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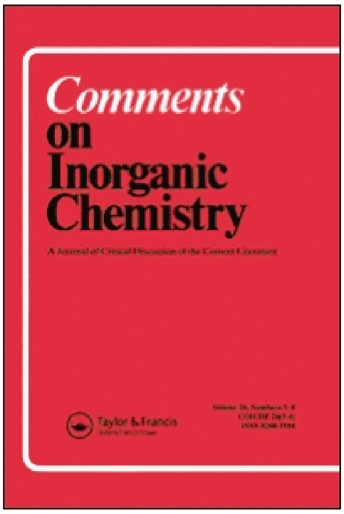

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Complex Transition Metal Hydrides

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Complex Transition Metal Hydrides

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Ternary metal hydrides $A_xM_yH_z$, in which A stands for an electropositive metal and M for a transition metal, can show salt-like or metallic behavior. The former often applies if the atomic arrangement contains complex $[M_yH_z]^{nx-}$ structure units, i.e., if the transfer of *n* electrons from the electropositive partner (A) makes up anionic frameworks. Investigations on the systems A/Pt/H and A/Pd/H with A ≙ Na, K, Rb or Cs show that complex transition metal hydrides $A_x[M_yH_z]$ do exist. Their crystal structures are analogous or related to those of corresponding halogenides. In addition to that, however, high temperature phase transitions are initiated through dynamic behavior of hydrogen ligands in the complex groups. Ternary hydrides with light alkali metals and with alkali earth metals show transitions from salt-like to metallic behavior of these complex compounds.

Key Words: *hydrides, crystal structures, neutron diffraction*

INTRODUCTION

Binary metal hydrides can be divided into three groups: (i) salt-like hydrides, in which electropositive main group metals are combined with hydrogen; (ii) covalent hydrides based on semimetals; (iii) metallic hydrides based on transition metals. There are, how-

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ever, no closely defined borderlines between these categories. Extending this classification to ternary hydrides, among the possible combinations a group of compounds is to be expected in which one metal (A) stems from salt-like, the other (M) from metallic hydrides. Consequently the general composition is expressed by the formula $A_xM_yH_z$. Such hydrides might show metallic or salt-like behavior. Especially the latter is the case when the atomic arrangement contains complex $[M_yH_z]^{nx-}$ units or frameworks, i.e., if according to the Zintl principle a transfer of n electrons from the electropositive partner (A) leads to complex anions. Following the electron configuration of hydrogen structure analogies to corresponding halogen compounds can be expected. These analogies become more prominent with a more electropositive partner (A), i.e., in those compounds, in particular, where A stands for a heavy alkali metal.

Which compounds are known in the field of complex hydrides $A_x[M_yH_z]$? With A $\triangleq$ alkali earth metal a series of compounds could be synthesized, where M is a transition metal of the eighth group.[1–8] Some of these hydrides show metallic behavior. Among those Mg_2NiH_4, with a view to its use as a storage system for hydrogen, was made the subject of intensive studies.[3,9] The crystal structure—there are obviously several phase transitions—is characterized by tetrahedral $[NiH_4]$ units. Other ternary hydrides with metals from the eighth group and alkali earth metals, such as Mg_2FeH_6[1] or Sr_2IrH_5,[7] show transitions to salt-like complex hydrides. Salt-like behavior should become more significant if the alkali earth metal is substituted by a more electropositive alkali metal. Little is known, however, of those ternary hydrides with the exception of K_2ReH_9 and K_2TcH_9.[10] The colorless salt-like compounds contain $[MH_9]^{2-}$ units in which the central atom M is coordinated by the hydrogen atoms forming a threefold capped trigonal prism. The exotic existence of these compounds begs the quest for additional alkali metal transition metal hydrides.

The following comments on complex metal hydrides $A_xM_yH_z$, where A means an alkali metal and M means platinum or palladium, suggest that, considering the possible variations arising from the periodic system, there must be a number of new and interesting hydrides.

