

SHORT COMMUNICATIONS

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Maximum entropy versus least-squares modeling of the electron density in K_2PtCl_6 . By RENZO RESTORI AND DIETER SCHWARZENBACH, *Institute of Crystallography, University of Lausanne, BSP, CH-1015 Lausanne, Switzerland*

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Abstract

The thermally smeared electron density in K_2PtCl_6 at room temperature is determined from accurate high-resolution X-ray data with the method of maximum entropy. Results are presented in the form of difference-density maps. In an earlier study, the charge density was derived from the same data by refining the parameters of various anharmonic and/or bonding density models with the method of least squares. The density of maximum entropy agrees closely with those results of the least-squares refinements producing flat residual maps.

Introduction

In a recent paper (Restori & Schwarzenbach, 1993; subsequently referred to as RS), we have reported a study of the thermally smeared electron density in K_2PtCl_6 at room temperature, based on high-quality high-resolution single-crystal X-ray diffraction data which were analyzed in terms of anharmonic displacement and/or bonding-density formalisms. In the present study, we apply the maximum-entropy formalism to the same data and demonstrate the close similarity of the results obtained with those from least-squares modeling.

The space group of K_2PtCl_6 is cubic, $Fm\bar{3}m$, $Z = 4$, $a = 9.743(3)$ Å. The X-ray data set of RS was measured to $(\sin\theta/\lambda)_{\max} = 1.3$ Å⁻¹ with Ag $K\alpha$ radiation ($\lambda = 0.56087$ Å) and contained 489 absorption-corrected inequivalent intensities (9007 observations, $R_{\text{int}} = 0.012$). Anharmonic displacements were represented with a Gram–Charlier series up to the fourth order (Johnson & Levy, 1974), and the asphericity of the atoms by a sum of multipolar deformation functions (Stewart, 1976). The variable parameters of the models were adjusted by least squares to the observed $|F_{\text{obs}}|^2$ values. The electron density in the vicinity of K and Cl was economically accounted for with nine anharmonic terms, but could also be parameterized with a very flexible multipole model; the density in the vicinity of Pt was accounted for only when both types of functions were used simultaneously. Weighted R values and goodness-of-fit values ranged from $wR(I^2) = 0.0091$ to 0.0071 , and $S = 1.213$ to 0.971 ; the corresponding total number of variable parameters was 18 and 40, respectively. The standard procrystal model composed of spherical atoms undergoing harmonic vibrations refined to $wR(I^2) = 0.0157$, $S = 2.080$. The results were presented as Fourier maps showing the difference between the total electron density computed for a given model and the total electron density of the procrystal model; the Fourier series included all structure factors to $(\sin\theta/\lambda)_{\max} = 1.762$ Å⁻¹. In order to reveal the aspherical features, the features with

spherical symmetry centered on the atomic sites (Fig. 2 of RS) were removed from these maps by fitting and then subtracting appropriate functions chosen by trial and error. Residual maps were calculated for each model with Fourier coefficients $(\text{sign}_{\text{calc}}|F_{\text{obs}}| - F_{\text{calc}})$. The main criteria used to judge the quality of a model were the flatness of the residual map and the economy in the number of variable parameters.

The maximum-entropy method has been applied successfully in recent years to powder and single-crystal X-ray data. It does not rely upon a partitioning of the total density into atomic contributions or into features resulting from anharmonic and bonding effects. Results from least-squares refinements are inherently biased by the model, *i.e.* by the type and number of functions it is composed of. Density maps may show features which are only weakly related to the data, in particular near the atomic centers. In contrast, the density from maximum entropy is unbiased in that the scale factor, the extinction and dispersion corrections and the phases calculated with the procrystal model are assumed to be correct. Comparison of this density with the total electron density obtained with least-squares modeling then provides, in principle, a model-independent test of the results.

