Crystal and Molecular Structure and Spectra of $K_4[Ni(NO_2)_6]\cdot H_2O$ and $K_3[Ni(NO_2)_4(O_2N)]$ *

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The crystal structure of the orange compound $K_4[Ni(NO_2)_6]\cdot H_2O$ has been determined. It shows that this contains an octahedral $[Ni(NO_2)_6]^{4-}$ complex anion with six *N*-bonded nitrite ligands and a water of crystallization. Dehydration at 100 °C produces a mixture of red $K_3[Ni(NO_2)_4(O_2N)]$ and KNO_2, with the latter occurring as microcrystallites ≈100 Å in size. Rehydration of the hygroscopic mixture at ≈20 °C causes $K_4[Ni(NO_2)_6]\cdot H_2O$ to be reformed. The nickel(II) in $K_3[Ni(NO_2)_4(O_2N)]$ has a distorted octahedral ligand environment, with four nitrites co-ordinated *via* nitrogen, and a fifth chelating. The infrared and electronic spectra of the compounds are discussed in terms of the difference in nitrite co-ordination.

The nitrite ion is a versatile ligand, co-ordinating to metal ions in several different ways.[1] The manner of bonding strongly influences the d-orbital splitting produced by this ligand, as well as the position and intensity of charge-transfer transitions,[2] so that a change in the mode of nitrite co-ordination to a transition-metal ion is usually accompanied by a significant alteration in colour. This is true of nickel(II) polynitrite complexes, where a variety of compounds of differing composition have been prepared. A range of compounds of the form $A_2B[Ni(NO_2)_6]$ are known, where A is a monovalent cation such as K^+, and B a divalent one such as Ca^{2+}. These are yellow-brown in colour, and X-ray crystal-structure analysis,[3] in conjunction with infrared spectroscopy,[4] has shown that all six nitrites bind to the Ni^{II} *via* nitrogen. The tetramethylammonium cation forms a highly insoluble yellow compound of stoichiometry $NMe_4[Ni(NO_2)_3]$ and infrared evidence suggests that this contains six-co-ordinate Ni^{2+} ions linked *via* the oxygen and nitrogen atoms of bridging nitrites.[5] With the larger alkali-metal ions Rb^+ and Cs^+ as counter cations, red compounds of the type $A_3[Ni(NO_2)_5]$ are formed, and on the basis of their infrared and electronic spectra it was suggested[6] that in these the Ni^{2+} is six-co-ordinate, with one nitrite bonding *via* both oxygen atoms. As the bands in the electronic spectrum appear relatively weak, it was inferred[6] that the Ni^{2+} ion in the $Cs_3[Ni(NO_2)_5]$ is probably in a centrosymmetric ligand environment, and hence that the bidentate nitrite group bridges, forming *trans* –ONO–Ni–ONO– linkages; however, it was pointed out[5] that the estimation of band intensities from reflection spectra is difficult, so that this conclusion is probably not warranted without further evidence.

It has been known for a hundred and fifty years that addition of Ni^{2+} ions to an aqueous solution of potassium nitrite produces an orange crystalline precipitate.[7] This was originally formulated as $K_4[Ni(NO_2)_6]$, and on the basis of a two-dimensional X-ray structure analysis[8] and an infrared study[9] it was proposed that it contains a $[Ni(NO_2)_6]^{4-}$ group involving six *N*-bonded nitrite ligands. It was subsequently shown that the compound is in fact a monohydrate, though the infrared and electronic spectra suggested that the water molecule is not bonded to the Ni^{2+} ion.[5] However, it was observed that on dehydration by heating to ≈100 °C the compound turns brick red in colour, reverting to the orange monohydrate on cooling to room temperature in the presence of water vapour. On the basis of the difference in the electronic transition energies and infrared spectra it was initially suggested[5,10] that on going from the orange to the red compound, two nitrite groups switch from nitrogen to monodentate oxygen co-ordination, so that the anhydrous compound has the form $K_4[Ni(NO_2)_4(ONO)_2]$. However, it was subsequently noted[11] that the spectral characteristics of the anhydrous potassium compound are very similar to those of the rubidium and cesium pentanitrite complexes. This implied that the former compound is probably better formulated as $K_4[Ni(NO_2)_4(O_2N)]\cdot NO_2$, with the Ni^{2+} co-ordinated to four nitro groups and the two oxygen atoms of a bidentate nitrite, with the remaining nitrite present as a free ion in the lattice. To investigate the cause of the above colour change in more detail, we have determined the structures of the anhydrous and monohydrated potassium nickel nitrite complexes by X-ray diffraction, and the present paper describes the results of this study, together with an interpretation of the infrared and electronic spectra of the two compounds.

Experimental

Preparation of Compounds and Measurement of Spectra.— Orange crystals of $K_4[Ni(NO_2)_6]\cdot H_2O$ were prepared as described previously.[5] The red, anhydrous compound was formed as previously reported,[5] by heating a finely ground sample of the orange monohydrate to constant weight in a vacuum at 100 °C using a drying pistol. This required about 24 h and the decrease in mass corresponded to the loss of one molecule of water per formula unit. Both compounds were characterized by comparing their infrared and electronic spectra with those already described.[5,10] As also noted previously,[5] a sample of the dehydrated compound left in the atmosphere was observed to revert to the orange monohydrate in about a day.

