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Chiral Polyoxotungstates. 1. Stereoselective Interaction of Amino Acids with Enantiomers of $[Ce^{III}(\alpha_1\text{-}P_2W_{17}O_{61})(H_2O)_x]^{7-}$. The Structure of DL-$[Ce_2(H_2O)_8(P_2W_{17}O_{61})_2]^{14-}$

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The ammonium salt of the 1:1complex (**1**) of Ce(III) with α_1-$[P_2W_{17}O_{61}]^{10-}$ was prepared and characterized by elemental analysis, vibrational and NMR spectroscopy (^{31}P, ^{183}W), cyclic voltammetry, and single-crystal X-ray analysis ($P\bar{1}$; $a = 15.8523(9)$ Å, $b = 17.4382(10)$ Å, $c = 29.3322(16)$ Å, $\alpha = 99.617(1)°$, $\beta = 105.450\ (1)°$, $\gamma = 101.132(1)°$, $V = 7460.9(7)$ Å^3, $Z = 2$). The anion consists of a centrosymmetric head-to-head dimer, $[\{Ce(H_2O)_4(P_2W_{17}O_{61})\}_2]$,$^{14-}$ with each 9-coordinate Ce cation linked to four oxygens of one tungstophosphate anion and to one oxygen of the other anion. On the basis of P NMR spectroscopy, a monomer−dimer equilibrium exists in solution with $K = 20 \pm 4$ M^{-1} at 22 °C. Addition of chiral amino acids to aqueous solutions of **1** results in splitting of the ^{31}P NMR signals as a result of diastereomer formation. No such splitting is observed with glycine or DL-proline, or when chiral amino acids are added to the corresponding complex of the achiral α_2-isomer of $[P_2W_{17}O_{61}]^{10-}$. From analysis of the ^{31}P NMR spectra, formation constants of the two diastereomeric adducts of **1** with L-proline are 7.3 ± 1.3 and 9.8 ± 1.4 M^{-1}.

Introduction

Polyoxometalates attract considerable attention because of their catalytic and biomedical applications.[1] In both of these areas it would be desirable to have chiral polyoxometalates, since chiral selectivity in catalysis is a major goal, and much biological activity involves chiral recognition. Although there are several readily accessible polyoxometalates with chiral structures,[2] there have been few studies that have focused on this aspect,[3] since many of these structures undergo rapid racemization via water exchange, partial hydrolysis, or as a result of fluxional behavior. Chirality that results from "substitution" of metal atoms into otherwise achiral parent structures, such as α_1-$[P_2W_{17}O_{61}Co(H_2O)]^{8-}$,[4] or the 1,5-isomer of $[PMo_{10}V_2O_{40}]^{5-}$,[5] is so subtle that it has not yet been possible to discriminate between enantiomers in solution, let alone to devise methods of resolution. In view of the considerable emphasis on the catalytic and stoichiometric reactivity of such "mixed metal" polyoxometalates in recent years,[6] we believe that efforts to effect partial or complete resolution of their enantiomers are of great importance.

We report here the interaction of amino acids with the 1:1 complexes of Ce(III) and α_1-$[P_2W_{17}O_{61}]^{10-}$. In contrast to complexes with transition metal cations, which bear a single terminal ligand as in α_1-$[P_2W_{17}O_{61}Co(H_2O)]^{8-}$, the larger lanthanide cations offer additional coordination sites. This often can lead to supramolecular assembly of such complexes.[7,8] In

