The Reduction of Pyridine by $K_{12}Si_{17}$ to the 4,4′-Bipyridine Radical Anion $[C_{10}H_8N_2]^{-\bullet}$: Crystal Structure and Spectroscopic Characterization of $[K([2.2.2]crypt)][C_{10}H_8N_2]$

Christian B. Benda and Thomas F. Fässler
Department Chemie, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

Reprint requests to Prof. Dr. T. F. Fässler. Fax: (+49) 89-289-13186.
E-mail: thomas.faessler@lrz.tum.de

Z. Naturforsch. **2014**, *69b*, 1119 – 1123 / DOI: 10.5560/ZNB.2014-4213
Received September 11, 2014

Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

From an anhydrous pyridine extract of the binary Zintl phase $K_{12}Si_{17}$ in the presence of the cation sequestering agent [2.2.2]crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) crystals of the compound $[K([2.2.2]crypt)][C_{10}H_8N_2]$ have been isolated which contains the 4,4′-bipyridine radical monoanion. This compound was fully characterized by X-ray diffraction, ^1H, ^{13}C NMR, EPR, IR and UV/Vis spectroscopy.

Key words: Organic Radicals, X-Ray Diffraction, NMR, EPR, UV/Vis, IR Spectroscopy

Introduction

There is an increasing interest in the reactivity of soluble polyhedral Zintl ions of the heavier tetrel elements (E) such as E_9 clusters [1, 2] due to their potential for the formation of novel tetrel allotropes based on nine-atom clusters [3]. In the case of $E = Ge$ various oxidation processes have been observed in solution with ethylenediamine as a solvent and in the absence of additional oxidizing agents. Despite the fact that in such solutions Ge_9 dimers $[Ge_9–Ge_9]^{6-}$, oligomers and polymers $[(Ge_9)^{2-}]_n$, $n = 3$, 4, and ∞ are formed, only hinted information on the role of the ethylenediamine as the oxidizing or proton-donating agent is available [4, 5], whereas the sodium and potassium amides of ethylenediamine have been indepently reported [6].

The isolation of compounds containing the nine-atom silicon cluster Si_9 has also been demonstrated using pyridine (py) as a solvent. Hitherto, the following compounds are known which were crystallized from pyridine solutions: $[K([2.2.2]crypt)]_3[Si_9]\cdot(py)_{2.5}$ [7], $[K([2.2.2]crypt)]_3[Si_9Zn(C_6H_5)]\cdot(py)_2$ [8] and $[K([18]crown\text{-}6)]_2[Si_9]\cdot(py)$ [9] ([18]crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane). In all three examples the silicide $K_{12}Si_{17}$ was firstly extracted using liquid ammonia as a solvent, followed by the removal of the solvent and re-dissolving of the residue in pyridine. The formation of these compounds in pyridine as well as the electrochemical investigations of the latter example in py and N,N'-dimethylformamide (dmf) qualified pyridine as a suitable and chemically inert solvent for $[Si_9]^{n-}$ polyanions ($n = 2$, 3). Interestingly the solutions of $A_{12}Si_{17}$ phases in liquid ammonia contain not only $[Si_9]^{4-}$ but also $[Si_4]^{4-}$ clusters, as it has been shown by the isolation of $Rb_4Si_9(NH_3)_5$ and $[Rb([18]crown\text{-}6)]_2Rb_{1.54}K_{0.46}[(MesCu)_2Si_4](NH_3)_{12}$, with the latter containing the MesCu complex $[(MesCu)_2(\eta^3\text{-}Si_4)]^{4-}$ (Mes = 2,4,6-$Me_3C_6H_2$) [10]. Due to their high charges per atom the clusters $[Si_9]^{4-}$ and especially $[Si_4]^{4-}$ are expected to be more reducing than the clusters $[Si_9]^{n-}$ ($n = 2$, 3) which have been isolated from pyridine solutions.

