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# Atomic Displacement Parameters for $Ni(ND_3)_4(NO_2)_2$ from 9 K X-ray and 13 K Time-of-Flight Neutron Diffraction Data

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## Abstract

Structural parameters derived from 9 (1) K X-ray diffraction data and 13 (1) K time-of-flight neutron diffraction data on perdeuterated tetraamminedinitronickel(II), $Ni(ND_3)_4(NO_2)_2$, are compared. It is shown that excellent agreement can be obtained for both positional and thermal parameters derived separately from the two experiments, provided that great care is taken in all steps of the process, including data collection, data reduction, and nuclear and electronic structure refinement. The mean difference in the thermal parameters, $<|\Delta U_{ij}|>$, is as low as 0.00034 $Å^2$ and $<(\Delta U_{ij}/\sigma)^2>^{1/2} = 1.92$, showing that, even without any form of scaling between the parameters, the same values can be obtained. This, compared with other such studies, indicates that time-of-flight neutron diffraction data can give structural information of a quality comparable to monochromatic neutron diffraction. The excellent correspondence between the thermal parameters derived separately from X-ray and neutron diffraction data gives confidence in the deconvolution of the thermal motion from the X-ray diffraction data, which is necessary for any study of a static electron density distribution.

## 1. Introduction

Bragg intensities contain information about the electron density (X-ray diffraction) or the nuclear density (neutron diffraction) smeared by motion or disorder. The thermal motion of the atoms in a crystal is normally parametrized by the use of isotropic, anisotropic or even anharmonic thermal structural models which are used in least-squares fits to the structure factors derived from the diffraction intensities. However, a number of systematic errors may affect the thermal parameters derived by this procedure (Blessing, 1995; Larsen, 1995). They include absorption, extinction, disorder, thermal diffuse scattering (TDS), multiple scattering and measurement errors such as scan truncation. For X-ray data the asphericity of the electron distribution caused by bonding effects is, especially for very light atoms, a further source of systematic error in the structural parameters. Differences in the various systematic errors between neutron and X-ray diffraction experiments very often result in a substantial discrepancy between the thermal parameters derived separately from the two experiments on the same crystal system. A clear example is documented by the IUCr project on comparison of structural parameters and electron density maps of oxalic acid dihydrate (Coppens, Dam, Harkema, Feil, Feld, Lehmann, Goddard, Krüger, Hellner, Johansen, Larsen, Koetzle, McMullan, Maslen & Stevens, 1984). This is unfortunate if the thermal parameters derived from the neutron diffraction experiment are to be used with fixed values in refinement of X-ray data for modelling the electron density of the crystal *via* the X-N method (especially for the H atoms). The effect of systematic errors on the derived values of the thermal parameters also makes any conclusions about the lattice dynamics of the crystal system less reliable. Only if we can derive identical parameters from the two completely different experiments can we believe that the parameters truly describe the thermal motion of the atoms.

To minimize the systematic errors, extensive data corrections are normally carried out both before and during the least-squares fitting procedure. For precise work, measurement of many equivalent reflections in a well ordered crystal system is necessary. Another consideration is the sample temperature. Proper correspondence between neutron and X-ray thermal parameters can only be obtained if the temperatures of the experiments match. This can be achieved with modern well regulated cooling devices (Henriksen, Larsen & Rasmussen, 1986; Larsen, 1991, 1995). Adequate absorption corrections can normally be carried out provided the crystal morphology is definable analytically and is carefully measured (Coppens, Leiserowich & Rabinovich, 1965). The same is true for the effects of extinction, which can be corrected for using empirical models during the least-squares procedure (Becker & Coppens, 1974). With regard to the asphericity of the electron densities for X-ray data, it is necessary to use very flexible electronic models in order to accurately determine the atomic displacement parameters [ADP's (Figgis, Iversen, Larsen & Reynolds, 1993)]. Correction for the effect of TDS is more difficult, because not only experimental conditions such as collimations, but also the elastic constants have to be known, which is only the case for a few simple crystal systems of rather limited chemical interest. This can be a very serious problem as the TDS contribution to the observed intensity easily can amount to more than 10% of the intensity of high-order reflections even at the temperature of liquid nitrogen (Larsen, Brown, Lehmann & Merisalo, 1982; Iversen, Nielsen & Larsen, 1995). Correct high-order intensities are very important for deriving proper ADP's. Anharmonic atomic motion can also seriously affect ADP's if it is not specifically accounted for in the thermal motion model. This can be done by introducing generalizations of the harmonic temperature factor expression (Kuhs, 1992). Anharmonic motion is temperature dependent, but even at the temperature of liquid nitrogen considerable anharmonicity may be present (Figgis, Khor, Kucharski & Reynolds, 1992).

