Heteropolymolybdates of As^{III}, Sb^{III}, Bi^{III}, Se^{IV}, and Te^{IV} Functionalized by Amino Acids[**]

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Polyoxoanions are a fascinating class of metal–oxygen cluster compounds with a unique structural variety and interesting properties which are of use in different fields including catalysis and medicine.[1–4] The first polyoxometalates were synthesized almost 200 years ago, but the structural identity of many species has only been established fairly recently. The availability of single-crystal X-ray diffraction has led to the discovery of a large number of novel polyoxoanions with different shapes and sizes.

During the last 20 years it has been established that the size, shape, and charge density of many polyoxoanions are of interest for pharmaceutical applications.[5] However, the main problem of many tested polyoxoanions has been insufficient selectivity. In many cases it would be desirable to slightly modify a given polyoxoanion core structure, but exactly this turns out to be a major problem. To date the mechanism of formation of polyoxometalates is not fully understood and usually described as self-assembly. Keeping this in mind it appears that a systematic derivatization of polyoxoanions is currently most feasible via attachment of organic groups to the surface of polyoxoanions.

Different groups worldwide have used a variety of approaches to incorporate organic or organometallic moieties in polyoxoanion frameworks. Many compounds have been synthesized and characterized over the years.[6] Interaction of polyoxovanadates with carboxylate functionalities has led to a large number of functionalized species, but only a few analogues of polyoxomolybdates and -tungstates with nuclearities of more than three are known.[6,7]

The reactivity of amino acids with polyoxovanadates has also been investigated in model studies for polyoxometalate-protein interactions.[8,9] To date the only examples of structurally characterized polyoxoanions with covalently bound amino acids are $[Mo_8O_{26}(\text{L-lysH}_2)_2]^{2-}$, $[HMo_6VO_{22}(NH_3CH_2COO)_3]^{2-}$, and $[Mo_{154}O_{462}H_{14}(H_2O)_{48}(HO_2C{-}(NH_3^+)HC{-}CH_2{-}S{-}S{-}CH_2{-}CH(NH_3^+){-}COO^-)_{11}]^{3-}$.[10–12] Recently Pope et al. studied the stereoselective interaction of amino acids with cerium-substituted, Dawson-type polyoxotungstates.[13] They proposed coordination of the amino acid to the cerium center by the carboxylate group in a monodentate fashion, accompanied by hydrogen bonding involving the amino group. Other interesting polyoxometalates are the polyoxovanadium cluster ion $[V_6O_{12}(OH)_3(O_2CCH_2CH_2NH_3)_3(SO_4)]^+$ and the neutral, polymeric $[Mo_4O_{12}(\text{glycylglycylglycine})_2]$.[14,15]

We decided to undergo a systematic study on the interaction of amino acids with polyoxomolybdates. The 20 natural amino acids with their variety of side chains represent a rich reservoir that perhaps can be employed to fine-tune the inhibition properties of polyanions (drug-design). In addition they are chiral, water-soluble, commercially available and non-toxic. Recently we have been particularly interested in the investigation of lone pair containing heteropolyanions.[16–18] Therefore we decided to study the following systems in some detail: X^{III}/Mo/L and X^{IV}/Mo/L (L = amino acid; X^{III} = As, Sb, Bi; X^{IV} = Se, Te).

Herein we report the synthesis and structural characterization of compounds **1–18**:

