

Figure 1. Values of advancing contact angles of water on polyethylene film functionalized at the surface with esters, PE-CO₂R (□), and amides, PE-CONHR (■); R = *n*-C_{*n*}H_{2*n*+1}. The cross-hatched line represents advancing contact angles for self-assembled monolayers of ω-mercapto ethers HS(CH₂)₁₆O-*n*-C_{*n*}H_{2*n*+1} on gold (taken from ref 4). The height of the symbols indicates the uncertainty in the measurement.

that determine wetting. These results imply that, to exhibit effective shielding, the functional groups need not be preoriented at the interface in a way that optimizes the presentation of the group R to the water.

We have carried out a limited investigation of structural isomers of the alkyl group (R) attached to N and O. The differences in contact angle with changes in structure are small; for example: C₄-C₅ groups R on CONHR, θ_a = 125° for (CH₂)₄CH₃, 123° for CH(CH₂CH₃)₂, 125° for *c*-C₅H₉, and 123° for C(CH₃)₃; for CO₂R, θ_a = 123° for (CH₂)₄CH₃, 115° for CH(CH₂CH₃)₂, 117° for *c*-C₅H₉, and 117° for C(CH₃)₃. Thus, the contact angle depends primarily on the size of the group that is a part of the ester or amide moiety rather than on the structural details of the group.

XPS data provide qualitatively useful information concerning the proximity of the ester or amide group to the solid-vacuum interface, and this information supplements that obtained from wetting. The ratio of the intensities of N 1s to C 1s peaks (normalized to the value for the unsubstituted amide CONH₂) and that of the O 1s to C 1s peaks (normalized either to the value for PE-CO₂H or for PE-CONH₂) decrease by only approximately a factor of 2 from *n* = 0 to *n* = 18. As the alkyl group becomes larger, the N or O nucleus in the polar functionality should be increasingly buried beneath the hydrocarbon of the R group, and the ratios of N or O to C should, in principle, decrease (ultimately to 0 for sufficiently large alkyl groups). The attenuation length (λ) of photoelectrons is ~40 Å in these systems.¹⁴ The relatively small decrease in these ratios thus indicates that the hydrocarbon structures overlying the amide and ester groups are thin. The conclusion of these experiments—that the size of the alkyl groups required to mask polar functionality in wetting is small compared to the thickness of hydrocarbon required to significantly attenuate XPS signals—is compatible with the proposed structures for the interfacial functional groups. These experiments also emphasize the high sensitivity of wetting as a probe of interfacial structure, relative to XPS.¹⁵

These results confirm that the interfacial region responsible for wetting, inferred to be thin in studies of well-ordered systems, is also thin in these disordered systems, at least for solvents that do not swell this region.^{16,17} The efficiency with which small groups R in the disordered solid-water interface of derivatives of PE-

CO₂H mask the influence of polar functionality (especially primary amides) on wetting is remarkable.^{18,19} The ability of a given alkyl group to mask a polar group in these disordered interfaces is similar to that observed previously for monolayers of alkyl thiolates on gold,^{4,5} systems we believe to be more ordered than PE-CO₂H and its derivatives. Establishing whether this similarity reflects intrinsic insensitivity of wetting to details of local structure around the polar group, or whether the monolayers are less ordered (or the polyethylene is more ordered¹⁹) than we have assumed, is a subject of continuing investigation.

(18) We cannot presently compare the data from self-assembled monolayers and surface-functionalized polymers in a way that provides a useful description of the structures and degree of order of the alkyl groups overlying the polar functional groups in these two types of surfaces.

(19) The dependence of wettability on pH for PE-CONH-C₆H₄-CO₂H is large (Wilson, M. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 8718-8719). We have rationalized this observation, assuming that polar groups are easily masked by overlying nonpolar groups, and that reorganization of the solid-liquid interface occurs readily.

Trigonal-Planar [M(SR)₃]¹⁻ Complexes of Cadmium and Mercury. Structural Similarities between Mercury-Cysteine and Cadmium-Cysteine Coordination Centers

Eric S. Gruff and Stephen A. Koch*

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794

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Mercury-cysteine coordination has recently been indicated in the mercury metalloregulatory protein (MerR), mercuric ion reductase, and related proteins.¹⁻⁴ The details of the coordination geometries of the metal centers in these proteins remain to be determined. The coordination of cysteine to the other group 2B metals, Zn and Cd, is well preceded in metalloproteins.⁵ The unique occurrence of two- and three-coordinate thiolate complexes in the chemistry of mercury^{6,7} has suggested the possibility that a low-coordinate metal-cysteine center could provide a structurally based method for preferential binding of mercury to Hg-cysteine proteins. We present the first evidence that low-coordinate complexes exist in the thiolate chemistry of cadmium as well as mercury and to emphasize the close structural similarity of monomeric Cd and Hg thiolate complexes.