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(2) (a) Strandberg. R. *Acta Chem. Scand.* **1973**, *27*, 1004. Pope, M. T. *Inorg. Chem.* **1976**, *15*, 2008−2010. Garvey, J. F.; Pope, M. T. *Inorg. Chem.* **1978**, *17*, 1115−1118 ($[X^{V}{}_2Mo_{18}O_{62}]^{6-}$ (X = P, As)). (b) Waugh, J. C. T.; Schoemaker, D. P.; Pauling, L. *Acta Crystallogr.* **1954**, *7*, 438. Baker, L. C. W.; Weakley, T. J. R. *J. Inorg. Nucl. Chem.* **1966**, *28*, 447−454. Nomiya, K.; Kobayashi, R.; Miwa, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3505−3506 ($[Mn^{IV}Mo_9O_{32}]^{6-}$). (c) Strandberg, R. *Acta Chem. Scand.* **1973**, *27*, 1004. Matsumoto, K. Y.; Kato, M.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 106−110. Hedman, B. *Acta Chem. Scand.* **1977**, *27*, 3335. Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc* **1981**, *103*, 1865−1867. $[X_2M_5O_{21}]^{n-}$ (X = OP, RP, S, Se; M = Mo, W). (d) Matsumoto, K. Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3284−3291 $[(MeAsO_3)Mo_6O_{18}(H_2O)_6]^{2-}$. (e) Tourné, C. M.; Tourné, G. F.; Zonnevijlle, F. J. *J. Chem. Soc., Dalton Trans.* **1991**, 143−155 $[WM_3(H_2O)_2(XW_9O_{34})_2]^{12-}$ ($X = M =$ Zn, Co). (f) Termes, S. C.; Pope, M. T. *Transition Met. Chem.* **1978**, *3*, 103−108 $[M(XW_{11}O_{39})_2]^{n-}$ (M = Ln, Ac; X = Si, P, etc.). (g) Xin, F.; Pope, M. T. *J. Am. Chem. Soc.* **1996**, *118*, 7731−7736 ($[Sn^{II}{}_3(XW_{11}O_{39})_2]^{n-}$ (X = Si, P)).

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(6) (a) Hill, C. L.; Brown, R. B., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 536−538. (b) Faraj, M.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1487−1489. (c) Katsoulis, D. E.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* **1989**, 1483−1489. (d) Neumann, R.; Abu-Gnim, C. *J. Am. Soc. Chem.* **1990**, *112*, 6025−6031. (e) Lyon, D. K.; Miller, W. K.; Novet, T.; Domaille, P. J.; Evitt, E.; Johnson, D. C.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7209−7221. (f) Mansuy, D.; Bartoli, J.-F.; Battioni, P.; Lyon, D. K.; Finke R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7222−7226. (g) Rong, C.; Pope, M. T. *J. Am. Chem. Soc.* **1992**, *114*, 2932−2938. (h) Mizuno, N.; Hirose, T.; Tateishi, M.; Iwamoto, M. *Chem. Lett.* **1993**, 1839−1842. (i) Khenkin, A. M.; Hill, C. L. *J. Am. Soc. Chem.* **1993**, *115*, 8178−8186. (j) Hill, C. L.; Zhang, X. *Nature* **1995**, *373*, 324−326. (k) Zhang, X.-Y.; Pope, M. T. *J. Mol. Catal. A: Chem.* **1996**, *114*, 201−208.

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the present case the complex is isolated in crystalline form as a DL-dimer, and participates in a monomer−dimer equilibrium in solution. By the use of Ce(III) as an internal “shift reagent”, it has been possible to distinguish between the binding constants of the diastereomers formed between L-proline and the heteropolytungstate enantiomers.

Experimental Section

Materials. All chemicals were reagent grade and used as supplied. The potassium−lithium salt of α$_1$-[$P_2W_{17}O_{61}$]$^{10-}$ (**2**) was prepared according to published methods[9a,b] and was identified by infrared spectroscopy and by ^{31}P NMR.

