Studies on Mixed Chelates. XI. Syntheses and Comparative Study of a New Series of Mixed Nickel(II) Chelates with Halide and Pseudohalide Ligands1)

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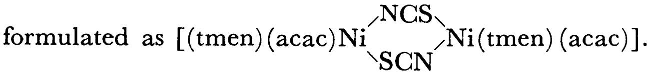
A new series of mixed chelates of nickel(II), Ni(diam) (β-dik)X·nH$_2$O (X=halide or pseudohalide anion, n=0—2), was prepared, and their structures in solid state and in various organic solvents were studied. Most of the chelates were octahedral, many of them being obtained as mono- or dihydrates. When the solid chelates were heated at reduced pressure, the main reactions were dimerization (X=pseudohalide), dehydration (X=I), and disproportionation (X=Br or Cl). On the other hand, the chelates showed complicated structural changes in organic solvents, some of which were not observed in solids, depending upon the nature of X and the polar characteristics of the solvent.

We previously reported that the mixed nickel(II) chelate, Ni(tmen)(acac)NCS·nH$_2$O(n=0 or 1)† shows interesting structural changes in various organic solutions.2) In a solvent of poor coordination ability(1,2-dichloroethane=DCE), it exists as a square pyramidal 5-coordinate complex [Ni(tmen)(acac)NCS] in a very dilute solution. However, with increase in concentration it forms a 6-coordinate species, probably a dimer formulated as  $[(\text{tmen})(\text{acac})\text{Ni}\overset{\text{NCS}}{\underset{\text{SCN}}{\rightleftarrows}}\text{Ni}(\text{tmen})(\text{acac})]$. In nitromethane, (=NM), ionic dissociation of these species leads to the formation of a small amount of square planar species [Ni(tmen)(acac)]$^+$. In more polar solvents, 6-coordinate solvated complexes such as [Ni(tmen)(acac)(Solv.)$_2$]$^+$ or [Ni(tmen)(acac)NCS(Solv.)] predominate.

A report was given on two related chelates, Ni(tmen)(acac) X·2H$_2$O(X=Br$^-$ or I$^-$).1) In this same study, we found that the bromide is thermally unstable, easily undergoing disproportionation by slight heating into [Ni(tmen)Br$_2$] and [Ni(tmen)(acac)$_2$], *i.e.* a tetrahedral 4-coordinate complex and an octahedral one. With the iodide, however, such disproportionation occurs only slightly, its main part being converted into [Ni(tmen)(acac)]I with the square planar cation by heating. When dissolved in DCE, both the bromide and iodide undergo disproportionation remarkably even at room temperature,†† but here again the ionization into [Ni(tmen)(acac)]$^+$ and X is favored in nitromethane.

We also prepared related complexes with other halide (Cl$^-$) and pseudohalide (NCO$^-$, NCSe$^-$, and N$_3^-$) ions. A comparative study of all these complexes is given in this paper.

Experimental

Preparation of the New Complexes. The general method of preparation adopted is shown in Scheme 1.

i) NCS-complexes: In addition to the complex Ni(tmen)(acac)NCS·nH$_2$O(n=0 or 1) reported,2) three new complexes Ni(tmen)(bza)NCS·H$_2$O, Ni(tmen)(dpm)NCS, and Ni(Et$_3$en)(acac)NCS·H$_2$O were prepared. In the course of preparation, crystals of [Ni(diam)(β-dik)$_2$] and [Ni(tmen)(NCS)$_2$] sometimes appeared first, obstructing isolation of the desired product. In general, the best yield could be obtained when the solution was concentrated at a relatively high temperature and quickly filtered after being cooled down to room temperature.

ii) NCSe-complex: Only Ni(tmen)(acac)NCSe·H$_2$O could be obtained. All operations had to be carried out under cooling: even at 25 °C, NCSe$^-$ ion tends to decompose, separating out red selenium. The decomposition also occurs when the isolated complex is heated gently in solid state or in solution, so that it must be kept in a freezer.

iii) NCO- and N$_3$-complexes: These complexes, both with tmen and acac, were hard to obtain in pure state; the products obtained by the general method were always impure, containing much ClO$_4^-$. Very small amounts of reasonably pure complexes were obtained when the filtrates of these trials were kept in a refrigerator for several months.

iv) Halide Complexes: In addition to the complexes Ni(tmen)(acac)X·2H$_2$O(X=Br$^-$ or I$^-$),1) Ni(tmen)(acac)Cl·H$_2$O, Ni(tmen)(bza) I·nH$_2$O(n=1 or 2), and Ni(tmen)(dpm)I·2H$_2$O were obtained. The two hydrates of the bza complex were obtained depending on the solvent for recrystallization, *i.e.* the dihydrate from methanol and monohydrate from an acetone-DCE mixture. The dpm complex loses its water easily in a desiccator or in dry open air, yielding a reddish orange, diamagnetic anhydrous chelate.

Chemicals. "Extra Pure" reagents and solvents were used. Nitromethane, DCE, acetone, and DMSO were distilled after being dried with Wako synthetic zeolite A-3.

Physical Measurements. Electronic spectra of solutions were obtained with Shimadzu MP-5000 and Hitachi 340 spectrophotometers, using quartz cells of 5 mm to 5 cm. Solid reflectance spectra were recorded with the latter instrument with a visible and near IR integrating sphere attachment, using BaSO$_4$ as a reference. Other instruments used in IR spectral, magnetic, and conductmetric studies were the same as those reported.2)

