

An experimental proof for negative oxidation states of platinum: ESCA-measurements on barium platinides

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ESCA-measurements on barium platinides provide the first spectroscopic evidence for negative oxidation states of platinum and are in excellent agreement with theoretical predictions based on quantum-chemical calculations.

Relativistic effects play an important role in the chemistry of heavy elements, among others, stabilizing their 6s and 6p_{1/2} shells.¹ Particularly strong contractions of the 6s shells were calculated for gold and platinum,² which is reflected by extremely high electron affinities as determined for these two metals (Au: 2.31 eV, Pt: 2.13 eV),³ in this respect approaching the values of halogens (I: 3.06 eV)³ and even surpassing the values of chalcogens (S: 2.08 eV).³ As a consequence, gold achieves the oxidation state -1 in many compounds.⁴ One of the most prominent examples is yellow-transparent CsAu consisting of caesium cations and auride anions.⁵ Auride ions have also been shown to exist in ternary alkali-metal auride oxides,⁶ in tetramethylammonium auride,⁷ or even as solvated anions in solutions of CsAu in liquid ammonia.⁸ In contrast to the rich auride family, the platinide chemistry was explored only recently. A full charge transfer, resulting in an oxidation state of -2 for platinum, thus far has been observed in red transparent Cs₂Pt, exclusively,⁹ while in compounds of platinum with another electropositive element, barium, intermediate charges ranging from -1.1 for BaPt, through -1.25 for Ba₃Pt₂, to -1.8 for Ba₂Pt were assigned to platinum atoms, by means of quantum-chemical analyses.^{4,10}

ESCA (Electron Spectroscopy for Chemical Analysis) is a versatile physical probe which is widely applied in analyzing valence states or partial charges of elements in given compounds.¹¹ Basically, in applying this method, the binding energy of a selected atomic level is correlated to a chemical environment of the investigated atom. For instance, ESCA-measurements conducted on a series of gold compounds revealed a virtually linear relationship between the binding energies of the Au(4f_{7/2}) levels and the oxidation states of gold.¹² The difference between binding energies of the Au(4f_{7/2}) level in rubidium or caesium auride and pure gold attained -1.1 eV, thus confirming the oxidation state of gold as -1 in both compounds. For platinum, ESCA investigations were carried out on compounds with positive oxidation states of the transition metal and proved to be a powerful tool for a charge assignment also in this case. The shifts of the Pt(4f_{7/2}) levels as compared to the metallic platinum achieved ~ 1.2 eV per one oxidation state unit.¹³ Herein we report on ESCA-measurements performed on barium platinides which confirm negative oxidation

states at platinum atoms to be realized in all investigated compounds.

Barium platinides (Ba_xPt, $x = 1, 1.5, 2$) were prepared by reaction of appropriate quantities of Ba pieces (99.99%, Sigma-Aldrich, twice distilled by a producer) and Pt sponge (99.9%, ChemPur/MaTeck, dried before use at 400 °C in a dynamic vacuum of 10⁻⁶ mbar) at 950 °C under argon in a welded tantalum ampoule followed by slow cooling of the reaction mixtures to room temperature. Further details on syntheses and characterizations are given elsewhere.¹⁰ Barium platinides are extremely air- and moisture-sensitive, therefore they were handled under strictly inert conditions (Schlenk technique or argon-filled glove box with H₂O, O₂ < 0.1 ppm). The samples were pressed into pellets (6 mm diameter \times ~ 1 mm thickness). Platinum foil was used as purchased (0.025 mm thickness, 99.9% ChemPur). ESCA spectra were recorded on an electron spectrometer (AXIS ULTRA, Kratos, UK) by use of monochromatized Al K _{α} radiation (1486.58 eV). The vacuum during the measurements was kept at *ca.* 3 \cdot 10⁻⁹ Torr. The sample surfaces were sputtered with high purity argon for 5 min; during this procedure no shifts of the Pt(4f) binding energies were observed. To account for charging, the spectra were calibrated with respect to an internal C(1s) line, assuming its invariance for all investigated samples (binding energy of 285.0 eV). The peak profiles were fitted with a Voigt function. To account for the asymmetric shape, besides the strongest peak corresponding to the binding energy, one additional peak was admitted in each case.

To prove the accuracy of the spectrometer, an ESCA-spectrum was taken first from a pure platinum foil. The resulting binding energy of the Pt(4f_{7/2}) level was 71.5(1) eV, which is in good agreement with the values reported in the literature for elemental platinum or Pt(0) compounds (71.2(1), 71.6(-), 72.0(2) eV).¹³ ESCA-spectra recorded for all compounds studied displayed a shift of the binding energy of the Pt(4f_{7/2}) level to lower energies (Fig. 1; maxima of Pt(4f_{7/2}) peaks are found at 70.2 eV for BaPt, 70.0 eV for Ba₃Pt₂ = Ba_{1.5}Pt, and 69.6 eV for Ba₂Pt) indicating an elevated electronic density on the platinum atoms as compared to elemental platinum, thus demonstrating a negative oxidation state at platinum. The binding energies vary monotonically with growing barium content, *i.e.* with increasing valence electron's concentration and virtually in accord with their formal descriptions [Ba²⁺·e⁻] \cdot Pt⁻, [(Ba²⁺)_{1.5}·1.5e⁻] \cdot Pt^{1.5-}, [(Ba²⁺)₂·2e⁻] \cdot Pt²⁻. In order to quantitatively assign a valence state to platinum, we used the known values for shifts in binding energies between elemental platinum and potassium tetrachloroplatinate (Pt(+2), $\Delta E = 2.4$ eV), or potassium hexachloroplatinate (Pt(+4), $\Delta E = 4.8$ eV),¹³ assuming for both these ionic compounds a

