The Magnetic, Spectral, and Structural Properties of *trans*-Tetraamminedinitronickel(II)

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The structural (295 and 130 K), magnetic, and spectral properties of *trans*-$[Ni(NH_3)_4(NO_2)_2]$ are reported. The crystal structure of the compound has been determined by single-crystal *X*-ray diffraction methods at 295 and 130 K. Crystals are monoclinic, space group $C2/m$, $Z = 2$, with $a = 1\,062.1(4)$ [1 062.8(4)], $b = 681.2(4)$ [688.7(2)], $c = 591.2(3)$ [597.4(3)] pm, and $\beta = 114.83(3)$ [114.80(3)]° where the 295 K values are in square parentheses. Diffractometry has provided significant Bragg intensities for 900 (130 K) and 1 264 (295 K) independent reflections and the structures have been refined by full-matrix least-squares methods to R 0.028 (130 K) and 0.051 (295 K). The molecule has a rectangular, almost square [N–Ni–N = 87.5(1)°] plane of ammonia molecules accurately perpendicular to the axis containing the *trans*-nitrite groups. The molecules are bound together by a fairly simple but strong hydrogen-bonding arrangement. The structure at 130 K is essentially the same as at 295 K. The Ni–N bond lengths, corrected for librational motions, are Ni–N(H_3) 210.9 (211.1) and Ni–N(O_2) 214.2 (215.2) pm where the 295 K values are in parentheses. The magnetic susceptibility follows a Curie–Weiss law with $\theta = -5.5$ K between 10 and 300 K, but departs from this below 10 K to become independent of temperature below 3 K. The data fit the theory for the ground $^3A_{2g}$ term with zero-field splitting represented by $D = 15.2$ K(10.4 cm^{-1}). This zero-field splitting, together with some limited data about the solid-state spectra, is reproduced by a ligand-field treatment with angular-overlap parameters $e_\sigma(NH_3) = 3\,700$, $e_\sigma(NO_2) = 12\,000$, $e_\pi(NO_2) = 5\,700$ cm^{-1}. The i.r. spectrum, including that of the deuteriated compound, is largely interpreted along conventional lines, but shows a band at 1 850 cm^{-1}. This band probably arises from strong hydrogen bonding involving one of the ammine hydrogen atoms in particular. This same hydrogen atom is also involved in an anomalously long N–H bond, and has large thermal parameters.

trans-TETRA-AMMINEDINITRONICKEL(II), $[Ni(NH_3)_4(NO_2)_2]$, has long been known as an octahedral bivalent nickel complex with a mixed-ligand co-ordination environment and as simple a formulation as is available.[1] The complex possesses an interesting combination of a square plane of ligands moderate in the spectrochemical series, together with two ligands high in the series in the axial positions. The four ammonia molecules are essentially σ-donating in character while the two *trans*-nitrite ions may be expected to show substantial π-bonding interaction with the nickel atom.

A preliminary report of the crystal structure [2] gives a monoclinic space group, $C2/m$ with highly pseudo-symmetric contents. Although the compound is not chemically very robust, tending to lose ammonia, it may be handled in the laboratory atmosphere for short periods and will keep indefinitely in a sealed container.

We have commenced an intensive study of the bonding in this compound, which will include detailed charge and spin-density distribution analyses. We report here the magnetic susceptibility at very low temperatures, the visible and i.r. spectral assignments for the compound in the solid state, and the main structural features at room temperature and at *ca.* 130 K. The literature seems to contain no estimate of the relative contributions of σ- and π-bonding character for the NO_2^- ion acting as a ligand, and it is of interest that our analysis of the magnetic and spectral data gives an estimate for that relationship, as expressed by the parameters of the angular-overlap model of ligand-field effects.

EXPERIMENTAL

The compound *trans*-$[Ni(NH_3)_4(NO_2)_2]$ was prepared by the method given in the literature.[3] Large dark claret-red single crystals were obtained by very slow cooling (*ca.* 1 K day^{-1}) of a solution of the compound in an aqueous solution of 0.880 ammonia (20% v/v). The crystals obtained showed much dendritic growth, and most were twinned. None of the larger crystals was well formed. The partially deuteriated compound (*ca.* 80% ND_3) was obtained by twice recrystallising the compound from a solution of NH_3 in D_2O (5% w/w) and then slowly recrystallising the product from the same medium.

