Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Rapid structure determination of the hydrogen-containing compound $Cs_2C_2O_4 \cdot H_2O$ by joint single-crystal X-ray and powder neutron diffraction

Mark T. Weller,* Paul F. Henry and Mark E. Light

School of Chemistry, University of Southampton, Southampton SO17 1BJ, England

Correspondence e-mail: mtw@soton.ac.uk

Received 23 February 2007
Accepted 27 March 2007

The structure determination of caesium oxalate monohydrate using single-crystal X-ray diffraction, powder neutron diffraction data and a combination of both has been undertaken. Results show that even for hydrogen-containing materials data collected rapidly on a high-flux neutron diffractometer improve the refinement such that accurate positional and thermal displacement parameters can be extracted for all atom types. This contrasts with structural models extracted from either data set alone that demonstrate the inherent limitations of the individual diffraction methods. The rapidity with which useful neutron diffraction data has been collected from hydrogen-containing compounds, 10 min in this study, indicates that the technique should be widely applicable allowing the facile and accurate extraction of hydrogen positions for many compounds.

1. Introduction

Hydrogen is a key element, with more compounds than any other, and whose functionality in both inorganic and organic compounds is central to controlling many of their structural and physical properties. In inorganic systems hydrogen-containing materials of interest stretch from geochemical materials (*e.g.* clay minerals, cements; Welch *et al.*, 2002), through functional inorganic compounds (*e.g.* catalysts, coordination complexes and hydroxides/hydrates; Hriljac *et al.*, 1995) and materials (*e.g.* ferroelectrics, hydrogen-storage media, fuel-cell components; Belushkin, 1997) to framework systems (*e.g.* zeolites, solvates and clathrates; Jobic, 2002). In organic systems hydrogen bonding between molecules is often crucial in determining crystal packing and the choice of structure in a polymorphic system (Allen & Motherwell, 2002; Aakeroy & Seddon, 1993).

For organic compounds and some light-atom inorganics, such as borohydrides, modern single-crystal X-ray diffractometers are normally sufficiently sensitive to scattering from hydrogen to allow the accurate determination of the centre of electron density associated with this atom. In many cases, though, this X-ray diffraction-determined position is perturbed from the nuclear centre producing artificially shortened $A-H$ distances, particularly for electronegative elements, A, such as O and N. Previously, the determination of H-atom positions using X-ray diffraction methods in inorganic compounds with heavier atoms present has proved impossible or has led to very inaccurate and imprecise extracted crystallographic information for hydrogen. Neutron diffraction methods are the obvious choice for locating hydrogen as its scattering length (-0.3739 fm) is comparable in magnitude to those of other atom types. Single-crystal neutron diffraction techniques can be applied to provide accurate and precise

Table 1
Experimental details for single-crystal X-ray diffraction.

Crystal data	
Chemical formula	$C_2H_2O_5Cs_2$
M_r	371.86
Cell setting, space group	Monoclinic, *C*2/*c*
Temperature (K)	289 (2)
a, *b*, *c* (Å)	10.0748 (5), 6.6473 (3), 11.2997 (6)
β (°)	107.189 (3)
V (Å^3)	722.94 (6)
Z	4
D_x (Mg m^{-3})	3.416
Radiation type	Mo *Kα*
μ (mm^{-1})	10.04
Crystal form, colour	Colourless, block
Crystal size (mm)	0.2 × 0.11 × 0.07
Data collection	
Diffractometer	Bruker–Nonius KappaCCD
Data collection method	2θ and ω scans
Absorption correction	Multiscan *SADABS*
$T_{\min}$	0.2060
$T_{\max}$	0.5005
No, of measured, independent and observed reflections	4032, 809, 700
Criterion for observed reflections	$I > 2\sigma(I)$
$R_{\rm int}$	0.0669
$\theta_{\max}$ (°)	27.31
Refinement	
Refinement on	F^2
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0249$, $wR_2 = 0.0513$
R indices (all data)	$R_1 = 0.0314$. $wR_2 = 0.0536$
S	1.168
No. of reflections	809
No of parameters	47
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0142P)^2 + 1.8270P]$, where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.956, −0.904