Synthesis: $(NH_4)_5KLi[\alpha_1\text{-}Ce(P_2W_{17}O_{61})]\cdot 9H_2O-(NH_4Cl)$. To a suspension of α$_1$-$K_9LiP_2W_{17}O_{61}\cdot xH_2O$ (2.0 g, ca. 0.44 mmol) in 1 M LiOAc solution (20 mL, pH 4.75) was added a solution of $Ce(NO_3)_3\cdot 6H_2O$ (0.72 g, 1.66 mmol) in 3 mL of water at room temperature. After 5 min, traces of a white powder remaining were removed by centrifugation and 10 mL of 4 N NH_4Cl was added to the solution. The solution was stored in a refrigerator, and after 3 days any white deposit was removed by filtration. The orange filtrate was returned to the refrigerator, and after 2 weeks the orange crystals which had formed were filtered off and air-dried (1.04 g, 0.223 mmol, 50 mol % based on W).

Elemental analysis (KANTI Technologies, Inc., Amherst, USA) of air-dried materials: calculated (found): N, 1.81 (1.81); H, 0.91 (0.77); Ce, 3.01 (2.59); P, 1.33 (1.36); W, 67.14 (67.40); Cl, 0.76 (0.80); K, 0.84 (0.70); Li, 0.15 (0.12).

IR (KBr disk, cm^{-1}) in metal−oxygen stretching region: 1132 (m), 1082 (s), 1056 (m), 1014 (m), 958 (vs), 945 (vs), 904 (vs), 827 (vs), 783 (vs), 729 (vs).

Physical Measurements. Phosphorus-31 NMR was measured on a Varian Mercury 300 MHz spectrometer (P resonance frequency 121.472 MHz) interfaced to a Sun Microsystems workstation with the following parameters: spectral width, 10 000 Hz; acquisition time, 6.4 s; pulse delay, 5 s; pulse width, 34.1° or 90.0° tip angle. All spectra were referenced to external 85% H_3PO_4, and the temperature was controlled by a VT temperature control unit. Tungsten-183 NMR spectra were recorded on a Bruker AM 300WB spectrometer (W resonance frequency 12.504 MHz), equipped with an Aspect 3000 computer with the following parameters: spectral width, 8064.516 Hz; acquisition time, 1.0158 s; pulse delay, 0.5 s; pulse width 45° tip angle. All spectra were referenced to external 2 M Na_2WO_4. Infrared spectra were recorded with a Nicolet FT-7000 spectrometer as KBr pellets. Cyclic voltammetry was measured at ambient temperature on a BAS100A System (Bioanalytical Systems, Inc., West Lafayette, IN). A glassy carbon working electrode (diameter 3 mm), a platinum wire counter electrode, and a Ag/AgCl reference electrode (3 M NaCl, Bioanalytical Systems, Inc.,) were used. Approximate formal potential values $E_{1/2}$ were calculated from the cyclic voltammograms as the average of the cathodic and anodic peak potentials for each corresponding oxidation and reduction wave.

Crystallography. An orange crystal suitable for X-ray analysis was obtained by the following procedure: To a suspension of α$_1$-$K_9LiP_2W_{17}O_{61}\cdot xH_2O$ (2.0 g, ca. 0.44 mmol) in 1 M LiOAc solution (20 mL, pH 4.75) was added a solution of $Ce(NO_3)_3\cdot 6H_2O$ (0.72 g, 1.66 mmol) in 3 mL of water at room temperature. After 5 min, 1.5 g of KCl was added to the reaction mixture and a small amount of white powder was filtered off. The filtrate was stored overnight in a refrigerator, and the resulting solid was filtered off and air-dried (1.65 g). Recrystallization of the crude solid from 12 mL of 2 N NH_4Cl at room temperature formed the desired orange crystals accompanied with white powder and red-brown crystals.[10]

Table 1. Crystal Data and Structure Refinement[a]

empirical formula	$H_{124}Ce_2K_{0.50}N_{13.50}O_{157}P_4W_{34}$	
formula weight	9500.70	
temperature	−100 °C	
wavelength	0.710 73 Å	
space group	$P\bar{1}$	
unit cell dimensions	$a = 15.8523(9)$ Å	$\alpha = 99.617(1)°$
	$b = 17.4382(10)$ Å	$\beta = 105.450(1)°$
	$c = 29.3322(16)$ Å	$\gamma = 101.132(1)°$
volume	7460.9(7) Å^3	
Z	2	
density (calcd)	4.229 mg/m^3	
abs coeff	26.866 mm^{-1}	
R1 [$I > 2\sigma(I)$]	0.0519	
wR2 (all data)	0.1346	

