

the C(12)-carboxylate groups of molecules related by the $0, \frac{1}{2}, \frac{1}{2}$ inversion centre are hydrogen bonded through O(2)^a—O(8), O(3)—O(8) [2.76 (1), 3.00 (1) Å]. At the phenyl ends, chain-chain interactions in the (202) layers are purely van der Waals, since up the **b** direction the phenyl rings are canted with respect to each other and do not overlap significantly; there is no π - π interaction. The only interanion interactions between (202) layers are van der Waals and ionic, since although the Ba ions and water molecules lie between the layers, acting as spacers, there are no hydrogen-bonding cross-linking interactions between the layers. Thus, though the water molecule O(6)H(61)H(62) provides the main spacing interaction between the phenyl rings, its hydrogen bonding is to N(1) in one molecule and to O(4) in a **b**-translationally equivalent one. Similarly, O(7)H(71)H(72) only provides an interanion link in the **b** direction between O(3) and O(4), O(5) of **b**-translationally equivalent molecules.

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References

- CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1, pp. 149–150. Birmingham: Kynoch Press.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A, pp. 72ff. Birmingham: Kynoch Press.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 866–870.
- HARVEY, E., LOBERG, M. & COOPER, M. (1975). *J. Nucl. Med.* **16**, 533.
- HUGHES, D. O. & SMALL, R. H. W. (1962). *Acta Cryst.* **15**, 933–940.
- HUGHES, R. R., KRISHNAMACHARI, N., LOCK, C. J. L., POWELL, J. & TURNER, G. (1977). *Inorg. Chem.* **16**, 314–319.
- JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- LIPPERT, B., LOCK, C. J. L., ROSENBERG, B. & ZVAGULIS, M. (1977). *Inorg. Chem.* **16**, 1525–1529.
- PIPPY, M. E. & AHMED, F. R. (1978). *Mean Plane and Torsion Angles*. Report NRC-22. National Research Council of Canada, Ottawa.
- SHELDRIK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
- STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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Comparison of Observed and Calculated Densities. XII.* Deformation Density in Complex Anions. II. Experimental and Theoretical Densities in Sodium Formate

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Abstract

X-*X* (high order) and *X*-*N* electron density difference maps are derived from low-temperature (120 K) neutron and X-ray diffraction studies on sodium formate (NaHCOO) crystals. For comparison,

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theoretical deformation density maps are presented based on 4-31G + BP SCF calculations. The overall agreement between the experimental and theoretical results is reasonable. [Crystal data at 120 K: space group *C2/c*, *a* = 6.239 (2), *b* = 6.749 (2), *c* = 6.097 (2) Å, β = 116.61 (2)°, *V* = 229.5 (1) Å³, *Z* = 4, *D_c* = 1.968 Mg m⁻³. *R(F)* for the conventional neutron refinement is 0.027 for 1081 reflections.]

Introduction

The deformation density of the formate ion (HCOO^-) was derived from measurements on lithium formate monohydrate ($\text{LiHCOO} \cdot \text{H}_2\text{O}$) crystals at about 298 K (Thomas, Tellgren & Almlöf, 1975; Harkema, de With & Keute, 1977; Thomas, 1978) and more recently on α -calcium formate [$\alpha\text{-Ca}(\text{HCOO})_2$] crystals at 100 K (Fuëss, Burger & Bats, 1981). Below we present X - X (high order) and X - N deformation density maps derived from low-temperature (120 K) neutron and X-ray diffraction studies on sodium formate (NaHCOO) crystals and compare the experimental with theoretical 4-31G + BP (bond polarization) AHF (approximate Hartree-Fock) results.

The crystal structure of NaHCOO was originally reported by Zachariasen (1940) and more recently was redetermined by Markila, Rettig & Trotter (1975).

Experiments

Suitable crystals of NaHCOO were obtained by recrystallization from methanol. Care had to be taken, as the crystals are slightly deliquescent. They are, however, stable in an environment with low humidity.

A summary of the data collection is given in Table 1, the crystal data of NaHCOO at 120 K are given in the *Abstract*.

Neutron diffraction

The neutron diffraction experiment was performed on the computer-controlled four-circle diffractometer D9 at ILL Grenoble. A crystal with approximate dimensions $1.1 \times 2.5 \times 2.8$ mm was mounted in an Air Products Displex cryostat cooled by a He refrigerator. A thermocouple, calibrated using a KH_2PO_4 crystal with a phase transition at 122.8 K, recorded a temperature of 120 K during the entire experiment. A hemisphere of data was measured with a wavelength 0.8409 Å up to $2\theta = 120^\circ$. Higher-order

beam contamination was eliminated by the use of an Er filter. Background corrections were made by profile analysis (Lehmann & Larsen, 1974). Three standard reflections were remeasured after every 50 reflections. They showed no significant fluctuations. Data were corrected for absorption using $\mu = 0.061 \text{ mm}^{-1}$. This value is based on an incoherent absorption cross section for H of $35 \times 10^2 \text{ fm}^2$. Each individual reflection was given a standard deviation according to $\sigma(I) = [\sigma^2(I)_{\text{counting}} + (0.03I)^2]^{1/2}$. The weight $[1/\sigma^2(I)]$ of an average reflection was taken as the sum of the weights of the individual reflections.