$[Se^{IV}Mo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ **1**

$[Se^{IV}Mo_6O_{21}\{O_2C(CH_2)_2NH_3\}_3]^{2-}$ **2**

$[Se^{IV}Mo_6O_{21}\{O_2C(CH_2)_3NH_3\}_3]^{2-}$ **3**

$[Se^{IV}Mo_6O_{21}(\text{L-}O_2CCHCH_3NH_3)_3]^{2-}$ **4**

$[Te^{IV}Mo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ **5**

$[Te^{IV}Mo_6O_{21}\{O_2C(CH_2)_2NH_3\}_3]^{2-}$ **6**

$[Te^{IV}Mo_6O_{21}\{O_2C(CH_2)_3NH_3\}_3]^{2-}$ **7**

$[As^{III}Mo_6O_{21}(O_2CCH_2NH_3)_3]^{3-}$ **8**

$[As^{III}Mo_6O_{21}\{O_2C(CH_2)_2NH_3\}_3]^{3-}$ **9**

$[As^{III}Mo_6O_{21}\{O_2C(CH_2)_3NH_3\}_3]^{3-}$ **10**

$[Sb^{III}Mo_6O_{21}(O_2CCH_2NH_3)_3]^{3-}$ **11**

$[Sb^{III}Mo_6O_{21}\{O_2C(CH_2)_2NH_3\}_3]^{3-}$ **12**

$[Sb^{III}Mo_6O_{21}\{O_2C(CH_2)_3NH_3)\}_3]^{3-}$ **13**

$[Sb^{III}Mo_6O_{21}(\text{L-}O_2CCHCH_3NH_3)_3]^{3-}$ **14**

$[Bi^{III}Mo_6O_{21}(O_2CCH_2NH_3)_3]^{3-}$ **15**

$[Bi^{III}Mo_6O_{21}\{O_2C(CH_2)_2NH_3\}_3]^{3-}$ **16**

$[Bi^{III}Mo_6O_{21}\{O_2C(CH_2)_3NH_3\}_3]^{3-}$ **17**

$[Bi^{III}Mo_6O_{21}\{\text{L-}O_2CCH[(CH_2)_4NH_2]NH_3\}_3]^{3-}$ **18**

The 18 polyanions represents a novel family of lone-pair containing heteropolymolybdates functionalized by five different amino acids: glycine ($HO_2CCH_2NH_2$), β-alanine ($HO_2C(CH_2)_2NH_2$), 4-aminobutyric acid ($HO_2C(CH_2)_3NH_2$),

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L-alanine (L-$HO_2CCHCH_3NH_2$) and L-lysine (L-$HO_2CCH\{(CH_2)_4NH_2\}NH_2$). These compounds can be represented by the general formula $[XMo_6O_{21}(O_2CRNH_3)_3]^{n-}$ ($n = 2$, $X = Se^{IV}$, Te^{IV}; $n = 3$, $X = As^{III}$, Sb^{III}, Bi^{III}; $R = CH_2$, C_2H_4, C_3H_6, $CHCH_3$, $CH(CH_2)_4NH_2$). Polyanions **4**, **14**, and **18** are the first examples of chiral, functionalized heteropolymolybdates.

Polyanions **1**–**18** consist of a heteroatom X surrounded by a ring of six MoO_6 octahedra which alternately share edges and corners. Three amino acid molecules are each bound to two edge-sharing Mo centers by their carboxylate group on the same side of the ring (see Figures 1–4). The central heteroatom, located slightly above the plane of six molybdenum atoms, is coordinated to three μ_3-oxo groups which leads to a trigonal-pyramidal coordination geometry. The lone pair is on the same side of the ring as the amino acids.

The molybdenum–oxo framework of the title compounds has been seen before in the species **19**–**22**:

$[CH_3AsO_3Mo_6O_{18}(H_2O)_6]^{2-}$ [19] **19**

$[(O_3PCH_2OPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ [20] **20**

$[(O_3POPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ [21] **21**

$[HMo_6VO_{22}(NH_3CH_2COO)_3]^{2-}$ [11] **22**

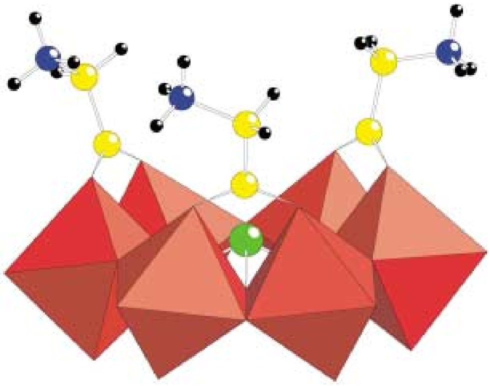

Figure 1. Combined polyhedral/ball and stick representation of **1**. The MoO_6 octahedra are shown in red and the balls represent selenium (green), carbon (yellow), nitrogen (blue), and hydrogen (black).

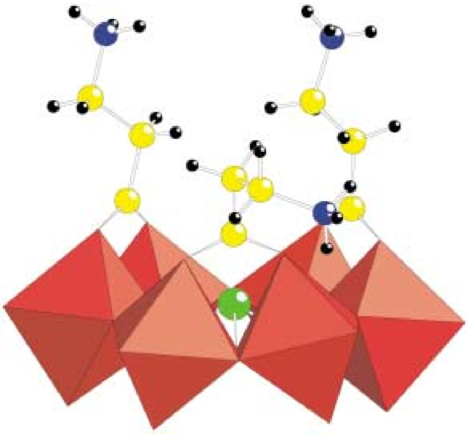

Figure 2. Combined polyhedral/ball and stick representation of **2**. The color code is the same as in Figure 1.

