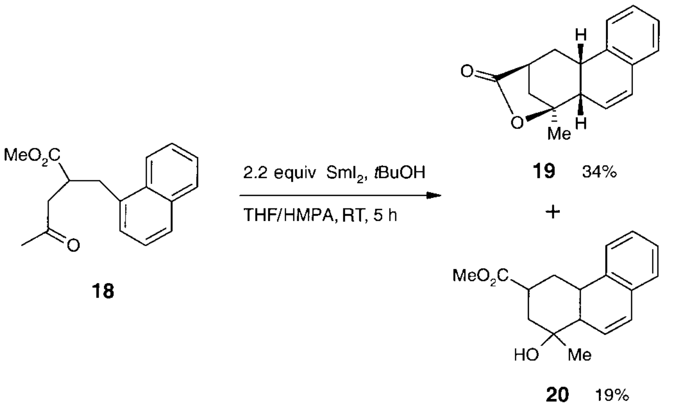
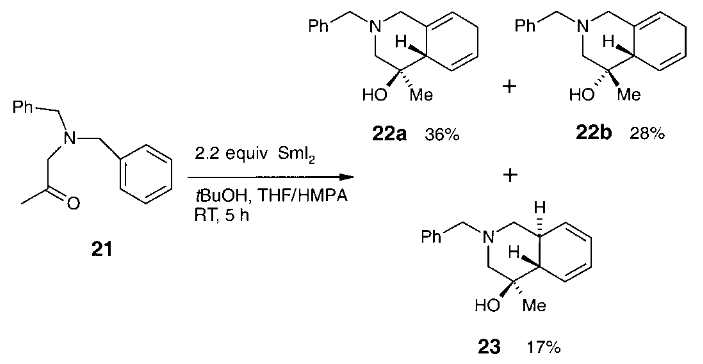
second compound **20** (configuration not yet defined), and for the reaction of *N,N*-dibenzyl-substituted amino ketone **21**, which produces isoquinoline derivatives **22** and **23**.





Experimental Section

In a typical experiment, a solution of 1,2-diiodoethane (0.270 g, 0.96 mmol) in anhydrous THF (20 mL) was added to samarium (0.160 g, 1.05 mmol) under an argon atmosphere. The reaction mixture was stirred for 1.5 h at room temperature, and the resulting deep blue solution was treated with HMPA (1.410 g, 7.88 mmol). Stirring was continued for 10 min, and argon was bubbled through the reaction mixture for a further 10 min. To the resulting solution was added a mixture of **8** (0.130 g, 0.44 mmol) and *t*BuOH (0.065 g, 0.87 mmol) in anhydrous THF (10 mL) over a period of 30 min. The mixture was then stirred for 4.5 h at room temperature, and a saturated solution (10 mL) of sodium bicarbonate was added. The organic layer was separated, the aqueous phase was extracted with diethyl ether (3 × 10 mL), and the combined extracts were washed with brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent and column chromatography of the crude product on silica gel (hexane/ethyl acetate 3/1) afforded **14** as colorless crystals (0.075 g, 60 %). M.p. 151 – 153 °C; ^{1}H NMR ($CDCl_3$): $\delta = 5.83$ (s, 2H; HC=CH), 3.72 (s, 3H; OCH_3), 3.99 (dd, $J = 4.1$, 13.5 Hz, 1H; CH_2), 2.89 (s, 3H; CH, CH_2), 2.79 (td, $J = 4.0$, 12.4 Hz, 1H; CH), 2.34 (t, $J = 13.5$ Hz, 1H; CH_2), 1.97 – 1.88 (m, 1H; CH), 1.56 – 1.43 (m, 7H; 3CH_2, OH), 1.38 – 1.30 (m, 2H; CH_2); ^{13}C NMR ($CDCl_3$): $\delta = 174.2$ (s, C=O), 150.9 (s, =C), 123.5, 122.4 (2d, HC=CH), 117.8 (s, =C), 104.7 (s, C≡N), 75.0 (s, C–OH), 52.0 (q, OCH_3), 50.0, 44.8, 43.3 (3d, 3CH), 36.0, 28.4, 28.0, 23.9, 20.9, 19.6 (6t, 6CH_2); IR (KBr): $\tilde{\nu} = 3515$ (br, O–H), 2940 – 2860 (C–H, =C–H), 2215 (C≡N), 1715 (C=O), 1640 cm^{-1} (C=C); elemental analysis calcd for $C_{17}H_{21}NO_3$ (287.4): C 71.05, H 7.36, N 4.87; found: C 71.10, H 7.58, N 4.85.