information on hydrogen positions where sufficiently large (0.1–1 mm^3), high-quality crystals are available, although this technique often requires several days for each data-set collection (Keen *et al.*, 2006). For powder neutron diffraction, the incoherent scattering of neutrons by the ^{1}H isotope using standard instrumentation leads to high backgrounds and noisy data sets from which the extraction of hydrogen positions is normally so poor as to be not worthwhile. Such problems have, in some cases, been overcome by sample deuteration (for polycrystalline materials) or by undertaking single-crystal neutron studies. However, these techniques are of very limited applicability owing to the cost and time for deuteration, the difficulty of growing the large single crystals and the high cost of lengthy experiments on neutron sources. In addition, deuteration may perturb the hydrogen position, particularly for strongly hydrogen-bonded systems, thus producing structural information of reduced relevance for materials whose functionality is dependent on hydrogen, *e.g.* hydrogen-storage materials, ferroelectrics and proton conductors (Deguchi *et al.*, 2005).

Studies of inorganic materials using a combination of X-ray and neutron diffraction data have been reported previously, although such work is rare. Most common are serial experiments where a structure is initially determined using X-ray diffraction and then specific structural elements, poorly determined in the X-ray work such as the light atom positions or the distributions of (near) isoelectronic species, fully delineated in subsequent powder or single-crystal neutron diffraction studies. Examples of such studies on hydrogenous compounds include those of the barium halide monohydrates $BaX_2{\cdot}H_2O$ (*X* = Cl, I; Moller *et al.*, 1993) and of Tutton's Salt, $K_2[Co(H_2O)_6](SO_4)_2$ (Kirfel *et al.*, 1998). The material is almost invariably deuterated prior to any powder neutron diffraction investigation.

Improved definition of the structure can often be obtained by combining the analyses into one refinement with a single crystallographic description used to model both the X-ray and the neutron diffraction sets. Such methods have most frequently been applied to combined powder X-ray and powder neutron diffraction data, and particularly to complex oxide systems; examples of recent applications of this method include studies of the lanthanum gallates (Guenter *et al.*, 2006) and $Li_xV_3O_8$ (Jouanneau *et al.*, 2005). The recent *ab initio* structure solution of the potential hydrogen storage material $Li_4(BH_4)(NH_2)_3$ using combined powder X-ray and neutron techniques is a noteworthy example of this approach (Chater *et al.*, 2006).

In some cases a combined single-crystal X-ray and single-crystal neutron diffraction analysis has been undertaken, *e.g.* the relatively recent study of $(Ph_4P)_3[Zr_6Cl_{18}H_5]$ (Cotton *et al.*, 1996) where a single crystallographic description has been used to model data from both experimental techniques. For data collection with single-crystal neutron diffraction deuteration is unnecessary as peak intensities can easily be integrated above the large incoherent background.

Very rarely has a combined analysis using single-crystal X-ray and powder neutron diffraction been employed, despite the quality of structural information inherent in such data. One of the few examples is the study of the jarosite $NaV_3(OD)_6(SO_4)_2$, where the combined approach enabled the excellent definition of all the structural elements (with sensitivity to all atom types present), although for the powder neutron diffraction analysis deuteration was undertaken and the data collection time was considerable, 18–24 h on a 4 cm^3 sample (Grohol *et al.*, 2003). Similarly, the modulated structure of $Bi_2Sr_2CaCu_2O_{8+y}$ has been more accurately delineated using a combined powder neutron diffraction–single-crystal X-ray diffraction method (SXD–PND; Gao *et al.*, 1993). The only previously combined SXD–PND work on a partly hydrogenous systems is that on $[Re_4(\mu_3\text{-}H)_4(CO)_{12}]{\cdot}2C_6D_6$ (Masciocchi *et al.*, 1997), although with limited-quality neutron data the definition in important bond lengths, *e.g.* Re—H = 1.88 (12) Å, is poor despite the low hydrogen percentage (7%) and extended experimental time.

Thus, a method that can yield accurate and precise hydrogen positions in inorganic compounds, in their typically produced forms and using reasonable experimental periods and costs, would be widely applicable and of considerable importance. In this article we describe how standard single-crystal X-ray diffraction methods coupled to rapid powder

Table 2
Experimental details for powder neutron diffraction and joint data-set refinement.

