In conclusion, cobalt on charcoal has been developed as an inexpensive, heterogeneous, and highly effective catalyst for intra- and intermolecular Pauson–Khand reactions. The reusability of the catalyst and the experimental simplicity are especially attractive and should encourage the use of this catalyst system among synthetic chemists and in industrial applications.

Experimental Section

The enyne shown in Equation (1) (0.30 g, 1.26 mmol) and Co/C (0.10 g, 12.2 wt% Co) in THF (15 mL) was heated under carbon monoxide (20 atm at room temperature) at 130 °C for 7 h. After workup and column chromatography, the corresponding cyclopentenone derivative was obtained 92% yield.

Characterization of the product of entry 10 in Table 1: IR (NaCl): $\tilde{\nu} = 1690$ (s; ν(CO)) cm^{-1}; m.p. 51 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.16$ (s, 2H), 6.28 (m, 2H), 6.20 (m, 2H), 2.90 (br.s, 2H), 2.70 (br.s, 2H), 2.66 (br.s, 2H), 2.27 (m, 2H), 2.15 (t, $J = 7.3$ Hz, 4H), 1.49 (q, $J = 7.4$ Hz, 4H), 1.37 (q, $J = 7.3$ Hz, 2H), 1.36 (d, $J = 9.2$ Hz, 2H), 1.19 (d, $J = 9.2$ Hz, 2H); elemental analysis (%): calcd: C 83.29, H 7.89; found: C 83.36, H 7.97.

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$(CuI)_2P_8Se_3$: An Adduct of D_3-Symmetrical P_8Se_3 Cage Molecules with Cu_2I_2 Rhomboids[**]

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Copper(I) halides have been established as a preparative tool for neutral and low charged molecules of the group 15 and 16 elements. Thus, several adducts of polymers, either of phosphorus or chalcogens, could be prepared in a crystalline state and characterized.[1] By this approach, the β-P_4Se_4 cage, which was not previously accessible, was synthesized in $(CuI)_3P_4Se_4$. This compound is an adduct of a neutral phosphoselenide cage with copper iodide.[2] Lowering the annealing temperature of the starting materials, copper iodide, phosphorus, and selenium, yields $(CuI)P_4Se_4$,[3] in which phosphorus and selenium are arranged as polymers consisting of P_4Se_3 cages, analogous to norbornane, bridged by selenium atoms. This finding is consistent with the behavior of free equimolar mixtures of phosphorus and selenium, that, at low temperatures, form a polymer[4] which depolymerizes at higher temperatures.[5] The depolymerization processes in phosphorus–selenium melts were subject of a series of experiments.[5] By means of NMR techniques, it was shown for P–Se mixtures of 48% P that, at about 375 °C, the depolymerization and the formation of oligomers becomes significant.[6] However, to date only four further phosphoselenide binary compounds have been crystallographically characterized. These compounds are P_2Se_5,[7] $P_{14}Se$,[8] P_4Se_5,[9] and P_4Se_3.[10] Therefore, information on the molecular structures of phosphoselenides is rather limited as compared to phoshosulfides.[11] The major problem that hinders the preparation of phosphoselenides seems to be their tendency to form amorphous polymers at ambient temperatures. Since oligomeric and polymeric P_4Se_4 can be obtained in copper iodide at different temperatures, we were encouraged to explore the system CuI-P-Se for the existence of further adducts of either oligomeric or polymeric phosphoselenides with copper iodide. Herein, we report the synthesis and the structural characterization of $(CuI)_2P_8Se_3$.

The adduct $(CuI)_2P_8Se_3$ was obtained as a red crystalline material from the reaction of stoichiometric mixtures of CuI, P, and Se (CuI:P:Se = 2:8:3). The crystal structure was determined from single crystals.[12] It consists of planar Cu_2I_2 rhomboids and P_8Se_3 phosphoselenide cages. It has been recently discussed that this building unit can adapt to a given coordination necessity due to the flexibility of both the ∢(Cu-I-Cu) and the ∢(I-Cu-I) angles.[3] Typical measures for these rhomboids are, for example, the distance d(Cu-Cu) and the angles mentioned above. For $(CuI)_2P_8Se_3$, the following

