CHEMISTRY LETTERS, pp. 437-440, 1979. Published by the Chemical Society of Japan

A NEW TYPE OF THERMAL DISPROPORTIONATION OF MIXED NICKEL(II) COMPLEXES[1)]

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Thermal decomposition of the mixed nickel(II) complexes, [Ni(tmen)(acac)$(OH_2)_2$]X(X=Br or I), occurs in the following two ways:

$$[Ni(tmen)(acac)(OH_2)_2]X \longrightarrow [Ni(tmen)(acac)_2] + [Ni(tmen)X_2] \qquad (1)$$

$$[Ni(tmen)(acac)(OH_2)_2]X \longrightarrow [Ni(tmen)(acac)]X \qquad (2)$$

The reaction(1) is favored by the bromide, and the reaction(2) by the iodide. Structures of these complexes in some organic solutions are also discussed.

The structures of a number of 6-coordinate nickel(II) complexes change from octahedral to square planar by heating, either in solid state or in solution. This kind of change was observed in our previous study of the mixed complex, [Ni(tmen)(acac)$(OH_2)_2$]ClO_4, which is dehydrated by heating as follows:[2)]

$$\underset{\text{(blue, octahedral)}}{[Ni(tmen)(acac)(OH_2)_2]ClO_4} \longrightarrow \underset{\text{(red, planar)}}{[Ni(tmen)(acac)]ClO_4} + 2H_2O$$

(tmen=N,N,N',N'-tetramethylethylenediamine, acac=acetylacetonate anion). It was also observed that this same change occurs in 1,2-dichloroethane(DCE) without heating, i.e. by mere dissolution of the complex. We have recently prepared and characterized two new complexes, [Ni(tmen)(acac)$(OH_2)_2$]X(X=Br or I), and studied their thermal changes.

The method of preparation of the complexes is similar to that of [Ni(tmen)(acac)]$B(C_6H_5)_4$ reported earlier;[2)] the only difference is that [Ni(tmen)(acac)$(OH_2)_2$]ClO_4 and KX(X=Br or I) are used instead of [Ni(tmen)(acac)(NO_3)] and $NaB(C_6H_5)_4$. Their analytical data, colors, and magnetic moments are shown in Table 1.

Table 1. Analytical data, colors and magnetic moments of Ni(tmen)(acac)X·$2H_2O$

Compound	C*	H*	N*	Color	μ_{eff}(B.M.)
X=Br	33.92(33.88)	6.90(6.98)	7.16(7.18)	blue	3.21(21.7°C)
X=I	30.24(30.24)	6.20(6.23)	6.48(6.41)	blue	3.21(22.6°C)

* Calculated values are in parentheses.

The ir and solid reflectance spectra of these complexes are very similar to each other, and also to those of the complex perchlorate, [Ni(tmen)(acac)$(OH_2)_2$]ClO_4. Therefore, they should be formulated as [Ni(tmen)(acac)$(OH_2)_2$]X, and thus are octahedral in the solid state.

When these solid complexes are heated at a relatively low temparature of 65°C under reduced pressure(2 Torr) for three days in dry air, characteristic thermal reactions are found to occur.

Thermal Decomposition of the Complex Bromide In this case, a part of the decomposition products remains as a violet powder in the reaction vessel, while another part of them sublimes away from it, and condenses as brilliant blue crystals at the top of the apparatus. More careful examination reveals that a trace amount of red crystals is also formed in the reaction vessel. The electronic spectrum of the violet powder, and that of the blue crystals, are shown in Fig. 1, together with their mean(curve 3) which shows the spectrum of a 1:1 mixture of the two main products. The spectrum of the violet powder is very similar to the spectrum of the tetrahedral complex, $[Ni(tmen)Br_2]$, reported by Sacconi et al.,$^{3)}$ while that of the blue crystals is nearly the same with the spectrum of $[Ni(tmen)(acac)_2]$ reported earlier.$^{2)}$ The elementary analysis of the blue crystals also comfirms its formulation as $[Ni(tmen)(acac)_2]$. Thus the predominant thermal reaction of the complex bromide can be fomulated as a disproportionation reaction:

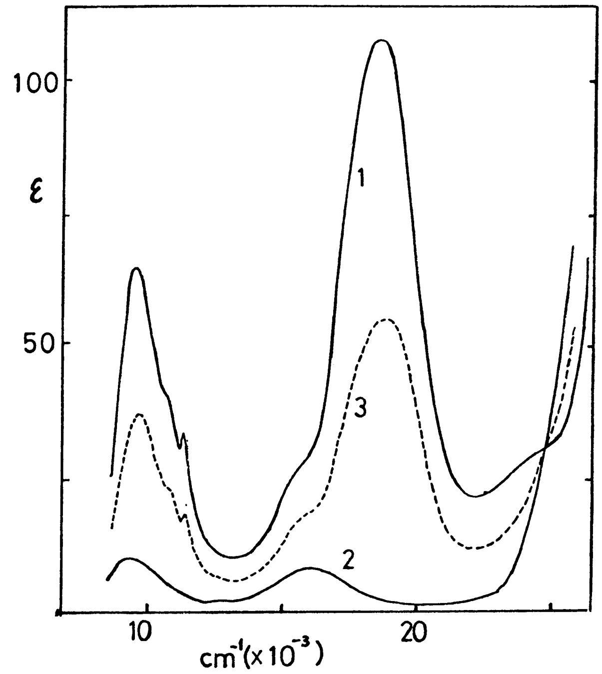

Fig. 1. Absorption spectra of the thermal decomposition products of the diaqua complex bromide dissolved in DCE: 1, violet powder; 2, blue crystals; 3, the curve obtained by taking the mean of 1 and 2.

$$[Ni(tmen)(acac)(OH_2)_2]Br \longrightarrow [Ni(tmen)(acac)_2] + [Ni(tmen)Br_2] + 2H_2O$$

The yield of the red crystals was too low for their characterization, but the results of the decomposition of the iodide complex(see below) suggest that they are crystals of the square planar complex $[Ni(tmen)(acac)]Br$, produced by the simple dehydration of the original complex:

$$[Ni(tmen)(acac)(OH_2)_2]Br \longrightarrow [Ni(tmen)(acac)]Br + 2H_2O$$

Thermal Decomposition of the Complex Iodide Here the main product is red crystals, and is evidently a square planar complex(ν_{max} in the reflectance spectrum: 21×10^3 cm^{-1}, i.e. nearly at the same position as that of $[Ni(tmen)(acac)]ClO_4$).$^{2)}$ Its ir spectrum shows no water bands. Thus the main reaction is simple dehydration:

$$[Ni(tmen)(acac)(OH_2)_2]I \longrightarrow [Ni(tmen)(acac)]I + 2H_2O$$

Sublimation of a trace amount of the blue crystals, $[Ni(tmen)(acac)_2]$, is observed here again, suggesting the occurence of the disproportionation

$$[Ni(tmen)(acac)(OH_2)_2]I \longrightarrow [Ni(tmen)(acac)_2] + [Ni(tmen)I_2] + 2H_2O$$

to a very limited extent. Another product of this reaction, $[Ni(tmen)I_2]$, which is expected to remain with the red crystals, could not be identified with certainty, but the weak paramagnetism(χ_g=3.37×10^{-6}) of the red crystals, which should be diamagnetic if it is purely square planar, may be an indication for its existence as an impurity.

Suggested Decomposition Mechanism The comparison of the two cases of the bromide and the iodide suggest the following decomposition sequence:

$$[Ni(tmen)(acac)(OH_2)_2]X \xrightarrow{\text{step 1}} [Ni(tmen)(acac)]X \xrightarrow{\text{step 2}}$$

$$([Ni(tmen)(acac)X]\ (a)\ \text{or}\ [Ni(tmen)(acac)X_2Ni(tmen)(acac)]\ (b)) \xrightarrow{\text{step 3}}$$

$$([Ni(tmen)(acac)_2]\ \text{and}\ [Ni(tmen)X_2])$$

When X=I, the reaction can proceed hardly over the step 1, so that the main product is [Ni(tmen)(acac)]I, and only a very small amount passes over to the step 2, where the anion gets into the coordination sphere, forming a 5-coordinate complex ([Ni(tmen)(acac)X]) or possibly its dimer($[Ni(tmen)(acac)X_2Ni(tmen)(acac)]$). These species are, however, unstable intermediates, and decomposed readily into the final products(step 3). When X=Br with much stronger coordination ability, the step 2(and then step 3) is much easier to occur, so that the main products are now $[Ni(tmen)(acac)_2]$ and $[Ni(tmen)Br_2]$, with only a small amount of [Ni(tmen)(acac)] Br formed in the step 1.

Solution Spectra of the Complex Halides The reaction sequence given above is supported by the facts that the formation of the complexes such as (a) and (b) was already observed when X=NCS in 1,2-dichloroethane(DCE), and that they coexist with the square planar complex, $[Ni(tmen)(acac)]^+$, in nitromethane(NM).[4] These facts led us to study the electronic spectra of the complex halides in these solvents.