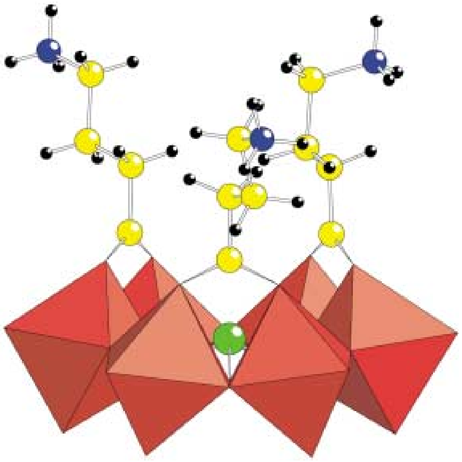

Figure 3. Combined polyhedral/ball and stick representation of **3**. The color code is the same as in Figure 1.

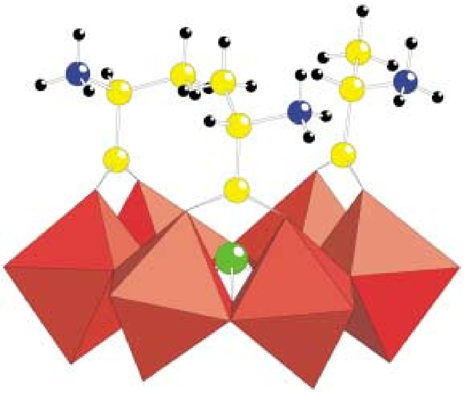

Figure 4. Combined polyhedral/ball and stick representation of **4**. The color code is the same as in Figure 1.

The new polyanions are synthesized by refluxing an aqueous solution containing sodium molybdate, heteroatom, amino acid, potassium chloride in the mole ratio 6:1.1:6:6 at pH 3.5 for 1 h.[22] The yields range from 23–97 %. Single crystals suitable for X-ray diffraction could be obtained for half of the compounds presented.[23] The characterization of the remaining species is based on FTIR spectroscopy and elemental analysis.[22]

In all the polyanions three amino acids are bound to the polyoxomolybdate framework by their carboxylate group. All species characterized by X-ray diffraction show complete protonation of the pendant amino groups, based on charge balance considerations. Therefore it can be concluded that glycine (**1**, **5**, **8**, **11**, **15**), β-alanine (**2**, **6**, **9**, **12**, **16**), 4-aminobutyric acid (**3**, **7**, **10**, **13**, **17**), L-alanine (**4**, **14**), and L-lysine (**18**) are bound as zwitterions. This is not a surprise keeping in mind that the pH value of the reaction mixture is 3.5, which is lower than the isoelectric point of the amino acids used (pH 6 for the neutral amino acids and pH 9.7 for L-lysine). Bond valence sum calculations did not indicate any protonation of the oxygen atoms bonded to the molybdenum atoms.[24] Therefore, the negative charge of each polyanion corresponds to the charge of the XO_3 heterogroup (−2 for $X = Se^{IV}$, Te^{IV}; −3 for $X = As^{III}$, Sb^{III}, Bi^{III}), which is located in the center of the metal–oxo framework. As a result **1**–**18** can be considered as "zwitteranions" and this property may be important for biological applications.

In addition to glycine, β-alanine, 4-aminobutyric acid, L-alanine, and L-lysine we investigated additional essential amino acids. It appears that some of them (e.g. L-asparagine) can also be bound to the title structure, but so far we have not been able to isolate pure products. Our studies allow us to conclude that it is more difficult to bind amino acids with bulky functional groups, most likely because of steric interactions.

Interestingly we observed little crystallographic disorder for the pendant alkyl amino groups of the amino acids. This is especially surprising for **3** and **7**, which contain 4-aminobutyric acid. A possible explanation involves the lone pair of the heterogroup, which seems to play an important structure-controlling role in all the polyanions. As a result, the three amino acids in each polyanion are orientated almost parallel to each other and perpendicular to the metal–oxo framework, this is especially true for the species with long alkyl groups (**3**, **7**, **10**, **13**, and **17**), which resemble a prawn with three legs.