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

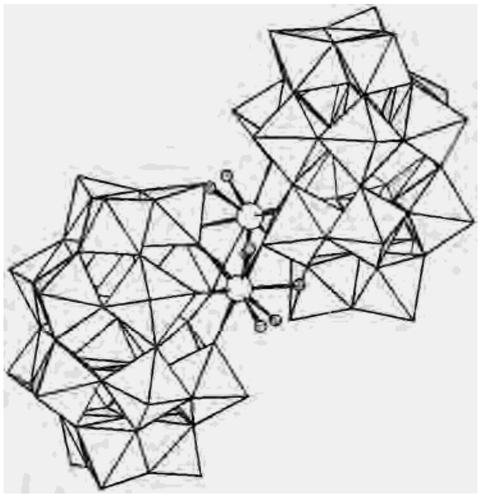

Figure 1. Polyhedral representation of $[Ce(\alpha_1\text{-}P_2W_{17}O_{61})(H_2O)_4]_2^{14-}$ in the ammonium salt (white circles, cerium; gray circles, water oxygen). Selected bond lengths: Ce−O(W) (oxygens in the uncapped face), 2.434(11)−2.495(12) Å; Ce−O (oxygens in the capped face), 2.543(13)−2.633(13) Å.

Single-crystal X-ray analyses were performed on a Bruker-Siemens SMART CCD single-crystal diffractometer equipped with a Mo Kα anode and graphite monochromator ($\lambda = 0.710\,73$ Å). The orange crystal (0.18 × 0.16 × 0.08 mm) was mounted on a glass fiber under mineral oil to prevent water loss, and placed in a nitrogen stream at 173 (2) K. The initial unit cell was determined using a least-squares analysis of a set of reflections obtained from three short (20 data frame) series of 0.3°-wide ω-scans which were well distributed in space. The intensity data were then collected using ω-scans (0.3° wide) with a crystal-to-detector distance of 5.0 cm to yield an approximate sphere of data with a maximum resolution of 0.75 Å. The final unit cell was calculated using a least-squares refinement of reflections culled from the entire data set. The data were corrected for Lorenz and polarization effects. An absorption correction based on multiple measurement of reflections[11] was applied as incorporated in the SADABS program.[12] All structures were solved using direct methods and refined against F^2 using the routines included in the SHELXTL-PC software suite.[13] Nitrogen atoms of ammonium cations were modeled as oxygen atoms because nitrogen atoms could not be distinguished from oxygen atoms. K, P, W, and Ce atoms were refined anisotropically; oxygen atoms were refined isotropically. Hydrogen atoms were not included in the

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(7) Müller, A.; Peters, F.; Pope, M.; Gatteschi, D. *Chem. Rev.* **1998**, *98*, 239−271 and references therein.

(8) Sadakane, M.; Dickman, M. H.; Pope, M. T. *Angew. Chem., Int. Ed.* **2000**, *36*, 2914−2916.

(9) (a) Contant, R.; Ciabrini, J. P. *J. Chem. Res.* **1977**, (S) 222, (M) 2601−2617. (b) Contant, R. *Inorg. Synth.* **1990**, *27*, 104−110. (c) Ciabrini, J. P.; Contant, R. *J. Chem. Res., Synop.* **1993**, 391; *J. Chem. Res., Miniprint* **1993**, 2720−2744.

(10) Characterization using IR, X-ray structure analysis, and ^{31}P NMR revealed that this red-brown crystal was the ammonium salt of $[Ce(\alpha_1\text{-}P_2W_{17}O_{61})(\alpha_2\text{-}P_2W_{17}O_{61})]^{17-}$.[4d] The white powder was not identified.

