SHORT COMMUNICATION

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Lithium formate monohydrate: a comparison of the $X-N$ difference density and structural parameters derived from different experiments.*

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Results of one neutron and four different X-ray diffraction experiments on lithium formate monohydrate ($LiCOOH.H_2O$) have been compared. Good qualitative agreement has been found in comparing $X-N$ difference densities of two independent X-ray determinations. Comparison of X-ray positional parameters of the heavier atoms shows no significant difference between the various determinations. All X-ray results are significantly different from the neutron results. A significant difference in thermal parameters is found in all (except one) parameter sets although the differences between different X-ray sets are smaller than those between the neutron set and the X-ray sets.

Introduction

The crystal structure of lithium formate monohydrate has been determined accurately by means of X-ray diffraction (Thomas, Tellgren & Almlöf, 1975; Enders-Beumer & Harkema, 1973) and neutron diffraction (Tellgren, Ramanujam & Liminga, 1974). A study of the electron density in the title compound has been published (Thomas, Tellgren & Almlöf, 1975). In our laboratory two other X-ray data sets have been collected. The purpose of this work is to compare the results of the different structure determinations.

Preliminary X-ray results have been published by Torre, Abrahams & Bernstein (1971). Mohano Rao & Viswamitra (1971) determined the crystal structure from data obtained by film methods. The results of these two determinations have not been examined.

Experimental

Crystals of lithium formate were prepared as described earlier (Enders-Beumer & Harkema, 1973). Data were collected on a Philips PW1100 four-circle diffractometer (Hornstra & Vossers, 1973) using Mo $K\alpha$ radiation (λ = 0·7107 Å, graphite monochromator). Two independent data sets from different crystals were collected. General information on the data sets considered is given in Table 1 (data sets 4 and 5). No absorption correction was carried out, since the difference between minimum and maximum transmission factors was estimated to be less than 1% (μ = 1·55 cm $^{-1}$). For data set 4 the scattering factors were those given by Enders-Beumer & Harkema (1973). Data set 5 was processed with the scattering factors given in *International Tables for X-ray Crystallography* (1974). Refinements were carried out with a local modification of *ORFLS* (Busing, Martin & Levy, 1962). Details of the parameters and structure factors obtained will not be given here, but can be obtained from the authors.

Comparison of $X-N$ charge distribution

With the structure factors of data set 5 and the neutron results of Tellgren, Ramanujam & Liminga (1974), $X-N$ difference density maps were calculated in the plane of the formate ion (Fig. 1) and the water molecule (Fig. 2). The calculations were performed with the program *SPFT* (van der Waal, 1975). Since the space group $Pna2_1$ is not centrosymmetric, special attention has to be paid to the phases of the contributions to the difference density. The phases of the amplitudes contributing to the $X-N$ maps were calculated in the way suggested by Coppens (1974). The same procedure was applied by Thomas, Tellgren & Almlöf (1975). Figs. 1(*a*) and 2(*a*) can be compared with Fig. 3(*a*) and (*d*) given by Thomas *et al.* (1975) and reproduced here as Figs. 1(*b*) and 2(*b*). A good qualitative resemblance is found. Maxima and minima in the difference density maps occur in corresponding regions. The actual value of the difference density at different places, however, shows quite appreciable deviations.

Comparison of positional and thermal parameters

The differences between the various data sets have been tested by two methods. Firstly a χ^2 test (Hamilton, 1969) has been applied to the positional and thermal parameters of the heavier atoms. In this test the quantity $\delta^2 p = \Sigma_i^N \delta^2 p_i$ is calculated. δp_i is given by $\delta p_i = \Delta p_i/\sigma(\Delta p_i)$ in which Δp_i is the difference between two corresponding parameters in two data sets and $\sigma(\Delta p_i)$ is the standard deviation of this difference. The resulting $\delta^2 p$ can be tested against χ^2 with N degrees of freedom at different levels of significance, giving an indication as to whether the differences found are drawn

