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On Some Mixed Chelates of Nickel(II) Which Are Highly Volatile, Fusible, and Soluble in Nonpolar Solvents

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It was found that the mixed chelates of nickel(II) with the general formula [Ni(diam)(β-dik)$_2$], where diam means an *N,N*- or *N,N'*-alkylated ethylenediamine and β-dik a β-diketonate anion, are highly volatile, fusible, and often amazingly soluble in nonpolar solvents like CCl_4, benzene, or heptane. Representative data on these properties are presented and their correlations with the structures of the ligands are discussed.

It is very well known that metallic acetylacetonates, and other β-diketonates like hexafluoroacetylacetonates and dipivaloylmethanates, are remarkably volatile, and soluble in a number of organic solvents. These properties have often been applied to the separation of metals by means of gas chromatography and extraction techniques.[1–4]

Recently, Hoshino *et al.* found that a mixed chelate of nickel(II) containing acetylacetonate anion, [Ni tmen (acac)$_2$],*** is highly volatile and can be sublimed at *ca.* 60 °C in a vacuum, when it is formed by the thermal disproportionation of the chelates Ni tmen acac X·nH$_2$O (X=halide ions).[5,6] This interesting observation lead us to a comparative study of the volatilities, melting points, and solubilities of this and related chelates to be reported here.

Experimental

All the chelates studied were prepared according to the literatures,[7–9] sometimes with certain modifications, and their identities were checked by elemental analyses. TG-DTA measurements on them were performed with a Rigaku Denki M8075 instrument in static air (heating rate 5 °C/min, sample weight *ca.* 9 mg, standard:Al_2O_3). Spectral measurements of their solutions in CCl_4, benzene, or heptane (all "Extra Pure") were made with a Hitachi 340 Recording Spectrophotometer from 7 to 25 kK (1 kK=1000 cm^{-1}), using 1 cm quartz cells at room temperature (*ca.* 20 °C).

Table 1. Abbreviations of the ligands

A: Diamines, $R_1R_2N(CH_2)_2NR_3R_4$

R_1	R_2	R_3	R_4	Abbreviation
CH_3	CH_3	CH_3	CH_3	tmen
C_2H_5	C_2H_5	C_2H_5	C_2H_5	teen
CH_3	CH_3	CH_3	H	Me$_3$en
C_2H_5	C_2H_5	C_2H_5	H	Et$_3$en
CH_3	H	CH_3	H	*sym*-dmen
C_2H_5	H	C_2H_5	H	*sym*-deen
CH_3	CH_3	H	H	*unsym*-dmen
C_2H_5	C_2H_5	H	H	*unsym*-deen

B: β-Diketonate Anions, $R_1COCHCOR_2^-$

R_1	R_2	Abbreviation
CH_3	CH_3	acac
CH_3	CF_3	tfa
CF_3	CF_3	hfa
$C(CH_3)_3$	$C(CH_3)_3$	dpm

Results

The chelates prepared are shown in Table 2. As reported formerly,[7–9] the mixed chelates I—XI are all blue to green crystals, and are typical 6-coordinate high-spin nickel(II) complexes.

Melting Points and Volatilities. The TG-DTA data of the mixed chelates studied are classified into three patterns A,B, and C (*cf.* Fig. 1). In the case of A, a sharp endothermic peak is observed on the DTA curve. The fact that this peak corresponds to the melting point of the chelate can be confirmed by visual observation. The chelate then begins to evaporate at a somewhat higher temperature(t_i), where a remarkable drop of the TG curve and a broad endothermic peak on the DTA begins to appear. In some cases t_i is lower than mp, that is, the evaporation begins to occur already in advance of melting.

Nearly quantitative evaporation takes place with some chelates; in such case, the ratio of the final weight (w_f) to the initial weight (w_i) of the chelate, w_f/w_i, is nearly zero. In many cases, however, decomposition of the chelates seems to occur at a later stage of evaporation and the sample remaining in the crucible is converted into a black nonvolatile residue, making the ratio w_f/w_i much higher.

