Hydration, Hydrolysis, and Dissociation of a Nickel(II) Bromide–Quinoline Complex

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The tetrahedral complex [$NiBr_2$(quin)$_2$] (quin = quinoline) will reversibly add two molecules of water or methanol on cooling to *ca.* −80 °C in chloroform or dichloromethane solution. In the presence of water there is an accompanying slow hydrolysis reaction, but anhydrous solutions maintained at room temperature slowly deposit the polymeric 1 : 1 complex, [{$NiBr_2$(quin)}$_n$], previously only obtained by thermal degradation reactions.

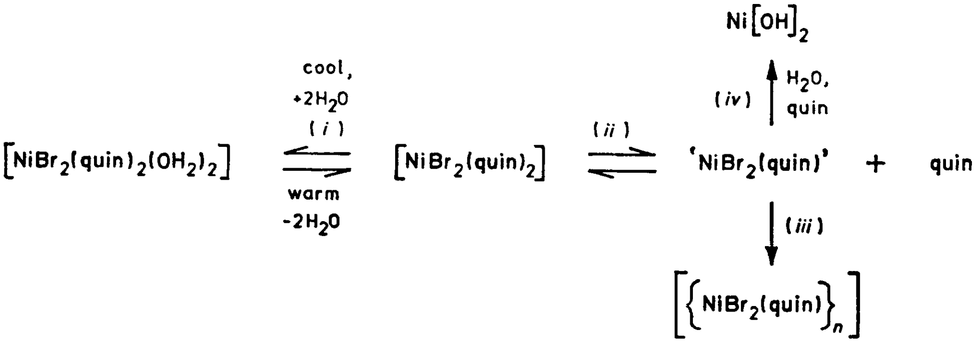
The tetrahedral complex [$NiBr_2$(quin)$_2$] (quin = quinoline) is obtained as the only direct product of the reaction of nickel(II) bromide with quinoline.[1] Thermal degradation of this complex yields the polymeric 1 : 1 compound [{$NiBr_2$(quin)}$_n$] in which the nickel has a distorted octahedral environment.[2,3] In addition to these two well defined and thoroughly characterised complexes, the experimental reports mention various unspecified 'solvolysis' or 'decomposition' reactions occurring in solutions of the 1 : 2 complex. An observation that the colour of [$NiBr_2$(quin)$_2$] in solution is strikingly temperature-sensitive prompted a more detailed examination of its behaviour in various solvent systems.

RESULTS AND DISCUSSION

The complex [$NiBr_2$(quin)$_2$] is moderately soluble in chloroform, dichloromethane, or acetone to form deep blue solutions which slowly deposit nickel(II) hydroxide under ambient conditions. Typically, solutions left exposed to the atmosphere hydrolyse completely in a few hours, or overnight. The colour of freshly prepared solutions (*ca.* 0.01 mol dm^{-3}) in reagent-grade solvents fades progressively on cooling and the solutions become colourless, to the naked eye, at *ca.* −80 °C. The complex does not precipitate from the cold solutions and the blue colour is restored on warming to room temperature.

Solutions in carefully dried, ethanol-free chloroform or dichloromethane do not decolourise on cooling: on the contrary, the principal visible absorption band ($\lambda_{max.}$ = 17 350 cm^{-1}) is slightly more intense at −80 °C than at room temperature. However, a further reaction occurs in the anhydrous solutions and leads to the slow crystallisation of the deep red polymeric 1 : 1 complex [{$NiBr_2$(quin)}$_n$].

The experimental observations are consistent with the reaction scheme below. In solutions containing traces of moisture, reversible hydration (*i*) yields the octahedral dihydrate [$NiBr_2$(quin)$_2$(OH_2)$_2$] at low temperature. At the experimental concentrations, this complex is colourless. The competing dissociation equilibrium (*ii*) becomes important in the anhydrous systems. This equilibrium must strongly favour the undissociated tetrahedral complex, even at room temperature, but association of the '$NiBr_2$(quin)' species leads eventually to the separation (*iii*) of the insoluble 1 : 1 complex.



