. The first peak height is slightly smaller than that of the second peak in EtOH, having the smallest ε_r in this group, which indicates that some TFA anions are still coordinated to the nickel(II) ion in EtOH. Comparing the results for the EtOH (smaller ε_r but slightly larger *DN*) and MeOH systems suggests that ε_r governs the coordination of the TFA anion rather than *DN*. A similarly dominant effect of ε_r over *DN* on the solvation of the FSA and Tf₂N salts is revealed upon comparing the MeCN and acetone solvents from the kinetic viewpoint, as described above.

Although most of the complexes with different counter anions are solvated to form Ni(solv)₂(alkyl-en)₂ in this group of solvents, a small peak at 470 nm, which is attributable to the square-planar configuration, is presented by some of the FSA and Tf₂N complexes (up-arrow in Fig. 6(c) and Fig. S3). This small peak is observed in the solvents of this group as well as in group (c) even at nearly infinite time (15h, Fig.7). The magnitude of this peak depends on the alkyl moiety of the metal complexes in the order, C6 > C8 >> C12 > C2C6, as shown in Fig. S3. This may be the reverse of the order of solvation. The magnitude of this small peak is larger in MeOH and EtOH than in DMF and DMSO. This trend indicates poorer solvation in the former two solvents, which is consistent with the solvent parameters (i.e., lower ε_{r} and *DN* values).

As the spectra of $Ni(DMF)_6^{2+}$ and $Ni(DMSO)_6^{2+}$ are significantly different from the present spectra in DMF and DMSO, respectively, [51,52] most of the alkyl-en ligands remain coordinated to the nickel(II) ion.

Conclusions

The solid-to-liquid transition temperatures for dipositive bis(alkyl-en)metal(II) (metal = nickel, copper,

and zinc) and tris(alkyl-en)nickel(II) complexes fall in the wide range of -44 to 200 °C depending on the molecular moieties. Some bis(alkyl-en)zinc(II) and tris(alkyl-en)nickel(II) complexes are liquids at room temperature despite the dipositive charge. The distance between the metal ion and the counter anion essentially governs the transition temperatures in these dipositive complexes. The extent of solvation of the bis(alkyl-en)nickel(II) complexes is dominated not only by the strength of the counter-anion binding to the nickel(II) ion but also by the polarity and the *DN* of the solvents. As a result, nickel(II) complexes containing the FSA or Tf₂N anion show a time-dependent solvation in acetone.

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Notes

The authors declare no competing financial interest.

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Synopsis: The solid-to-liquid transition temperatures (T_{MP}) for dipositive analogous bis(alkyl-en)metal(II) (metal = nickel, copper, and zinc) and tris(alkyl-en)nickel(II) complexes fall in a wide range of -50 to 250 °C depending on the molecular structures.



Highlights:

- Some divalent zinc(II) and nickel(II) complexes form room temperature ionic liquids •
- Analogous divalent complexes take a wide range of melting temperatures •
- Some rules were found concerning the formation of ionic liquids of divalent complexes •
- Alkylethylenediamine nickel(II) complexes show time-dependent acetone solvation •

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