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[20] According to this charge distribution, one would expect the shortest distances to be found between the Na and Sn3 atoms. A shortening of the Na–Sn3 distances would result in lengthening of the Na–Sn1 distances;[4] these are already relatively long (3.625 Å), even for four-coordinate tin atoms.

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Small Potassium Clusters**

Andreas Kornath*, Ralf Ludwig, and Anja Zoermer

The investigation of ligand-free atomic clusters presents an ideal opportunity for studying the transition from a single atom to a macroscopic particle. Moreover, the basic properties of small metallic clusters are believed to be an important link in the understanding of the fundamental mechanisms of catalysis and numerous chemical transformations.[1] Despite considerable recent effort, the structures of small atomic metal clusters remain largely unknown.[2, 3] This attests to the intrinsic difficulties associated with experimental work in this field. Even the generation and isolation of the smallest species requires an extensive experimental setup.[4] On the other hand, the number of theoretical calculations and predictions has increased explosively during this decade due to the increasing computer capacity available. Alkali metal clusters are one of the main subjects for theoretical work, but even the diatomic species have yet to be isolated experimentally.

A simplified method for the generation of diatomic potassium molecules was developed during experiments for the simulation of stratospheric phenomena. The apparatus consists of a regular low-pressure plasma tube which is connected to a cryostat with a copper cold surface (15 K).[5] The metal sample is sputtered by a microwave-induced low-pressure krypton plasma, and the material stream is frozen immediately on the cold surface. After one hour of deposition time, a blue layer of solid krypton and potassium molecules was formed. Figure 1 shows the Raman spectrum of the krypton matrix with diatomic potassium molecules. The fundamental frequency of 91.0 cm^{-1} is in excellent agreement with the value obtained from gas-phase experiments (92.0 cm^{-1}), and from density functional theory (DFT) calculations (see Table 1).[6] The surprising result of the microwave sputtering experiment is the efficient formation of the diatomic species. Thermal evaporation under similar conditions (ca. 80 °C) would yield more than 99 % potassium atoms.[7] This was verified by thermal evaporation experiments which yielded red matrices of potassium atoms without any detectable molecular species. These experiments also confirm that the blue color of the krypton matrix is due to the

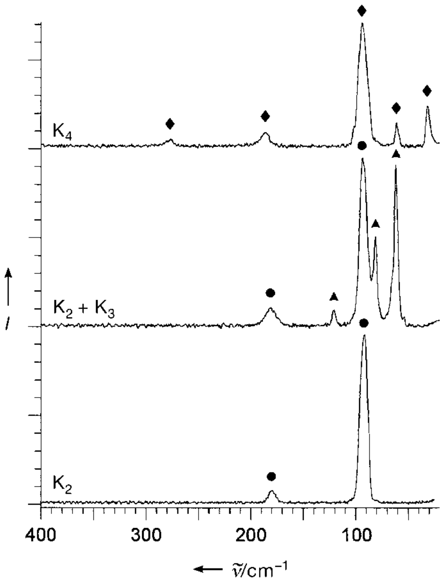

Figure 1. Raman matrix spectra of K_2, K_4, and a mixture of K_2 and K_3 in krypton at 15 K (experimental conditions: 100 µm layer, laser wavelength 514.5 nm, laser power 125 mW, resolution 0.6 cm^{-1}). I = intensity. ●: lines from K_2, ▲: from K_3, ◆: from K_4.

Table 1. Experimental and calculated (DFT) Raman frequencies [cm^{-1}], and vibration modes for K_2, K_3, and K_4.

K_n	DFT[a]	Exp.	Assignment	
K_2	90.0	91.0	ν (K_2)	Σ_g
		181.5	2ν (K_2)	Σ_g
K_3	57.2	(61.0)	δ (K_3)	A_1
	58.9	61.0	δ (K_3)	B_2
	83.0	81.5	ν (K_3)	A_1
		120.0	2δ (K_3)	A_1
K_4	31.2	30.0	δ (K_4)	A_g
	60.0	61.5	δ (K_4)	B_{3g}
	92.4	93.0	ν (K_4)	A_g
		185.0	2ν (K_4)	A_g
		276.0	3ν (K_4)	A_g

[a] DFT calculations with the Slater exchange function and the local spin density correlation function of Vosko, Wilk, and Nusair (SVWN5)[10] and the basis set LANL2DZ[11] performed with the Gaussian 94 package.[16]

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[*] Dr. A. Kornath, Dr. R. Ludwig, Dipl.-Chem. A. Zoermer
Anorganische Chemie, Fachbereich Chemie der Universität
Otto-Hahn-Strasse 6, D-44221 Dortmund (Germany)
Fax: (+49) 231-755-3797
E-mail: kornath@citrin.chemie.uni-dortmund.de

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diatomic potassium, and does not result from solvated electrons, as observed in solutions of alkali metals in aprotic solvents.