Sample data and data collection	Powder neutron diffraction data	Joint data-set refinement
Neutron wavelength (Å)	1.36	
Sample	1 g polycrystalline in 5 mm diameter vanadium can	
Temperature (K)	298	289/298
a, *b*, *c* (Å)	10.1126 (5), 6.6533 (4), 11.3255 (6)	10.1125 (5), 6.6535 (4), 11.3255 (6)
β (°)	107.190 (4)	107.191 (4)
V (Å^3)	727.97 (7)	727.97 (7)
Data collection		
Diffractometer	D20, ILL Grenoble	
Data collection method	High-resolution mode, 10 min	
θ range (°) collected, used	0–154, 10–140, step size 0.1°, 1300 observations	
Refinement		
Refinement on	$I_{\rm net}$	$F^2/I_{\rm net}$
Neutron		
$R(F^2)$	0.051	0.063
wR_P (fitted), R_P (fitted)	0.0124, 0.0090	0.0132, 0.0095
wR_P (minus background)	0.0232	0.0252
R_P (minus background)	0.0124	0.0134
Single crystal		
$R(F)$, $wR(F_o)$	–	0.0247, 0.032
χ^2	2.08	2.80 (total)
No. of reflections	809	809/818
No of parameters	71 (including profile parameters)	73 (including profile parameters)
Weighting scheme	$w = 1/\sigma(Y_{\rm obs})^2$	As single data sets; equal weighting to neutron and X-ray data

neutron diffraction on a hydrogen-containing powder can resolve this problem, and produce precise and accurate positions on all atom types present in a hydrogenous material. The method employs short experimental times and would be applicable to most materials, as produced in the laboratory, *i.e.* polycrystalline, 0.1–1 g, and as small, < 50 µm, single crystals.

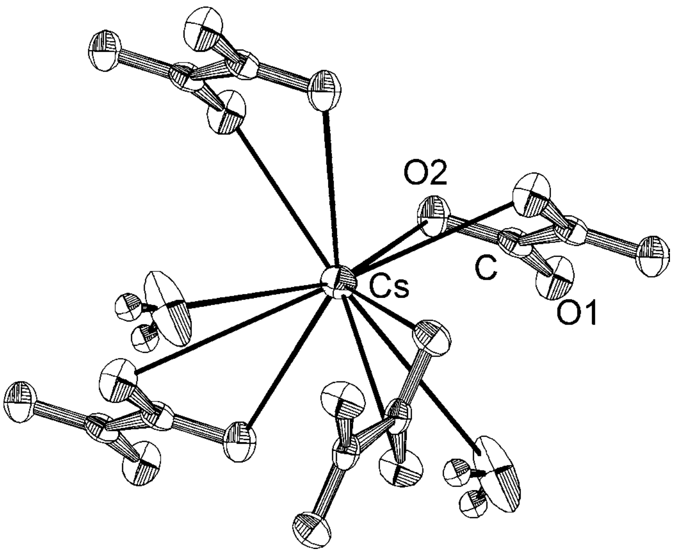

Figure 1
The structure of $Cs_2C_2O_4{\cdot}H_2O$ as initially obtained from single-crystal X-ray diffraction data alone. Displacement ellipsoids are drawn at the 50% probability level with H atoms depicted as spheres with arbitrary radius. The asymmetric unit is labelled.

2. Experimental

A sample of caesium oxalate monohydrate, $Cs_2(C_2O_4){\cdot}H_2O$, a compound previously unreported in the structural chemistry literature, was prepared as follows: 8.196 g of 50 wt% CsOH (Aldrich; 27.34 mmol of CsOH) was diluted with 25 ml of distilled water and added to a solution of 1.2302 g (13.67 mmol) of oxalic acid dihydrate, $C_2O_4H_2{\cdot}2H_2O$, dissolved in 25 ml of water. The solution was evaporated to dryness either by heating to 343 K in a flow of air or leaving it in a Petri dish in a desiccator over concentrated H_2SO_4. The compound crystallized as a fine white powder (solvent evaporation at 343 K) or as large crystals, typically with several cubic millimetres in dimension (desiccator evaporation). Powder X-ray diffraction data collected from the product showed no match with JCPDS database patterns for caesium oxalate dihydrate, $Cs_2C_2O_4{\cdot}2H_2O$, 77-0629 (Kholodkovskaya *et al.*, 1990), or caesium hydrogen oxalate oxalic acid dihydrate, $Cs(HC_2O_4)(H_2C_2O_4){\cdot}2H_2O$ (Clegg, 1984).

