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The Nature of the Blue Isomer of Ni(1,2-diaminoethane)$_2$(NO$_2$)$_2$

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The nitrite ion is unusual as a ligand, because of the large number of ways it can coordinate to metal [1]. This gives rise to the possibility of linkage isomerism, best known in the nitro and nitrito isomers of cobalt(III) [2] and nickel(II) [3, 4]. The colour of a nitrite complex often depends upon its coordination type. Thus, nickel(II) complexes containing nitrogen bonded nitrites are typically red, while those in which oxygen bound nitrites occur are blue. The red compound $Ni(en)_2(NO_2)_2$, en = 1,2-diaminoethane, is known to be a *trans* nitrocomplex at room temperature [5], but it was observed that on heating to ~120 °C this complex turns blue [6, 7]. The change is reversible and was interpreted in terms of a nitro–nitrito equilibrium of the form:

$$Ni(en)_2(NO_2)_2 \text{ (red)} \rightleftharpoons Ni(en)_2(ONO)_2 \text{ (blue)}$$

A nitrito complex is expected to occupy a larger volume than the corresponding nitro complex, and in several systems it has been found that the application of high pressure shifts a nitro–nitrito equilibrium in favour of the nitro isomer [8]. The pressure dependence of the electronic spectrum of $Ni(en)_2(NO_2)_2$ has also been interpreted in terms of a nitro-nitrito equilibrium of the above kind on this basis [9].

It has been pointed out, however, that the nitrite infrared spectrum reported for blue $Ni(en)_2(NO_2)_2$ is inconsistent with the presence of monodentate nitrito groups and it was suggested that the red to blue conversion might involve a change of the form:

$$Ni(en)_2(NO_2)_2 \text{ (red)} \longrightarrow [Ni(en)_2(NO_2)]NO_2 \text{ (blue)}$$

with the blue isomer containing one bidentate and one ionic nitrite per nickel [10]. Various modes of bidentate coordination are feasible, as complexes of general formula $[Ni(en)_2(NO_2)]X$ are known in which the nitrite is bound in several different ways. When X = Cl^-, Br^- or NO_3^-, the nitrite chelates [11], while when X = ClO_4^- or BF_4^-, μ(N, O) bridging nitrite ligands occur [12]. When X = $(C_6H_5)_4B^-$, the novel complex $[Ni_2(en)_4(NO_2)_2][(C_6H_5)_4B]_2$ occurs, containing dimers involving one tridentate nitrite and a monodentate nitrito group [13]. The present study provides evidence to suggest that this second hypothesis is in fact correct, with blue $Ni(en)_2(NO_2)_2$ containing one chelating and one ionic nitrite *per* nickel ion.

Experimental

Preparation of the Complexes

The red isomer of $Ni(en)_2(NO_2)_2$ and $Zn(en)_2(NO_2)_2$ were prepared as described previously [4, 14] and characterised by means of their infrared spectra. The metastable blue form of $Ni(en)_2(NO_2)_2$ was prepared as described by Green [7], by heating a sample of the red isomer for two hours in boiling 1-butanol, producing a suspension of a dark blue solid.

Physical Measurements

X-ray powder diffraction measurements were made using a Phillips PW 1010/25 automatic diffractometer, infrared spectra were recorded as KBr disks using a Digilab FTS20E spectrometer, and electronic spectra were measured as mulls in silicone vacuum grease at 295 K and ~30 K using a Cary 17 spectrophotometer, the samples being cooled using a Cryodyne 21 cryostat.

Results and Discussion

The nitrite ion has three infrared active vibrations, the symmetric and antisymmetric NO stretches, γ_s and γ_{as}, and the wagging mode δ_{NO_2}. These occur at 1335 cm^{-1} (very weak), 1250 cm^{-1} (strong) and 830 cm^{-1} (weak, sharp), respectively, in $NaNO_2$ [15]. In a complex the energy of γ_{as} shifts in a manner characteristic of the manner of nitrite coordination [1]. The red form of $Ni(en)_2(NO_2)_2$ shows a strong peak at 1285 cm^{-1} which may be assigned to γ_{as} of the nitro groups in this complex [1]. In the blue isomer of $Ni(en)_2(NO_2)_2$ this is replaced by a peak of similar intensity at 1242 cm^{-1}, the other bands shifting only slightly in position. This was interpreted by Green [8] as indicating a change to nitrito coordination of the nitrite groups. However, an energy of 1242 cm^{-1} is inconsistent with values observed in other complexes where monodentate nitrito coordination to nickel(II) is known to occur, when the corresponding band occurs in the range 1100–1140 cm^{-1} [16]. The observed value of γ_{as} is in fact very similar to that of the uncoordinated nitrite ion, being also in the range observed for bidentate chelating or μ(NO) bridging nitrite groups (1200–1250

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cm^{-1}) [1]. The complex Zn(en)$_2$(NO$_2$)$_2$ is known to be of the form [Zn(en)$_2$(O$_2$N)]NO$_2$, with one ionic and one chelating nitrite per Zn(II) [17], and the infrared spectrum of this was found to be very similar to that of the blue form of Ni(en)$_2$(NO$_2$)$_2$, with an intense nitrite absorption also occurring at 1242 cm^{-1}. This is presumably due to a superposition of the peaks arising from γ_{as} of the ionic and chelating nitrite ions. X-ray powder diffraction patterns were recorded for the red and blue forms of Ni(en)$_2$(NO$_2$)$_2$, and Zn(en)$_2$(NO$_2$)$_2$. The diffraction pattern of blue Ni(en)$_2$(NO$_2$)$_2$ was quite different from that of red Ni(en)$_2$(NO)$_2$, the Bragg angles of the peaks being very similar to those observed for Zn(en)$_2$(NO$_2$)$_2$. This suggests that the blue isomer and Zn(en)$_2$(NO$_2$)$_2$ have similar unit cell dimensions and probably also nitrite coordination, with the nickel compound also containing one chelating and one ionic nitrite per formula unit.

