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Neutron Diffraction of Mixed-Valence $CsAuCl_3$ at High Pressure

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Wells's salt,[1] whose empirical formula is $CsAuCl_3$, is a classical example of a class II[2] mixed-valence compound. Its crystal structure, first determined by Elliot and Pauling[3] in 1938, and recently refined,[4] reveals that half the gold atoms are surrounded by four chlorine atoms in a plane while the other half have two chlorine nearest neighbors in a linear arrangement. Since square-planar coordination is typical of the low-spin d^8 configuration and linear coordination of d^{10}, it is clear that to a first approximation the lattice contains Au(I) and Au(III), and not Au(II). This agrees with the facts that it is diamagnetic and at ambient pressure is a high-resistance semiconductor. Nevertheless, in contrast to the $AuCl_4^-$ and $AuCl_2^-$ ions, which are both pale yellow, it is black. Thus, the Franck–Condon barrier to intervalence electron transfer cannot be greater than about 2 eV, and, in fact, in a closely related ammonium salt an absorption edge was found at 2.2 eV.[5]

Recently, however, it has been reported[6] that the electrical conductivity of $CsAuCl_3$ is a very steep function of hydrostatic pressure, increasing continuously by 9 orders of magnitude up to 60 kbar, when it behaves as a metal. Clearly, such a transformation must be accompanied by some alteration in the structure. At first sight $CsAuCl_3$ appears to contain chains of alternate $AuCl_4^-$ and $AuCl_2^-$, the planes of the former perpendicular to the *c* axis and the axes of the latter along this axis. However, as pointed out by Wells[7] the three-dimensional structure of $CsAuCl_3$ can be considered formally as derived from the cubic perovskite structure by displacing the chloride ions from the centers of the cube edges in the fashion shown in Figure 1. Thus, a reasonable hypothesis would be that the transformation of $CsAuCl_3$ from a high-resistance semiconductor at ambient pressure to a metal at 60 kbar is brought about by the movement of the chloride ions toward the centers of the lines joining every nearest-neighbor pair of gold atoms. Every gold atom would have an identical environment and the Franck–Condon barrier to electron transfer between the metal sites would disappear; i.e., the compound would become a class III[2] mixed-valence material. In an attempt to verify this hypothesis we have performed powder neutron diffraction measurements on $CsAuCl_3$ under pressure. This note reports our results.

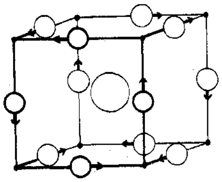

Figure 1. Relation between the structure of $CsAuCl_3$ and the cubic perovskite structure. Small filled circles are Au, smaller open circles are Cl, and the large open circle is Cs.

Table I. Neutron Diffraction and Unit Cell Parameters of $CsAuCl_3$ at Various Pressures

	P, kbar	2θ(obsd)	2θ(calcd)	a_0	c_0
(110)	0	13.15 ± 0.05		7.53	
	1	13.18		7.52	
	20	13.42		7.38	
	28	13.50		7.34	
(202,022)	0	22.90	22.75		
	1	22.95	22.80		
	20	23.35	23.23		
	28	23.40	23.38		
(004)	0	26.03			10.84
	1	26.05			10.83
	20	26.60			10.61
	28	26.80			10.53

Experimental Section

$CsAuCl_3$ was prepared according to Wells.[1] The powder neutron diffraction data were collected at room temperature on the D2 diffractometer at the Institut Laue-Langevin, Grenoble, using a wavelength of 1.222 Å. The sample was contained in an aluminum can within a portable and compact high-pressure clamped cell[7] made of Lucalox (high-density alumina). A small quantity of NaCl was placed inside the sample can as an internal pressure calibrant. Scans were also run on the sample within its can but without the pressure cell.

