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Molecular Motions in the Solid State: the Thermochromic Nitro–Nitrito Interconversion in Nickel(II) Bis(diamine) Complexes

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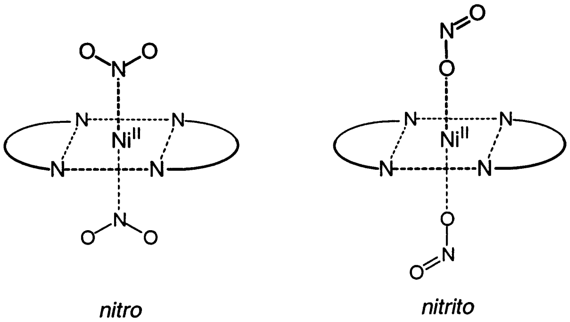
The NO_2^- ion, in the trans-octahedral $[Ni^{II}(N,N'\text{-dimethylethylenediamine})_2(NO_2)_2](H_2O)$ complex, coordinates the metal through the nitrogen atom (*nitro* form). On heating the solid complex, the anion rotates to give *nitrito* coordination (oxygen bound), according to a reversible process. The coordination mode of NO_2^- to Ni^{II} is related to the steric interplay between the anion and the alkyl substituents on the diamine.

Linkage isomerism is observed in coordination compounds when an ambidentate ligand (e.g., NCS^-) binds the metal center through the one or the other of its two terminal donor atoms, giving rise to two different complexes. The relative stability of the two isomers is associated primarily with the donating tendencies of the two donor atoms: the more stable isomeric form will be that in which the ambidentate ligand is bound through its more donating atom. Moreover, also steric effects can play a determining role, when the two binding modes involve different steric hindrance toward coligands present in the coordination sphere. A classical example in this sense refers to the nitro−nitrito isomerism in complexes of formula $Ni^{II}L_2(NO_2)_2$, in which L indicates an *N*-alkyl substituted ethylenediamine.[1] A trans-octahedral stereochemistry has been observed for these complexes, with the two diamine ligands coordinated in the equatorial plane and the two NO_2^- ions occupying the axial sites.

In the absence of serious steric effects (steric repulsion between the anions and the alkyl substituents on the amine nitrogen atoms), the NO_2^- ions are bound to the metal through the nitrogen atoms (*nitro* form, $Ni^{II}L_2(NO_2)_2$), whereas, in the presence of a heavier alkyl substitution, the *nitrito* isomer forms (oxygen atom coordinated, $Ni^{II}L_2(ONO)_2$). Formation of either isomer can be visually perceived, as the nitro complexes show a pink-red color (which is associated with a d−d band centered at around 500 nm, as measured in a noncoordinating solvent, e.g., $CHCl_3$). On the other hand, nitrito complexes exhibit a blue color (d−d band centered at ca. 600 nm). Moreover, it has been observed that nitro complexes in a $CHCl_3$ solution undergo conversion to the nitrito form on heating, through a fast and reversible equilibrium: in fact, on cooling, the pink-red form is quickly restored.[2] Such a behavior represents an interesting example of thermochromism in solution, associated wiht a well-defined motion of the NO_2^- ion.



We were interested in verifying the occurrence of thermochromic changes in the *solid* phase for this type of complex. In particular, we considered the $Ni^{II}L_2(NO_2)_2$ complexes of the two substitutionally isomeric diamines: *N*,*N′*-dimethylethylenediamine, **1**, and *N*,*N*-dimethylethylenediamine, **2**.

The $[Ni^{II}(\mathbf{1})_2(NO_2)_2](H_2O)$ complex was obtained as a pink-red microcrystalline solid: the absorption spectrum of the solid complex, finely ground and spread on filter paper, showed a band centered at 500 nm (see Figure 1), which is indicative of a *nitro* coordination. Binding through the NO_2^- nitrogen atom had been demonstrated by X-ray analysis on a single crystal of the $[Ni^{II}(\mathbf{1})_2(NO_2)_2](H_2O)$ complex.[3]

On the other hand, the corresponding complex of **2**, $[Ni^{II}(\mathbf{2})_2(NO_2)_2]$, is blue (absorption band of the solid complex centered at 590 nm, see the spectrum in Figure 1), which indicates *nitrito* coordination. Most importantly, a previously reported crystallographic investigation on the same complex had shown that each NO_2^- ion is axially coordinated through one of the oxygen atoms.[3]

