



HAL
open science

Ternary Transition Metal Acetylides $A(I)_2M(0)C_2$ ($A(I) = K, Rb; M(0) = Pd, Pt$): Neutron Diffraction Studies and Electronic Properties

Uwe Ruschewitz, Heinrich Billetter, Tim Wallraff, Ronald I. Smith, Ulrich Schwarz

► **To cite this version:**

Uwe Ruschewitz, Heinrich Billetter, Tim Wallraff, Ronald I. Smith, Ulrich Schwarz. Ternary Transition Metal Acetylides $A(I)_2M(0)C_2$ ($A(I) = K, Rb; M(0) = Pd, Pt$): Neutron Diffraction Studies and Electronic Properties. *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2010, 636 (9-10), pp.1834. 10.1002/zaac.201000108 . hal-00599865

HAL Id: hal-00599865

<https://hal.science/hal-00599865>

Submitted on 11 Jun 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Ternary Transition Metal Acetylides $A(I)2M(O)C_2$ ($A(I) = K, Rb$; $M(O) = Pd, Pt$): Neutron Diffraction Studies and Electronic Properties

Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.201000108.R1
Wiley - Manuscript type:	Article
Date Submitted by the Author:	11-Apr-2010
Complete List of Authors:	Ruschewitz, Uwe; Universität zu Köln, Department für Chemie Billetter, Heinrich; Universität zu Köln, Department für Chemie Wallraff, Tim; Universität zu Köln, Department für Chemie Smith, Ronald I.; Harwell Science and Innovation Campus, ISIS Facility, Rutherford Appleton Laboratory Schwarz, Ulrich; Max Planck Institute for Chemical Physics of Solids
Keywords:	Acetylide , Alkali Metal, Neutron Diffraction, Palladium, Platinum



ARTICLE

DOI: 10.1002/zaac.200((will be filled in by the editorial staff))

Ternary Transition Metal Acetylides $A^I_2M^0C_2$ ($A^I = K, Rb$; $M^0 = Pd, Pt$): Neutron Diffraction Studies and Electronic Properties

Heinrich Billetter^[a], Tim Wallraff^[a], Ulrich Schwarz^[b], Ronald I. Smith^[c], and Uwe Ruschewitz^{*[a]}

Dedicated to Prof. Bernd Harbrecht on the Occasion of his 60th birthday.

Keywords: Acetylide; Alkali Metal; Band Structure; Neutron Diffraction; Palladium; Platinum

The crystal structures of K_2PdC_2 , K_2PtC_2 , and Rb_2PdC_2 ($P\bar{3}m1$, $Z = 1$) were refined from time-of-flight powder neutron diffraction data (Polaris, ISIS/RAL) at room temperature and 4.5 K. The resulting C-C distances within the C_2^{2-} anion are in the range 124.4 – 124.7 pm (295 K). This is distinctively longer than the expected distance for a C-C triple bond (120 pm). At low temperatures slightly longer C-C distances are found (125.0 – 126.7 pm), which is due to an increasing wobbling of the C_2 dumbbells around their centre of gravity with increasing temperature. This is also reflected in the temperature dependence of the lattice parameters a and c . Lattice parameter c , which is parallel to the C_2

dumbbell, decreases with increasing temperature, whereas a shows a typical positive thermal expansion. Differing to previous work ternary palladium acetylides A_2PdC_2 were obtained as red ($A = Na$) and yellow powders ($A = K, Rb$) by using a slightly improved synthesis. By means of diffuse reflectivity direct band gaps were determined to 2.09 eV ($A = Na$), 2.55 eV ($A = K$), and 2.77 eV ($A = Rb$). This is in good agreement with direct band gaps obtained from band structure calculations. These band structure calculations indicate very small indirect band gaps of only a few tenth of an eV.

[a] Department of Chemistry, University of Cologne, Greinstraße 6, D-50939 Köln (Germany)
Fax: +49-(0)-221-470-3933
E-mail: Uwe.Ruschewitz@uni-koeln.de

[b] Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Straße 40, D-01187 Dresden (Germany).

[c] ISIS Facility, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, OX11 0QX (UK).

these compounds indicative for a weaker backbonding from the metal M^+ into the antibonding states of the C_2 units. But the different electronic properties of compounds of composition $A_2M^0C_2$ and $AM^I C_2$ despite their similar crystal structures are intriguing and still not fully understood, although some explanations based on band structure calculations have been given [3].

Introduction

In the last decade we have been able to synthesize and characterize numerous ternary alkali metal transition metal acetylides [1]. Na_2PdC_2 and Na_2PtC_2 were the first examples of this new class of compounds [2]. Their crystal structures consist of ${}^\infty[M^0(C_2)_{2/2}^-]$ chains, which are separated by sodium cations. In a more detailed analysis it was shown that the C-C distances are elongated compared to a C-C triple bond [3]. Based on band structure calculations this finding was attributed to a strong backbonding from palladium and platinum into the antibonding states of the C_2 units. This was confirmed by Raman spectroscopic data. Measurements of the electrical conductivity and band structure calculations revealed that these compounds are semiconductors with very small indirect band gaps (approx. 0.2 eV). In these investigations Na_2PdC_2 and Na_2PtC_2 were always obtained as black powders. In subsequent work also the analogous potassium [3], rubidium and cesium compounds [4] were prepared, again as black powders.