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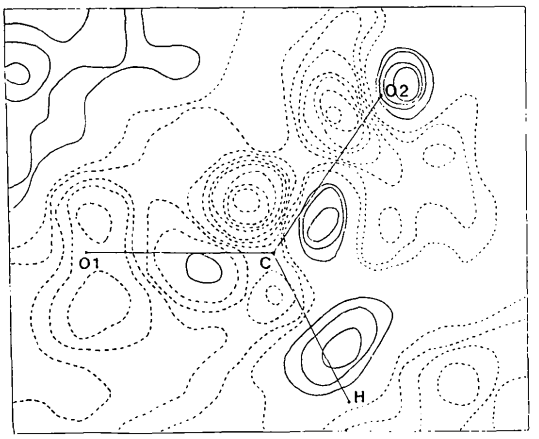
Table 1. *Reference information for the different experiments*

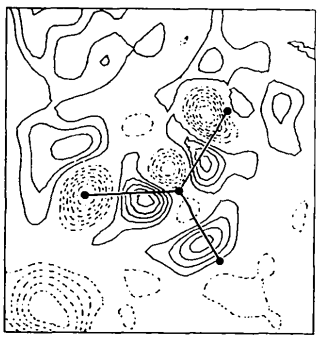
Experiment	1[a]	2[b]	3[c]	4[d]	5[d]
Radiation	neutron	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
R(%)	2·5	3·3	4·9	4·7	4·5
R_w(%)	2·8	4·1	3·7	3·4	3·3
Number of reflexions	555	1027	1027	1027	2797
Significant reflexions: $>2\sigma$	424	866	861	969	1044
$(\sin\theta)/\lambda_{max}$	0·693	0·904	0·904	0·904	1·455
Absorption correction	yes	yes	no	no	no
Extinction correction	isotropic	isotropic	isotropic	isotropic	isotropic
Diffractometer	Hilger & Watts	Philips–Stoe	Nonius AD-3	Philips PW1100	Philips PW1100
Temperature (K)	298	298	295	293	293

References: (*a*) Tellgren, Ramanujam & Liminga (1973). (*b*) Thomas, Tellgren & Almlöf (1975). (*c*) Enders-Beumer & Harkema (1973). (*d*) This work.

from a normal distribution with unit variance and zero mean (standard normal distribution). Therefore, when the calculated value of $\delta^2 p$ exceeds the expected value of $\chi^2_{N,\alpha}$, it may be concluded that the two data sets are significantly different at the $100\,\alpha\%$ significance level. The results of this test have been compiled in Tables 2 and 3 for the positional and thermal parameters respectively. As far as positional parameters are concerned it can be concluded that there is no significant difference (at the 5% level) between the various X-ray experiments. All X-ray experiments are found to give results significantly (1%) different from the neutron results. Systematic differences between X-ray and neutron parameters can be expected because in X-ray diffraction one determines the centroid of the charge density around the

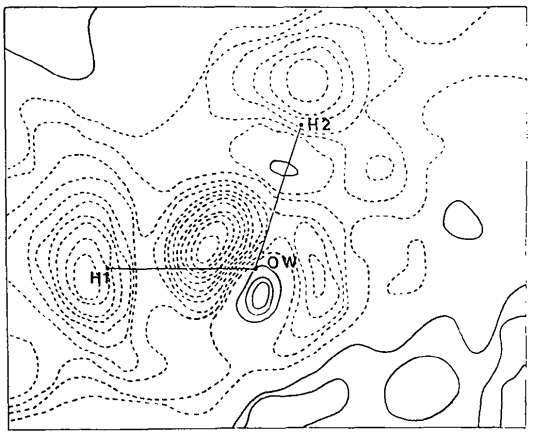


(*a*)

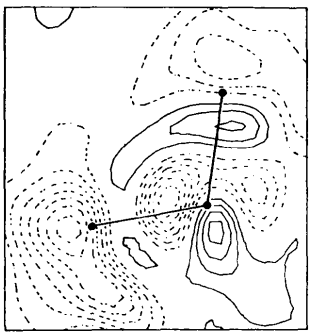


(*b*)

Fig. 1. $X - N$ difference density in the plane of the formate ion. Contours are drawn at intervals of 0·05 e Å^{-3}, regions of electron excess are indicated by unbroken lines. The zero-level contour has been omitted. (*a*) This work. (*b*) Results of Thomas, Tellgren & Almlöf (1975).



(*a*)



(*b*)

Fig. 2. $X - N$ difference density in the plane of the water molecule. For contouring see Fig. 1. (*a*) This work. (*b*) Results of Thomas, Tellgren & Almlöf (1975).

