



Cs₂Pt, a Platinide(-II) Exhibiting Complete Charge Separation



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Introduction

The importance of relativistic effects grows with increasing atomic number and becomes rather prominent when reaching the 6th period. The effects are particularly noticeable for gold, which exhibits the highest electron affinity among all metals (2.31 eV). The Au⁻ anion is stable in the gas phase, in solution^[1] and in the solid state^[2]. Furthermore crystal-chemical parallels to halogenides and a reactivity partly analogous to the halogens, as the alkali induced disproportionation^[3], have found a straightforward explanation in the relativistic stabilisation of Au⁻.

Platinum is the metal with the second highest electron affinity (2.13 eV) after gold exceeding that of any chalcogen (highest value 2.08 eV; sulphur), which readily form, as typical non-metals, negatively charged dianions. Due to this fact it appeared promising to attempt the synthesis of platinides containing platinum with a twofold negative ionic charge realizing the closed-shell valence state. After numerous failures we have now succeeded in obtaining Cs₂Pt.

Experimental

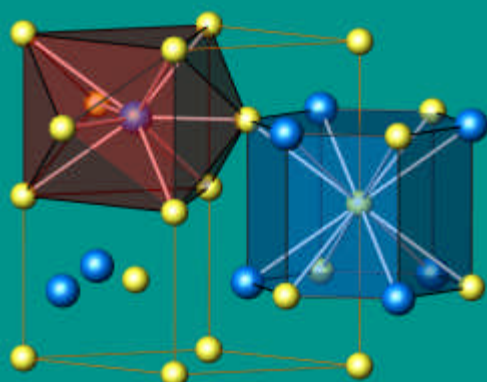
Cs + Pt (3:1 ratio) sealed under Ar in a Ta-ampoule reacted at 700°C

Temperature, °C vs Time, h graph showing a heating ramp of 50°C/h to 700°C, a 2-day hold at 700°C, and a cooling ramp of 10°C/h.

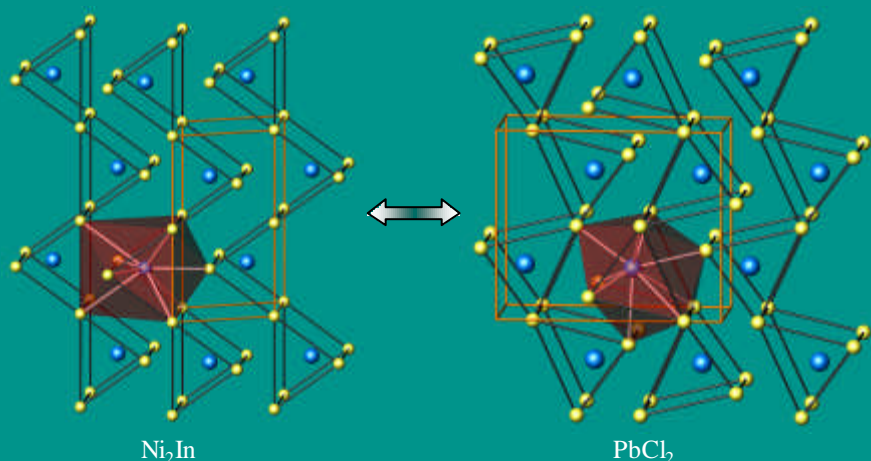
Cs-distillation at 100°C crystal search red, transparent needles of Cs₂Pt

Crystal Structure

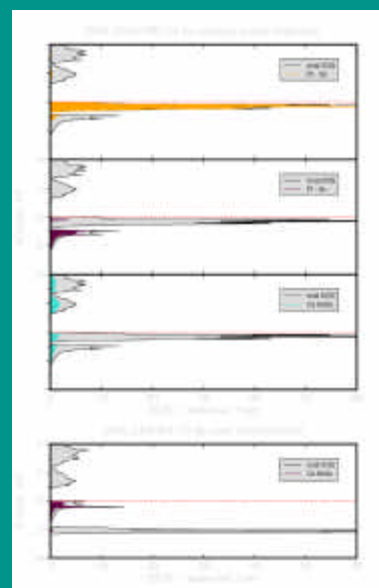
Cs₂Pt crystallizes in the Ni₂In-type. Platinum (blue balls) is surrounded by nine caesium atoms (yellow balls, 328(3×) and 405(6×) pm) in the form of a three fold capped trigonal prism, with two additional neighbours at a distance of 473 pm. The environments of the two independent caesium atoms differ significantly: Cs1 is coordinated by six Pt and six Cs2 atoms at the same distance of 405 pm, Cs2 by three Pt (328 pm) and six Cs1 (405 pm). Nevertheless, in an ionic picture (Cs⁺, Pt²⁻) both caesium atoms are energetically balanced, with respect to their partial Madelung energies.



The Ni₂In-type is the end member of a series of polymorphous modifications, arising from compounds in the fluorite-type under increased hydrostatic pressure. The sequence *anti*-CaF₂-type → *anti*-PbCl₂-type → Ni₂In-type is also observed in the alkali metal monochalcogenides.^[4] The close structural relationship between the PbCl₂- and Ni₂In-types, which can be transformed into each other via a displacive rearrangement mechanism, explains why ionic solids can also crystallize in the Ni₂In-structure. In accordance with the pressure-homologue-rule, Cs₂S, Cs₂Se and Cs₂Te already exist under normal pressure in the PbCl₂-type. Rb₂Te^[5] marks a transition, since it exists in the CaF₂-, PbCl₂- and, at high temperatures, in the Ni₂In-structure. In this sense Pt²⁻ might be considered as a higher homologue of the chalcogenides.