${}^\infty[M^0(C_2)_{2/2}^-]$ chains were observed in compounds of composition $AM^I C_2$ ($A = Li-Cs$, $M^I = Cu$ [5], Ag [6], Au [7]). These compounds are insulators and colorless ($M^I = Cu$, Ag) or yellow ($M^I = Au$). Only slightly elongated C-C distances with respect to a C-C triple bond were found in

In the following we will present a detailed structural analysis of some compounds of composition $A_2M^0C_2$ as well as new measurements and calculations of the electronic properties of these compounds. The former have been feasible as by a slightly improved synthesis samples of ternary palladium acetylides A_2PdC_2 have been accessible, which show a red ($A = Na$) and yellow colour ($A = K, Rb$), resp.

Results and Discussion

The crystal structures of K_2PdC_2 , K_2PtC_2 , and Rb_2PdC_2 were refined in space group $P\bar{3}m1$ using time-of-flight powder neutron diffraction data. These refinements confirm the crystal structures already obtained from X-ray powder diffraction data [3, 4]. All compounds crystallize isostructural to Na_2PdC_2 [2]. As an example the crystal structure of K_2PdC_2 is shown in Figure 1. Each Pd atom (d^{10}) is coordinated *end-on* by two C_2 dumbbells, which link two Pd atoms. Thus linear ${}^\infty[Pd(C_2)_{2/2}^-]$ chains are formed, which run parallel to each other along the c axis. These chains are separated by the K^+ cations. Each C_2 dumbbell is coordinated by six K^+ cations that form a distorted octahedral coordination. The K^+ cations are surrounded very asymmetrically by three Pd atoms and three C_2 anions in a more or less *side-on* fashion.

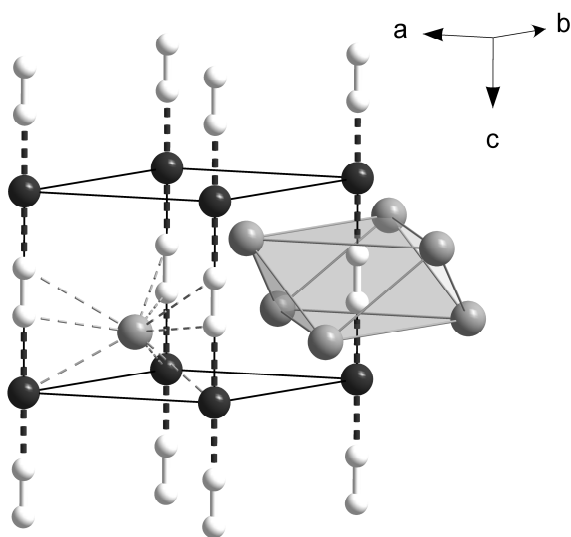


Figure 1. Crystal structure of K_2PdC_2 with K (large grey balls), Pd (large dark balls) and C (small white balls). C-C bonds are drawn as white solid lines, Pd-C (dark), K-C (grey), and K-Pd (grey) contacts are drawn as dotted lines. The K_6 polyhedron around one C_2 unit is emphasized.

Details of the structural investigations on K_2PdC_2 at 295 K and 4.5 K as well as selected distances and angles are given in Table 1. At low temperatures (4.5 K) the C-C distance within the C_2 anion was determined to 125.6 pm, which is distinctly larger than the value expected for a C-C triple bond (120 pm) [8]. This is in agreement with the results obtained for Na_2PdC_2 and Na_2PtC_2 [3]. It was shown that a strong backbonding from Pd/Pt into the antibonding states of the C_2 unit is responsible for these elongated C-C bonds [3]. This is confirmed by the Pd-C distances (201.9 pm at 4.5 K), which are shorter than the values calculated from theoretical radii [8]. Therefore the following mesomeric Lewis structures can be formulated:



K_2PdC_2 is best described by a mixture of both structures, (2) takes the backbonding from palladium into the antibonding orbitals of the C_2 unit into account. The K-C distances are similar to those found in K_2C_2 [9], and the K-Pd distances (328.1 pm) are short, but not unprecedented in the literature (e.g. K_3PdD_3 : K-Pd = 302.6 pm [10]).

Table 1. K_2PdC_2 : summary of neutron powder diffraction investigations (*time-of-flight* method, 3 detector banks, Polaris at ISIS, Rutherford Appleton Laboratory, UK).