X-ray diffraction

The X-ray diffraction experiments were performed on a Syntex $P2_1$ diffractometer with Nb-filtered Mo $K\alpha$ radiation. A temperature of 120 K was maintained during the experiments using an Enraf-Nonius universal low-temperature device. A thermocouple mounted in the cold-air stream had been calibrated by studying the phase transition of KH_2PO_4 at 122.8 K.

Two sets of X-ray data were collected using different crystals (Table 1). To obtain a high accuracy and reduce errors due to fluctuations, the reflections were repeatedly remeasured at different stages of the experiments. For the number of equivalent reflections see Table 1.

Background corrections were made by profile analysis, using the method of Blessing, Coppens & Becker (1974). Three standard reflections were observed after every 60 reflections. They showed a maximum fluctuation of 3% for crystal 1 and 5% for crystal 2, probably due to variations in the incident-beam intensity and detector sensitivity. These effects were corrected by rescaling the data with respect to the standards. An absorption correction was made by numerical integration over $6 \times 6 \times 6$ Gaussian sampling points. The equivalent reflections were averaged. A weighting scheme was applied as in the neutron diffraction case.

Structure refinement

Least-squares refinements were performed with a modified version of the program *ORFLS* (Busing, Martin & Levy, 1962). Refinement was on F with weights according to $w = 1/\sigma^2(F)$.

Neutron diffraction

Scattering lengths for C, O and H were taken from Koester (1977). The scattering length of Na is less well known. Koester & Knopf (1972) reported a value of $b_{\text{Na}} = 3.63$ (2) and Shull & Wollan (1951) a value of 3.51 fm. Therefore we decided to consider b_{Na} as a parameter to be determined during the structure

Table 1. Summary of data collection

	Neutron	X-ray 1	X-ray 2
Crystal volume (mm^3)	7.7	0.015	0.0032
μ (mm^{-1})	0.061	0.357	0.357
Transmission range	0.856–0.939	0.914–0.934	0.945–0.971
λ (Å)	0.8409	0.71069	0.71069
$(\sin \theta/\lambda)_{\text{max}}$ (Å $^{-1}$)	1.03	1.08	1.00
Number of equivalents	2	8 ($\sin \theta/\lambda < 0.24$) 6 ($\sin \theta/\lambda = 0.24\text{--}0.81$) 4 ($\sin \theta/\lambda = 0.81\text{--}0.86$) 3 ($\sin \theta/\lambda = 0.86\text{--}1.08$)	13 ($\sin \theta/\lambda < 0.90$) 2 ($\sin \theta/\lambda = 0.90\text{--}1.00$)
$\Sigma I - \langle I \rangle / \Sigma I$	0.015	0.019	0.029
Total number of reflections	2602	6502	10705
Independent reflections	1081	1205	948
Reflections with $I \geq 0$	1056	1177	912

Table 2. Summary of least-squares refinements

	Number of reflections	Number of parameters	$R(F)$	$R_w(F)$	S^*	Scale
Neutron						
Conventional refinement	1081	27	0.027	0.021	1.36	5.956 (10)
Third-cumulant refinement	1081	48	0.026	0.020	1.28	5.959 (9)
X-ray 1						
All-data refinement	1177	23	0.028	0.031	3.18	4.463 (10)
$\sin \theta/\lambda > 0.65 \text{ \AA}^{-1}$	916	20	0.031	0.023	1.82	4.532 (13)
$\sin \theta/\lambda > 0.80 \text{ \AA}^{-1}$	686	19	0.035	0.023	1.40	4.532†
X-ray 2						
All-data refinement	912	23	0.038	0.033	3.69	2.392 (6)
$\sin \theta/\lambda > 0.65 \text{ \AA}^{-1}$	655	20	0.051	0.026	1.91	2.455 (12)
$\sin \theta/\lambda > 0.80 \text{ \AA}^{-1}$	432	19	0.066	0.030	1.59	2.455†

$$* S = \{ \sum w(|F_o| - |F_c|)^2 / (no - nv) \}^{1/2}$$

† Not refined.

refinement and obtained the value $b_{\text{Na}} = 3.585$ (9) fm. An isotropic extinction correction was made (Larson, 1969). The minimum value of $y = F_{\text{obs}}^2 / F_{\text{corrected}}^2$ was $y = 0.576$ for the 020 reflection. An attempt to make an anisotropic extinction correction (Coppens & Hamilton, 1970) did not lead to any improvement, indicating that the extinction can be considered to be isotropic.

The details about the least-squares refinements are reported in Table 2, the resulting positional and thermal parameters in Table 3.

