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Tris(ethylenediamine)nickel(II) Sulphate at 110 K. Structure Determination in the Presence of Twinning

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Abstract

The structure of $[Ni(C_2H_8N_2)_3]SO_4$ has been determined at 110 K. Upon cooling a reversible phase transition occurs at 180 (1) K with an enthalpy change $\Delta H_t = 0{\cdot}35$ (2) kJ mol.$^{-1}$ Crystal symmetry is lowered from $\bar{3}m$ (space group $P\bar{3}1c$) to $\bar{3}$ (space group $P\bar{3}$) and twinning with exact superposition of the non-equivalent reflections *hkl* and *khl* occurs. Other crystal data for the low-temperature phase are: $a = b = 8{\cdot}822$ (3), $c = 9{\cdot}689$ (3) Å, $Z = 2$; 3 symmetry is imposed for Ni and S sites. With a modified least-squares program the data were used as measured. The structure and an extra twinning variable were refined on F^2 to R and R_w of 0·043 and 0·064 using 1352 unique data including $F_o^2 < 0$ up to $(\sin\theta)/\lambda = 0{\cdot}7156$ Å^{-1}. The final refined twin ratio was 0·5663 (1):0·4337. The $Ni(en)_3^{2+}$ cation approximately retains the 32 symmetry of the room-temperature phase; Ni—N: 2·121 (2), 2·129 (2) Å; torsional angles: Ni—N—C—C −39·8 (2) and −43·6 (2)°, and N—C—C—N 56·8 (2)°. The conformation is the expected $\delta\delta\delta$ configuration. At low temperature the sulphate group is completely ordered, and no close C—H···O contacts occur. Thermoanalytical results for this system and the analogous Cu system are discussed with respect to structural results.

Introduction

Order–disorder structural phase transitions and translations from static to dynamic Jahn–Teller distortions are of wide interest (for example: Dubler, Matthieu & Oswald, 1975; Ammeter, Bürgi, Gamp, Meyer-Sandrin & Jensen, 1979; Reinen, Friebel & Reetz, 1972; Noda, Mori & Yamada, 1978; Bertini, Gatteschi & Scozzafava, 1977). In this connection the complexes $[M(\text{ethylenediamine})_3]SO_4$, M = Cu, Ni, have been extensively studied and compared since the former is a Jahn–Teller system while the latter is not (Mitra & Sengupta, 1973; Bertini, Gatteschi & Scozzafava, 1974, 1977; Bertini & Gatteschi, 1972; Mackey, 1977). At room temperature both the Ni (Mazhar-ul-Haque, Caughlan & Emerson, 1970) and Cu complexes (Cullen & Lingafelter, 1970) are isomorphous and isostructural. The Cu complex shows dynamic (or static statistically disordered) Jahn–Teller distortions, which disappear below 182 K. There is also a partial ordering of the disordered sulphate group (Bertini, Dapporto, Gatteschi & Scozzafava, 1979). Crystal symmetry is lowered from $\bar{3}m$ (Cu and S at 32 symmetry sites) to $\bar{1}$. The Ni complex also undergoes a structural phase transition at 180 K, but in this case $\bar{3}$ symmetry is still apparent. In order to relate thermoanalytical data on this system to the crystal and molecular structures, we have determined the structure of $[Ni(en)_3]SO_4$ at 110 K. Bertini *et al.* (1979) guided their Cu complex through the transition without twinning occurring; in our case twinning seemed unavoidable and special refinement techniques were used (Jameson, 1982). With regard to twinned crystals the following references may be noted: Buerger (1960, and references therein), Catti & Ferraris (1976), Britton (1972), Hawthorne (1974), Sudarsanan, Young & Donnay (1973), Grainger (1969), Marezio, Dernier & Santoro (1973), Santoro (1974). Some examples of structure solution with data collected from twinned crystals are reported by Zalkin, Forrester & Templeton

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(1964), Grainger & McConnell, (1969), Wei (1969), Dunitz, Gehrer & Britton (1972), Murray-Rust (1973), Sabelli, Tangocci & Zanazzi (1969), Losman, Karlsson & Sheldrick (1977), Pratt, Coyle & Ibers (1971), Perenthaler, Schulz & Beyeler (1981). In most cases the twinning ratios could be determined from non-overlapped data and thereby the overlapping data could be detwinned.