Magnetic Susceptibility.—The magnetic susceptibility of the polycrystalline compound was measured on equipment previously described,[4,5] The temperature scale was established with reference to the susceptibility of $[Cu(bipy)_2(thiourea)][ClO_4]_2$ (bipy = 2,2′-bipyridyl), which obeys a Curie law,[6] apart from a small temperature-independent paramagnetism term and the diamagnetic correction for the ligand molecules. This temperature-independent paramagnetism was taken to have a value typical for bivalent copper complexes,[7] $\chi_{Cu} = 750 \times 10^{-12}$ m^3 mol^{-1}, and the diamagnetism to be $\chi_{diam.} = -3\,970 \times 10^{-12}$ m^3 mol^{-1}.[8] The measurements on $[Ni(NH_3)_4(NO_2)_2]$ were made at 28 temperatures between 1.85 and 33 K, at 84 K, and at three temperatures near ambient. They had a scatter of 1% in the low-temperature region, but the high-temperature values were not as accurate since the net paramagnetism is then rather small. The magnetic susceptibility best fitting to the experimental points is listed at a series of suitably spaced temperatures in Table 1. Between 10 and 300 K a Curie–Weiss law is obeyed, with $\theta = -5.5$ K. Below 10 K the susceptibility rises less rapidly than the Curie–Weiss law, and becomes independent of temperature below 3 K. The values of the magnetic moments derived from the susceptibilities, after correction for the diamagnetism, were fitted by least-squares methods to the expression for the magnetic moment of the $^3A_{2g}$ ground term of the d^8 configuration in octahedral stereochemistry, in the presence of zero-field splitting. The expression is given in equation (1) where g is the gyromagnetic ratio and $x = D/k_BT$ (k_B = Boltzmann constant) with D the zero-field splitting parameter.[9] The

value of $\Delta(A_2 - T_2)$ was estimated (see later) as *ca.* 8 000 cm^{-1} and k, the orbital-angular momentum reduction parameter, was set at 0.8; D was found to be 15.2(5) K (10.4 cm^{-1}), with the value of the reliability index R, defined below, 0.025; g was evaluated as 2.18(5).

$$\mu_{eff.}^2 = 2\bar{g}^2[2 - 2x\exp(-x) + \exp(-x)]/[1 + 2\exp(-x)]x + 24k^2k_BT/\Delta(A_2 - T_2) \quad (1)$$

TABLE 1

Magnetic susceptibility and moment of *trans*-$[Ni(NH_3)_4(NO_2)_2]$ at various temperatures. $\chi_{diam.} = -0.96$ mm^3 mol^{-1}

T/K	χ_{Ni}/mm^3 mol^{-1}	$\mu_{eff.}$/B.M.*
1.85	1 700	1.415
2.0	1 720	1.478
2.5	1 700	1.642
3.0	1 670	1.784
4.0	1 560	1.995
4.2	1 540	2.030
5.0	1 430	2.13
7.5	1 180	2.37
10	921	2.42
15	742	2.66
20	582	2.72
30	411	2.80
40	322	2.86
80	178.1	3.01
150	98.1	3.06
200	74.6	3.08
300	50.4	3.10

* 1 B.M. = 9.274 × 10^{-24} A m^2.

Spectra.—The compound decomposes in any solvent but ammonia solution, and the main species present there is obviously not $[Ni(NH_3)_4(NO_2)_2]$, since the colour is royal blue. The visible and near-i.r. region of the spectrum was recorded in the solid state at *ca.* 295 K by diffuse reflectance, using a Beckman Acta MIV spectrometer equipped with integrating reflecting spheres. It was also recorded perpendicular to the (001) crystal face by cementing a thin (*ca.* 0.1 mm) plate-like crystal over a 2-mm hole in a blackened aluminium sheet and placing this in the sample beam of the same spectrometer, with a similar crystal-free sheet in the reference beam.

The diffuse reflectance spectrum consisted of broad bands at 11 000 and 20 000 (with a shoulder at *ca.* 16 000) cm^{-1}, with absorption rising rapidly above 28 000 cm^{-1}. There was also a series of relatively sharp bands apparently overlapping a broad weaker absorption below 6 000 cm^{-1}. The single-crystal spectrum showed broad bands at 11 800 and at 19 000 cm^{-1}, with absorption rising rapidly to high values above 25 000 cm^{-1}. There also may be absorption bands below 6 000 cm^{-1}, some with sharp features being shifted to lower frequencies in the spectrum of the deuteriated compound.

The i.r. spectrum of $[Ni(NH_3)_4(NO_2)_2]$ was recorded as mulls in Nujol and hexachlorobutadiene. That of the *ca.* 80% deuteriated compound was obtained in the same mulls. The bands observed, together with assignments, are listed in Table 2. The assignment of the various $\delta(NH_3)$, $\delta(ND_3)$, and $\delta(ND_2H)$ bands rests upon known regions for such NH_3 bands,[10] the frequency ratios corresponding to mass changes, and the changing relative intensities as the percentage deuteriation is increased. From the relative intensities of the $\delta_{asym}(ND_3)$ and $\delta_{asym}(ND_2H)$ bands, we estimate the final percentage deuteriation as 80 ± 5%.