To investigate how well the thermal motion in NaHCOO can be described by the ordinary anisotropic thermal parameters, a subsequent refinement was done, including third-cumulant coefficients (Johnson, 1970). Such a treatment would be useful in the case of curvilinear thermal motion (librations) or anharmonic thermal motion. The inclusion of third cumulants did lower $R_w(F)$ from 0.0213 to 0.0198. Application of an R -factor-ratio test (Hamilton, 1965) indicated an improvement of the model with a more than 99.5% probability. Inspection of the resulting coefficients shows, however, that the effect comes entirely from the motion of the H atom. It has a rather large vibration perpendicular to the plane of the molecule, giving rise to a significant non-linear motion.

X-ray diffraction

Scattering factors for Na, C and O were taken from *International Tables for X-ray Crystallography* (1974), those for H from Stewart, Davidson & Simpson (1965). Anomalous-scattering factors (Cromer & Liberman, 1970) were applied to Na, C and O. An isotropic extinction correction was made (Larson, 1969). The H atom was refined with an isotropic thermal parameter. For each data set three refinements were made: using (i) all data (conventional refinement); (ii) only those reflections with $\sin \theta/\lambda > 0.65 \text{ \AA}^{-1}$ and keeping the extinction coefficient and the H parameters fixed; (iii)

only those reflections with $\sin \theta/\lambda > 0.80 \text{ \AA}^{-1}$. In the last refinement the scale factor had to be kept fixed at the value for the previous refinement, in order to avoid serious correlation (85–90%) with the thermal parameters. A summary of the refinements is given in Table 2. The atomic parameters resulting from refinements (i) and (iii) are reported in Table 3 for comparison with the neutron results.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36296 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Positional and equivalent isotropic temperature parameters

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_j$$

X1A: X-ray, crystal I, all-data refinement.

X1H: X-ray, crystal I, high-angle refinement ($> 0.80 \text{ \AA}^{-1}$).

X2A: X-ray, crystal II, all-data refinement.

X2H: X-ray, crystal II, high-angle refinement ($> 0.80 \text{ \AA}^{-1}$).

N: neutron data.

	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
Na X1A	0.0	-0.13699 (3)	0.25	0.0089 (1)
X1H	0.0	-0.13697 (4)	0.25	0.0092 (1)
X2A	0.0	-0.13692 (5)	0.25	0.0092 (1)
X2H	0.0	-0.13695 (9)	0.25	0.0096 (1)
N	0.0	-0.13697 (6)	0.25	0.0087 (1)
O X1A	0.14108 (5)	0.19289 (4)	0.18448 (5)	0.0104 (1)
X1H	0.14093 (4)	0.19296 (4)	0.18460 (5)	0.0107 (1)
X2A	0.14110 (7)	0.19309 (7)	0.18440 (8)	0.0105 (1)
X2H	0.14080 (10)	0.19293 (9)	0.19437 (11)	0.0111 (1)
H N	0.14096 (3)	0.19311 (3)	0.18456 (3)	0.0099 (1)
C X1A	0.0	0.27845 (7)	0.25	0.0097 (2)
X1H	0.0	0.27831 (6)	0.25	0.0100 (1)
X2A	0.0	0.27847 (12)	0.25	0.0100 (3)
X2H	0.0	0.27840 (14)	0.25	0.0106 (3)
N	0.0	0.27832 (3)	0.25	0.0091 (1)
H X1A	0.0	0.4246 (18)	0.25	0.021 (3)
X2A	0.0	0.4277 (24)	0.25	0.028 (4)
N	0.0	0.44137 (10)	0.25	0.0390 (5)

Quantum-chemical calculations

The AHF GTO (approximate Hartree–Fock Gaussian-type orbital) HCOO⁻ molecular and H, C and O atomic wavefunctions were calculated with the closed-shell and the open-shell [Roothaan (1960) open-shell procedure] parts of the *POLYATOM* program system (Csizmadia, Harrison, Moskowitz & Sutcliffe, 1966) using the 4-31G (Ditchfield, Hehre & Pople, 1971) + BP [bond functions (Hase & Schweig, 1977)] basis set [one *s* function with orbital exponent 1.25, and one *s* and a set of *p* functions with orbital exponents 1.35 and 0.80 in the middle of the C–H and C–O bonds, respectively (Breitenstein, Dannöhl, Meyer, Schweig, Seeger, Seeger & Zittlau, 1981)]. Thermal smearing was performed with the method of Hase, Reitz & Schweig (1976) using the thermal parameters of the present study.

Discussion

A stereoscopic view of the NaHCOO structure, showing the thermal ellipsoids at 120 K, is depicted in Fig. 1. Bond distances and angles derived from the three data sets are reported in Table 4. They agree very well, except that the C–H distance is 0.10 Å too short in the X-ray refinements, as generally found in comparisons of X-ray and neutron diffraction results.

The positional parameters of the non-hydrogen atoms are very similar in the different refinements. Only for the *y* parameter of the O atom are there differences of 5σ and 3σ respectively when the results of the all-data refinement and the high-angle refinement of crystal 1 are compared with the neutron results. From X-ray data set 2, which has larger standard deviations, this difference is no longer apparent.