(11) Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.

(12) Sheldrick, G. M. *SADABS Absorption Correction Method*; University of Goettingen: Germany, 1996.

(13) Sheldrick, G. M. *SHELXTL 97. Program for the Refinement of Crystal Structures. Release 97−2, Bruker Analysis Instruments*; Madison, WI.

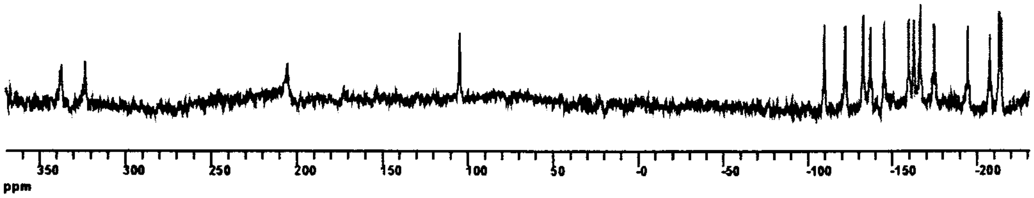

Figure 2. ^{183}W NMR spectrum of **1** in D_2O (1.0 g in 3.0 mL, 48 000 scans).

refinement model. Although one lithium atom, one potassium atom, and one chloride atom were found in the elemental analysis, only 0.5 potassium atom was found in the crystal analysis, due either to disorder or to a difference between crystal and bulk sample. Less water was found in the elemental analysis than the crystal structure, because the bulk sample was air-dried.

Crystal data and structure refinement parameters are listed in Table 1, and all crystallographic data are available as Supporting Information.

Results and Discussion

The 1:1 Ce(III) complex of **2**, $[Ce(\alpha_1\text{-}P_2W_{17}O_{61})(H_2O)_x]^{7-}$ (**1**), was prepared and isolated as an ammonium salt by modifying previously reported methods.[8,9c] X-ray structure analysis of a crystal of this salt shows that the anion exists as a dimeric meso (D,L) form in the solid state (Figure 1). Each cerium cation occupies a distorted monocapped square antiprism defined by the four oxygens that surround the vacant site of one lacunary anion, four water molecules, and a terminal oxygen of the second heteropolyanion.

In solution, the ^{183}W NMR spectrum of **1** consists of 17 lines of similar intensity, consistent with the C_1 symmetry of the α_1-isomer (Figure 2). Thirteen lines appear between −110 and −215 ppm, but four are observed between +100 and +340 ppm and are assigned to the W atoms adjacent to the paramagnetic Ce atom. In the previous report,[8] we found that the analogous Keggin complex $[Ce(\alpha\text{-}SiW_{11}O_{39})]^{5-}$ existed as a polymer in the solid state, but, based on ^{183}W NMR, dissociated into monomeric species in aqueous solution. In the present case ^{183}W NMR spectra cannot discriminate between monomeric or dimeric solute species or a mixture of both under fast exchange conditions. However, the ^{31}P NMR studies discussed below strongly indicate that the dimer dissociates in solution.

The ^{31}P NMR spectrum of **1** shows two lines of equal integrated intensity at −13.44 and −15.88 ppm assigned respectively to the phosphorus atoms remote from (P2) and close to (P1) the paramagnetic Ce(III) atom (Figure 3 , top). The spectrum reveals that other phosphorus-containing species (most likely the α_2-isomer) are present in insignificant amounts (<2%).[14] The chemical shifts show a concentration dependence, indicating a rapidly established dimer−monomer equilibrium in aqueous solution (eq 1). The concentration effect is greater for P1 than P2, and the concentration effect on δ(P1) is depicted in Figure 4. The data were fitted to a dimerization isotherm yielding a dimerization constant $K_d = 20 \pm 4\ M^{-1}$ at 22 °C.[15]

$$2[(\alpha_1\text{-}P_2W_{17}O_{61})Ce(H_2O)_4]^{7-} \rightleftharpoons [((\alpha_1\text{-}P_2W_{17}O_{61})Ce(H_2O)_4)_2]^{14-} \quad (1)$$