The effects of some of the systematic errors can be drastically reduced by decreasing the temperature of the crystal to around 10 K. At very low temperatures the thermal motion is close to constant at the zero-point motion over a fairly large temperature range and, thus, small differences in the temperature between the neutron and the X-ray diffraction experiment produce negligible effects. Also, anharmonic motion experimentally seems to become negligible at 10 K (Figgis *et al.*, 1993; Iversen, Nielsen *et al.*, 1995), as is theoretically expected. Of even more importance is that the TDS intensity at this temperature is much reduced. We have earlier shown that very good agreement between X-ray and neutron thermal parameters can be obtained even for rather complex transition metal systems such as $(ND_4)_2Cu(SO_4)_2.6H_2O$, copper Tutton's salt or CuTS, provided that the measurements are carried out near 10 K and if a very flexible electron density model is used in the modelling of the X-ray data (Figgis *et al.*, 1993). However, even at 10 K small, but noticeable, systematic differences in the thermal parameters were still found. It was shown that these are probably due to multiple scattering effects. Such effects can in principle be avoided by recording the same reflection at different azimuthal settings around the diffraction vector, but beamtime limitations, particularly at neutron sources, usually prohibit carrying out such procedures. In our study of CuTS a monochromatic beam was used in the neutron diffraction measurements and this simplified the highly important corrections for absorption and extinction.

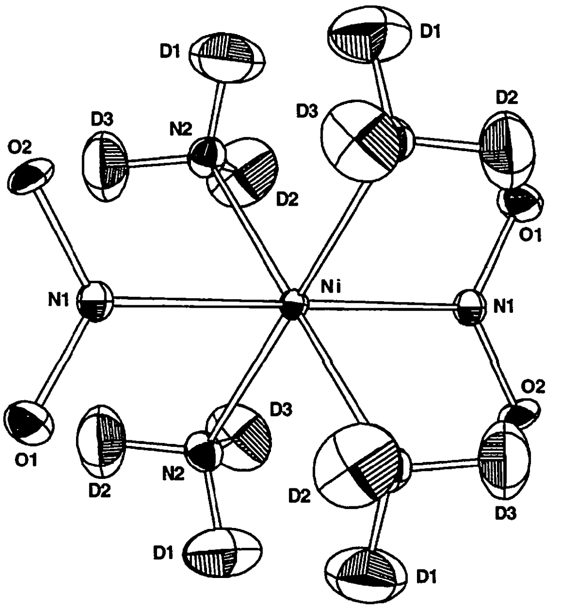

Fig. 1. *ORTEP*II drawing (Johnson, 1976) of $Ni(ND_3)_4(NO_2)_2$ at 9 K showing the atom-numbering scheme and 90% thermal ellipsoids.

The present paper deals with 9 (1) K X-ray and 13 (1) K neutron diffraction measurements on tetraamminedinitronickel, $Ni(ND_3)_4(NO_2)_2$ (NiTA, Fig. 1). The NiTA structure has previously been studied by a number of different methods, including X-ray diffraction (Porai-Koshits & Dikareva, 1960; Figgis, Reynolds, White, Williams & Wright, 1981; Figgis, Reynolds & Wright, 1983) and monochromatic neutron diffraction (Figgis, Reynolds & Williams, 1981). The present neutron experiment was carried out with the use of the white beam time-of-flight technique (Schultz, Srinivasan, Teller, Williams & Lukehart, 1984). Because of the many wavelength-dependent factors which must be measured or evaluated, the accuracy of thermal parameters derived from such time-of-flight Laue data requires establishment. In a previous study, comparison of the results of time-of-flight constant-wavelength neutron and γ-ray diffraction from the same $MnF_2$ crystal demonstrated that highly accurate thermal parameters can be obtained for small structures at least (Jauch, Schultz & Schneider, 1988; Jauch, McIntyre & Schultz, 1990). In this paper we discuss the data collection and reduction, and compare the structural parameters derived separately from X-ray and time-of-flight neutron diffraction experiments for the more complex structure of $Ni(ND_3)_4(NO_2)_2$. In a forthcoming paper we will discuss the details of the electron density distribution in the crystal derived from a combined analysis of the two data sets (Iversen, Larsen, Figgis & Reynolds, 1996*a*).

## 2. Data collection

The protonated form of the title compound *trans*-$[Ni(ND_3)_4(NO_2)_2]$ was prepared by standard methods (Soret & Robineau, 1889). A 78.5% deuterated crystal was obtained by recrystallizing the hydrogenous

Table 1. *Crystal data and experimental conditions for the X-ray experiment*

| | |
|---|---|
| Unit cell at 9 (1) K | |
| $a$ (Å) | 10.609 (1) |
| $b$ (Å) | 6.773 (1) |
| $c$ (Å) | 5.879 (1) |
| $\beta$ (°) | 114.86 (1) |
| $V$ (Å$^3$) | 383.3 |
| $\rho_{\text{calc}}$ (Mg m$^{-3}$) | 1.978 |
| Space group | $C2/m$ |
| Z | 2 |
| Crystal dimensions (mm) (from arbitrary centre) | $\pm(001)$ 0.13, $\pm(20\bar{1})$ 0.09, $(1\bar{1}\bar{1})$ 0.12, $(\bar{2}\bar{4}\bar{1})$ 0.11, $(2\bar{4}1)$ 0.14, (010) 0.32 |
| $V_{\text{crystal}}$ (mm$^3$) | 0.002835 |
| Radiation | Ag $K\alpha$ |
| $\lambda$ (Å) | 0.5603 |
| Monochromator | Graphite (002) |
| No. of measured reflections | 9231 (after removal of suspect measurements, see text) |
| No. of unique reflections | 4016 |
| $(\sin\theta_{\max}/\lambda)$ (Å$^{-1}$) | 1.4 |
| $\mu$(Ag $K\alpha$) (cm$^{-1}$) | 13.11 |
| Transmission factors | 0.69–0.81 |