	295 K	4.5 K
Space group, Z	$P\bar{3}m1$ (no. 164), 1	$P\bar{3}m1$ (no. 164), 1
a / pm	510.575(4)	507.646(5)
c / pm	528.211(7)	529.392(8)
V / nm ³	0.119249(2)	0.118149(2)
K on 2 d	$z = 0.2788(2)$	$z = 0.2787(2)$
U_{iso} / pm ²	239(3)	31(2)
Pd on 1 a		
U_{iso} / pm ²	143(2)	14(1)
C on 2 c	$z = 0.38207(8)$	$z = 0.38135(7)$
U_{iso} / pm ²	134(1)	25(1)

No. of reflections	601/669/77 ^[a]	598/1403/77 ^[a]
R_{Bragg}	0.129/0.086/0.042 ^[a]	0.030/0.019/0.039 ^[a]
R_p	0.032/0.032/0.034 ^[a]	0.018/0.015/0.017 ^[a]
wR_p	0.029/0.026/0.035 ^[a]	0.012/0.009/0.018 ^[a]
No. of refined parameters	47	47
K – K / pm	376.17(9) 3x	375.23(9) 3x
K – Pd / pm	329.52(5) 3x	328.13(5) 3x
K – C / pm	299.78(2) 3x	298.08(2) 3x
	344.94(6) 3x	343.93(6) 3x
Pd – C / pm	201.81(4) 2x	201.88(4) 2x
C – C / pm	124.58(6)	125.62(5)

[a] Bank 1/Bank 2/Bank 3 (see Experimental Section)

In Table 1 structural parameters obtained at 295 K and 4.5 K are given. Surprisingly, some distances and lattice parameter c increase with decreasing temperature. This is also shown in Figure 2, where the temperature dependence of lattice parameters of K_2PdC_2 is shown, as investigated in the temperature range 295 – 4.5 K. This negative thermal expansion of c is due to the fact that the C_2 dumbbells, which are aligned parallel to c , wobble around their centre of gravity. As this wobbling increases with increasing temperature, c decreases, whereas a increases with increasing temperature. This behavior is also reflected in the C-C and Pd-C distances. The C-C distance obtained at 4.5 K can be assumed as being the “real” distance, whereas at 295 K only a projection of the vibrating C_2 dumbbell is obtained, which necessarily leads to a shorter C-C distance. The same effect can be found – in a less pronounced form – for the Pd-C distance.

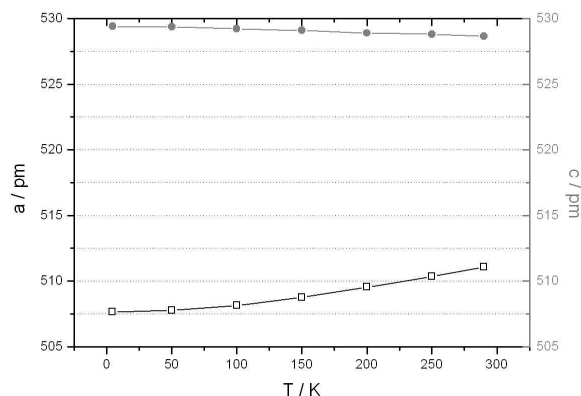


Figure 2. Temperature dependence of lattice parameters of K_2PdC_2 as obtained from neutron powder diffraction data (Polaris, ISIS/RAL): a (empty squares), c (filled circles).

Table 2. K_2PtC_2 : summary of neutron powder diffraction investigations (*time-of-flight* method, 3 detector banks, Polaris at ISIS, Rutherford Appleton Laboratory, UK). The sample contains 27(1) wt. % platinum.

	295 K	4.5 K
Space group, Z	$P\bar{3}m1$ (no. 164), 1	$P\bar{3}m1$ (no. 164), 1
a / pm	512.322(7)	509.41(1)
c / pm	521.81(1)	522.69(2)
V / nm ³	0.118612(3)	0.117467(5)
K on 2 d	$z = 0.2754(5)$	$z = 0.2746(4)$
U_{iso} / pm ²	224(7)	58(5)

1			
2	Pt on 1 a		
3	$U_{\text{iso}} / \text{pm}^2$	119(3)	10(2)
4	C on 2 c	$z = 0.3805(2)$	$z = 0.3804(2)$
5	$U_{\text{iso}} / \text{pm}^2$	120(3)	17(2)
6	No. of reflections	596/1394/76 ^[a]	587/1384/76 ^[a]
7	R_{Bragg}	0.075/0.094/0.056 ^[a]	0.031/0.026/0.086 ^[a]
8	R_{p}	0.033/0.027/0.036 ^[a]	0.015/0.013/0.015 ^[a]
9	wR_{p}	0.027/0.020/0.041 ^[a]	0.010/0.008/0.021 ^[a]
10	No. of refined parameters	59	59
11	K – K / pm	377.4(2) 3x	376.9(2) 3x
12	K – Pt / pm	328.9(1) 3x	327.26(9) 3x
13	K – C / pm	300.83(5) 3x	299.26(4) 3x
14		346.0(2) 3x	345.0(1) 3x
15	Pt – C / pm	198.6(1) 2x	198.8(1) 2x
16	C – C / pm	124.7(2)	125.0(2)
17			