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Discovery and Optimization of Heterogeneous Catalysts by Using Combinatorial Chemistry[**]

Selim M. Senkan[*] and Sukru Ozturk

Solid catalysts are used in the manufacturing of a vast array of chemicals and fuels, and as such significantly contribute to our economy and high living standards.[1] In addition, catalysts provide important environmental benefits, such as in catalytic converters for automobiles. However, in spite of their significance and broad utility, the discovery of new catalysts continues to be an arduous and rather unpredictable trial-and-error process. Catalysts traditionally are developed by using a large variety of tedious, time-consuming, and often one at a time methods, characterized and tested for activity, modified,

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[*] Prof. Dr. S. M. Senkan, S. Ozturk
University of California, Los Angeles
Department of Chemical Engineering
Los Angeles, CA 90095-1592 (USA)
Fax: (+1) 310-206-4107
E-mail: senkan@seas.ucla.edu

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characterized and retested until no further improvements are justified. In addition, these investigations have often been conducted independently by different groups, rendering the comparison of activity information difficult. This approach, although time consuming, has been employed successfully for the discovery of a significant number of solid-state catalysts over many decades.[2] However, there remains a large unexplored universe of binary, ternary, quaternary, and higher order solid-state materials and other complex metal compounds that can have superior catalytic properties. Conventional approaches clearly are inadequate to rapidly synthesize and then screen this vast universe of catalytic materials; therefore, the development of new approaches that will accelerate the process of discovery, optimization, and understanding of heterogeneous catalysts will have a significant impact in catalysis science and engineering.

Combinatorial chemistry, in which a large diversity of chemical compounds are rapidly produced and processed, and the resulting libraries of compounds are then screened for desirable properties to identify lead compounds in a high-throughput fashion, is a particularly attractive approach for the discovery and optimization of heterogeneous catalysts. At present two primary methods exist for the preparation of solid-state libraries: 1) synthesis based on thin film deposition[3–6] and 2) synthesis using solution-based technologies.[7, 8] These methods were then used for the discovery of superconducting,[3] magnetoresistive,[4] and luminescent[5–7, 9] materials, and electrochemical catalysts.[8]

The discovery of heterogeneous catalysts is a great challenge because unlike superconductivity, magnetoresistivity, and electrochemical reactions, which can be tested by contact probes, or non-specific luminescence/fluorescence, the screening of heterogeneous catalysts requires the unambiguous detection of a specific molecule (i.e., a product) in the vicinity of small catalyst sites. To date three methods have been proposed to screen catalyst libraries: 1) in situ optical screening using infrared (IR) thermography[10, 11] or fluorescence acid–base indicator,[8] 2) microprobe sampling and scanning mass spectrometry (MS),[12] and 3) in situ resonance-enhanced multiphoton ionization (REMPI) spectroscopy with microelectrode detection.[13] The optical methods, although they provide high-speed data on activity, generally provide limited information on selectivity or different reaction products. The mass spectrometric investigation using microprobes involves the sampling and transfer of very small quantities of gases containing product species that are also at low concentrations. In addition, the sampling probe must physically be moved from site to site to screen the entire library. The REMPI technique combines the speed of optical methods and the selectivity of mass spectrometry and allows the high-speed screening of large solid-state catalyst libraries for activity and selectivity without the need to remove samples.

We report herein on the application of REMPI together with novel array microreactors for the discovery of an optimal composition in the ternary Pt/Pd/In metal catalyst system for the dehydrogenation of cyclohexane to benzene. Array microreactors allow the screening of a large number of catalysts in parallel and under identical (standard) operating conditions. Consequently, measurements become primarily sensitive to the method of preparation of the catalysts. This represents a significant advance over the current practice in catalyst research, in which different catalysts are often studied under different operating conditions, rendering comparisons difficult.