We have recently structurally characterized the first example of a trigonal-planar thiolate complex of zinc, [Zn(S-2,3,5,6-Me₄C₆H)₃]¹⁻.⁸ An attempt to prepare the Cd analogue gave the dimeric compound [(*n*-Pr₄N)]₂[Cd₂(S-2,3,5,6-Me₄C₆H)₆]. Increasing the steric hindrance of the thiolate ligand resulted in the

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(15) Changing the take-off angle in the XPS measurements on these systems does not significantly change the surface sensitivity.⁹ We attributed this insensitivity to roughness of the interfaces.

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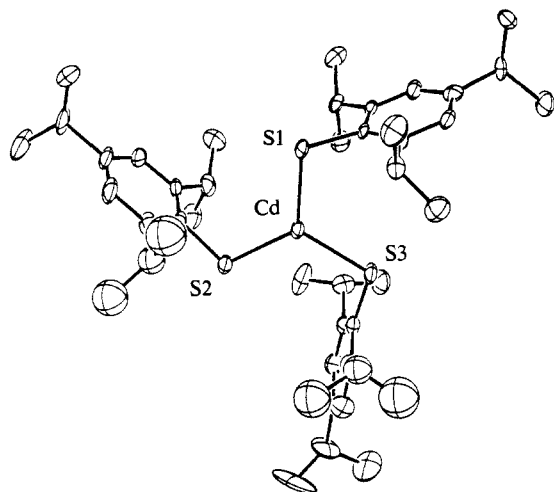


Figure 1. ORTEP diagram of $[\text{Cd}(\text{S-2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2)_3]^{1-}$ (**1**). Selected bond distances (angstroms) and angles (degrees): Cd-S1, 2.419 (3); Cd-S2, 2.421 (3); Cd-S3, 2.428 (3); S1-Cd-S2, 122.7 (1); S1-Cd-S3, 117.6 (1); S2-Cd-S3, 119.7 (1); Cd-S1-C11, 104.4 (3); Cd-S2-C21, 105.4 (4); Cd-S3-C31, 104.7 (4).

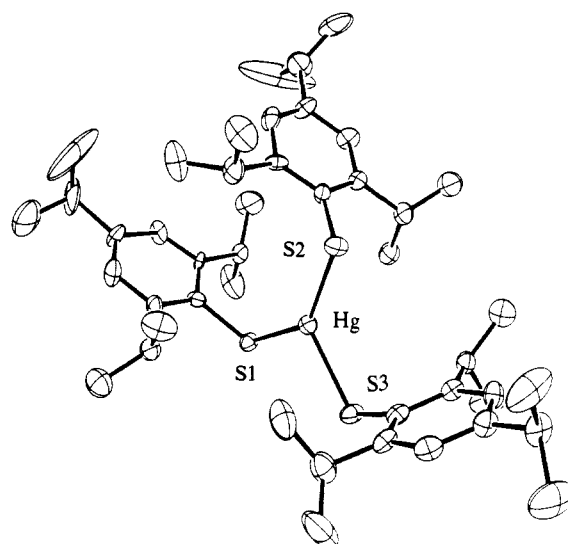


Figure 2. ORTEP diagram of $[\text{Hg}(\text{S-2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2)_3]^{1-}$ (**2**). Selected bond distances (angstroms) and angles (degrees): Hg1-S1, 2.460 (4); Hg1-S2, 2.397 (4); Hg1-S3, 2.469 (4); S1-Hg1-S2, 136.6 (1); S1-Hg1-S3, 101.3 (1); S2-Hg1-S3, 121.9 (1); Hg1-S1-C11, 109.4 (5); Hg1-S2-C21, 105.4 (5); Hg1-S3-C31, 108.2 (5).