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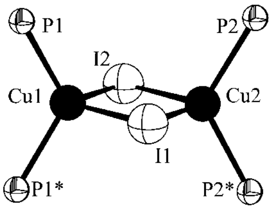

Figure 1. Labeling scheme and coordination pattern of the Cu_2I_2 rhomboids and copper-coordinated P atoms in $(CuI)_2P_8Se_3$ (symmetry generated atoms are marked by a star). The bond distances d(Cu-I) are slightly longer for I1 than for I2, due to the larger angles $\sphericalangle$(I-Cu-P) for I2.

values are found: $d(\text{Cu-Cu}) = 3.039$ Å, $\sphericalangle(\text{Cu-I-Cu}) = 69.36°$ (I1) and 71.79° (I2), $\sphericalangle(\text{I-Cu-I}) = 109.39°$ (Cu1) and 109.46° (Cu2). A slight deviation of an ideal rhomboid is present since both copper atoms and both iodine atoms of each rhomboid are crystallographically inequivalent. Thus, the bond length d(I1-Cu) is about 0.08 Å longer than the corresponding bond length d(I2-Cu). As shown in Figure 1, the reason for this bond length difference is because of the coordination of each copper atom to two phosphorus atoms. Due to the arrangement in the crystal structure, the angle $\sphericalangle$(I-Cu-P) is larger for I2 than for I1. Thus, repulsion by the bulky P_8Se_3 molecules can be regarded as the reason for the slight elongation of the Cu-I1 bonds.

The most remarkable feature of the crystal structure of $(CuI)_2P_8Se_3$ are the novel P_8Se_3 cage molecules. Their D_3 symmetry is crystallographically reduced to C_2 symmetry, as shown in Figure 2. The slight deviations from ideality are due to the crystal structure arrangement. The P_8Se_3 cages under discussion can be derived from a P_8 cube by inserting selenium into three edges related by a threefold axis of the cube. The deviations from the ideal D_3 symmetry become obvious when the lengths and angles within this covalent molecular arrangement are discussed. The threefold axis is defined by P1 and P1′, which are symmetry related. P1 has three covalent bonds to the phosphorus atoms P2, P3, and P4 (Figure 2). The distances d(P-P) for P1 range from 2.226 to 2.246 Å and the angles $\sphericalangle$(P-P-P) are in the narrow range from 104.35° to 105.06°. In contrast, P2, P3, and P4 have only two covalent bonds to other phosphorus atoms. In addition, each of them is covalently bonded to one selenium atom. The averaged bond length $\bar{d}(\text{P-P}) = 2.23$ Å is only slightly smaller than the averaged bond lengths $\bar{d}(\text{P-Se}) = 2.26$ Å. The bond angles $\sphericalangle$(P-Se-P) of 93.13° (Se1) and 98.96° (Se2) are typical for phosphoselenides.

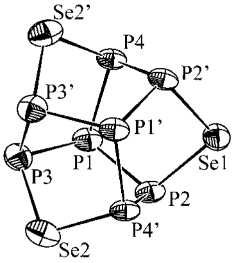

Figure 2. Labeling scheme of the P_8Se_3 molecules in $(CuI)_2P_8Se_3$. The cages are coordinated to copper through P1/P1′ and P2/P2′. The molecular D_3 symmetry is lowered in the crystal structure and only one C_2 axis remains. Atoms marked by ′ are generated by this twofold axis. Ellipsoids are drawn at a 80% probability level.

Figure 3 shows a section of the crystal structure of $(CuI)_2P_8Se_3$. Each P_8Se_3 cage is coordinated by four copper ions belonging to four different Cu_2I_2 rhomboids by Cu1-P1 (P1′) and Cu2-P2 (P2′) bonds. The crystal structure consists of alternating layers of the phosphoselenide cages and of the Cu_2I_2 rhomboids. These layers are oriented along (001). The single cages are well separated due to their coordination to copper iodide. The shortest interlayer and intralayer distances between different P_8Se_3 units are about 3.8 Å.