There is further evidence that the complex dissociates into monomeric species in aqueous solution. Addition of selected chiral amino acids (AA) to solutions of **1** causes the ^{31}P NMR lines to split; see Figure 3 and Table 2.[17] Achiral or racemic amino acids (glycine, DL-proline) have no effect. Significantly, addition of L-proline to the achiral (C_{2v}) isomer of **1**, $[Ce(\alpha_2\text{-}P_2W_{17}O_{61})(H_2O)_x]^{7-}$, had no effect on the ^{31}P NMR spectrum. The splitting increases as the molar ratio of AA:**1** is increased

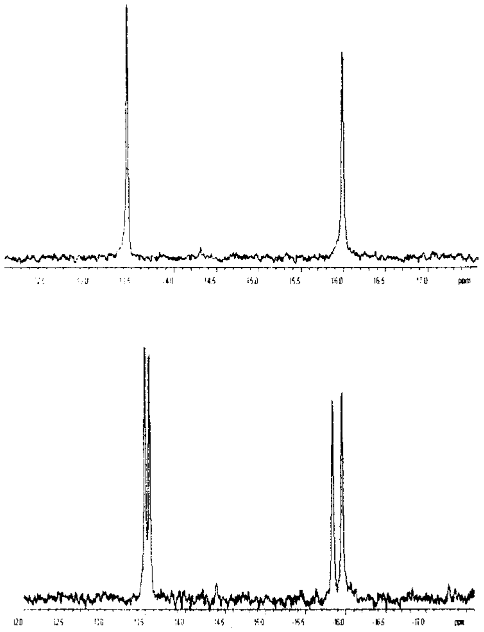

Figure 3. ^{31}P NMR spectrum of **1** (ca. 10 mM in D_2O) without (top) and with L-proline (ca. 100 mM) (bottom), 40 scans.

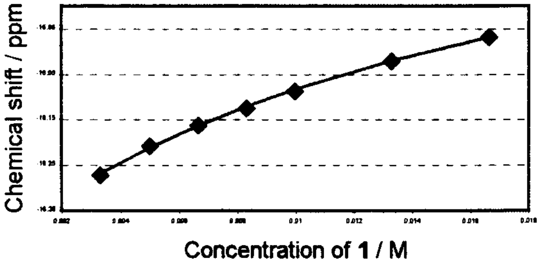

Figure 4. ^{31}P NMR chemical shift (P1) of **1** as a function of concentration. The line is the best fit to the dimerization isotherm.[15]

(Figure 5), and we attribute this behavior to the formation of diastereomeric pairs of *monomeric*[18] polyoxometalate−amino acid complexes that are in fast exchange with the unbound amino acids. We suggest that the amino acids interact with **1** through coordination of the carboxylate to Ce^{3+} and hydrogen

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(14) The corresponding chemical shifts for **2** under the same conditions are −8.56 ppm (P1) and −12.90 ppm (P2), and chemical shifts for $[Ce(\alpha_2\text{-}P_2W_{17}O_{61})(H_2O)_x]^{7-}$ are −17.40 ppm (P1) and −14.44 ppm (P2). (Sadakane, M.; Ostuni, A.; Pope, M. T. Manuscript in preparation.)

(15) Dimerization constant (K_d) for eq 1 was obtained via ^{31}P NMR titration, with δ(P1) followed as a function of concentration.[16] To provide K_d, the data were fitted (Mathematica version 4.0.1.0; Wolfram Research Inc.: 1988−1999) to the equation $\delta_{obs} = \delta_m + ((\delta_d - \delta_m)/[P])(([P] + 1/(4K_d)) - (([P] + 1/(4K_d))^2 - [P]^2)^{1/2})$, where the experimentally determined parameters are as follows: [P] is the total concentration of analyte and δ_{obs} is the observed shift. Parameters obtained are δ_m (−16.42 ± 0.02), the shift of the monomer, δ_d (−14.98 ± 0.12), the shift of the dimer, and K_d (20 ± 4), the dimerization constant.