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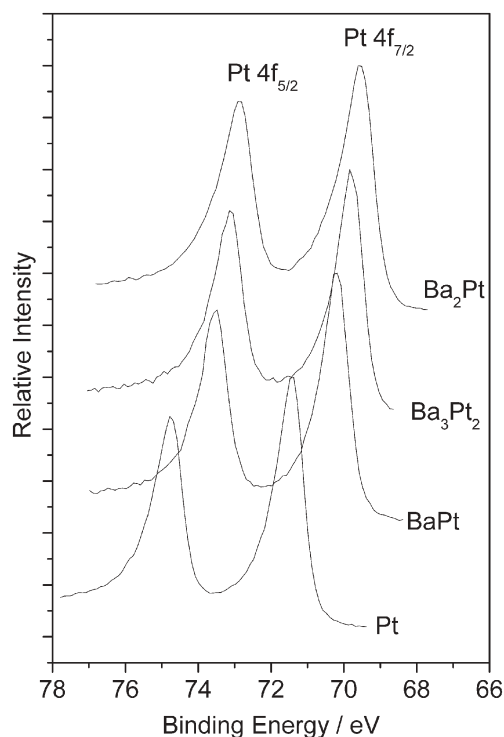


Fig. 1 Pt 4f region of ESCA spectra of barium platinides.

complete charge transfer from platinum to chlorine. Plotting the shifts in Pt(4f_{7/2}) binding energies against the formal oxidation states produces a linear relationship for oxidation states between 4 and -1, slightly deviating to lower shift values for Ba₃Pt₂ and Ba₂Pt (Fig. 2). From the linear dependence, “partial oxidation states” of platinum in barium platinides can be easily deduced: -1.1 for BaPt, -1.25 for Ba₃Pt₂ and -1.6 for Ba₂Pt. We expect that a further increase of the Ba/Pt ratio would shift the “partial

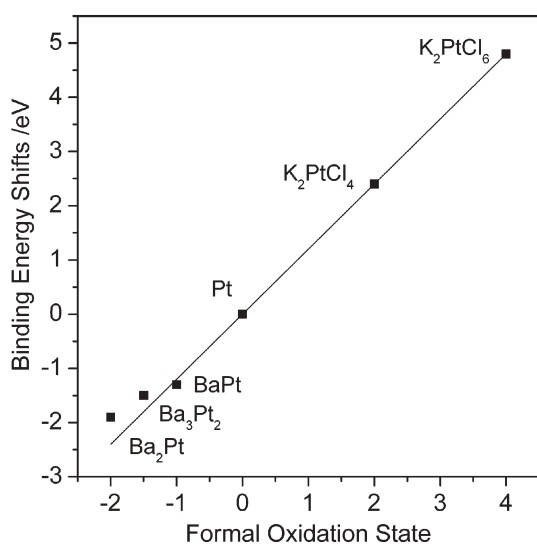


Fig. 2 Graphical presentation of the correlation between formal oxidation state of platinum and the 4f_{7/2} binding energy shift, for selected compounds. The formal oxidation state of platinum in the barium platinides is defined according to the notation [Ba²⁺₂e⁻]₂Pt⁻, [(Ba²⁺)_{1.5}⁺e⁻]₂Pt^{1.5-}, and [(Ba²⁺)₂e⁻]₂Pt²⁻.

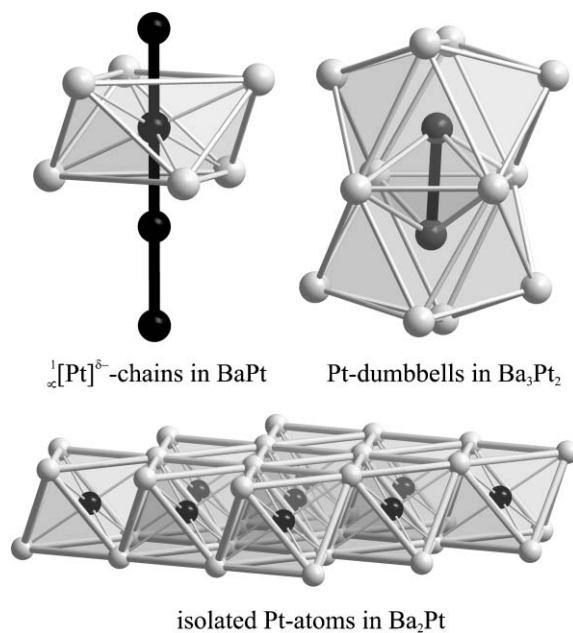


Fig. 3 Platinum coordination in selected barium platinides.

oxidation state” of platinum closer to -2, the state corresponding to a quasi-inert electronic configuration 5d¹⁰6s². Noteworthy is the excellent correspondence of the spectroscopically determined values of the “partial oxidation state” of platinum to the effective charges as determined by quantum-chemical analyses¹⁰ (see above). However, one should bear in mind that the absolute match is accidental rather than rational because there seems to be no simple functional relationship between the two different probes employed. Nevertheless, even if one resorts just to the very well agreeing relative differences between the charges assigned, the ESCA results nicely corroborate us classifying BaPt, Ba₃Pt₂ and Ba₂Pt as platinides, and furthermore regarding them as the first examples of Zintl phases where the anionic part, including the formation of polyanionic entities, is played by a transition element. As can be seen from Fig. 3, the degree of catenation of platinum increases with dropping number of valence electrons provided by the electropositive constituent from isolated atoms (Ba₂Pt), through dumbbells (Ba₃Pt₂) to chains (BaPt).

In conclusion, in this work we provide the first physical evidence for negative oxidation states of platinum in solid state compounds. We present also an independent physical verification for theoretical predictions of charge assignments based on quantum-chemical analyses using barium platinides as model compounds.

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