The First Trigonal Planar Transition Metal−Hydrogen Complex in $NaBaPdH_3$

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A new quaternary hydride, $NaBaPdH_3$, has been synthesized. The novel structure type was refined, in the hexagonal space group $P6_3/mmc$, from single-crystal X-ray data complemented by neutron powder diffraction data from the corresponding deuteride. The unit cell dimensions at 150 K were determined to be $a = 6.049(1)$ Å and $c = 6.061(3)$ Å. The structure consists of trigonal planar PdH_3 complex anions, with formally zerovalent palladium, in a framework of sodium and barium counterions. It is related to the CaCuP structure, with the PdH_3 unit at the P atom site and Ba and Na at the Cu and Ca atom sites, respectively.

Introduction

In recent years, a number of new ternary and quaternary metal hydrides of group VIII (Fe−Os, Co−Ir, Ni−Pt) transition metals (TMs) with electropositive alkali and alkaline earth metals or their corresponding binary hydrides have been synthesized by hot sintering in hydrogen.[1] These new hydrides, in contrast to the now classical K_2ReH_9, consist of formally low-valent TM−hydrogen fragments in a framework of electropositive metal counterions, which have donated their valence electrons to form TM−hydrogen bonds in the new complexes.

The apparent ability of the hydrogen ligand to stabilize formally low-valent oxidation states is remarkable. For middle and late transition metals to adopt low oxidation states, certain electron-accepting properties of the ligand are usually required; i.e., it should be a π-acid with unoccupied orbitals available for bonding. In homoleptic complexes with hydrogen ligands, this mechanism cannot be realized, but there still exist a few formally very low-valent TM−hydrogen complexes with electron-dense bonds in, for example, the ternary hydrides $Li_2[PdH_2]$, $Na_2[PdH_2]$, $Mg_2[NiH_4]$, and $Mg_3[RuH_3]$.[2−5] In these compounds, the TM−hydrogen complexes force even highly electropositive alkali and alkaline earth atoms to participate in covalent bonding, beyond the role of the classical undeformed cations, by accepting additional electron density from the anionic transition metal complex. This behavior has also been suggested by Miller et al., from extended Hückel calculations for Mg_3RuH_3, where the valence orbitals of Mg interact covalently with Ru and H, leading to increased stability and a more metallic character.[6]

It is interesting to note, for the palladium hydrides, how the formation of $[Pd(0)H_2]$ complexes is favored over that of a more common square planar arrangement in $[Pd(II)H_4]$. Na_2PdH_4, containing the latter four-coordinated complex, was recently synthesized but could only be obtained at an extreme 2 kbar H_2 pressure![7] K_2PdH_4, containing the larger and more electropositive potassium ion, was synthesized at a more moderate pressure.[8] Both hydrides are nonmetallic, and the Pd−H distances are short, 1.61 and 1.63 Å, respectively, indicating more conventional, covalent bonding than the longer Pd−H distances, 1.68 Å, in the metallic Li_2PdH_2 and Na_2PdH_2 hydrides.

In the present article, we will describe the synthesis and characterization of the new quaternary hydride $NaBaPdH_3$, containing unprecedented 16-electron $[PdH_3]$ complexes that contain formally zerovalent palladium with planar trigonal D_{3h} symmetry. The crystal structure was determined and refined from single-crystal X-ray diffraction data and was verified by a neutron powder diffraction experiment on a deuterated sample.

Experimental Section

Syntheses. All materials were sensitive toward air and moisture and were stored and handled in an Ar-filled glovebox. Ruby-red single crystals of $NaBaPdH_3$ were obtained from a solid-state reaction between cold-pressed powders of sodium hydride (NaH, claimed purity 97%, Aldrich-Chemie; NaD was synthesized by reacting sodium metal with deuterium gas, which was bubbled through the molten metal), barium hydride (Ba rods 99.9+%, Aldrich Chemical Company, Inc.; heated under 50 bar of hydrogen (deuterium) pressure at 450 °C for 4 h), and palladium (Pd <60 μm, claimed purity 99.9+%, Chempur) in a 1:1:1 molar ratio. The reaction was performed in an Al_2O_3 crucible, placed in a stainless steel reactor under a hydrogen pressure of 90 bar, at 510 °C during 48 h. The temperature and pressure were then decreased and held at 400 °C and 50 bar for 1 week. Several attempts at varying both temperature and pressure were made, to find the optimal reaction conditions. Phase analysis of the products was performed with a Guinier−Hägg focusing camera, using Si as internal standard. The unknown reflections in the powder photographs were indexed with the

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(1) (a) Bronger, W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 759. (b) Bronger, W. *J. Alloys Compd.* **1995**, *229*, 1. (c) Yvon, K. In *Encyclopedia of Inorganic Chemistry*; King, B., Ed.; John Wiley & Sons Ltd.: Chichester, England, 1994; Vol. 3.

