The Transition-metal Chemistry of Quinuclidinone-containing Ligands. Part VI. A Study of the Thermal Properties of Several Complexes with *trans*-2-(2-Quinolyl)methylenequinuclidin-3-one[1]

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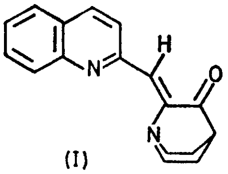
A thermochemical determination of the relative solid-state stabilities of the yellow [{Ni(qnqn)Cl$_2$}$_2$] and violet [Ni(qnqn)Cl$_2$] isomers (where qnqn is *trans*-2-(2-quinolyl)methylenequinuclidin-3-one) has indicated that the violet isomer is the metastable isomer at room temperature. D.t.a.-t.g. measurements have been obtained for the iron, cobalt, nickel, and copper chloride and nickel bromide complexes of qnqn and reveal in the case of the nickel chloride isomers an endothermic structural transformation of the yellow dimer to the violet monomer at 230 °C. No related transformation is observed in the remaining complexes. The unusual inter-related thermal properties of the nickel chloride isomers are discussed in terms of the various properties of the two complexes.

The structural properties of several transition-metal complexes of *trans*-2-(2-quinolyl)methylenequinuclidin-3-one (I) (qnqn) and the *X*-ray structure of [{Ni(qnqn)Cl$_2$}$_2$] have been reported.[1,2] The latter complex, which is a yellow dimeric molecule containing nickel(II) ions in a square pyramidal geometry, exhibits unusual thermal properties.[2] At high temperature (*ca.* 230 °C), this yellow dimer is converted *via* a solid-state transformation into its violet, tetrahedral monomeric isomer. Upon cooling to room temperature, this complex remains violet; however, upon further cooling (to *ca.* −78 °C), the solid violet isomer is again converted into the dimeric yellow isomer, which remains yellow on warming to room temperature. This paper reports the details of a calorimetric study of the relative solid-state stability of the two nickel isomers and a d.t.a.–t.g. study of qnqn and several of its complexes.



(I)

EXPERIMENTAL

The ligand and its complexes were prepared by methods previously described.[2,3] Anhydrous nickel chloride was prepared by heating reagent grade NiCl$_2$·6H$_2$O to 230 °C for 24 h. The results of Pechkovskii *et al.*[4] indicate that the last water of hydration is lost at 208 °C and that the anhydrous material is stable relative to the oxide below 600 °C. Evlanov[5] reports 215 °C as the dehydration temperature.

The solution calorimeter used in this work has been described.[6] The measurements on the nickel complexes were carried out on two separate preparations of each. The decomposition products of the two nickel complexes in 0·1N-HCl have identical visible absorption spectra; hence, they are assumed to be identical.

The relative density of the yellow and violet nickel complexes was measured by simultaneous flotation in a CCl$_4$–CBr$_4$ solution.

The d.t.a.–t.g. results were obtained on *ca.* 10 mg of powdered samples in platinum crucibles by using a Mettler Thermoanalyzer. The d.t.a. reference standard was Al$_2$O$_3$, the heating rate was 8 °C/min. The d.t.a. circuit utilized a platinum–rhodium couple along with a platinum thermocouple. The heating chamber and balance were evacuated three times to *ca.* 0·1 Torr and then filled with dry helium in order to minimize the residual oxygen in the sample chamber. During the heating, a stream of dry helium passed through the sample chamber. In some instances, in order to detect small weight changes, larger samples were used.

The *X*-ray powder diffraction patterns were obtained with a Siemanns Crystalloflex IV diffractometer equipped with a copper tube.

RESULTS

The calorimetric measurements of the heat of solution of anhydrous nickel chloride, qnqn, violet [Ni(qnqn)Cl$_2$], and yellow [{Ni(qnqn)Cl$_2$}$_2$] in 0·1N-HCl are presented in Table 1 along with some derived thermochemical results.

The simultaneous measurement of the relative densities of violet [Ni(qnqn)Cl$_2$] and yellow [{Ni(qnqn)Cl$_2$}$_2$] indicates that the yellow isomer has the higher density. The density of the yellow isomer has been determined[1] to be 1·66 g/cm^3 by flotation and *X*-ray measurements.