Results and Discussion

An inevitable consequence of the experimental setup is the presence of a large number of intense reflections from the Al_2O_3, Al, and NaCl which obscure about two-thirds of the reflections from the sample in the 2θ range studied. At ambient pressure $CsAuCl_3$ is tetragonal, I4/*mmm*, and the values of a_0 and c_0 from X-ray diffraction are 7.495 and 10.880 Å. From the scans with and without the pressure cell we identified three main peaks due to $CsAuCl_3$ and followed them at 1, 20, and 28 kbar, the last being the upper limit for the cell. The peak at 13.15° is a composite of (002) and (110) but calculation of the structure factors indicates that it is dominated by (110). The other identifiable peaks are (202,022) and (004). By monitoring (004) we can, therefore, follow the variation of c_0 with pressure, while from (110) we can find a_0. The values obtained can then be checked by calculating the position of (202,022) and comparing it with that observed.

The results are shown in Table I, and the (110), (202,022), and (004) reflections at 1 and 28 kbar are shown in Figure 2. Both a_0 and c_0 decrease with increasing pressure. In fact the ratio $2^{1/2}a_0/c_0$ remains remarkably constant: at 0, 1, 20, and 28 kbar it takes the values 0.983, 0.982, 0.984, and 0.986, respectively. At the same time the volume of the unit cell decreases to 99.4, 94.0, and 92.2% of its volume at ambient pressure. The unit cell of the ideal cubic perovskite structure shown in Figure 1 corresponds to a ratio $2^{1/2}a_0/c_0$ equal to 1.0, so it is clear that over the pressure range we have been able to study no transformation to this structure has taken place. On the other hand, the conductivity data[6] suggest a smoothly continuous increase throughout the range, from a room-

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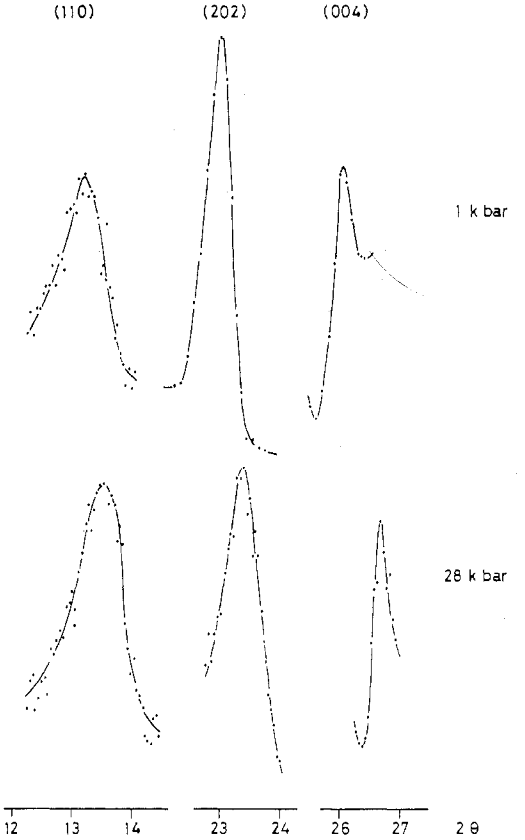

Figure 2. The (110), (202), and (004) powder neutron diffraction peaks of $CsAuCl_3$ at 1 and 28 kbar.

temperature conductivity of $10^{-6}\ \Omega^{-1}\ cm^{-1}$ at ambient pressure up to $10^{-1}\ \Omega^{-1}\ cm^{-1}$ at 28 kbar. Because the two Au sites in the unit cell must still remain crystallographically inequivalent at 28 kbar, this very large increase must be due to a lowering of the activation energy in a semiconducting phase rather than the transformation of the semiconducting phase into a metallic phase. In other words at 28 kbar $CsAuCl_3$ is still a class II mixed-valence salt.

