plane through this carbon atom, whereas the other set H*i*10, H*i*30 is split into two doublets (6.20 ppm, $J = 15.7$ Hz; 4.78 ppm, $J = 15.8$ Hz) due to their nonequivalent positions and geminal $H_A,H_B$ coupling.

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**Supplementary Material Available:** Tables SI–SIV, listing details of the crystal data collection, anisotropic thermal parameters, positional parameters for the hydrogen atoms, distances, and angles, a packing diagram, and a UV–vis spectrum (6 pages); a listing of observed and calculated structure amplitudes (54 pages). Ordering information is given on any current masthead page.

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# Structure and Properties of Bis(D-penicillaminato-*N*,*S*)nickelate(II) Tetrahydrate: A Monomeric Nickel Complex of D-Penicillamine, the Antidote for Nickel Toxicity

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## Introduction

For some time D-penicillamine (D-$H_2$Pen)[1] has been in use for removing excess copper from patients with Wilson's disease.[2,3] In recent years, D-$H_2$Pen has also afforded promising results in the treatment of acute intoxication with other metals, especially nickel.[4–7] We report here the structure and spectral parameters of a genuine $[NiL_2]^{2-}$ complex of D-$H_2$Pen formed under the condition of excess drug (therapeutic level). In addition, the structural features of this complex, namely potassium bis(D-penicillaminato-*N*,*S*)nickelate(II) tetrahydrate (**1**) are compared with those of potassium bis(L-cysteinato-*N*,*S*)nickelate(II) sesquihydrate (**2**), recently reported by this group.[8] Since (a) solution studies by us as well as other groups[9–15] have demonstrated the existence of only the $[NiL_2]^{2-}$ species and (b) the complex **1** is extremely stable in aqueous and saline solutions in the pH range 6–10, it is quite possible that excess nickel is excreted from the body in this form.[16]

## Experimental Section

**Preparation of Compounds.** D-Penicillamine was purchased from Aldrich Chemical Co. In the following preparation, all manipulations were performed under a pure dinitrogen atmosphere.

**$K_2[Ni(SC(CH_3)_2CH(NH_2)COO)_2]\cdot 4H_2O$ (1).** To a solution of dipotassium D-penicillaminate ($KSC(CH_3)_2CH(NH_2)COOK$), prepared from 1.0 g (6.7 mmol) of D-$H_2$Pen and 0.75 g (13.4 mmol) of KOH in 25 mL of 1-butanol, was added with stirring a solution of 0.4 g (1.68 mmol) of $NiCl_2\cdot 6H_2O$ in 20 mL of 3:1 1-butanol/methanol when a cloudy red solution was obtained. After 1 h of stirring, the reaction mixture was filtered to remove KCl. Next, the filtrate was heated to 50 °C and 0.5 mL of water was added to it. The clear red solution was then allowed to slowly cool and stand at room temperature for 24 h. The red crystals thus obtained were collected by filtration and dried under dinitrogen. Yield: 0.65 g (73%). Selected IR bands (KBr pellet, $cm^{-1}$): 3400 (s, br), 3200 (s), 2960 (s), 1595 (s), 1577 (s), 1400 (s), 1360 (s), 1135 (m), 1050 (m), 930 (m), 790 (m). Anal. Calcd for $C_{10}H_{26}N_2O_8S_2K_2Ni$: C, 23.84; H, 5.21; N, 5.56. Found: C, 23.71; H, 5.23; N, 5.70.

**Table I.** Summary of Crystal Data, Intensity Collection, and Structure Refinement Parameters for $K_2[Ni(SC(CH_3)_2CH(NH_2)COO)_2]\cdot 4H_2O$ (**1**)

| | | | |
|---|---|---|---|
| formula (mol wt) | $C_{10}H_{26}N_2O_8S_2K_2Ni$ (503.26) | $\beta$, deg | 117.50 (3) |
| | | $V$, Å$^3$ | 2139.7 (14) |
| $T$, K | 130 | $Z$ | 4 |
| cryst syst | monoclinic | $d_{calcd}$, g cm$^{-3}$ | 1.57 |
| space group | $P2_1$ | abs coeff, $\mu$, cm$^{-1}$ | 15.20 |
| $a$, Å | 10.949 (3) | | |
| $b$, Å | 19.292 (7) | $R^a$ | 6.48 |
| $c$, Å | 11.420 (5) | $R_w{}^b$ | 6.84 |

[a] $R = (\sum||F_o - F_c||)/\sum|F_o|$. [b] $R_w = \{[\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2\}^{1/2}$.