(16) Conners, K. *Binding Constants*; Wiley and Sons: New York, 1987.

Table 2. Splitting of Phosphorus-31 NMR Lines of $[Ce(\alpha_1\text{-}P_2W_{17}O_{61})(H_2O)_x]^{7-}$ (**1**) in the Presence of Selected Amino Acids[a]

amino acid	splitting/Hz P1[b]	splitting/Hz P2[c]
L-proline	14.6	6.8
L-*N*-methylproline	10.3	d
L-asparagine	11.4	12.2
L-glutamic acid γ-methyl ester	d	4.9
L-serine	6.3	3.9
L-methionine	10.0	3.4
L-*S*-methylcysteine	4.4	5.3
L-lysine HCl[e]	21.4	2.7

[a] 10 mM **1**, 100 mM amino acids in D_2O except where noted. No splitting observed with glycine, DL-proline, L-proline methyl ester hydrochloride. [b] Phosphorus close to Ce(III); −15.88 ppm. [c] Phosphorus remote from Ce(III); −13.44 ppm. [d] Unresolved (broad line). [e] 36 mM amino acid.

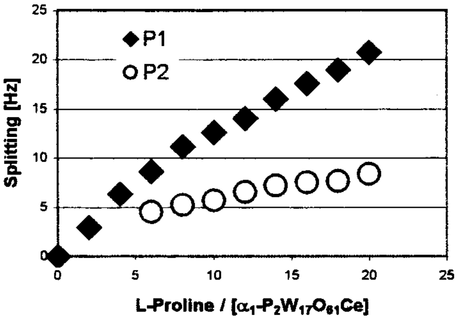
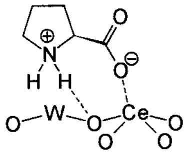


Figure 5. Splitting width plotted against the molar ratio of L-proline/heteropolyanion.

Scheme 1. Possible Interaction between **1** and Amino Acid (L-Proline as a Model)



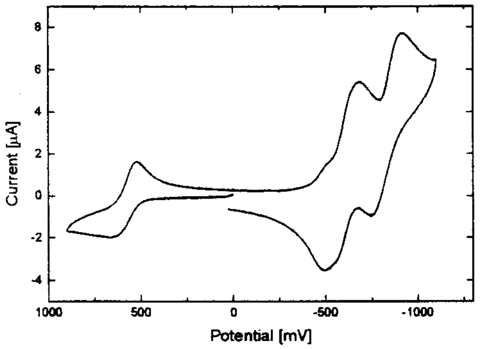


Figure 6. Cyclic voltammogram of **1** in 0.1 M Na_2SO_4 solution (pH 4.50).

Table 3. Ce(IV/III) Redox Potentials in Selected Polytungstates[a]

polytungstate	redox potential [mV]
$[Ce(\alpha\text{-}SiW_{11}O_{39})]^{4-/5-}$	581 (590)[b]
$[Ce(\alpha_1\text{-}P_2W_{17}O_{61})]^{6-/7-}$ (**1**)	600
$[Ce(\alpha\text{-}GeW_{11}O_{39})]^{4-/5-}$	639 (632)
$[Ce(\alpha_2\text{-}P_2W_{17}O_{61})]^{6-/7-}$	654 (651)
$[Ce(\alpha\text{-}PW_{11}O_{39})]^{3-/4-}$	747 (740)

[a] 1.0 mM ammonium polytungstate[8,14,24] in 0.1 M Na_2SO_4 (pH 4.50), glassy carbon electrode, scan rate 10 mV/s, Ag/AgCl (3 M NaCl) reference electrode. [b] Literature value[25] for complexes prepared in situ.