The above conclusion is supported by the electronic spectra of the two forms of Ni(en)$_2$(NO$_2$)$_2$ (Fig. 1). The spectrum of the red isomer at ~30 K shows band maxima at 13,000 cm^{-1} (with a shoulder at 11,600 cm^{-1}) and 19840 cm^{-1}, these being similar in energy to those reported for a single crystal of this complex at room temperature [18]. In the spectrum of the blue isomer, the lower energy peak is shifted to 11,500 cm^{-1}, this being consistent with the lower ligand field strength of oxygen compared with nitrogen bonded nitrite groups. Of more significance, however, is the fact that the peak at 19840 cm^{-1}, which has been assigned as a weak metal → ligand charge transfer transition [19] is replaced by a pair of bands centred at 18,350 cm^{-1} and 21,650 cm^{-1}, the latter being relatively weak. The disappearance of the band at ~20,000 cm^{-1} which is characteristic of nitrite groups bound to nickel(II) via nitrogen confirms that no μ(NO) bridging groups are present in blue Ni(en)$_2$(NO$_2$)$_2$ (the spectrum of [Ni(en)$_2$(NO$_2$)]ClO$_4$, which contains linkages of this kind, has bands centred at 12,500 cm^{-1} and 20,450 cm^{-1} [20]). The peaks at 18,350 and 21,650 cm^{-1} observed for blue Ni(en)$_2$(NO$_2$)$_2$ are very similar in energy and relative intensity to those reported for [Ni(NN'diethylethenediamine)$_2$(O$_2$N)]NO$_2$ [21] and [Ni(1,2-diphenylethylenediamine)$_2$(O$_2$N)]NO$_2$ each of which contains one chelating and one ionic nitrite per nickel [21, 22]. For these, the lower energy band was assigned to the $^3T_{1g}(F) \leftarrow {}^3A_{2g}$d–d transition, whilst that at ~21,600 cm^{-1} was assigned as a spin-forbiddent $\pi^* \leftarrow n$ internal nitrite transition [21]. It was suggested [21] that the latter band, which has so far only been observed for complexes containing chelating nitrite groups, is most likely characteristic of this manner of nitrite coordination. The low temperature spectrum of blue Ni(en)$_2$(NO$_2$)$_2$ also shows a series of weak, sharp peaks in the region 405–370 nm. These consist of two progressions, each of energy 597 ± 15 cm^{-1} built upon initial members centred at 24,832 cm^{-1} and 24,950 cm^{-1}. Similar progressions have been observed in NaNO$_2$ [23] and various nitrite complexes and it was concluded that they are part of the band structure of a $\pi^* \leftarrow n$ internal nitrite transition, the progressional interval of ~600 cm^{-1} being in the δ_{NO_2} wagging mode of the excited electronic state, coupled for the higher energy progression to the excitation of a single quantum of a lattic mode of energy ~115 cm^{-1}.

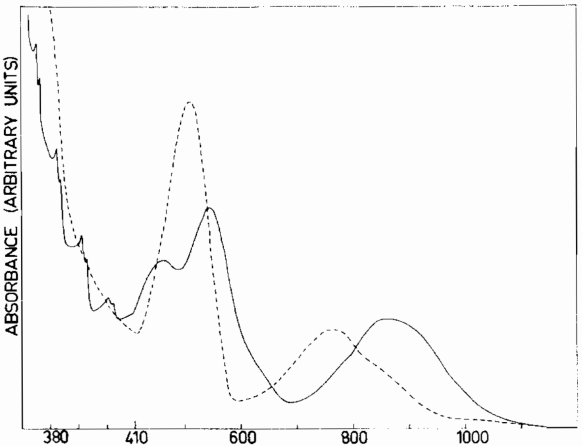

Fig. 1. Electronic spectrum at ~30 K of mulls of the blue (solid line) and red (dashed line) isomers of Ni(en)$_2$(NO$_2$)$_2$. Spectra were also recorded at 298 K and differed from those at low temperature only in being more poorly resolved and in slight shifts of some of the band maxima to lower energy. Note the change in the wavelength scale at 410 nm.

Conclusions

The reversible change from the low temperature red to the high temperature blue form of Ni(en)$_2$(NO$_2$)$_2$ most likely involves an equilibrium of the type:

$$\mathrm{Ni(en)_2(NO_2)_2\ (red)} \rightleftharpoons \mathrm{[Ni(en)_2(O_2N)]NO_2\ (blue)}$$

in which the blue isomer contains one chelating and one ionic nitrite per metal. A previous study of the pressure dependence of the electronic spectrum showed that subjecting the blue form to 30 Kbar pressure at ~126 °C converted it reversibly to the red form [9]. This was previously interpreted in terms of the intramolecular nitro–nitrito equilibrium proposed by Green [8]:

$$\mathrm{Ni(en)_2(NO)_2\ (red)} \rightleftharpoons \mathrm{Ni(en)_2(ONO)_2\ (blue)},$$

but the results are equally consistent with the present proposal, as it is likely that the blue isomer has a lower density than the red form [7]. It was noted that the red → blue conversion was favoured by an increase in entropy [9]. This is also in agreement with the present formulation of the blue isomer, as the red → blue transition involves an increase in the number of independent species in the system.

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