Table 4. Bond distances (Å) and angles (°)

	Neutron	X-ray 1*	X-ray 2*
2 × Na–O	2.3855 (6)	2.3862 (6)	2.3868 (9)
2 × Na–O	2.4186 (8)	2.4186 (8)	2.4174 (10)
2 × Na–O	2.4918 (7)	2.4908 (6)	2.4905 (10)
2 × C–O	1.2560 (3)	1.2561 (4)	1.2567 (9)
C–H	1.1004 (7)	0.99 (1)	1.01 (2)
O–C–O	125.50 (3)	125.41 (4)	125.35 (9)
2 × O–C–H	117.25 (1)	117.30 (2)	117.33 (4)

* Results from high-angle refinement with $\sin \theta/\lambda > 0.80 \text{ \AA}^{-1}$; H atom from refinement on all data.

Table 5. Differences in thermal parameters averaged over the Na, C and O atoms

	U_{11}	U_{22}	U_{33}	U_{13}
X-ray 1 ($\sin \theta/\lambda > 0.80 \text{ \AA}^{-1}$) – neutron	0.00118 (11)	0.00062 (12)	0.00030 (13)	0.00032 (10)
X-ray 2 ($\sin \theta/\lambda > 0.80 \text{ \AA}^{-1}$) – neutron	0.00110 (21)	0.00186 (23)	0.00061 (21)	0.00045 (17)
X-ray 1 ($\sin \theta/\lambda > 0.80 \text{ \AA}^{-1}$) – X-ray 2 ($\sin \theta/\lambda > 0.80 \text{ \AA}^{-1}$)	0.00008 (20)	–0.00124 (22)	–0.00031 (20)	–0.00013 (16)

The situation is very different, however, when the thermal parameters of the three data sets are compared. The neutron refinement gives significantly smaller thermal parameters than the X-ray refinements. The differences are, however, not isotropic, but are larger in U_{11} and U_{22} than in U_{33} . Also among the two X-ray data sets there are significant differences. They occur, however, mainly in U_{22} . The discrepancies in thermal parameters are analysed in two ways. A normal probability plot (Abrahams & Keve, 1971) comparing the thermal parameters is shown in Fig. 2. The deviation between observed and expected values is obvious. The curve describing the differences between

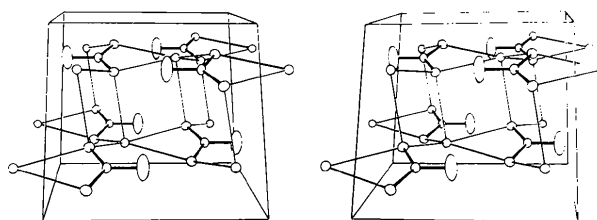


Fig. 1. Stereoscopic view of the sodium formate structure along *a*. The thermal ellipsoids are the 50% probability surfaces.

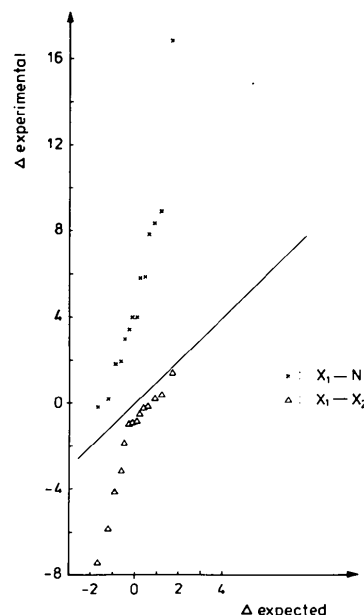


Fig. 2. Normal probability plot comparing the thermal parameters of the neutron and the X-ray diffraction results (X_1 : X-ray data set 1, X_2 : X-ray data set 2, N : neutron data).

the two X-ray data sets consists of two parts: a steep curve corresponding to U_{22} and U_{33} values and a curve with a slope of about 1.0 corresponding to U_{33} , U_{12} , U_{13} and U_{23} values. The anisotropy of the differences in thermal parameters averaged over the Na, C and O atoms is given in Table 5 and gives a similar picture.

It is obvious that systematic errors in the neutron and X-ray data sets have not been accounted for. Temperature differences among the three experiments are unlikely to explain these results, as more isotropic differences would be expected, neither are errors in the absorption and extinction corrections, as both effects were satisfactorily corrected. It was pointed out (Scheringer, Kutoglu & Mullen, 1978) that the neglect of a TDS correction will generally result in smaller thermal parameters in neutron diffraction than in X-ray diffraction. The effect of TDS can lead to different results for the two X-ray data sets, as the crystals were mounted in different orientations and data were collected up to different $\sin \theta/\lambda$ values.

Systematic differences among thermal parameters obtained by X-ray and neutron diffraction have also been reported by other authors (Bats, Coppens & Koetzle, 1977). Harkema, de With & Keute (1977) have compared four different X-ray data sets and one set of neutron data for lithium formate monohydrate. They found substantial differences in thermal parameters between the various sets; only two agreed.