To learn more about the solution properties of **1**–**18** we analyzed the freshly prepared polyanions by ^{1}H and ^{13}C NMR spectroscopy. We also measured the spectra of aqueous solutions of the redissolved salts of **1**–**18** as well as solutions of amino acids as references. However, we discovered that NMR spectroscopy did not allow us to distinguish free from bound amino acids. It is possible that binding of an amino acid to two molybdenum centers in **1**–**18** does not induce a detectable chemical-shift change for its hydrogen and carbon atoms. The hydrogen atoms on the α-carbon atoms should be most affected, but they are already four bonds away from the closest molybdenum atom. In addition, the bonds between molybdenum atoms and carboxylate oxygen atoms are weak (e.g. in **1**: $d_{\text{Mo-OC}} = 2.260$–$2.322(5)$). This observation indicates that in aqueous solution the amino acids are probably labile, which would lead to a relatively fast exchange of free and bound amino acids. We performed temperature-dependent NMR spectroscopy between 5–25 °C, but these studies did not allow us to draw additional conclusions.

Our work has shown that the structural type of the title polyanions can accommodate a variety of amino acids. Furthermore there appears to be variability related to the central heteroatom site. We were able to synthesize isostructural species although we changed the size of the heteroatom and its lone pair ($\text{As}^{\text{III}} < \text{Sb}^{\text{III}} < \text{Bi}^{\text{III}}$) as well as its charge ($\text{As}^{\text{III}}/\text{Sb}^{\text{III}}/\text{Bi}^{\text{III}}$ vs. $\text{Se}^{\text{IV}}/\text{Te}^{\text{IV}}$). Therefore, the open structural type of **1**–**18** is a rare example of a polyoxoanion family that can be easily and systematically derivatized at two different sites. In addition the terminal amino groups of the amino acids present sites for further functionalization.

Currently we are in the process of preparing additional derivatives of the title compounds, with an emphasis on phosphorus-containing species. A detailed investigation of the biological properties of the title polyanions is also underway and the results will be reported elsewhere.

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[22] The synthetic details, elemental analyses, and IR spectral data for all the compounds are available in the Supporting Information.

[23] X-ray structural analyses: Bruker SMART CCD, Mo anode, graphite monochromator, $\lambda = 0.71073$ Å, refinement (SHELXS-97, SHELXL-97),[25] absorption correction (SADABS),[25] hydrogen-atom positions calculated. $\text{K}_2[\text{Se}^{\text{IV}}\text{Mo}_6\text{O}_{21}(\text{O}_2\text{CCH}_2\text{NH}_3)_3]\cdot 8\,\text{H}_2\text{O}$: $0.24 \times 0.18 \times 0.08$ mm^3, orthorhombic, space group *Pnma*, $Z = 4$, $T = 167(2)$ K, $a = 14.0414(14)$, $b = 20.724(2)$, $c = 12.2628(12)$ Å, $V = 3568.3(6)$ Å^3, $2\theta_{\text{max}} = 56.6°$, $\rho_{\text{calcd}} = 2.638$ Mg m^{-3}, $\mu = 3.417$ mm^{-1}, min/max transmission 0.553/0.779, 38537 reflections collected, 4537 independent reflections ($R_{\text{int}} = 0.041$), 4290 observed reflections with $I > 2\sigma(I)$, 144 parameters, max residual electron density 1.41 e Å^{-3}, $R_1 = 0.048$, $wR_2 = 0.109$; K, Se, Mo refined anisotropically. $\text{K}(\text{H}_3\text{N}(\text{CH}_2)_2\text{COOH})[\text{Se}^{\text{IV}}\text{Mo}_6\text{O}_{21}(\text{O}_2\text{C}(\text{CH}_2)_2\text{NH}_3)_3]\cdot 2.5\,\text{H}_2\text{O}$: $0.20 \times 0.16 \times 0.14$ mm^3, monoclinic, space group $P2_1/c$, $Z = 4$, $T = 173(2)$ K, $a = 10.5238(16)$, $b = 20.342(3)$, $c = 17.224(3)$ Å, $\beta = 97.626(2)$, $V = 3654.6(9)$ Å^3, $2\theta_{\text{max}} = 56.7°$, $\rho_{\text{calcd}} = 2.592$ Mg m^{-3}, $\mu = 3.220$ mm^{-1}, min/max transmission 0.555/0.685, 40850 reflections collected, 8922 independent reflections ($R_{\text{int}} = 0.067$), 6696 observed reflections with $I > 2\sigma(I)$, 265 parameters, max residual electron density 2.755 e Å^{-3}, $R_1 = 0.079$, $wR_2 = 0.177$; K, Se, Mo refined anisotropically. $\text{K}_2[\text{Se}^{\text{IV}}\text{Mo}_6\text{O}_{21}(\text{O}_2\text{C}(\text{CH}_2)_3\text{NH}_3)_3]\cdot\text{KCl}\cdot 10\,\text{H}_2\text{O}$: $0.20 \times 0.14 \times 0.10$ mm^3, monoclinic, space group $P2_1/n$, $Z = 4$, $T = 173(2)$ K, $a = 12.3206(12)$, $b = 22.059(2)$, $c = 17.3546(16)$ Å, $\beta = 106.130(2)$, $V = 4530.9(7)$ Å^3, $2\theta_{\text{max}} = 56.6°$, $\rho_{\text{calcd}} = 2.364$ Mg m^{-3}, $\mu = 2.856$ mm^{-1}, min/max trans-

