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Observations of a Pressure Induced Nitrito → Nitro Conversion in Solid Ni(iso-quinoline)$_4$(NO$_2$)$_2$

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On the basis of electronic and infrared spectral measurements it was suggested [1] that solid Ni(i-quin)$_4$(NO$_2$)$_2$, i-quin = iso-quinoline, contains both oxygen and nitrogen bonded nitrite groups. This is surprising, since other complexes of the type Ni(amine)$_4$(NO$_2$)$_2$ formed by heterocyclic bases such as pyridine, 3 and 4-methylpyridine, pyrazole and 2-methylimidazole have all been found to be *trans* nitritocomplexes [2]. The fact that the nitrite bonds *via* oxygen rather than nitrogen in these latter complexes has been attributed to the lesser degree of steric interference with the amine ligands expected for this type of nitrite coordination and this interpretation has received support from an analysis of the crystal structures of the complexes [2]. Originally, it was proposed that the electronic spectrum of the isoquinoline complex implied the presence of two distinct isomers of the type Ni(i-quin)$_4$(–NO$_2$)$_2$ and Ni(i-quin)$_4$(–ONO)$_2$, probably with a somewhat different packing of the aromatic ring systems in each molecular form, one favoring nitro and the other nitrito coordination [1]. However, more recent studies [3] suggest that the electronic spectrum is equally consistent with the solid containing a single type of molecule of general formula Ni(i-quin)$_4$(–NO$_2$)$_x$(–ONO)$_{2-x}$. This might either be a stoichiometric nitro-nitritocomplex (corresponding to x = 1) or have the two types of nitrite statistically distributed throughout the lattice. Unfortunately, although quite large crystals of Ni(i-quin)$_4$(NO$_2$)$_2$ can be prepared, these exhibit severe twinning problems so that a determination of the structure of the complex by X-ray methods has so far proved impossible.

It is known that the complexes Ni(diamine)$_2$(NO$_2$)$_2$, diamine = N,N-dimethylethylenediamine and N,N′-diethylethylenediamine, exhibit nitro-nitrito equilibria upon solution in inert organic solvents [4], and recently it has been found that the application of pressure shifts the equilibria in favour of the presumably more compact nitro isomer [5, 6]. We therefore decided to test the effect of pressure upon the nature of the metal–nitrite bonding in Ni(i-quin)$_4$(NO$_2$)$_2$ by measuring its infrared spectrum over a pressure range. Typical spectra measured over the range 1050 cm^{-1} to 1450 cm^{-1} as a powder compressed between diamond windows using a Perkin-Elmer Model 180 spectrophotometer, are shown in Fig. 1. The pressure was calibrated by observing the shift in frequencies of a small amount of polyethylene incorporated with the sample [7].

The infrared spectrum of Ni(i-quin)$_4$(NO$_2$)$_2$ at atmospheric pressure shows strong peaks at ~1315 cm^{-1} and 1125 cm^{-1} and these have been assigned [1] to the antisymmetric NO stretching frequency of the nitro and nitrito groups, respectively. The symmetric NO stretch of the nitrito group has been assigned to the shoulder occurring at 1400 cm^{-1}, that of the nitro group being too weak to distinguish unambiguously from the peaks due to the amine [1]. When the pressure was increased by increments to 18

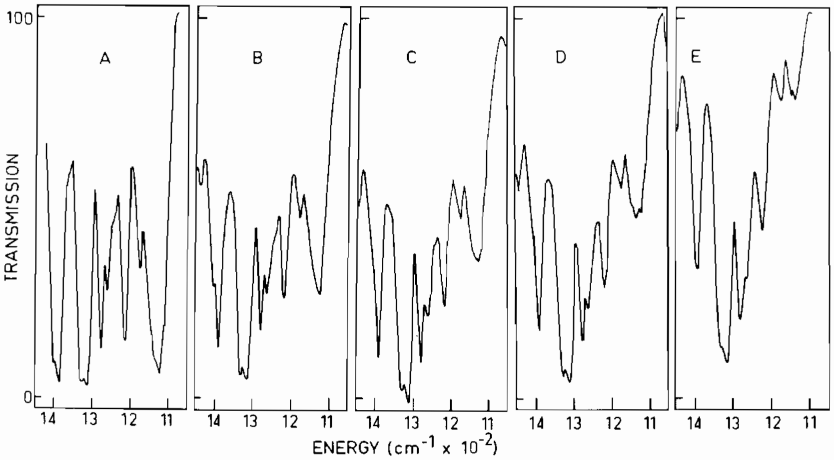

Fig. 1. The infrared spectrum of Ni(i-quin)$_4$(NO$_2$)$_2$ measured at: A 0, B 3.5, C 7, D 11 and E 18 kbar applied pressure.

kbar, and back to atmospheric pressure again, the peak at 1125 cm^{-1} decreased progressively in intensity and the shoulder at 1400 cm^{-1} gradually disappeared, while the peak at 1325 cm^{-1} became broader and relatively more intense. The changes were quite reversible and occurred without any detectable hysteresis effects. These results suggest that at atmospheric pressure $Ni(i\text{-}quin)_4(NO_2)_2$ does indeed contain a mixture of nitro and nitrito groups, and that as the pressure is raised the proportion of nitrogen to oxygen bound nitrite ions increases progressively until by ~20 kbar essentially only nitro groups are present.

The fact that the nitro form is favored at high pressure is in agreement with the previous studies of solution equilibria [5], and with the supposition that a nitrocomplex occupies a smaller effective volume than the corresponding nitritocomplex. In order to see whether the change in nitrite coordination was accompanied by an alteration in the crystal structure, the X-ray powder pattern of the complex was measured by the Debye-Scherrer method at atmospheric pressure, and ~25 kbar. Although the compound gave a poorly resolved diffraction pattern, this showed no change either in the relative intensity, or number of the diffraction lines upon increasing the pressure, suggesting that no change in the gross crystal structure of the complex accompanies the change in the manner of coordination of the nitrite groups. When considered in conjunction with the fact that the infrared spectra show that the nitrito to nitro conversion takes place continuously and reversibly over the pressure range 0–20 kbar this suggests that the complex may well consist of $Ni(i\text{-}quin)_4(NO_2)_2$ molecules having a statistically disordered distribution of nitro and nitrito groups, rather than distinct isomers of the type $Ni(i\text{-}quin)_4(-NO_2)_2$ and $Ni(i\text{-}quin)_4(-ONO)_2$. Further efforts are being made to grow crystals of the compound of satisfactory quality for X-ray studies to clarify this point.

Acknowledgements

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