Quantum Chemical Calculations



The densities of states and their projections onto certain atomic orbitals shown on the left side, were calculated within DFT using the TB-LMTO-ASA program. The three diagrams above are taken from calculations with the gradient corrected functional of Perdew and Wang. The Cs 5p orbitals were treated as valence states. The partial waves within the MT spheres were obtained by solving the one particle Dirac equation. The band gap amounts to 1.3 eV.

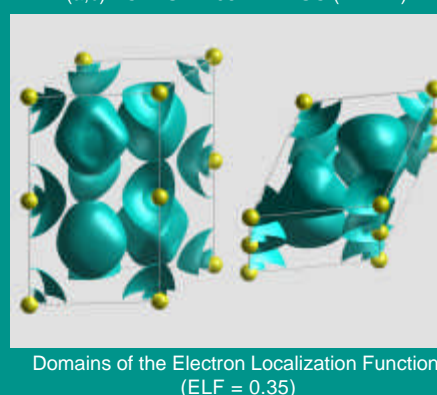
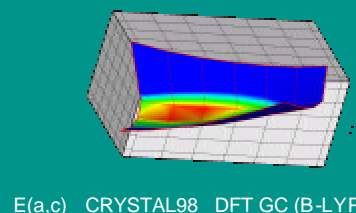
The nonrelativistic error can be seen in the lower diagram, where the s and d bands change their position. Nevertheless even in the nonrelativistic case, Cs₂Pt still is a semiconductor with a band gap of 0.9 eV.

Hartree-Fock and DFT calculations were performed with the CRYSTAL98 program. Relativity was considered by using the Stuttgart-Dresden quasi-relativistic pseudopotentials (Pt: 18 valence electrons, Cs: 9 valence electrons).

Method	Lattice parameters		Mulliken Charge			Band Gap / eV
	a / Å	c / Å	q(Pt)	q(Cs2)	q(Cs1)	
HF	6.19	8.85	-1.92	+0.97	+0.94	7.1
LDA BH	5.53	7.40	-1.93	+0.98	+0.95	2.1
GC B-LYP	5.95	8.59	-1.85	+0.94	+0.91	2.1
Exp.	5.68	9.47				

Optimized lattice parameters (CRYSTAL98)

The Cs ₂ Pt molecule, calculated with GAUSSIAN98:			
Method:	CCSD(T)		
Basis set:	Pt [6s5p4d2f]; Cs [5s4p2d1f]		
Pseudopot.:	quasirelativistic; Pt 18 ve; Cs 9 ve		
R _{Cs-Pt} :	2.96 Å		
θ _{Cs-Pt-Cs} :	133°		
Mulliken charge	HF:	Pt	Cs
	CCD:	-1.48	+0.74
		-1.79	+0.89



Optimized lattice parameters are given in the table above. Concerning the bonding in the Cs₂-Pt-planes as reflected by the *a* parameter, the same trends with respect to the computational details can be observed as for the hypothetical Cs₂Pt molecule. The stability is not only caused by relativistic effects, but also by the polarizability of the ions, including the Cs⁺ ion. The bonding along the *c*-axis has a significant dispersion contribution. This cannot be calculated properly by DFT or HF. Thus the changes in energy are only a few mH when varying the *c* parameter by 1 Å.

The topological analysis of the electron density obtained with the WIEN2k program gives the following charges: q(Pt) = -1.3; q(Cs2) = +0.6; q(Cs1) = +0.7.

Both, relativity and dynamical correlation enhance the charge separation in Cs₂Pt.

Crystal Data of Cs₂Pt

Formula weight	460.91
Temperature /K	293
Wavelength /pm	71.073
Crystal system	Hexagonal
Space group	P6 ₃ /mmc (No. 194)
<i>a</i> /pm	567.6(1)
<i>c</i> /pm	947.1(3)
<i>V</i> /pm ³	264.3(1) × 10 ⁶
<i>Z</i>	2
Crystal size /mm ³	0.2 x 0.2 x 0.4
X-ray density /g cm ⁻³	5.783
Absorption coefficient /mm ⁻¹	39.86
2θ range /deg.	8 – 68
Number of variable parameters	8
Independent reflections	243
R ₁ (all data), R ₁ [I > 2σ(I)] ^{b)}	0.0221, 0.0265
wR ₂ (all data), wR ₂ [I > 2σ(I)] ^{c)}	0.0529, 0.0557

Atomic parameters and equivalent displacement parameters U_{eq} (pm²/10)

Atom	x	y	z	U _{eq}
Pt	1/3	2/3	1/4	26(1)
Cs1	0	0	0	44(1)
Cs2	1/3	2/3	3/4	32(4)

Selected interatomic distances (Å) and angles (deg.)

Pt – Cs2	327.9(1) 3x
– Cs1	404.5(1) 6x
Cs1 – Cs2	404.5(1) 6x
Cs2 – Pt – Cs2	120.0

References

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