mission 0.634/0.756, 51123 reflections collected, 11056 independent reflections ($R_{int} = 0.056$), 8979 observed reflections with $I > 2\sigma(I)$, 308 parameters, max residual electron density 1.544 e Å^{-3}, $R_1 = 0.040$, $wR_2 = 0.092$; K, Se, Mo, Cl refined anisotropically. $\mathrm{K_2[Se^{IV}Mo_6O_{21}(O_2CCHCH_3NH_3)_3]\cdot 4.5\,H_2O}$: 0.30 × 0.20 × 0.10 mm^3, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $T = 293(2)$ K, $a = 11.2576(16)$, $b = 16.655(2)$, $c = 19.285(3)$ Å, $V = 3616.0(9)$ Å^3, $2\theta_{max} = 56.6°$, $\rho_{calcd} = 2.587$ Mg m^{-3}, $\mu = 3.364$ mm^{-1}, min/max transmission 0.375/0.621, 40856 reflections collected, 8833 independent reflections ($R_{int} = 0.067$), 7967 observed reflections with $I > 2\sigma(I)$, 267 parameters, max residual electron density 1.316 e Å^{-3}, $R_1 = 0.038$, $wR_2 = 0.097$; K, Se, Mo refined anisotropically. $\mathrm{K_2[Te^{IV}Mo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8\,H_2O}$: 0.30 × 0.14 × 0.10 mm^3, orthorhombic, space group *Pnma*, $Z = 4$, $T = 173(2)$ K, $a = 13.9561(18)$, $b = 20.805(3)$, $c = 12.3770(16)$ Å, $V = 3593.7(8)$ Å^3, $2\theta_{max} = 56.6°$, $\rho_{calcd} = 2.709$ Mg m^{-3}, $\mu = 3.176$ mm^{-1}, min/max transmission 0.596/0.719, 39150 reflections collected, 4557 independent reflections ($R_{int} = 0.051$), 4156 observed reflections with $I > 2\sigma(I)$, 144 parameters, max residual electron density 1.663 e Å^{-3}, $R_1 = 0.057$, $wR_2 = 0.132$; K, Te, Mo refined anisotropically. $\mathrm{K(H_3N(CH_2)_2COOH)[Te^{IV}Mo_6O_{21}(O_2C(CH_2)_2NH_3)_3]\cdot 3\,H_2O}$: 0.20 × 0.16 × 0.08 mm^3, monoclinic, space group $P2_1/c$, $Z = 4$, $T = 173(2)$ K, $a = 10.7020(14)$, $b = 20.831(3)$, $c = 16.771(2)$ Å, $\beta = 97.527(2)$, $V = 3706.6(9)$ Å^3, $2\theta_{max} = 56.7°$, $\rho_{calcd} = 2.657$ Mg m^{-3}, $\mu = 2.966$ mm^{-1}, min/max transmission 0.634/0.704, 42108 reflections collected, 9096 independent reflections ($R_{int} = 0.062$), 6903 observed reflections with $I > 2\sigma(I)$, 265 parameters, max residual electron density 1.660 e Å^{-3}, $R_1 = 0.043$, $wR_2 = 0.090$; K, Te, Mo refined anisotropically. $\mathrm{Cs_2[Te^{IV}Mo_6O_{21}(O_2C(CH_2)_3NH_3)_3]\cdot 5.25\,H_2O}$: 0.18 × 0.16 × 0.10 mm^3, monoclinic, space group $P2_1/n$, $Z = 4$, $T = 293(2)$ K, $a = 11.3740(16)$, $b = 22.231(3)$, $c = 16.887(2)$ Å, $\beta = 102.535(2)$, $V = 4168.3(10)$ Å^3, $2\theta_{max} = 56.7°$, $\rho_{calcd} = 2.697$ Mg m^{-3}, $\mu = 4.259$ mm^{-1}, min/max transmission 0.507/0.612, 46889 reflections collected, 10230 independent reflections ($R_{int} = 0.051$), 8117 observed reflections with $I > 2\sigma(I)$, 282 parameters, max residual electron density 1.471 e Å^{-3}, $R_1 = 0.039$, $wR_2 = 0.086$; Cs, Te, Mo refined anisotropically. $\mathrm{K_2Na[As^{III}Mo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 6\,H_2O\cdot 0.5\,Cl}$: 0.22 × 0.06 × 0.04 mm^3, monoclinic, space group $P2_1$, $Z = 2$, $T = 173(2)$ K, $a = 11.7166(17)$, $b = 13.753(2)$, $c = 11.8154(17)$ Å, $\beta = 115.121(2)$, $V = 1723.8(4)$ Å^3, $2\theta_{max} = 56.8°$, $\rho_{calcd} = 2.749$ Mg m^{-3}, $\mu = 3.479$ mm^{-1}, min/max transmission 0.636/0.856, 20056 reflections collected, 7708 independent reflections ($R_{int} = 0.076$), 6330 observed reflections with $I > 2\sigma(I)$, 277 parameters, max residual electron density 1.320 e Å^{-3}, $R_1 = 0.050$, $wR_2 = 0.102$; K, Na, As, Mo, Cl refined anisotropically. $\mathrm{K_{2.5}Na[Sb^{III}Mo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 6\,H_2O\cdot 0.5\,Cl}$: 0.10 × 0.08 × 0.02 mm^3, monoclinic, space group $P2_1$, $Z = 2$, $T = 173(2)$ K, $a = 11.7166(17)$, $b = 13.753(2)$, $c = 11.8154(17)$ Å, $\beta = 115.121(2)$, $V = 1723.8(4)$ Å^3, $2\theta_{max} = 56.8°$, $\rho_{calcd} = 2.877$ Mg m^{-3}, $\mu = 3.354$ mm^{-1}, min/max transmission 0.705/0.819, 20076 reflections collected, 8344 independent reflections ($R_{int} = 0.068$), 6870 observed reflections with $I > 2\sigma(I)$, 277 parameters, max residual electron density 1.682 e Å^{-3}, $R_1 = 0.051$, $wR_2 = 0.097$. K, Na, Sb, Mo, Cl refined anisotropically. CCDC-190479–190487 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Preparation and Characterization of a Model Bimetallic Catalyst: Co–Pd Nanoparticles Supported on Al_2O_3**