The pattern B is observed when the chelate has water of crystallization. Here two peaks appear on the DTA curve, one corresponding to the dehydration temperature (t_d), and the other to the mp. The TG curve also decreases in two steps, the first of which indicates the quantitative loss of water in the formula.

The pattern C also show two DTA peaks, but here the chelate is anhydrous, and the first peak probably indicates some kind of solid phase transition, which takes place in advance of melting. This temperature is designated as t_t.

All these data are summarized in Table 2, together with those of the simple acetylacetonates of nickel (II) and copper(II).

The volatilities of these chelates can now be studied by taking the temperature at which 25% of the weight of a chelate is lost by evaporation ($t_{1/4}$; *cf.* Table 2),

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***As to the abbreviations of ligands, *cf.* Table 1.

TABLE 2. TG-DTA DATA OF THE MIXED CHELATES, $Ni(acac)_2$ AND $Cu(acac)_2$
As to the meaning of t_i, t_f *etc.*, *cf.* text and Fig. 1.

	Chelate	Pattern	Mp	t_i	t_f	t_d	t_t	w_f/w_i	$t_{1/4}$
I	Ni(teen)(acac)$_2$	A	90	95	322			0.43	180
II	Ni(Et$_3$en)(acac)$_2$·H$_2$O	B	59	112	236	45		0.38	187
III	Ni(*sym*-deen)(acac)$_2$·H$_2$O	B	78	108	216	74		0.21	184
IV	Ni(*unsym*-deen)(acac)$_2$·H$_2$O	B[a]	151	137	216	72, 119		0.65	202
V	Ni(tmen)(acac)$_2$	A	97	114	208			0.067	170
VI	Ni(Me$_3$en)(acac)$_2$·H$_2$O	B	100	104	230	48, 59[c]		0.17	173
VII	Ni(*sym*-dmen)(acac)$_2$·H$_2$O	B	134	118	255	82, 104[c]		0.24	186
VIII	Ni(*unsym*-dmen)(acac)$_2$	A	187	135	230			0.37	204
IX	Ni(tmen)(hfa)$_2$	C	130	80	185		102	0.018	153
X	Ni(tmen)(tfa)$_2$	A	81	114	199			0.013	163
XI	Ni(tmen)(dpm)$_2$	A	162	148	264			0.017	221
	Ni(acac)$_2$	[b]		224	338			0.72	315
	Cu(acac)$_2$	[b]		178	260			0.043	228

a) The DTA curve of this chelate was anomalous, and showed one more strong peak of unknown nature at 157 °C, *i.e.*, just above the mp. This may be related to the high value of w_f/w_i, *i.e.*, the remarkable tendency for thermal decomposition of this chelate. b) Simple sublimation without melting; with Ni(acac)$_2$, much decomposition took place along with it. c) These double peaks may be an indication for stepwise dehydration, *e.g.* by way of hemihydrate formation.

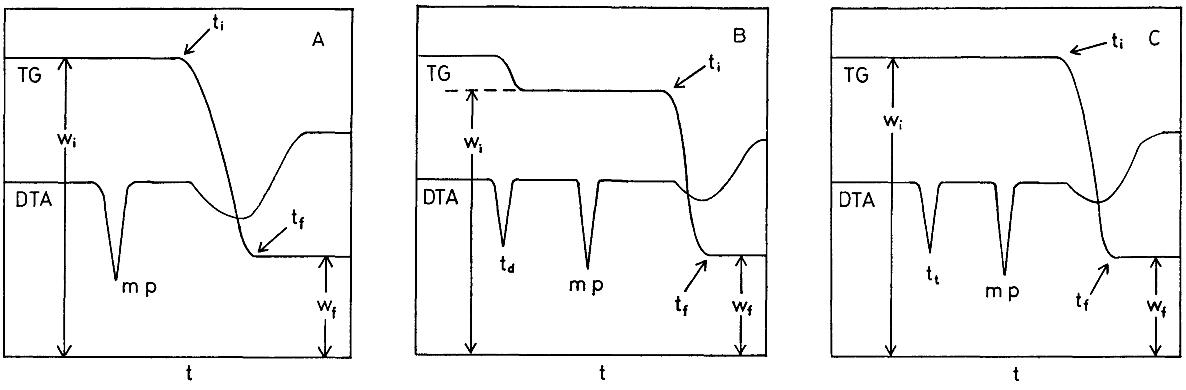

Fig. 1. Typical patterns of the TG-DTA curves (schematic).