Obviously, even in careful experiments, a number of factors introduce systematic trends and give rise to larger errors in the thermal parameters than indicated by their standard deviations. In electron density studies using a combination of X-ray and neutron data, this effect may easily lead to an erroneous deformation density synthesis.

The deformation density in NaHCOO has been calculated in two ways: (i) an $X-X$ (high-angle) synthesis based on the atomic parameters from the refinements of the X-ray reflections with $\sin \theta/\lambda > 0.80 \text{ \AA}^{-1}$; maps showing the density in the plane of the formate group are shown in the left parts of Fig. 3(a) and (b); (ii) the corresponding $X-N$ maps are represented in the right parts of the same figure. In these calculations, spherical atoms are placed at the positions obtained from the neutron diffraction experiment. The problem arises which set of thermal parameters should be used. If one suggests that the differences in thermal parameters among the data sets result from unaccounted effects like diffuse scattering, none of the parameter sets would correspond to the real thermal parameters of the atoms. Then, if no correction for diffuse scattering is made, the best deformation density would be the one in which the absolute value of the thermal parameters is derived from the X-ray data used in the difference synthesis. Consequently, in the $X-N$ syntheses we used modified thermal parameters that were constructed by adding the correction terms of Table 5 to the neutron

parameters. RHF scattering factors (*International Tables for X-ray Crystallography*, 1974) were used for H in the $X-N$ synthesis. All deformation maps were calculated up to $\sin \theta/\lambda = 0.90 \text{ \AA}^{-1}$. An indication of the statistical error in the maps is given by $\sigma(\rho) = (2/V)\{\sum[\sigma(F)/k]^2\}^{1/2}$ (Rees, 1976) and gives 0.023 and 0.036 e \AA^{-3} for Fig. 3(a) and (b) respectively. This does not include errors in the scale factor or atomic parameters. Consequently, near the atomic positions the errors will be larger and these values serve mainly as a lower estimate of the density in a general position.

Except near the H atom the $X-X$ and $X-N$ maps are very similar. The refinement on the neutron diffraction data had shown that use of a third-cumulant refinement gave slightly better R values than the conventional refinement due to a nonlinear motion of the H atom. To investigate which errors are made by neglecting the curvilinear motion of the atoms, subsequent $X-N$ syntheses were calculated by including the third-cumulant coefficients obtained from the neutron refinement. The anisotropic thermal parameters were again modified as described above. The difference with the previous maps was, however, only 0.02 e \AA^{-3} in the binding regions of the molecule. Obviously, the neglect of the curvilinear motion in the present case does not lead to any significant errors.

Fig. 4 shows the final $X-N$ density averaged over the two data sets. General features of the electron density in NaHCOO are similar to those in LiHCOO.H₂O (Thomas, 1978) and α -Ca(HCOO)₂ (Fuess, Burger & Bats, 1981). Electron density is accumulated in the C-O and C-H bonds. Rather diffuse lone-pair regions appear on the O atoms. From the electron density derived from X-ray data set 1 (Fig. 3a), it appears that there is an asymmetry between the two lone-pair lobes of the O atom. The one pointing toward the 'chelate-forming' Na atom is lower (0.13 vs 0.26 e \AA^{-3}) than the lobe on the other side. As this difference corresponds, however, to the limit of the accuracy obtained

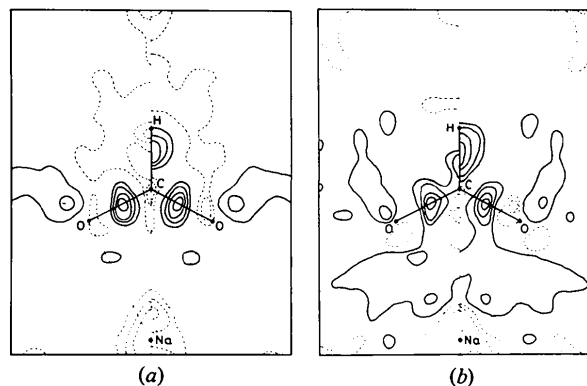


Fig. 3. The deformation density in the plane of the formate group. Contour interval 0.1 e \AA^{-3} ; the zero contour is omitted. (a) Using X-ray data set 1; (b) using X-ray data set 2. The left side of each shows the $X-X$ density, the right side the $X-N$ density.

($3\sigma \approx 0.08 \text{ e } \text{Å}^{-3}$), the study of the second X-ray data set might help clear up the point as to whether the difference is artificial or due to interactions with the neighbouring Na atoms. The electron density derived from data set 2, however, does not reproduce this result (Fig. 3*b*), so it may be an artifact. The two independent measurements agree, however, in showing a rather diffuse lone-pair density at the O atom with lower peak heights than generally found in carboxylic acids.

The density in cross sections through the midpoints of the C—H and C—O bonds is shown in Fig. 5(*a, b*). The C—H bond peak is slightly extended out of the plane of the molecule following the vibration of the H atom which is largest perpendicular to the plane. At

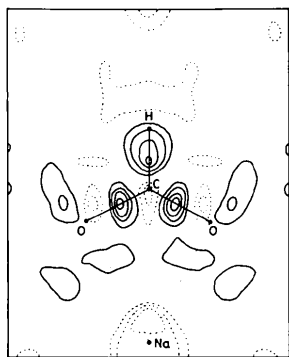


Fig. 4. The deformation density of sodium formate. The average of the two $X - N$ densities, including third-cumulant coefficients. Contours as in Fig. 3.