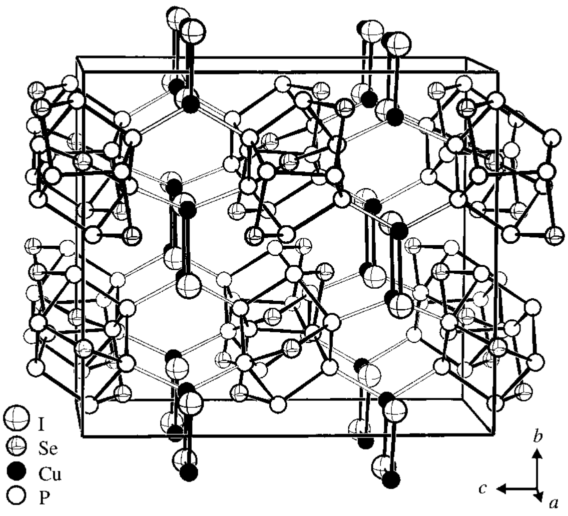

Figure 3. Section of the crystal structure of $(CuI)_2P_8Se_3$. The P_8Se_3 cages and the Cu_2I_2 rhomboids are arranged in layers parallel to (001).

The P_8Se_3 cage molecules are closely related to P_{11}^{3-} polyanions, the so-called "ufosane", which are present in Na_3P_{11} and K_3P_{11}.[8, 16] The negatively charged two-coordinate phosphorus atoms of P_{11}^{3-} are replaced by selenium, consistant with the Zintl–Klemm concept. Thus, the polyanion P_{11}^{3-} is transformed to the neutral heteroatomic molecule P_8Se_3. The most important function of copper iodide is to support the crystallization and, in addition, to hinder the polymerization of the cage molecules.[1] If this concept holds, one might expect a large number of new adduct compounds of phosphoselenides with copper iodide when the impressive group of polyphosphide ions[8] is regarded.

Experimental Section

$(CuI)_2P_8Se_3$ was synthesized in quantitative yield by the reaction of stoichiometric amounts of CuI (>98%, Merck), red phosphorous (99.999%, Hoechst), and grey selenium (99.999%, Chempur). CuI was purified by recrystallisation from an aqueous HI solution prior to use.[1] The reaction mixture of CuI, P, and Se (CuI:P:Se = 2:8:3) was sealed in dried and evacuated quartz glass ampoules, heated slowly to 600 °C, and then cooled to 350 °C. A pure microcrystalline product containing small dark red crystals was obtained after an annealing period of four weeks. The purity of the samples was checked by X-ray powder diffraction (flat sample in transmission geometry, Siemens D5000, $Cu_{K\alpha 1}$, $\lambda = 1.54051$ Å, Si as an external standard). Thermal analyses were performed with a DTA L62 apparatus (Linseis) with Al_2O_3 as reference material. $(CuI)_2P_8Se_3$ has a melting point of 408 ± 2 °C.

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[12] Single crystal X-ray structure: orthorhombic, space group *Pbcm* (no. 57), $a = 9.1348(6)$, $b = 12.351(1)$, $c = 13.873(1)$ Å, $V = 1565.2(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.673$ g cm^{-1}. Data collection: STOE IPDS, 8639 reflections, 1446 independent reflections, $R_{int} = 0.0931$, room temperature, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $2\theta_{max} = 50°$, $-10 \leq h \leq 9$, $-14 \leq k \leq 14$, $-16 \leq l \leq 16$, crystal size $0.36 \times 0.30 \times 0.04$ mm^3, numerical absorption correction (X-RED,[13] X-SHAPE[14]). The structure was solved by direct methods and refined against F^2 (SHELX-97[15]). The refinement of 75 parameters converged to $R = 0.0369$ and $wR = 0.0771$ ($I > 2\sigma(I)$) and $R = 0.0545$ and $wR = 0.0816$ (all reflections). Min./max. electron density (final difference Fourier extremes) $-0.995/1.772$ e Å^{-3}. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411332.