Far less common are systems where there is exact lattice overlap (twinning by merohedry) which may be subdivided into two classes (I and II in the nomenclature of Catti & Ferraris, 1976). Britton (1972) and Murray-Rust (1973) have noted that for class II twinning [where the true (nontwinned) crystal symmetry is a subclass of that for the overall twinned lattice] this need not be a barrier to successful detwinning of the data. What certainly remains as a barrier is, firstly, recognition of a twinning problem, particularly if the twinning ratio is close to 0·5 or if the minor twin component is relatively small (of the order of ~0·1). In the former case, false pseudosymmetry occurs which may lead to incorrect structures (for a review see Catti & Ferraris, 1976) and, in the latter case, refinement dies with poor agreement between observed and calculated structure factors. With few exceptions (for example: Grainger & McConnell, 1969; Wei, 1969; Pratt, Coyle & Ibers, 1971; Perenthaler *et al.*, 1981) recourse is usually made to a detwinning of the data by removing the contribution(s) of the minor component(s) to the measured intensities.

Experimental

Slightly flattened hexagonal needles were prepared by a small modification of the method of Werner (1899). Identity of these crystals with those used in the room-temperature structure determination (Mazhar-ul-Haque, Caughlan & Emerson, 1970) was shown by X-ray diffraction photographs and by a redetermination of the room-temperature structure which also confirmed the unusual sulphate disorder previously reported.

On cooling to low temperature a reversible phase transition could be monitored by crystallographic and thermoanalytical methods (Fig. 1). Additional reflections corresponding to the systematic absences of space group $P\bar{3}1c$ appeared and equivalence of *hkl* and *khl* reflections weakened. Data collection at 110 K encountered obstacles: various glues, resins and greases all exerted forces upon the crystal leading to fracture at the glue–crystal interface. Eventually, we smothered a crystal completely in Araldite and upon passage through the phase transition a crystal with very high mosaicity, particularly for reflections *hkl* $h,k \ll l$, was generated. Nevertheless, a data set was collected and processed in the usual way. Starting with the parameters for the Ni(en)$_3$ moiety from the room-temperature structure, all refinements in diverse space groups ($P\bar{3}$,$P3$,$P\bar{1}$,$P1$) expired at values of R ~0·20 with a very large positive and a similar-sized negative peak in the difference Fourier synthesis on the z axis. The sulphate group appeared to be ordered, although strong ghosts appeared at both the S and Ni sites. Finally, a crystal was placed in a capillary with a paraffinic oil (m.p. 279–281 K). Now the crystal mosaicity was not affected. Crystal data and data-collection details have been deposited.* Data were corrected for Lorentz and polarization effects. Intensities, however, and subsequent calculations were very similar to before. Since little crystallographic sense could be made of the ghost molecules in difference Fourier maps, models involving disorder were abandoned (those tried gave values for R and R_w of ~0·18). We then carefully checked long-exposure rotation and Weissenberg photographs of crystals at low temperature for evidence that one or more axes had doubled. No evidence was found. In the absence of warning signs such as split peaks, non-characterizable systematic absences, and suspect crystal quality, we were reluctantly forced to conclude that at low temperature crystals of [Ni(en)$_3$]SO$_4$ become twinned.

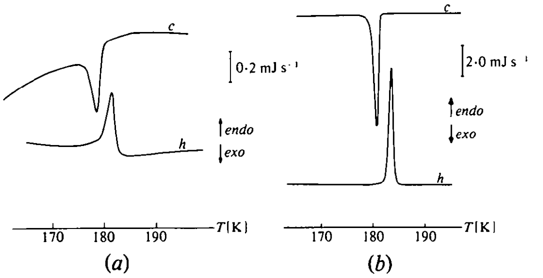

Fig. 1. Differential scanning calorimetry curves for microcrystalline samples of (*a*) [Ni(en)$_3$]SO$_4$ (T^h_{eo} = 178·9, T^c_{eo} = 180·2 K), and (*b*) [Cu(en)$_3$]SO$_4$ (T^h_{eo} = 182·6, T^c_{eo} = 182·0 K) (T_{eo} denotes the extrapolated onset temperature for the transition). Heating and cooling are denoted *h* and *c*, respectively.