**Physical Measurements.** Infrared spectra were obtained with a Perkin-Elmer 1600 FTIR spectrometer. Absorption spectra were monitored on a Perkin-Elmer Lambda 9 spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were recorded on a General Electric GN-300 (300 MHz) instrument. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA.

**X-ray Data Collection, Structure Solution, and Refinement.** Dark red blocks were obtained from a solution of **1** in moist butanol. Diffraction experiments were performed on a Siemens R3m/V machine equipped with graphite monochromator and a modified LT-1 low-temperature apparatus. Mo K$\alpha$ radiation was employed. The intensities of two standard reflections, recorded after every 198 reflections, remained unchanged during the period of data collection. The structure was solved by direct methods (SHELXTL PLUS (VMS)). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions, and a riding model was used with fixed isotropic thermal parameters. A total of 4479 reflections with $F > 4\sigma(F)$ were used in the refinement (full-matrix least squares), and the data were corrected for absorption effects by the use of the program XABS.[17]

Machine parameters, crystal data, and data collection parameters are summarized in Table I. Positional parameters are listed in Table II, while selected bond distances and angles are collected in Table III. The rest of the crystallographic data have been submitted as supplementary material.

## Results and Discussion

Cysteine[8,10,13,14] and other S-containing ligands[18] form $[NiL_2]^{2-}$ type of complexes with bivalent nickel in the presence of large excess of L—at lower L:$Ni^{2+}$ ratios, the propensity of thiolato

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0020-1669/91/1330-3967$02.50/0

**Table II.** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **1**

| | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Ni(1) | 4167 (1) | −782 (1) | 3282 (1) | 16 (1) |
| S(1) | 3599 (3) | −1699 (1) | 2066 (3) | 20 (1) |
| S(2) | 6308 (3) | −1050 (2) | 4097 (3) | 22 (1) |
| N(1) | 2209 (8) | −560 (5) | 2551 (9) | 19 (3) |
| N(2) | 4680 (9) | 47 (5) | 4381 (9) | 21 (3) |
| O(1) | −355 (7) | −206 (4) | 520 (8) | 27 (3) |
| O(2) | −1203 (8) | −1228 (4) | 714 (8) | 28 (3) |
| O(3) | 7553 (8) | 1116 (4) | 6499 (9) | 29 (3) |
| O(4) | 5741 (9) | 754 (4) | 6710 (8) | 28 (3) |
| C(1) | 1824 (11) | −1462 (5) | 896 (10) | 22 (4) |
| C(2) | 1239 (10) | −1112 (5) | 1713 (10) | 21 (4) |
| C(3) | 1063 (12) | −2139 (6) | 304 (13) | 33 (5) |
| C(4) | 1828 (12) | −974 (7) | −174 (11) | 28 (4) |
| C(5) | −238 (9) | −822 (6) | 899 (10) | 18 (3) |
| C(6) | 7026 (11) | −447 (6) | 5534 (10) | 25 (4) |
| C(7) | 6154 (10) | 226 (5) | 5036 (10) | 19 (3) |
| C(8) | 6883 (13) | −785 (7) | 6676 (11) | 32 (4) |
| C(9) | 8515 (12) | −333 (7) | 5906 (14) | 37 (5) |
| C(10) | 6501 (9) | 745 (5) | 6175 (10) | 18 (3) |
| Ni(2) | 4460 (1) | 2134 (1) | 3944 (1) | 16 (1) |
| S(3) | 2566 (3) | 1621 (2) | 2623 (2) | 24 (1) |
| S(4) | 4912 (3) | 2339 (2) | 2327 (2) | 23 (1) |
| N(3) | 3943 (8) | 2030 (5) | 5352 (8) | 18 (3) |
| N(4) | 6249 (8) | 2496 (5) | 5133 (8) | 18 (3) |
| O(5) | 1918 (10) | 980 (4) | 6377 (10) | 39 (4) |
| O(6) | 2341 (8) | 2098 (4) | 6667 (7) | 26 (3) |
| O(7) | 9113 (7) | 2642 (4) | 6294 (8) | 25 (3) |
| O(8) | 8876 (8) | 3656 (4) | 5303 (8) | 32 (3) |
| C(11) | 1653 (9) | 1670 (5) | 3670 (10) | 18 (3) |
| C(12) | 2781 (9) | 1532 (5) | 5041 (10) | 18 (3) |
| C(13) | 562 (10) | 1117 (7) | 3191 (12) | 28 (4) |
| C(14) | 1026 (11) | 2396 (6) | 3523 (11) | 24 (4) |
| C(15) | 2306 (9) | 1545 (6) | 6129 (9) | 18 (3) |
| C(16) | 6751 (10) | 2542 (6) | 3246 (10) | 21 (4) |
| C(17) | 6932 (10) | 2923 (5) | 4515 (10) | 19 (3) |
| C(18) | 7558 (11) | 1853 (6) | 3563 (11) | 27 (4) |
| C(19) | 7141 (12) | 3002 (7) | 2392 (11) | 29 (4) |
| C(20) | 8442 (10) | 3086 (6) | 5437 (10) | 21 (4) |
| K(1) | 4689 (3) | 92 (2) | 8125 (3) | 33 (1) |
| K(2) | 14064 (3) | 1952 (2) | 9308 (2) | 29 (1) |
| K(3) | 11562 (2) | 3370 (1) | 6987 (2) | 24 (1) |
| K(4) | 10145 (2) | 1458 (1) | 7367 (2) | 22 (1) |
| O(9) | 16164 (10) | 1619 (5) | 8719 (10) | 43 (4) |
| O(10) | 13618 (12) | 600 (6) | 9757 (11) | 31 (5) |
| O(11) | 6041 (8) | −1116 (5) | 8944 (8) | 30 (3) |
| O(12) | 2710 (9) | −232 (4) | 5634 (10) | 37 (4) |
| O(13) | 11079 (10) | 748 (5) | 9816 (10) | 38 (4) |
| O(14) | 14158 (8) | 3320 (5) | 8983 (8) | 31 (3) |
| O(15) | 11737 (8) | 2345 (4) | 9517 (7) | 25 (3) |
| O(16) | 7285 (10) | 402 (6) | 10257 (12) | 51 (5) |
| O(17) | 6080 | 187 | 11905 | 18 (5) |
| C(21) | 4557 | 440 | 11081 | 19 (8) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table III.** Selected Bond Distances and Angles for **1**