The simultaneous d.t.a.–t.g. plot for the ligand in helium from 100 to 700 °C is presented in Figure 1 and is summarized in Table 2. The sharp endotherm at 150 °C corresponds to the ligand's melting point, which has been reported[3] as being 150—151 °C. The initial weight loss begins at *ca.* 170 °C, and there is a 6% by weight residue at *ca.* 850 °C. The complexity of the decomposition indicates that a more detailed study will be required to yield any conclusions regarding the mechanism of decomposition. The d.t.a.–t.g. of the ligand measured in air is similar from 25 °C to *ca.* 900 °C to that shown in Figure 1 except that a large exotherm accompanied by a weight loss is centred at 575 °C.

The thermogram for yellow [{Ni(qnqn)Cl$_2$}$_2$] in helium is presented in Figure 2. The d.t.a.–t.g. for the violet [Ni(qnqn)Cl$_2$] isomer is essentially identical to that exhibited by the yellow isomer *except* that the endotherm at 230 °C is *not* observed.

The d.t.a.–t.g. plots for [Fe(qnqn)Cl$_2$], [Co(qnqn)Cl$_2$], and

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[1] Part V, G. J. Long and E. O. Schlemper, *J.C.S. Dalton*, 1975, 96; *Inorg. Chem.*, 1974, **13**, 279.

[2] G. J. Long and D. L. Coffen, *Inorg. Chem.*, 1974, **13**, 270.

[3] D. L. Coffen and T. E. McEntee, jun., *J. Org. Chem.*, 1970, **35**, 503.

[4] V. N. Pechkovskii, N. I. Vorob'ev, and T. V. Ostrovskaya, *Zhur. neorg. Khim.*, 1964, **9**, 778.

[5] G. A. Evlanov, *Izvest. V.U.Z. Khim. i khim. Tekhnol.*, 1963, **6**, 3.

[6] G. L. Bertrand, R. D. Beaty, and H. A. Burns, *J. Chem. and Eng. Data*, 1968, **13**, 436.

TABLE 1

Thermochemical data at 25 °C [a]

	ΔH/kcal mol^{-1}
$\mathrm{NiCl_2\ (s)} \longrightarrow \mathrm{NiCl_2(0{\cdot}1\,N\text{-}HCl)}$	$-19{\cdot}58 \pm 0{\cdot}17$
$\mathrm{qnqn\ (s)} \longrightarrow \mathrm{qnqn(0{\cdot}1\,N\text{-}HCl)}$	$-0{\cdot}43 \pm 0{\cdot}06$
$\mathrm{violet[Ni(qnqn)Cl_2]\ (s)} \longrightarrow \mathrm{NiCl_2(0{\cdot}1\,N\text{-}HCl) + qnqn(0{\cdot}1\,N\text{-}HCl)}$	$-13{\cdot}14 \pm 0{\cdot}06$
$\tfrac{1}{2}\mathrm{yellow[\{Ni(qnqn)Cl_2\}_2](s)} \longrightarrow \mathrm{NiCl_2(0{\cdot}1\,N\text{-}HCl) + qnqn(0{\cdot}1\,N\text{-}HCl)}$	$-10{\cdot}54 \pm 0{\cdot}02$
Derived results	
$\mathrm{violet[Ni(qnqn)Cl_2](s)} \longrightarrow \tfrac{1}{2}\mathrm{yellow[\{Ni(qnqn)Cl_2\}_2](s)}$	$-2{\cdot}60 \pm 0{\cdot}07$
$\mathrm{NiCl_2(s) + qnqn\ (s)} \longrightarrow \mathrm{violet[Ni(qnqn)Cl_2](s)}$	$-6{\cdot}87 \pm 0{\cdot}19$
$\mathrm{NiCl_2\ (s) + qnqn\ (s)} \longrightarrow \tfrac{1}{2}\mathrm{yellow[\{Ni(qnqn)Cl_2\}_2]\ (s)}$	$-9{\cdot}47 \pm 0{\cdot}18$

[a] These results represent the average of at least three separate measurements, and the uncertainties indicate the root-mean square deviation; the final solutions were *ca.* 3 × 10^{-3}M.