We observed that the two solid isomeric complexes $[Ni^{II}(\mathbf{1})_2(NO_2)_2](H_2O)$ and $Ni^{II}(\mathbf{2})_2(ONO)_2$ display very different

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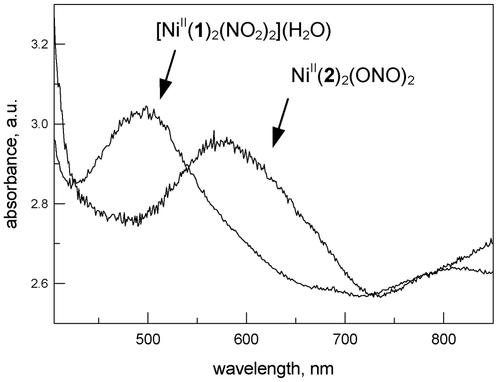

Figure 1. Spectra of the solid complexes spread on filter paper, at 25 °C: $[Ni^{II}(\mathbf{1})_2(NO_2)_2](H_2O)$, nitro; $Ni^{II}(\mathbf{2})_2(ONO)_2$, nitrito.

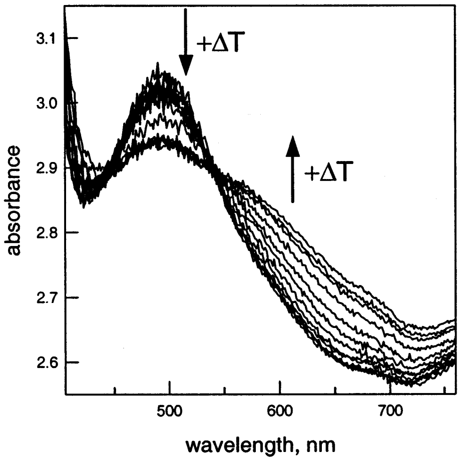

Figure 2. d−d absorption spectra of the solid $[Ni^{II}(N,N'\text{-dimethylethylenediamine})_2(NO_2)_2](H_2O)$ complex, spread on filter paper, over the temperature range 25−132 °C. On heating, the band at 500 nm (nitro) decreases, whereas the band at ca. 600 nm (nitrito) increases.

thermal behavior. In fact, on heating the solid $Ni^{II}(\mathbf{2})_2(ONO)_2$ blue complex, neither color change nor spectral modifications were observed. On the contrary, on heating the solid $[Ni^{II}(\mathbf{1})_2(NO_2)_2](H_2O)$ complex, the color gradually changed from pink-red toward blue and distinct variations were observed in the absorption spectrum of the powder spread on the filter paper. The family of spectra measured over the 25−132 °C temperature range is shown in Figure 2.

At temperatures higher than 132 °C, spectra were not reproducible, probably due to modifications of the paper support. It is observed that, on heating, the band of the nitro complex, with λ_{max} at 500 nm, decreases in intensity (see Figure 2), while a new band develops at ca. 600 nm (to be ascribed to the nitrito isomer). This spectral behavior can be explained by supposing that, on heating, the nitro form of $[Ni^{II}(\mathbf{1})_2(NO_2)_2](H_2O)$ smoothly converts to the nitrito derivative. Notice, however, that at the highest investigated temperature, 132 °C, the conversion is not yet complete: assuming that the limiting spectrum of the $Ni^{II}(\mathbf{1})_2(ONO)_2$ complex is similar to that observed for the $Ni^{II}(\mathbf{2})_2(ONO)_2$ complex (Figure 1), conversion has taken place to ca. 50%. Noticeably, the family of spectra discloses well-defined isosbestic points, which demonstrates that only *two* species coexist in the solid state equilibrium. It is suggested that the two trans NO_2^- ions, on heating, rotate simultaneously, moving from the nitro to the nitrito coordination mode, and no mixed species (e.g., $Ni^{II}(\mathbf{1})_2(NO_2)(ONO)$) form as an intermediate, during the conversion process.