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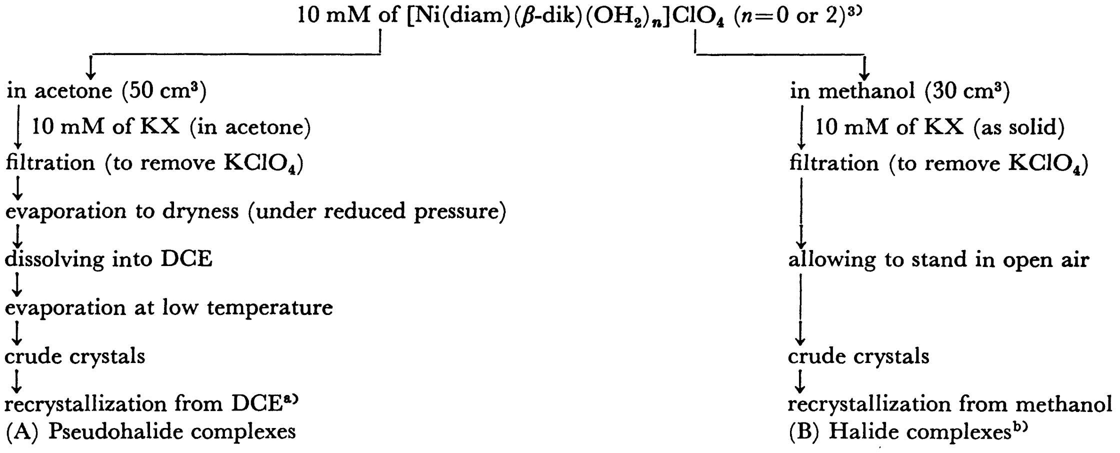
† Abbreviations: diam=N-alkylated ethylenediamine such as N,N,N',N'-tetramethylethylenediamine(tmen) or N,N,N'-triethylethylenediamine(Et$_3$en); β-dik=β-diketonate ion such as acetylacetonate(acac), benzoylacetonate(bza), or dipivaloylmethanate (dpm); X=halide or pseudohalide ions such as Cl$^-$, Br$^-$, I$^-$, NCS$^-$, NCSe$^-$, NCO$^-$, or N$_3^-$.

†† This view is different from that reported;1) for detail, see text.



Scheme 1. Preparation of the complexes, Ni(diam) (β-dik)X·nH_2O (n=0, 1, or 2)

a) When X=NCS^- and diam=Et_3en, acetone or methanol should be used instead of DCE, and the solution must be kept in a refrigerator. b) When X=Cl^-, this method was found to be inadequate, so that the complex was obtained by direct reaction of $NiCl_2 \cdot 6H_2O$, tmen and acac in methanol.

Results and Discussion

The analytical data of the new mixed complexes together with those reported are summarized in Table 1, and their magnetic moments and $\tilde{\nu}_{max}$ values of their reflectance spectra in Table 2. All the complexes are blue to green and in high spin state (μ_{eff}: 3.0—3.2 BM) except XII which is reddish orange and diamagnetic (*cf.* Experimental). These results and the spectral evidence given below lead to the formulation of the complexes as shown in Table 2.

Table 1. Analytical data of complexes[a)]

No.-n[b)]	Complex	C/%	H/%	N/%
I-1	Ni(tmen)(acac)(NCS)(H_2O)	40.48 (41.16)	7.06 (7.21)	12.11 (12.00)
II-1	Ni(tmen)(acac)(NCSe)(H_2O)	36.25 (36.30)	6.31 (6.35)	10.64 (10.58)
III	Ni(tmen)(acac)(NCO)	44.91 (45 61)	7.24 (7 34)	13.01 (13 30)
IV	Ni(tmen)(acac)(N_3)	41.05 (41.81)	7.23 (7.34)	22.11 (22.16)
V-1	Ni(tmen)(bza)(NCS)(H_2O)	48.95 (49.54)	6.54 (6.60)	10.09 (10.19)
VI	Ni(tmen)(dpm)(NCS)	51.23 (51.94)	8.42 (8.47)	10 08 (10.09)
VII-1	Ni(Et_3en)(acac)(NCS)(H_2O)	45.29 (44.47)	7.74 (7.73)	11.43 (11.11)
VIII-2	Ni(tmen)(acac)(I)$(H_2O)_2$	30.24 (30.24)	6.20 (6.23)	6.48 (6.41)
IX-2	Ni(tmen)(acac)(Br)$(H_2O)_2$	33.92 (33.88)	6.90 (6.98)	7.16 (7.18)
X-1	Ni(tmen)(acac)(Cl)(H_2O)	39.94 (40.34)	7.61 (7.69)	8.55 (8.56)
XI-2	Ni(tmen)(bza)(I)$(H_2O)_2$	38.50 (38.51)	5.95 (5.86)	5.57 (5.61)
XI-1	Ni(tmen)(bza)(I)(H_2O)	39.82 (39.95)	5.66 (5.66)	5.88 (5.82)
XII-2	Ni(tmen)(dpm)(I)$(H_2O)_2$	40.77 (39.18)	7.84 (7.54)	5.22 (5.38)
XII	Ni(tmen)(dpm)(I)	41.03 (42 09)	7.16 (7 22)	5.73 (5.77)

a) Calculated values are in parentheses. b) Number of water molecules. 0 is omitted for n=0.

(A) Pseudohalide Complexes. *(i) Solid Structures*: All the pseudohalide complexes (Table 2, I-1 to VII-1) show two d-d bands in their reflectance spectra which can be ascribed to $\tilde{\nu}_1(^3T_{2g} \leftarrow {}^3A_{2g})$ and $\tilde{\nu}_2(^3T_{1g} \leftarrow {}^3A_{2g})$ of octahedral complexes of Ni(II).