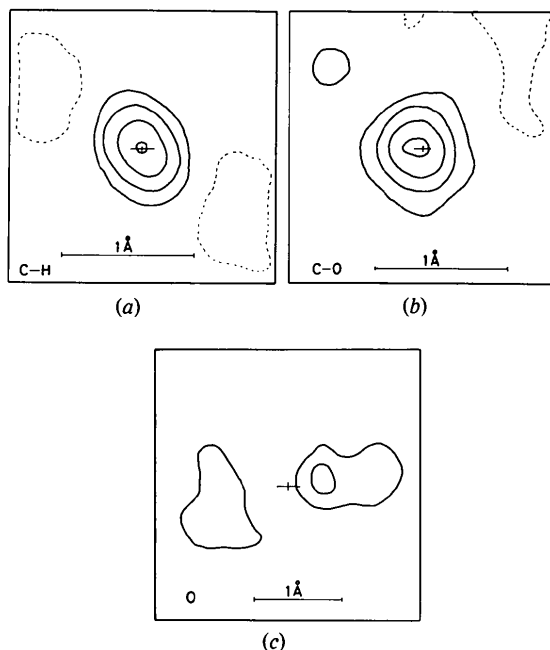


Fig. 5. $X - N$ deformation density in specific sections (*a*) through the midpoint of the C—H bond; (*b*) through the midpoint of the C—O bond; (*c*) perpendicular to the C—O axis through the O lone-pair region. Contours as in Fig. 3.

this intersection the C—O bond shows almost cylindrical symmetry about the bond axis. The deformation density in a section perpendicular to the C—O bond and 0.16 Å away from the O atom is shown in Fig. 5(*c*). There is no indication that the directions of the lone-pair lobes are affected by the Na—O interactions.

The theoretical static and dynamic (thermally smeared) deformation densities of the formate ion in the molecular plane are presented in Fig. 6(*a*) and (*b*), respectively.

The static density of Fig. 6(*a*) bears little resemblance to the static density presented in the paper by Thomas, Tellgren & Almlöf (1975). A calculation using the same basis set as chosen by these authors, led to a static density that perfectly agreed with the 4-31G + BP one of Fig. 6(*a*), suggesting that the density given previously is erroneous.

Strictly, the static density of Thomas, Tellgren & Almlöf (1975) incorporates effects of the crystal environment. From our previous experience with the calculation of crystal effects in sodium salts (Dannöhl, 1978; Dannöhl, Meyer & Schweig, 1980) and the explicit consideration of the effects of the crystal environment on a formate ion (Breitenstein *et al.*, 1981), the large differences between the previous static density and the density of Fig. 6(*a*) cannot arise because of crystal-field effects (see below).

Although there are some distortions in the shape of the experimental density (*cf.* Fig. 4) relative to the theoretical dynamic density (Fig. 6*b*) there is a rather good overall agreement between both results except for the oxygen lone-pair regions, where the experimental density turns out to be lower than the calculated one and, additionally, exhibits the asymmetry mentioned above. In order to have a closer look at both effects a calculation of the formate-ion density was performed including crystal effects by mimicking its crystal environment by point charges and additional bond functions (BP's) and incorporating these charges and BP's into the SCF calculations (Dannöhl, 1978; Breitenstein *et al.*, 1981). The main results are: (i) The C—H and C—O bonding regions are practically not

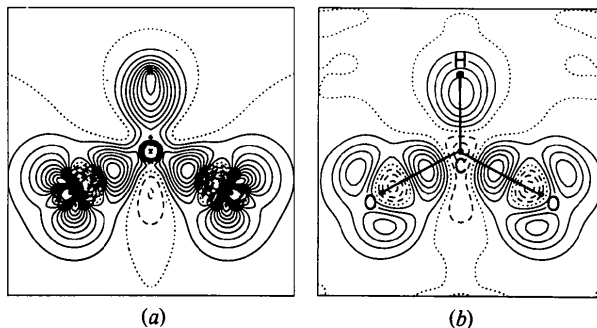


Fig. 6. Theoretical (*a*) static and (*b*) dynamic deformation densities. Contour interval $0.1 \text{ e } \text{Å}^{-3}$. Positive contours are solid, zero contours are dotted and negative contours are dashed.