(2) Kadir; K.; Noréus, D. *Z. Phys. Chem. (Munich)* **1989**, *163*, 231.

(3) (a) Noréus, D.; Törnroos, K. W.; Börje, A.; Szabó, T.; Bronger, W.; Spittank, H.; Auffermann, G.; Müller, P. *J. Less-Common Met.* **1988**, *139*, 233. (b) Kasowski, R. V.; Noréus, D.; Wang, L.; Whangbo, M.-H. *Inorg. Chem.* **1992**, *31*, 4737.

(4) (a) Zolliker, P.; Yvon, K.; Jorgensen, D.; Rotella, F. J. *Inorg. Chem.* **1986**, *25*, 3590. (b) Noréus, D. *Z. Phys. Chem. (Munich)* **1989**, 163, 575. (c) Gavra, Z.; Kimmel, G.; Gefen, Y.; Mintz, M. H. *J. Appl. Phys.* **1985**, *57*, 4548. (d) Gavra, Z.; Mintz, M. H.; Kimmel, G.; Hadari, Z. *Inorg. Chem.* **1979**, *18*, 3595.

(5) Bonhomme, F.; Yvon, K.; Fischer, P. *J. Alloys Compd.* **1992**, *186*, 309.

(6) Miller, G. J.; Deng, H.; Hoffmann, R. *Inorg. Chem.* **1994**, *33*, 1330.

(7) Bronger, W.; Auffermann, G. *J. Alloys Compd.* **1995**, *228*, 119.

(8) Kadir, K.; Kritikos, M.; Noréus, D.; Andresen, A. F. *J. Less-Common Met.* **1991**, *172−174*, 36.

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Table 1. Atomic Parameters from Single-Crystal X-ray Diffraction Data for $NaBaPdH_3$[1] and Rietveld-Fitted Neutron Powder Diffraction Data for $NaBaPdD_3$[2] (Space Group $P6_3/mmc$; $Z = 2$)[a]

atom	position	x	y	z	U_{eq} (Å^2)[b]	U_{iso} (Å^2)[c]	occ
Pd	2*c*	$^1/_3$	$^2/_3$	$^1/_4$	0.0088(1)[1]	0.009(3)[2]	1
Ba	2*d*	$^2/_3$	$^1/_3$	$^1/_4$	0.0071(1)[1]	0.006(3)[2]	1
Na	2*a*	0	0	0	0.0168(8)[1]	0.018(8)[2]	1
H	6*h*	0.170(7)	0.34(1)	$^1/_4$		0.03(1)[1]	1
D	6*h*	0.169(2)	0.338(3)	$^1/_4$		0.042(3)[2]	1

[a] Standard deviations are given in parentheses. [b] U_{eq} values are the equivalent isotropic thermal parameters of the anisotropically refined atoms, defined as $^1/_3$·trace (**U**). [c] U_{iso} values are the isotropically refined thermal parameters.

program TREOR,[9] and least-squares refinements of the unit cell dimensions were performed with the program PIRUM.[10] The new $NaBaPdH_3$ was found to crystallize with hexagonal unit cell dimensions $a = 6.0611(6)$ Å and $c = 6.0859(8)$ Å at room temperature. A deuterated sample for the powder neutron diffraction study was also synthesized as described above, and its unit cell dimensions were determined to be $a = 6.0513(4)$ Å and $c = 6.0813(19)$ Å at room temperature. The deuteride powder sample contained a small amount of impurities, identified as BaO[11] and $Ba(OD(H))_2{\cdot}3D(H)_2O$[12] from Guinier−Hägg films.

The hydrogen content of the title compound was determined by degassing a sample of crystals at high temperature into a calibrated volume, while the increase in gas pressure was monitored. The hydrogen content per formula unit was found to be close to 3.