and comparing it with those of other chelates.[****] The following general trends can be deduced in this way.

1) All the mixed chelates are readily fusible, with melting points which are sometimes much lower than 100 °C. They are also highly volatile, even in static air of 1 atm pressure. In contrast to these observations, the simple acetylacetonates Ni(acac)$_2$ and Cu(acac)$_2$ do not melt by heating, and they are much less volatile (in the case of Ni(acac)$_2$, much part of it is thermally decomposed before sublimation) under the same conditions.

2) Among the mixed chelates with acac and methylated diamines, the volatility increases in the following order of diamines:

$$\text{tmen} \gtrsim \text{Me}_3\text{en} > \textit{sym}\text{-dmen} > \textit{unsym}\text{-dmen}. \quad (1)$$

3) Among the mixed chelates with acac and ethylated diamines, the volatility increases in the following order of diamines:

$$\text{teen} > \text{Et}_3\text{en} \lesssim \textit{sym}\text{-deen} > \textit{unsym}\text{-deen}. \quad (2)$$

4) The volatilities of the *unsym*-dmen and *unsym*-deen chelates are comparable, but among other mixed chelates with acac, those of methylated diamines are slightly more volatile than those of ethylated diamines.

5) Among the mixed chelates containing tmen and various β-diketonate anions, the volatility increases in the following order of β-diketonates:

$$\text{hfa} > \text{tfa} > \text{acac} \gg \text{dpm}.$$

The plot of $t_{1/4}$ in Fig. 2 illustrates these trends.

Solubilities in Nonpolar Solvents. The high volatilities and fusibilities of chelates clearly show that the intermolecular forces acting in their crystals are quite weak. Thus we can expect that they will be soluble in nonpolar solvents. The measurements of their solubilities in C_6H_6, CCl_4, and heptane, which were carried out spectrophotometrically, confirmed this expectation.

From the data in Table 3, we can deduce the following trends:

[****] Nearly the same trends are observed when we take the temperature at which 5 or 10% of the weight is lost; at these earlier stages of evaporation, the effect of thermal decomposition thus seems to be negligible. The identity of the sublimed chelates with the original ones was also confirmed by their visible and IR spectra.

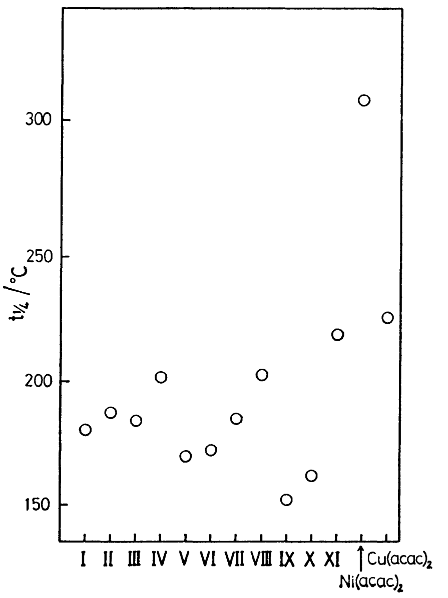

Fig. 2. $t_{1/4}$ values of the chelates. I—XI are those for the mixed chelates (*cf.* Table 2).