Table 2. *Crystal data and experimental conditions for the neutron experiment*

| | |
|---|---|
| Moderator | Liquid $CH_4$ |
| Effective detector dimension (mm) | 263 × 265 |
| Histogram dimensions ($X \times Y \times T$) | 85 × 85 × 120 channels |
| Detector channel width ($\Delta X \times \Delta Y$) (mm) | 3.1 × 3.1 |
| Relative time channel width ($\Delta t/t$) | 0.15 |
| Counting time per histogram (h) | 6.5 |
| Sample to detector distance (cm) | 32 |
| Wavelength range (Å) | $0.7 < \lambda < 4.2$ |
| $(\sin\theta/\lambda)_{\max}$ (Å$^{-1}$) | 1.17 |
| Unit cell at 13 (1) K | |
| $a$ (Å) | 10.647 (2) |
| $b$ (Å) | 6.799 (1) |
| $c$ (Å) | 5.891 (1) |
| $\beta$ (°) | 114.82 (1) |
| $V$ (Å$^3$) | 387.1 |
| $\rho_{\text{calc}}$ (Mg m$^{-3}$) | 1.959 |
| Crystal morphology | Box shaped with side length of 2.5 mm |
| Linear absorption coefficient (cm$^{-1}$) (78.5% deuteration) | |
| $\mu_a$ (true absorption at $\lambda = 1.8$ Å) | 0.549 |
| $\mu_s$ (total scattering) | 1.202 |
| No. of reflections for least-squares | 2436 |

compound twice from a 5% solution of $ND_3$ in $D_2O$. For neutron diffraction studies deuteration serves to reduce incoherent scattering, but considerable gains can also be obtained in X-ray scattering experiments at low temperature due to the reduced zero-point motion of deuterium relative to hydrogen.

### 2.1. *X-ray data*

For the X-ray data collection a prismatic crystal was encapsulated in a glass capillary, using a tiny amount of vacuum grease to secure the crystal. The capillary was fitted on the cold station of a type 202 DISPLEX refrigerator mounted on a type 512 Huber four-circle diffractometer. During 6 weeks of data collection using graphite-monochromatized Ag $K\alpha$ radiation the temperature was kept constant at 9 (1) K. Unit-cell parameters were determined by least-squares fitting to the setting angles of well centred medium range reflections. A full sphere of data was collected in the region $2\theta < 60°$, whereas only the half sphere of positive $k$-indices was collected for the region $60 < 2\theta < 110°$. Two standards, 600 and 002, were measured every 50 reflections. The orientation matrix was redetermined every few days. A few times a gradual drop in the intensity of the standard reflections of up to 10% over half a day was noticed. Data collection was stopped and redetermination of the orientation matrix brought back the intensity. An $\omega/2\theta$ scan was used with widths $\Delta\theta$ at $\theta$ values: (1.20, 0°), (1.30, 15°), (1.50, 30°), (2.00, 45°) and (2.60, 60°). Further experimental details as well as crystal data are summarized in Table 1.

### 2.2. *Neutron data*

For the neutron diffraction measurements an almost equidimensional box-shaped crystal was glued to an aluminum pin using Goo rubber base adhesive (Hobsco, Milwaukee, USA). Earlier neutron diffraction measurements on NiTA were carried out on a twinned crystal specimen (Figgis, Reynolds & Williams, 1981) and indeed, several twinned crystal specimens had to be discarded before a single crystal was found for the present study. The twinning problem in the earlier neutron diffraction study caused the thermal parameters of that study to be inaccurate and thus useless for a combined X-N study. It is a virtue of time-of-flight area-detector measurements that sample crystals can be quickly checked and twinning and high mosaicity are both easily detected. This makes the search for an optimum crystal feasible, even with necessarily strict beamtime limits.

The crystal was encapsulated in aluminum foil to reduce deuterium exchange. The aluminum pin attached to the sample was fitted on the cold station of a Model CS-202 DISPLEX refrigerator; itself mounted on a type 512 Huber four-circle diffractometer at the SCD beamline at the Intense Pulsed Neutron Source, Argonne National Laboratories. This device employs the white beam of a spallation source and the diffractometer is also equipped with a position-sensitive area detector. The instrument uses $\omega$ fixed at 45° and different volumes of reciprocal space are recorded by setting $\varphi$ and $\chi$ at a number of values. A total of 40 three-dimensional data histograms ($x$ and $y$ spatial coordinates on the detector and the time-of-flight $t$) were recorded, restricting those reflections considered observed to those where the wavelength of the neutrons was between 0.7 and 4.2 Å.