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The Structure of the Fe^{IV}O$_4^{4-}$ Ion**

Mark T. Weller* and Andrew L. Hector

Most of the complex oxide chemistry of iron is restricted to the oxidation states 2 and 3 though tetravalent, pentavalent, and hexavalent iron compounds can be formed in combination with Group 1 and 2 cations. Hexavalent iron is well known as the red-purple tetrahedral ferrate(VI) ion, FeO_4^{2-}, in compounds such as Cs_2FeO_4[1] and Na_2FeO_4.[2] The FeO_4^{3-} ion, containing iron(V), has also been structurally characterized in K_3FeO_4.[3] Iron(IV) compounds include the alkali metal iron oxides such as Sr_2FeO_4,[4] $Sr_3Fe_2O_7$,[5] $SrFeO_3$,[6] and $CaFeO_3$,[7] which contain distorted FeO_6 octahedra sharing vertices; unusual electronic properties are exhibited by some of these d^4 materials due to a spin-pairing mechanism.[8] The existence of a phase of the stoichiometry Ba_2FeO_4, reported by Scholder et al.[9] as adopting the β-Ca_2SO_4 structure on the basis of similarities in the powder X-ray diffraction patterns, has not been substantiated. Fe^{3+} adopts octahedral coordination to oxygen in most of its complex oxides though the tetrahedral FeO_4^{5-} ion is known in the compound Na_5FeO_4.[10]

Scholder et al.[9] reported the synthesis of a sodium iron(IV) oxide of the stoichiometry Na_4FeO_4 but no structural data exist for this material, which might be expected to contain tetrahedral FeO_4^{4-} by analogy with other Na_4MO_4 (M = Ti, Cr, Co, Ge) compounds.[11–14] Indeed the structure of the ferrate(IV) ion has not been described to date. Iron(IV) is isoelectronic with manganese(III) and both ions exhibit Jahn–Teller distortions, due to their high-spin d^4 configurations. The observation of unusual colossal magnetoresistive properties in some Mn^{III} and Fe^{IV} compounds[15] is associated with structural distortions in these d^4 species. Herein we report for the first time the geometry of the FeO_4^{4-} ion as determined in sodium ferrate(IV).

The structure of Na_4FeO_4 consists of discrete FeO_4^{4-} ions separated by sodium ions as shown in Figure 1. Each unit cell contains two ferrate(IV) ions related by a center of symmetry, and the sodium ions coordinate to four (Na1, Na2, and Na3) or five (Na4) oxygen atoms at 2.3–2.5 Å, though Na1 has two and Na3 has one longer, additional interactions to an oxygen atom. The most remarkable feature of the structure is that the FeO_4^{4-} tetrahedron is strongly distorted (Figure 2). The unit is squashed along one C_2 axis to give the ion approximately D_{2d} symmetry, rather than perfect tetrahedral, and two of the

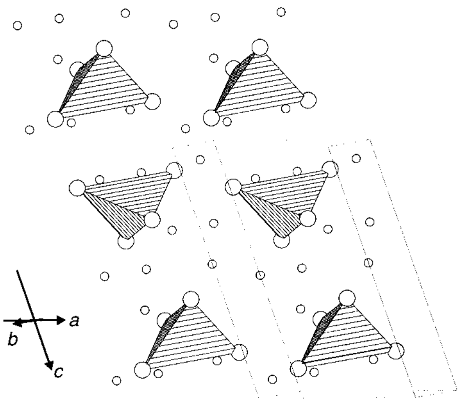

Figure 1. Unit cell of Na_4FeO_4. FeO_4^{4-} units are shown as polyhedra and sodium atoms as spheres.

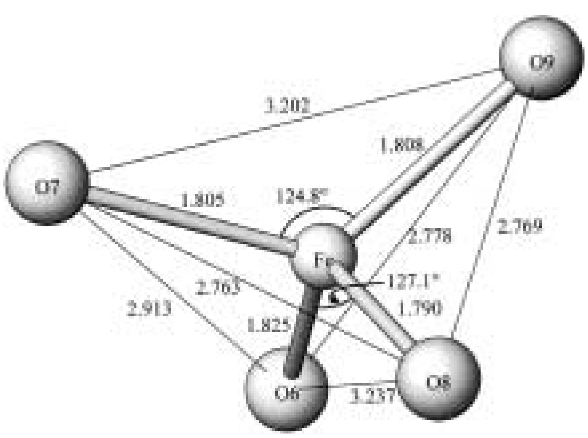

Figure 2. Geometry of the FeO_4^{4-} ion. Other bond angles [°] not shown for clarity are O6-Fe-O7 106.7(2), O6-Fe-O9 99.8(2), O7-Fe-O8 100.5(2), O8-Fe-O9 100.6(2).

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