Ac magnetic susceptibility data were collected on polycrystalline $NaBaPdH_3$, in the temperature range 11−325 K at 500 Hz and 500 $A{\cdot}m^{-1}$, using a Lake Shore Inc. ac susceptometer, model 7130, equipped with a helium cryostat. The sample was contained in a sealed glass capillary, and the experimental susceptibilities were corrected for sample-holder diamagnetism. The diamagnetic contributions from atomic core electrons were taken into account by using Pascal's constants.[13] A weak, almost temperature-independent paramagnetic signal indicated minor impurities of palladium metal. This presence of palladium in its elemental state probably originates from sample decomposition. The expected diamagnetic contribution from $NaBaPdH_3$ was thus obscured by the palladium metal contamination. However, a temperature-dependent paramagnetic behavior of, e.g., Curie−Weiss type was absent in the measured temperature range. From this observation it was suggested that $NaBaPdH_3$ is diamagnetic.

Single-Crystal X-ray and Neutron Powder Diffraction Data Collection and Structure Refinements. An irregularly shaped single crystal of the size 0.22 × 0.27 × 0.30 mm^3 was mounted and sealed in a glass capillary. X-ray diffraction data were collected at 150 K on a STOE four-circle diffractometer using Mo Kα radiation ($\lambda = 0.710\,73$ Å). The unit cell parameters were refined from 30 well-centered reflections in the region $36.1° < 2\theta < 41.3°$. Systematic absences in the diffraction data were consistent with space group $P6_3/mmc$ (No. 194). A total of 1134 reflections were scanned ($3° < 2\theta < 69°$) with the $\omega-2\theta$ technique, of which 187 were unique and 183 observed. The data were corrected for background, Lorentz, and polarization effects using the program package X-shape.[14] A numerical absorption correction[14] was applied, with a linear absorption coefficient of 14.72 mm^{-1} and the internal R value (R_{int}) was 0.0355.

In the subsequent structure refinement, the $\sum w(\Delta F^2)$ function was minimized with a full-matrix least-squares method.[15] The barium atoms were found by Patterson methods,[16] and the palladium and the sodium atoms were located from a difference Fourier map. Due to the reduced thermal motions of the atoms at 150 K, the hydrogens were distinguished as weak, but significant, peaks in the difference Fourier map. In the final refinement, 10 parameters were allowed to vary. Anisotropic displacement parameters were refined for the metal atoms, and isotropic, for the hydrogen atoms. The agreement factors (R values) decreased significantly, from R1 = 0.0248 and wR2 = 0.0558 to R1 = 0.0227 and wR2 = 0.0421 when the hydrogen atoms were included in the refinement.

A neutron powder diffraction study on a deuterated sample at room temperature was performed at NFL, Studsvik, Sweden, using the NDP diffractometer with $\lambda = 1.470$ Å at 295 K. The data were collected in the $4.00 < 2\theta < 139.92°$ interval, with a step size of 0.08°. The profile refinement[17] used 30 reflections in the $4.00° < 2\theta < 72.00°$ range. To avoid problems with overlapping peaks from the impurity phases, the higher angles were not used. The major impurity phase BaO[11] is indicated in the Rietveld plot (Figure 1). The amount was, however, too small to be allow a convergent refinement, which was also the case for the minor impurity phase $Ba(OD(H))_2{\cdot}3D(H)_2O$.[12] A Gaussian profile function was used to describe the reflections. The background was interpolated between 15 given points, and 13 parameters (5 structural and 8 profile) were included in the final structure refinement using the Rietveld program FULLPROF.[18] The final Rietveld R values were $R = 0.047$, $R_B = 0.077$, and $R_F = 0.055$. The results from the refinements are shown in Table 1, the Rietveld-fitted profile and difference plot in Figure 1, and the shortest interatomic distances in Table 2.

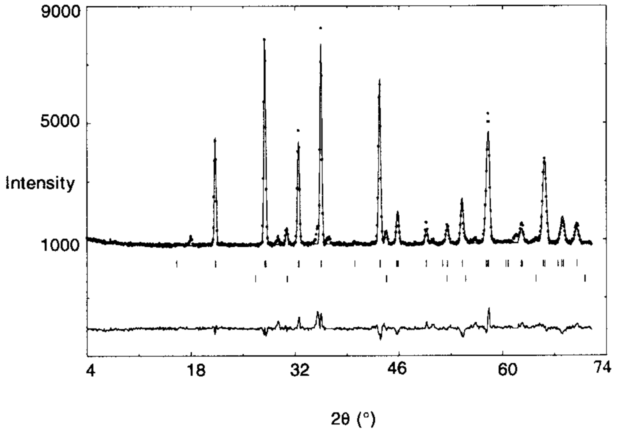

Figure 1. Rietveld-fitted profile and difference plot for $NaBaPdD_3$. BaO is indicated as a second phase in the difference plot.