TABLE 2

Observed i.r. frequencies in $[Ni(NH_3)_4(NO_2)_2]$ and $[Ni(ND_3)_4(NO_2)_2]$ together with assignments (ref. 10)

NH_3 compound		ND_3 compound	
ν/cm^{-1}	Assignment	ν/cm^{-1}	Assignment
3 330 (s) 3 320 (s) 3 310 (s)	ν(NH)	2 500 (s) 2 440 (w) 2 400 (m) 2 330 (w)	ν(ND)
1 850 (m)			
1 640 (s) 1 620 (s)	$\delta(NH_3)_{asym.}$		
1 425 (m) 1 400 (m) 1 360 (m)	$\nu(NO_2)_{asym.}$	1 435 (m) 1 410 (w) 1 370 (s)	$\nu(NO_2)_{asym.}$
1 310 (m) 1 270 (s)	$\nu(NO_2)_{sym.}$	1 315 (s) 1 265 (m)	$\nu(NO_2)_{sym.}$
1 240 (s) 1 210 (w) 1 190 (w)	$\delta(NH_3)_{asym.}$	1 225 (w) 1 190 (m)	$\delta(ND_2H)_{asym.}$
		1 135 (s)	$\delta(ND_3)_{asym.}$
840 (w) 810 (w)	$\sim\delta(NO_2)$	1 020 (s)	$\delta(ND_2H)_{asym.}$
		935 (s)	$\delta(ND_3)_{asym.}$
670 (m) 635 (w)	$\sim NO_2$ wag	810 (w)	$\sim\delta(NO_2)$
		720 (w) 620 (m)	$\sim NO_2$ wag

X-*Ray Crystallography.*—Crystals suitable for X-ray diffraction measurements were obtained by cleavage of twinned crystals along the (001) twinning plane. The crystals were coated with a thin layer of Canada balsam or of Araldite to minimise decomposition. This decomposition leads to a bright green powder product on the surface and causes an increase in the mosaic spread of the crystal, detectable by X-ray photography. Oscillation and Weissenberg photographs at 295 K of apparently perfect crystals showed that the space group was C-centred monoclinic. The crystals used were prismatic, bounded by {001}, {010}, {20$\bar{1}$} and/or {100} faces. Data were collected using a Syntex $P2_1$ four-circle diffractometer equipped with a graphite single-crystal monochromator, and a Syntex LT-1 low-temperature attachment. Two data sets were collected, one at 295(1) and the other at 130(10) K. The error in the second temperature reflects the uncertainty in temperature calibration. Periodic recentring of the six reflections used in cell-constant determination showed no changes in cell axis lengths which would be equivalent to a temperature change of greater than ±4 K. At 295 K a complete sphere of data out to a 2θ limit of 100° was measured using an ω—2θ scan mode. At 130 K about three-quarters of a complete data set out to a 2θ limit of 70° was collected. Both at room temperature and at 130 K the six standard reflections, which were measured every 50 reflections, showed a steady decrease in intensity, finishing at 0.95 of the original values. This drift in the intensities of the standard reflections perhaps indicates some decomposition of the crystal.

After allowance for variation in the standards, the data were corrected for absorption by the use of a local adaptation of the program CAMEL-JOCKEY.[11] This program is much faster in execution than the usual analytical absorption corrections but doubt remains as to its applicability in monoclinic symmetry without use of azimuthal scans.[11] We employed 18 unique sets of four equivalent, relatively intense, reflections to determine the anisotropy correction to be made. The results were checked by comparing the

CAMEL-JOCKEY transmission coefficients with those from the analytical absorption correction program ABSCOR.[12] The coefficients varied between 0.45 and 0.59, with the two programs agreeing to within 0.02. The crystal data are presented in Table 3.

TABLE 3

Crystal data for $[Ni(NH_3)_4(NO_2)_2]$

Space group	$C2/m$	$C2/m$
T/K	295(1)	130(10)
a/pm	1 062.8(4)	1 062.1(4)
b/pm	688.7(2)	681.2(4)
c/pm	597.4(3)	591.2(3)
β/°	114.80(3)	114.83(3)
U/nm^3	0.3969	0.3882
Z	2	2
D_c/Mg m^{-3}	1.831	1.872
D_m/Mg m^{-3}	1.82(1)	
λ(Mo-K_α)/pm	71.069	71.069
μ/mm^{-1}	2.42	2.47
Crystal dimensions/mm	0.14 × 0.23 × 0.22	0.37 × 0.30 × 0.21
Unique data [$I > 3\sigma(I)$]	1 264	900
$(\sin\theta_{max.})/\lambda$ (nm^{-1})	10.78	8.07

Structure Refinements.—Initial non-hydrogen atomic co-ordinates used in the refinement of the asymmetric unit of structure in the space group $C2/m$ were those previously reported.[2] The successful refinement of the structure confirmed this choice of the centrosymmetric space group. Least-squares refinement of atomic co-ordinates and anisotropic thermal parameters was performed by use of the program CRYLSQ [12] in the full-matrix mode, the function minimised being $\Sigma w(\Delta F)^2$ where w is the weight assigned to the $|F_o|$ values and $\Delta F = |F_o| - |F_c|$. Difference-Fourier syntheses yielded the positions of the three independent hydrogen atoms. These were included in the scattering models, and their positional co-ordinates and isotropic temperature factors were refined. A weighting scheme of the form $w = [\sigma^2(|F_o|) + 0.000\,6|F_o|^2]^{-1}$ was used. Neutral-atom scattering factors for non-hydrogen atoms were taken from ref. 13, and were modified for the real and imaginary anomalous dispersion corrections.[14] The scattering-factor curve for H was taken from ref. 15. Structural refinement and analysis were performed using the *X*-RAY '76 program system.[12]