Table I. Metal-Sulfur Bond Distance in Monomeric Cd and Hg Thiolate Complexes

metal	bond distance, Å		
	$[\text{M}(\text{SR})_4]^{2-}$	$[\text{M}(\text{SR})_3]^{1-}$	$[\text{M}(\text{SR})_2]$
Cd	2.52-2.53 ^a	2.420 (4) ^b	
Hg	2.52-2.54 ^a	2.44 (3) ^b	2.322 (6) ^b

^aReferences 11, 12, 23. ^bThis work.

monomeric complex, $[\text{PPh}_4][\text{Cd}(\text{S-2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2)_3]$ (**1**), which was structurally characterized.^{9,10} The $[\text{Cd}(\text{SR})_3]^{1-}$ anion has a pinwheel conformation with approximately C_{3h} symmetry (Figure 1). The individual S-Cd-S angles are close to 120° , and the sum of the three angles is 360° . As a result of the reduced coordination number, the Cd-S distances are substantially shorter than those in $[\text{Cd}(\text{SR})_4]^{2-}$ compounds (Table I).^{11,12} Structurally characterized examples of three-coordinate complexes of Cd are very rare.¹³ The three-coordinate structure is maintained in solution: the ^{113}Cd chemical shift of **1** (577 ppm) is the same in CDCl_3 and in DMF; the shift in the solid state (590 ppm) is quite similar.¹⁴ The steric hindrance of the thiolate ligands does not prevent the coordination of a fourth ligand to the metal; the

analogous cobalt(II) complex, $[\text{Co}^{\text{II}}(\text{S-2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2)_3(\text{DMF})]^{1-}$, is four-coordinate.

The corresponding Hg and Zn complexes are isomorphous and presumably isostructural with **1**, but full X-ray characterization of these complexes was precluded by rapid loss of solvent of crystallization. A change in the cation provided $[(n\text{-Pr})_4\text{N}][\text{Hg}(\text{S-2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2)_3]$ (**2**), which was structurally characterized (Figure 2).¹⁵

The $[\text{Hg}(\text{SR})_3]^{1-}$ anion has a different conformation of the thiolate ligands and a considerably distorted $[\text{HgS}_3]$ unit. The $[\text{HgS}_3]$ unit is planar (the sum of the S-Hg-S angles = 359.8°), but the S-Hg-S angles ($101.3 (1)^\circ$, $121.9 (1)^\circ$, $136.6 (1)^\circ$) deviate significantly from 120° . There is also a considerable range in the individual Hg-S distances (2.397 (4)-2.469 (4) Å). There is a relationship between the S-Hg-S angle and the length of the opposite Hg-S bond; a large angle correlates with a long Hg-S bond. Similar structural effects have been seen in other $[\text{M}(\text{SR})_3]^{2-/1-}$ compounds of d^{10} metals.^{8,16,17} The deviations in S-Hg-S angles from 120° result from the steric interactions between the thiolate ligands. The easy deformability of the coordination sphere is characteristic of d^{10} metal ions.

Although $[\text{Hg}(\text{SPh})_3]^{1-}$ is the only other example of a structurally characterized, trigonal-planar mercury thiolate complex,¹⁶ spectroscopic studies have indicated three-coordinate $[\text{Hg}(\text{SR})_3]^{1-}$ complexes for a variety of different thiolate ligands.¹⁸⁻²⁰ In the case of Zn and Cd, it has been necessary to use sterically hindered thiolate ligands to achieve $[\text{M}(\text{SR})_3]^{1-}$ complexes. In a metalloprotein, the arrangement of the cysteine residues in the polypeptide chain could have an equivalent effect.

(9) Synthesis of $[\text{Ph}_4\text{P}][\text{Cd}(\text{S-2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2)_3]$: $\text{Li-S-2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2$ (1.13 g, 4.7 mmol), CdCl_2 (0.18 g, 1.0 mmol), and Ph_4PBr (0.80 g, 1.9 mmol) were combined in a mixture of 5 mL of DMF and 50 mL of *i*-PrOH, and the pale yellow mixture was stirred for 2 h. The mixture was then cooled to -20°C overnight, and the resultant crystalline white solid was filtered, washed with *i*-PrOH, and dried. Yield: 0.50 g (45%). $^1\text{H NMR}$ (CDCl_3): 1.00 (d, 36 H, *o*- CH_3), 1.13 (d, 18 H, *p*- CH_3), 2.72 (m, 3 H, *p*- CH), 4.09 (m, 6 H, *o*- CH), 6.67 (s, 6 H, *m*- H), 7.4-8.0 ppm (m, 20 H, Ph_4P^+).