Calculations and results

The maximum-entropy electron-density (*MEED*) program used in the present study was developed by Sakata & Sato (1990). The input consists of phased structure factors and their estimated standard deviations. The observed structure amplitudes $|F_{\text{obs}}|$ were scaled and corrected for extinction (Becker & Coppens, 1974) and for dispersion (Patterson, 1963) using the results of the standard procrystal refinement. The corresponding anomalous scattering factors were taken from Cromer & Ibers (1974). The phases of the structure factors were also derived from the procrystal refinement; they are probably accurate since the structure of K_2PtCl_6 is centrosymmetric and all intensities have been observed with $I > 4\sigma(I)$. We believe the e.s.d.'s of the uncorrected $|F_{\text{obs}}|^2$ to be trustworthy (see RS for a description of the data set and the values of the goodness-of-fit obtained for the various models refined by least squares). The e.s.d.'s of $|F_{\text{obs}}|$ were calculated with the usual expression $\sigma(|F_{\text{obs}}|) = \sigma(|F_{\text{obs}}|^2)/2|F_{\text{obs}}|$. The uncertainties of the extinction and dispersion corrections contributing to the e.s.d.'s of F_{obs} and the correlations of the latter are difficult to estimate and were neglected. A grid of $96 \times 96 \times 96$ was used in the *MEED* calculations. The $C1$ statistic (the convergence criterion which corresponds to the square of the goodness-of-fit in least squares) was set to 1.0. Final agreement factors between the observed

and calculated structure factors at convergence were $R(F) = 0.0088$ and $wR(F) = 0.0049$, comparable to the agreement obtained for the different least-squares fitted models.*

For two reasons, however, the corresponding total electron density is not suitable for direct comparison with the results of the least-squares calculations of RS. First, the least-squares results are presented as difference-density maps, not as total density maps. Second, the density from maximum entropy has an essentially infinite resolution, while both the total and the difference density obtained by Fourier summation subsequent to least squares are affected by strong series termination effects (Fig. 2 of RS). The difference density required for a meaningful comparison is the difference between the total electron densities from maximum entropy and of the procrystal model. It may be obtained with a Fourier summation using the differences of the structure factors of the latter densities, at the expense of introducing a series termination effect. Alternatively, relativistic free-atom densities in direct space at infinite resolution may be calculated with a quantum chemistry program, and must be convoluted with the atomic displacement probability density function. We have opted for the difference between two *MEED* maps: the computed structure factors of the procrystal model are used in a *MEED* calculation as if they were observations. The e.s.d.'s of these computed pseudo-observations are zero by definition, but in practice they must be assigned nonzero values: experience shows that very small values for the e.s.d.'s result in narrow oscillation ripples of the electron density near the core of the Pt atom (see also, Benjamin, 1980). Therefore, the electron density of the procrystal was calculated twice with different e.s.d.'s, viz. the e.s.d.'s of the observed structure factors, and unitary e.s.d.'s. Apart from the value of $wR(F)$, the results were very nearly identical. Agreement factors between the pseudo-observations and the corresponding calculated structure factors of the *MEED* at convergence were $R(F) = 0.0053$ and 0.0049 for the two sets of e.s.d.'s, respectively. Thus, the *MEED* calculation does not exactly reproduce the structure factors of the procrystal model. Judging from the very low R values, the difference between the maximum entropy and the true procrystal density is certainly minor.

As was the case for the difference-density maps obtained with least-squares refinements (e.g. Fig. 2 of RS), the corresponding map obtained with the *MEED* formalism shows spherically symmetric peaks or troughs centered on the atomic sites which partly obscure aspherical features. They may be due, at least in part, to systematic errors in the F_{obs} values arising from imperfect dispersion and extinction corrections. In order to better reveal the aspherical features and permit a comparison with the results from least squares, these spherical features were subtracted by trial and error in a way similar to the earlier work. The spherical density on each of the three atomic sites was represented by the sum of a Lorentzian and a Gaussian function

$$P(r) = L[1 + (\beta r)^2]^{-n} + E \exp[-(\beta r)^m],$$

where L , E , β , n and m were optimized by least squares. Fig. 1(a) shows the resulting *MEED* difference map in the