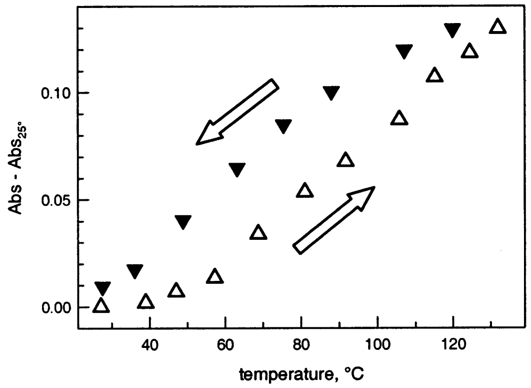

Figure 3. Thermal behavior of the solid $Ni^{II}(N,N'\text{-dimethylethylenediamine})_2(NO_2)_2$ complex, spread on filter paper, over the temperature range 25−132 °C. Vertical axis reports the difference between current absorbance at 610 nm (nitrito form) and the absorbance at 610 nm, measured at 25 °C. Open triangles: increasing temperature. Filled triangles: decreasing temperature.

Moreover, making the rather rough assumption that an equilibrium exists in the solid state, the constant *K* of the nitro-to-nitrito conversion can tentatively be evaluated from spectral data. In particular, it was assumed that the limiting spectrum of the nitrito form of the $[Ni^{II}(\mathbf{1})_2(NO_2)_2]$ complex corresponds to that of $Ni^{II}(\mathbf{2})_2(ONO)_2$, as shown in Figure 1. Then, the valves of *K* for the nitro-to-nitrito conversion $Ni^{II}L(NO_2) \leftrightarrows Ni^{II}L(ONO)_2$ were calculated at each temperature over the 25−132 °C temperature range.[4] The ln *K* vs $1/T$ plot was found reasonably linear and produced the following thermodynamic quantities: $\Delta H° = 8.5 \pm 0.4$ kcal mol^{-1}, $\Delta S° = 21 \pm 1$ cal mol^{-1} K^{-1}. The endothermic enthalpy change reflects the variation of the energy of the axial bonds on replacing nitrogen with oxygen. The distinctly positive entropy change indicates an increase of disorder probability associated with the nitro−nitrito conversion, which should include a rearrangement of the carbon backbone of the ligands. In fact, the mere statistical contribution of the $M{-}NO_2 \rightarrow M{-}ONO$ change (NO_2^- offers only one donor atom, ONO^- two) is only 1.37 cal mol^{-1} K^{-1} per anion ($= R \ln 2 - R \ln 1$).

Very interestingly, on cooling, the band of the nitrito species decreases, while the band of the nitro form is progressively restored. The reversible thermochromic change shows a moderate hysteresis, as demonstrated by the diagram in Figure 3, in which the difference between absorbance at 610 nm (band of the nitrito complex) at varying temperatures and the absorbance at 610 nm measured at 25 °C is plotted vs temperature: it is observed that the heating curve (open triangles) and the cooling curve (filled triangles) are distinctly separated. In particular, over the 60−110 °C interval, the temperature delay, i.e., the additional Δ*T* necessary to reach the same degree of nitrito-to-nitro conversion, is about 20−25 °C.

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[4] The constants were calculated as follows (Abs = absorbance): K = [current Abs of $[Ni^{II}(\mathbf{1})_2(NO_2)_2](H_2O)$ at 600 nm/Abs of $[Ni^{II}(\mathbf{2})_2(NO_2)_2]$ at 600 nm]/[current Abs of $[Ni^{II}(\mathbf{1})_2(NO_2)_2](H_2O)$ at 500 nm/Abs of $[Ni^{II}(\mathbf{1})_2(NO_2)_2](H_2O)$ at 25 °C]. Absorbances of each band were corrected for the contribution due to the other band.

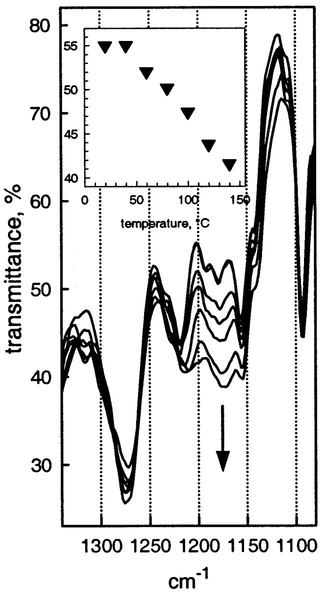

Figure 4. IR diffuse reflectance spectra of the solid $[Ni^{II}(N,N'$-dimethylethylenediamine$)_2(NO_2)_2](H_2O)$ complex, in a 5:95 mixture with KBr, over the temperature range 20−140 °C. The transmittance at 1170 cm^{-1} (stretching of the oxygen-bound ONO^- anion) decreases with increasing temperature (see also inset).