A sketch of the array microreactor system developed is shown in Figure 1. The reactor array consisted of 17 rectangular channels that were micromachined on a flat nonporous silica ceramic slab ($7.5 \times 3.75 \times 0.63$ cm^3). Each channel was 0.1 cm wide, 0.1 cm deep, and 2 cm long, and possessed a cylindrical well (0.3 cm diameter by 0.2 cm deep) to hold cylindrical catalyst pellets (0.3 cm diameter and 0.1 cm high). In this configuration, the flat surface of the catalyst pellet, when placed into the well, would be flush with the bottom of the reactor channel. A similar flat ceramic slab was used to cover the microreactor array slab and to form isolated channels. This design results in unobstructed gas flow rates through the channels with only wall skin friction providing flow resistance. Consequently, the establishment of nearly identical flow rates in each channel, and therefore identical

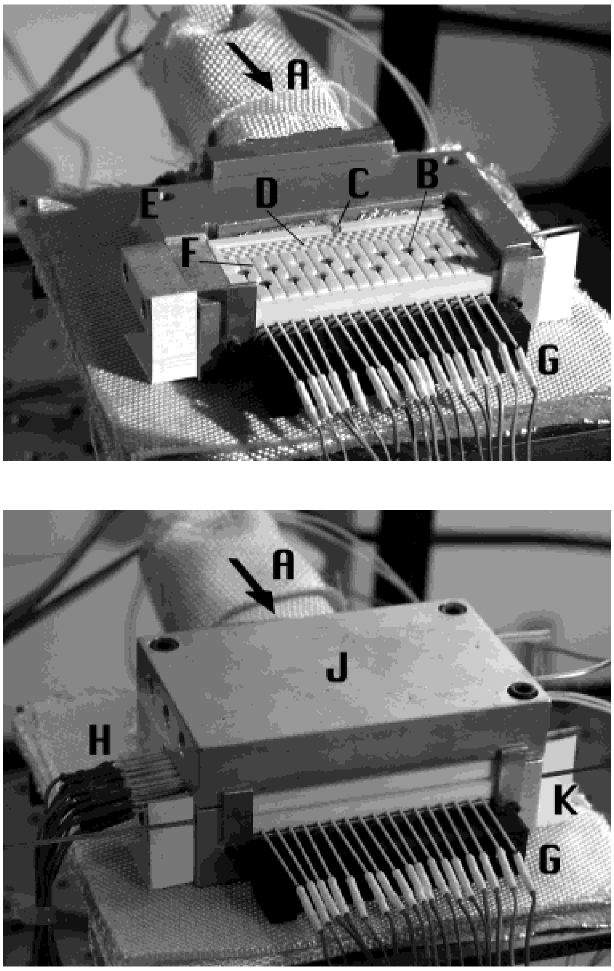

Figure 1. Array microreactor system: Internal details (top); entire reactor system (bottom): A: feed gas preheater; B: catalyst pellets; C: reactant gas inlet; D: flow distribution baffles; E: bottom aluminum heating block; F: reactor channels; G: signal detection microelectrodes; H: power supply microelectrodes; J: top aluminum heating block; K: laser beam.

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contact times between the reactant gases and the catalyst pellets in each microreactor were feasible. The flat and rigid nature of the ceramic slabs also result in the formation of a good gas seal, thereby isolating each channel from one another under a broad range of temperatures.

Ceramic slabs were also machined for optical access and the placement of dedicated microelectrodes as shown in Figure 1. The reactor array was cradled between two aluminum metal heating blocks. In addition, a separate heating block was used to preheat the feed gases to the desired reaction temperature. The temperature of each heating block was independently regulated by using electrical heating elements embedded into the aluminum body and PID controllers (Omega, Stamford, CT). Gas temperatures in the vicinity of the catalyst sites were separately monitored by small thermocouples inserted from the reactor exit to assess their uniformity across the microreactor library, and to establish the time periods for heat up and cool down. These studies revealed the presence of a nearly uniform temperature, within 1 °C, across the entire catalyst library. In addition, the reactor array was shown to heat up and/or cool down to a desired temperature within 30 min of the set point change.

The reactant gases were introduced into the microreactor array through a quartz feed tube and a series of flow distribution baffles that were also micromachined to the bottom ceramic slab (Figure 1). The baffles were used to establish uniform gas flow rates through each channel. The feed stream composition was about 10 % cyclohexane in helium carrier gas; this mixture was prepared by bubbling helium gas (1000 $cm^3 min^{-1}$) through liquid cyclohexane in a sparger at about 25 °C. These conditions correspond to a nominal contact time of about 0.04 s to cross the flat surface of the 0.3 cm diameter catalyst pellet in each microreactor. The uniformity of gas flow rates in each channel was checked by passing smoke through the reactor array and by measuring the lengths of the smoke plume jets emanated from each channel. These studies indicated that gas flow rates were approximately the same in each channel.