| | | | |
|---|---|---|---|
| | Bond Lengths (Å) | | |
| Ni(1)–S(1) | 2.155 (3) | Ni(1)–S(2) | 2.147 (3) |
| Ni(1)–N(1) | 1.956 (9) | Ni(1)–N(2) | 1.949 (9) |
| S(1)–C(1) | 1.837 (10) | S(2)–C(6) | 1.863 (11) |
| S(2)–K(3b) | 3.300 (5) | N(1)–C(2) | 1.497 (12) |
| N(2)–C(7) | 1.472 (13) | O(1)–C(5) | 1.251 (14) |
| O(2)–C(5) | 1.252 (13) | O(2)–K(3c) | 2.933 (11) |
| O(3)–C(10) | 1.258 (13) | O(3)–K(4) | 2.621 (8) |
| O(4)–C(10) | 1.239 (17) | O(4)–K(1) | 2.700 (11) |
| C(1)–C(2) | 1.513 (19) | C(1)–C(3) | 1.527 (15) |
| C(1)–C(4) | 1.545 (18) | C(6)–C(7) | 1.556 (14) |
| Ni(2)–S(3) | 2.161 (3) | Ni(2)–S(4) | 2.158 (4) |
| Ni(2)–N(3) | 1.946 (11) | Ni(2)–N(4) | 1.926 (7) |
| S(3)–C(11) | 1.882 (13) | S(4)–C(16) | 1.832 (10) |
| S(4)–K(2a) | 3.218 (4) | N(3)–C(12) | 1.500 (13) |
| O(5)–C(15) | 1.248 (15) | O(5)–K(4d) | 2.814 (14) |
| O(6)–K(2d) | 2.734 (7) | O(6)–K(3d) | 2.678 (9) |
| O(6)–K(4d) | 3.118 (10) | O(7)–K(3) | 2.799 (8) |
| O(7)–K(4) | 2.592 (8) | O(8)–K(3) | 2.726 (7) |
| K(2)–O(9) | 2.753 (13) | K(2)–O(10) | 2.746 (12) |
| | Bond Angles, deg | | |
| S(1)–Ni(1)–S(2) | 90.8 (1) | S(1)–Ni(1)–N(1) | 88.4 (3) |
| S(2)–Ni(1)–N(1) | 178.6 (3) | S(1)–Ni(1)–N(2) | 180.0 (4) |
| S(2)–Ni(1)–N(2) | 89.2 (3) | N(1)–Ni(1)–N(2) | 91.6 (4) |
| Ni(1)–S(1)–C(1) | 99.1 (4) | Ni(1)–S(2)–C(6) | 99.4 (4) |
| Ni(1)–S(2)–K(3a) | 137.5 (1) | C(6)–S(2)–K(3a) | 117.3 (4) |
| Ni(1)–N(1)–C(2) | 115.5 (7) | Ni(1)–N(2)–C(7) | 116.2 (8) |
| S(1)–C(1)–C(2) | 105.6 (6) | S(1)–C(1)–C(4) | 109.8 (8) |
| C(3)–C(1)–C(4) | 111.8 (9) | N(1)–C(2)–C(1) | 109.6 (10) |
| N(1)–C(2)–C(5) | 111.2 (8) | C(1)–C(2)–C(5) | 114.4 (8) |
| O(1)–C(5)–O(2) | 126.3 (8) | O(1)–C(5)–C(2) | 117.5 (9) |
| S(3)–Ni(2)–S(4) | 90.7 (1) | S(3)–Ni(2)–N(3) | 88.7 (2) |
| S(4)–Ni(2)–N(3) | 174.5 (3) | S(3)–Ni(2)–N(4) | 173.7 (3) |
| S(4)–Ni(2)–N(4) | 88.6 (3) | N(3)–Ni(2)–N(4) | 92.5 (4) |
| Ni(2)–S(3)–C(11) | 98.8 (3) | Ni(2)–S(4)–C(16) | 100.1 (4) |
| Ni(2)–S(4)–K(2a) | 143.9 (1) | C(16)–S(4)–K(2a) | 111.1 (4) |
| Ni(2)–N(3)–C(12) | 114.2 (7) | Ni(2)–N(4)–C(17) | 115.8 (6) |