A final point of interest concerns the compressibility of the salt. Defining the linear axial compressibility as the compressive strain per unit pressure $-(1/l)(dl/dP)$, where $l = a$ and c, we calculate values of 0.95×10^{-2} and $1.03 \times 10^{-2}\ cm^2\ dyn^{-1}$ along the a and c axis, respectively. These are to be compared with values[9] for simple ionic salts such as NaCl ($1.42 \times 10^{-2}\ cm^2\ dyn^{-1}$) and CsCl ($1.98 \times 10^{-12}\ cm^2\ dyn^{-1}$) and indicate that despite the very large increase in conductivity brought about by pressure, the elastic properties of $CsAuCl_3$ are not notably unusual. We hope to extend our measurements to higher pressures using a newly constructed[10] sapphire cell.

After the experiments described here were completed, we became aware of a parallel investigation of the high-pressure structure of $CsAuCl_3$ by X-ray diffraction.[11] We are grateful to Professor Dr. H. Schulz and Dr. W. Denner for communicating these results to us and helping to index the 26–27° region of our scans.

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A Five-Coordinate Palladium(II) Complex Containing Tris(2-(dimethylamino)ethyl)amine, $N(CH_2CH_2N(CH_3)_2)_3$

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Although five-coordinate complexes of the type $[M(trenMe_6)X]X$ (M = a first-row transition metal; $trenMe_6 = N(CH_2CH_2N(CH_3)_2)_3$; X = an anionic ligand) are known,[1-4] analogous five-coordinate derivatives containing a second- or third-row transition metal have not yet been reported.

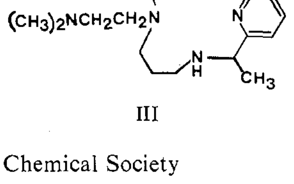
Results and Discussion

The molecular structure of the four-coordinate cation $[PdCl(trenMe_6H)]^{2+}$ isolated as $[PdCl(trenMe_6H)]ClPF_6$ has been determined.[5] We now report that when the foregoing cation is formed in situ in aqueous solution and the pH of the solution is adjusted to about 11.5 with Na_2CO_3, the protonated *N,N*-dimethylaminoethyl portion of the coordinated ligand is neutralized and coordinates to the palladium center according to eq 1. The product, II, may be readily isolated as the chloride salt, $[PdCl(trenMe_6)]Cl$ (see Experimental Section).

$$\underset{\mathrm{I}}{[PdCl(trenMe_6H)]^{2+}} + CO_3^{2-} \rightarrow \underset{\mathrm{II}}{[PdCl(trenMe_6)]^{+}} + CO_2 + OH^- \qquad (1)$$

At pH ≤7.0, $[PdCl(trenMe_6H)]^{2+}$ is present in solution and may be isolated as the chloride salt $[PdCl(trenMe_6H)]Cl_2$. The proton NMR spectrum of I in D_2O exhibits a doublet (3.27 and 3.17 ppm) and a singlet (2.70 ppm) in a ratio of 2:1 downfield from DSS and is shown in Figure 1. The doublet resonance may be attributed to the magnetically nonequivalent methyl hydrogens of the *N,N*-dimethylaminoethyl groups bonded to palladium and the singlet may be attributed to the methyl groups of the protonated *N,N*-dimethylaminoethyl group. At pH ~12, II is present in solution and its proton NMR spectrum is characterized by a sharp, singlet methyl resonance (2.6 ppm) in D_2O.

The proton NMR spectrum shown in Figure 1 is consistent with the presence of six magnetically equivalent methyl groups, i.e., the ligand is acting as a tetradentate ligand. The geometry about the palladium is presumably trigonal bipyramidal, similar to that observed for other five-coordinate complexes containing $trenMe_6$.[6] The chloride salt of II behaves as a 1:1 electrolyte in aqueous solution (see Experimental Section). These data together with the analytical data presented in Table I are consistent with the formation of a five-coordinate palladium(II) complex according to eq 1. Recently, a pH-induced geometrical change similar to that described herein has been reported for the macrocyclic ligand III coordinated to nick-



III

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