The supported multimetallic catalyst formulations were prepared by using the conventional co-impregnation method, in which porous alumina pellets were immersed into the aqueous solutions of catalyst precursors at different concentrations. Pellets were prepared by compacting 30 mg of high surface area γ-Al_2O_3 powder (Alfa Aesar, Ward Hill MA, 150 $m^2 g^{-1}$) into a cylindrical shape (0.3 cm diameter and 0.1 cm height) using a die. These pellet dimensions allow for easy scale up of newly discovered and/or optimized catalysts for commercial applications. This is in contrast to much smaller scale microreactors proposed by other investigators,[14] which can possess significant scale up problems. Metal precursor stock solutions of Pt, Pd, and In were prepared from high purity H_2PtCl_6, $PdCl_2$, $InCl_2$, and aqueous HCl (Alfa Aesar, Ward Hill MA). The catalyst precursor solution library was prepared automatically by mixing predetermined volumes of different catalyst precursor solutions into individually addressable test tubes in an array using a computer-controlled x,y,z translation table and a high accuracy liquid delivery system. The system utilizes stepper motor controlled syringe pumps and micro solenoid valves to dispense aqueous solutions within 10 nL accuracy. Following the dispensation of catalyst precursor solutions, deionized water was jetted into each test tube to induce further mixing and to render the final volume to be 50 μL.

Alumina pellets added to each test tube were allowed to impregnate under the competition of HCl in solution for 24 h in order to attain homogeneous metal distribution within the particles. Subsequently, the solutions were evaporated and the pellets were dried first at 90 °C for 4 h then at 120 °C for 4 h. Finally, the impregnated pellet library was calcined at 500 °C for 2 h and cooled down to ambient temperature in the furnace. The catalyst library consisted of 66 ternary combinations of Pt, Pd, and In in 0.1 % wt increments of each with 1 wt % total metal loading on alumina support. In addition, the final chlorine content of the pellets was also kept at about 1 %. The compositions of the 66 pellets prepared are shown in Figure 2. All the catalyst pellets were prepared and processed in an identical manner without any human intervention.

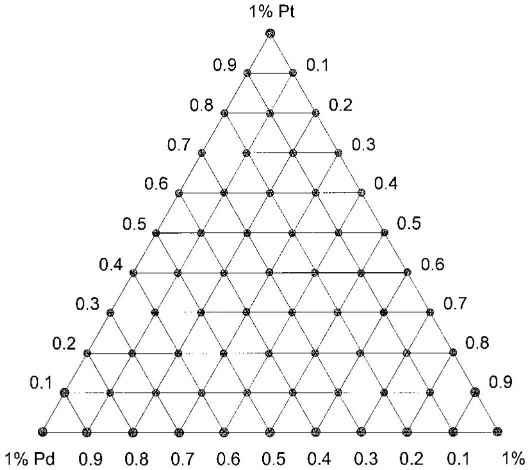

Figure 2. Compositions of the 66 Pt/Pd/In ternary catalyst combinations investigated (1 % wt total metal on 30 mg gamma alumina pellet in 0.1 % increments).

The catalysts were tested by using the following procedure: After the placement of new catalyst pellets into the wells of the array microreactor, the system was heated to 350 °C under helium flow. A blank alumina pellet was always placed into the central microreactor (9th well from either side) in all experiments to serve as an internal reference standard. After the temperature had reached 350 °C, the helium flow was switched to pure hydrogen for 2 h to reduce the platinum, palladium, and indium chlorides into metallic form. Following the catalyst reduction step, the reactor temperature was decreased to 300 °C again under helium gas flow. Once the proper operating temperature was reached, cyclohexane feed was introduced. With the existing array microreactor system, this procedure had to be repeated five times to screen the entire library of 66 catalysts. Additional experiments were also undertaken to check the reproducibility of the measurements, including the placement of catalyst pellets at different locations in the array microreactor and duplicate preparation and testing of different combinations. All these studies resulted in similar results within the limits of accuracy of the measurements (i.e. ±15%).

All the catalysts were subjected to an identical pretreatment (i.e. reduction) process before screening in order to standardize the initial conditions. This way the activities of the catalysts can be compared to one another having been on-stream the same time period, thereby minimizing complications related to catalyst deactivation, poisoning etc. In addition, visual inspection of the pellets immediately after the reduction steps also revealed a uniform catalyst metal distribution across the pellet.