The blue color of the potassium molecules is the first visible difference in the transition from potassium atoms to metallic material. Investigation of diffusion-controlled clustering processes,[8] which occur during warm-up cycles of the krypton layers above their diffusion temperature, revealed that two relatively stable clusters exist. The first one is the diatomic potassium cluster, which reacts relatively slowly to form the second stable species, a tetraatomic potassium cluster (Figure 1). Further annealing results in spontaneous deposition of silvery metallic potassium. To obtain the elusive triatomic species, which has already been detected by ESR spectroscopy,[9] a mixture of mono- and diatomic potassium was prepared and annealed. During the clustering process, we first observed an increase in the intensity of the K_2 lines in the Raman spectra and the appearance of three additional lines (Figure 1), which we assigned to the trimer. Two of these lines disappeared completely (the third line overlaps with a line from K_4 cluster) after further warm-up cycles. The final Raman spectrum shows only lines for the K_4 cluster, and there are no indications for larger clusters.

The vibrational data provide a reliable way to determine the cluster geometry from quantum mechanical calculations. To choose the appropriate theoretical method for the clusters, we compared results from Hartree–Fock (HF), Moeller–Plesset (MP2), and two DFT calculations (B3LYP and SVWN5) with different basis sets for alkali metal dimers. The HF and MP2 calculations yielded frequencies which deviated widely (up to 10%) from the experimental gas-phase data. Finally, the SVWN5 method, with the LANL2DZ basis set augmented with polarization and diffuse functions, produced data with deviations of less than 1–2% from the experimental values.[10, 11] The careful choice of a theoretical method at this stage is of great importance, since the discrepancies are carried over to the larger clusters and can lead to somewhat erratic results, as discussed in the literature.[12] The observed frequencies and the symmetry (derived from spectroscopic selection rules) of the clusters agree well with the calculated data summarized in Table 1 (Figure 2).

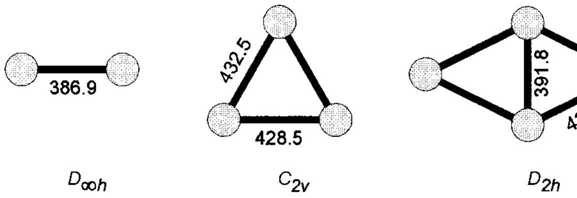

Figure 2. Symmetry and bond lengths of K_2, K_3, and K_4.

The vibrational frequency and the bond length of K_2 (386.9 pm), which is 15% shorter than the atomic distance in the body-centered cubic lattice of potassium (454.4 pm),[13] indicates the presence of a single σ bond. Therefore the nature of the bonding in dipotassium should be similar to that of diatomic nonmetal molecules. This is to be expected based on classical valence bond theory (overlap of two 4s orbitals), but earlier theoretical investigations have predicted that this kind of bonding would be influenced by the core electrons.[14] A comparison of the results from different theoretical methods enabled us to confirm earlier predictions that core electron polarization (CVP) causes additional contraction of the single bond (Figure 3).[14] The contribution of this effect to a classical single bond is already in the range of 8% for diatomic potassium, and it persists for the K_3 and K_4 clusters. Therefore, the tri- and tetraatomic potassium clusters do exist, in contrast to predictions made on the basis of valence-only (without CVP) calculations.[15] When all the experimental observations and theoretical calculations are summarized, it appears at this stage, that bond strengthening due to CVP plays a significant role in the formation of clusters.

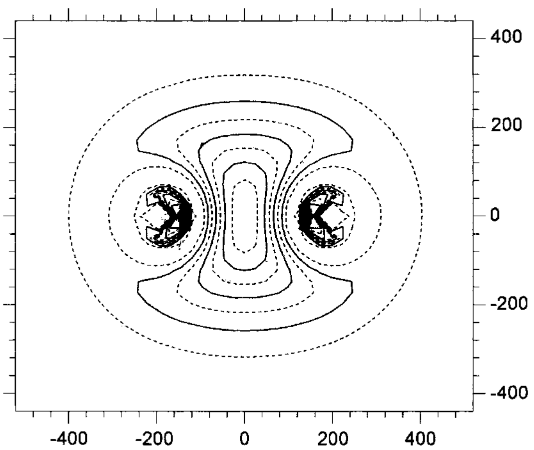

Figure 3. Contour-line diagram of the electron density $\rho(r)$ of K_2 in the ground state ($^1\Sigma_g^+$). Scale in pm.