3. Data collection and initial structure solution (Sheldrick, 1997, 2003; Farrugia, 1999; Otwinowski & Minor, 1997; Hooft, 1998)

Cell dimensions and intensity data were recorded at 289 K on a Bruker–Nonius KappaCCD, Table 1. The structure was solved using direct methods and refined using full-matrix least-squares *via SHELX*97 (Sheldrick, 1997). All non-H atoms were refined with anisotropic temperature factors and the hydrogen positions were located from the difference map and fully refined. Results are summarized in the supplementary material;[1] Fig. 1 shows the asymmetric unit.

Powder neutron diffraction data were collected using the D20 high-flux diffractometer operating in a high-resolution mode (Convert *et al.*, 1997), Table 2. No attempt was made to optimize the data collection method in terms of wavelength or sample mounting. The large incoherent scattering from hydrogen contributes strongly to the diffraction profile, but is isotropic and rapidly averaged to a smooth function on this

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK5052). Services for accessing these data are described at the back of the journal.

high-flux instrument. Data were treated using the standard data reduction protocols for the D20 instrument in LAMP. A few data points were excluded from the data-set analyses owing to inconsistencies in the normalization process resulting from electronic noise.

4. Further and combined data analysis

Limited software is available for structure solution and refinement using both single-crystal and powder diffraction data. The *GSAS* suite of programs (Larson & Von Dreele, 2004) has this functionality; while this software is normally used for the analysis of powder diffraction data, it has been used successfully to solve single-crystal data (Grey *et al.*, 1997). For refinements using multiple data sets these may be read into the structure refinement suite as separate histograms and the weighting factors applied to the histograms may be modified.

In order to confirm that the single-crystal X-ray diffraction data could also be modelled with the *GSAS* program package, the solution and refinement was repeated using this software with the raw 289 K diffraction data; the supplementary material summarizes the refined model and refinement statistics obtained from this analysis. Consideration of the extracted crystallographic descriptions at 289 K using the *SHELX* and *GSAS* analysis methods show only minor differences, well within the s.u.s, in their extracted crystallographic information.

Analysis of the powder neutron diffraction data was initially undertaken using the single-crystal determined structural model and this data set alone. Profile fitting was undertaken using the standard methodology with the *GSAS* refinement suite including all profile parameters (lattice parameters, peak half-width descriptions, zero point *etc.*) and atomic positional parameters; no constraint was used. Note that a slight difference in the data collection temperatures (298 K for neutron *versus* 289 K for single-crystal refinement) results in a small observed expansion in the extracted lattice parameter from the neutron data. Anisotropic thermal displacement parameters were included for all atoms in the final stages of the refinement. The intense background varies smoothly as a function of angle and was well fitted using a simple ten-term, cosine Fourier series. The final extracted positional parameters and derived bond lengths/angles of interest are summarized in the supplementary material. Fig. 2 shows the unit-cell content including the refined H-atom positions; Figs. 3(*a*) and (*b*) show, respectively, the profile fits achieved without and with background subtraction.

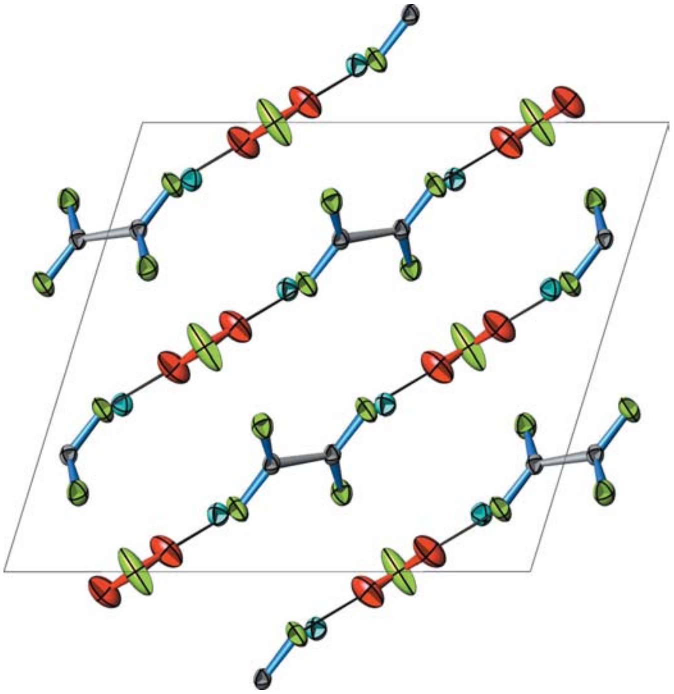

Figure 2
The structure of $Cs_2C_2O_4{\cdot}H_2O$ as extracted from the joint powder neutron diffraction–single-crystal X-ray diffraction analysis, viewed down the *b* axis. Cs cyan; C dark grey, O dark blue and H red. Displacement ellipsoids are shown at 50% probability.