Since the formation of 4,4′-bipyridine radical monoanions in solutions of alkali metals in pyridine is well documented, we investigated the *direct* reaction of $K_{12}Si_{17}$ with pyridine. From the reaction of pyridine with alkali metals it is known that pyridine undergoes a coupling reaction to 4,4′-bipyridine without any observed evolution of hydrogen gas which leads to the radical monoanion [11, 12]. The existence of the 4,4′-bipyridine radical was deductively observed before by a subsequent treatment of the solutions with water or moisture yielding neutral 4,4′-bipyridine and its derivatives [13, 14]. Recently the reduction of 4,4′-bipyridine with sodium metal in ethylenediamine resulted in the isolation of the 4,4′-bipyridine radical anion and the 4,4′-bipyridine dianion (bipy) in the compounds Na(4,4′-bipy)·(en), Na_2(4,4′-bipy)$_2$·(en)$_2$ and Na_2(4,4′-bipy)·(en) [15]. Similarly, the reduction of 2,4′- and 2,2′-bipyridine with potassium and rubidium in ethylenediamine yielded both the bipy radical in the compounds [K(2,2′-bipy)]x·(en)x ($x = 1$ and 4), K(2,4′-bipy)·(en), A_4(2,4′-bipy)$_2$·(en)$_{3.5}$ and Rb_4(2,4′-bipy)$_2$·(en)$_{3.5}$ ($A =$ K, Rb), and the dianion in the compound Rb_2(2,2′-bipy)·(en) [16]. Even though there was no direct evidence, the role of pyridine as the oxidizing agent and the formation of the 4,4′-bipyridine radical anion was also assumed in the rather complex reaction of $[GaBi_3]^{2-}$ to $[Bi_{11}]^{3-}$ in pyridine as a solvent. The presence of 4,4′-bipyridine was evidenced from GC-MS measurements of the residue of the reaction solution. However, a more detailed characterization of the bipyridine was not given [17].

Here we report on the reduction of pyridine with $K_{12}Si_{17}$ as reducing agent. Attempts to extract deltahedral silicion polyanions $[Si_4]^{4-}$ and $[Si_9]^{4-}$ from $K_{12}Si_{17}$ using exclusively pyridine as a solvent led to the isolation of the 4,4′-bipyridine radical monoanions in form of deep-purple crystals of [K([2.2.2]crypt)][$C_{10}H_8N_2$] (**1**) (see Experimental Section). The 4,4′-bipyridine radical monoanion does not coordinate to solvent molecules and due to the presence of the sequestering agent [2.2.2]crypt not to the cations. Therefore **1** represents the first compound with an isolated paramagnetic 4,4′-bipyridine radical.

Results and Discussion

The treatment of the Zintl phase $K_{12}Si_{17}$ with anhydrous pyridine in the presence of [2.2.2]crypt results within a few minutes in a light-brown solution the color of which changes to deep purple within 12 hours at ambient temperature. The color of this solution is typical of paramagnetic bipyridine species [11, 12]. After filtration of the purple solution and layering with toluene deep-purple crystals started to grow at the bottom of the vial.

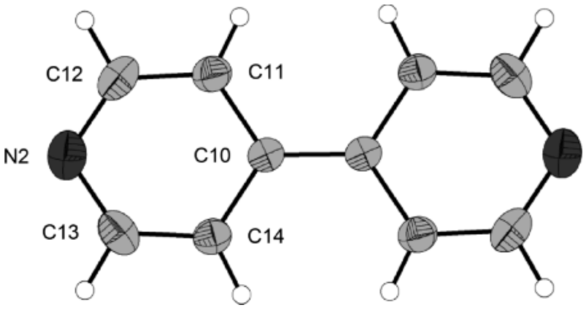

Fig. 1. Molecular structure of the 4,4′-bipyridine radical monoanion $[C_{10}H_8N_2]^{\bullet-}$. C and N atoms are shown as grey and black filled ellipsoids, respectively. Anisotropic displacement ellipsoids of C and N atoms are drawn at the 50 % probability level at 150 K. Selected bond lengths (Å) and angles (deg): C12–N2 1.347(2), C13–N2 1.352(2), C10–C10^{ii} 1.421(3), C10–C11 1.417(2), C10–C14 1.424(2), C11–C12 1.361(2), C13–C14 1.362(2); C12–N2–C13 112.8(2), C11–C10–C14 112.9(1).