(10) $[\text{Ph}_4\text{P}][\text{Cd}(\text{S-2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2)_3]\cdot\text{DMF}\cdot i\text{-PrOH}$ crystallizes in the monoclinic space group $\text{P}1$ with $a = 15.379 (6) \text{ \AA}$, $b = 21.255 (7) \text{ \AA}$, $c = 13.585 (6) \text{ \AA}$, $\alpha = 95.04 (3)^\circ$, $\beta = 114.85 (3)^\circ$, $\gamma = 104.40 (3)^\circ$, $V = 3808 (6) \text{ \AA}^3$, $Z = 2$. Final least-squares refinement using 4704 unique reflections with $I > 3\sigma(I)$ gave $R(R_w) = 0.072 (0.095)$.

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(15) $[(n\text{-Pr})_4\text{N}][\text{Hg}(\text{S-2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2)_3]\cdot\text{CH}_3\text{OH}$ crystallizes in the monoclinic space group $\text{P}2_1/c$ with $a = 14.298 (10) \text{ \AA}$, $b = 18.710 (5) \text{ \AA}$, $c = 24.543 (8) \text{ \AA}$, $\beta = 106.14 (4)^\circ$, $V = 6307 (9) \text{ \AA}^3$, $Z = 4$. Final least-squares refinement using 2932 unique reflections with $I > 3\sigma(I)$ gave $R(R_w) = 0.041 (0.047)$.

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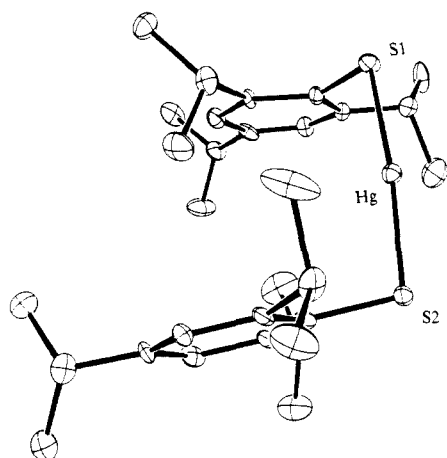


Figure 3. ORTEP diagram of $[\text{Hg}(\text{S}-2,4,6\text{-}i\text{-Pr}_3\text{C}_6\text{H}_2)_2]$ (3). Selected bond distances (angstroms) and angles (degrees): Hg1-S1, 2.322 (6); Hg1-S2, 2.322 (5); S2-Hg1-S1, 174.2 (2); Hg1-S1-C11, 97.8 (6); Hg1-S2-C21, 101.1 (7).

The reaction of 2 equiv of $\text{LiS}-2,4,6\text{-}i\text{-Pr}_3\text{C}_6\text{H}_2$ with HgCl_2 gives the two-coordinate complex $[\text{Hg}(\text{S}-2,4,6\text{-}i\text{-Pr}_3\text{C}_6\text{H}_2)_2]$ (3) (Figure 3).²¹ The Hg-S bond distance (2.322 (6) Å) is similar to those of other $[\text{Hg}(\text{SR})_2]$ complexes.²² Linear $[\text{M}(\text{SR})_2]$ complexes of Cd and Zn remain a synthetic objective.

The average M-S distances in 1 and 2 are nearly equal (Table 1). The close similarity of Hg-S and Cd-S distances is also found in $[\text{M}(\text{SR})_4]^{2-}$ compounds.²³ Our studies suggest that cadmium should be an excellent spectroscopic probe for monomeric Hg-cysteine centers particularly in cases where there is a protein-imposed coordination geometry. EXAFS studies have indicated a Hg-S distance of 2.42 Å for the MerR protein.³ This distance is in close agreement with the trigonal-planar $[\text{Hg}(\text{SR})_3]^{1-}$. Very recent biochemical studies have provided strong evidence for $[\text{Hg}(\text{S-cys})_3]$ coordination.²⁴ If this is indeed the case, a Cd derivative of the MerR protein might be expected to also have $[\text{M}(\text{S-cys})_3]$ coordination.²⁵

Continued study of the similarity and differences in the coordination chemistry of the group 2B metals with thiolate ligands should provide insight in the metal-binding specificity of group 2B metal-cysteine proteins.

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Registry No. 1-Ph₃P, 124511-86-0; 1-Ph₃P-DMF-*i*-PrOH, 124511-87-1; 2-*n*-Pr₄N-CH₃OH, 124511-90-6; 3, 124511-91-7.