[a] Bank 1/Bank 2/Bank 3 (see Experimental Section)

Structural details of K_2PtC_2 and Rb_2PdC_2 are summarized in Table 2 and 3, resp. Again C-C distances of approx. 125.0 pm and 126.7 pm are found comparable to that of K_2PdC_2 . Similar effects for the temperature dependence of lattice parameters, C-C, and Pd/Pt-C distances are observed for these compounds. It should be mentioned that despite the negative thermal expansion of lattice parameter c the unit cell volume shows the usual positive thermal expansion. The resulting distances are also comparable to those of known compounds (e.g. Rb_2C_2 : Rb-C = 308.6 pm [11]; Rb_3PdD_3 : Rb-Pd = 323.6 pm [12]) so that K_2PtC_2 and Rb_2PdC_2 also fit nicely into the trend of ternary palladium and platinum acetylides.

Comparing some structural features of K_2PdC_2 and K_2PtC_2 it is intriguing that the unit cell volume and lattice parameter c are distinctively smaller in the platinum compound. Furthermore the Pd-C distance is 3 pm longer than the Pt-C distance. All these effects are due to relativistic effects, which should peak at the pair Ag/Au, but are still significant for Pd/Pt [13].

As noted in Table 2 and 3 K_2PtC_2 and Rb_2PdC_2 contain some unreacted Pt and Pd, resp., whereas K_2PdC_2 was obtained as a single-phase product. This result of the refinements is somewhat surprising, as a surplus of the respective alkali metal acetylide was used in all syntheses, which was not detected in the neutron diffraction patterns. K_2PdC_2 and Rb_2PdC_2 were obtained as yellowish powders with no visible amounts of black palladium powder.

Table 3. Rb_2PdC_2 : summary of neutron powder diffraction investigations (*time-of-flight* method, 3 detector banks, Polaris at ISIS, Rutherford Appleton Laboratory, UK). The sample contains 14(1) wt. % palladium.

	295 K	4.5 K
54		
55	Space group, Z	$\text{P}\bar{3}\text{m1}$ (no. 164), 1
56	a / pm	535.675(4)
57	c / pm	528.888(6)
58	V / nm^3	0.131431(2)
59	Rb on 2 d	$z = 0.2786(1)$
60	$U_{\text{iso}} / \text{pm}^2$	232(2)
	Pd on 1 a	
	$U_{\text{iso}} / \text{pm}^2$	141(2)
	C on 2 c	$z = 0.3824(1)$

	$U_{\text{iso}} / \text{pm}^2$	147(1)	30(1)
	No. of reflections	658/1545/80 ^[a]	649/1538/80 ^[a]
	R_{Bragg}	0.089/0.148/0.036 ^[a]	0.022/0.013/0.032 ^[a]
	R_{p}	0.034/0.027/0.030 ^[a]	0.021/0.019/0.020 ^[a]
	wR_{p}	0.024/0.018/0.032 ^[a]	0.013/0.009/0.022 ^[a]
	No. of refined parameters	59	58
	Rb – Rb / pm	387.93(5) 3x	386.27(5) 3x
	Rb – Pd / pm	342.58(2) 3x	341.08(2) 3x
	Rb – C / pm	314.10(1) 3x	311.97(1) 3x
		357.48(4) 3x	356.32(4) 3x
	Pd – C / pm	202.25(5) 2x	201.64(5) 2x
	C – C / pm	124.39(7)	126.65(7)

[a] Bank 1/Bank 2/Bank 3 (see Experimental Section)

Based on the crystal structures obtained at 4.5 K band structures were calculated for K_2PdC_2 , K_2PtC_2 , and Rb_2PdC_2 . They all look similar and are comparable to the one published for Na_2PdC_2 [3]. As an example the band structure obtained for K_2PdC_2 is shown in Figure 3. As a characteristic feature a very small indirect band gap (A-L) of approx. 0.2 eV and a direct band gap (A-A) of more than 2 eV is found. The small indirect band gap is mainly caused by a large dispersion of the conduction band between A and L [3]. The direct band gaps obtained from the band structure calculations of K_2PdC_2 and Rb_2PdC_2 are given in Table 4. They range from 2.30 eV to 2.37 eV and should lead to absorptions in the visible region of the electromagnetic spectrum.

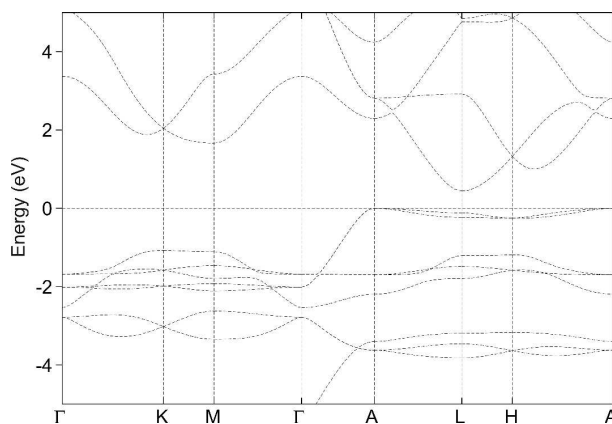


Figure 3. Band structure of K_2PdC_2 . The Fermi level is at $E = 0$ eV, the symmetry points are given in the standard notation for the hexagonal cell.