TERNARY HYDRIDES $A_xM_yH_z$ WITH A ≙ Na, K, Rb OR Cs AND M ≙ Pt OR Pd—EXAMPLES OF COMPLEX TRANSITION METAL COMPOUNDS

The synthesis of the compounds A_xPtH_z and A_xPdH_z is achieved by the reaction of alkali metal hydrides with the corresponding noble metal in a hydrogen atmosphere:

$$xAH + M + (z - x)/2\ H_2 \rightarrow A_xMH_z$$

Owing to the extreme sensitivity of the hydrides to oxygen and humidity it is necessary to use very pure initial materials and to work in a closed system.[11] The alkali metal hydrides can be synthesized in an autoclave from the distilled metals and hydrogen of high purity taken from a tank filled with $FeTiH_x$.[12] Reactive platinum and palladium can be obtained by the reduction of $(NH_4)_2PtCl_6$ and of $Pd(NH_3)_2Cl_2$ with hydrogen at 200–250°C. The handling of educts and products in a closed system is made possible by manipulators.[11] The reaction temperatures vary from 280 to 400°C. The progress of a reaction can be gauged by the absorption or desorption of hydrogen; it can be used to determine the composition of the resulting compounds.

By this procedure the ternary hydrides were obtained in microcrystalline samples. To determine their crystal structures X-ray and neutron diffraction experiments were carried out, the latter on deuterated samples, thereby precisely ascertaining the positions of the light atoms. The deuterated samples can be synthesized in analogy to the hydrides as described above.

In the system Na/Pt/H a violet-red compound of the composition Na_2PtH_4 could be synthesized.[11] Structure investigations led to a hitherto unknown structure type (space group I4/mmm, $Z = 2$). The atomic arrangement is outlined in Fig. 1. Characteristic structure units are planar $[PtH_4]^{2-}$ groups. This structure is closely related to the K_2PtCl_4-type which is included in Fig. 1 for comparison. The atomic arrangements differ only in that the $[PtX_4]^{2-}$ groups in the K_2PtCl_4-type lie one on the other in the direction of the *c*-axis, whereas in the Na_2PtH_4-type the packing is staggered. The result is a doubling of the *c*-axis in the Na_2PtH_4-type. Cal-

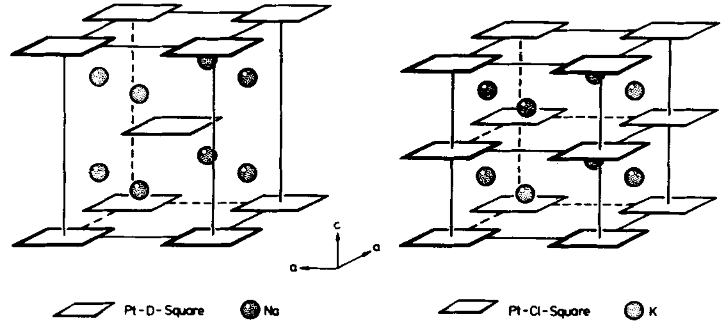

FIGURE 1 The structure of Na_2PtD_4 (left side) and the structure of K_2PtCl_4 (right side).

culations of the electrostatic part of lattice energy show that the Na_2PtH_4-type is favored compared with the K_2PtCl_4-type. An evident explanation for the existence of the K_2PtCl_4-type would be the assumption of an additional energy gain arising from interactions between the d^8-atoms, which are caused by the relatively high electron density above and below the planar $[PtCl_4]^{2-}$units. This favors the positioning of positive ions in the *c*-direction.