The X-ray powder pattern of the above anhydrous compound suggested that this in fact consists of a mixture of potassium nickel(II) pentanitrite and potassium nitrite, so may be formulated as $K_3[Ni(NO_2)_4(O_2N)]\cdot KNO_2$ (see Discussion below). It was hoped that it might be possible to stabilize the pure pentanitrite by removing the potassium nitrite by extraction with a suitable solvent. Tests showed that dry potassium

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Crystallographic data for $K_4[Ni(NO_2)_6]\cdot H_2O$ and $K_3[Ni(NO_2)_4(O_2N)]$

	$K_4[Ni(NO_2)_6]\cdot H_2O$	$K_3[Ni(NO_2)_4(O_2N)]$
M	509.1	406.0
Crystal system	Rhombohedral	Monoclinic
Space group	$R3$	$P2_1/m$
a/Å	7.5988(8)	7.240(1)
b/Å		10.946(2)
c/Å	22.400(3)	7.120(1)
β/°		98.086(6)
U/Å^3	1120.2	558.6
D_c/g cm^{-3}	2.26	2.41
Z	3	2
μ(Mo-Kα)/cm^{-1}	24.2	28.9
Crystal size/mm	0.26 × 0.30 × 0.17	0.06 × 0.15 × 0.17
Scan speed/° min^{-1}	2	1.2
Data collection range	$\pm h, \pm k, \pm l$, 4–60° (2 θ)	$\pm h, \pm k, \pm l$, 4–70°
No. of measured reflections	2350	3969
No. of independent reflections used in refinement	673	1262
R_{int} for averaged reflections	0.037	0.046
R (unit weights)	0.040	0.056

Details in common: θ–2θ scans; scan width 2.4 + $\Delta\theta$° where $\Delta\theta = \alpha_1 - \alpha_2$ separation.

nitrite is slightly soluble in dry ethanol ($\approx$0.4 g per 100 cm^3), and very slightly soluble in dry acetonitrile ($\approx$0.05 g per 100 cm^3). About 0.1 g of the red, anhydrous $K_3[Ni(NO_2)_4(O_2N)]\cdot KNO_2$ was extracted with boiling dry ethanol (25 cm^3) (BDH Analar grade dried over 3 Å molecular sieves) in a Soxhlet extractor for 24 h. After this time, several small, pale green patches had developed on the residue, presumably due to impurities formed by reaction with the ethanol. However, the residue proved largely stable to exposure to a moist atmosphere, and a small quantity of stable red material was separated by hand from the green material and traces of the orange monohydrate and the infrared spectrum of this suggested that it was largely the desired pentanitrite (see following section). The solvent from the extraction contained a mixture of white crystals, presumably KNO_2, and small red needles. X-Ray analysis suggested that the latter might be $K_3[Ni(NO_2)_4(O_2N)]$, but they invariably exhibited evidence of twinning. Extraction in an identical manner with acetonitrile dried over 3 Å molecular sieves produced a residue which largely reverted to the orange hydrate on exposure to a moist atmosphere, but produced in the extracting solvent, together with a white residue, small red crystals which proved quite stable in the atmosphere and amenable to analysis by X-ray diffraction. As described below, these proved to be $K_3[Ni(NO_2)_4(O_2N)]$.

Infrared spectra were measured using a Digilab FTS-20E spectrometer and KBr discs prepared with potassium bromide freshly dried by heating to 110 °C.

Structure Determinations.—Crystals of both compounds were verified as single crystals using precession photographs, and transferred to a Siemens AED diffractometer for intensity data collections (Mo-Kα radiation). The crystal of $K_3[Ni(NO_2)_4(O_2N)]$ was coated with silicone grease to protect it from reaction with atmospheric moisture. Lattice parameters were determined by the least-squares technique applied to the setting angles of 18 reflections with $2\theta > 18°$. A standard reflection was monitored every 50 reflections to correct for intensity drift during the data collection. Details of the data collection and refinement are summarized in Table 1.

For $K_4[Ni(NO_2)_6]\cdot H_2O$, the published coordinates of Ferrari *et al.*[8] were used as starting values for the refinement. Some problems were encountered initially due to the different setting (reverse setting[8]) of the rhombohedral cell in the earlier study. These were overcome and the refinement proceeded smoothly, allowing the location to be established of the water molecule oxygen, O_w, which was not found in the earlier study. With anisotropic thermal parameters for all atoms except O_w the refinement converged at a final R value (unit weights) of 0.040. The largest Δ/σ was 0.04 and the largest peak in the Fourier difference map was 0.4 e Å^{-3}.

For $K_3[Ni(NO_2)_4(O_2N)]$ the coordinates of the nickel and potassium atoms were established by direct methods and the nitrogen and oxygen atoms were located in Fourier maps. One of the oxygen atoms, O(6), was found to be disordered over sites located 0.25 Å on either side of the mirror plane at $y = \frac{1}{4}$. Refinement using anisotropic thermal parameters for all atoms converged at a final R value (unit weights) of 0.056. The largest Δ/σ was 0.02 and the largest peak in the Fourier difference map was 1.2 e Å^{-3}, close to the nickel atom. The atomic scattering factors for neutral atoms and anomalous dispersion coefficients were taken from ref. 12. All computing was performed with the SHELX 76 system of programs.[13] Final atomic coordinates are reported in Tables 2 and 3 for $K_4[Ni(NO_2)_6]\cdot H_2O$ and $K_3[Ni(NO_2)_4(O_2N)]$ respectively, bond lengths and angles are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Crystal Structure.—The crystal structure of $K_4[Ni(NO_2)_6]\cdot H_2O$ has been described by Ferrari *et al.*[8] The present refinement confirms the details of the atomic arrangement at a higher precision than obtained in the earlier study based on film data and in addition, reveals the location of the water molecule. The nickel atom is octahedrally co-ordinated to six equivalent nitrite groups, through the nitrogen atom, with *trans* ligands being coplanar in an arrangement similar to that observed for the salts $K_2A[Ni(NO_2)_6]$, where A is Ba, Sr or Pb.[3] The Ni–N bond length and internal dimensions of the nitrite groups are also very similar to those in the other nickel(II) hexanitro complexes. The nickel and potassium atoms stack along the trigonal axis in the sequence Ni–K(1)–K(2)–K(2)–K(1)–Ni, with Ni–K(1) and K(1)–K(2) separations of 4.3 Å, and K(2) ··· K(2) 5.4 Å. The water molecule is located halfway between the pair of K(2) atoms, but displaced slightly off the trigonal axis to increase the K(2)–O_w distance. Possibly, the reason that the basic lattice of $K_4[Ni(NO_2)_6]\cdot H_2O$ becomes unstable on dehydration is because the water molecule is necessary to cushion the electrostatic repulsion between the K(2) ions.