Table 6. Peak heights in electron deformation densities of the formate ion (in $e \text{ \AA}^{-3}$)

For the labelling of the O atom consult Fig. 2(a) in the paper by Thomas (1978) for $\text{LiHCOO} \cdot \text{H}_2\text{O}$ and Figs. 4, 5 in the paper by Fuess, Burger & Bats (1981) for $\alpha\text{-Ca}(\text{HCOO})_2$; the theoretical peak heights for $\alpha\text{-Ca}(\text{HCOO})_2$ and $\text{LiHCOO} \cdot \text{H}_2\text{O}$ are based on unpublished maps by Dannöhl, Meyer & Schweig (1981); the experimental peak heights for $\alpha\text{-Ca}(\text{HCOO})_2$ and $\text{LiHCOO} \cdot \text{H}_2\text{O}$ are taken from maps obtained by Fuess, Burger & Bats (1981) and by Thomas (1978), respectively; l.p. stands for lone pair; first value of the l.p. peak heights refers to the l.p. lobe that is directed towards the C-H bond; $M-A$ stands for multipole deformation density.

Molecular region	Theoretical			Experimental			
	$\alpha\text{-Ca}(\text{HCOO})_2$ 100 K	NaHCOO 120 K	$\text{LiHCOO} \cdot \text{H}_2\text{O}$ 298 K	$\alpha\text{-Ca}(\text{HCOO})_2$ 100 K $X-N$	NaHCOO 120 K $X-N$	$\text{LiHCOO} \cdot \text{H}_2\text{O}$ 298 K $X-N$	$\text{LiHCOO} \cdot \text{H}_2\text{O}$ 298 K $M-A$
C-H	0.45	0.45	0.30	0.40	0.45	0.20	0.25
C-O(1)	0.55		0.35	0.45	0.50	0.25	0.30
C-O(2)	0.55		0.35	0.25	0.50	0.30	0.35
O(1) l.p.	0.45 and 0.40		0.35 and 0.30	0.30 and 0.35	0.20 and 0.15	0.10 and 0.20	0.20 and 0.25
O(2) l.p.	0.45 and 0.40	0.45 and 0.40	0.30 and 0.30	0.45 and 0.40	0.20 and 0.15	0.15 and 0.20	0.15 and 0.20

affected; (ii) no asymmetry (in the sense that the peak height in the lone-pair lobe that is directed towards the Na atom would be lower than the peak height in the other lobe) is introduced; (iii) but the lone-pair density in both lobal regions is reduced by $0.1 e \text{ \AA}^{-3}$. Hence now, even in the lone-pair regions, the discrepancy between experiment and theory is not higher than 0.1 and $0.2 e \text{ \AA}^{-3}$, respectively.

To summarize previous and present results and to make them easily comparable, the peak heights of all available dynamical theoretical (isolated anion) and experimental (crystal) densities are collected in Table 6. Considering that the chemical environment of the formate ion drastically differs from one crystal to the other, the overall agreement of the data is quite astonishing (except for the slight tendency of the experimental lone-pair peaks to be slightly lower than the theoretical ones, which may partly be due to crystal effects as mentioned above in the NaHCOO case). As expected, the room-temperature data give lower peak heights than the low-temperature results, but nonetheless correspond quite well to the theoretical data. The results demonstrate again that well-founded calculations [for the particular suitability of the $4\text{-}31\text{G} + \text{BP}$ basis set *cf.* Breitenstein *et al.* (1981)] and carefully measured data may lead to deformation density data that agree within ± 0.1 to $0.2 e \text{ \AA}^{-3}$.

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References

- ABRAHAM, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157-165.
- BATS, J. W., COPPENS, P. & KOETZLE, T. F. (1977). *Acta Cryst.* **B33**, 37-45.
- BLESSING, R. H., COPPENS, P. & BECKER, P. (1974). *J. Appl. Cryst.* **7**, 488-492.
- BREITENSTEIN, M., DANNÖHL, H., MEYER, H., SCHWEIG, A., SEEGER, R., SEEGER, U. & ZITTLAU, W. (1981). In preparation.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71-83.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.
- CSIZMADIA, I. G., HARRISON, M. C., MOSKOWITZ, J. W. & SUTCLIFFE, B. T. (1966). *Theoret. Chim. Acta*, **6**, 191-216; Quantum Chemistry Program Exchange, Indiana Univ. Program No. 199.
- DANNÖHL, H. (1978). Thesis, Univ. Marburg.
- DANNÖHL, H., MEYER, H. & SCHWEIG, A. (1981). *Chem. Phys. Lett.* **69**, 75-77.
- DITCHFIELD, R., HEHRE, W. J. & POPLE, J. A. (1971). *J. Chem. Phys.* **54**, 724-728.
- FUESS, H., BURGER, N. & BATS, J. W. (1981). *Z. Kristallogr.* **156**, 219-232.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502-510.
- HARKEMA, S., DE WIT, G. & KEUTE, J. C. (1977). *Acta Cryst.* **B33**, 3971-3973.
- HASE, H.-L., REITZ, H. & SCHWEIG, A. (1976). *Chem. Phys. Lett.* **39**, 157-159.
- HASE, H.-L. & SCHWEIG, A. (1977). *Angew. Chem.* **89**, 264-265; *Angew. Chem. Int. Ed. Engl.* **16**, 258-259.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1970). *Thermal Neutron Diffraction*, edited by B. T. M. WILLIS, pp. 132-160. Oxford Univ. Press.
- KOESTER, L. (1977). *Neutron Physics. Springer Tracts in Modern Physics*, edited by G. HÖHLER, Vol. 80. Berlin: Springer.
- KOESTER, L. & KNOPF, K. (1972). *Z. Naturforsch. Teil A*, **27**, 901-905.
- LARSON, A. C. (1969). *Crystallographic Computing*, edited by F. R. AHMED, pp. 291-294. Copenhagen: Munksgaard.

- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A30, 580–584.
- MARKILA, P. L., RETTIG, S. J. & TROTTER, J. (1975). *Acta Cryst.* B31, 2927–2928.
- REES, B. (1976). *Acta Cryst.* A32, 483–488.
- ROOTHAAN, C. C. J. (1960). *Rev. Mod. Phys.* 32, 179–185.
- SCHERINGER, C., KUTOGLU, A. & MULLEN, D. (1978). *Acta Cryst.* A34, 481–483.
- SHULL, C. G. & WOLLAN, E. O. (1951). *Phys. Rev.* 81, 527–535.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.
- THOMAS, J. O. (1978). *Acta Cryst.* A34, 819–823.
- THOMAS, J. O., TELLGREN, R. & ALMLÖF, J. (1975). *Acta Cryst.* B31, 1946–1955.
- ZACHARIASEN, W. H. (1940). *J. Am. Chem. Soc.* 62, 1011–1013.

Acta Cryst. (1982). B38, 743–748

Interaction of Methylmercury(II) with Bidentate Ligands Containing Pyridine and Pyrazole Rings. Synthesis and Structure of Methyl[1-(2-pyridyl)pyrazole]mercury(II) Nitrate and [Di(1-pyrazolyl)methane]methylmercury(II) Nitrate

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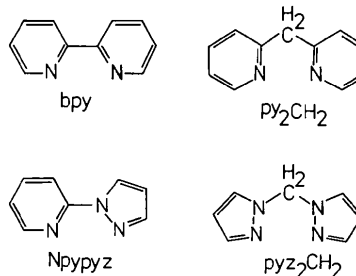
Abstract

The complexes $[\text{MeHg}L]\text{NO}_3$ [$L = 1$ -(2-pyridyl)pyrazole or di(1-pyrazolyl)methane] have L present as bidentate ligands to give irregular three coordination for Hg in the CHgN_2 moieties. The 1-(2-pyridyl)pyrazole complex, $[\text{Hg}(\text{CH}_3)(\text{C}_8\text{H}_7\text{N}_3)]\text{NO}_3$, is triclinic, with $a = 10.201$ (9), $b = 10.347$ (9), $c = 7.650$ (7) Å, $\alpha = 91.16$ (2), $\beta = 106.89$ (3), $\gamma = 127.07$ (2)°, $U = 596.0$ Å³, $Z = 2$, $D_c = 2.355$, $D_m = 2.36$ (2) Mg m⁻³, $F(000) = 392$, and space group $P\bar{1}$. The structure was refined for 869 counter-measured observed reflections to $R = 0.066$. The complex has C(1)–Hg–N(1) 168 (2)° and Hg–N(1) 2.21 (3) Å [N(1) is the pyrazole donor atom], Hg–N(1') (pyridine ring) 2.61 (5) Å, and nitrate O atoms 2.97 (3), 3.07 (3), and 3.14 (3) Å from Hg. The di(1-pyrazolyl)methane complex, $[\text{Hg}(\text{CH}_3)(\text{C}_7\text{H}_8\text{N}_4)]\text{NO}_3$, is triclinic, with $a = 8.457$ (9), $b = 10.461$ (7), $c = 8.455$ (5) Å, $\alpha = 100.68$ (1), $\beta = 107.73$ (2), $\gamma = 114.39$ (2)°, $U = 605.74$ Å³, $Z = 2$, $D_c = 2.334$, $D_m = 2.34$ (22) Mg m⁻³, $F(000) = 396$, and space group $P\bar{1}$; $R = 0.043$ for 1112 reflections; the cation has C(1)–Hg–N(1) 179 (1)°, Hg–N(1) 2.16 (1), Hg–N(1') 2.96 (2) Å, and nitrate O atoms 2.88 (2) and 2.90 (2) Å from Hg. In both structures the cations

and anions are grouped to form $\{[\text{MeHg}L]\text{NO}_3\}_2$ dimeric units *via* $\text{Hg}\cdots\text{O}$ interactions.

Introduction

In studying the tendency of methylmercury(II) to form complexes with coordination numbers for Hg greater than two we have employed aromatic N donor ligands that can potentially act as either unidentate or polydentate donors. Thus, 2,2'-bipyridyl (bpy) and 4,4',4''-triethyl-2,2':6',2''-terpyridyl act as bidentate and tridentate ligands, respectively, towards MeHg^{II} in the solid state, although ¹H nuclear magnetic resonance spectra show that both these ligands act as bidentate in methanol; di(2-pyridyl)methane (py_2CH_2) has a methylene bridge between the pyridyl rings and coordinates



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