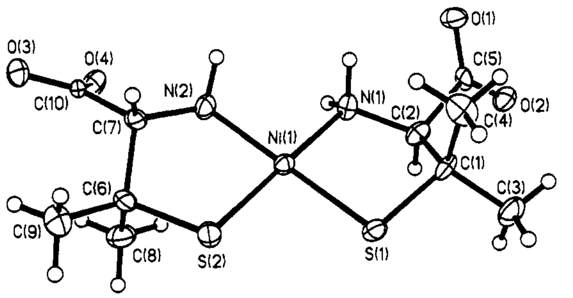

**Figure 1.** Thermal ellipsoid plot at the 50% probability level of one of the two anions of **1** in the asymmetric unit. Hydrogen atoms are given an arbitrary size.

sulfur to form bridges between metal centers gives rise to multinuclear species of the type $[Ni_xL_y]^{n-}$. Even when isolated $[NiL_2]^{2-}$ complexes with such ligands are dissolved in protic or aprotic solvents, $[Ni_xL_y]^{n-}$ species are rapidly formed in solution due to the same reason. In contrast, the reaction between $Ni^{2+}$ and D-$H_2$Pen (which is $\beta,\beta$-dimethylcysteine) is clean[9-11] and exclusively affords $[NiL_2]^{2-}$ in the pH range 5–10. Clearly, the presence of the two methyl groups on the $\beta$-carbon prevents the bridge formation by the thiolato sulfur atoms.[19] Though several groups have reported the formation and some spectral parameters of the bis(D-penicilaminato)nickelate(II) anion, prior to this work, neither has the complex been isolated in pure crystalline state nor has its structure been determined. The synthetic procedure described above provides $K_2[Ni(D\text{-}Pen)_2]\cdot 4H_2O$ (**1**) in high yield.

**Structure of $K_2[Ni(SC(CH_3)_2CH(NH_2)COO)_2]\cdot 4H_2O$ (1).** The crystal structure consists of $K^+$ ions, two independent but very similar types of anions (there are two of each type in the asymmetric unit), and water molecules. The $K^+$ ions strongly interact with several oxygen atoms (distance range 2.592 (8)–2.814 (14) Å) from the carboxylate groups of D-penicilaminate (D-$Pen^{2-}$) and the water molecules. Additional bonding interaction is present between each $K^+$ and at least one S atom (average distance 3.3 Å). In these regards, the structure of **1** is closely related to potassium bis(L-cysteinato-*N*,*S*)nickelate(II) sesquihydrate (**2**).[8] A computer-generated thermal ellipsoid plot of one of the two essentially similar anions is shown in Figure 1. Plots of the two anions with the $K^+$–oxygen interaction network are included in the supplementary material.