Table 2 Atomic coordinates for $K_4[Ni(NO_2)_6]\cdot H_2O$

Atom	X/a	Y/b	Z/c
Ni	0.0	0.0	0.0
K(1)	0.0	0.0	0.192 01(6)
K(2)	0.0	0.0	0.379 81(8)
N	0.871 8(4)	0.743 3(4)	0.054 9(1)
O(1)	0.965 1(4)	0.728 3(4)	0.098 9(1)
O(2)	0.694 1(4)	0.602 9(4)	0.047 3(1)
O_w*	0.246(2)	0.662(3)	0.169(1)

* 1/6 occupancy of general site by disordered atom O_w.

Table 3 Atomic coordinates for $K_3[Ni(NO_2)_4(O_2N)]$

Atom	X/a	Y/b	Z/c
Ni	0.2890(2)	0.25	0.7594(2)
K(1)	0.6883(3)	0.25	0.2258(3)
K(2)	0.8041(2)	0.9926(2)	0.7256(2)
N(1)	0.3027(8)	0.0577(6)	0.7768(8)
N(2)	0.6188(13)	0.25	0.6780(15)
N(3)	0.0544(10)	0.25	0.5656(10)
N(4)	0.1698(11)	0.25	0.9976(11)
O(1)	0.2068(9)	0.0010(6)	0.8797(8)
O(2)	0.4056(8)	0.9971(6)	0.6869(9)
O(3)	0.4785(11)	0.25	0.5603(10)
O(4)	0.5788(11)	0.25	0.8470(11)
O(5)	0.9838(7)	0.3472(5)	0.5006(8)
O(6)*	0.0027(16)	0.2258(36)	0.0028(20)
O(7)	0.2747(12)	0.25	0.1548(10)

* 0.5 Occupancy of general site by disordered atom O(6).

In $K_3[Ni(NO_2)_4(O_2N)]$, octahedral co-ordination to nitrite groups is maintained by having four monodentate bonds through the nitrogen atom, as in $K_4[Ni(NO_2)_6]\cdot H_2O$, and one bidentate nitrito ligand with bonding through the oxygen atoms, O(3) and O(4). To our knowledge this is the first reported example of this particular configuration for a metal atom octahedrally co-ordinated by nitrite groups. In the corresponding copper compound $K_3[Cu(NO_2)_5]$, one copper atom is octahedrally co-ordinated to four monodentate and one bidentate NO_2 groups but two of the monodentate ligands are bonded through oxygen.[15] The participation of the bidentate ligand in the octahedral co-ordination results in a considerable angular distortion of the octahedron. The O(3)–Ni–O(4) angle is lowered to 59° in $K_3[Ni(NO_2)_4(O_2N)]$ whereas the octahedral bonds in $K_4[Ni(NO_2)_6]\cdot H_2O$ are within a relatively narrow range and close to 90°, see Table 4. The angle *trans* to the chelating nitrite [N(3)–Ni–N(4) 99°], is somewhat higher than the octahedral value. The bidentate nitrite is symmetrically chelated, as is generally the case when such a group is bonded to Ni^{2+},[15] in contrast to metal ions such as Cu^{2+}, Zn^{2+} and Cd^{2+}, where asymmetric co-ordination is usually observed.[14,16] In line with observations on other complexes,[17] it may be noted that the internal angle of the chelated nitrite [O(3)–N(2)–O(4) 111.7(9)°], is somewhat reduced from the value observed in $NaNO_2$, 114.9(5)°,[18] while those of the nitro groups are raised somewhat to 116–118° (Table 4). The geometries of the octahedra in $K_4[Ni(NO_2)_6]\cdot H_2O$ and $K_3[Ni(NO_2)_4(O_2N)]$ are compared in Fig. 1.

The structures of $K_4[Ni(NO_2)_6]\cdot H_2O$ and $K_3[Ni(NO_2)_4(O_2N)]$ are quite closely related as can be seen by viewing them along equivalent projection axes. For $K_3[Ni(NO_2)_4(O_2N)]$ an

Table 4 Bond lengths (Å) and angles (°) for $K_4[Ni(NO_2)_6]\cdot H_2O$ and $K_3[Ni(NO_2)_4(O_2N)]$