Structure refinement now proceeded with a modified least-squares program (Jameson, 1982). With an eye to the cupric analogue (Bertini *et al.*, 1979), we first examined and rejected various triclinic trillings, before turning to trigonal twinning. For convenience we

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* Tables of (1) structure factors [$10|F_o|$ *vs* $10|F_c|$ where $|F_o|$ (and analogously F_c) is derived from $F_o^2 = \alpha F_{o1}^2(hkl) + (1-\alpha)F_{o2}^2(khl)$, and a negative entry denotes $F_o^2 < 0$]; (2) anisotropic thermal parameters; (3) crystal data and data-collection details; (4) metrical details and (5) hydrogen-bonding networks of both low- and high-temperature-phases of [Ni(en)$_3$]SO$_4$ and [Cu(en)$_3$]SO$_4$; (6) transition enthalpies and temperatures for these complexes and some Cu salts; and (7) stereoscopic diagrams of triclinic [Cu(en)$_3$]SO$_4$, which show more clearly than the originally published diagrams (Bertini *et al.*, 1979) the similarities and differences of the Ni and Cu crystal structures, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38036 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic positions and isotropic thermal parameters for* $[\mathrm{Ni(en)_3}]\mathrm{SO_4}$ *at* 110 K

Estimated standard deviations in the least significant figure are given in parentheses in this and all subsequent tables. For non-hydrogen atoms $B_{\mathrm{eq}} = \frac{1}{3}\sum_i\sum_j B_{ij}\, a_i^*\, a_j^*\, \mathbf{a}_i\cdot\mathbf{a}_j$.

	x	y	z	B_{eq} (Å^2)
Ni	$\frac{2}{3}$	$\frac{1}{3}$	0·23439 (6)	0·60 (1)
S	$\frac{1}{3}$	$\frac{2}{3}$	0·24420 (8)	0·66 (2)
N(1)	0·4611 (2)	0·1319 (3)	0·1179 (2)	0·88 (5)
C(1)	0·2946 (3)	0·1132 (3)	0·1657 (2)	1·00 (5)
N(2)	0·4540 (3)	0·3027 (3)	0·3584 (2)	0·95 (5)
C(2)	0·3008 (3)	0·1318 (3)	0·3224 (2)	1·08 (5)
O(1)	0·3151 (2)	0·5001 (2)	0·1928 (2)	1·30 (4)
O(4)	$\frac{1}{3}$	$\frac{2}{3}$	0·3959 (3)	1·80 (8)
H1(N1)	0·472 (5)	0·151 (5)	0·033 (4)	1·3
H2(N1)	0·467 (6)	0·042 (6)	0·133 (4)	1·3
H1(C1)	0·273 (5)	0·200 (6)	0·127 (4)	1·5
H2(C1)	0·120 (6)	0·003 (6)	0·137 (4)	1·5
H1(N2)	0·431 (5)	0·383 (5)	0·354 (4)	1·4
H2(N2)	0·478 (5)	0·305 (6)	0·438 (4)	1·4
H1(C2)	0·312 (5)	0·038 (5)	0·363 (4)	1·6
H2(C2)	0·195 (6)	0·126 (6)	0·359 (4)	1·6

continued in space group $P\bar{1}$. The values for R and R_w (on F^2, 4061 data) dropped to 0·088 and 0·123 for a model involving *hkl* and *khl* twinning; the value α (twin ratio) went from a value of 0·66 to 0·57. Anisotropic refinement lowered R and R_w (on F^2) to 0·081 and 0·115. Since the refined positions differed insignificantly from point symmetry 3 for the $\mathrm{Ni(en)_3}$ and $\mathrm{SO_4}$ moieties, the data were averaged assuming space group $P\bar{3}$; the R value (on F^2) for averaging was 0·035. Isotropic refinement (27 variable parameters and 1352 data) led to values for R and R_w (on F^2) of 0·079 and 0·115. H atoms were included at their calculated idealized positions with a temperature factor, $B_{\mathrm{H}} = B_{\mathrm{C,N}} + 0{\cdot}5$ Å^2. Non-hydrogen atoms were allowed anisotropic thermal parameters and the positional parameters of all atoms were now refined. At convergence the values for R and R_w (on F^2) were 0·043 and 0·064. The final refined value for α was 0·5663 (1).