A suitable crystal for single-crystal X-ray diffraction revealed the composition [K([2.2.2]crypt)][$C_{10}H_8N_2$] (**1**) containing the 4,4′-bipyridinyl anion (Figs. 1, 2 and Fig. S1, Supporting Information available online; see note at the end of the paper for availability). Due to the positive charge of the sequestered potassium cation one negative charge can be attributed to the bipyridine unit expecting a paramagnetic monoanion.

Compound **1** crystallizes in the monoclinic space group $P2/n$ (no. 13). The unit cell contains two K atoms (Wyckoff site: 2f:2) sequestered by a [2.2.2]crypt molecule and two bipyridine units (see Fig. S1, Supporting Information). Mean C–C and C–N distances in the planar anion range from d(C–C) = 1.361(2) to 1.424(2) Å and d(C–N) = 1.347(2) to 1.352(2) Å and are in agreement with previously reported values [15]. Crystallographic and refinement data are collected in Table 1. Crystals of **1** were further characterized by powder X-ray diffraction at 298(2) K. The obtained pattern matches well with the calculated pattern based on the data set of the single-crystal diffraction experiment at 150 K (see Fig. S2, Supporting Information).

^{1}H NMR measurement of the deep-purple solution of crystals of **1** in deuterated acetonitrile did not show any signal related to the 4,4′-bipyridine unit indicating its paramagnetic nature. Only the resonances at 3.55, 3.51 and 2.52 ppm indicative of [2.2.2]crypt were observed (Fig. S3a). When the solution is ex-