$K_4[Ni(NO_2)_6]\cdot H_2O$			
Ni–N	2.090(3) (× 6)	N–Ni–N	88.9(1) (× 6), 91.1(1) (× 6)
N–O(1)	1.251(4)	O(1)–N–O(2)	116.8(3)
N–O(2)	1.245(4)		
K(1)–O(1)	2.852(3), 2.872(2)	K(2)–O(2)	2.867(3), 3.013(3)
K(1)–O(2)	2.872(3)	K(2)–O_w	2.71(1), 2.82(1)
$K_3[Ni(NO_2)_4(O_2N)]$			
Ni–N(1) (× 2)	2.110(6)	N(1)–Ni–N(3)	93.9(1) (× 2)
Ni–N(3)	2.032(7)	N(1)–Ni–N(4)	88.4(2) (× 2)
Ni–N(4)	2.008(8)	N(1)–Ni–O(3)	90.6(2) (× 2)
Ni–O(3)	2.107(8)	N(1)–Ni–O(4)	86.9(1) (× 2)
Ni–O(4)	2.103(7)	N(3)–Ni–O(3)	96.0(3)
		N(3)–Ni–N(4)	99.0(3)
		N(4)–Ni–O(4)	106.2(3)
		O(3)–Ni–O(4)	58.8(3)
N(1)–O(1)	1.244(9)	O(1)–N(1)–O(2)	117.6(6)
N(1)–O(2)	1.240(9)		
N(2)–O(3)	1.22(1)	O(3)–N(2)–O(4)	111.7(9)
N(2)–O(4)	1.28(1)		
N(3)–O(5) (× 2)	1.241(6)	O(5)–N(3)–O(5)	118.0(7)
N(4)–O(6)	1.24(2)		
N(4)–O(7)	1.26(1)	O(6)–N(4)–O(7)	116.1(9)
K(1)–O(1) (× 2)	2.975(7)	K(2)–O(1)	2.823(6), 2.969(6)
K(1)–O(2) (× 2)	2.878(7)	K(2)–O(2)	2.860(6), 3.113(7)
K(1)–O(3)	2.999(8)	K(2)–O(4)	3.427(5)
K(1)–O(4)	2.702(8)	K(2)–O(5)	2.860(6)
K(1)–O(5) (× 2)	2.891(5)	K(2)–O(6)	3.26(3), 3.42(3)
K(1)–O(6) (× 2)	2.96(1)	K(2)–O(7)	2.870(4)
K(1)–O(7)	2.966(9)	K(2)–N(2)	3.118(4)
K(1)–N(3)	3.328(7)	K(2)–N(4)	3.296(5)
K(1)–N(2)	3.33(1)		
K(1)–N(1) (× 2)	3.369(6)		

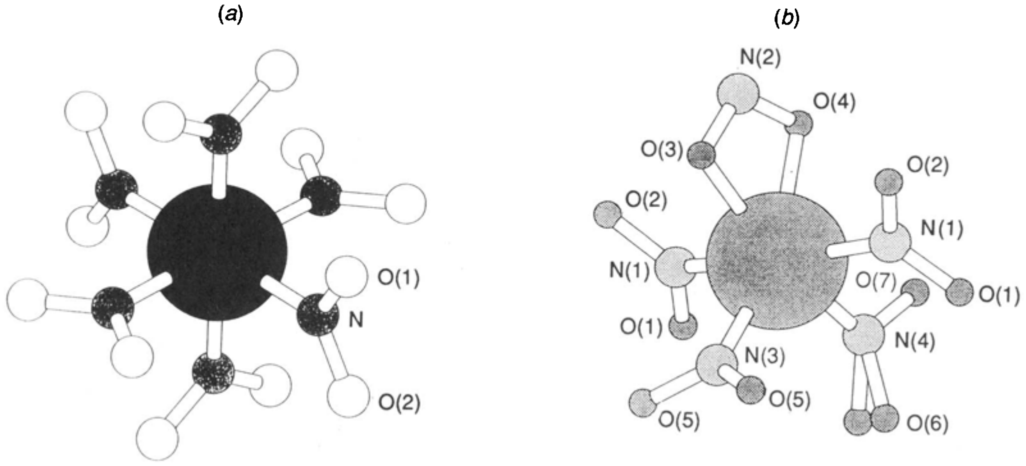

Fig. 1 Geometry of NiX_6 in (*a*) $K_4[Ni(NO_2)_6]\cdot H_2O$ and (*b*) $K_3[Ni(NO_2)_4(O_2N)]$

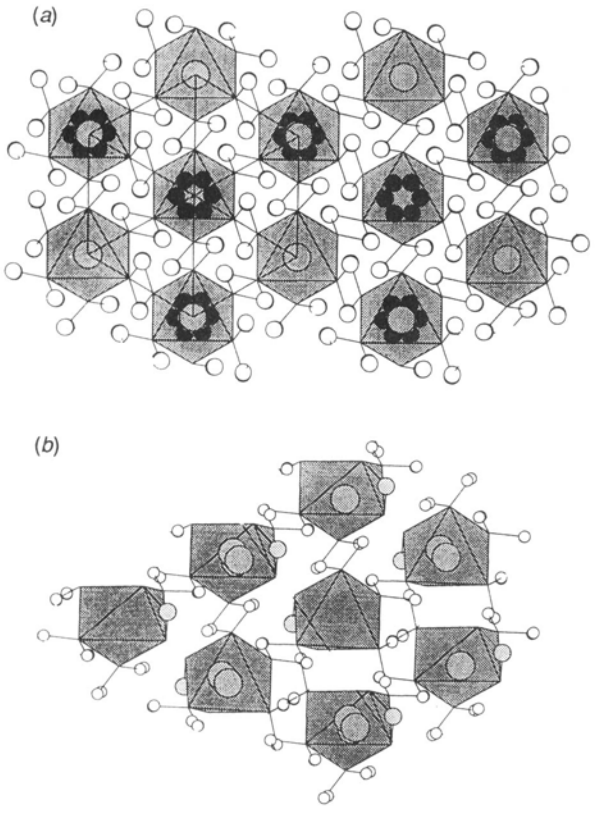

Fig. 2 (*a*) Projection of the structure of $K_4[Ni(NO_2)_6]\cdot H_2O$ along [001]. Large shaded circles, K; small open circles, O; small shaded circles, N; small filled circles, O_w; (*b*) projection of structure of $K_3[Ni(NO_2)_4(O_2N)]$ along [210]