For the 1 264 data at 295 K, refinement converged with $R(=\Sigma|\Delta F|/\Sigma|F_o|)$ 0.051, and R' $\{=[\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ 0.058. The maximum parameter shift-to-error ratio at convergence was 0.05 : 1. A final difference synthesis showed no peaks greater than $|0.6| \times 10^{-6}$ e pm^{-3}, except for some stronger features of maximum density $|2| \times 10^{-6}$ e pm^{-3} near the nickel atom. Further analysis of these residual features, present in both the data sets, will be presented in a subsequent publication. The refined value of the isotropic extinction parameter was small [$0.6(2) \times 10^3$].[12,16]

The refinement of the 900 data at 130 K converged with R 0.028 and R' 0.036, with a maximum parameter shift-to-error ratio of 0.09 · 1. A final difference synthesis showed no peaks greater than $|0.6| \times 10^{-6}$ e pm^{-3}, except for features close to the nickel atom, of maximum density $|1.4| \times 10^{-6}$ e pm^{-3}. The refined value of the isotropic extinction parameter, $0.1(3) \times 10^3$, was not significantly different from zero.

Observed and calculated structure factors, with standard deviations in the observed values, and thermal parameters are listed in Supplementary Publication No. SUP 22933 (14 pp.).* Final atomic positional co-ordinates, with estimated standard deviations in parentheses, are listed in Table 4.

TABLE 4

Final atomic positional co-ordinates for $[Ni(NH_3)_4(NO_2)_2]$ †

Atom	x/a	y/b	z/c
Ni(1)	0	0	0
N(1)	0.200 5(2)	0	−0.007 6(4)
	0.200 0(1)	0	−0.006 6(2)
N(2)	0.065 7(2)	0.220 7(3)	0.268 6(3)
	0.065 5(1)	0.223 5(1)	0.271 4(2)
O(1)	0.308 6(2)	0	0.185 4(5)
	0.308 6(1)	0	0.191 1(2)
O(2)	0.213 5(3)	0	−0.207 0(5)
	0.213 4(1)	0	−0.209 1(2)
H(1)	0.097 6(61)	0.174 6(137)	0.419 8(97)
	0.100 4(36)	0.179 2(86)	0.437 0(60)
H(2)	0.119 8(43)	0.287 7(72)	0.247 5(71)
	0.118 6(25)	0.301 4(38)	0.247 9(42)
H(3)	0.001 2(41)	0.294 1(77)	0.243 5(73)
	−0.000 7(25)	0.302 3(43)	0.242 4(43)

† Upper and lower values quoted are for structure refinements at 295 and 130 K respectively.

RESULTS AND DISCUSSION

The molecular geometry and atom numbering of the centrosymmetric *trans*-$[Ni(NH_3)_4(NO_2)_2]$ molecule is shown in Figure 1. The packing of the molecules in the unit cell is shown in Figure 2. Interatomic distances,

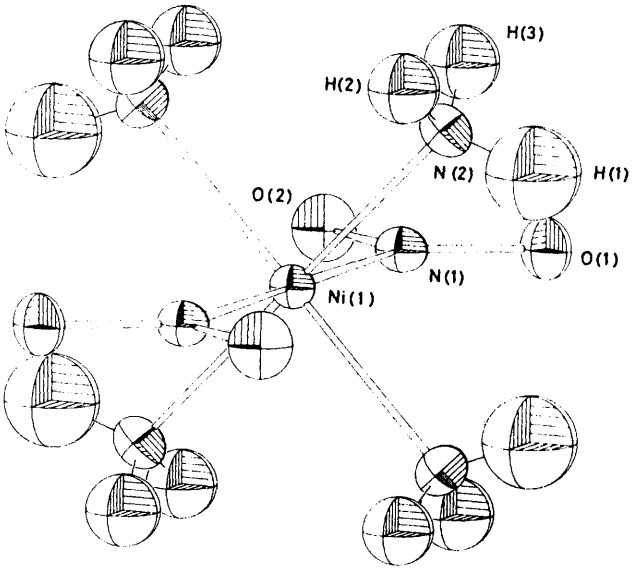

FIGURE 1 An ORTEP drawing of *trans*-$[Ni(NH_3)_4(NO_2)_2]$ (295 K parameters) showing the molecular geometry and atom numbering. Thermal ellipsoids are drawn at the 30% probability level

angles, and correlated estimated standard deviations derived from the refinement are given in Tables 5 and 6.