Supplementary Material Available: Tables of crystallographic parameters, atomic coordinates, thermal parameters, and bond distances and angles for 1-3 (30 pages); tables of observed and calculated structure factors for 1-3 (69 pages). Ordering information is given on any current masthead page.

(21) $[\text{Hg}(\text{S}-2,4,6\text{-}i\text{-Pr}_3\text{C}_6\text{H}_2)_2]$ crystallizes in the monoclinic space group $C2/c$ with $a = 37.56$ (1) Å, $b = 8.645$ (4) Å, $c = 21.05$ (1) Å, $\beta = 113.87$ (5)°, $V = 6251$ Å³, $Z = 8$. Final least-squares refinement using 2356 unique reflections with $I > 3\sigma(I)$ gave $R(R_w) = 0.066$ (0.081).

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Synthesis of $[1\text{-}^{15}\text{N}]$ Purine Ribonucleoside by a Novel Rearrangement

Jon Adler, Walda Powell, and Richard Wolfenden*

Department of Biochemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Received August 7, 1989

We report the facile conversion of the 1-methylpurinium ribonucleoside cation (I, Scheme I) in aqueous ammonia to purine ribonucleoside (II, Scheme I). This reaction, which appears to involve addition of ammonia at C-6, followed by a rearrangement with elimination of methylamine, offers a method for specific incorporation of ^{15}N into heterocyclic compounds.

In basic solution, cation I was earlier found to undergo reversible addition of oxygen and sulfur nucleophiles at C-6, with a change of λ_{max} from 269 nm to much longer wavelengths, 284 nm for oxygen addition and 302 nm for sulfur addition.¹ In ammonia buffers, we observed very different behavior. When cation I (0.2 M, prepared as described earlier¹) was dissolved in aqueous $^{15}\text{NH}_4\text{Cl-KOH}$ (1 M) at pH 9.2, its UV absorption spectrum underwent complete conversion in a few minutes at room temperature from that of I ($\lambda_{\text{max}} = 269$ nm) to that of II ($\lambda_{\text{max}} = 263$ nm). The elution behavior of the product, upon C-18 reverse-phase HPLC, was identical with that of an authentic sample of II, and proton-coupled ^{15}N NMR spectroscopy of the reaction solution at pH 7 revealed a doublet of doublets 248 ppm downfield from ^{15}N ammonium ion, with a principal $^{15}\text{N-H}$ coupling constant of 14.3 Hz. This chemical shift is approximately 4 ppm downfield from chemical shifts reported for N-1 of purine and 7-methylpurine, each of which also shows a doublet of doublets ($J_{15\text{N-H}} = 14.3$ and 14.6 Hz, respectively).² Thus, I rearranges to II with incorporation of ammonia from the solvent. The other reaction product was identified as *N*-methylamine by GC-MS analysis of the waxy yellow crystals obtained by derivatizing the reaction mixture with 2,4-dinitrofluorobenzene, revealing *N*-methyl-2,4-dinitroaniline.

In ammonia buffers of varying pH, the velocity of this reaction was found to reach a sharp maximum near pH 10, with a half-time of approximately 4 min at 25 °C in aqueous NH_4Cl (5 M in total ammonia), with 100% conversion to purine ribonucleoside. In separate experiments, the rate of reaction was found to vary in direct proportion to the concentration of I ($2.5\text{--}12.5 \times 10^{-3}$ M) and of NH_4Cl (2-8 M). At pH values near 10, attack by NH_3 at C-6 appears to determine the overall rate of reaction, but at more basic pH values, instantaneous equilibrium formation of the pseudobase (accompanied by slower irreversible ring opening¹) competes with this process. Rearrangement was found to proceed at a similar rate in dry DMSO and in water, at equivalent concentrations of ammonia, so that mechanisms involving hydrated intermediates can be excluded. The reaction probably proceeds instead by a mechanism involving addition of ammonia, followed by ring opening, ring closing, and elimination of methylamine as shown in Scheme I. In the only previous synthesis that appears to have been reported, 1-aminoadenosine after long exposure to methanolic ^{15}N ammonia at elevated temperature yielded a mixture of products that included purine ribonucleoside in which ^{15}N was partially incorporated at the 1-position.³

The scope of the present reaction may be general, since rearrangement was also found to proceed smoothly to completion with the 3-methylquinazolinium ion under similar conditions. The product of the present reaction, purine ribonucleoside, is of interest as the parent compound from which major constituents of nucleic acids are derived, and because it exists in equilibrium with an extremely rare 1,6-hydrated species.⁴ The active site of adenosine

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