Table 3. Solubilities (10^{-2} mol/dm^3, 20 °C) of the mixed chelates, Ni(acac)$_2$ and Cu(acac)$_2$

Chelate	C_6H_6	CCl_4	Heptane
Ni(teen)(acac)$_2$	100	140	55
Ni(Et$_3$en)(acac)$_2\cdot H_2O$	46	65	16
Ni(*sym*-deen)(acac)$_2\cdot H_2O$	13	7.6	0.30
Ni(*unsym*-deen)(acac)$_2\cdot H_2O$	16	7.3	0.30
Ni(tmen)(acac)$_2$	140	100	60
Ni(Me$_3$en)(acac)$_2\cdot H_2O$	130	77	13
Ni(*sym*-dmen)(acac)$_2\cdot H_2O$	33	22	0.60
Ni(*unsym*-dmen)(acac)$_2$	14	14	0.23
Ni(tmen)(hfa)$_2$	39	5.0	1.4
Ni(tmen)(tfa)$_2$	130	64	13
Ni(tmen)(dpm)$_2$	43	28	29
Ni(acac)$_2$	0.97	[a]	[a]
Cu(acac)$_2$[b]	0.32	—	0.025

a) Too insoluble to measure. b) Taken from Ref. 10.

1) The mixed chelates studied are all highly soluble in typically nonpolar solvents. For example, the solubility of [Ni(*unsym*-dmen)(acac)$_2$] in heptane is 48 g/dm^3, and that of [Ni(tmen)(acac)$_2$] in the same solvent is 220 g/dm^3 (in CCl_4 it is still higher, being 370 g/dm^3!). These figures are very much higher than those of Ni(acac)$_2$ and Cu(acac)$_2$.

2) Among the mixed chelates with acac, there are certain relations between the volatilities and solubilities. For example, in CCl_4 and heptane, the solubility increases with the number of alkyl groups in both the methylated and ethylated diamine series. However, the relation among the chelates with different β-diketonate anions is not clear as yet.

Discussion

All the data obtained show that the intermolecular forces acting among the mixed chelate molecules in crystal are very much weaker than those acting in the crystals of simple acetylacetonates of Ni(II) and Cu(II). This is evidently the consequence of structural differences; it is known that the crystals of Ni(acac)$_2$ is composed of complicated trimeric molecules, and those of Cu(acac)$_2$ contain planar monomeric molecules, in which Cu^{2+} and polar ligand groups are exposed to outer influence.[11,12] Thus we can imagine that a lot of energy is needed to sublime them, or to dissolve them in solvents with nearly no solvating power, because the intermolecular forces in them will be relatively high, and, in the case of Ni(acac)$_2$, energy will also be needed to dissociate the trimer into monomeric gaseous molecules.[†]

On the other hand, all the mixed chelates studied here are monomeric octahedral, and their polar groups are buried deep under a large number of protruding alkyl (or fluoroalkyl) groups, so that the intermolecular forces acting in them will be essentially weaker than those in Ni(acac)$_2$ or Cu(acac)$_2$. It will be especially weak when the number of alkyl groups on the diamine is large[††] (*cf.* the order (1) and (2) mentioned above); however, when their size is too large, the increase of van der Waals force will make the chelate slightly less volatile (*cf.* the $t_{1/4}$ values of the methylated and ethylated complexes). The same effect may be responsible for the lower volatility of the dpm chelate. The higher volatilities of the tfa and hfa chelates are probably due to the partial negative charge on their fluorine atoms, which act to decrease the intermolecular attraction; similar increase in volatility in going from acac to tfa and hfa is already well known among their simple chelates.[1,2]

Our results thus clearly show that the volatility, fusibility, and solubility in nonpolar solvents of a chelate can be drastically augmented by mixed chelate formation with ligands containing bulky groups.

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[†] The occurence of such a dissociation in diphenylmethane solution at 200 °C[13] suggests the monomeric nature of this chelate in gaseous phase.

[††] It is possible that, in the mixed chelates containing N–H bonds (*i.e.* those of Me$_3$en, Et$_3$en, *sym*- and *unsym*-dmen and deen), hydrogen bond formation between them and the C–O bonds of neighboring molecules contributes to the intermolecular attraction.

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