TABLE 2

D.t.a.–t.g. results obtained in helium

Compound (sample wt.)	D.t.a. (t/°C) Initial	Max.	End	Wt. loss mg	% Wt. loss	Comments
qnqn	145	150	155 (en)	0	0	Melting
(8·8 mg)	175	200	210 (ex)	0·2	2·2	Initial decomposition
				6·05	68·0	Wt. loss 210—430 °C
				2·05	23·0	Wt. loss 430—900 °C
$[\mathrm{Fe(qnqn)Cl_2}]$	280	285	290 (ex)	0·25	2·4	Initial decomposition
(10·4 mg)				3·75	36·0	Wt. loss 290—420 °C
				0·90	8·6	Wt. loss 420—580 °C
				1·90	18·2	Wt. loss 580—670 °C
				0·80	7·6	Wt. loss 670—900 °C
$[\mathrm{Co(qnqn)Cl_2}]$	295	315	325 (ex)	0·50	4·6	Initial decomposition
(10·7 mg)				2·85	26·6	Wt. loss 325—390 °C
				1·00	9·3	Wt. loss 390—530 °C
				0·85	7·9	Wt. loss 530—590 °C
				0·85	7·9	Wt. loss 590—900 °C
Yellow$[\{\mathrm{Ni(qnqn)Cl_2}\}_2]$	220	230	240 (en)	0	0	Yellow → violet transformation
(10·0 mg)	350	310	320 (ex)	0·85	8·5	Initial decomposition
				2·10	21·0	Wt. loss 320—360 °C
				2·55	25·5	Wt. loss 360—900 °C
Violet$[\mathrm{Ni(qnqn)Cl_2}]$	300	310	315 (ex)	0·80	8·6	Initial decomposition
(9·3 mg)				2·00	21·5	Wt. loss 315—360 °C
				2·40	25·8	Wt. loss 360—900 °C
$[\mathrm{Ni(qnqn)Br_2}]$	315	320	330 (ex)	0·65	5·9	Initial decomposition
(11·1 mg)				2·05	18·5	Wt. loss 330—380 °C
				4·10	36·9	Wt. loss 380—500 °C
$[\mathrm{Cu(qnqn)Cl_2}]$	190	205	225 (ex)	0·35	3·4	Initial decomposition
(10·4 mg)	225		375 (en)	3·00	28·8	Wt. loss 225—375 °C
				1·40	13·5	Wt. loss 375—900 °C

$[\mathrm{Ni(qnqn)Br_2}]$ are all similar to those obtained for violet $[\mathrm{Ni(qnqn)Cl_2}]$ and are summarized in Table 2. It should be noted that none of these complexes exhibits the endotherm at 230 °C that is observed with the yellow $[\{\mathrm{Ni(qnqn)Cl_2}\}_2]$ complex. The copper complex, $[\mathrm{Cu(qnqn)Cl_2}]$ is quite different from the others in that a small initial weight loss occurs at a lower temperature (180 °C) and is accompanied by an exotherm centred at 205 °C. The t.g. plots for each of the complexes exhibit several overlapping weight-loss steps, which no doubt correspond to overlapping processes. As a result, it is almost impossible to say anything specific about the mode of thermal decomposition.