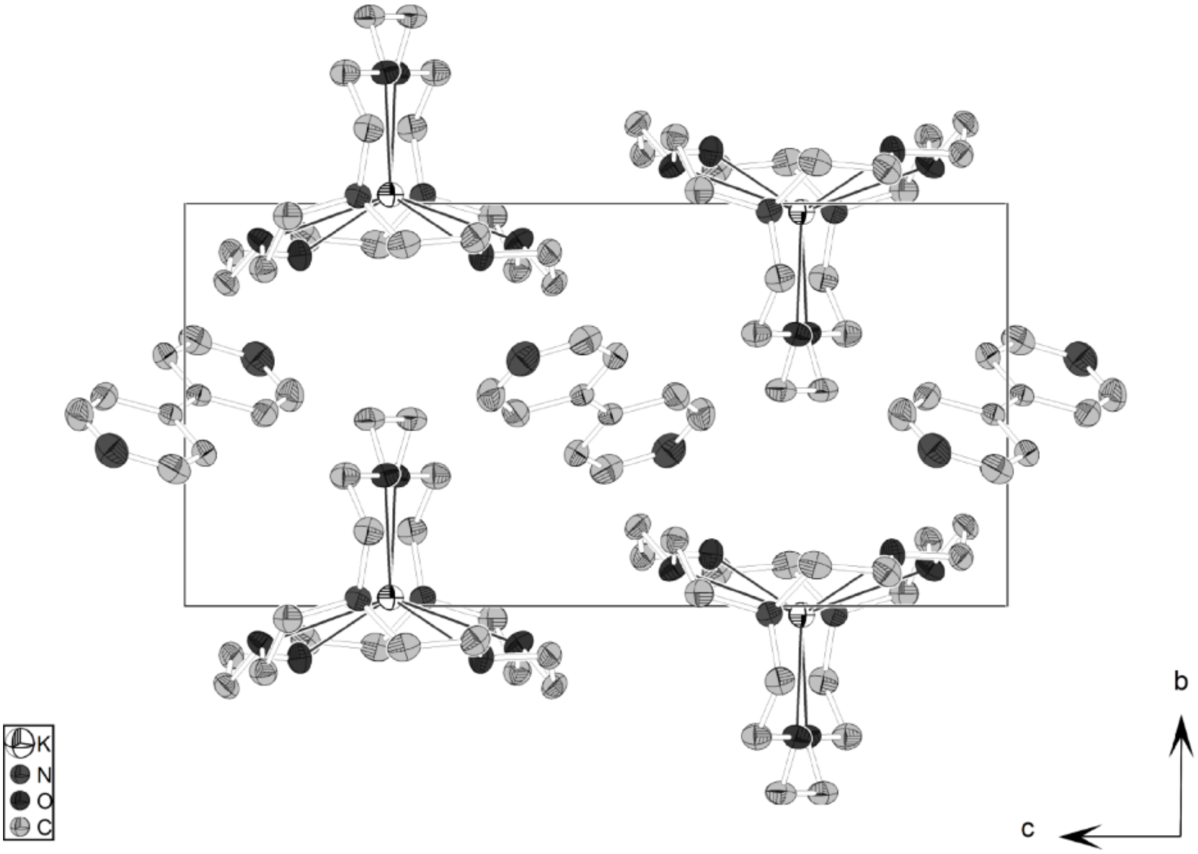

Fig. 2. Unit cell of compound **1** viewed along the crystallographic *c* axis. C, O and N atoms are shown as grey, dark grey and black filled ellipsoids, respectively.

posed to air its color turns first to light brown and then to almost colorless after a few seconds. This colorless solution shows two additional signals in the ^{1}H NMR spectrum (doublet of doublet, coupling constants: 1.6 and 4.5 Hz) in the region of aromatic protons at 8.70 and 7.67 ppm confirming the presence of the 4,4′-bipyridine unit (Fig. S3b, Supporting Information). From this observation we conclude that the paramagnetic radical anion becomes oxidized by oxygen or moisture to the neutral and diamagnetic 4,4′-bipyridine which is detectable *via* ^{1}H NMR spectroscopy. ^{13}C NMR spectral data are also available (see Fig. S4, Supporting Information).

The paramagnetic nature of compound **1** was confirmed by EPR spectroscopy (Fig. S5, Supporting Information). Measurements were obtained both from a well ground mixture of single crystals of compound **1** and diamond powder, and from a solution of compound **1** in ethylenediamine at 286(2) K. The *g* factor was determined to $g = 1.95069$ relative to an Mn standard which is comparable with the *g* factor obtained for Na(4,4′-bipy)·(en) of 2.00429 [15]. The coupling pattern and constants of the EPR spectrum of compound **1** (Fig. S5) match very well with the reported ones [8, 18], and the UV/Vis and IR spectra are also in accordance with those reported previously (see Figs. S6/7, Supporting Information).

Conclusion

Our investigations have shown that pyridine is reduced by $K_{12}Si_{17}$. It is not clear yet whether the clusters dissolve without decomposition in pyridine and whether $K_{12}Si_{17}$ similar to the alkali metals gives rise to solvated electrons upon dissolution, or whether the

Table 1. Selected crystallographic and refinement data for compound $[K([2.2.2]crypt)][C_{10}H_8N_2]$ (**1**).

Compound	**1**
Empirical formula	$C_{28}H_{44}KN_4O_6$
Formula weight, g mol^{-1}	571.77
Temperature, K	150(2)
Crystal size, mm^3	$0.18 \times 0.18 \times 0.02$
Crystal system	monoclinic
Space group	$P2/n$
Unit cell dimensions	
a, Å	11.2185(6)
b, Å	8.0351(4)
c, Å	16.4222(9)
β, deg	91.868(5)
Volume, Å^3; Z	1479.54(14); 2
Calculated density, g cm^{-3}	1.28
Absorption coefficient, mm^{-1}	0.2
$F(000)$, e	614
Θ range, deg	2.82–26.99
Measured reflections	18862
Independent reflections / R_{int}	3228 / 0.0596
Completeness, %	99.9
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3228 / 0 / 266
Goodness-of-fit on F^2	0.789
R-indices R_1 / wR_2 [$I > 2\sigma(I)$]	0.0340 / 0.0487
R-indices R_1 / wR_2 (all data)	0.0755 / 0.0535
Largest diff. peak and hole, e Å^{-3}	0.21 / −0.23

reduction of pyridine takes place at the surface in a topotactic reaction.