In the presence of water, the free base liberated in the dissociation reaction (*ii*) will promote onward hydrolysis (*iv*) to Ni[OH]$_2$. Additionally, hydrolysis may occur by decomposition of the hydrate [$NiBr_2$(quin)$_2$(OH_2)$_2$] or related species.

Detailed study of the hydration reaction (*i*) is complicated by the simultaneous hydrolysis process, but similar results can be obtained by adding small quantities of dry methanol to anhydrous solutions of the tetrahedral complex. The temperature dependence of the spectrum of a solution containing a 2.66 : 1 methanol : [$NiBr_2$(quin)$_2$] mixture is illustrated in Figure 1 and the effect of various quantities of added methanol on the 17 350 cm^{-1} absorption intensity (measured as peak height) between 25 and −90 °C is shown in Figure 2 (*a*)—(*c*). The cold solutions are completely colourless but a very weak band ($\epsilon < 1$) which can be assigned to the ν_2 transition in octahedral $[NiBr_2(quin)_2(HOMe)_2]$ is just detectable at *ca.* 14 000 cm^{-1} in spectra measured at −85 °C. The very low molar absorbance strongly suggests a centrosymmetric *trans*-octahedral (D_{2h}) structure for the complex. The formation of the octahedral product is favoured by raising the methanol concentration, the colour being discharged at progressively higher temperatures as the methanol : nickel ratio is increased. With a sufficient excess of methanol, the solutions are colourless even at room temperature.

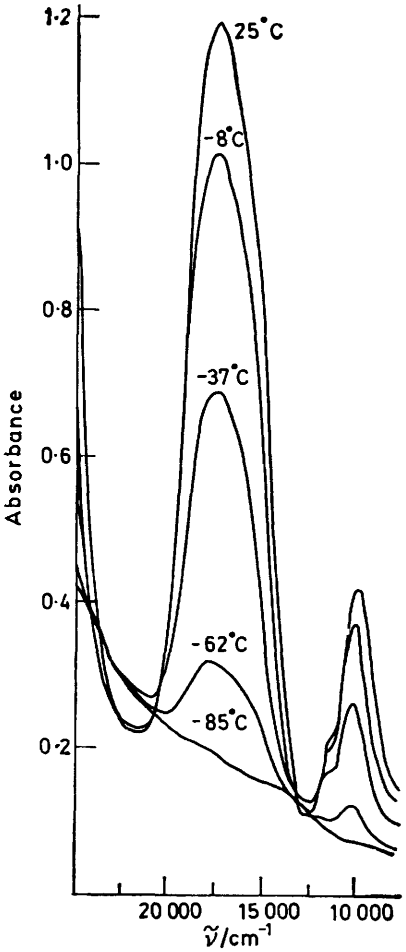


FIGURE 1 Visible absorption spectrum of CH_2Cl_2 solution containing $[NiBr_2(quin)_2]$ (0.009 mol dm^{-3}) and MeOH (0.024 mol dm^{-3}) (1 : 2.66) between 25 and −85 °C

The complete disappearance of the tetrahedral-nickel absorption bands in solutions with methanol : nickel ratios as low as 2.66 : 1 indicates that the process involved must be one of addition, to yield $[NiBr_2(quin)_2(HOMe)_2]$, rather than ligand replacement, giving $[NiBr_2(HOMe)_4]$ or $[Ni(HOMe)_6]^{2+}$. There is no evidence in the spectra for the formation of significant quantities of five-co-ordinate species, and when the methanol : nickel ratio is reduced to less than 2 : 1 [Figure 2(*a*)] the blue colour is only partially discharged on cooling. It should be emphasised here that although these results are reasonably reproducible for freshly prepared and very carefully dried solutions, they are not strictly quantitative because the slow precipitation of $[\{NiBr_2(quin)\}_n]$, which cannot be prevented, progressively removes nickel from the experimental solutions.