Results and Discussion

The novel $NaBaPdH_3$ structure is related to the CaCuP type[19] and thus consists of layers of anionic PdH_3 complexes (P position) and barium ions (Cu position) interspersed by sodium

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(9) Werner, P.-E.; Eriksson, L.; Westdahl, M. *J. Appl. Crystallogr.* **1985**, *18*, 367.

(10) Werner, P.-E.; Eriksson, L. *World Directory of Powder Diffraction Programs*, Release 2.2; Report to the IUCr Commission on Powder Diffraction; Program Exchange Bank: Leiderdorp, The Netherlands, 1995.

(11) Gerlach, W. *Z. Phys.* **1922**, *9*, 184.

(12) (a) Leshchenko, P. P.; Kobzareva, V. P.; Lykova, L. N.; Kovba, L. M. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1980**, *25*, 1100. (b) Lutz, H. D.; Kellersohn, T.; Vogt, T. *Acta Crystallogr.* **1990**, *C46*, 361.

(13) Boudreaux, E. A.; Mulay, L. N. *Theory and applications of molecular paramagnetism*; Wiley: New York, 1976.

(14) *X-SHAPE revision 1.01: Crystal Optimisation for Numerical Absorption Correction*; STOE: Darmstadt, Germany, 1996.

(15) Sheldrick, G. M. *SHELXL93: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.

(16) Sheldrick, G. M. *SHELXS86: Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1985.

(17) Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, *2*, 65.

(18) Rodriguez-Carvajal, J. *FULLPROF Version 3.1 Jul95-LLB-JRC*; CEA-CNRS: Gif-sur-Yvette, France, 1995.

(19) Mewis, A. *Z. Naturforsch.* **1978**, *33B*, 983.

Table 2. Shortest Interatomic Distances Found in $NaBaPdD_3$ (Esd's in Parentheses)

atoms	multiplicity	dist (Å)	atoms	multiplicity	dist (Å)
Pd−D[a]	3	1.719(8)	Pd−Ba[c]	2	3.041(1)
Na−D	6	2.337(6)	Na−Na	2	3.041(1)
D−D[a]	2	2.98(1)	Pd−Na	6	3.810(1)
Ba−D[b]	6	3.03(1)	Ba−Na	6	3.810(1)

[a] Intramolecular distances. [b] In the *ab* plane. [c] In the *c* direction.

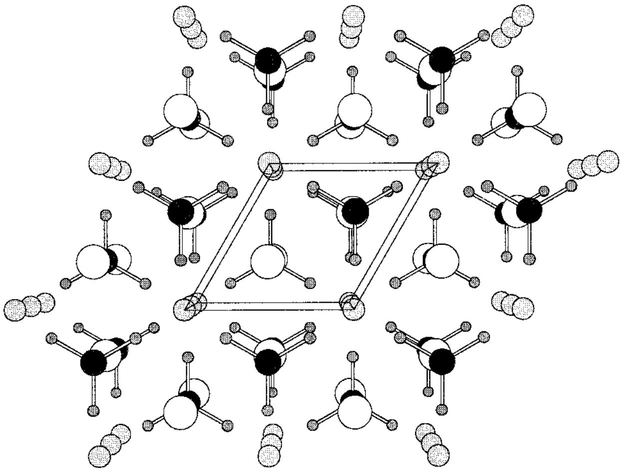

Figure 2. Structure of $NaBaPdH_3$ viewed along the *c* axis. The unit cell is marked with bold lines. The Pd atoms (black circles) are connected to the H atoms (small, gray circles). The PdH_3 units are surrounded by Ba atoms (large, white circles) and Na atoms (light gray circles).

ions (Ca position) (Figure 2). The presence of planar PdH_3 complexes in the *ab* plane elongates the corresponding axes, yielding the low c/a axis ratio of 1.00, compared to $c/a = 1.92$ in CaCuP.