In order to probe the optical band gap, diffuse reflectivity spectra of several ternary palladium and platinum acetylides were recorded. Meaningful spectra were obtained only for compounds, whose powders show a non-black color (Na_2PdC_2 : red; K_2PdC_2 , Rb_2PdC_2 : yellow). The results are shown in Figure 4. The band gaps were taken as the inflection points of these spectra. They are listed in Table 4. K_2PtC_2 and Cs_2PdC_2 [4] could only be obtained as black powders. Their diffuse reflectivity spectra did not give any significant inflection points to determine the band gaps of these compounds.

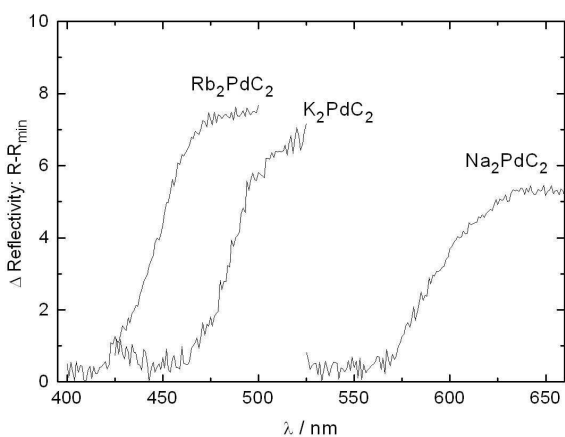


Figure 4. Diffuse reflectivity of Na_2PdC_2 , K_2PdC_2 , and Rb_2PdC_2 depending on the radiation wavelength.

In Table 4 theoretically and experimentally obtained direct band gaps of Na_2PdC_2 , K_2PdC_2 , and Rb_2PdC_2 are summarized. The experimental data fit nicely to the colors of the compounds under investigation. The size of the direct band gaps obtained from band structure calculations is in good agreement with the experimental band gaps. But the trend – increasing band gaps from Na_2PdC_2 to Rb_2PdC_2 – is not reproduced. On the other hand it is surprising at all that such a good agreement between experimental and theoretical band gaps is obtained, as theoretical calculations based on the LMTO method usually tend to underestimate band gaps by up to 50 %.

Table 4. Theoretical and experimental direct band gaps of ternary acetylides $\text{A}'_2\text{Pd}^0\text{C}_2$ ($\text{A}' = \text{Na}, \text{K}, \text{Rb}$) as determined by band structure calculations and measurements of diffuse reflectivity.

	Colour	Experimental direct band gap	Theoretical direct band gap
Na_2PdC_2	Red	$594 \text{ nm} \equiv 2.09 \text{ eV}$	2.78 eV
K_2PdC_2	Yellow	$486 \text{ nm} \equiv 2.55 \text{ eV}$	2.30 eV
Rb_2PdC_2	Yellow	$448 \text{ nm} \equiv 2.77 \text{ eV}$	2.37 eV

Conclusions

Neutron diffraction studies on K_2PdC_2 , K_2PtC_2 , and Rb_2PdC_2 confirm the structural trends found for Na_2PdC_2 and Na_2PtC_2 [3]. C-C bond distances are elongated compared to a C-C triple bond. For Na_2PdC_2 and Na_2PtC_2 it was shown that this is due to a backbonding from the metal (Pd, Pt) into the antibonding states of the C_2 anion [3]. Similar effects must be assumed for the ternary acetylides of the heavier alkali metals.

By a slightly modified synthesis, which mainly consists of a repeated grinding and heating of the resulting samples, ternary palladium acetylides A_2PdC_2 ($\text{A} = \text{Na}, \text{K}, \text{Rb}$) were obtained as colored powders ($\text{A} = \text{Na}$: red; $\text{A} = \text{K}, \text{Rb}$: yellow). Using these samples the direct band gaps could be determined. Na_2PdC_2 and K_2PdC_2 were obtained as samples free of unreacted palladium. Rb_2PdC_2 however contains 14 wt. % palladium. But the amount seems to be small enough so that a determination of the direct band gap was still possible. Despite several attempts to optimize their syntheses Cs_2PdC_2 as well as all ternary alkali metal

platinum acetylides could only be obtained as black powders so that a determination of their optical (direct) band gaps was not possible. From neutron diffraction studies it was determined that the sample of K_2PtC_2 contains 27 wt. % unreacted platinum. It must be assumed that this amount is too high to obtain a colored powder suitable for diffuse reflectivity measurements.