F-centred pseudo-cubic unit cell can be defined with $a_c = a - c$, $b_c = b$ and $c_c = a + c$. One of the body diagonals of this cell is equivalent to the trigonal c axis for $K_4[Ni(NO_2)_6]\cdot H_2O$. The correct body diagonal was found by inspection and found to be oriented along [210] (monoclinic cell indices). Diagrams of the projected structures of $K_4[Ni(NO_2)_6]\cdot H_2O$ and $K_3[Ni(NO_2)_4(O_2N)]$ along [001] and [210] respectively are compared in Fig. 2. The close relationship between the two structures is evident in the same orientation and packing of the octahedra in the projection plane, the same orientation of the monodentate nitrite groups and the same colinear strings of octahedra and potassium atoms along the projection axis. The major structural change from $K_4[Ni(NO_2)_6]\cdot H_2O$ to $K_3[Ni(NO_2)_4(O_2N)]$ is a large contraction in the (001) layer separation. The c axis of 22.4 Å in $K_4[Ni(NO_2)_6]\cdot H_2O$ decreases to 18.2 Å in $K_3[Ni(NO_2)_4(O_2N)]$. The corresponding separation between adjacent (001) layers of octahedra (*i.e.* the primitive cell repeat) decreases from 7.5 to 6.1 Å. This difference in layer separation is shown in Fig. 3, in which the structure of $K_4[Ni(NO_2)_6]\cdot H_2O$ is viewed along [210] and that of $K_3[Ni(NO_2)_4(O_2N)]$ along the equivalent direction. It is seen that the main dimensional changes are related to removal of H_2O and K from the interlayer region.

Reversible dissociation of $K_4[Ni(NO_2)_6]\cdot H_2O$.—The structure refinement on the dehydration product from $K_4[Ni(NO_2)_6]\cdot H_2O$ showed that its composition was $K_3[Ni(NO_2)_5]$. This confirmed that the dehydration was accompanied by phase separation into $K_3[Ni(NO_2)_4(O_2N)]$ and KNO_2. Evidence for the decomposition reaction was in fact first obtained from X-ray powder diffraction patterns of the dehydration product, which showed broad peaks due to the rhombohedral form of KNO_2, with $a_r = 5.1$ Å, $c_r = 10.1$ Å. The powder patterns for $K_4[Ni(NO_2)_6]\cdot H_2O$ and its product after heating in air for 20 min at 110 °C are compared in Fig. 4.

The remarkable feature of the decomposition reaction is that it is rapidly and completely reversible at room temperature. Fig 4 shows the powder pattern of the decomposition product after standing in air at 22 °C for 2 h. There is no remaining trace of $K_3[Ni(NO_2)_4(O_2N)]$ or KNO_2 and the peaks of the restored $K_4[Ni(NO_2)_6]\cdot H_2O$ are as sharp as in the original sample. There are a number of factors that may contribute to the ease of reconstruction of $K_4[Ni(NO_2)_6]\cdot H_2O$ from KNO_2 and $K_3[Ni(NO_2)_4(O_2N)]$. The domains of exsolved KNO_2 are small (≈ 100 Å estimated from peak broadening) and so atomic diffusion paths are relatively short. The unit-cell dimensions of KNO_2 and $K_3[Ni(NO_2)_4(O_2N)]$ are closely related ($a = 2a_r$, $c = 2c_r$) and so coherent interfaces between domains of the two phases are possible. Potassium nitrite is very hygroscopic and so there is the possibility of an aqueous solution being formed as an intermediate stage, followed by recrystallization of $K_4[Ni(NO_2)_6]\cdot H_2O$.

Infrared and Electronic Spectra.—The nitrite vibrations, ν_{sym}, ν_{asym} and δ, are often diagnostic of the way in which this ligand co-ordinates to the metal.[1] It is thus of interest to compare the spectra observed for the present compounds, and these are shown in Fig. 5. The spectrum of the monohydrate, Fig. 5(*a*), shows a pair of weak, sharp peaks at 810 and 831 cm^{-1} due to the δ mode, split by lattice forces, an intense peak at 1319 cm^{-1} (ν_{asym}) and a medium peak at 1346 cm^{-1} (ν_{sym}). In addition, peaks at 3551 and 3630 cm^{-1} occur due to the O–H stretching vibrations of the water molecule, and a weak peak at 1628 cm^{-1} due to the H_2O deformation mode plus the first overtone of the