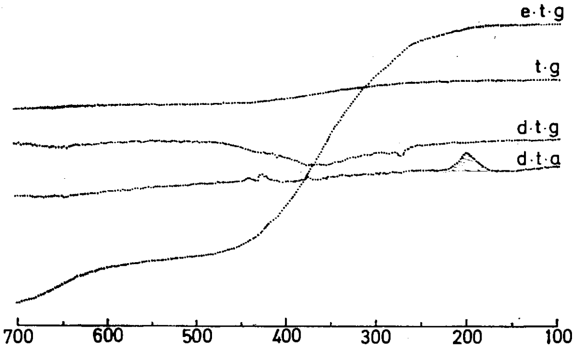

FIGURE 1 D.t.a.–t.g. plot for qnqn in helium

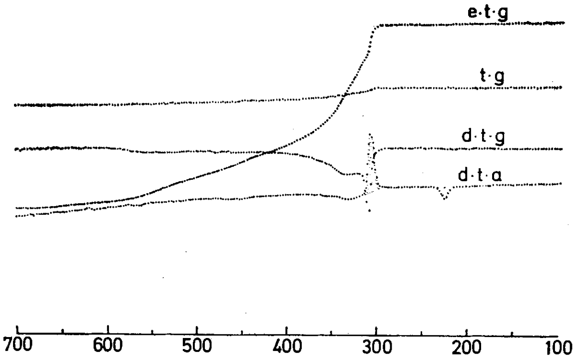

FIGURE 2 D.t.a.–t.g. plot for yellow $[\{\mathrm{Ni(qnqn)Cl_2}\}_2]$ in helium

The d.t.a.–t.g. plot for yellow $[\{\mathrm{Ni(qnqn)Cl_2}\}_2]$ in air is illustrated in Figure 3. In air, as in helium, the yellow and violet nickel chloride isomers have identical d.t.a.–t.g. plots above 250 °C; however, the yellow complex again shows a small endotherm centred at 230 °C which is not observed in the violet complex. Because of the identical results obtained for the yellow and violet complexes above 250 °C, we decided to study in more detail the endotherm centred at 230 °C in the yellow isomer. A visual observation of the yellow isomer in a sealed melting-point tube revealed a change in colour from yellow to violet centred at *ca.* 230 °C.[2] The *X*-ray powder pattern of the violet sample obtained by heating the yellow isomer to 240 °C is identical to that of the violet isomer prepared directly.[2] The d.t.a.–t.g. results at 230 °C with larger samples (Figure 4) reveal no endotherm at 230 °C for the violet isomer (Figure 4a). The weight loss is less than 0·05%, the limit of measurability. The yellow complex exhibits an endotherm at 230 °C (Figure 4b) accompanied by a 0·2% weight loss. This small weight loss is undetectable in Figures 2 and 3. Heating of this sample (initially the yellow isomer) was stopped at 250 °C, and the violet [Ni(qnqn)Cl$_2$] complex was obtained either by furnace cooling or by slow cooling (*ca.* 1 °C/min) the sample to room temperature. Again, the *X*-ray powder pattern of the violet complex obtained in this manner is identical with the pattern of the violet complex synthesized directly. This sample, in a sealed tube, was then immersed in liquid nitrogen for a few minutes yielding the dimeric yellow [{Ni(qnqn)Cl$_2$}$_2$] complex as discussed previously.[2] The d.t.a.–t.g. for the resulting yellow complex reveals the presence of the endotherm at 230 °C (Figure 4c) which corresponds to the yellow to violet structural transformation. In this case, there was no weight loss.

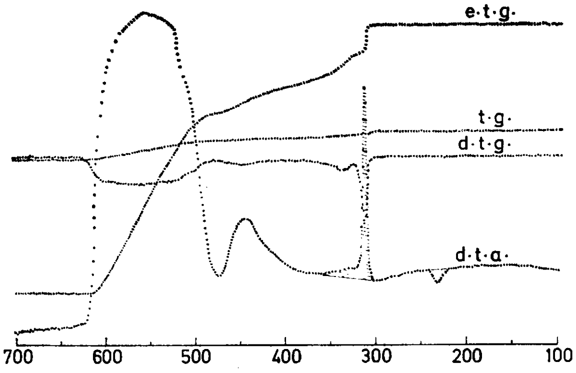

FIGURE 3 D.t.a.–t.g. plot for yellow [{Ni(qnqn)Cl$_2$}$_2$] in air

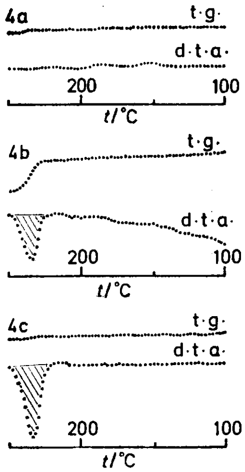

FIGURE 4 D.t.a.–t.g. plot between 100 and 250 °C for (a) 115·9 mg of violet [Ni(qnqn)Cl$_2$], (b) 214·6 mg of yellow [{Ni(qnqn)-Cl$_2$}$_2$], and (c) 130·3 mg of yellow [{Ni(qnqn)Cl$_2$}$_2$] after its initial conversion into the violet isomer followed by reconversion into the yellow isomer at 80 K (see text). The ordinate scale is different for different plots of d.t.a.