The final refinement type undertaken involved fitting both single-crystal X-ray and powder neutron diffraction data within the *GSAS* suite. Weightings of unity were given to each data set; lattice parameters were only determined using the neutron diffraction data. Final cycles of refinement, which converged rapidly, included all refineable profile, atomic and thermal displacement parameters. The extracted positional and thermal displacement parameters for this analysis are given in the supplementary material.

5. Discussion

5.1. Structure description

The structure of dicaesium oxalate monohydrate, $Cs_2C_2O_4{\cdot}H_2O$, consists of chains of hydrogen-bonded oxalate anions ($C_2O_4^{2-}$) and water molecules, which run in the *ac* direction, and coordinate through the O atoms of both species to caesium ions. The caesium ion is in tenfold coordination to two water molecule O atoms and eight oxalate-group oxygen sites. The water molecule lies on the twofold axis with symmetry-related hydrogen positions. The hydrogen bond lies between two O atoms separated by 2.727 Å and the off-axis angle O—H···H is $\sim 164^\circ$, which is typical of a hydrogen bond of this length. The displacement parameter ellipsoid for the water O atom is elongated along the direction perpendicular to the water molecule plane and along the direction between two caesium ions.

5.2. The methodology

The structural results extracted from the single-crystal X-ray diffraction experiment alone demonstrate all the well known limitations of this method for inorganic compounds and particularly those containing moderately or very heavy elements, Table 3. The hydrogen position is poorly defined with s.u.s on its atomic coordinates over an order of magnitude larger than those on the other atoms in this material. As would be expected, it was impossible to model any anisotropic thermal displacement behaviour for this atom. Furthermore, the extracted hydrogen position and derived O—H bond length (~ 0.8 Å) is typical of this contact which is artificially shortened by the measurement of the electron distribution in this bond (Bacon, 1975).

The structural parameters extracted from the neutron data alone (Table 3) also reflect the inherent limitations in this analytical method; these derive from the specific scattering lengths of the nuclei present, a limited number of uncorrelated data {with 1300 observable reflections covering 1033 reflections compared with 809 uniquely determined $[I > 2\sigma(I)]$ reflections for single-crystal refinement} and problems in determining the exact background position, particularly in the low *d*-spacing range. The overall correlation between integrated Bragg peak intensities and the true measure of uncorrelated independent reflections has been discussed by David (1999); in the case of this sample and the relatively low-resolution data from D20 (Convert *et al.*, 1997), the fraction of independent peaks/total Bragg peaks is around 0.35. Thus, the crystallographic model obtained from the neutron data alone has greater s.u.s (by factors of typically 2–3) on most positional and displacement parameters, and on the derived bond lengths, when compared with the single-crystal X-ray model. The exception is obviously the H atom whose position and thermal motion is defined with similar accuracy to that of the other elements, Fig. 4. The extracted O—H distance of 0.98 Å is typical of the true internuclear separation and the water molecule internal angle at 111 (1.0)° is much more realistic than the 101 (6)° (average value for the two analyses) extracted from the X-ray diffraction data.

The structural model extracted from combined data-set refinement benefits from the information inherent in both diffraction techniques. This leads to a full structural model with all atom positions well defined, and derived bond lengths and angles accurately and precisely measured, Table 3.