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The First Specific Ti^{IV}–Protein Complex: Potential Relevance to Anticancer Activity of Titanocenes**

Hongzhe Sun, Hongyan Li, Richard A. Weir, and
Peter J. Sadler*

Biological interest in titanium complexes arises from current clinical trials of two anticancer agents $[Ti^{IV}(bzac)_2(OEt)_2]$ (Hbzac = 1,3-diphenyl-1,3-propanedione) and $[Ti^{IV}Cp_2Cl_2]$,[1, 2] and the potential radiopharmaceutical use of compounds containing ^{45}Ti isotopes.[3] Moreover, since enormous amounts of titanium occur in a wide variety of materials, especially TiO_2, there are abundant opportunities for Ti ions to enter into biochemical pathways in living systems. However, very little is known about the biological chemistry of Ti compounds. There appear to be no reports of specific binding of Ti ions to proteins, and the mode of action of Ti anticancer complexes is poorly understood. We chose to study the binding of Ti^{IV} ions to the blood plasma protein transferrin since this protein has been implicated in the transport and delivery of metal ions such as Ga^{III} (as ^{67}Ga) and Ru^{III} to cancer cells.[4, 5] We show here that Ti^{IV} forms a strong complex with human serum transferrin (hTF) by binding to the specific Fe^{III} binding sites in this protein. This appears to be the first characterization of a specific Ti–protein complex, one which may play a role in the mechanism of action of the titanium anticancer drugs.

Our initial experiments focussed on the reaction of titanium(IV) citrate[6] with human serum apotransferrin.[7] When titanium(IV) citrate was added to an aqueous solution of apo-transferrin (apo-hTF), three new bands gradually appeared in the UV difference spectrum and increased in intensity over a period of 12 h, Figure 1. The wavelengths of the two sharp bands at 241 and 295 nm are typical of phenolate groups generated by the binding of metal ions to Tyr residues (Tyr 95 and Tyr 188 in the N-lobe, Tyr 426 and Tyr 517 in the C-lobe) in the specific iron binding sites.[8] The third, broader band at 315 nm ($\Delta\varepsilon = 4700 \pm 300\,\text{M}^{-1}\text{cm}^{-1}$) is likely to be a ligand-to-metal charge-transfer (LMCT) band. However, we could find no reports of such LMCT bands for titanium(IV) phenolate complexes in the literature. To confirm this assignment, titanium(IV) citrate was titrated into a solution of the model ligand ethylenebis(*o*-hydroxyphenylglycine) (EHPG, pH 7.4, 10 mM Hepes buffer), a ligand used previously for mimicking Fe^{III} binding.[9] The UV difference spectra were almost identical to those from reaction of titanium(IV) citrate with transferrin and ^1H NMR shifts of the aromatic protons of EHPG induced by titanium(IV) citrate are consistent with the binding of Ti^{IV} ions to phenolate groups on the ligand.

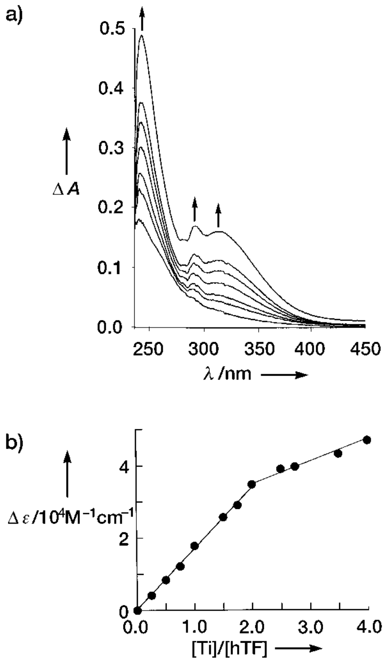

Figure 1. a) UV difference spectra of apo-hTF (13 μM in 10 mM Hepes, 5 mM HCO_3^-, pH 7.4, 310 K) after addition of 2 molequiv titanium(IV) citrate. Reaction times (from bottom to top): 1, 5, 10, 20, 40, 150, and 720 min. b) Titration curve for addition of titanium(IV) citrate to apo-hTF (conditions as above). Each solution was left > 12 h to reach equilibrium. $\Delta\varepsilon$ is the absorbance at 241 nm divided by the transferrin concentration.

Analysis of the titration curve for reaction of apo-hTF with titanium(IV) citrate (Figure 1 b) suggests that two Ti^{IV} ions bind strongly to transferrin (i.e. one in each lobe). A similar stoichiometry of Ti:hTF = 1.9(± 0.1):1 was obtained from the measurement of the titanium content of purified titanium transferrin by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The value of the extinction coefficient for the first step of Ti^{IV} binding to transferrin (occupation of one lobe), $\Delta\varepsilon_1$, is $17000 \pm 400\,\text{M}^{-1}\,\text{cm}^{-1}$ at 241 nm, which is the same as the value determined for Ti^{IV} binding to ethylenebis(*o*-hydroxyphenylglycine) ($\Delta\varepsilon \approx 17000\,\text{M}^{-1}\,\text{cm}^{-1}$), suggesting that two tyrosines are involved in binding Ti^{IV} in both the N- and C-lobes (linear increase in $\Delta\varepsilon$ with occupation of sites, see Figure 1 b). The resulting yellow Ti_2–hTF solution was stable at ambient temperature.

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[*] Prof. Dr. P. J. Sadler, Dr. H. Sun, H. Li, R. Weir
Department of Chemistry, University of Edinburgh
West Mains Road, Edinburgh EH9 3JJ (UK)
Fax: (+44) 131-650-6452
E-mail: p.j.sadler@ed.ac.uk

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