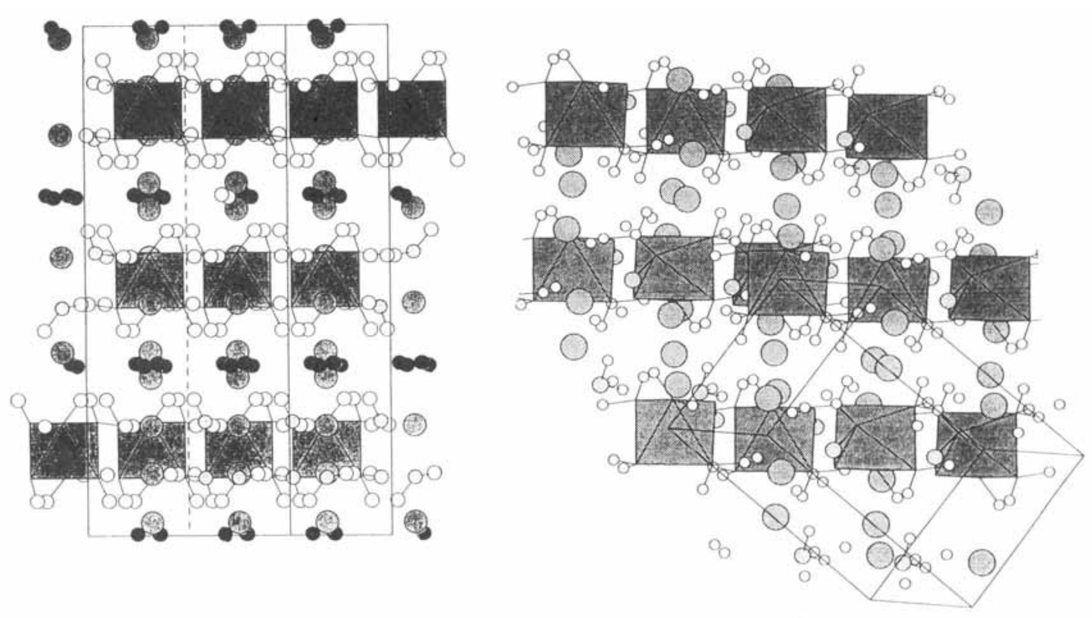

Fig. 3 (*a*) Projection of structure of $K_4[Ni(NO_2)_6]{\cdot}H_2O$ along [210]; (*b*) equivalent projection for $K_3[Ni(NO_2)_4(O_2N)]$. Unit-cell outlines shown

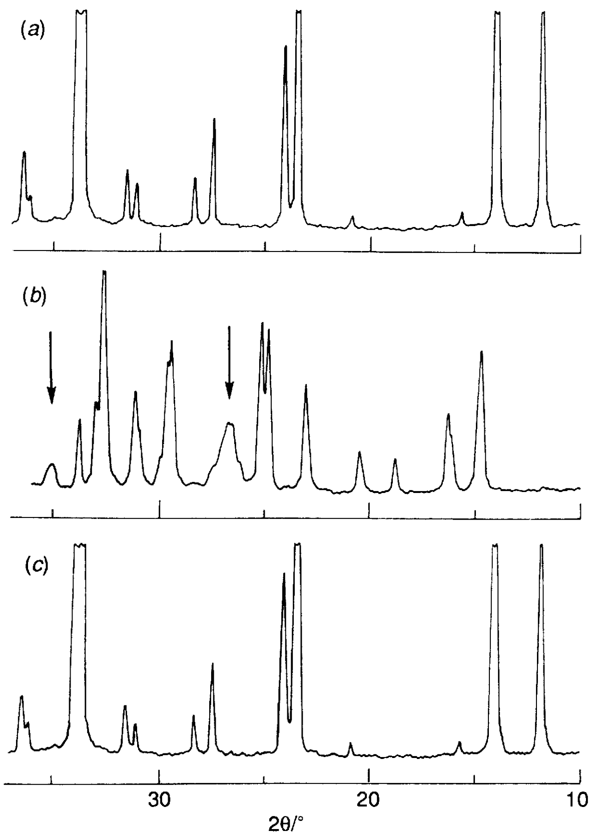

Fig. 4 Powder X-ray patterns (Cu-Kα radiation) for (*a*) $K_4[Ni(NO_2)_6]{\cdot}H_2O$, (*b*) product from heating (*a*) for 20 min at 110 °C, arrows indicate KNO_2 peaks, (*c*) product obtained from (*b*) after standing in air for 2 h at 22 °C

nitrite wagging vibration. The peak positions and assignments are in good agreement with those reported previously[5,10] and ν_{sym} and ν_{asym} are very similar to those of other nickel(II) nitro complexes.[1,4]

The spectrum of the product of dehydration, Fig. 5(*b*), is also similar to that reported previously,[5,10] though the present assignment of some peaks differs because of the recognition that dehydration produces a mixture of pentanitrite and potassium nitrite. This mixture, $K_3[Ni(NO_2)_4(O_2N)] + KNO_2$, shows peaks with similar energies and relative intensities to those in the monohydrate, at 810, 826, 1321 and 1346 cm^{-1}, and these are assigned to the nitro groups in the $[Ni(NO_2)_4(O_2N)]$ moiety. In addition, a peak of moderate intensity occurs at 1271 cm^{-1}, and this is assigned to ν_{asym} of KNO_2. A well resolved spectrum of pure KNO_2 could not be obtained for comparison, as all attempts to grind a sample produced a compacted mass. Similar problems have been described by others,[19] but it was reported[19] that KNO_2 has a similar spectrum to that of $NaNO_2$, for which ν_{asym} occurs as an intense broad peak at 1261 cm^{-1}.[19] For the latter, ν_{sym} occurs as a very weak peak at 1328 cm^{-1}, with δ being at 828 cm^{-1}, so that these peaks for KNO_2 are probably obscured by those at 1321 and 824 cm^{-1} due to the

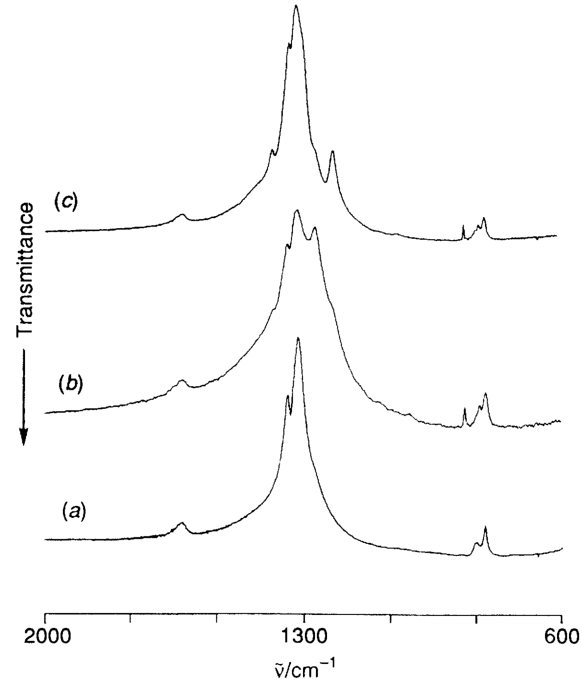

Fig. 5 Infrared spectra of $K_4[Ni(NO_2)_6]{\cdot}H_2O$ (*a*), the red product of dehydration, $K_3[Ni(NO_2)_4(O_2N)]{\cdot}KNO_2$ (*b*) and the residue of $K_3[Ni(NO_2)_4(O_2N)]$ remaining after extraction of the $K_3[Ni(NO_2)_4(O_2N)]{\cdot}KNO_2$ with anhydrous ethanol (*c*)