The shorter Pd−D distance of 1.719(8) Å, compared with the Pd−D distance of 2.01 Å in palladium deuteride,[20] supplies a picture of covalently bonded PdH_3 complexes in a framework of Na and Ba ions. Ac magnetic susceptibility measurement on $NaBaPdH_3$ also supports a d^{10} electron configuration on Pd. The Pd−D distances in $NaBaPdD_3$ are however longer than 1.68(1) Å found in the low-melting, metallic Li_2PdD_2 and Na_2PdD_2, both containing formally zerovalent Pd. Furthermore, they are significantly longer than the Pd−D distances of 1.625(8) Å found in K_2PdD_4 and 1.606(3) Å in Na_2PdD_4, containing divalent palladium and a more conventional covalently bonded anionic species with ionic bonding to the cations. A picture thus emerges of the new hydrides, containing electron-dense d^{10} complexes, as interesting systems between the interstitial metallic transition metal hydrides and the more salt-like hydrides, where the electrons are localized in the covalent bonds of the TM complexes.

The bonding situation in $NaBaPdH_3$, with two different cations, seems to be even further complicated. As seen in Figure 2, the sodium atoms form chains within a tunnel of neighboring hydrogen atoms. The sodium−hydrogen distance in the tunnel is short at 2.337(6) Å, compared with 2.440(1) Å in NaH.[21] This indicates a larger degree of interaction between the hydrido ligands and the sodium atoms than in NaH. The sodium−sodium distances in the chain are also rather short at 3.0406(10) Å; depending on the sodium−hydrogen interaction, this may open up possibilities for interesting electron transport phenomena along the chain. The more electropositive Ba atoms are found at a rather long distance, 3.025(11) Å, from the hydrido ligands, indicating a low degree of Ba−D interaction, at least compared to the shortest Ba−D distance of 2.570(11) Å in BaD_2.[22] From this we suggest that barium can be regarded as Ba^{2+} ions in $NaBaPdH_3$, donating the two 6s electrons completely to the complexes, and that sodium atoms are involved in the stabilization of the anionic $[PdH_3]$ complexes by accepting some electron density. A detailed band structure calculation is needed to better describe the bonding situation in this compound.

The ruby-red color of $NaBaPdH_3$ crystals cannot be reconciled with a metallic behavior. But even if $NaBaPdH_3$ is not a metal, we believe that it is not far from being one, and impurity doping can probably make it metallic. The solidified bulk has a metallic luster, similar to that of Na_2PdH_2, and with a conventional multimeter a measurable electric conductivity is found. The ruby-red crystals, obtained after carefully crushing the bulk, are transparent only if they are very thin (<0.01 mm), which is in contrast to the more salt-like K_2PdH_4,[8] which directly forms a yellow-greenish powder upon reaction.

The ability of hydrogen, as a ligand, to stabilize both high ($[ReH_9]^{2-}$)[23] and low ($[PdH_2]^{2-}$) formal oxidation states on the central TM atom is unique. TM−hydrido complexes are often compared with, and often crystallize with the same type of structures as, TM−fluoro and −chloro complexes, in which the halogens are well-known as electron donors stabilizing high formal oxidation states of the TM atoms. On the other hand, formally low oxidation states on the TM atoms are frequently stabilized by electron-withdrawing ligands such as π-acids. Therefore it is interesting to note that hydrogen is found in the latter context in a growing number of compounds. And with palladium, hydrogen even seems to favor the lowest oxidation state.

But as we have pointed out above, the bonding situation in these compounds is not appropriately described by conventional models.

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Supporting Information Available: Text giving experimental powder diffraction details and tables of observed and calculated powder diffraction data and calculated interatomic distances (3 pages). One X-ray crystallographic file, in CIF format, is available on the Internet only. Ordering and access information is given on any current masthead page.

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(20) The Pd−D distance in $PdD_{0.6}$ was estimated as the *a* axis (4.02 Å)/2. See: Worsham, J. E.; Wilkinson, M. K.; Shull, C. G. *J. Phys. Chem. Solids* **1957**, *3*, 303.

(21) The Na−H distance in NaH was estimated as the *a* axis (4.880(1) Å)/2. See: Zintl, E.; Harder, A. *Z. Phys. Chem.* **1931**, *B14*, 265.

(22) Bronger, W.; Chi-Chien, S.; Müller, P. *Z. Anorg. Allg. Chem.* **1987**, 545, 69.

(23) (a) Abrahams, S. C.; Ginsberg, A. P.; Knox, K. *Inorg. Chem.* **1964**, *3*, 558. (b) Stetson, N. T.; Yvon, K.; Fischer, P. *Inorg. Chem.* **1994**, *33*, 4598. (c) Stetson, N. T.; Yvon, K. *J. Alloys Compd.* **1995**, *223*, L4.