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The development of well-defined model systems is an important precondition for studies aimed at an understanding of catalytic mechanisms at the microscopic level. In this context, the bridging of the so-called "materials gap", that is the adjustment of the model systems to the complexity of real catalysts, is essential. Accordingly, in the case of supported metal catalysts, the focus has shifted from single crystals, which were studied in the beginning to understand adsorption and reaction on extended surfaces, to metal particles deposited on oxide supports.[1,2] The latter systems allow the investigation of particle size effects as well as metal–support interactions, that is factors that can equally be decisive for the overall catalytic performance. Although some progress has been achieved in recent years in this field, the question remains how model systems for more complex systems can be prepared in a defined and reproducible manner.

Herein, we deal with this question for bimetallic catalysts. Such materials represent a highly interesting class of catalysts because one metal can tune and/or modify the catalytic properties of the other metal as the result of both ligand (electronic) and ensemble (structural) effects.[3] Bimetallic Pd–Co particles, for example, have shown improved selectivity over pure Co particles in Fischer–Tropsch reactions.[4–8] Since the conversion of natural resources into syngas (CO + H_2) and then to clean fuels through the Fischer–Tropsch reaction will likely become evermore important with changing supplies and environmental concerns,[9] a detailed understanding of such effects by means of suitable model systems is needed.

Our approach is based on metal vapor deposition on a suitable oxide support under ultrahigh vacuum (UHV) conditions. For the present study, a thin alumina film grown on a metallic NiAl(110) substrate was used,[10] which enabled us to apply scanning tunneling microscopy (STM) as well as temperature-programmed desorption (TPD) for the charac-

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