The geometry of the coordination sphere of nickel in **1** is square planar with the two thiolato S and two amine N atoms of the two D-$Pen^{2-}$ ligands bonded to the metal center (Figure 1). The average Ni(II)–S and Ni(II)–N distances (2.155 (3) and 1.944 (9) Å) are within the range observed in the nickel(II) complexes of $\beta$-mercaptoethylamine,[21] cysteine,[8] and *N*,*N*-dimethyl-$\beta$-

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[19] Polynuclear complexes of $Ni^{2+}$ with cysteine, $\beta$-mercaptopropionic acid,[20] and $\beta$-mercaptoethylamine[21] are all reported.

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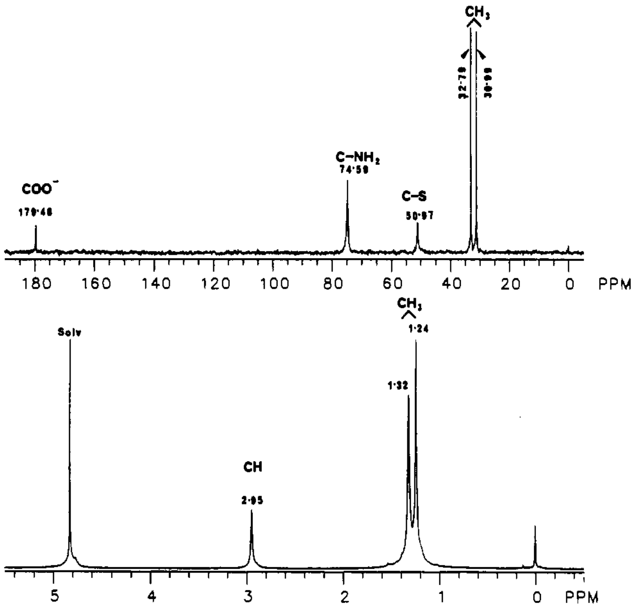

**Figure 2.** $^{13}C$ (top trace) and $^1H$ (bottom trace) NMR spectra (300 MHz, 293 K) of **1** in $D_2O$ (pD = 10.4). The chemical shift values from TSP are indicated.

mercaptoethylamine.[22] The most unusual feature of the structure of the anion (Figure 1) is the cis disposition of the two D-Pen$^{2-}$ ligands despite the presence of the two $CH_3$ groups on the $\beta$-carbon atom of the ligand. On steric grounds, a trans geometry is clearly the preferred one.[23] In **2**, the two L-cysteinate ligands are trans to each other.[8] The cis geometry of D-Pen$^{2-}$ ligands is also found in the tetranuclear heterometallic anion $[Au^I_2Ni^{II}_2(SC(CH_3)_2CH(NH_2)COO)_4]^{2-}$ (**3**).[24] That coordination to the Au(I) centers is not the reason for the cis geometry of the D-Pen$^2$ ligands in **3** is evident from the present result—in **1**, the two D-Pen$^{2-}$ ligands are cis to each other even though no bridge formation occurs. Another interesting aspect of the structure of **1** is the occurrence of the two carboxylate groups of the D-Pen$^{2-}$ ligands on the same side of the mean coordination plane (Figure 1). This feature is also observed in the structures of **2**[8] and **3**.[24] Presumably, this arrangement of the carboxylate groups allows better coordination to $K^+$ ions as well as effective H-bonding in the crystal lattice. The bond angles (Table III) and other metric parameters of the chelate rings in **1** are unexceptional.