According to the differences of the two structure types mentioned above a dynamic behavior of the hydrogen ligands is observed above 300°C. The atomic arrangement in the high temperature form corresponds to the K_2PtCl_6-type with a statistical $2/3$ occupation of the chlorine positions by hydrogen atoms. Figure 2

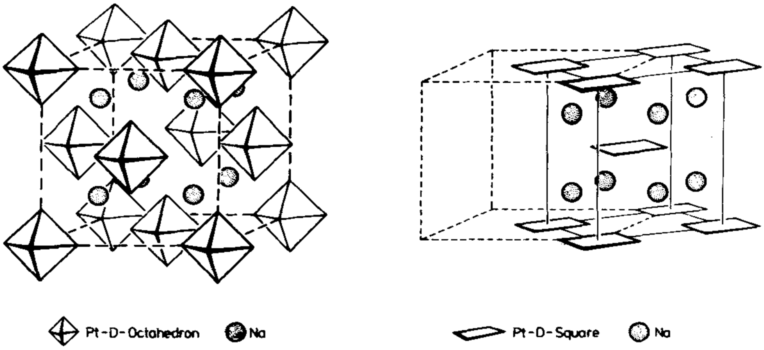

FIGURE 2 Na_2PtD_4, the structure of the low temperature form (right side) and the high temperature form (left side).

shows the correlation of the atomic arrangements in the two Na_2PtH_4-modifications; Fig. 3 shows the change of the lattice constants with temperature.

In the system K/Pt/H a colorless hydride of the composition K_2PtH_4 exists.[13] Its structure shows, even at room temperature, an atomic arrangement corresponding to that of K_2PtCl_6. Neutron diffraction experiments on the deuterated compound K_2PtD_4 made it possible to characterize the atomic arrangement including the ⅔-occupation of the D-positions (24e, space group Fm3m). Measurements of the magnetic susceptibility in the temperature range between 3.7 and 295 K resulted in diamagnetism which points to a planar configuration of the d^8-atoms. The assumption that the

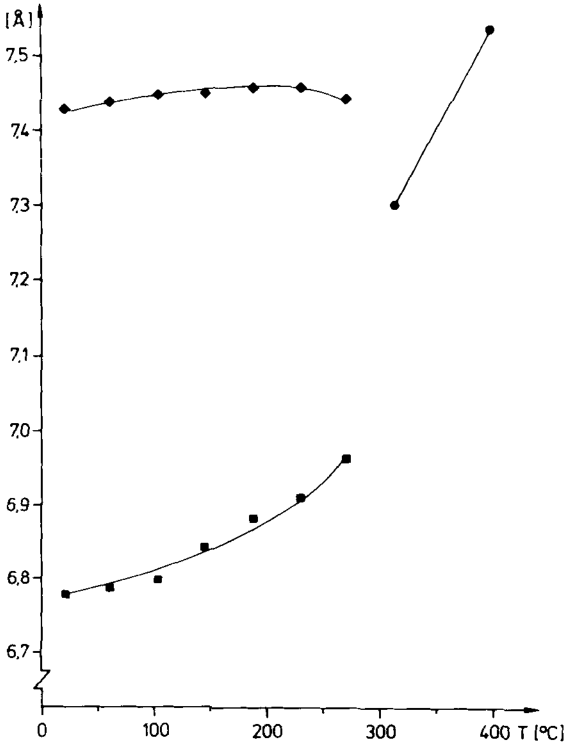

FIGURE 3 Na_2PtD_4, the change of the lattice constants with temperature (LT: ◆ ≙ $a\cdot\sqrt{2}$, ■ ≙ c, HT: ● ≙ a).

statistical distribution of the hydrogen atoms represents a dynamic effect is once again confirmed by a low temperature modification below 195 K (see Fig. 4). Furthermore, at room temperature ^1H-NMR-investigations show a sharp signal which becomes broader at temperatures around 200 K, thereby indicating a restriction of hydrogen movements. The structure of the low temperature modification of K_2PtH_4 indicates a new type in which $[PtH_4]^{2-}$ groups are not arranged in a parallel manner as in the Na_2PtH_4-type, but vertically to (001) of a tetragonal unit cell (see Fig. 4)[14]. The relationships of the above mentioned crystal structures is given in Fig. 5 by means of group–subgroup relations. Rb_2PtH_4 and Cs_2PtH_4, too, crystallize in two modifications with atomic arrangements corresponding to those of K_2PtH_4.[13] Complete structure determinations were achieved through neutron diffraction experiments on the deuterated compounds.