A complete set of unique data to a maximum $\sin\theta/\lambda$ of 0.82 $Å^{-1}$, with many additional data out to 1.17 $Å^{-1}$, was obtained during 2 weeks of data collection, showing that the time-of-flight neutron diffraction technique allows a large sampling of reciprocal space even within strict beamtime limitations. The histograms were measured in the unique part of reciprocal space, with overlap between adjacent histograms resulting in some redundancy in the data. During the data collection period the temperature was kept fixed at 13 (1) K. A summary of experimental conditions for the neutron experiment is given in Table 2. There is a slight difference between the X-ray and neutron cell parameters. In general, cell parameters determined on the SCD instrument are less accurate than X-ray cell parameters. We have, therefore, used the X-ray cell parameters in the neutron data refinements.

## 3. Data reduction

### 3.1. *X-ray data*

Integrated intensities were obtained using the profile analysis program *COLL5N*, which is based on the minimization of $\sigma(I)/I$ (Lehmann & Larsen, 1974). Plots of the intensities of standard reflections showed, as expected from the observations during data collection, a few cases of fairly sudden drops in intensity. As adequate rescaling of such intensity drops is impossible, these groups of reflections were removed. This hardly affected the completeness of the data below $\sin\theta/\lambda < 0.89$ $Å^{-1}$, because many equivalents of each reflection were collected. For the high-order reflections there are some random holes in the data set, although overall only ~ 100 unique reflections are missing up to $(\sin\theta/\lambda)_{\max} = 1.4$ $Å^{-1}$. The remaining standard reflections showed intensity changes of less than 5%, with somewhat larger fluctuations of the 600 reflection than the 002 reflection. The data were rescaled using only the 002 reflection. One block of high-order reflections (1865 reflections) recorded immediately after a 3 d halt to data collection was scaled separately from the other reflections, because this block showed an almost constant intensity decrease of 6%. In further refinements this block of data was also allowed a separate scale factor from the main block of data.

At this point it was detected that some $+k$ reflections had profile shapes showing contamination by aluminum powder lines. This was due to the crystal position in the capillary being too close to the tip of the aluminum pedestal which is mounted on the cold station of the DISPLEX. Since the contamination by aluminum powder lines was in many cases too subtle to detect in the reflection profiles with the naked eye, we chose to remove all $+k$ reflections within 1° of the four strongest Al powder lines, $(\theta, I/I_0)$ = (14.49°, 100), (16.09°, 47), (23.01°, 24) and (27.28°, 22). Again, this had little effect on the completeness of the data set, because a full sphere of reflections was collected for $2\theta < 60°$. The data were corrected for absorption with a 512-point Gaussian grid using the program *DATAP* (Coppens, 1974). The equivalent reflections were then averaged using the program *SORTAV* (Blessing, 1989). Severe outliers were removed, resulting in a total of 4026 unique reflections. The main block of reflections had an internal agreement factor $R_I = \Sigma\,(I - I_{\rm av})/\Sigma I_{\rm av}$ = 0.023 for 7366 reflections averaged to 3192 unique. The minor data block consisting of the less intense 1865 reflections with $\sin\theta/\lambda > 1.20$ $Å^{-1}$ had $R_I$ = 0.058 for 834 unique reflections. The data were not corrected for TDS due to the lack of knowledge of elastic constants. Based on earlier experiences with diffraction data at very low temperatures, it seems likely that TDS effects at 9 K are suppressed to a point where they are negligible (Figgis *et al.*, 1993; Iversen, Nielsen *et al.*, 1995).

### 3.2. *Neutron data*

Local Argonne programs were used in all steps of the data acquisition, data reduction and structure refinement (Schultz & Leung, 1986; Schultz, 1987). One set of programs searches for intensity maxima in the histograms, indexes the peaks and refines an orientation matrix. When examining the peak profiles it was apparent that the peak widths for some reflections were quite wide (20–25 channels in the $x$ or $y$ directions compared with 7–8 normally). In addition to the mosaicity of the crystal, it was subsequently determined that a detector problem had led to a degradation of the positional resolution. However, since all peaks could be properly indexed, the crystal was deemed to be single. Extremely wide peaks may cause problems with peak overlap and subsequent integration errors, but outliers in the final structure refinement neither corresponded to particularly broad peaks nor did they affect the refined parameters. They were therefore kept untouched. The peak intensities were integrated using a two-dimensional Lehmann–Larsen-type box integration. The algorithm locates the integration rectangle which yields the minimum $\sigma(I)/I$ value and before integration one channel is added in each spatial direction to counter any bias in the method. Up to five time-slices are then added to obtain a minimum $\sigma(I)/I$ for the total peak. Border peaks which could not be integrated were discarded since they were also recorded on adjacent histograms. The intensities were corrected for the Lorentz factor and normalized based on the known measured spectral distribution of the incident beam and detector efficiency. The data were also corrected for absorption using an initial estimate of the deuterium content (75%). An approximation of a spherical crystal with 2.5 mm diameter was employed. This data set was used in structural refinements including refinement of the deuterium scattering length. In a second data reduction the refined deuterium content (78.5%) was used in the calculation of the absorption coefficients. Neutron scattering lengths and absorption cross sections were taken from Sears (1992). For hydrogen, cross sections measured by Howard, Johnson, Schultz & Stringer (1987) were used. Since 'equivalent' reflections were recorded at different wavelengths they could not be averaged. The final data set comprised 2436 reflections.