DISCUSSION

The interconversion between the dimeric yellow and monomeric violet isomers of [Ni(qnqn)Cl$_2$] is unusual in that the transition from yellow to violet occurs at 230 °C, whereas the reverse transition does not occur in the solid state until the sample is cooled to *ca.* −80 °C. We interpret this phenomenon as indicating that the yellow isomer is the more stable form of the complex below 230 °C and that some type of an activation barrier prevents the solid-state rearrangement of the violet complex to the more stable yellow isomer between −80 and 230 °C The calorimetric results presented in Table 1 reveal that in the solid state the yellow isomer is energetically more stable than the violet isomer at 25 °C. The structural transition at 230 °C, observed both visually and with d.t.a., reveals that the violet form is more stable above this temperature even though the yellow to violet transition is endothermic. The yellow to violet transition is thus observed to be endothermic at both 25 and 230 °C. The dissociation of the dimeric yellow complex to the monomeric violet form is expected to have a positive change in entropy. Thus the change in Gibbs free energy for this process is more negative (and more favourable) at higher temperatures. If we assume that the change in enthalpy for the process of dissociation is independent of temperature, we calculate that the entropy change (yellow $\longrightarrow$ violet) is $+5{\cdot}0$ cal mol^{-1} K^{-1}. The temperature range of this transition (*ca.* 20 °C) detracts from our interpretation of this process as a first-order transition; however, visual observation reveals that individual single crystals undergo the structural transformation within a short time span (*ca.* 1 s) and over a very small (*ca.* 0·1 °C) range of temperature.[2] This indicates that the temperature range of the complete transition is due mainly to differences in the individual crystals—perhaps crystal defects.

Several other observations indicate that the violet isomer is metastable at temperatures below 230 °C. In the preparation of the violet complex, it must be rapidly precipitated from a high-temperature solution by quenching.[2] A slow cooling of the solution or a failure to dry the violet complex completely after filtration results in contamination with the yellow isomer. Precipitation of the complex from every solvent studied to date has resulted in the yellow isomer. Solution of either isomer in methylene chloride at room temperature produces a violet solution from which the yellow isomer precipitates on slow evaporation of the solvent. In addition, grinding and the application of pressure [7] converts the violet

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[7] G. J. Long and J. R. Ferraro, *J.C.S. Chem. Comm.*, 1973, 719.

isomer into the yellow isomer. This is not surprising, because the yellow isomer has a higher density and presumably a smaller unit-cell volume than the violet isomer.

The d.t.a.–t.g. results indicate that the order of increasing initial temperature of decomposition is [Cu(qnqn)Cl_2], [Fe(qnqn)Cl_2], violet [Ni(qnqn)Cl_2], [Co(qnqn)Cl_2], and [Ni(qnqn)Br_2]. In this sequence, the temperature for the copper complex is significantly lower than the temperature for the remaining complexes, which are all rather similar. This is consistent with previous conclusions [2] which reveal that the iron, violet nickel chloride, cobalt, and nickel bromide complexes are structurally similar and significantly different from the structure of the copper complex.

Our detailed study of the d.t.a.–t.g. results for the yellow to violet transition (Figure 4) reveals that the very small weight loss at 230 °C (*ca.* 0·2 weight %) is probably the result of the loss of entrapped solvent molecules and surface adsorbed gases and not the result of a weight loss accompanying the structural transition. This is confirmed by the absence of a similar weight loss accompanying the same transformation after the initial transformation and reconversion of the resulting violet isomer into the yellow isomer at low temperature (Figure 4c).

All the above observations are compatible with our interpretation of the violet isomer as the solid-state metastable isomer at room temperature. The transition of the violet monomer [1] to the yellow dimer would thus require movement and alignment of the molecules prior to the formation of the dimer. The details of this alignment have been discussed elsewhere.[1] This alignment process constitutes an activation barrier, which is principally entropic rather than energetic, and, as a result, is not particularly favoured by high temperatures (between −80 and 230 °C). Certainly an activation barrier of this type could be circumvented by compression or by solution and recrystallization. The effect of cooling the violet isomer to *ca.* −80 °C may be similar to the effect of compression that overcomes the activation barrier and permits the entropically unfavoured dimerization to occur.

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