As shown in Fig. 2, the spectra of the two complexes in NM both show a strong band at ca. 20×10^3 cm^{-1} which indicates the predominance of $[Ni(tmen)(acac)]^+$. The band of the bromide, however, is somewhat weaker and slightly shifted toward red, and there are also bands at ca. 15×10^3, 12×10^3 and 10×10^3 cm^{-1} in the

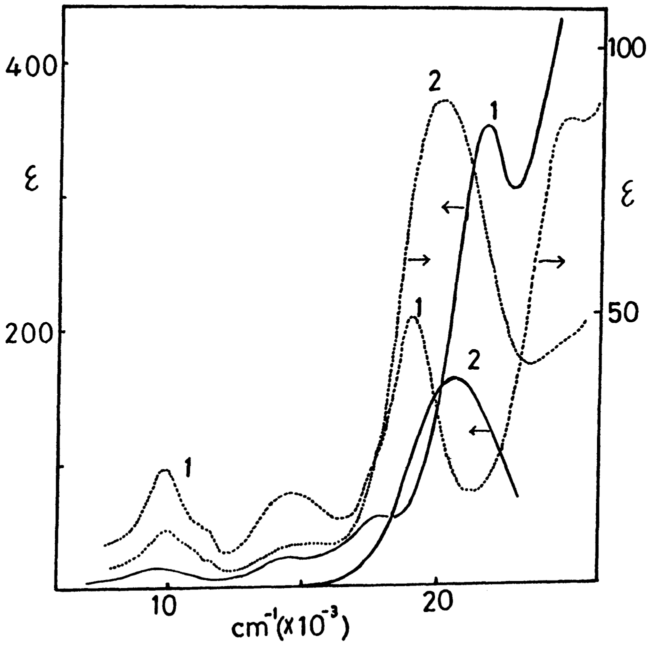

Fig. 2. Absorption spectra of the diaqua complex halides dissolved in DCE (1) and NM(2). Curves for the bromide are shown with------(ε scale on the right side), and those for the iodide with —— (ε scale on the left).

spectrum of the bromide, which are still much weaker and cannot be found in the spectrum of the iodide. These changes can be explained reasonably well, if we assume that the disproportionation into [Ni(tmen)(acac)$_2$] and [Ni(tmen)Br$_2$] occurs also in this solution to some extent, and their absorption bands are superposed on the band of [Ni(tmen)(acac)]$^+$.

In the DCE solutions, however, the situation is quite different. Here the spectrum of the iodide with bands at 21×10^3, 18×10^3, 14×10^3 and 9×10^3 cm^{-1} is very similar to that of [Ni(tren-Me)Cl]Cl*, a typical trigonal bipyramidal 5-coordinate complex reported by Ciampolini et al.5) In a non-polar and non-coordinating solvent like DCE, therefore, even the I$^-$ ion can get into the coordination sphere, forming a 5-coordinate trigonal bipyramidal complex, [Ni(tmen)(acac)I]. On the other hand, the spectrum of the bromide can be considered essentially as the spectrum of the disproportionation products(cf. Fig. 1, Curve 3).6)

Thus we can recognize that, also in DCE solutions, the bromide can get further along the reaction sequence(1 → 2 → 3) postulated above, owing to its much smaller size and higher coordination ability. In NM, the high dielectric constant (ε=35.8) favors the ionization into [Ni(tmen)(acac)]$^+$ and X$^-$, but here also some disproportionation occurs with the bromide. In both solvents, it seems that the water molecules get away readily on dissolution, indicating that they are held only very weakly in the original complexes, as in the case of the complex perchlorate.2)

References and Notes

1) Part X of the series "Studies on Mixed Chelates". As for Part IX, see 4).

2) Y. Fukuda and K. Sone, Bull. Chem. Soc. Jpn., 43, 2282(1970); Y. Fukuda and K. Sone, J. Inorg. Nucl. Chem., 34, 2315(1972).

3) L. Sacconi, I. Bertini and F. Mani, Inorg. Chem., 6, 262(1967).

4) N. Hoshino, Y. Fukuda and K. Sone, Transition Met. Chem., in press(1979).

5) M. Ciampolini, N. Nardi and G. P. Speroni, Coord. Chem. Rev., 1, 222(1966) and references therein(tren-Me= tri(2-dimethylaminoethyl)amine, $N(CH_2CH_2N(CH_3)_2)_3$).

6) There are, however, a new band at 24.8×10^3 cm^{-1} and another at 14.6×10^3 cm^{-1} in the spectrum of the bromide in DCE, which are absent in Curve 3 of Fig. 1. It is interesting to note that, in acetone, these new bands almost disappear, and the curve of the bromide looks very much like Curve 3 in Fig. 1. The shape of the curve of the iodide in acetone is essentially the same as that in DCE, so that the difference between the two halides is more clear-cut in this solvent. Further details on these problems will be discussed elsewhere.

(Received February 17, 1979)