JOURNAL OF SOLID STATE CHEMISTRY **100**, 191–196 (1992)

Ab Initio Structure Determination of $LiCF_3SO_3$ from X-Ray Powder Diffraction Data Using Entropy Maximization and Likelihood Ranking

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Communicated by J. B. Goodenough, June 22, 1992

Entropy maximization combined with likelihood ranking has been applied to the determination of a previously unknown inorganic crystal structure—lithium triflate, $LiCF_3SO_3$—from X-ray powder diffraction data. This technique partitions the intensities of overlapping reflections in a rational fashion and has the potential to solve more complex structures from powder diffraction data than has been possible previously. Structure solution of $LiCF_3SO_3$ by this technique revealed a partially determined structure which was completed via difference Fourier and Rietveld refinement methods. Final refinement of the structure involved the use of both X-ray and neutron powder diffraction data. The structure is in the monoclinic system, space group $P2_1/c$, $a = 10.2432(2)$ Å, $b = 5.0591(1)$ Å, $c = 9.5592(3)$ Å, $\beta = 90.319(2)°$.

Introduction

Recent advances in powder diffraction instrumentation and software have generated a great deal of activity in the ab initio determination of crystal structures from powder diffraction data (*1*). This activity has concentrated largely on relatively simple inorganic systems, but has recently been extended to small organometallic and organic

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0022-4596/92 $5.00

molecular systems (*2*, *3*). In these studies, the problem of peak overlap in the powder pattern is the factor which limits the complexity of structures that can be determined successfully by this method. Overlap of nonequivalent reflections arises either by symmetry-imposed degeneracy, in the case of high-symmetry systems, or by accidental degeneracy, especially at high scattering angle, in the case of low-symmetry systems. Ab initio structure determination relies on the ability to assign intensities to individual reflections, therefore overlap limits the amount of useful data available for structure solution. According to Sheldrick's rule (*4*), a structure will be difficult to solve by conventional direct methods if less than 50% of the available data in the resolution range 1.1–1.2 Å is "observed." Exceptions to this rule are very small structures or heavy-atom structures. Patterson methods have the advantage of requiring less data and have been applied successfully to heavy-atom structures (*1*, *2*) and also to small molecular structures of fixed geometry (*5*). However, it is clear that for significant progress to be made, such that the complexity of structures which can be *solved* from powder diffraction data is comparable to that which can be meaningfully *refined* from the same data, a more sophisticated method of extracting useful information from heavily overlapped powder patterns is required.

The most promising method is the Maximum Entropy and Likelihood approach. Most current approaches to ab initio structure determination from powder diffraction data either ignore overlapping reflections or partition their intensities in an arbitrary manner (for example, fully overlapping reflections are commonly assigned equal intensities). The method of entropy maximization and likelihood ranking, however, is a significant improvement in that overlapped data are treated in a rational manner (*6*, *7*), as discussed below. It should also be noted that David (*8*) has applied a related method to Patterson deconvolution from powder data for TiO_2.

We believe that the maximum entropy and likelihood technique has the potential to become the most effective method for ab initio structure determination from powder diffraction data. However, the technique has not, as yet, been tested extensively. This paper contains the first reported determination of a previously unknown structure by the maximum entropy and likelihood method from powder diffraction data. Due to the relatively poor scattering of X-rays by lithium, the structure of $LiCF_3SO_3$ has been refined by the combined use of X-ray and neutron diffraction data.

Summary of the Method

The theoretical basis of the maximum entropy and likelihood method has been described elsewhere (*9*, *10*). Its intuitive content may be understood by reference to "structure factor graphs" (*11*) as used, for instance, in solving the structure of penicillin (*12*). We view an unknown crystal structure as made up of atoms with known chemical identity, but unknown positions, and initially consider the latter as random with a uniform distribution in the asymmetric unit. Structure determination consists in the gradual removal of this randomness. For this purpose, a strong Bragg reflection is interpreted as indicative of a bias, away from uniformity, in the distribution of atomic positions. This leads to placing any strong scatterers near the maxima of the structure factor graph for that reflection in accordance with its known or assumed phase. For very small structures, a strong scatterer placed in this fashion can be used as a "heavy atom," which itself may represent a sufficiently good initial structural model for subsequent structure refinement. Success will depend on whether this tentative heavy-atom position can account for salient features in the pattern of intensities in the rest of the data and not just for the strong reflection(s) used in inferring this position.

Our method is a statistical generalization of this idea in which assumed phases for a "basis-set" of strong reflections give rise not to a tentative position for some dominant scatterer, but to a tentative redistribution of random positions of all scatterers. By virtue of the maximum entropy criterion used in its construction, this redistribution is the most noncommital with respect to the data outside the basis-set; nevertheless, it still predicts certain biases in the intensity distribution within these data. The "log-likelihood gain" (LLG) affords an optimal measure of the degree of corroboration of that prediction (and hence of the basis-set phase assumptions from which it is derived) by the observed intensities of the reflections not in the basis-set. The intensities of overlapped reflections are used in the calculation of the LLG. Each such measurement is interpreted as the squared radius of a hypersphere (*6*), and the single-crystal LLG is integrated over all possible separations of the total intensity into individual intensities for the members of the overlap. This allows optimal use of all available data while avoiding the bias inherent in simply equipartitioning the intensities of overlapping reflections.