The screening protocol demands the unambiguous detection of benzene in a cyclohexane, hydrogen, and helium background, as well as other reaction by-products. In order to accomplish this goal using the REMPI technique one must identify a suitable UV laser wavelength that selectively produces benzene REMPI ions. One such wavelength was identified to be 259.6 nm in our previous studies using time-of-flight mass spectrometry (TOF-MS).[13] At this wavelength, the first photon energizes the benzene molecule to an excited electronic state, P* [Eq. (1)], and the second photon ionizes this intermediate state [Eq. (2)].

$$C_6H_6 + h\nu \rightarrow C_6H_6^* \quad (1)$$

$$C_6H_6^* + h\nu \rightarrow C_6H_6^+ + e^- \quad (2)$$

In the present work, the reactor exhaust gases were also analyzed by TOF-MS using the same 259.6 nm laser light to find out if species other than benzene could have contributed to the signals measured by the microelectrodes.[15] No photoions, other than those with mass 78, were detected by TOF-MS. The laser light in the experiments was obtained by frequency doubling the output of a dye laser (Laser Analytical Systems, LDL 2051) using a second harmonic generator (BBO I). The dye laser was pumped by an excimer laser (Lambda Physik, Compex 102). The energy of the laser beam was maintained at about 300 μJ per pulse during the entire screening process.

The pulsed UV laser light was passed through the optical access windows of the heating block and the ceramic slab, simultaneously crossing the exhaust streams of all the microreactors. The laser beam also passed between the dedicated microelectrodes that were embedded into the top and bottom ceramic slabs (Figure 1). The microelectrodes were made from 0.1 mm diameter steel wires and their tips were flush with the ceramic slab surfaces. This design significantly simplified the process of alignment and calibration of the microelectrodes and the laser beam between catalyst changes and thus improved the speed and accuracy of the catalyst screening process. Multichannel switches were used to individually apply 100 V DC power to each microelectrode sequentially (Stanford Research Systems, PS 350). REMPI signals were detected by using a digital oscilloscope (Hewlett-Packard 54540C). The screening of the catalysts in the array microreactor took two to three minutes.

Figure 3 shows the bar chart of benzene REMPI signals (voltage E in mV) as measured by the oscilloscope for each catalyst (66 total). These measurements correspond to an average of 10 laser shots. Signal-to-noise ratios were better than 20 throughout the entire screening process. As evident from Figure 3, both Pt and Pd individually exhibited catalytic activities, with Pt being more active than Pd. On the other hand In was not catalytically active for benzene production from cyclohexane. These results are in complete agreement with the previous measurements reported by other investigators.[16, 17]

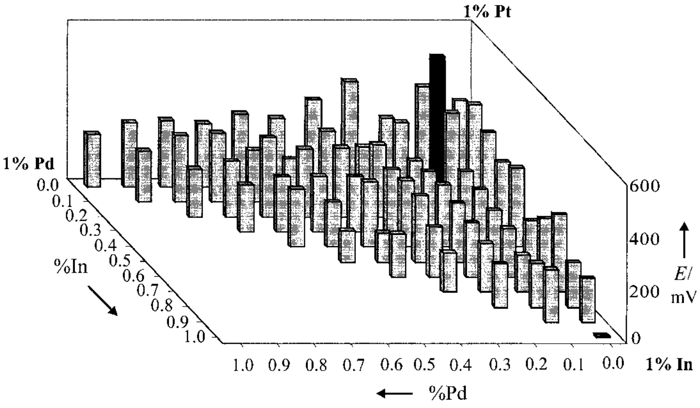

Figure 3. Array microreactor screening results for the ternary Pt/Pd/In catalyst combinations (bar chart for the activities (voltage of measured REMPI signals) plotted against catalyst composition).

The reproduction of the reactivity trends of individual metals is important in generating confidence with regard to the suitability of the system developed for the intended catalyst screening studies. As seen in Figure 3, we also made the significant discovery that a ternary mixture (0.8% Pt, 0.1% Pd, and 0.1% In) exhibited the best benzene productivity of all the metal combinations investigated. These results demonstrate the feasibility of using array microreactors coupled with REMPI screening for the discovery and optimization of heterogeneous catalysts.

In Table 1 the approximate times associated with the execution of each step in the preparation, processing, and screening of the catalyst library are given. As noted earlier, the present array microreactor accommodates a total of 17 catalyst pellets. Consequently, the complete testing of the

Table 1. Time elements associated with the preparation, processing, and screening of catalysts.