As in the case of I-1 formulated formerly as [Ni(tmen)-(acac)(H_2O)NCS], the complexes II-1, V-1, and VII-1 can be formulated as [Ni(tmen)(β-dik)(H_2O)NCX]; the IR data (Table 3) which indicate the N-coordination of NCS^- or $NCSe^-$ in the complexes also support these formulas. The water molecules are only loosely held, and driven off by slight heating or mere dissolution in

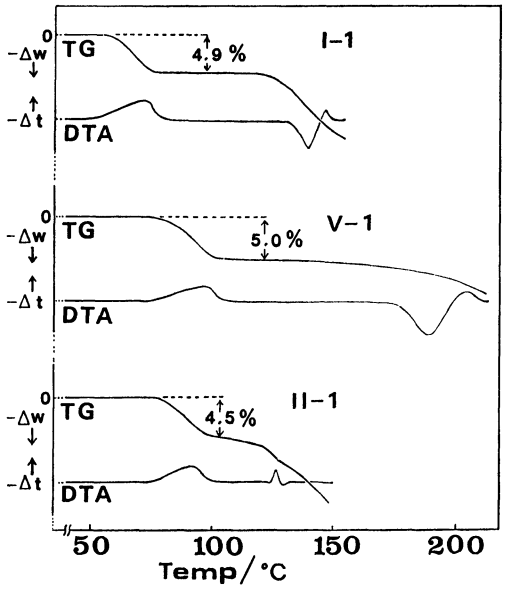


Fig. 1. TG and DTA data of three monohydrated complexes; I-1, V-1, and II-1. Numbers (%) on TG curves show the observed mass losses; the theoretical values are 5.1%, 4.4%, and 4.5%, respectively.

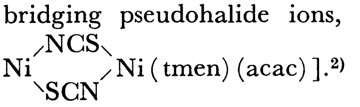
TABLE 2. MAGNETIC MOMENTS AND REFLECTANCE SPECTRA OF SOLID COMPLEXES

No.-*n*	Complex	μ_{eff}/BM	$\tilde{\nu}_{max}/10^3$ cm^{-1}	
I-1	$[Ni(tmen)(acac)(H_2O)(NCS)]$	3.16(19 °C)	9.64	15.80
I	$[Ni(tmen)(acac)(NCS)]_2$	3.14(18 °C)	9.15	16.05
II-1	$[Ni(tmen)(acac)(H_2O)(NCSe)]$	3.20(18 °C)	9.70	15.85
III	$[Ni(tmen)(acac)(NCO)]_2$	3.20(18 °C)	—	—
IV	$[Ni(tmen)(acac)(N_3)]_2$	3.02(18 °C)	—	—
V-1	$[Ni(tmen)(bza)(H_2O)(NCS)]$	3.21(21 °C)	9.42	16.18
VI	$[Ni(tmen)(dpm)(NCS)]_2$	3.09(17 °C)	8.77	16.05
VII-1	$[Ni(Et_3en)(acac)(H_2O)(NCS)]$	3.14(17 °C)	9.63	16.00
VIII-2	$[Ni(tmen)(acac)(H_2O)_2]I$	3.21(23 °C)	9.30	15.87
IX-2	$[Ni(tmen)(acac)(H_2O)_2]Br$	3.21(22 °C)	9.27	15.92
X-1	$[Ni(tmen)(acac)(H_2O)Cl]$	3.29(18 °C)	8.90	15.40
XI-2	$[Ni(tmen)(bza)(H_2O)_2]I$	3.18(18 °C)	9.60	16.03
XI-1	$[Ni(tmen)(bza)(H_2O)I]$	3.18(18 °C)	8.45	15.55
XII-2	$[Ni(tmen)(dpm)(H_2O)_2]I$	3.08(19 °C)	9.53	15.85
XII	$[Ni(tmen)(dpm)]I$	diamagnetic	20.50	

TABLE 3. IR SPECTRA OF COMPLEXES (ν, δ/cm^{-1})

No.-*n*	Complex	ν(O-H)	δ(OH)	ν(CN)[a]	ν(CS)[b]	ν(C=C) ν(C=O)	
I-1	$[Ni(tmen)(acac)(H_2O)(NCS)]$	3475—3200	1655	2100[c]	772	1595	1523
I	$[Ni(tmen)(acac)(NCS)]_2$	—	—	2150	760	1600	1518
II-1	$[Ni(tmen)(acac)(H_2O)(NCSe)]$	3475—3200	1652	2105	625	1593	1520
III	$[Ni(tmen)(acac)(NCO)]_2$	—	—	2230 2200	1305	1610	1515
IV	$[Ni(tmen)(acac)(N_3)]_2$	—	—	2120	1292	1605	1518
V-1	$[Ni(tmen)(bza)(H_2O)(NCS)]$	3140	1660	2090	760	—[d]	—[d]
VI	$[Ni(tmen)(dpm)(NCS)]_2$	—	—	2140	—[d]	—[d]	—[d]
VII-1	$[Ni(Et_3en)(acac)(H_2O)(NCS)]$	3390—3240	1660	2100	760	1595	1513
VIII-2	$[Ni(tmen)(acac)(H_2O)_2]I$	3370	1665	—	—	1595	1518
IX-2	$[Ni(tmen)(acac)(H_2O)_2]Br$	3350	1670	—	—	1593	1518
X-1	$[Ni(tmen)(acac)(H_2O)Cl]$	3401, 3225	1680	—	—	1600	1515
XI-2	$[Ni(tmen)(bza)(H_2O)_2]I$	3240	1650	—	—	—[d]	—[d]
XI-1	$[Ni(tmen)(bza)(H_2O)I]$	3240	1650	—	—	—[d]	—[d]
XII-2	$[Ni(tmen)(dpm)(H_2O)_2]I$	3260	—[d]	—	—	—[d]	—[d]

a) ν_a(NCO) and ν_a(NNN) for III and IV. b) ν_s(NCO) and ν_s(NNN) for III and IV. c) The value in the former report (2170 cm^{-1})[2] was a misprint. d) This band could not be assigned clearly.

nonpolar solvents; TG measurements in static air (heating rate: 1°/min) show that I-1, II-1, and V-1 lose their water quantitatively at 58—76, 78—100, and 75—100 °C, respectively (Fig. 1). The anhydrous complexes of I and V could be easily prepared in this way, but decomposition of NCSe$^-$ ion hindered the preparation of anhydrous II. On the other hand, no monohydrate could be obtained in the system tmen–dpm–NCS, only the anhydrous complex VI being isolated. Since the anhydrous complexes V and VI are also of high spin and show octahedral spectra (Table 2, VI), they are probably dimeric chelates with bridging pseudohalide ions, such as  $[(tmen)(acac)Ni\begin{smallmatrix}NCS\\ SCN\end{smallmatrix}Ni(tmen)(acac)]$.[2] Similar dimeric structures can be tentatively assigned to the complexes of NCO$^-$ and N$_3^-$ (III and IV) which are also anhydrous, of high spin and similar in color, although other types of bridging and polymerization can not be ruled out.[5,6]