We use a phasing tree as a convenient bookkeeping device for recording the hierarchy between successive phase assumptions, and their acceptance or rejection as the basis-set is progressively enlarged. Phase assumptions for the most recently incorporated reflections are generated by considering all possible signs for the real and/or imaginary parts of the associated structure factors. A statistical analysis of their LLG's is then used to select significant phase indications and to prune the tree accordingly.

Experimental

Polycrystalline anhydrous lithium triflate, $^7LiCF_3SO_3$, was prepared by slow addition of aqueous trifluoromethane sulphonic acid (triflic acid) (0.667 mol dm^{-3}, Aldrich) to $^7Li_2CO_3$ (AEA Technology, Harwell) while stirring. The solution was filtered through a fine sinter and the water removed on a rotary evaporator. The hydrated salt was transferred to a drying tube and was dried by heating under vacuum for two days.

X-ray powder diffraction data were collected on a Stoe STADI/P high-resolution diffractometer using Ge-monochromatized Cu$K_{\alpha 1}$ radiation and a position-sensitive detector covering ~6° in 2θ. The sample was mounted in a 0.5-mm diameter capillary and data was collected in the range $7.5° < 2\theta < 80°$ in 0.02° steps. The total data collection time was ~15 hr. Time-of-flight neutron diffraction data were collected on the Polaris diffractometer at ISIS, Rutherford–Appleton Laboratory. A sample of approximately 5 g was sealed under nitrogen in a cylindrical vanadium can. Only data from the backscattering detector banks were used in the refinement, covering the resolution range $0.65 < d < 3.0$ Å.

Structure Determination

Solution of the structure was carried out with the X-ray diffraction data only. The powder pattern was indexed with the program TREOR (*13*) on the basis of the first 25 observable lines. The best solution left two very weak lines unindexed but gave a good figure-of-merit and sensible unit-cell dimensions, and so was accepted. Systematic absences unambiguously determined the space group as $P2_1/c$. Integrated intensities were extracted from the profile over the range $5° < 2\theta < 60°$ with a modified Rietveld method (*14*) incorporated into the GSAS program (*15*). This produced a total of 142 intensities, of which 95 were nonoverlapping and 47 overlapping according to a visually judged criterion. The overlapping reflections were grouped into 20 groups with a maximum of four reflections within any one of these groups. For subsequent analysis, the overlapped reflections within each group were summed to produce a combined effective intensity for the group.

These data were input into the conventional direct methods program MITHRIL91 (*16*), and the standard NORMAL and CONVERGE modules were executed to give normalized U values and three origin-defining reflections. It is important to stress that the set of overlapped reflections is used, and is very significant, in the normalization of the data, but is not currently used within the basis-set of reflections in subsequent analysis. The normalized U magnitudes were then input into the maximum entropy and likelihood program MICE (*17*). The three origin-defining reflections from MITHRIL91 were used as the initial basis-set reflections. Six further basis-set reflections were then chosen automatically from amongst the largest 30 nonoverlapped data according to the criteria set out in Ref. (*7*). Permuting the phases of these reflections led to 64 nodes (sets of U's) on the phasing tree. By analysis of the LLGs of each of these, eight nodes were kept for further extrapolation. A further two reflections were then chosen manually for permutation. It is important at this stage in particular to choose reflections with maximum "surprise," i.e., those with small extrapolated magnitudes and small d-spacing, the principle being to first define an approximate molecular envelope onto which atomic detail can be added subsequently. After maximization of these 32 nodes, centroid maps corresponding to several of the best (i.e., highest likelihood) phase sets were inspected. The best solution (likelihood = 8.04, vs 6.51 for the next solution) showed four peaks well above the noise level. Inspection of the geometry of these peaks suggested that they may represent S, F, F, and O atoms in the triflate anion. These atoms were therefore used as an initial structural model in a Rietveld refinement of the whole X-ray diffraction profile ($7.5° < 2\theta < 80°$).