The deep red insoluble complex $[\{NiBr_2(quin)\}_n]$ is identical with the material obtained by Goodgame *et al.*[2] by thermal degradation of $[NiBr_2(quin)_2]$. A number of similar red, polymeric 1 : 1 complexes of $NiCl_2$ and $NiBr_2$ are obtained with pyridine and substituted pyridine ligands:[4,5] the unusually deep colours are attributed to the distorted environment of the metal atom. All of these complexes are obtained by thermal degradation of the 1 : 2 compounds[2-5] and are amorphous or very poorly crystalline: the present example appears to be the first reported case of separation of a well crystallized 1 : 1 complex from solution at room temperature.

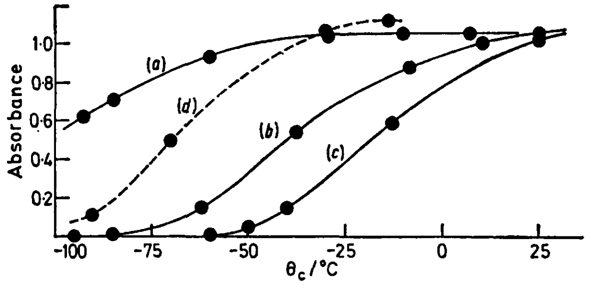


FIGURE 2 Temperature dependence of 17 350 cm^{-1} absorption intensity in CH_2Cl_2 solutions of $[NiBr_2(quin)_2]$ (0.009 mol dm^{-3}) containing (*a*) 0.0135, (*b*) 0.024, and (*c*) 0.05 mol dm^{-3} MeOH; (*d*) 17 100 cm^{-1} absorption intensity for $[NiBr_2(4Me\text{-}quin)_2]$ (0.009 mol dm^{-3}) with 0.1 mol dm^{-3} MeOH

The quinoline liberated in the formation of the 1 : 1 complex tends to oppose further dissociation of the tetrahedral complex, and eventually reaches a sufficient concentration to bring the precipitation reaction effectively to a halt. Thus, only a proportion of the nickel initially present can be separated as $[\{NiBr_2(quin)\}_n]$, and solutions left to stand for prolonged periods still contain substantial quantities of undissociated $[NiBr_2(quin)_2]$.

The reactions of $NiBr_2$ with 4-methyl-, 6-methyl-, and 7-methyl-quinoline yield deep blue tetrahedral complexes $[NiBr_2L_2]$, exactly analogous to $[NiBr_2(quin)_2]$, with no evidence of other products. With 2-methylquinoline the only solid product was a pale blue-green non-crystalline material which failed to yield satisfactory or consistent analytical data and clearly is not comparable with the simple tetrahedral complexes. No reaction occurred with 8-methylquinoline: the methyl group in this position will seriously obstruct access to the ligand nitrogen atom.

The effect of temperature on the $[NiBr_2(4Me\text{-}quin)_2]$–methanol system is illustrated in Figure 2(*d*). A much higher methanol concentration, and a significantly lower temperature, are required for the formation of the octahedral $[NiBr_2(4Me\text{-}quin)_2(HOMe)_2]$ complex than for the corresponding quinoline–methanol complex. The 4-

methyl substituent will tend to enhance the N ⟶ Ni donor interaction and hence to reduce the effective positive charge on the nickel atom; on this simple basis we would expect additional ligands to bind less readily to $[NiBr_2(4Me\text{-}quin)_2]$ than to $[NiBr_2(quin)_2]$. However, the visible absorption spectra of the two complexes are very similar (Table 1) and certainly do not reveal any large differences in the ligand field at the nickel atom.