The temperature-induced nitro-to-nitrito isomerization could also be followed through the diffuse reflectance IR spectra of a $[Ni^{II}(\mathbf{1})_2(NO_2)_2](H_2O)$/KBr mixture (5:95), over the 20−140 °C range (see Figure 4). In particular, it was observed that a band at 1170 cm^{-1} distinctly develops with increasing temperature. This band has to be ascribed to the stretching of the oxygen-bound ONO^- ion (to be compared to the similar stretching observed in the diffuse reflectance IR spectrum of the $[Ni^{II}(\mathbf{2})_2(ONO)_2]$ complex: 1150 cm^{-1}). Noticeably, the decrease with temperaure of the transmittance at 1170 cm^{-1} (inset of Figure 4) parallels the increase of the d−d band intensity at ca. 600 nm (open triangles in Figure 3).

Finally, a comment should be made on the possible role of the water molecule of the $Ni^{II}(\mathbf{1})_2(NO_2)_2(H_2O)$ complex in the thermochromic conversion. The question is whether the water molecule participates in the thermochromic transition. Thermogravimetric analysis on the $Ni^{II}(\mathbf{1})_2(NO_2)_2(H_2O)$ complex showed that no weight loss occurred until 140 °C. At this temperature weight loss began with a flex in the weight vs temperature curve at 175 °C: this corresponds to a weight loss of 6.0% (calculated value for the loss of a water molecule from $Ni^{II}(\mathbf{1})_2(NO_2)_2(H_2O)$: 5.5%). Afterward, a further continuous weight loss was observed, to be ascribed to the decomposition of the complex salt. The above evidence indicates that the water molecule does not interfere with the red-to-blue color change, being lost at a temperature at which most of the nitro-to-nitrito conversion has taken place.

Solid phase reversible thermochromism is an interesting and rather rare phenomenon in coordination chemistry.[5] For nitro−nitrito complexes, no quickly reversible temperature dependent interconversion had been previously noticed in the solid state.

The reversible red-to-blue interconversion of $Ni^{II}(\mathbf{1})_2(NO_2)_2$ can be visually followed by exposing a piece of filter paper spread with the thermochromic complex to the heat produced by a hot electrical plate. Quick color changes are observed when moving the paper consecutively close to and far away from the plate.

The intimate nature of the red-to-blue thermochromic conversion of the $[Ni^{II}(\mathbf{1})_2(NO_2)_2](H_2O)$ complex can be tentatively explained by considering that, on heating, vibrations of the diamine backbone and, in particular, of the methyl substituents increase their amplitude. As a consequence, the space available for the axially bound anions is reduced: thus, each NO_2^- ion prefers to rearrange to the less space demanding nitrito mode of coordination. The intrinsic mechanism of the nitro−nitrito interconversion (a pirouette of the NO_2^- ion) is kinetically uncomplicated and is characterized by a moderate energy barrier (which is expressed by the hysteresis observed during heating−cooling cycles). The above arguments also account for insensitivity to heating of the blue $Ni^{II}(\mathbf{2})_2(ONO)_2$ complex, in which the anion has been forced to adopt the less space demanding coordination mode even at room temperature and cannot undergo any further rearrangement.

It has to be noted that for the temperature-induced nitro-to-nitrito transition of the $[Ni^{II}(N,N'$-dipropylethylenediamine$)_2(NO_2)_2]$ complex a different mechanism has been observed.[6] In particular, one of the NO_2^- ions leaves the coordination sphere, while the other chelates the Ni^{II} center with the two oxygen atoms. A similar structural rearrangement had been proposed for the Ni^{II}(ethylenediamine$)_2(NO_2)_2$ complex.[7] However, in the present case, IR reflectance spectra at varying temperatures showed the development of a band of the oxygen-bound ONO^- anion (at 1170 cm^{-1}, see Figure 4), supporting the mechanism of the simultaneous rotation of the two NO_2^- ions.

Solid state thermochromic behavior is of special interest in the design of devices for visual and prompt monitoring of temperature changes. The reversible nitro−nitrito interconversion in nickel(II) bis(diamine) complexes can provide a class of thermochromic materials whose mechanism has been well understood and whose behavior can be designed at will, through a well-thought choice of the substituents on the diamine coligand.

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Supporting Information Available: Plot of ln *K* vs 1/*T* from spectral data in Figure 2 and thermogravimetric profile for the $Ni^{II}(\mathbf{1})_2(NO_2)_2(H_2O)$ complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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