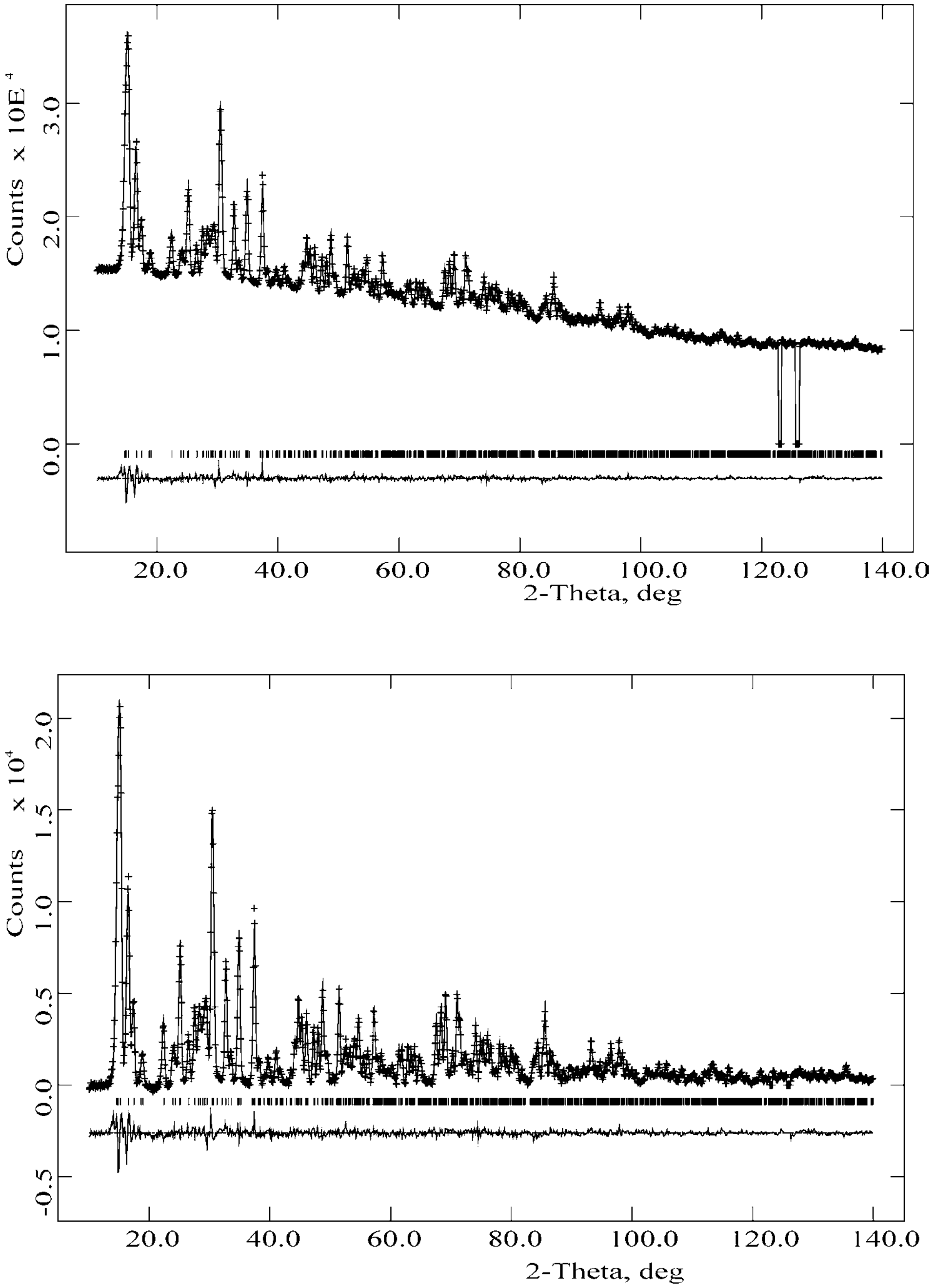

Figure 3
Profile fit achieved to the powder neutron diffraction data from $Cs_2C_2O_4 \cdot H_2O$ (*a*) including the background counts and showing a smooth background function from the incoherent scattering and (*b*) with the background subtracted. The crosses show measured intensity, the upper continuous line the calculated profile and the lower continuous line the difference. Tick marks show the reflection positions. Small excluded regions corresponding to electronic noise are marked.

6. Conclusions

Combining X-ray and neutron data sets in structure determination has been used previously, albeit not widely. Examples of its recent application are mainly limited to powder X-ray and powder neutron diffraction data, and in the studies of oxides and some framework structures. In such cases the combined refinement often helps with specific structural problems, such as distinguishing neighbouring elements or defining accurate oxygen positions in heavy metal

Table 3
Extracted bond lengths (Å) and angles (°) at 298 K for the various data-analysis methods employed.