Thermal Motion and its Structural Effect.—On decrease of temperature from 295 to 130 K, the thermal parameters decrease uniformly by a factor of between 2.5 and 3. This is about the change expected for a well behaved, harmonic crystal. The apparent lengths of

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

those bonds involving H and O atoms are all increased at 130 K. This effect is no doubt caused by the smaller amount of librational motion at 130 K. We have made a correction for the effect of thermal motion on the non-hydrogen bond lengths using the program RIGBY.[17] The observed thermal motion tensors U_{ij} were fitted to a *TSL* rigid body model.[18] We have assumed a model consisting of a rigid NiN_6 unit and two NO_2 groups having additional librational degrees of freedom. The

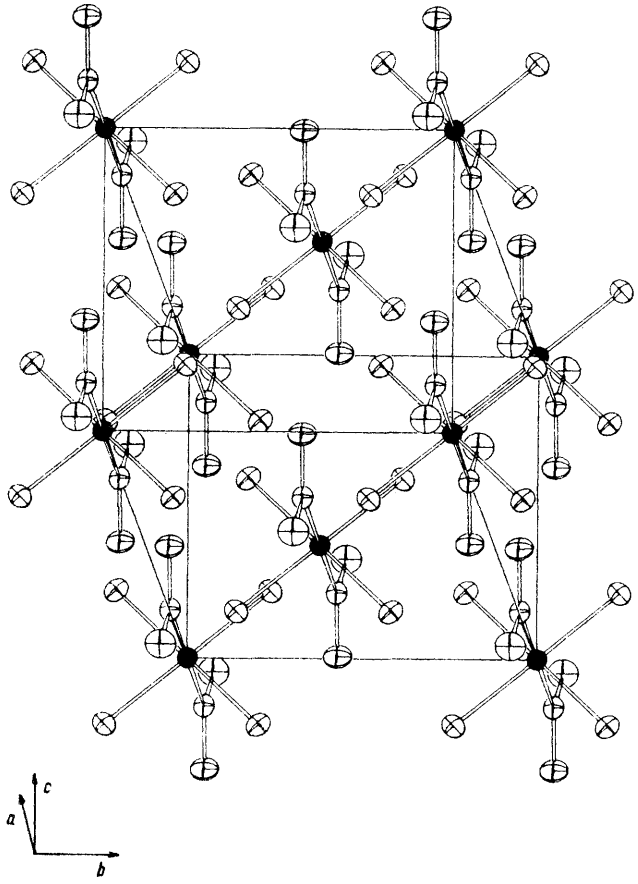

FIGURE 2 An ORTEP drawing showing the unit-cell contents in the *trans*-$[Ni(NH_3)_4(NO_2)_2]$ crystal (295 K parameters). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level

two NO_2 groups and the NiN_6 unit are coupled through the 'joint' atoms N(1) and its symmetry equivalent. The 12-variable model gave an acceptable fit to the 22 independent U_{ij} elements at 295 K, with an R factor of 0.06. The T and L matrices for the NiN_6 unit and the NO_2 groups are listed in SUP 22933. The translational motion at 295 K corresponds to a $\langle U^2 \rangle$ value of 200 to 300 pm^2. The librational motion about the b and c axial directions is relatively small (3—23 degrees squared). The NO_2 groups show a large (61 degrees squared) libration about the Ni–N(1) bond, as expected. The NiN_6 unit also shows its largest librational component (13 degrees squared) about this direction, as expected for low-energy librational modes of NO_2 about the Ni–N(1) vector.

TABLE 5

Intramolecular interatomic distances (pm) and angles (°) in $[Ni(NH_3)_4(NO_2)_2]$ from refined co-ordinates, and those corrected for the effects of thermal motion (refs. 17 and 18)

	130 K		295 K	
	Refined	Corrected	Refined	Corrected
(*a*) Distances				
Ni–N(1)	214.1(2)	214.2(2)	215.0(2)	215.2(2)
Ni–N(2)	210.7(1)	210.9(1)	210.5(2)	211.1(2)
N(1)–O(1)	125.0(2)	125.8(2)	124.0(3)	125.7(3)
N(1)–O(2)	126.4(2)	127.0(2)	125.5(4)	127.1(4)
N(2)–H(1)	94(4)		88(6)	
N(2)–H(2)	83(3)		78(5)	
N(2)–H(3)	84(3)		81(5)	
(*b*) Angles				
N(1)–Ni–N(2)	90.1(1)	90.1(1)	90.1(1)	90.0(1)
N(2)–Ni–N(2′) *	87.5(1)	87.5(1)	87.6(1)	87.6(1)
Ni–N(1)–O(1)	121.1(1)	121.0(1)	121.3(2)	121.1(2)
Ni–N(1)–O(2)	121.6(1)	121.5(1)	121.7(2)	121.5(2)
O(1)–N(1)–O(2)	117.3(2)	117.5(2)	117.0(3)	117.4(3)
Ni–N(2)–H(1)	115(3)		113(6)	
Ni–N(2)–H(2)	112(2)		109(3)	
Ni–N(2)–H(3)	109(2)		109(3)	
H(1)–N(2)–H(2)	112(3)		113(5)	
H(1)–N(2)–H(3)	110(4)		110(6)	
H(2)–N(2)–H(3)	97(3)		103(5)	

* The primed atom is related by the co-ordinate transformation $(-x, y, -z)$.