A few interesting trends may be pointed out as to the ease of dehydration of these complexes. In the series [Ni(tmen)(β-dik)(H$_2$O)NCS], the water beoomes more tightly held in the order:

$$\text{dpm (no hydrate isolated)} \ll \text{acac} < \text{bza}$$

and in the series [Ni(tmen)(acac)(H$_2$O)X]:

$$NCO^- \approx N_3^- \text{ (no hydrate isolated)} \ll NCS^- < NCSe^-$$

The order seems to indicate that the bonding of water is strengthened by the weakening of the ligand field strength (l.f.s.) produced by other ligands.[3,7]

Another interesting complex prepared was [Ni(Et$_3$en)(acac)(H$_2$O)NCS] (VII-1), containing a diamine with very bulky alkyl groups. The spectral feature is essentially similar to that of (I-1), showing that H$_2$O can still be coordinated in this complex. No corresponding complex with Et$_4$en(teen),[8] [Ni(teen)(acac)(H$_2$O)-NCS], could be isolated, but the formation of a 5-coordinate complex (probably [Ni(teen)(acac)NCS]) in

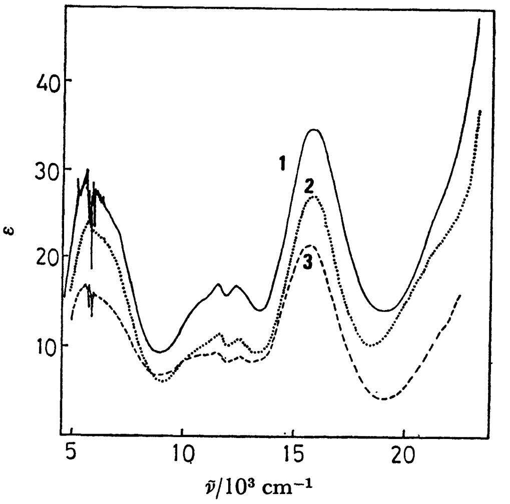


Fig. 2. Electronic spectra of VII-1 in various organic solvents (1=DCE; 2=NM; 3=acetone). Strong noises observed at *ca.* 6×10^3 cm^{-1} in the spectra of 1 and 3 were due to the absorption bands of the solvents.

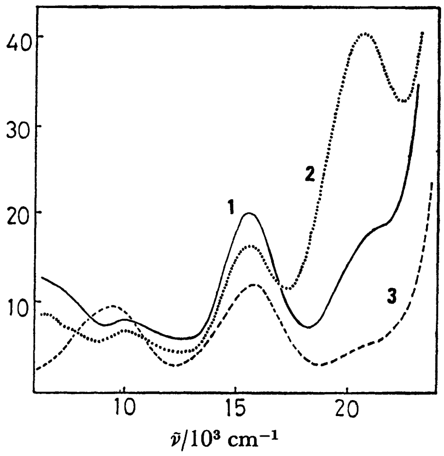


Fig. 3. Electronic spectra of VI in various solvents. For the numbering of curves, *cf.* Fig. 2.

an acetone solution of its components could be confirmed by its electronic spectrum. Coordination of solvent molecule is thus strongly hindered by the increase of the number of ethyl groups in the diamine (see below).

(ii) Structures in Organic Solutions: The structural changes of the complexes I-1 and I in various organic solvents were described in detail.[2] The spectral curves of VII-1 (Fig. 2) are most interesting in this connection; the curve in DCE is typically square pyramidal,[9] showing four bands assigned as follows:

$^3E(F) \leftarrow {}^3B_1(F)$, 5750 cm^{-1}; $^3A_2(F) \leftarrow {}^3B_1(F)$, 11550 cm^{-1}; $^3B_2(F) \leftarrow {}^3B_1(F)$, 12470 cm^{-1}; $^3E(F) \leftarrow {}^3B_1(F)$, 15900 cm^{-1}.

Two other spin allowed bands ($^3A_2(P)\leftarrow{}^3B_1(F)$ and $^3E(P)\leftarrow{}^3B_1(F)$) are probably under the strong CT band observed in the ultraviolet. Thus the water molecule escapes easily on dissolution, causing a structural change from 6- to 5-coordination. The 5-coordinate structure is also retained fairly well in more polar solvents (nitromethane or acetone), but the decrease in band intensity suggests that it is partially converted into other forms, such as planar [Ni(Et_3en)(acac)]$^+$ (in nitromethane) or [Ni(Et_3en)(acac)(solv.)NCS] (in acetone), as in the case of I. However, it can be seen that the dimerization observed with I in DCE or nitromethane is hindered by the bulky substituents in Et_3en, and the 5-coordinate structure is notably stabilized in comparison with the case of I.

The case of VI (Fig. 3) is in strong contrast with that of VII-1. Here the spectrum depends much more (and seemingly more than I) on the solvent, and the 5-coordinate species in DCE (which coexists with some [Ni(tmen)(dpm)]$^+$, as indicated by a notable hump at about 20000 cm^{-1}) is converted easily into [Ni(tmen)(dpm)]$^+$ in nitromethane, and solvated 6-coordinate species (probably [Ni(tmen)(dpm)(Solv.)NCS]) in acetone. The bulky substituents in dpm are somewhat apart from the central metal ion, so that the 5th and 6th coordination sites around it are not so sterically hindered as in the case of VII-1. The NCS^- can be dissociated away in nitromethane of relatively high dielectric constant (35.9), while a polar solvent molecule can enter into the coordination sphere. The effect of dimerization on the spectra is not so apparent as with I, probably owing to the stronger ligand field of dpm and larger interligand repulsion in the dimer.