The optical band gap of A_2PdC_2 ($\text{A} = \text{Na}, \text{K}, \text{Rb}$) is shifted from $594 \text{ nm} \equiv 2.09 \text{ eV}$ ($\text{A} = \text{Na}$) to $448 \text{ nm} \equiv 2.77 \text{ eV}$ ($\text{A} = \text{Rb}$). Unfortunately, samples of Cs_2PdC_2 could not be measured, but following the trend a larger band gap can be expected for this compound. One could even think of a “band gap tuning” by using quaternary acetylides with a mixed occupancy of the alkali metal sites. Actually, we have been able to synthesize compounds of composition $\text{AA}'\text{PdC}_2$ ($\text{A}, \text{A}' = \text{alkali metal}$) [14], but up to now all these compounds could only be obtained as black powders. The optimization of their syntheses is part of our current research efforts in this field as well as the synthesis of the “missing” members $\text{Li}_2\text{M}^0\text{C}_2$ ($\text{M}^0 = \text{Pd}, \text{Pt}$). But their synthesis seems to be difficult. It can be speculated that Li_2C_2 , which is the only thermodynamically stable binary alkali metal acetylide [15], is less reactive than the binary acetylides of the heavier alkali metals. Possibly for the same reasons all our attempts to synthesize ternary alkaline earth metal acetylides of composition $\text{A}^{\text{II}}\text{M}^0\text{C}_2$ ($\text{A}^{\text{II}} = \text{Mg} - \text{Ba}$; $\text{M}^0 = \text{Pd}, \text{Pt}$) have also failed up to now. CaC_2 , SrC_2 , and BaC_2 are thermodynamically stable compounds, whereas MgC_2 shows a low thermal stability and decomposes at approx. 770 K [16]. Therefore it seems to be necessary to develop a completely new synthetic strategy for the synthesis of these compounds.

Experimental Section

Synthesis. Na_2PdC_2 , K_2PdC_2 , K_2PtC_2 , and Rb_2PdC_2 were synthesized by reacting the respective alkali metal acetylide in a slight surplus and fine Pd/Pt sponge [17] in an inert Argon atmosphere. Na_2C_2 , K_2C_2 , and Rb_2C_2 were obtained as described in the literature [9, 11]. Prior to the reaction the purity of these alkali metal acetylides was checked by X-ray powder diffraction (Huber G670, $\text{CuK}\alpha_1$ radiation, capillary $\varnothing 0.3 \text{ mm}$).

K_2PdC_2 : In a typical reaction 613 mg (6 mmol) K_2C_2 and 530 mg (5 mmol) Pd powder were mixed, carefully ground and sealed in a glass ampoule in an argon atmosphere (1 bar). The glass ampoule was heated in a furnace at 553 K over night. The resulting powder was ground again and the whole procedure was repeated up to three times, until a yellow powder was obtained.

Na_2PdC_2 , K_2PtC_2 , and Rb_2PdC_2 were obtained in analogous reactions. The resulting samples are red (Na_2PdC_2) and yellow (Rb_2PdC_2), only K_2PtC_2 remained as a black powder after this treatment.

All sample handling was carried out in a glovebox in an argon atmosphere. Sample purity was checked by X-ray powder diffraction (Huber G670, $\text{CuK}\alpha_1$ radiation, capillary $\varnothing 0.3 \text{ mm}$). K_2PtC_2 and Rb_2PdC_2 contain minor amounts of unreacted Pt and Pd, resp. This was confirmed by neutron powder diffraction data (see Table 2 and 3).

Neutron powder diffraction. Time-of-flight neutron powder diffraction data were collected on the Polaris diffractometer [18] at the ISIS spallation source (Rutherford Appleton Laboratory, UK). Approx. 3 g of each sample (K_2PdC_2 , K_2PtC_2 , Rb_2PdC_2) were

loaded into thin-walled cylindrical vanadium sample cans (\varnothing 6 mm, height \approx 50 mm, wall thickness \approx 0.15 mm), which were sealed air-tight with indium wire. All sample handling was carried out in a glovebox (argon atmosphere). For low temperature measurements an AS Scientific "orange" helium cryostat was used, which allowed measurements at temperatures down to 4.5 K. Data collected in three detector banks centred at $2\theta = 90^\circ$ ($d_{\max} = 4.2\text{\AA}$, Bank 1), $2\theta = 145^\circ$ ($d_{\max} = 3.2\text{\AA}$, Bank 2), and $2\theta = 35^\circ$ ($d_{\max} = 8.2\text{\AA}$, Bank 3) were used in structure refinement.

All refinements were carried out with the GSAS suite of programs [19]. Further details of the crystal-structure investigations may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-421489 (K_2PdC_2 , RT), CSD-421490 (K_2PdC_2 , 4.5 K), CSD-421491 (K_2PtC_2 , RT), CSD-421492 (K_2PtC_2 , 4.5 K), CSD-421493 (Rb_2PdC_2 , RT), CSD-421494 (Rb_2PdC_2 , 4.5 K) (<http://www.fiz-karlsruhe.de/>).