## 4. Refinements

### 4.1. *X-ray data*

In a forthcoming paper describing the electron density distribution of NiTA we will discuss in detail the various electron density refinements that have been carried out. These all included the same temperature factor model with anisotropic harmonic temperature factors. In the present context, the details of the various adequate refinements are not important because the structural parameters are almost unchanged between the different multipole models. This is probably due to the fact that a very large number of precise high-order data are present in the X-ray data set and these reflections effectively fix the positional and thermal parameters, while being relatively insensitive to small changes in the choices of electron deformation functions. In the following we therefore only present what we believe to be the best multipole model. With regard to further description of multipole modelling of electron densities, readers are referred to a review by Coppens (1992) or our paper on CuTS (Figgis *et al.*, 1993).

The model we used can be termed a partial X-N model because only positional and thermal parameters for the hydrogens were kept fixed at the values found in the neutron study. These parameters are not well determined by the X-ray data. The heavy-atom structural parameters on the other hand are well determined by the X-ray data and the partial X-N procedure therefore allows us to directly compare the X-ray and neutron parameters. The electron density model we have used contains full multipole expansions up to fourth order on Ni, up to third order on N1, N2, O1 and O2, and to second order on D1, D2 and D3. On the Ni atom a very flexible model containing two sets of multipoles was used. For N1 separate expansion/contraction parameters, so-called $\kappa$ parameters, were refined for each multipole order, whereas for the other atoms one $\kappa$ parameter was refined for the spherical valence term and one for multipolar terms. Thus, for O1, O2, N2, D1, D2 and D3, a standard Hansen & Coppens model was used (Hansen & Coppens, 1978), whereas for Ni and N1 extra radial flexibility was added compared with the standard model. The refinement contained an isotropic extinction parameter [type I, Becker & Coppens (1974), Lorentzian distribution] and two scale factors (one for each data block, see above). Earlier studies (Figgis *et al.*, 1983) as well as the present have shown that the complex has a small orthorhombic distortion and that the two O atoms not are chemically equivalent. Even though the data extend far out into reciprocal space we show that anharmonic parameters are not necessary to obtain a good description of all the data. This demonstrates that at very low temperatures anharmonicity is negligible here. The refinements were carried out using the *XD* program (Koritzansky, Howard, Mallison, Su, Richter & Hansen, 1995). It became clear that the strongest reflection, $\bar{4}01$, was very poorly fitted with the multipole model. The reflection profile was then reanalysed and it became clear that this reflection intensity was suffering from an inadequate dead-time correction. It was discarded. Large systematic discrepancies were also observed for nine reflections recorded at very high $\chi$ angles (> 87.5°). The crystal may have moved partly out of the beam presumably because of the high torque produced by the almost horizontal DISPLEX at these $\chi$ angles. These reflections were also removed, leaving a total of 4006 reflections with $I > 0$, which were all used in the least-squares refinements on $w(F_o^2 - F_c^2)$. In Table 3 the residual indices for the refinement are listed, in Table 4 the positional parameters are given and in Table 5 the thermal parameters are shown.*

### 4.2. *Neutron data*

The refinement of the time-of-flight neutron diffraction data was performed using a multiwavelength program based on *ORFLS* (Busing, Martin & Levy, 1962). Besides positional and thermal parameters, the refinement included separate scale factors for each of the 40 histograms. Initially only one isotropic extinction parameter [type I, Becker & Coppens (1974), Lorentzian distribution] was refined for the whole data set based on the appropriate path lengths calculated for a spherical crystal. However, this was found to be an inadequate description. To model the effect of different path lengths and anisotropy in extinction coefficents for different reflections, separate extinction parameters were introduced for each histogram. For two histograms the refinement resulted in negative extinction parameters and these parameters were set to zero. Several reflections were severely affected by extinction, the four worst being: $(hkl, \lambda, y) = (\bar{4}01, 3.803\ \text{Å}, 0.157)$, $(021, 3.888\ \text{Å}, 0.384)$, $(021, 3.389\ \text{Å}, 0.453)$ and $(\bar{2}22, 3.403\ \text{Å}, 0.489)$. It is questionable if a simple extinction model can adequately correct for extinction in such extreme cases. We therefore performed a series of refinements in which the most affected reflections were succesively removed (up to $y < 0.7$). While this slightly improved the refinement residuals, it did not significantly change the values of the structural parameters. Since we do not know what level of data removal is appropriate, we

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* A list of structure factors has been deposited with the IUCr (Reference: SH0080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Refinement residuals*

| | $N_o$ | $N_v$ | Cut off | $S$ | $R(F)$ | $R(F^2)$ | $R(wF^2)$ |
|---|---|---|---|---|---|---|---|
| X-ray | 4006 | 125 | $0\sigma$ | 1.26 | 0.0235 | 0.0303 | 0.0541 |
| Neutron | 2436 | 136 | $0\sigma$ | 1.92 | 0.0705 | 0.1006 | 0.0634 |

Table 4. *Positional parameters for NiTA in fractional coordinates (×10⁵ for Ni, O and N atoms, ×10⁴ for D atoms*

First entry is the X-ray value, second entry is the neutron value. For the D atoms only the neutron value is given. The third entry is the difference between the X-ray and neutron values divided by the e.s.d. $[\sigma = (\sigma_X^2 + \sigma_N^2)^{1/2}]$.