Bond/angle	Analysis method	Kappa CCD *SHELX*97	Kappa CCD *GSAS*	D20 Neutron only *GSAS*	Combined *GSAS*
Cs—O1		3.120 (3)	3.116 (2)	3.111 (6)	3.1253 (21)
Cs—O2		3.116 (3)	3.118 (2)	3.129 (6)	3.1267 (19)
Cs—O1		3.123 (3)	3.124 (3)	3.127 (5)	3.1260 (19)
Cs—O2		3.131 (2)	3.133 (3)	3.130 (7)	3.1418 (18)
Cs—O2		3.149 (2)	3.148 (2)	3.169 (6)	3.1557 (18)
Cs—O2		3.205 (2)	3.203 (2)	3.197 (7)	3.2075 (19)
Cs—O3		3.217 (4)	3.215 (3)	3.227 (7)	3.2278 (23)
Cs—O1		3.343 (3)	3.347 (2)	3.351 (6)	3.3547 (20)
Cs—O1		3.579 (3)	3.579 (3)	3.591 (6)	3.5831 (21)
Cs—O3		3.716 (1)	3.717 (2)	3.733 (4)	3.7278 (23)
O3—H		0.81 (6)	0.78 (3)	0.979 (9)	0.964 (7)
O2—H		2.05 (5)	2.09 (3)	1.853 (9)	1.881 (7)
O3—H···O2		161 (6)	162.2 (1.3)	165.4 (7)	164.5 (6)
H—O3—H		104 (6)	97 (5)	111.4 (1.0)	111.0 (1.1)
O1—C5		1.244 (6)	1.249 (4)	1.269 (5)	1.251 (3)
O2—C5		1.256 (5)	1.254 (4)	1.254 (6)	1.256 (3)
C5—C5		1.566 (9)	1.556 (7)	1.573 (6)	1.573 (4)
O2—C5—O3		125.6 (4)	125.2 (3)	125.1 (4)	125.71 (23)

oxides. Previously, experiments combining single-crystal X-ray and powder neutron diffraction data have not been undertaken; in essence, such studies have rarely been worthwhile as the desired structural information has either been available from one such technique alone or the time and effort involved in carrying out two diffraction experiments deemed unnecessary or problematic. Where the full structural information is of importance it usually pertains to hydrogen positions and researchers have where possible resorted to single-crystal neutron diffraction or powder neutron diffraction on deuterated materials. However, application of either of these methods is often challenging or impractical.

Single-crystal neutron diffraction requires the growth of large crystals and/or extended experiments; even with high-flux modern instrumentation, *e.g.* VIVALDI at ILL and SXD at ISIS, a crystal of a volume of a few cubic millimetres and 3–7 d beamtime are typical. In some cases growing crystals of sufficient size and quality is extremely time-consuming, in many others it is just not possible. Effort to tackle these problems is still ongoing and involves, for example, the construction of even higher flux instrumentation, and the development of methods for analysing data sets obtained from multiple crystals and of partial data sets. Currently the method remains of limited application and relevance but is crucial for some systems, such as hydrogen-containing organometallics and complexes as it can yield information unobtainable by any other technique. For structurally complex hydrogenous materials, with very large asymmetric units, the application of single-crystal neutron diffraction is still likely to be necessary if the crystal can be easily obtained.

Powder neutron diffraction studies of hydrogenous materials generally require deuteration, which is time consuming, expensive and difficult to ensure. In some cases deuteration may also affect the properties of the materials under investigation, for example many hydrogen-bonded ferroelectrics, (Wilson *et al.*, 1991) and also their formation, *e.g.* in zeolite synthesis (Burkett & Davis, 1995). Furthermore, using such powder diffraction data alone for structure refinement limits the complexity of the system that can be studied, even with high-resolution instrumentation.

By combining the techniques of single-crystal X-ray and powder neutron diffraction (on a high-flux, medium-resolution instrument) we have shown that very high-quality structural data on all atom types, including hydrogen, can be obtained. With a high-flux neutron diffractometer, moderate-resolution data sets of sufficient quality to bias the refinement appropriately in terms of accurate (the hydrogen nuclear position) and precise definition of the H atom may be collected rapidly and on reasonably small samples. The incoherent scattering from hydrogen is rapidly averaged on a high-flux instrument to a smooth background function that can be fitted easily as part of the profile analysis. Thus, the complete diffraction data can be obtained very quickly – in this case with total data collection over ~ 1 h – and a full structure solution completed soon thereafter.