Diffuse reflectivity. Optical band gaps were determined from diffuse reflection (Varian Cary 500, white standard BaSO_4 , ratio 10 : 1) under inert conditions at room temperature. The absorption energy was taken as the inflection point of the step-like decrease of the diffuse reflectivity.

Band-structure calculations. For electronic band-structure calculations, the LMTO method [20, 21] within the local density approximation (LDA), taking the von Barth-Hedin approximation, was used [22]. Atomic-sphere radii were chosen by an automated procedure for the TB-LMTO-ASA calculations. Scalar relativistic corrections were included and the calculations were checked for k -point convergence.

Acknowledgments

The help of Dr. Winfried Kockelmann with collecting neutron powder diffraction data is greatly acknowledged.

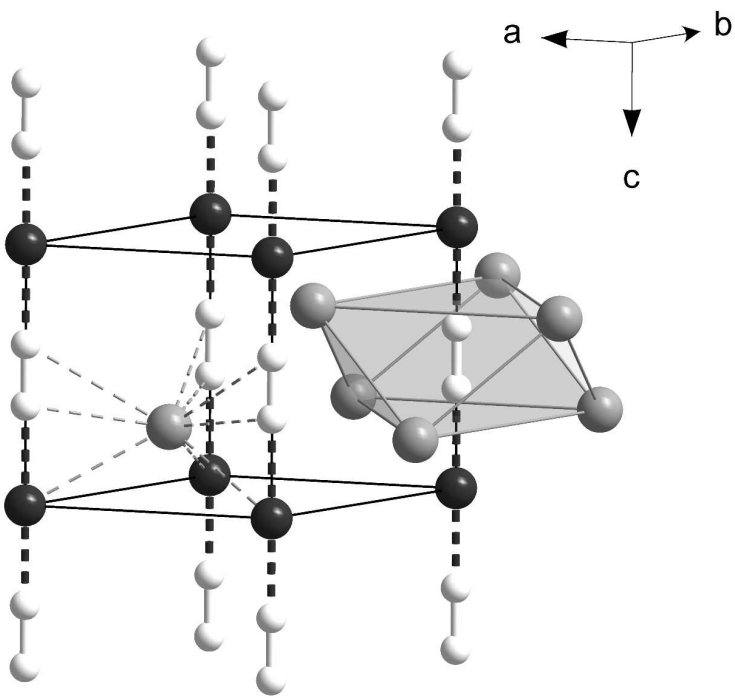
- [1] U. Ruschewitz, *Z. Anorg. Allg. Chem.* **2006**, 632, 705-719.
- [2] M. Weiß, U. Ruschewitz, *Z. Anorg. Allg. Chem.* **1997**, 623, 1208-1210.
- [3] S. Hemmersbach, B. Zibrowius, W. Kockelmann, U. Ruschewitz, *Chem. Eur. J.* **2001**, 7, 1952-1958.
- [4] U. Ruschewitz, *Z. Anorg. Allg. Chem.* **2001**, 627, 1231-1235.
- [5] U. Cremer, W. Kockelmann, M. Bertmer, U. Ruschewitz, *Solid State Sci.* **2002**, 4, 247-253.
- [6] W. Kockelmann, U. Ruschewitz, *Angew. Chem.* **1999**, 111, 3697-3700; *Angew. Chem. Int. Ed.* **1999**, 38, 3492-3495.
- [7] J. Offermanns, U. Ruschewitz, C. Kneip, *Z. Anorg. Allg. Chem.* **2000**, 626, 649-654.
- [8] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**.
- [9] S. Hemmersbach, B. Zibrowius, U. Ruschewitz, *Z. Anorg. Allg. Chem.* **1999**, 625, 1440-1446.
- [10] W. Bronger, G. Auffermann, *J. Less-Common Met.* **1990**, 158, 163-167.
- [11] U. Ruschewitz, P. Müller, W. Kockelmann, *Z. Anorg. Allg. Chem.* **2001**, 627, 513-522.