TABLE 6

Significant intermolecular interatomic distances (pm) and angles (°) in $[Ni(NH_3)_4(NO_2)_2]$

	130 K	295 K
(*a*) Distances		
H(1) · · · O(2^{I})	228(4)	237(6)
H(2) · · · O(2^{II})	233(3)	239(5)
H(3) · · · O(1^{III})	234(3)	239(5)
N(2) · · · O(2^{I})	318.9(2)	323.5(3)
N(2) · · · O(2^{II})	315.1(2)	317.3(3)
N(2) · · · O(1^{III})	318.3(2)	320.6(3)
(*b*) Angles		
N(2)–H(1) · · · O(2^{I})	162(15)	166(24)
N(2)–H(2) · · · O(2^{II})	174(19)	176(30)
N(2)–H(3) · · · O(1^{III})	174(19)	177(30)

Roman numeral superscripts refer to the following co-ordinate transformations: I $x, -y, 1 + z$; II $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; III $x - \frac{1}{2}, y + \frac{1}{2}, z$.

Before turning to the molecular geometry, we should also note that the H(2) and H(3) thermal parameters [$\langle U^2 \rangle$ *ca.* 700 (100) pm^2 at 295 K] are reasonable for an NH_3 group riding on the NiN_6 unit and undergoing some extra librational/torsional motion. The H(1) thermal parameter [1 200 (100) pm^2], however, seems anomalously large. This anomaly persists at 130 K and is discussed further below.

After correction for thermal motion effects, the agreement between the 295 and 130 K molecular bond lengths is much improved (Table 5), in particular for the N(1)–O(1) and N(1)–O(2) distances.

Intramolecular Structure.—The local symmetry around the nickel atom is higher than that required by its 2/*m* crystallographic site symmetry. The four N(2) (ammine) atoms and the nickel atom are constrained to be coplanar by the *C*2/*m* site symmetry, and are also found to be perpendicular [90.1(1)°] to the N(1)–Ni–N(1′) (nitro) vector. However, the N(2)–Ni–N(2′) angle of 87.5(1)°

is significantly different from 90°. The Ni–N(1) distance of 214.2(2) pm (130 K) is comparable to other similar distances in, for example, $[Ni(en)_2(NO_2)]$ (en = ethylenediamine),[19] as are the N(1)–O bond lengths and the ONO angle of 117.5(2)°. The significant difference between N(1)–O(1) and N(1)–O(2) bond distances [125.8(2) and 127.0(2) pm respectively] is an intermolecular effect, and is discussed below.

The N(2)–H distances are shorter than the expected internuclear separation, partly due to thermal motion but mostly due to the well known difference in positions between the centroid of charge density in the N–H bond and the true hydrogen nuclear position.[20] The N(2)–H(1) distance is significantly longer than the other two N–H distances [94(4) compared with 83(3) and 84(3) pm respectively]. The various angles in the $Ni–NH_3$ fragment are not distinguishably different from ideal tetrahedral symmetry, given the poor accuracy inevitable with *X*-ray determined hydrogen positions, with one exception. The H(2)–N(2)–H(3) angle is 97(3)°. The dihedral angle of N(2′)–Ni–N(2)–H(1) [where the primed atom is related by the transformation $(-x, y, -z)$] is 180°, within the errors, maintaining an approximate mirror plane in *bc**.

Intermolecular Structure.—There are three different significant intermolecular contacts, all involving a nearly linear N–H · · · O arrangement. Otherwise, there are no intermolecular contacts of non-hydrogen atoms (X · · · Y) of less than 340 pm, of X · · · H less than 295 pm, nor of H · · · H less than 255 pm. The approximate local molecular symmetry is maintained, even though it is not crystallographically required, in that two of these bonds appear to be almost related by a non-crystallographic *bc** mirror plane through the nickel atom, while the third is in this plane. It is *not* possible to make this symmetry perfect. While the hydrogen atoms of a given molecule *may* be bonded in this symmetrical manner, that is *not* possible for its oxygen atoms. Each O(2) atom participates in four hydrogen bonds while each O(1) atom participates in only two. This presumably causes the observed difference in the two N–O bond lengths. The crystal is thus held together by a network of linear hydrogen bonds. Four N(2)–H(2) · · · O(2^{II}) and four N(2)–H(3) · · · O(1^{III}) bonds (Table 6) connect the molecule at 0, 0, 0 with those at $\pm\frac{1}{2}, \pm\frac{1}{2}, 0$. The *ab* planes of molecules are connected together, between 0, 0, 0 and 0, 0, ±1, by four N(2)–H(1) · · · O(2^{I}) bonds.