Although pyridine is a useful solvent for dissolving the residues of the reactions of the Zintl phase $K_{12}Si_{17}$ in liquid ammonia, it cannot be recommend as a solvent for the pure phase, since in this case $K_{12}Si_{17}$ acts as reducing agent. The clusters $[Si_4]^{4-}$ or $[Si_9]^{4-}$ are oxidized and pyridine gets coupled to give bipyridine and subsequently is reduced to its radical anion which could be trapped in compound **1**.

Experimental Section

General procedures

All manipulations were carried out under argon atmosphere using standard Schlenk and glove box techniques. [2.2.2]Crypt was dried *in vacuo*. Pyridine was dried over calcium hydride and stored over molecular sieve in an argon-filled glove box. Toluene was purchased from an MBraun solvent purification system. $K_{12}Si_{17}$ was prepared from stoichiometric mixtures of 469 mg (12 mmol) K, 477 mg (17 mmol) Si sealed in a tantalum container, which was encapsulated in an evacuated fused silica tube and heated to 900 °C (2 °C min^{-1}) for 1 h and slowly cooled to room temperature with a rate of 0.1 °C min^{-1}.

$[K([2.2.2]crypt)][C_{10}H_8N_2]$ (1)

$K_{12}Si_{17}$ (60 mg; 0.063 mmol based on Si_9) and [2.2.2]crypt (100 mg; 0.27 mmol) were weighted into a Schlenk tube and dissolved in 1.5 mL of anhydrous pyridine (19 mmol). The resulting deep-purple solution was filtered and layered with 3.5 mL toluene. This solution was kept at −30 °C. Compound **1** crystallized as deep-purple/black plates and was isolated after 12 months with a yield of 15 mg.

Single-crystal structure determination

The very air- and moisture-sensitive crystals of **1** were transferred from the mother liquor into perfluoropolyalkyl ether oil inside a glove box. A single crystals was fixed on a glass capillary and positioned in a 150 K cold N_2 stream. Data collection at 150(2) K: Oxford-Diffraction Xcalibur3 diffractometer (MoK_α radiation). The structure was solved by Direct Methods and refined by full-matrix least-squares calculations against F^2 (SHELXL-97) [19, 20].

CCDC 1015641 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Powder X-ray diffraction

Phase analyses of $K_{12}Si_{17}$ and compound **1** were performed using a Stoe STADI P diffractometer (Ge(111) monochromator; Cu$K_{\alpha1}$ radiation) equipped with a linear position-sensitive detector (Mythen). For sample preparation the products were finely ground in an agate mortar and filled into sealed glass capillaries. Diamond was used as an internal standard. The samples were measured in Debye-Scherrer mode. Data analysis was carried out using the Stoe WINXPOW software package [21].

NMR spectroscopy

Approximately 2 mg of crystals of compound **1** were collected inside a glove box and transferred into a J. Young NMR tube and dissolved in 0.4 mL deuterated acetonitrile (99.5 %, Merck, stored over activated molecular sieve). NMR data were recorded with a Bruker Ultrashield400 spectrometer and a Bruker Avance-III 400 FT-system (400 MHz, 298(2) K).

EPR spectroscopy

Crystals of **1** (approx. 0.5 mg) were dissolved in dried ethylenediamine (200 μL) and transferred into a glass capillary (inner diameter: 0.5 mm, length: 30 mm), sealed with wax and inserted into a common silica EPR tube (sealed with a cap and Parafilm®). EPR spectroscopic investigations were carried out at ambient temperature using a Jeol JES-FA 200 spectrometer at X-band frequency ($\nu \sim 9.07$ GHz, field center: 324 mT, field width: 5 mT, modulation frequency: 100 kHz, modulation width: 0.01 mT, power: 4.5 mW). g values were calculated in relation to signals of an Mn standard.

IR spectroscopy

Due to the high oxygen sensitivity of compound **1** 50 mg of anhydrous KBr was pressed to a disc at 5 tons for 30 seconds inside a glove box. A mixture of 100 mg anhydrous KBr and a few crystals of **1** were ground in an agate mortar. The resulting light-blue powder was layered onto the ground KBr disc and pressed at 5 tons for 30 seconds. Finally, 50 mg of pure KBr was added and pressed at 10 tons for 30 min. The spectrum was recorded at 298(2) K with an FT-IR Varian Spectrometer.