An analysis of the weighting scheme $[1/w = \sigma^2(F_o^2)$ where $\sigma^2(I) = \sigma^2_{\mathrm{counting}} + (0{\cdot}03I)^2$; I intensity corrected only for background scattering$]$ revealed no dependence of the minimized function upon the magnitude of F_o^2 or $(\sin\theta)/\lambda$. The conventionally quoted but here meaningless values for R and R_w (on F) for those 1238 data having $F_o^2 > 3\sigma(F_o^2)$ are 0·027 and 0·032. Final atomic parameters are given in Table 1. Differential scanning calorimetry measurements were made on a Perkin–Elmer DSC2 instrument using both microcrystalline and single-crystal samples.

Description and discussion of the structure

General description

The structure consists of $\mathrm{Ni(en)_3^{2+}}$ cations and $\mathrm{SO_4^{2-}}$ anions. Fig. 2 illustrates the $\mathrm{Ni(en)_3}$ moiety. Bond angles are listed in Table 2. An extensive hydrogen-bonding network links sulphate O atoms to amine H atoms (Fig. 2). At low temperature the $\mathrm{Ni(en)_3}$ group has only point symmetry 3, in contrast to 32 at room temperature, although deviations from idealized 32 symmetry are small. The sulphate group becomes completely ordered, with an S—O bond lying on a threefold axis in contrast to the extensive 32 symmetry imposed disorder for the room-temperature form. The Ni and S centres move along the c axis such that $z \neq \frac{1}{4}$. In the room-temperature structure Ni and S atoms were separated by $c/2 = 4{\cdot}822$ (3) Å; at low temperature the values are 5·052 (2) and 4·637 (2) Å – a substantial structural reorganization. Note that whereas the a and b axes decrease by 0·15 Å on cooling the c axis *increases* by 0·06 Å.

The twinning

The *hkl* and *khl* twinning corresponds to twinning by merohedry through reflection across the $(\bar{1}10)$, the (100) or the (010) planes in real space, which are coincident with glide planes in space group $P\bar{3}1c$. The same twinning law can also be described by rotations

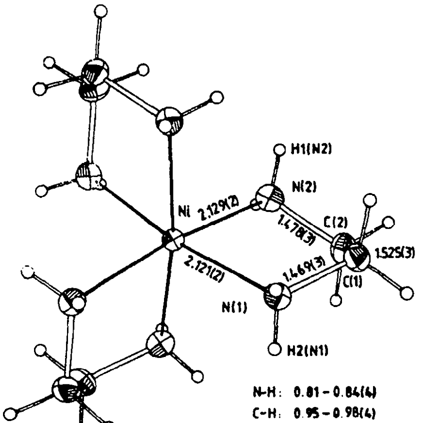

Fig. 2. A view down the trigonal axis of the $\mathrm{Ni(en)_3^{2+}}$ cation at 110 K. Thermal ellipsoids are drawn at the 70% probability level except for H atoms which are shown artificially small. The atom-labelling scheme is also defined. Bond distances are in Å.