The synthesis of the hydrides A_2PtH_4 with $A \triangleq$ K, Rb or Cs, in each case was started with a surplus of alkali metal hydride. Whereas at temperatures above 350°C the A_2PtH_4-phases were formed, at lower temperatures hydrides of the stoichiometry A_3PtH_5 exist. Its structure is shown in Fig. 6. Investigations led to a tetragonal unit cell (space group P4/mbm, $Z = 2$). The atomic arrangement contains differently bonded hydrogen atoms: On the one hand, here again the characteristic $[PtH_4]^{2-}$ units were found; on the other hand, hydrogen atoms exist which are octahedrally

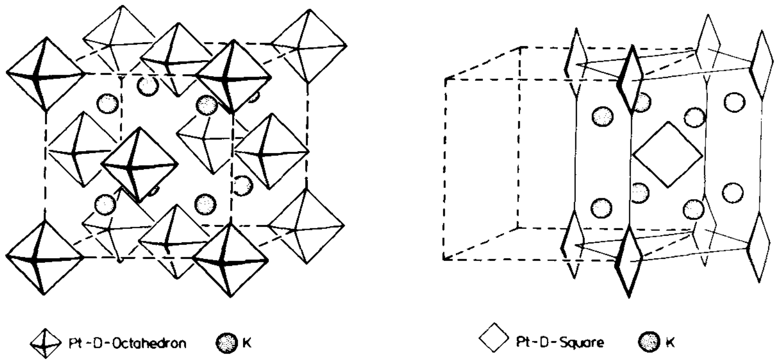

FIGURE 4 K_2PtD_4, the structure of the low temperature form (right side) and the high temperature form (left side).

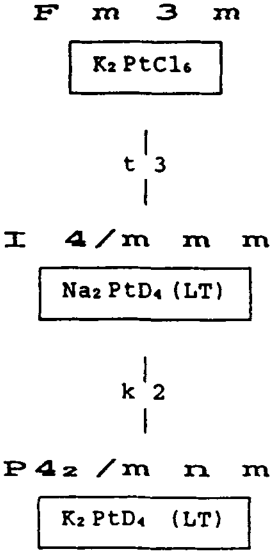

FIGURE 5 Group–subgroup relations (LT ≙ low temperature form).

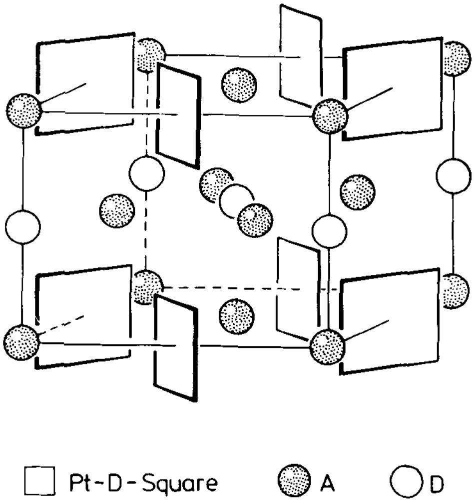

FIGURE 6 A_3PtD_5 (A ≙ K, Rb or Cs), the structure of the low temperature form.