As regards the complex with $NCSe^-$ (II-1), its spectrum in DCE is generally similar to spectra of I-1 and V-1, indicating an equilibrium between 5- and 6-coordinate species. Not much could be done with this complex, however, owing to its thermal instability.

The complexes with NCO^- (IV) and N_3^- (VI) could not be studied in sufficient detail owing to their poor yield, but they show typically octahedral spectra in DCE. This fact, and the non-conductivity of their solutions, indicate that their 6-coordinate dimeric (or polymeric) structure is retained also in solution, probably owing to the higher coordination and bridge formation ability of the NCO^- and N_3^- ions than NCS^- and $NCSe^-$ ions.[5,6] The $\tilde{\nu}_{max}$ and ε_{max} values of the solution spectra are summarized in Table 4.

(B) Halide Complexes. *(i) Solid Structures*: Unlike the pseudohalide complexes, almost all the complexes obtained (Table 1) are dihydrates. Their appearance and solid spectra are very similar to those of [Ni(tmen)(acac)(H_2O)$_2$]ClO_4,[3] suggesting their formulation as [Ni(diam)(β-dik)(H_2O)$_2$]X.

When β-dik=bza and $X=I^-$, both the mono- and dihydrate can be obtained, the latter being partially transformed into the former in a desiccator (*cf.* Experimental). Careful observation of the dehydration process of IX-2 by heating also shows that it is first converted into a yellowish green mass, apparently very similar to the complex [Ni(tmen)(bza)(H_2O)I]. Thus the number (n) in the hydrates Ni(tmen)(β-dik)X·$n$$H_2O$ varies as follows:

a) β-dik=acac

X=	I	Br	Cl
n=	2	2	—
	—	(1)	1

b) X=I

β-dik=	dpm	acac	bza
n=	2	2	2
	—	—	1

TABLE 4. SPECTRAL DATA OF SOLUTIONS OF PSEUDOHALIDE COMPLEXES, $\tilde{\nu}_{max}/10^3$ cm^{-1} (ε_{max} IN PARENTHESIS)

I-1	[Ni(tmen)(acac)(H_2O)(NCS)]						
	1,2-dichloroethane		6.0—9.5(8.4—11.0)		15.67(16.9)		c*
	nitromethane		6.0—9.5(7.3—8.5)		15.60(15.5)	20.92(16.7)	c*
	acetonitrile		9.76(11.3)		16.21(10.4)		c*
	acetone		9.35(11.0)		15.80(11.7)		c*
	DMSO		9.48(10.0)		15.77(7.6)		c*
I	[Ni(tmen)(acac)(NCS)]$_2$						
	1,2-dichloroethane	6.67(12.5)	9.80(9.3sh)		15.46(20.4)		c*
	nitromethane	6.67(10.1)	9.76(9.8sh)		15.55(18.6)	20.83(20.7)	c*
	acetonitrile		9.73(11.1)		16.21(10.8)		c*
	acetone		9.22(10.8)		15.75(13.0)		c*
	DMSO		9.43(9.9)		15.70(7.6)		c*
II-1	[Ni(tmen)(acac)(H_2O)(NCSe)]						
	1,2-dichloroethane		6.0—9.5(9.3—7.6)		15.87(16.6)		c
III	[Ni(tmen)(acac)(NCO)]$_2$						
	1,2-dichloroethane		9.20(9.2)		15.15(8.3)		b
IV	[Ni(tmen)(acac)(N_3)]$_2$						
	1,2-dichloroethane		9.28(13.8)		15.27(12.2)		b
V-1	[Ni(tmen)(bza)(H_2O)(NCS)]						
	1,2-dichloroethane		6.0—9.5(8.7—11.0)		15.63(20.2)		b
VI	[Ni(tmen)(dpm)(NCS)]$_2$						
	1,2-dichloroethane	6.17(12.8)	10.20(8.0)		15.63(20.2)	20.6(17sh)	b
	nitromethane	6.17(9.0)	10.05(6.8)		15.60(16.5)	20.70(40.8)	d
	acetone		9.47(9.6)		15.80(12.2)	20.6(5.2sh)	b
VII-1	[Ni(Et_3en)(acac)(H_2O)(NCS)]						
	1,2-dichloroethane	5.75(30)	10.4(14sh)	11.55(17.0)	12.47(17.0)	15.90(34.8)	b
	nitromethane	5.80(24)	10.4(9.2sh)	11.60(11.7)	12.50(11.0)	15.85(27.1)	a
	acetone	5.60(16.8)	10.4(9.0)	11.50(9.4)	12.50(8.8)	15.80(21.6)	b

Concentration: a *ca.* 1.0×10^{-2} M, b *ca.* 2.0—2.9×10^{-2} M, c *ca.* 5.1×10^{-2} M, d *ca.* 5.0×10^{-3} M (1 M=1 mol dm^{-3}). Temperature: *=25 °C; otherwise, room temperature (17—21 °C). sh=shoulder.