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ni | 0 | 0 | 0 |
| O1 | 30820 (6) | | 19184 (11) |
| | 30843 (9) | 0 | 19170 (20) |
| | 2.23 | | 0.64 |
| O2 | 21357 (5) | | −20938 (10) |
| | 21350 (10) | 0 | −20880 (20) |
| | 0.63 | | 2.64 |
| N1 | 20063 (6) | | −625 (8) |
| | 20037 (6) | 0 | −630 (10) |
| | 3.33 | | 0.41 |
| N2 | 6547 (3) | 22449 (5) | 27298 (6) |
| | 6553 (4) | 22459 (7) | 27296 (8) |
| | 1.30 | 1.16 | 0.21 |
| D1 | 1082 (1) | 17250 (2) | 4513 (2) |
| D2 | 1379 (1) | 3126 (2) | 2538 (2) |
| D3 | −146 (1) | 3136 (23) | 2569 (2) |

Table 5. *Thermal parameters for NiTA in Å² (×10⁵ for Ni, O an N atoms, ×10⁴ for O atoms)*

First entry is the X-ray value, second entry is the neutron value. For the D atoms only the neutron values are given. The third entry is the ration of $U_X/U_N$. The fourth entry is the absolute difference $\Delta U = |U_X - U_N|$, whereas the fifth entry is the ratio beween the difference and the estimated standard deviation $[\sigma = (\sigma_X^2 + \sigma_N^2)^{1/2}$.

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Ni | 273 (6) | 369 (8) | 323 (6) | 0 | 134 (4) | 0 |
| | 270 (20) | 390 (30) | 340 (20) | | 100 (20) | |
| | 1.011 | 0.946 | 0.950 | | 1.340 | |
| | 3 | 21 | 17 | | 34 | |
| | 0.14 | 0.67 | 0.81 | | 1.67 | |
| O1 | 481 (13) | 1071 (24) | 576 (13) | 0 | 125 (12) | 0 |
| | 480 (30) | 1110 (4) | 610 (30) | | 130 (30) | |
| | 1.002 | 0.965 | 0.944 | | 0.962 | |
| | 1 | 39 | 34 | | 5 | |
| | 0.03 | 0.87 | 1.04 | | 0.15 | |
| O2 | 686 (15) | 898 (21) | 588 (12) | 0 | 385 (11) | 0 |
| | 720 (30) | 1000 (40) | 630 (30) | | 380 (30) | |
| | 0.953 | 0.898 | 0.933 | | 1.013 | |
| | 34 | 102 | 42 | | 5 | |
| | 1.01 | 2.26 | 1.30 | | 0.16 | |
| N1 | 376 (10) | 521 (17) | 492 (10) | 0 | 209 (7) | 0 |
| | 390 (20) | 600 (30) | 570 (20) | | 200 (20) | |
| | 0.964 | 0.868 | 0.863 | | 1.045 | |
| | 14 | 79 | 78 | | 9 | |
| | 0.63 | 2.29 | 3.48 | | 0.42 | |
| N2 | 581 (9) | 526 (12) | 603 (9) | −44 (5) | 251 (6) | −109 (5) |
| | 590 (20) | 680 (20) | 630 (20) | −50 (10) | 230 (20) | −120 (10) |
| | 0.985 | 0.774 | 0.957 | 0.880 | 1.091 | 0.908 |
| | 9 | 154 | 27 | 6 | 21 | 11 |
| | 0.41 | 6.61 | 1.23 | 0.54 | 1.79 | 0.98 |
| D1 | 206 (5) | 204 (6) | 94 (4) | 16 (4) | 35 (4) | 20 (4) |
| D2 | 157 (5) | 188 (6) | 197 (5) | −74 (4) | 96 (4) | −34 (4) |
| D3 | 120 (4) | 148 (5) | 187 (5) | 40 (4) | 62 (4) | −22 (4) |

have conservatively chosen to include all reflections, even those most affected by extinction, in the final refinement.

A number of reflections were observed to have quite large discrepancies (large $|F_o - F_c|$) at convergence of the refinement. We have not been able to detect any systematic trend among these reflections: such as the poorly fitting reflections being particularly wide, or weak, or on the border, or in any particular region of reciprocal space or always having the same sign of $F_o - F_c$. Refinements in which the worst misfits were removed also did not alter the structural parameters, although again their removal improves the residuals. As before we have chosen the conservative course of retention of all reflections in the final refinement, that is a zero $\sigma(F^2)$ cut-off level. In the final cycles a robustness criterion was used, which multiplies the minimum of $(F_o/F_c,\ F_c/F_o)$ on the least-squares weights, thereby downweighting outliers in the refinement. Again, the effect on the structural parameters was negligible. In Table 3 the refinement residuals are shown, in Table 4 the positional parameters and finally in Table 5 the thermal parameters are listed. Figure 1 shows the thermal ellipsoids at the 90% level, because the conventional 50% is too small at these temperatures. Notice that the ellipsoid principal axes are aligned with the bonds as we expect.