We postulate that in this substance the hydrogen bonds are sufficiently strong that there is significant energy gain by establishing not only an N · · · O distance of *ca.* 320 pm (Table 6), but also N–H · · · O linearity. This situation cannot be satisfied by variation of the cell parameters *a*, *b*, *c*, and β alone, and some intramolecular distortion is required. Presumably the anomalies mentioned above, involving the H(2)–N(2)–H(3) and N(2)–Ni–N(2′) angles and the N(2)–H(1) distance, are the distortions which require the least expenditure of free energy.

The N · · · O contacts of 318.9(2), 315.1(2), and 318.3(2) pm are relatively long for hydrogen bonding. However, the enhancement of the NH dipole (over that in an alkylamine) due to charge transfer to the nickel atom and the substantial charge on the nitrite oxygen atom (over that in a carbonyl group, for example) will both increase the attractive electrostatic component of the energy over that in a ' normal ' hydrogen bond.

Infrared Spectrum and Hydrogen Bonding.—The assignment of the i.r. spectra of $[Ni(NH_3)_4(NO_2)_2]$ and $[Ni(ND_3)_4(NO_2)_2]$ is quite straightforward. There is, however, a medium intensity band at 1 850 cm^{-1} in the H compound only. The only reasonable explanation is that of a hydrogen stretch whose frequency has been much reduced by hydrogen bonding. This is concordant with the long N(2)–H(1) bond length (compared to the other two) and the high thermal motion of H(1).

Spectra and Magnetism.—The absorption spectrum of *trans*-$[Ni(NH_3)_4(NO_2)_2]$, in common with those of some other octahedral nitro–ammine complexes of bivalent nickel,[19] shows a band in the region of 11 000 to 12 000 cm^{-1} and a stronger one at *ca.* 20 000 cm^{-1}, with a shoulder to lower energy.[21] The 20 000 cm^{-1} absorption appears to be due to an internal transition of the nitrite ion rather than a *d*–*d* transition of the nickel ion.[19] The shoulder at *ca.* 16 000 cm^{-1} is probably a *d*–*d* band.[19] If an octahedral crystal field is assumed, then the transition $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$ would be identified with the lower energy band, giving 10 Dq = 11 500 cm^{-1}, in agreement with the average for four ammonia molecules and two nitrite ions,[19] 11 800 cm^{-1}. The transition $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ would be identified with the 16 000 cm^{-1} band, and this would be compatible with a value of *ca.* 1 000 cm^{-1} for the Racah parameter for interelectronic repulsion, B. In this interpretation, B would be reduced to some 90% of the free Ni^{2+} ion value. The transition $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ would be predicted to lie at *ca.* 28 000 cm^{-1}, and so be hidden by the charge-transfer absorption which sets in above that energy.

The assumption of a cubic ligand field which was the basis for the preceding paragraph is, however, at variance with our observation of a large zero-field splitting of the ground $^3A_{2g}$ term. The main origin of this zero-field splitting is the lifting of the orbital degeneracy of the $^3T_{2g}(F)$ term through the departure of the ligand field from cubic symmetry.[9] We have employed the angular-overlap model of ligand-field effects.[22–24] Since the information available is so limited, we restrict ourselves to the assumptions that the parameter $e_\pi(NH_3)$ is zero and that $e_{\pi\parallel}(NO_2) = e_{\pi\perp}(NO_2)$. The value of $e_\sigma(NH_3)$ is then fixed at 3 700 cm^{-1} from the knowledge of 10 Dq for the ion $[Ni(NH_3)_6]^{2+}$, 11 100 cm^{-1}. We then put $e_\pi(NO_2) = fe_\sigma(NO_2)$, and constrain this relationship by the knowledge that in the ion $[Ni(NO_2)_6]^{4-}$: $3e_\sigma(NO_2) - 4e_\pi(NO_2)$ = 13 400 cm^{-1}. It is then possible to investigate how the spectrum and the zero-field splitting may be rationalised by variation of the parameter f. In this way an estimate of the relative contributions of the para-

meters $e_\sigma(NO_2)$ and $e_\pi(NO_2)$ in the angular-overlap model may be obtained.

In general, the zero-field splitting of the ground term is not completely accounted for by the lifting of the orbital degeneracy of the next higher term of the same multiplicity.[25] It is necessary to take into account the effect of the departure from cubic symmetry on the many other terms arising from a d^n configuration, in order to obtain a good account of the experimental observations. A computer program was written which calculated the energies arising from the entire d^2 (d^8) configuration under the perturbation of the Hamiltonian in equation (2).

$$\mathscr{H} = \sum_{i=1}^{2} e^2/r_{ij} + V_{\text{L.F.}} + \sum_{i=1}^{2} \zeta_{3d} l_i \cdot s_i \qquad (2)$$

The first term on the right-hand side of this expression represents the interelectronic repulsions, and these were incorporated as the Condon–Shortley [26] parameters F_2 and F_4. The second term is the ligand-field potential, parametrised by $e_\sigma(NH_3)$, $e_\sigma(NO_2)$, and $e_\pi(NO_2)$, and the last term is the spin–orbit coupling. Values of F_2 = 1 400 and F_4 = 100 cm^{-1}, reduced by 10 to 20% from those of the free Ni^{2+} ion, were employed. The angular-overlap model parameters were constrained as described above, and ζ_{3d} was set at 500 cm^{-1}, again somewhat below the free-ion value.