* Lists of parameters and agreement factors of least-squares models, and structure factors have been deposited with the IUCr (Reference: AN0506). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

plane $(0\bar{1}1)$, Fig. 1(b) the corresponding map obtained by least squares with the simplest anharmonic model [18 variable parameters, $wR(|F|^2) = 0.0091$, $S = 1.213$, Fig. 3 of RS]. The close similarity of the two maps corroborates the earlier work and shows that the anharmonic model does not introduce appreciable bias near K and Cl. The maxima near Pt are at a larger distance from the center in the *MEED* map than

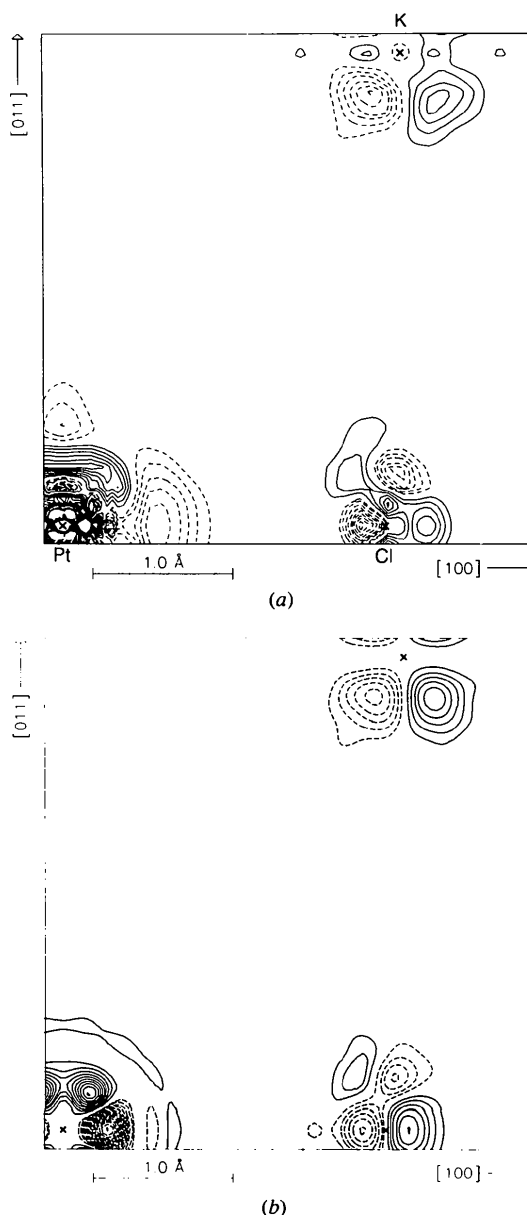


Fig. 1. (a) Difference between the observed and standard electron densities resulting from *MEED* calculations. Contour interval is $0.1 \text{ e} \text{ \AA}^{-3}$; the zero contour is omitted. (b) Difference between the anharmonic and standard electron densities resulting from the least-squares refinement of an anharmonic model. Intervals are as in (a). The functions used to subtract spherically symmetric features centered on the atoms are slightly different from those used to produce Fig. 3 of RS.

in the map obtained with anharmonic model functions; they more resemble Fig. 7 of RS obtained with a combination of electron density and anharmonic functions. Uncertainties of the charge distribution are indeed expected to be largest in the region of Pt. These results may depend on the convergence criterion prescribed by the C1 statistic. Calculations were therefore repeated for $C1 = 0.9$ and 1.1 . Corresponding maps differ from Fig. 1(a) only inside a sphere of radius 0.25 \AA about the center of Pt, *i.e.* in the region where Fig. 1(a) is unintelligible. Densities within 0.1 \AA of the centers of K and Cl change by $0.1 e \text{ \AA}^{-3}$. All features farther removed from the atomic centers are not affected by the change of C1. Finally, we state the obvious fact that a modeling method such as *MEED* gives no clue as to the interpretation of the map in terms of anharmonic motions or bonding effects. Work on low-temperature diffraction data of K_2PtCl_6 is in progress.

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