## 5. Comparison of X-ray and neutron parameters

In several previous combined X-ray and neutron diffraction studies it has been shown that for non-H atoms satisfactory correspondence between positional parameters determined by the two techniques can be obtained, see for instance the IUCr oxalic acid dihydrate project (Coppens *et al.*, 1984). In Table 4 the positional parameters for NiTA are compared. Excellent agreement is achieved with an overall average value of $<(\Delta X_i/\sigma)^2>^{1/2} = 1.73$, which is similar to the

Table 6. *Comparison of relative thermal parameters from different X and N studies*

| | NiTA[a] | CuTS[b] | Alloxan[c] | $CoSO_4.6D_2O$[d] | Acetamide[e] |
|---|---|---|---|---|---|
| $\langle U_{ii}^X/U_{ii}^N\rangle$ | 0.93 (6) | 0.97 (7) | 1.02 (5) | 1.17 (28) | 1.62 (15) |
| $\langle \lvert\Delta U_{ij}\rvert\rangle$ | 0.00034 (37) | 0.00031 (23) | 0.00049 (39) | 0.00094 (72) | 0.0027 (19) |
| $\langle\Delta U_{ij}^2\rangle^{1/2}$ | 0.00050 | 0.00039 | 0.00063 | 0.00118 | 0.0033 |
| $\langle(\Delta U_{ij}/\sigma)^2\rangle^{1/2}$ | 1.92 | 3.17 | 0.83 | 3.59 | 11.14 |

(*a*) Present study; (*b*) Figgis *et al.* (1993); (*c*) Swaminathan *et al.* (1985); (*d*) Kellersohn *et al.* (1993); (*e*) Zobel *et al.* (1992); Jeffrey *et al.* (1980).

findings of the oxalic acid dihydrate project. On the contrary, agreement between the *thermal* parameters determined in parallel by X-ray and neutron experiments is very often less satisfactory. Blessing (1995) has recently carried out extensive cross comparisons of the thermal parameters obtained from the different data sets measured in the IUCr oxalic acid project. This was an attempt to derive correction schemes for the neutron-determined thermal parameters to be used in refinement of X-ray data. Blessing noted that for oxalic acid the r.m.s. value of $\Delta U/\sigma$ very often is considerably larger than 2. For simple inorganic structures very good agreement can be obtained between thermal parameters derived from X-ray and neutron data. Iversen, Larsen, Souhassou & Takata (1995) in a detailed study of metallic beryllium obtained a r.m.s. difference of $<\Delta U_{ij}^2>^{1/2} = 0.00012$ Å$^2$ between X-ray and monochromatic neutron diffraction data. In studies of $MnF_2$ (Jauch *et al.*, 1988, 1990) it has been shown, by comparison with $\gamma$-ray diffraction data, that the neutron time-of-flight technique can give structural parameters of comparable quality to measurements with monochromatic neutrons. The r.m.s. difference between time-of-flight neutron and $\gamma$-ray thermal parameters was found to be $<\Delta U_{ij}^2>^{1/2} = 0.00032$ Å$^2$ compared with $<\Delta U_{ij}^2>^{1/2} = 0.00026$ Å$^2$ for the thermal parameters determined from $\gamma$-ray and monochromatic neutron diffraction. In complex crystal structures such agreement is rarely achieved between X-ray and neutron diffraction thermal parameters.

In Tables 5 and 6 various measures for comparing the NiTA thermal parameters have been calculated. Also listed in Table 6 are the values obtained from comparisons of our CuTS X-ray and monochromatic neutron data. Both for NiTA and CuTS very good agreement is observed and we obtain $<(\Delta U_{ij}/\sigma)^2>^{1/2} = 1.92$ for NiTA and $<(\Delta U_{ij}/\sigma)^2>^{1/2} = 3.17$ for CuTS. However, for combined X-N refinements it is probably more important that the absolute differences between the thermal parameters are small. Only for very low temperature studies does a small value for the r.m.s. value of $\Delta U/\sigma$ also imply small absolute values for $<|\Delta U_{ij}|>$. This is because the higher the temperature, the less far data extend in reciprocal space and the greater is $\sigma$. For NiTA $<\Delta U_{ij}^2>^{1/2} = 0.00050$ Å$^2$ and CuTS $<\Delta U_{ij}^2>^{1/2} = 0.00039$ Å$^2$. This is an agreement similar to that obtained for the simple inorganic structures cited above. The difference is smaller than that observed for high quality data on simple rigid organic molecules measured at liquid nitrogen temperature, even though such structures in some cases can have very small $\Delta U/\sigma$ values. Blessing (1995) noted that after introducing various empirical correction schemes to scale the oxalic acid X-ray and neutron data a correspondence of 0.0001–0.0005 Å$^2$ was achieved. This is a reduction of a factor of 2–20 compared with the uncorrected data. We obtain this level of correspondence without introducing any type of correction or scaling between the parameters. If such a scaling is performed for NiTA the (unbelievable) correspondence is better than $10^{-8}$ Å$^2$. The ratio of $U_X$ to $U_N$ also yields results satisfyingly close to unity for NiTA. This result is obtained even though the ratio is between small numbers, which makes such comparisons unfavourable for very low temperature data.