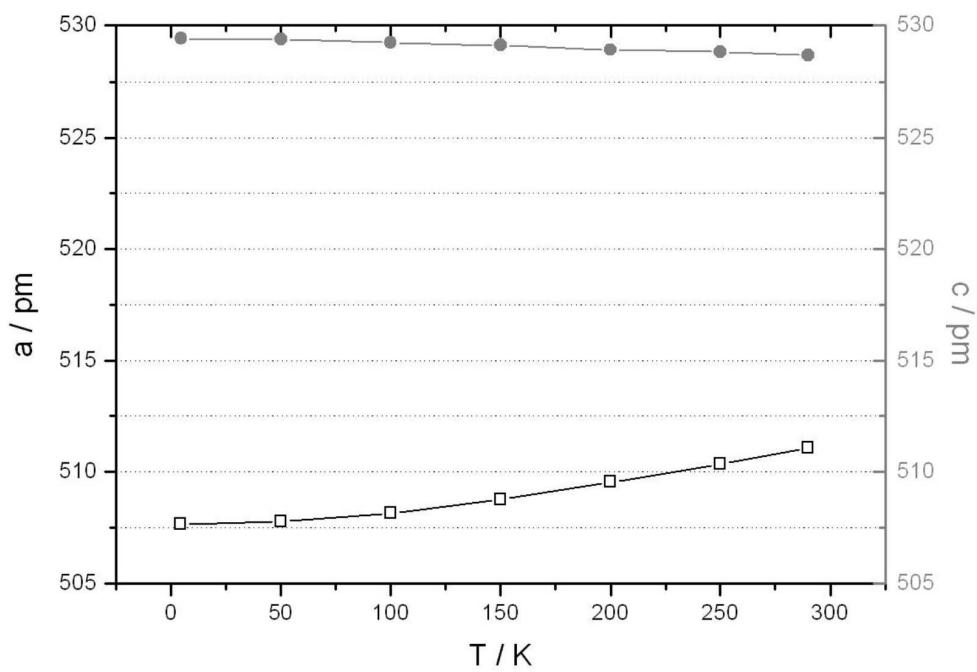
- [12] W. Bronger, G. Auffermann, *J. Alloys Compd.* **1992**, 179, 235-240.
- [13] P. Pyykkö, *Chem. Rev.* **1988**, 88, 563-594.
- [14] H. Billetter, U. Ruschewitz, unpublished results.
- [15] U. Ruschewitz, R. Pöttgen, *Z. Anorg. Allg. Chem.* **1999**, 625, 1599-1603.
- [16] U. Ruschewitz, *Coord. Chem. Rev.* **2003**, 244, 115-136.
- [17] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, 3rd vol., 3rd ed., F. Enke Verlag, Stuttgart, **1981**; differing to the described procedure the final reduction with H_2 was performed at 473 K.
- [18] S. Hull, R. I. Smith, W. I. F. David, A. C. Hannon, J. Mayers, R. Cywinski, *Phys. B* **1992**, 180/181, 1000-1002.
- [19] A. C. Larson, R. B. von Dreele, *Los Alamos Laboratory, Rep. No. LA-UR* **1987**, 86, 748.
- [20] O. K. Andersen, C. Arcangeli, R. W. Tank, T. Saha-Dasgupta, G. Krier, O. Jepsen, I. Dasgupta, *Tight-Binding Approach to Computational Materials Science*, MRS Symposia Proceedings, no. 491, MRS, Pittsburgh, PA, **1998**.
- [21] G. Krier, O. Jepsen, A. Burkhardt, O. K. Andersen, TB-LMTO-ASA program, v. 4.7.
- [22] U. von Barth, L. Hedin, *J. Phys. C* **1972**, 5, 1629-1642.

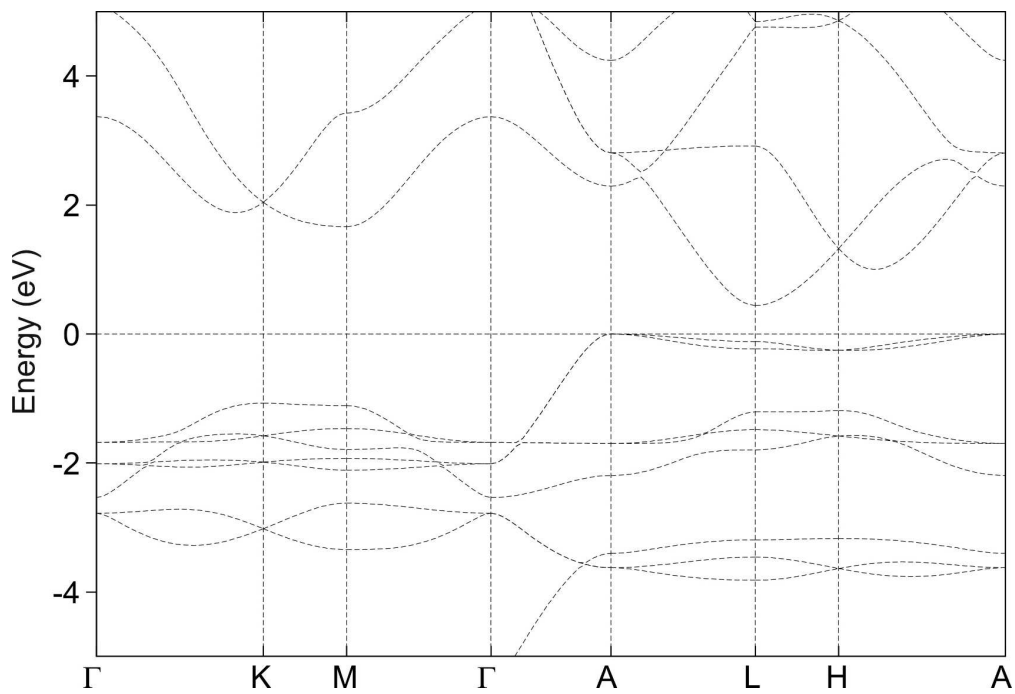
Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60







1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