TABLE 5. SPECTRAL DATA OF SOLUTIONS OF HALIDE COMPLEXES, $\tilde{\nu}_{max}/10^3$ cm^{-1}
(ε_{max} IN PARENTHESIS, sh=SHOULDER)

VIII-2	[Ni(tmen)(acac)(H_2O)$_2$]I					
	1,2-dichloroethane	9.43(16.6)	14.49(21.2)	17.80(51.2)	21.72(342)	b
	nitromethane	20.60(154)				b
	acetone	9.45(16.2)	14.50(12.5)	17.82(40.1)	21.96(264)	b
	methanol	9.52(8.1)	15.90(6.4)			e
	DMSO	9.44(8.7)	15.73(6.4)			e
IX-2	[Ni(tmen)(acac)(H_2O)$_2$]Br					
	1,2-dichloroethane	9.80(22.5)	14.60(17.8)	19.05(50.1)	24.75(86.8)	b
	nitromethane	9.90(11.1)	14.70(8.0)	20.10(91.6)		d
	acetone	9.85(29.4)	15.74(13.6)	19.05(65.7)	24.2 (46.7sh)	d
	methanol	9.55(7.5)	15.95(5.8)			d
X-1	[Ni(tmen)(acac)(H_2O)Cl]					
	1,2-dichloroethane	9.80(10.4)	14.40(12.0)	19.87(12.9)	24.6 (54sh)	d
	nitromethane	10.00(11.6)	14.60(11.0)	19.90(24.4)	24.6 (52sh)	d
	acetone	10.00(18.9)	14.15(8sh)	16.13(9.0)	18.18(18sh)	d
		19.74(32.1)	24.6 (35sh)			
XI-1	[Ni(tmen)(bza)(H_2O)I]					
	1,2-dichloroethane	9.52(21.1)	14.60(26.6)	17.80(58.4)	21.85(418)	b
XII	[Ni(tmen)(dpm)]I					
	1,2-dichloroethane	14.40(9.7)	20.83(133)			b
IX′	[Ni(tmen)Br_2][a]					
	1,2-dichloroethane	9.85(65.0)	15.6 (26sh)	19.00(108)	24.2 (29sh)	c
XIII	[Ni(tmen)(acac)$_2$][a]					
	1,2-dichloroethane	9.43(10.3)	16.23(8.3)			c

Concentration: b *ca.* 5.0—5.9×10^{-3} M, c *ca.* 2.5×10^{-3} M, d *ca.* 1.0×10^{-2} M, e *ca.* 2.7×10^{-2} M. Temperature: room temperature (13—20 °C). a) The data on these complexes[3,4] are given for comparison.

We see that there is a competition between the water molecules and halide ions in the coordination sphere, and the nature of the β-diketonate (probably its steric requirement) also affects this competition. The water molecules are combined only weakly,[3] and easily lost on dissolution in relatively nonpolar solvents.

[Ni(tmen)(dpm)]I, a reddish orange diamagnetic solid with a typically square planar reflectance spectrum (a band at 20500 cm^{-1}), is obtained easily from the hydrate (*cf.* Experimental). On the other hand, the complexes VIII-2 and XI-1 dehydrate with more difficulty, losing their water at 80—120 and 100—145 °C, respectively, under the same conditions as in the case of pseudohalide complexes.††† Their anhydrous complexes are both reddish orange but slightly paramagnetic ($\chi_g = 3.4\times10^{-6}$ and 4.3×10^{-7}, respectively) and show weak bands (9300, 11000(sh), and 12150 cm^{-1} in XI, and 9550 cm^{-1} in VIII) together with a strong square planar band (20500—21000 cm^{-1}). VIII is remarkably hygroscopic; its paramagnetism may be due to the formation of its hydrate during storage. However, XI is apparently not very hygroscopic and a very small amount of blue crystals were observed to deposit at the top of the vessel during the course of dehydration in a vacuum (50—60 °C, 2 d). Thus the paramagnetism of XI, and at least a part of that of VIII, seem to be due to the product of decomposition which, to a small extent, accompanies their dehydration.

The nature of decomposition is understandable, if we compare the results with those of IX-2 and X-1.[1] With IX-2, the water is lost between 70 and 100 °C, but the weight decreases steadily on further heating, and when it is heated at under 60 °C for 17 d, it separates into a violet powder and a pale blue sublimate. The analysis of the latter (Found: C, 51.49; H, 8.08; N, 7.61%. Calcd: C, 51.50; H, 8.10; N, 7.51%) confirms its formulation as $[Ni(tmen)(acac)_2]$, while that of the former indicates that it is chiefly composed of $[Ni(tmen)Br_2]$ (Found: C, 23.29; H, 4.82; N, 7.77%. Calcd for: C, 21.53; H, 4.82; N, 8.37%). The deviations from the calculated values can be ascribed to a small amount of red crystals contained in the former (probably [Ni(tmen)(acac)]Br) which can be discerned by careful observation. Thus the decomposition of this complex can be formulated as:

$$[Ni(tmen)(acac)(H_2O)_2]Br \longrightarrow \begin{cases} [Ni(tmen)Br_2] + [Ni(tmen)(acac)_2]\cdots\cdots\text{(A)} \\ \qquad\qquad\qquad\qquad\qquad\text{Disproportionation}^{\dagger\dagger\dagger\dagger} \\ [Ni(tmen)(acac)]Br\cdots\cdots\text{(B) Dehydration.} \end{cases}$$

(A) is the main reaction. With X-1, this reaction seems to occur nearly exclusively; after being heated at 90 °C for 7 d it decomposed perfectly into $[Ni(tmen)(acac)_2]$ (subliming away from the vessel) and green $[Ni(tmen)Cl_2]$ with no trace of red complex.

Thus we can summarize the thermal decompositions of XII-2, VIII-2, XI-1, IX-2 (or IX-1), and X-1 as follows:

$$\text{XII-2} \rightarrow \text{(B) (no(A))} \qquad \left.\begin{matrix}\text{VIII-2}\\ \text{XI-1}\end{matrix}\right\}\begin{matrix}\nearrow\text{(B)}\\ \searrow\text{(A)}\end{matrix}$$

$$\text{IX-2}\begin{matrix}\nearrow\text{(B)}\\ \searrow\text{(A)}\end{matrix} \qquad \text{X-1} \rightarrow \text{(A) (no (B))}$$

if we assume that the reaction (A) occurs to a small extent with VIII-2 and XI-1, producing the blue sublimate observed with VIII-2, and paramagnetic impurity (presumably $[Ni(tmen)I_2]$) in the dehydration products.