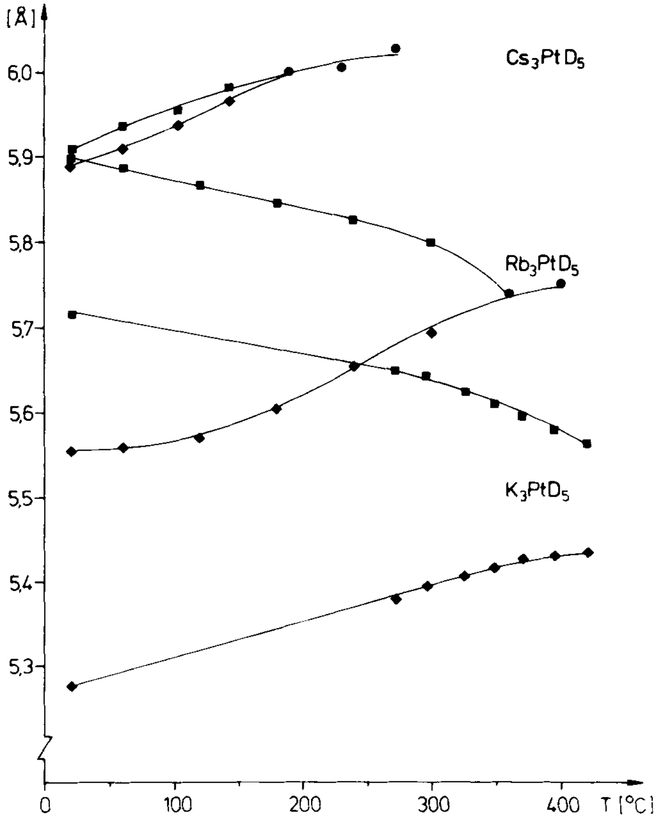

FIGURE 7 A_3PtD_5 (A ≙ K, Rb or Cs), the change of the lattice constants with temperature (LT: ◆ ≙ $a/\sqrt{2}$, ■ ≙ c, HT: ● ≙ a).

surrounded by six alkali metal atoms in the same manner as in the binary alkali metal hydrides.[15] This, too, runs parallel to the structural chemistry of ternary halogenides: Rb_3PdF_5 and Cs_3PdF_5 crystallize in isotypical atomic arrangements.[16] Structural investigations at varying temperatures on the compounds A_3PtH_5 again show the high mobility of the hydrogen atoms. It explains the fact that in the range where A_3PtH_5-phases with A ≙ Rb, Cs are stable the tetragonal structural type at higher temperatures turns into a cubic one before the decomposition according to $A_3PtH_5 \rightarrow A_2PtH_4 + AH$ takes place. The potassium compound also gets close to this phase transition without, however, achieving it (see Fig. 7). Regarding the atomic arrangements the situation can be described as follows: In the tetragonal low temperature structure type the $[PtH_4]^{2-}$ units cause a torsion of the alkali metal octahedra around the fourfold axis parallel to the *c*-axis at an angle of approximately 14° (see Fig. 8, left side). The alkali metal atoms occupy two different crystallographic positions which could be held by two different alkali metals in quaternary hydrides such as K_2RbPtH_5 and K_2CsPtH_5. As evident in the high temperature modification the movements of the hydrogen atoms again result in an octahedral surrounding of the platinum atoms with an occupation factor of ⅔ for the hydrogen atoms; the torsion of the alkali metal octahedra around the fourfold axis is cancelled (see Fig. 8, right side). The result is a cubic symmetry (space group Pm3m). Taking the $[PtH_4]^{2-}$ group as one particle the atomic arrangement corresponds to that of a perowski: $[PtH_4]HA_3$!

In the system Na/Pd/H a hydride of the composition Na_2PdH_2 could be synthesized.[17] The crystal structure is outlined in Fig. 9. Linear $[PdH_2]^{2-}$ dumbbells take the place of anionic units. They, together with the sodium atoms, have the same atomic arrangement as was found in Na_2HgO_2.[18] With the assumption of oxidation number zero for the palladium atoms the analogy with the linear coordinations as often found in complexes with central atoms of