Table 2. *Bond angles* (°) *for* $[\mathrm{Ni(en)_3}]\mathrm{SO_4}$ *at* 110 K

N(1)—Ni—N(1)′	94·31 (7)	C(1)—N(1)—H1(N1)	110 (3)
N(2)—Ni—N(2)′	91·24 (7)	C(1)—N(1)—H2(N1)	112 (3)
N(1)—Ni—N(2)	82·18 (7)	C(2)—N(2)—H1(N2)	112 (3)
N(1)—Ni—N(2)′	92·65 (7)	C(2)—N(2)—H2(N2)	111 (3)
N(1)—Ni—N(2)″	172·42 (7)	N(1)—C(1)—H1(C1)	112 (2)
Ni—N(1)—C(1)	108·3 (1)	N(1)—C(1)—H2(C1)	110 (2)
Ni—N(2)—C(2)	107·1 (1)	N(2)—C(2)—H1(C2)	110 (2)
N(1)—C(1)—C(2)	108·8 (2)	N(2)—C(2)—H2(C2)	109 (3)
N(2)—C(2)—C(1)	108·1 (2)	C(2)—C(1)—H1(C1)	108 (2)
Ni—N(1)—H1(N1)	113 (3)	C(2)—C(1)—H2(C1)	111 (2)
Ni—N(1)—H2(N1)	106 (3)	C(1)—C(2)—H1(C2)	109 (2)
Ni—N(2)—H1(N2)	116 (3)	C(1)—C(2)—H2(C2)	112 (2)
Ni—N(2)—H2(N2)	110 (3)		

either about the *c* axis or, more usefully, about the numerous crystallographic twofold axes perpendicular to the *c* axis which exist in the room-temperature $P\bar{3}1c$ phase. The situation is not dissimilar to that encountered by Zalkin *et al.* (1964). With exactly superimposed trigonal lattices we were in an excellent position to utilize fully an extensive data set. For data sets where intensity drops rapidly with increasing values of (sin θ)/λ the distinction between a disordered structure and a twinned structure may become blurred. Further, the domains here are large – as judged crudely by crystal mosaicity they may be similar in size to the optically coherent regions composing the crystal prior to cooling.

The phase transition and comparison with related compounds

At room temperature the Ni and Cu complexes are isomorphous and closely isostructural (see deposited table). Significant differences are, respectively: *M*—N 2·124 (6) and 2·150 (2) Å; N—*M*—N 82·0 (2) and 80·9 (1)°; C—C 1·544 (9) and 1·507 (5) Å.

The transition enthalpy (for groups of single crystals) for $[Cu(en)_3]SO_4$ [2·57 (2) kJ mol^{-1}] is about 7× greater than that for $[Ni(en)_3]SO_4$ [0·35 (2) kJ mol^{-1}], more or less as expected for a system which includes a Jahn–Teller ordering. On the other hand, the transition temperatures for the Cu and Ni $[M(en)_3]SO_4$ systems are remarkably similar, a coincidence derived from entropic $T\Delta S$ effects. In both systems ordering of the sulphate groups occurs. For the Cu system it is incomplete since an S—O bond remains approximately *perpendicular* to the *c* axis. There is, therefore, an interesting dichotomy in entropic effects between the disordered $P\bar{1}$ Cu system and the twinned $P\bar{3}$ Ni system.

Thus we can make only an approximate estimate of the magnitude of the Jahn–Teller component in the structural phase transition for the Cu system, insofar as it is justified to separate the Jahn–Teller effect from the sulphate-ordering effect. The value of 2·57 (2) − 0·35 (2) = 2·22 (4) kJ mol^{-1} thereby obtained represents a lower limit since incomplete sulphate ordering occurs for the Cu system. The transition enthalpies for a number of octahedrally coordinated Cu^{II} systems may be found in another deposited table. The phase transitions involved are of the type

static Jahn–Teller distortion ⇌ dynamic (or static statistically disordered) Jahn–Teller distortion.

The value observed for $[Cu(en)_3]SO_4$ is large (39·2 J g^{-1} Cu) compared to the values for purely inorganic salts, such as $K_2PbCu(NO_2)_6$ (16·1 J g^{-1} Cu), which lie in the range 14·6–25·9 J g^{-1} Cu.

The low-temperature Ni complex – with corresponding values for the low-temperature Cu system given in square brackets – shows some asymmetry in the ethylenediamine coordination (see also deposited table): *M*—N 2·121 (2) and 2·129 (2) Å [2·03 (1) to 2·24 (1) Å]; *M*—N—C 107·1 (3) and 108·3 (3)° [103·7 (9) to 109·9 (9)°]; *M*—N—C—C −39·8 (2) and −43·6 (2)° [−41 (1) to −45 (2)°]; N—C—C—N 56·8 (2)° [58 (2) to 60 (2)°]; displacements of C atoms from *M*NN plane: −0·302 and 0·424 Å [−0·32 to 0·40 Å].