Table 7. *$\Delta U$ values along internuclear vectors of bonded atoms*

| | Bond length (Å) | $\Delta U$ (Å$^2$ × $10^5$) |
|---|---|---|
| Ni—N1 | 2.142 (1) | 80 |
| Ni—N2 | 2.106 (1) | 110 |
| N1—O1 | 1.244 (1) | 10 |
| N1—O2 | 1.255 (1) | 0 |
| N2—D1 | 1.015 (1) | 280 |
| N2—D2 | 1.015 (1) | 360 |
| N2—D3 | 1.014 (1) | 230 |

It is common to perform a 'rigid-bond analysis' of the thermal parameters (Hirshfeld, 1976) to test the physical meaning of the model parameters. The basic premise of rigid-bond analysis is that the bonds are rigid and thus bonded atoms should have identical mean-square displacement amplitudes along the bond. However, this is not true at very low temperatures. Near to 0 K the thermal motion of the atoms, now mainly zero-point motion, is relatively more dominated by internal modes than at higher temperatures where the external modes are more important. In Table 7 we have listed the $\Delta U$ values along the internuclear vectors for the bonded atoms. The $\Delta U$ values for the N—D bonds are relatively large due to the much larger zero-point motion of the D atoms. In the Debye model the zero-point amplitude scales with the inverse of the square root of the atomic mass. This is reflected in the observed $\Delta U$ values.

It is interesting to compare the $\Delta U$ values found for NiTA and CuTS with some of the best X-N studies of complex molecules from the literature. In Table 6 we have included results from X-N studies of alloxan (Swaminathan, Craven & McMullan, 1985), $CoSO_4.6D_2O$ (Kellersohn, Delaplane, Olovsson & McIntyre, 1993) and acetamide (Jeffrey, Ruble, McMullan, DeFrees, Brinkley & Pople, 1980; Zobel, Luger, Dreissig & Koritzansky, 1992). The alloxan study is an example of a high-quality study of a small rigid organic molecule, in which measurements were carried out at 100 K. The $CoSO_4.6D_2O$ study is an example of a 25 K X-N study of a compound very similar to CuTS and provides an excellent opportunity for comparison. Finally, acetamide provides direct comparison with an X-N study of a small organic molecule carried out at the low temperature of 23 K. In the study of alloxan excellent agreement based on $\Delta U/\sigma$ was achieved (see Table 6). However, as can be seen, the average difference in $U$ values is considerably larger for alloxan than for NiTA and CuTS, even though the transition metal complexes are less rigid and more complex systems. This is a demonstration of the advantages gained by lowering the temperature to 10 K compared with studies employing only liquid nitrogen cooling. Not only do the absolute $U$ values become smaller at 10 K, but uncorrected systematic errors are effectively reduced. However, as was discussed by Iversen, Larsen, Figgis & Reynolds (1996*b*), it is also essential to use extremely flexible electron density models to obtain good agreement. To demonstrate this in Table 6 we have included a comparison with the X-ray and neutron thermal parameters obtained in a high-quality 25 K X-N study of $CoSO_4.6D_2O$. The quality of both the X-ray and neutron $CoSO_4.6D_2O$ data seems to be similar to both the CuTS and the NiTA data, but in its analysis a more rigid electron density model was used. This probably results in the X-ray thermal parameters attempting to correct inadequacies in the electron density model, thereby causing a larger discrepancy between the X-ray and neutron parameters. The last entry in Table 6 is the $\Delta U$ values found for acetamide at 23 K. In this study the difference between X-ray and neutron thermal parameters is an order of magnitude larger than for NiTA and CuTS. It is difficult to point out what causes the relatively large discrepancy for acetamide, but it demonstrates that lowering the temperature alone is not necessarily sufficient in obtaining good agreement.

## 6. Conclusions

The present study has shown that it is possible, even for chemically complex transition metal systems, to obtain thermal parameters for non-H atoms, presumably substantially free of systematic errors from both X-ray and neutron diffraction. We further show that the time-of-flight neutron diffraction technique yields structural parameters of comparable quality to measurements employing monochromatic neutrons. It should also be noted that the time-of-flight technique also allows quick examination of crystal quality and a more complete survey of reciprocal space, compared with what can normally be obtained with monochromatic neutron diffraction measurements. However, to obtain very accurate structural parameters care should be taken in every step of the process of data collection, data reduction and nuclear and electronic structure refinement. Most important is the use of a temperature of 15 K or less, where it seems that thermal diffuse scattering and anharmonicity in the thermal motion are reduced to negligible proportions. The fact that excellent agreement between X-ray and neutron thermal parameters can be obtained even for transition metal systems provides confidence in the deconvolution of the thermal motion from X-ray data to yield static electron density distributions.

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