Figure 4
Displacement ellipsoids, 50% probability, for caesium linked to one water molecule and one oxalate ion. Data were extracted from, left to right, single-crystal X-ray diffraction data, powder neutron diffraction data and joint data-set analyses.

We are extremely grateful to the ILL for providing beamtime for this study and Professor C. C. Wilson, University of Glasgow, for useful discussions.

References

Aakeroy, C. B. & Seddon, K. R. (1993). *Chem. Soc. Rev.* **22**, 397–407.
Allen, F. H. & Motherwell, W. D. S. (2002). *Acta Cryst.* B**58**, 407–422.
Bacon, G. E. (1975). *Neutron Diffraction*, 3rd Ed, pp. 352–357. Oxford: Clarendon Press.
Belushkin, A. V. (1997). *Crystallogr. Rep.* **42**, 501–524.
Burkett, S. L. & Davis, M. E. (1995). *Chem. Mater.* **7**, 1453.
Chater, P. A., David, W. I. F., Johnson, S. R., Edwards, P. P. & Anderson, P. A. (2006). *Chem. Commun.* pp. 2439–2441.
Clegg, W. (1984). *Z. Kristallogr.* **169**, 211–215.
Convert, P., Hansen, T., Oed, A. & Torresgrossa, J. (1997). *Physica B*, **241**, 195–197.
Cotton, F. A., Chen, L. & Schultz, A. J. (1996). *C. R. Acad. Sci. Ser. II*, **323**, 529–544.
David, W. I. F. (1999). *J. Appl. Cryst.* **32**, 654–663.

Deguchi, K., Azuma, S. & Kobayashi, Y. (2005). *J. Phys. Soc. Jpn*, **74**, 2506–2509.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Gao, Y., Coppens, P., Cox, D. E. & Moodenbaugh, A. R. (1993). *Acta Cryst.* A**49**, 141–148.

Grey, I. E., Roth, R. S. & Balmer, M. L. (1997). *J. Solid State Chem.* **131**, 38–42.

Grohol, D., Huang, Q. Z., Toby, B. H., Lynn, J. W., Lee, Y. S. & Nocera, D. G. (2003). *Phys. Rev. B*, **68**, Art No 094404.

Guenter, M. M., Lerch, M., Boysen, H., Toebbens, D., Suard, S. & Baehtz, C. (2006). *J. Phys. Chem. Solids*, **67**, 1754–1768.

Hooft, R. W. W. (1998). *Collect.* Nonius BV, Delft, The Netherlands.

Hriljac, J. A., Torardi, C. C. & Vogt, T. (1995). *J. Phys. Chem. Solids*, **56**, 1339–1343.

Jobic, H. (2002). *Curr. Opin. Solid State Mater. Sci.* **6**, 415–422.

Jouanneau, S., Verbaere, A. & Guyomard, D. (2005). *J. Solid State Chem.* **178**, 22–27.

Keen, D. A., Gutmann, M. J. & Wilson, C. C. (2006). *J. Appl. Cryst.* **39**, 714–722.

Kholodkovskaya, L. N., Trunov, V. K. & Tskhelashvili, N. B. (1990). *J. Struct. Chem.* **31**, 154–158.

Kirfel, A., Klapper, H., Schafer, W. & Schwabenlander, F. (1998). *Z. Kristallogr.* **213**, 456–460.

Larson, A. C. & Von Dreele, R. B. (2004). *GSAS*, Report LAUR86-748. Los Alamos National Laboratory, New Mexico, USA.

Masciocchi, N., D'Alfonso, G., Kockelmann, W., Schafer, W. & Sironi, A. (1997). *Chem. Commun.* pp. 1903–1904.

Moller, H., Kellersohn, T., Schmidt, M., Lutz, H. D. & Cockcroft, J. K. (1993). *Z. Kristallogr.* **208**, 19–26.

Otwinowski, Z. & Minor, W. (1997). *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, edited by C. W. Carter & R. M. Sweet, Part A, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELX*97, Release 97–2. University of Göttingen, Germany.

Sheldrick, G. M. (2003). *SADABS*, Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Welch, M. D., Marshall, W. G., Ross, N. L. & Knight, K. S. (2002). *Am. Mineral.* **87**, 154–159.

Wilson, C. C., Cox, P. J. & Stewart, N. S. (1991). *J. Crystallogr. Spectrosc. Res.* **21**, 589–593.