nitro groups in $K_3[Ni(NO_2)_4(O_2N)]$ + KNO_2. The remaining peak at 866 cm^{-1}, and shoulders at ≈1225 and 1385 cm^{-1}, are assigned to the chelating nitrite in the $[Ni(NO_2)_4(O_2N)]$ complex.

This is confirmed by the spectrum of the sample of $K_3[Ni(NO_2)_4(O_2N)]$ prepared by extraction of KNO_2 from the anhydrous residue, where the peak at 1271 cm^{-1} assigned to KNO_2 has almost disappeared, and the peaks at 1225 and 1389 assigned to ν_{asym} and ν_{sym} of the chelating nitrite are clearly resolved [Fig. 5(*c*)]. The rather high energy of the wagging mode δ is consistent with symmetrical nitrite chelation, this typically occurring in the range 860–870 cm^{-1} for this co-ordination.[20] The energies of ν_{asym} and ν_{sym} are somewhat higher than is generally observed for nitrite chelated to Ni^{2+}, these generally falling in the range 1200–1215 cm^{-1} and 1270–1300 cm^{-1}, respectively.[20,21] However, a high value of ν_{asym} ≈1260 cm^{-1} was also observed for symmetrically chelated nitrite groups in other complexes with potassium as the counter ion, $K_2[M(NO_2)_4]$ (M = Cd or Hg),[22] the weak peak due to ν_{sym} being unresolved for these two salts. The infrared spectrum reported[5] for $Cs_3[Ni(NO_2)_4(O_2N)]$ is very similar to that of $K_3[Ni(NO_2)_4(O_2N)]$, with peaks at 809, 821, 833, 1208, 1325, ≈1348 and 1372 cm^{-1}, suggesting similar nitrite co-ordination in the two compounds.

The electronic spectra of $K_4[Ni(NO_2)_6]\cdot H_2O$ and the product of dehydration, $K_3[Ni(NO_2)_4(O_2N)]\cdot KNO_2$, have been reported previously.[5] The hexanitro complex in the monohydrate exhibits peaks at 13 200 and 20 700 cm^{-1}, with a weak shoulder at ≈11 000 cm^{-1}. The peak at 13 200 cm^{-1}, due to the $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition of octahedrally co-ordinated Ni^{2+}, is a measure of the ligand-field splitting parameter Δ. The high value is consistent with the strong ligand field associated with nitrogen bound nitrite groups, and with the rather short Ni–N bond lengths in $K_4[Ni(NO_2)_6]\cdot H_2O$; depending upon the nature of the counter cation, the ligand-field splitting has been observed to vary from 13 300 to 12 000 cm^{-1} in a range of nickel hexanitro complexes.[23] The weak shoulder at ≈11 000 cm^{-1} may be assigned to the spin-forbidden $^3A_{2g} \longrightarrow {}^1E_g$ transition, and the band at 20 700 cm^{-1} is probably due to a superposition of the $^3A_{2g} \longrightarrow {}^3T_{1g}$ (F) d–d transition, and a charge-transfer transition.[23,24] It has been shown that a weak charge-transfer transition in this region, probably metal ⟶ ligand in nature,[24] is characteristic of nitrite groups bound to Ni^{2+} *via* nitrogen.

The red pentanitrite complex has band maxima at 12 050 and 19 200 cm^{-1} with a pronounced shoulder at ≈10 500 cm^{-1}.[5] The peak at 19 200 cm^{-1} is again probably due largely to the charge-transfer transitions associated with the nitro groups in the complex. The shift of all peaks to lower energy compared with $K_4[Ni(NO_2)_6]\cdot H_2O$ is consistent with the replacement of two nitro groups in the nickel(II) co-ordination sphere by a chelating nitrite, since the ligand-field strength is much lower when the nitrite ion co-ordinates *via* oxygen rather than nitrogen.[24] The significant angular deviations of the metal–ligand bond directions from the cartesian axes are also expected to influence the d orbital energies, and to investigate this aspect the excited state energies were estimated using the computer program CAMMAG developed by Gerloch and co-workers.[25] This parameterises metal–ligand bonding using angular overlap parameters e_σ, $e_{\pi x}$ and $e_{\pi y}$ to describe the σ- and π-antibonding interactions, the geometry being defined by the crystal structure.[26] The ligand-field splitting in a regular octahedral complex is given by equation (1).[26]