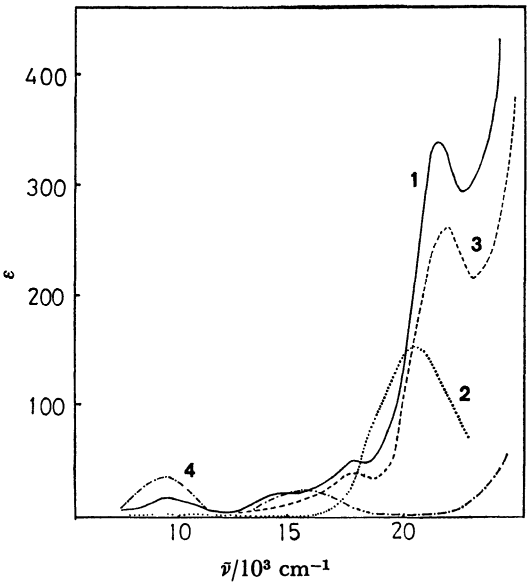


Fig. 4. Electronic spectra of VIII-2 in various solvents (1=DCE; 2=NM; 3=acetone; 4=DMSO (ε×5 as ordinate)).

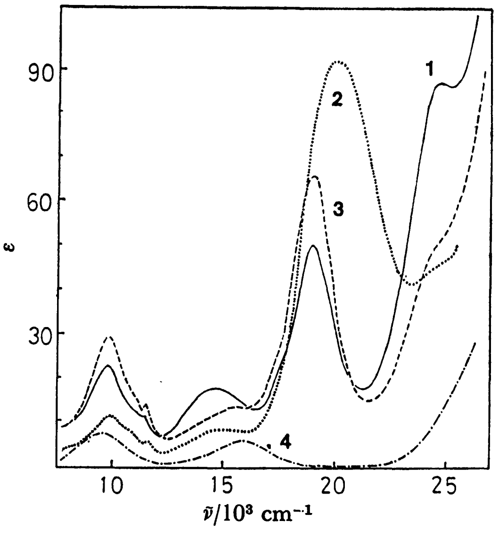


Fig. 5. Electronic spectra of IX-2 in various solvents. For the numbering of curves, *cf.* Fig. 4.

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††† The ease of dehydration is in the order dpm ≫acac> bza, *i.e.* the same as in the case of pseudohalide complexes. XI-1 and XI-2 both melt between 98 and 104 °C, seemingly leading to the same product.

†††† This reaction can be reversed, *i.e.*, when we mix the violet powder and blue sublimate in a 1 : 1 molar ratio in DCE, concentrate, and add some acetone, the crystals of $[Ni(tmen)(acac)(H_2O)_2]Br$ appear again.

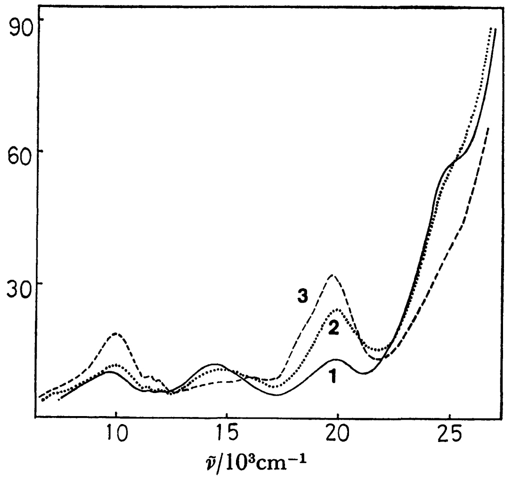

Fig. 6. Electronic spectra of X-1 in various solvents. For the numbering of curves, *cf.* Fig 2.

Table 6. Conductivity of DCE and NM solutions (1.0×10^{-3} M, 25 °C; $\Lambda_M/\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}$)[a]

		DCE	NM
I-1	$[\text{Ni(tmen)(acac)(H}_2\text{O)(NCS)}]$	≈0	16.6
I	$[\text{Ni(tmen)(acac)(NCS)}]_2$	≈0	18.8
III	$[\text{Ni(tmen)(acac)(NCO)}]_2$	1.1	—
VI	$[\text{Ni(tmen)(dpm)(NCS)}]_2$	2.5	—
VIII-2	$[\text{Ni(tmen)(acac)(H}_2\text{O)}_2]\text{I}$	19.0[b]	85.0
IX-2	$[\text{Ni(tmen)(acac)(H}_2\text{O)}_2]\text{Br}$	2.1	67.1
X-1	$[\text{Ni(tmen)(acac)(H}_2\text{O)Cl}]$	0.7	21.0
XII	$[\text{Ni(tmen)(dpm)}]\text{I}$	24.3	—
Standard 1 : 1 electrolytes		10—24	75—95

a) Care must be taken in comparing these data with the spectral ones, since the latter were mostly obtained with much more concentrated solutions. b) At 5×10^{-3} M, Λ_M drops to 12 $\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}$.

(ii) Structures in Organic Solutions. Figures 4, 5, and 6 show the spectra of VIII-2, IX-2, and X-1 in various organic solvents. Their $\tilde{\nu}_{max}$ and ε_{max} values are summarized in Table 5.

In general, in highly polar and coordinating solvents like DMSO or methanol, the spectra show that the complexes tend to form 6-coordinate species ($[\text{Ni(tmen)(acac)(Solv.)}_2]^+$ or $[\text{Ni(tmen)(acac)(Solv.)X}]$), as in the case of the pseudohalide complexes. However, the situation is quite different in solvents of low polarity and/or coordination ability (DCE, nitromethane, or acetone).

As to IX-2 (Fig. 5), the curve in DCE indicates the occurrence of reaction (A),[1] since it is very similar to that of 1 : 1 mixture of the products, $[\text{Ni(tmen)Br}_2]$ and $[\text{Ni(tmen)(acac)}_2]$. The similarity is still more pronounced in acetone, and the band at 14600 cm^{-1}, which should be ascribed to some unidentified by-product formed in DCE, apparently disappears. Thus it is clear that reaction (A) occurs quite easily by mere dissolution of this complex in these solvents.