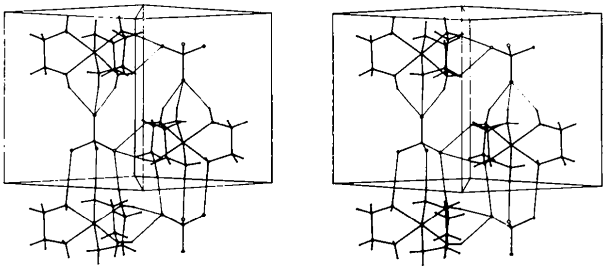

Fig. 3. Unit-cell diagram of $[Ni(en)_3]SO_4$ at 110 K. Hydrogen bonds are indicated with thin lines.

Substantial differences exist in the hydrogen-bonding networks for the room- and low-temperature phases of the Ni and Cu crystal structures. These are summarized in another deposited table and illustrated in Fig. 3 and a deposited figure. Generally, each O atom in both the room- and low-temperature structures makes three hydrogen bonds. Noticeably shorter separations occur for the room-temperature structures and for the low-temperature Cu system, although for the former two some of this may be an artefact of thermal foreshortening. The most remarkable difference is the absence of close C—H···O contacts in the Cu, and especially the Ni, low-temperature phases. Indeed, in the room-temperature structures there exist C···O and C—H···O contacts shorter than some of the purported hydrogen bonds; for example: C···O [C—H···O], 3·16 (5) [2·32 (7)] and 3·18 (3) [2·30 (6)] Å, for the Ni and Cu room-temperature phases, respectively; N···O [NH···O], 3·16 (4) [2·69 (7)], 3·30 (4) [2·56 (6)] and 3·17 (3) [2·50 (6)], 3·23 (4) [2·38 (4)] Å.

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(*N*-Methylimidazole)(2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)copper(II) Hexafluorophosphate

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Abstract

$[Cu(C_4H_6N_2)(C_{14}H_{24}N_4)].(PF_6)_2$, $C_{18}H_{30}CuN_6^{2+}.2PF_6^-$, $Pna2_1$, $a = 17{\cdot}535\ (4)$, $b = 18{\cdot}527\ (3)$, $c = 8{\cdot}569\ (2)$ Å, $V = 2784$ Å^3, $Z = 4$, $d_{\rm exp} = 1{\cdot}64\ (2)$, $d_{\rm calc} = 1{\cdot}632$ g cm^{-3}, Mo $K\alpha$, $\mu = 10$ cm^{-1}. The structure was refined by full-matrix least squares to $R = 0{\cdot}051$ and $R_w = 0{\cdot}037$, with 5718 F values in the $hk\pm l$ quadrant. The coordination of the copper atom is square pyramidal, the four nitrogen atoms of the macrocycle forming the basal plane and the unsubstituted *N*-methylimidazole nitrogen atom the apex. The copper atom is displaced out of the coordination plane toward the axial ligand by 0·44 (1) Å.

Introduction

As part of an effort to model and understand copper proteins, we have undertaken the determination of the structures of a series of four- and five-coordinated compounds of divalent copper with the macrocycle 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene which we call TIM, see Fig. 1. The crystals of the present compound, royal blue in color, were provided by M. J. Maroney. The cation is five-coordinate square pyramidal, the apical ligand being *N*-methylimidazole, and the TIM nitrogen atoms forming the basal plane.

Oscillation, Weissenberg, and precession photographs indicated orthorhombic symmetry; the systematic absences, $0kl$ for $k + l = 2n + 1$ and $h0l$ for $h = 2n + 1$, suggested that the space group is $Pna2_1$ or $Pnam$; and the Wilson statistics narrowed the choice to $Pna2_1$. The cell parameters were determined by a least-squares fit of the parameters of the orientation matrix to the setting angles of 12 reflections with 2θ between 35 and 43°. The experimental density was measured by flotation in a solution of chloroform and 1,3-dibromopropane.

Intensity data: 0·4 × 0·4 × 0·5 mm crystal; $\theta/2\theta$ scans, 2° min^{-1} in 2θ, 20 s background counts fore

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