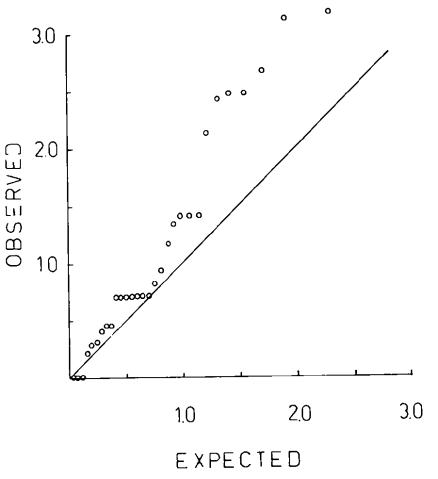


Fig. 3. Half-normal probability plot for the data sets 2 and 4 (thermal parameters).

different atoms, which may differ from the mean position of the nucleus found by neutron diffraction. To a large extent these systematic differences can be eliminated by applying special refinement procedures such as high-order refinement or multipole expansion of the charge density. In this case a high-order refinement proved impossible because of the lack of sufficient high-order data.

Table 2. *Positional-parameter results*

Combination		χ^2 realized	Slope*	Intercept*
1	2	37·20	1·81 (0·11)	−0·25 (0·11)
1	3	37·55	1·79 (0·05)	−0·20 (0·05)
1	4	46·00	2·08 (0·13)	−0·36 (0·13)
1	5	46·99	1·87 (0·13)	−0·07 (0·12)
2	3	7·47	0·89 (0·04)	−0·21 (0·04)
2	4	17·20	1·20 (0·09)	−0·13 (0·08)
2	5	9·34	0·98 (0·09)	−0·23 (0·08)
3	4	4·60	0·68 (0·05)	−0·15 (0·05)
3	5	8·69	0·65 (0·06)	0·14 (0·06)
4	5	21·10	1·12 (0·08)	0·11 (0·08)

* Standard deviations are given in parentheses. $\chi^2_{15,0\cdot05} = 25\cdot00$, $\chi^2_{15,0\cdot01} = 30\cdot6$.

Table 3. *Thermal-parameter results*

Combination		χ^2 realized	Slope*	Intercept*
1	2	148·81	2·51 (0·11)	−0·33 (0·11)
1	3	160·37	2·50 (0·04)	−0·19 (0·04)
1	4	229·38	2·95 (0·06)	−0·19 (0·06)
1	5	187·47	3·02 (0·11)	−0·64 (0·11)
2	3	75·60	1·80 (0·06)	−0·25 (0·06)
2	4	95·36	2·00 (0·11)	−0·28 (0·11)
2	5	61·87	1·59 (0·09)	−0·20 (0·09)
3	4	27·61	1·17 (0·05)	−0·27 (0·05)
3	5	68·50	1·59 (0·11)	−0·11 (0·11)
4	5	109·36	2·15 (0·13)	−0·31 (0·12)

* Standard deviations are given in parentheses. $\chi^2_{30,0\cdot05} = 43\cdot77$, $\chi^2_{30,0\cdot01} = 50\cdot9$.

The thermal parameters of all experiments (except one) are significantly different. It should be noted that there is a clear indication that differences between X-ray experiments are smaller than between neutron and X-ray experiments. Differences in thermal parameters may occur, at least partly, because some X-ray sets have not been corrected for absorption and because different scattering factors have been used.

Secondly, the δp_i distributions have been analysed by means of half-normal probability plots (h.n.p. plots) (Abrahams & Keve, 1971). The δp_i are ordered in increasing magnitude and plotted against the expected quantiles for a half-normal distribution. For small samples (up to 41) the expected quantiles are tabulated by Hamilton & Abrahams (1972). If the distribution of the δp_i is normal, the resulting plot is a straight line of unit slope and zero intercept. A straight line was fitted by least squares through the points of the plots. The resulting slopes and intercept are presented in Tables 2 and 3. As an example the h.n.p. plot comparing thermal parameters of data sets 2 and 4 is given in Fig. 3. The results of the h.n.p. plot analysis confirm the results of the χ^2 test.

Conclusions

As far as positional parameters are concerned, no significant difference between the various X-ray sets has been found. The neutron results differ significantly from all the X-ray sets. With regard to thermal parameters significant differences between all sets exist (except for one combination of X-ray sets). The comparison between the various X-ray sets is better than the comparison of the neutron set with all the X-ray sets.

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