bonding of the ammonium cation to an adjacent oxygen; see Scheme 1. There are several lines of evidence to support this: (1) The amino acids are in zwitterionic form at the pH (ca. 6.0) of the experiment. Under these conditions, only carboxylate anions coordinate to lanthanide cations with 1:1 AA−lanthanide cation ratio in aqueous solution.[19] (2) The methyl ester of L-proline causes no splitting, demonstrating that the carboxylate anion is necessary. (3) Previous studies of amino acids with polyoxometalates have shown hydrogen-bonding interactions, and that amino acids and peptides can serve as countercations.[20] (4) The bridging oxygen atoms between Ce and W are the most basic sites on the polyoxometalate surface, and precedents exist for complexes in which the lanthanide acts as a Lewis acid and its adjacent oxygen as a Lewis base.[21] From ^{31}P NMR spectra of millimolar solutions of **1** (99% monomer) containing 10−50 mM L-proline, the formation constants of the two diastereomers were determined to be 9.8 ± 1.4 and 7.3 ± 1.3 M^{-1}.[22] These values are comparable to the binding constants reported for complexes of AA and europium chelates in aqueous solution.[23]

The cyclic voltammogram of **1**, measured in 0.1 M Na_2SO_4 (pH 4.50) is shown in Figure 6. Three pseudoreversible redox pairs, a one-electron redox cycle for Ce(IV/III) and two two-electron reductions of the polytungstate, were observed. The redox potentials of Ce incorporated into polytungstates are summarized in Table 3.

Conclusion

Although it has long been evident that $\alpha_1\text{-}[P_2W_{17}O_{61}]^{10-}$ and its derivatives are chiral and optically nonlabile, discrimination between enantiomers has hitherto not been possible, since these have very similar molecular shapes. The trivalent cerium complex, $\alpha_1\text{-}[P_2W_{17}O_{61}Ce]^{7-}$, was isolated and characterized. The complex exists as a dimeric meso (D**,**L) form in the solid state, but dissociates into monomeric species in aqueous solution. The use of a paramagnetic lanthanide cation magnifies the chemical shift differences between the diastereomers that result from interactions with chiral amino acids, and permits deter-

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(17) In all cases addition of amino acid in excess of the amounts shown in Table 1 led to precipitation of the polyoxometalate before a limiting value of the splitting could be observed.

(18) The dimeric species is not chiral.

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(22) Assuming that only 1:1 L-proline:**1** complexes are formed with binding constant *K*, the following equation can be used:[16] $1/\Delta_{obs} = 1/\Delta_0 K[L] + 1/\Delta_0$, where Δ_{obs} is the measured chemical shift difference of **1** (P1 signal) in the presence and absence of L-proline, Δ_0 is the chemical shift difference between **1** and the L-proline:**1** complex, and [L] is total L-proline concentration. By plotting $1/\Delta_{obs}$ vs 1/[L] (see Supporting Information) for each of the split P1 lines, values of *K* and Δ_0 could be determined as 7.3 ± 1.3 M^{-1}, 0.53 ± 0.09 ppm, and 9.8 ± 1.4 M^{-1}, 0.70 ± 0.09 ppm.

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mination of both binding constants. We are currently exploring the possibility of these and other stereoselective interactions that could result in partial or complete resolution of the polyoxometalate enantiomers.[26]

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Supporting Information Available: Crystal and structure refinement data for the ammonium salt of **1** (figures showing atom labels; table of atomic coordinates; CIF file). Plots of $1/\Delta_{obs}$ vs 1/[L] for determination of proline binding constants. Mathematica output for calculated line of Figure 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Once resolved, the cerium or other lanthanide complexes can readily be converted to the corresponding enantiomers of transition metal substituted polyoxotungstates that are known to have higher formation constants [Contant, R.; Ciabrini, J. P. *J. Chem. Res. (S)* **1982**, 50. Ciabrini, J.-P.; Contant, R. *J. Chem. Res.* (*S*) **1993**, 391.]