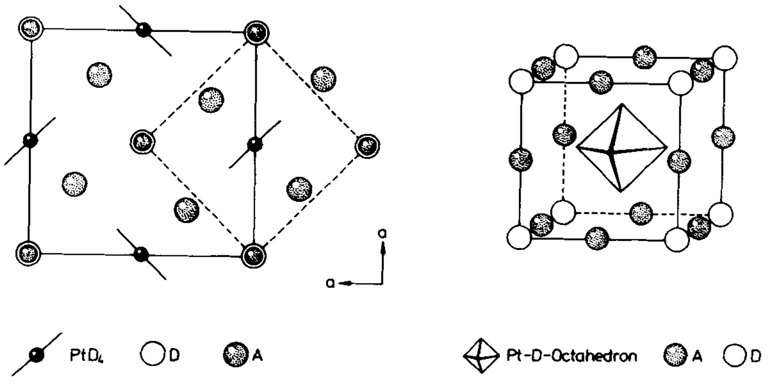

FIGURE 8 A_3PtD_5, the structure of the low temperature form (left side) and the high temperature form (right side).

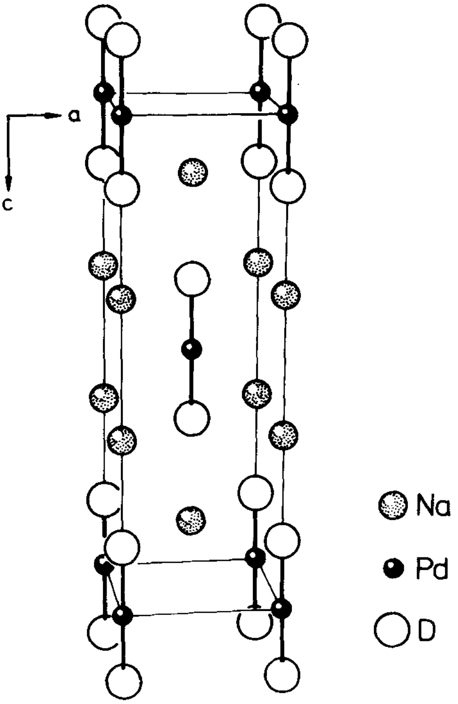

FIGURE 9 The structure of Na_2PdD_2.

a d^{10}-configuration becomes apparent. However, Na_2PdH_2 does show more metallic behavior. But this property can also be put into the present context: In the systems Li/Pt/H and Li/Pd/H the metallic behavior prevails in the hydrides with palladium.[19] Therefore Na_2PtH_4 with its violet-red color should have more ionic properties than Na_2PdH_2 so that more metallic behavior of the latter falls into the pattern. In the systems A/Pd/H with A ≙ K, Rb or Cs again complex compounds with ionic behavior were found. Yellow hydrides of the compositions K_3PdH_5, Rb_3PdH_5 and Cs_3PdH_5 have been synthesized.[20] The crystal structure determinations are in progress.

With other platinum metals, too, corresponding ternary hydrides do exist. Thus with iridium and rhodium, two colorless compounds, K_2IrH_5 and K_2RhH_5, were synthesized,[20] but structure analyses have not been completed.

CONCLUSIONS

Investigations of the systems A/Pt/H and A/Pd/H with A $\triangleq$ Na, K, Rb or Cs have shown that complex transition metal hydrides $A_xM_yH_z$ do exist. Furthermore, it is safe to assume that other compounds $A_xM_yH_z$ will be discovered. The synthesis of pure compounds is not easy, which is the reason why so little is known in this area. The scope of accessible hydrides, however, can surely be expanded if experiments with high hydrogen pressure are included.

The ascertained crystal structures are analogous with or related to those of corresponding halogenides. There are, however, two main differences: (i) additional phase transitions initiated by movements of the hydrogen ligands in the complex groups; (ii) transitions from salt-like to metallic behavior of these complex compounds in the range of the lighter alkali metals as well as the alkali earth metals. Both characteristics attract a great deal of interest and merit further investigations. The key to a deeper understanding is the analysis of the movements of the hydrogen atoms. In this context the complex platinum and palladium hydrides with their simple crystal structures can be considered as suitable model substances for NMR-investigations as well as incoherent neutron diffraction experiments.

This promises to be a fascinating part of inorganic solid state chemistry research that may lead to new and interesting results!

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