UV/Vis spectroscopy

One crystal of compound **1** was dissolved in approximately 0.5 mL of anhydrous acetonitrile in a Schlenk tube attached to a silica cuvette (QS). The spectrum was recorded at 298(2) K with a Jasco V-550 spectrophotometer.

Supporting information

The Supporting Information includes an ORTEP representation of the asymmetric unit of $[K([2.2.2]crypt)][C_{10}H_8N_2]$ (**1**) (Fig. S1); the experimental and calculated powder X-ray patterns for compound **1** (Fig. S2); the ^{1}H and ^{13}C NMR data of the oxidized compound **1′** (Figs. S3/4, Table S1); the EPR spectrum (Fig. S5), and the IR and UV/Vis spectra of **1** (Figs. S6/7). Tables S2–S4 summarize atom coordinates, atomic displacement parameters and bond lengths and angles (12 pages, available online, DOI: 10.5560/ZNB.2014-4213).

Acknowledgement

We thank Oliver Dachwald and Prof. Klaus Köhler for the EPR measurements.

---

[1] S. Scharfe, F. Kraus, S. Stegmaier, A. Schier, T. F. Fässler, *Angew. Chem. Int. Ed.* **2011**, *50*, 3630 – 3754.

[2] T. F. Fässler, *Structure and Bonding*, Vol. 140, Springer-Verlag, Heidelberg **2011**.

[3] A. J. Karttunen, T. F. Fässler, M. Linnolahti, T. A. Pakkanen, *Chem. Phys. Chem.* **2010**, *11*, 1944 – 1950.

[4] M. W. Hull, S. C. Sevov, *J. Am. Chem. Soc.* **2009**, *131*, 9026 – 9037.

[5] We reported about the protonation of $Zn(C_5Me_5)_2$ to C_5Me_5H in ethylenediamine as evidenced by ^{1}H NMR spectroscopic investigations. See Supporting Information in: C. B. Benda, R. Schäper, S. Schulz, T. F. Fässler, *Eur. J. Inorg. Chem.* **2013**, 5964 – 5968.

[6] W. R. Heumann, A. Bouchard, L. Šafarík, *Can. J. Chem.* **1969**, *47*, 3509 – 3513.

[7] J. M. Goicoechea, S. C. Sevov, *J. Am. Chem. Soc.* **2004**, *126*, 6860 – 6861.

[8] J. M. Goicoechea, S. C. Sevov, *Organometallics* **2006**, *25*, 4530 – 4536.

[9] J. M. Goicoechea, S. C. Sevov, *Inorg. Chem.* **2005**, *44*, 2654 – 2658.

[10] M. Waibel, F. Kraus, S. Scharfe, B. Wahl, T. F. Fässler, *Angew. Chem. Int. Ed.* **2010**, *49*, 6611 – 6615.

[11] R. L. Ward, *J. Am. Chem. Soc.* **1961**, *83*, 3623 – 3626.

[12] C. D. Schmulbach, C. C. Hinckley, D. Wasmund, *J. Am. Chem. Soc.* **1968**, *90*, 6600 – 6602.

[13] H. Weidel, M. Russo, *Monatsh. Chem.* **1882**, *3*, 850 – 885.

[14] C. R. Smith, *J. Am. Chem. Soc.* **1924**, *46*, 414 – 419.

[15] M. S. Denning, M. Irwin, J. M. Goicoechea, *Inorg. Chem.* **2008**, *47*, 6118 – 6120.

[16] E. Gore-Randall, M. Irwin, M. S. Denning, J. M. Goicoechea, *Inorg. Chem.* **2009**, *48*, 8304 – 8316.

[17] B. Weinert, A. R. Eulenstein, R. Ababei, S. Dehnen, *Angew. Chem. Int. Ed.* **2014**, *53*, 4704 – 4708.

[18] A. Carrington, J. d. Santos-Veiga, *Mol. Phys.* **1962**, *5*, 21 – 29.

[19] SHELXTL, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **1998**.

[20] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.

[21] WINXPOW (version 2.08), Stoe & Cie GmbH, Darmstadt (Germany) **2003**.