TABLE I

FINAL REFINED ATOMIC PARAMETERS (JOINT REFINEMENT) FOR $LiCF_3SO_3$, SPACE GROUP $P2_1/c$, a = 10.2432(2) Å, b = 5.0591(1) Å, c = 9.5592(3) Å, β = 90.319(2)°

Atom	x	y	z	U(iso)/Å^2
S	0.8287(4)	0.3950(6)	0.0944(4)	0.010(1)
C	0.6620(6)	0.2434(13)	0.1081(6)	0.030(2)
Li	1.0869(14)	0.119(4)	0.0796(17)	0.034(4)
F1	0.5766(5)	0.4366(12)	0.1426(6)	0.048(2)
F2	0.6264(6)	0.1413(11)	−0.0121(7)	0.060(2)
F3	0.6627(6)	0.0571(12)	0.1942(7)	0.063(2)
O1	0.8583(6)	0.5016(10)	0.2283(6)	0.046(2)
O2	0.9121(5)	0.1680(11)	0.0584(6)	0.021(2)
O3	0.8109(6)	0.5996(13)	−0.0091(7)	0.025(2)

Note. X-ray data: 7.5–80°, 3624 data points, 309 reflections, R_{wp} = 7.6%; Neutron data: 0.65–3.0 Å, 2842 data points, 2014 reflections, R_{wp} = 7.1%.

Structure development then proceeded in a conventional manner. A series of least-squares refinement/difference-Fourier cycles were used to locate the remaining F, O, C, and, finally, Li atoms. All atoms were located straightforwardly, the Li being the highest peak in the penultimate difference map. The refined molecular geometry was good given the quality of the data, although the Li environment was, as expected, less well defined than the remainder of the structure. For this reason it was decided to carry out a joint refinement of the model against both X-ray and neutron diffraction data. This can be carried out within the GSAS program package. The resulting refinement allowed individual isotropic temperature factors to be refined for all atoms and resulted in a molecular geometry which is in very good agreement with that observed in similar systems, discussed below.

Results and Discussion

Final refined atomic coordinates and other data from the joint refinement are given in Table I, and selected bond distances

TABLE II

SELECTED BOND DISTANCES (Å) AND ANGLES (°)

S–O1	1.420(8)	C–F1	1.354(8)
S–O2	1.472(6)	C–F2	1.310(8)
S–O3	1.443(6)	C–F3	1.251(8)
S–C	1.877(6)	Li–O1	2.02(2)
		Li–O2	1.82(1)
		Li–O2′	1.96(2)
		Li–O3	1.89(2)
O1–S–O2	113(1)	O1–Li–O2	115(1)
O1–S–O3	112(1)	O1–Li–O2′	113(1)
O1–S–C	106(1)	O1–Li–O3	113(1)
O2–S–O3	118(1)	O2–Li–O2′	92(1)
O2–S–C	103(1)	O2–Li–O3	114(1)
O3–S–C	106(1)	O2′–Li–O3	108(1)
F1–C–F2	109(1)	F2–C–F3	106(1)
F1–C–F3	113(1)	F2–C–S	111(1)
F1–C–S	108(1)	F3–C–S	112(1)

and angles in Table II. A view of the molecular packing within the unit cell is shown in Fig. 1. This is the first anhydrous triflate to have been structurally characterized (single crystals are difficult to prepare), but the geometry of the triflate group may be compared with that in several hydrated salts, such as $M(H_2O)_9(CF_3SO_3)_3$ (M = La, Gd, Lu, Y (*18*) and Nd or Ho (*19*)). The S–C (1.88 Å), average C–F (1.31 Å), and average S–O (1.42 Å) bond lengths for $LiCF_3SO_3$ are in excellent agreement with those in the above compounds (1.82–1.88, 1.29–1.33, and 1.42–1.44 Å, respectively), and the Li–O bond lengths are typical of Li in a tetrahedral oxygen-coordinated environment. It should be stressed that a significant improvement in both accuracy and precision of all structural parameters was obtained on using both the X-ray and neutron diffraction data sets in the combined refinement.

Gilmore *et al.* (*7*) have previously demonstrated the use of the maximum entropy and likelihood method in the determination of two previously known crystal structures from their powder diffraction data. The results reported here additionally demonstrate the feasibility of applying this method for the determination of unknown crystal structures directly from powder diffraction data. We firmly believe that future work will reveal the advantages of the method when more challenging problems involving more extensive peak overlap or lower resolution data are considered. We are currently testing the technique on more difficult problems, including low-symmetry systems larger than that considered here and high-symmetry systems involving a high degree of exact overlap of nonequivalent reflections.

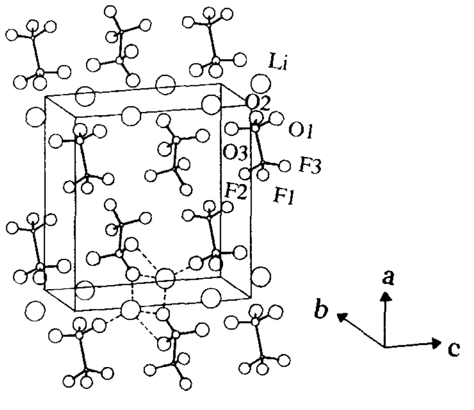

FIG. 1. Unit cell packing diagram for $LiCF_3SO_3$.

Acknowledgments

We are grateful to the SERC for support. PGB thanks the Royal Society for the award of a Pickering Research Fellowship. We thank Dr. R. I. Smith for collection of the neutron diffraction data.

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