Operation	t [h]
Library preparation	
preparation of precursor solutions	0.50
preparation of solution library	0.25
impregnation of pellets	24.00
drying	8.00
calcining (Including heating and cooling)	6.00
total catalyst preparation time	38.00
Library screening (16 pellets per cycle)	
catalyst reduction (Including heating and cooling)	3.50
REMPI screening	0.03
cooling and replacement	1.00
cycle time	4.53
total catalyst screening time (cycle time ×5)	22.65
Total time to discovery and optimization	60.65 or 2.5 days

entire library of 66 catalysts involved five sequential runs. As shown in Table 1 the preparation and screening of the Pt/Pd/In ternary catalyst library took about 2.5 days to complete. Although this represents a significant advance over conventional methods, which may take months to achieve the same objectives, further acceleration of the overall process is clearly possible. For example, increasing the number of microreactors in each array, that is increasing the level of parallel processing, and decreasing the times for impregnation, drying, calcination, and reduction can significantly speed up the process. However, the latter issues must be carefully implemented as even minor modifications in catalyst preparation methods can dramatically alter the performance of the catalysts. On the other hand, the minimization of catalyst preparation times can be the objective of a combinatorial study such as that described here.

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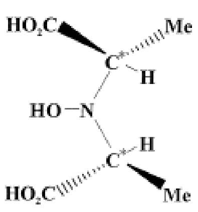
The Structural Characterization of Amavadin**

Robert E. Berry, Elaine M. Armstrong,
Roy L. Beddoes, David Collison, S. Nigar Ertok,
Madeleine Helliwell, and C. David Garner*

One fascinating aspect of bioinorganic chemistry is that of metal accumulation by living organisms, for example, to provide an appropriate concentration for the use of the metal in one or more specific biochemical functions and/or as a means of protection against toxicity that arises from an excess of metal. A striking example of metal accumulation is provided by three species of *Amanita* mushrooms: *A. muscaria*, the "fly agaric"; *A. regalis*; and *A. velatipes*. Each species concentrates vanadium to levels of up to 400 times those typically found in plants. Studies by Ter Meulen,[1] Bertrand,[2, 3] and Meisch et al.[4] have shown that the accumulation of vanadium by these species of *Amanita* is independent of the age of the mushrooms, unrelated to the vanadium content of the soil, and essentially equally distributed between the stem, skin, and cap.

In 1972 Bayer and Kneifel[5] isolated a blue, vanadium-containing compound from *A. muscaria* collected in the Black Forest. They named this compound "amavadin" and showed that it is constituted as a 1:2 complex of vanadium and the pro-ligand (*S*,*S*)-2,2′-(hydroxyimino)dipropionic acid ((*S*,*S*)-hidpaH$_3$).[6] Further studies[7–10] led to the proposal that the vanadium center of amavadin exists as an eight-coordinate, non-oxo complex with a novel structure. Herein, we report confirmation of this postulate by X-ray crystallographic determinations on a sample of amavadin crystallized as a phosphoric acid derivative;[11] and as the salt **1** with Ca^{2+} countercations.[12]



(*S*, *S*)-hidpaH$_3$

$[Ca(H_2O)_5][\Delta\text{-}V((S,S)\text{-hidpa})_2]\cdot 2\,H_2O$ **1**

The use of Ca^{2+} counterions to crystallize amavadin proved valuable in obtaining good quality crystals for X-ray diffraction analysis, as demonstrated previously for related chemical systems.[13] The lattice of **1** is comprised of $[Ca(H_2O)_5]^{2+}$ and $[\Delta\text{-}V((S,S)\text{-hidpa})_2]^{2-}$ ions that are linked in the form of infinite chains; a portion of a chain is shown in Figure 1. Each anion is bound by two Ca^{2+} ions through a carboxylate group

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[*] Prof. C. D. Garner, R. E. Berry, Dr. E. M. Armstrong, R. L. Beddoes, Dr. D. Collison, Dr. M. Helliwell
Department of Chemistry, University of Manchester
Manchester, M13 9PL (UK)
Fax: (+44) 161-275-4616
E-mail: dave.garner@man.ac.uk

Dr. S. N. Ertok
Ege Üniversitesi, Fen Facültesi Dekanligi
Kimya Bölümü (Turkey)

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