**Properties.** The IR spectrum of **1** exhibits no band in the region 2600–2500 cm$^{-1}$, indicating coordination of the ligand as thiolate. That the carboxylate group of D-Pen$^{2-}$ is not involved in coordination to nickel is suggested by the appearance of the antisymmetric and symmetric $\nu(COO^-)$ at 1595 and 1400 cm$^{-1}$, respectively.[8] The red color of the aqueous solution of **1** arises from a band at 462 nm ($\epsilon$ = 126 M$^{-1}$ cm$^{-1}$) with a shoulder at 560 nm ($\epsilon$ = 45 M$^{-1}$ cm$^{-1}$). In addition, the electronic absorption spectrum of **1** exhibits two strong charge-transfer bands with maxima at 312 nm (3100 M$^{-1}$ cm$^{-1}$) and 270 nm (14000 M$^{-1}$ cm$^{-1}$). Several groups[10-12] have generated the $[Ni(D\text{-}Pen)_2]^{2-}$ ion in aqueous solution and recorded the absorption spectrum in the visible region. We report the entire spectrum here for the first time. The features at 560 and 462 nm have been tentatively assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively, by another group.[11] The $^1H$ and $^{13}C$ NMR spectra of **1** in $D_2O$ are shown in Figure 2. Assignments of the various peaks rely on area integration, APT data,[25] and the proton-coupled spectra. The clean and simple spectra confirm the stability of **1** in aqueous solution.

In conclusion, comment must be made on the unusual stability of the $[Ni(D\text{-}Pen)_2]^{2-}$ anion in relation to the role of D-$H_2$Pen as an antidote for acute nickel toxicity. Unlike most square-planar thiolato complexes of nickel, **1** in aqueous (pH 6–10), saline, or urine (pH 7.2) solution is stable over long periods of time. These solutions are quite resistant to air oxidation.[26] In fact, complex **1** is formed under aerobic conditions as well. When $Ni^{2+}$ is mixed with excess (>4 equiv) D-$H_2$Pen in water (pH 8),[27] the characteristic red color is rapidly developed and the extinction coefficient of the 462-nm band reaches its maximum value of 125 within 1 min. No change in the absorption spectrum is noted over the next 24 h. The same result is obtained when the reaction mixture contains an equivalent amount of albumin.[28] It is known that the major $Ni^{2+}$-binding substance in human blood is albumin.[7] Thus, serum nickel can be extracted with excess D-$H_2$Pen and complex **1** is expected to be the product of this reaction. It therefore appears that chemotherapy with high doses of D-$H_2$Pen could remove nickel in the form of the bis complex $[Ni(D\text{-}Pen)_2]^{2-}$.

**Acknowledgment.** We wish to acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

**Supplementary Material Available:** Computer-generated drawings of the two independent anions of **1** showing the $K^+$–oxygen atom interactions and H-bonding by the water molecules and complete tables of crystal data, bond distances, bond angles, anisotropic displacement coefficients, and the H atom coordinates (8 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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(26) The extinction of the visible band shows less than 2% decomposition over 24 h. No decomposition is observed when the aqueous solution (pH ~7) contains 2–3 equiv of D-$H_2$Pen. The stability constant (log $\beta_2$) of $[Ni(D\text{-}Pen)_2]^{2-}$ has been determined in aqueous solution. The value of log $\beta_2$ is 22.88 ± 0.14.[9-11,13]

(27) The p$K_a$'s for the –COOH, –SH, and –$NH_2$ groups of D-$H_2$Pen are 1.99–2.00, 8.1, and 10.6, respectively.[11]

(28) In this experiment, $Ni^{2+}$ was preincubated with an equivalent amount of albumin (24 h) before it was mixed with D-$K_2$Pen solution.

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## A New Material with Alternating Metal–Oxide and Metal–Phosphide Layers: $Ba_2Mn_3P_2O_2$

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With the discovery of high-temperature superconductors, there is a renewed interest in complex layered metal–oxide compounds.[1] In addition, there is a significant amount of interest in two-dimensional compounds due to their anisotropic physical properties. Our interest in the synthesis and properties of ternary transition-metal pnictide compounds[2] prompted our investigation of the synthesis and characterization of the novel layered oxide–pnictide compounds: $A_2Mn_3X_2O_2$ (A = Sr, Ba; X = As, Sb, Bi).[3] Although the single-crystal structure of these compounds has been reported, no other physical characterizations have been performed. We have successfully modified the reaction procedure to produce pure materials for physical property measurements. In addition, the new compound $Ba_2Mn_3P_2O_2$ has been synthesized in high yield. This new compound is isostructural with the heavier group 15 (group VA) element analogues and has a unique two-dimensional structure with alternating metal–oxide and metal–phosphide layers separated by alkaline-earth-metal cations. This is one of the few examples of a solid-state compound that contains both oxygen and phosphorus atoms without direct bonding between them.[4]

The structure for these compounds is shown in Figure 1. They crystallize in the tetragonal system, *I*4/*mmm* (*Z* = 2). Manganese

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