In nitromethane, however, a strong band at *ca.* 20000 cm^{-1} appears, showing a remarkable dissociation into $[\text{Ni(tmen)(acac)}]^+$ and Br^- (*ca.* 60%, if the true ε_{max} of this band is assumed to be *ca.* 150).[3] On the other hand, the bands of products of reaction (A) are correspondingly weakened. This indicates that the higher polarity of nitromethane as an ionizing medium as compared with those of DCE and acetone (*cf.* their dielectric constants and E_T values,[11] and note that the latter decreases as nitromethane≫DCE≈acetone) favors the formation of charged species (*i.e.* ionization) in comparison with that of non-charged species (*i.e.* reaction (A)).

The data on X-1 (Fig. 6) can be understood on the same basis. Here the curve for acetone is similar to that of IX-2, indicating that reaction (A) occurs remarkably. The curves in nitromethane and DCE are essentially similar to that in acetone, although a band of some unidentified byproduct appears again at 14400—14600 cm^{-1}, and the band at *ca.* 10000 cm^{-1} and 19900 cm^{-1} are weakened. The band at 19900 cm^{-1} in nitromethane is much higher than that in DCE; this is probably due to the partial ionization (*ca.* 10%) into $[\text{Ni(tmen)(acac)}]^+$ and Cl^- which takes place in nitromethane (Table 6), and the overlap of the band of $[\text{Ni(tmen)(acac)}]^+$ on that of $[\text{Ni(tmen)Cl}_2]$ which is in the same region.

The data on VIII-2 (Fig. 4) are more complicated. However, it is clear that, in nitromethane, there is almost perfect ionization into $[\text{Ni(tmen)(acac)}]^+$ and I^-, since the spectrum is very similar to those of $[\text{Ni(tmen)(acac)}]\text{X}(\text{X}=\text{ClO}_4^-$ or $\text{B(C}_6\text{H}_5)_4^-)$ in highly non-coordinating media.[3] Comparing the data of the three complexes in nitromethane, we can conclude that: (i) the coordinated water is easily lost on dissolution, (ii) the complex then either ionizes into $[\text{Ni(tmen)(acac)}]^+$ and X, or undergoes disproportionation into $[\text{Ni(tmen)X}_2]$ and $[\text{Ni(tmen)(acac)}_2]$. The ionization is nearly complete when $\text{X}=\text{I}^-$, and occurs strongly when $\text{X}=\text{Br}^-$, but only weakly when $\text{X}=\text{Cl}^-$. The anions tend to remain coordinated in the order $\text{I}^-<\text{Br}^-<\text{Cl}^-$, as can be expected from their l.f.s.

The spectra of VIII-2 in DCE and acetone present some questions. Since their general appearance is similar to the spectrum of the trigonal bipyramidal [Ni(tren-Me)Cl]Cl reported by Ciampolini *et al.*,[10] we mistakenly ascribed the curves to the complex [Ni(tmen)(acac)I].[1] We have found, however, that they are very similar to the spectrum of $[\text{Ni(tmen)I}_2]$[4] in DCE. The bands in the former spectra are much weaker, and it can be estimated that only 10—15% of VIII-2 dissolved in DCE are converted into $[\text{Ni(tmen)I}_2]$, *i.e.* 20—30% undergo disproportionation into $[\text{Ni(tmen)I}_2]$ and $[\text{Ni(tmen)(acac)}_2]$ (the bands of $[\text{Ni(tmen)(acac)}_2]$ are much weaker than those of $[\text{Ni(tmen)I}_2]$, and will be completely covered by them, if the two species coexist in equimolar amounts).

On the other hand, the Λ_M values (Table 6) show that a large part of VIII-2 (50% or more in a 5×10^{-2} M solution) is converted into ionic species in DCE. A similar situation is also expected in acetone. There is no spectral indication for these ionic species, but this may be due to the fact that the bands of the expected ionic species ($[\text{Ni(tmen)(acac)}]^+$, $[\text{Ni(tmen)(acac)(acetone)}_2]^+$, and possibly $[\text{Ni(tmen)(H}_2\text{O)}_4]^{2+}$ produced by the hydrolysis of $[Ni(tmen)I_2]$) are considerably weaker than those of $[Ni(tmen)I_2]$. They would thus be nearly buried under the strong bands of $[Ni(tmen)I_2]$, even if a considerable amount of the ionic species is present in solution.

Comparing the data in DCE and acetone, we see that reaction (A) takes place with IX-2 or X-1 but VIII-2 mainly ionizes, showing that I^- is held more weakly to the metal ion than Br^- and Cl^-.

Spectral data were also obtained in DCE with complexes XI-1 and XII, containing bza and dpm instead of acac. XI-1 shows nearly the same spectrum as VIII-2; the curve of XII, however, is similar to that of VIII in nitromethane, and together with the high Λ_M value of its solution (Table 6), shows that most of it is dissociated into $[Ni(tmen)(dpm)]^+$ and I^- in DCE, although a weak band at 14400 cm^{-1} might indicate a slight occurrence of reaction (A). This is evidently due to the bulkiness and strong l.f.s. of dpm, which stabilizes the square planar cation.

Concluding Remarks. Although only limited information could be obtained with complexes containing NCO^-, $NCSe^-$, and N_3^-, there are clear-cut differences between the behavior of the pseudohalide complexes and that of the halide complexes. The most characteristic feature of the latter is the peculiar disproportionation reaction (A), which occurs both in solid state and in non-polar solvents, with ease which increases with the l.f.s. of the halide anion. The behavior of all these complexes in solution is governed not only by the donor number of the solvent, but also by other polarity parameters, such as dielectric constant and E_T value, especially when the polarity is relatively low.

Some of these solutions are notably thermochromic; for example, when an acetone solution of IX-2 was frozen in liquid nitrogen, and the spectral change of its melt with the rise of temperature was followed up to room temperature, the band *ca.* 19000 cm^{-1} was found to increase several times, indicating strong shift of the disproportionation equilibrium.

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