$$\Delta = 3e_\sigma - 2e_{\pi x} - 2e_{\pi y} \qquad (1)$$

The nickel(II) co-ordination geometry in $K_4[Ni(NO_2)_6]\cdot H_2O$ is very close to octahedral (Table 4) and the observed $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition energy is reproduced by e_σ = 4400 cm^{-1} if it is assumed, as has been concluded from other studies,[27] that the π-bonding interaction of the nitro group is negligible. The ligand-field splitting parameter of the nitrite ion co-ordinated to Ni^{2+} *via* oxygen has been estimated[23] as Δ = ≈9000 cm^{-1} for bond lengths similar to those in $K_3[Ni(NO_2)_4(O_2N)]$. Assuming that the in-plane π interaction is negligible, and that the out-of-plane π bonding is ≈25% as strong as the σ interaction, as has been done in previous studies,[29] leads to the estimates e_σ = ≈3600, $e_{\pi x}$ = 0 and $e_{\pi y}$ = ≈900 cm^{-1} for the oxygen atoms of the chelating nitrite group in the pentanitrite. The nitro groups in this complex were assumed to have similar bonding parameters to those in $K_4[Ni(NO_2)_6]\cdot H_2O$, except for minor corrections for the slight differences in Ni–N bond distances (Table 4). Both theory[30] and experiment[31] suggest that the ligand-field splitting varies inversely as between the fifth and sixth power of the bond distance, and in the present case the latter was assumed. The calculated energies of the components of the $^3T_{2g}$ excited state obtained using these bonding parameters are 9870, 10 750 and 11 590 cm^{-1}. If the deviations of the metal–ligand bond vectors from 90° are ignored, energies of 11 590 (doubly degenerate) and 13 220 cm^{-1} (non-degenerate) are obtained, showing that the distortions have a large effect upon the energy levels. The observed transition energies of ≈10 500 and 12 050 are somewhat higher than those calculated using the true geometry of the complex, but close agreement is not to be expected considering the simplistic way in which the bonding is represented. In particular, given the small 'bite' angle of the chelating ligand, it seems possible that the directions of the nitrite lone pair orbitals may deviate from the Ni–O bond vectors, and this is expected to influence the e_σ and $e_{\pi x}$ bonding parameters.[32] However, in the absence of a detailed assignment of the electronic spectrum, which does not seem feasible at present since the small size of the crystals precludes the measurement of single-crystal spectra, a more detailed analysis of the bonding is in our view not warranted.

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References

1 M. A. Hitchman and G. L. Rowbottom, *Coord. Chem. Rev.*, 1982, **42**, 55.
2 D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1964, **3**, 1389; A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. White, *Aust. J. Chem.*, 1981, **34**, 2085.
3 S. Tagaki, M. Joesten, P. Galen-Lenhert, *Acta Crystallogr., Sect. B*, 1975, **31**, 1970.
4 I. Nakagawa, T. Shimanouchi and K. Yamasaki, *Inorg. Chem.*, 1964, **3**, 772; 1968, **7**, 1332.
5 D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1967, **6**, 813.
6 B. J. Hathaway and R. C. Slade, *J. Chem. Soc. A*, 1966, 1485.
7 N. W. Fisher, *Poggendorffs Annalen*, 1848, **74**, 115.
8 A. Ferrari, L. Cavalca and M. Nardelli, *Gazz. Chim. Ital.*, 1951, **81**, 945.
9 M. Le Postollec and J. P. Mathieu, *Compt. Rend.*, 1962, **254**, 1800; M. Le Postollec, J. P. Mathieu and H. Poulet, *J. Chim. Phys.*, 1963, **60**, 1319.
10 M. H. Brooker and D. E. Parish, *Inorg. Chem.*, 1969, **8**, 219.
11 Ref. 1, p. 112.
12 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
13 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
14 K. A. Klanderman, W. C. Hamilton and I. Bernal, *Inorg. Chim. Acta*, 1977, **23**, 117.
15 A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. White, *Aust. J. Chem.*, 1981, **34**, 2163.

16 E. Luukkonen, *Suom Kemistil.*, 1973, 46, 302; P. Phavanantha, Ph.D. Thesis, University of London, 1970.
17 Ref. 1, p. 71.
18 M. I. Kay and B. C. Frazer, *Acta Crystallogr., Sect. B*, 1961, **14**, 56.
19 R. E. Weston and T. F. Brodasky, *J. Chem. Phys.*, 1957, **27**, 683.
20 D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1965, **4**, 721.
21 A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. White, *Aust. J. Chem.*, 1981, **34**, 2113.
22 D. M. L. Goodgame and M. A. Hitchman, *J. Chem. Soc. A*, 1967, 612.
23 D. Reinen, C. Friebel and K. P. Reetz, *J. Solid State Chem.*, 1972, **4**, 103.
24 Ref. 1, pp. 88–91.
25 D. A. Cruse, J. E. Davies, M. Gerloch, J. H. Harding, D. Mackey and R. F. McMeecking, CAMMAG a FORTRAN computing package, University Chemical Laboratory, Cambridge, 1979.
26 M. Gerloch, *Magnetism and Ligand Field Analysis*, Cambridge University Press, Cambridge, 1983.
27 D. Reinen and C. Freibel, *Struct. Bonding (Berlin)*, 1979, **37**, 1; B. J. Kennedy, K. S. Murray, M. A. Hitchman and G. L. Rowbottom, *J. Chem. Soc., Dalton Trans.*, 1987, 825.
28 A. J. Finney, M. A. Hitchman, C. L. Raston, G. L. Rowbottom and A. White, *Aust. J. Chem.*, 1981, **34**, 2095.
29 A. B. P. Lever, I. M. Walker and P. J. McCarthy, *Can. J. Chem.*, 1982, **60**, 495; D. W. Smith, *Struct. Bonding (Berlin)*, 1972, **12**, 50.
30 D. W. Smith, *J. Chem. Phys.*, 1969, **50**, 2784; M. Bermejo and L. Paeyo, *J. Chem. Phys.*, 1983, **78**, 854.
31 H. G. Drickamer and C. W. Frank, *Electronic Transitions and the High Pressure Chemistry and Physics of Solids*, Chapman-Hall, London, 1972.
32 R. J. Deeth and M. Gerloch, *Inorg. Chem.*, 1987, **26**, 2573, 2578.

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