It has been pointed out [19] that in the point group D_{4h}, which applies for *trans*-$[Ni(NH_3)_4(NO_2)_2]$, the 4*s* and $3d_{z^2}$ orbitals both have the same symmetry (a_{1g}), and consequently mix. For square-planar cobalt(II) complexes it was estimated that this mixing lowered the energy of the d_{z^2} orbital by some 2 000 cm^{-1}. We have included the possibility of mixing of d_{z^2} with the 4*s* orbital by performing the calculations outlined in the previous paragraph, but with the energy of the d_{z^2} orbital lowered by (*a*) 1 000 cm^{-1} and (*b*) 2 000 cm^{-1}.

It was found that, with the data resulting from the above discussion, and a value of *f* between 0.47 and 0.48, depending on the lowering of the d_{z^2} orbital by 4*s* mixing, the two spectral bands (11 800 and 17 000 cm^{-1}) and the zero-field splitting (10.4 cm^{-1}) were reproduced. This result may be used to deduce the individual angular-overlap model parameters for the nitrite ion co-ordinated to bivalent nickel: $e_\sigma(NO_2)$ = 12 000 cm^{-1}, $e_\pi(NO_2)$ = 5 700 cm^{-1}. In this analysis the $^3T_{2g}(F)$ term is predicted to be split by 5 500 cm^{-1}, so that the band at 11 800 cm^{-1} is the transition $^3B_{2g} \leftarrow {}^3A_{2g}$ in D_{4h} symmetry and the band at *ca.* 16 000 cm^{-1} is $^3E_g \leftarrow {}^3A_{2g}$. The other component of the $^3T_{1g}(F)$ term, $^2A_{2g}$, would lie at *ca.* 18 000 cm^{-1}, obscured by the internal transition of the nitrite group.[19] It is predicted that the second component of the $^3T_{2g}(F)$ term of cubic symmetry, ^3E_g, should lie at 6 500 cm^{-1} above the ground $^3A_{2g}$ term, and indeed there may be some absorption near that region of the spectrum but it is confused by sharp features which are obviously overtones of the i.r. vibrational fundamentals. A high harmonic content in the vibrational spectrum of $[Ni(NH_3)_4(NO_2)_2]$ is not unexpected in view of the strong hydrogen bonding present in the crystal.

The value of the parameter *f* deduced above is dependent upon the assumptions made about the assignment of the spectral bands, about the amount of s–d_{z^2} mixing, and most particularly about the value of the spin–orbit coupling constant for the nickel ion. The major contribution to the zero-field splitting parameter, *D*, comes from the splitting of the $^3T_{2g}(F)$ term, equation (3). By use of this relationship, it is possible to estimate

$$D \simeq 2\zeta_{3d}^2[1/\Delta(E - A_2) - 1/\Delta(B_2 - A_2)] \qquad (3)$$

the sensitivity of the determination of *f* to the spin–orbit coupling constant. It is found that in the region of $f \sim 0.5$ that $\partial f/\partial\zeta_{3d} \simeq 1.0$. Consequently, if it is accepted that our estimate of ζ_{3d} carries a 10% uncertainty, the uncertainty in our deduced value for the parameter *f* is *ca.* 0.05.

In principle, information about the value of ζ_{3d} could come from the magnetic susceptibility through the gyromagnetic ratio, *g*. In cubic symmetry we have, for the d^8 configuration to first order in perturbation theory, equation (4). Here, *k* is the effective orbital-

$$\bar{g} = 2[1 + 2k\zeta_{3d}/\Delta(T_2 - A_2)] \qquad (4)$$

angular-momentum reduction factor. In D_{4h} symmetry the same result should hold with $\Delta(T_2 - A_2)$ an appropriate average for the separation of the $^3T_{2g}(F)$ components from the ground term. However, the uncertainty in the value of $\bar{g}$ together with the need to estimate an additional parameter, *k*, means that the relationship cannot be used to do more than confirm that the observed value of $\bar{g}$, 2.18, is consistent with the average $^3T_{2g}(F)$ term position in the complex, together with a reasonable value for *k*. If $\Delta(T_2 - A_2)$ is taken to be 8 000 cm^{-1} and *k* to be 0.8, the calculated value for $\bar{g}$ is 2.20, indeed agreeing with observation.

The ratio $e_\pi(NO_2)/e_\sigma(NO_2)$ that we have deduced for the nitrite ligand in $[Ni(NH_3)_4(NO_2)_2]$ ($f \sim 0.48$) is quite similar to that obtained for donor atom systems in which a good deal of π interaction is expected. For example,[27] the nitrogen donor atoms in some macrocycles forming square-planar complexes with bivalent cobalt show $e_\pi/e_\sigma \simeq 0.4$.

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