Recent Structural Studies of PtI


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Abstract

The halogen-bridged mixed-valence metal complexes (MX) have been the object of numerous studies probing the properties of their quasi-one-dimensional M-X sublattice in which the charge disproportionation δ of the metal (M^{3+}/M^{2+}) can be tuned from 0 to 1. We have recently investigated the structure of a fully deuterated sample of [Pt(en)2][Pt(en)2]2(CIO4)4 at room temperature by using pair-distribution-function analysis X-ray powder diffraction data and regular single crystal diffraction in order to study the relationship between the local structure and the charge density wave strength of this class of materials.

Keywords: X-ray diffraction, Structural phase transition

Introduction

The mixed-valence [M(L2)2][M(X2)L2]Y4 systems where M represents a mixed-valence metal (Pt, Ni, ...), X a halogen (Cl, Br, I), (L-L) a ligand such as ethylenediamine and Y a counterion (ClO4, I) have been the subject of numerous investigations over the last decade. Characterized by the existence of quasi-one dimensional chains of alternating metal M and halide X, these materials have been recognized as charge density wave (CDW) systems [1] in which the charge disproportionation δ of the metal (M^{3+}/M^{2+}) can be tuned from 0 to 1. The electronic properties of the MX chains have previously been well described by Peierls-Hubbard models [2] and one-dimensional models gave a good description of the longitudinal vibrations [3-5].

Recent investigations have been devoted to the structural and dynamical characterization of inter-chain interactions [6-8] of the perdeuterated form of [Pt(en)2][Pt(en)2]2(CIO4)4 referred to as d8-PtI. X-ray studies suggested a new structure with existence of two types of chains distinguished by a slight difference in the charge disproportionation in a cell with doubled a (perpendicular to the chains) and b (parallel to the chains) parameters [7]. More recent neutron diffraction studies allowed the solution of the average structure at 20 K in the C2/c monoclinic space group and revealed a new phase transition at 160 K [8]. We also provided evidence of the existence of extra peaks at 20 K and at room temperature indicating a doubling of the whole a, b and c parameters.

We report here on the studies of d8-PtI at room temperature by rotating anode X-ray diffraction on single crystal and by high energy X-ray scattering on powder. These studies provide information on the local and average structures of this system, including a splitting of Pt-I distance along the a axis.

Experimental

A gold needle shaped crystal, of dimensions 0.10 x 0.21 x 0.31 mm, was attached to a glass fiber using 5 minute epoxy.

The capillary was then placed on a Bruker P4/CCD/PC diffractometer. The data were collected using a sealed, graphite monochromatized MoKα X-ray source. The lattice was determined using 44 reflections. A hemisphere of data was collected using a combination of psi and omega scans, with 45 second frame exposures and 0.13° frame widths. Data collection, initial indexing, and cell refinement were handled using MART software. Frame integration and final cell parameter calculation were carried out using SAINT software. The final cell parameters were determined using a least-squares fit to 8192 reflections. The data were corrected for absorption using the SADABS program; decay of reflection intensity was not observed.

The d8-PtI powder was dispersed in a plate and the experiment carried out on the A2 wiggler beamline of Cornell High Energy Synchrotron Source. The measurements were performed at room temperature with a fixed energy of 58.8 kev. The pair distribution function presented in Figure 1 was obtained from the data following a procedure previously reported for the non-periodic systems [9-10].

Results

23378 reflections have been collected and assigned in the monoclinic unit cell with a = 33.915(2), b = 11.6626(7) c = 14.897(1) Å and β=98.447(1). Preliminary analysis of the data collected on the single crystal shows that the reflections with h, k and l odd represent 15% of the sum of reflections and 96% of the sum of intensities collected; hence, the other 85% weak reflections provide evidence for an increasing of the cell and a doubling of the a, b and c parameters. According to the data, taking into account the collected reflections with approximatively I > 3 σ(I), it appears that the possible space groups are P21/m or P2/m. Although the structural refinement is not complete, preliminary work in the big cell (2a, 2b, 2c) and the analysis of
the difference Fourier map systematically suggest a location for
the extra atoms close (at ~0.5 Å) to the platinum.

Discussion
The number and the intensity of the new reflections observed
with X-ray provide more evidence for the doubling of the whole
parameters than was observed during the neutron studies.
Nevertheless, with regard to the reflections collected and to the
preliminary X-ray results, we observed a stronger signature for
systematic disorder along the chains than between chains as
previously observed [7].

The analysis of the diffuse scattering using the pair
distribution function was recently applied to study the local
structure of the PtI compound. Figure 1 clearly shows the two
shorter Pt-I distances along the chain, i.e. 2.72 and 3.04 Å.
These values confirm those determined by neutron at 20 K [8], i.e.
2.712 (3) and 3.048(3) Å respectively, and are in good agreement
with those calculated for the Pt\textsuperscript{2+}-I and Pt\textsuperscript{4+}-I spacing [11]; no
evidence of Pt\textsuperscript{3+}-I distance was exhibited from the PDF.

By comparison to the PDF obtained and the average structure
previously [7] reported by X-ray at room temperature, it appears
there is a splitting of the Pt-I distances along the a axis. The
indicated Pt-I distances are at about 8.3 and 8.6 Å, which is
compared to the average distance determined from the cell
parameter at 8.48 Å. This result is consistent with our preliminary
refinements of data obtained on the single crystal and suggests
that the Pt chains are not straight but in “zigzag”. According to
this result, since the Pt-I distances are similar along the chains at
room temperature and at 20 K, and since the overall unit cell
shrinks, we should observe an increase of the zigzag and hence
the new reflections at low temperature. More investigations are
necessary but such a result could be helpful in explaining the fine
structure recently reported [12].

Conclusion
We report on recent X-ray structural investigations of d8-PtI
using regular single crystal diffraction and pair distribution
function. Preliminary analysis gave new results emphasizing a
doubling of the whole a, b and c parameters at room temperature.
In addition, we show a splitting of the Pt-I distances along the a
axis. This result consistently obtained by two different
techniques, gives the first evidence of the existence of chains in
zigzag for this compound. More quantitative information could
be extracted from these data by modeling in the real space,
comparing consistent analyses of the single crystal experiment
and the PDF in order to extract the local structure. Such
information may be helpful in improving the theoretical models
and the understanding of relations between structural and
dynamical properties for this class of materials.

Fig. 1 : Portion of the PDF of PtI at room
temperature. The main distances involving platinum and iodine
are indicated by arrows.

References
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