TABLE 1

Visible spectra (cm^{-1}) of $[NiBr_2(quin)_2]$ and $[NiBr_2(4Me\text{-}quin)_2]$

$[NiBr_2(quin)_2]$		$[NiBr_2(4Me\text{-}quin)_2]$		
Solid [a]	CH_2Cl_2 [b]	Solid [a]	CH_2Cl_2	Assignment [b]
ca. 17 900 (sh)	*ca.* 17 350	*ca.* 17 350	*ca.* 17 100	${}^3T_1(F) \rightarrow {}^3T_1(P)$
16 400	*ca.* 15 750	*ca.* 15 600 (sh)	*ca.* 16 000 (sh)	
ca. 11 100 (sh)	*ca.* 11 400	*ca.* 11 000 (sh)	*ca.* 11 400	${}^3T_1(F) \rightarrow {}^1\Gamma_5({}^1D_2)$
10 000	9 950	9 650	10 050	${}^3T_1(F) \rightarrow {}^3A_2$

[a] Nujol mulls. [b] See also ref. 1.

The methylquinoline complexes all hydrolyse on exposure to the atmosphere but, unlike $[NiBr_2(quin)_2]$, do not yield detectable quantities of 1 : 1 complexes from anhydrous solutions.

EXPERIMENTAL

Solvents.—Chloroform, dichloromethane, and methanol were purified and dried as described elsewhere.[6]

Tetrahedral Complexes.—The deep blue 1 : 2 quinoline and methylquinoline complexes listed in Table 2 were prepared as described by Goodgame and Goodgame.[1]

TABLE 2

Analytical data

	Analysis (%) *			
Complex	C	H	Ni	Br
$[NiBr_2(quin)_2]$	45.2	3.0	12.2	33.4
	(45.3)	(3.0)	(12.3)	(33.5)
$[\{NiBr_2(quin)\}_n]$	31.0	2.0	16.9	45.8
	(31.1)	(2.0)	(16.9)	(46.0)
$[NiBr_2(4Me\text{-}quin)_2]$	47.1	3.6	11.6	31.6
	(47.6)	(3.6)	(11.6)	(31.7)
$[NiBr_2(6Me\text{-}quin)_2]$	48.6	3.6	11.4	31.6
	(47.6)	(3.6)	(11.4)	(31.7)
$[NiBr_2(7Me\text{-}quin)_2]$	47.0	3.4	11.6	30.8
	(47.6)	(3.6)	(11.6)	(31.7)

* Calculated values are given in parentheses.

$[\{NiBr_2(quin)\}_n]$. A solution of $[NiBr_2(quin)_2]$ in dry CH_2Cl_2 (0.015 mol dm^{-3}, 750 cm^3) deposited *ca.* 1 g of the deep red crystalline complex $[\{NiBr_2(quin)\}_n]$ on standing at room temperature for a period of four weeks.

Reactions with methanol. The visible spectra of solutions of $[NiBr_2(quin)_2]$ or $[NiBr_2(4Me\text{-}quin)_2]$ in dry chloroform or dichloromethane, with various proportions of added methanol, were observed over the temperature range 25 to −95 °C using a Beckman-R11C variable-temperature cell and TDM-1 controller in conjunction with a Unicam SP700 spectrophotometer. The system was allowed to stabilise for at least 45 min before each individual reading was made, and the temperature accuracy was estimated to be better than ±3 °C throughout. Absorbances were recorded on an arbitrary linear scale (Figures 1 and 2) chosen to maximise the 17 350 cm^{-1} peak height at room temperature. The measured absorption coefficient[1] for $[NiBr_2(quin)_2]$ at 17 450 cm^{-1} in CH_2Cl_2 at room temperature is 169 dm^3 mol^{-1} cm^{-1}: because of problems with side reactions, this figure must be regarded as approximate. The absorption intensity (measured as peak height) in anhydrous CH_2Cl_2 increases by *ca.* 3% on cooling to −90 °C.

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