

Cu–Cu distances so far reported.¹² This occurrence of such a short Cu–Cu distance unsupported by a bridge exemplifies Hoffmann's "weak soft interaction"¹³ between d^{10} ions. In this connection we note that the Cu(I) ions are pulled slightly (0.182 Å) out of the trigonal plane toward each other, an observation which is at least consistent with the existence of bonding interaction between Cu(I) ions. While we failed (presumably on account of solution instability) to grow crystals of **3** or **4** of sufficient size for X-ray crystallography, we did succeed in obtaining a crystal of **2** quite heavily (~30% as judged by intensity of the near-IR absorption) doped with a mixed-valence species. This blue crystal exhibits a 7-line EPR spectrum in the polycrystalline state, as is typical of magnetically dilute, doped species. X-ray diffraction measurements showed it to be isomorphous¹⁴ with **2**, a finding which rules out any significant change of internuclear distance or coordination geometry in $[\text{Cu}_2\text{L}]^{3+}$ as vs $[\text{Cu}_2\text{L}]^{2+}$.

Cyclic voltammetry of **2** in dmf solution shows two almost reversible waves, one at -1160 mV ($\Delta E = 60$ mV) vs Ag/AgCl attributable to ligand- or metal-based reduction and the other at +310 mV ($\Delta E = 110$ mV) vs Ag/AgCl corresponding to Cu(I) oxidation.¹⁵ Quantitative chemical oxidation of **2** with AgClO_4 confirms that this is a one-electron process and the electronic spectrum of the oxidized solution is identical with that of **3**. There is no sign of any oxidation wave at potentials more positive than 310 mV, although following application of potentials above +1900 mV, an irreversible cathodic peak appears at -536 mV, demonstrating severe chemical change consequent on this further oxidation.

The intense near-infrared absorption of **3** and **4** is exceptional in several respects. It is solvent independent and unusually narrow, with an intensity greater by an order of magnitude than any so far observed for mixed-valence copper, comparable, indeed, with that observed¹⁶ for the intervalence transfer band of the most highly delocalized mixed-valence ruthenium example, the Creutz-Taube ion. However, for class III average-valence species the IT description of electronic absorption becomes invalid. The

near-infrared absorption presumably originates in an allowed transition between ground and excited state orbitals of the $\text{Cu}^{1.5}\text{Cu}^{1.5}$ assembly; more precise assignment must await the results of our spectroscopic experiments, now in an early stage.

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Note Added in Proof. By adjustment of the pH in the preparation of the perchlorate salt, we have succeeded in isolating a mixed-valence complex with the formula $[\text{Cu}_2\text{L}](\text{ClO}_4)_3$. The spectroscopic (EPR and electronic) properties of this complex are nearly identical with those of **3**.

Registry No. **2**, 137040-30-3; **3**, 137040-32-5; **4**, 137040-33-6; $\text{Cu}(\text{MeCN})_4\text{ClO}_4$, 14057-91-1; Cu , 7440-50-8.

Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients, H-atom coordinates, and isotropic displacement coefficients, and a table of analytical data for **2** and **3** (2 pages); listing of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

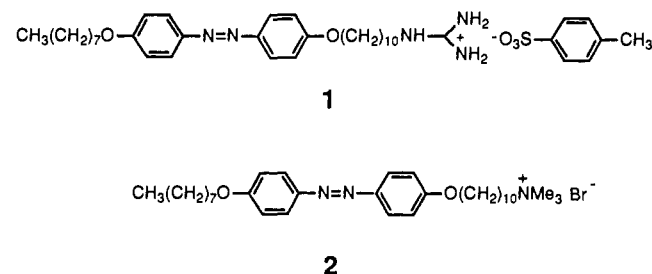
Specific, Multiple-Point Binding of ATP and AMP to a Guanidinium-Functionalized Monolayer

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Multiple-point interaction between host and guest systems is a key element for molecular recognition. It amplifies the host-guest binding energy and provides orientational effects between the interacting bodies that result in highly specific recognition.¹ We have detected strong, specific binding of ATP and AMP with the monolayer of guanidinium-functionalized **1**.²



The guanidinium moiety is an important interaction unit for many biological receptors,³ in particular those for RNA.⁴ Its

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(1) For comprehensive reviews of synthetic receptors, see: (a) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (b) Lehn, J.-M. *Design and Synthesis of Organic Molecules Based on Molecular Recognition*; Van Binst, G., Ed.; Springer-Verlag: Berlin, 1986.

(2) The synthesis of **1** will appear in a future publication. Crystalline **1**: golden yellow flakes; mp 165–168 °C. ¹H NMR spectra were obtained on a JEOL JNM-GSX 400 spectrometer (DMSO): δ 7.82 (dd, $J = 2.1, 8.8$ Hz, 4 H, azobenz), 7.49 (d, $J = 7.93$ Hz, 2 H, PTS aromatic), 7.12 (d, $J = 7.93$ Hz, 2 H, PTS aromatic), 7.09 (dd, $J = 1.22, 8.3$ Hz, 4 H, azobenz), 4.06 (t, $J = 6.41$ Hz, 4 H, CH_2O), 3.08 (br t, 2 H, CH_2NH), 2.29 (s, 3 H, PTS- CH_3), 1.74 (m, 4 H, $\text{CH}_2\text{CH}_2\text{O}$), 1.43 and 1.28 (m, 24 H, alkyl tail and spacer), 0.87 (t, $J = 7.01$ Hz, 3 H, CH_3). IR (KBr): 3178, 2920, 1677, 1631, 1600, 1580, 1246, 1146, 840 cm^{-1} . Anal. Calcd for $\text{C}_{38}\text{H}_{57}\text{N}_5\text{O}_5\text{S}$: C, 65.58; H, 8.26; N, 10.06. Found: C, 65.50; H, 8.24; N, 10.05.

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(14) Crystal data for **2**: $[\text{Cu}_2(\text{GT})(\text{ClO}_4)_2 \cdot \text{C}_{18}\text{H}_{30}\text{Cl}_2\text{N}_5\text{O}_8]$, brown crystal with dimensions $0.5 \times 0.6 \times 0.2$ mm, rhombohedral, space group $R\bar{3}2$, $a = 8.804$ (4) Å, $c = 30.95$ (2) Å, $V = 2078$ (2) Å³, $Z = 3$, λ (Mo K α) = 0.71069 Å, $\mu = 1.7$ mm⁻¹. Intensities of 641 unique reflections ($4 < 2\theta < 55^\circ$) were measured at room temperature on a Siemens R3v diffractometer and were corrected for Lorentz, polarization, and absorption effects. The structure was solved by direct methods (TREF: Sheldrick, G. M. SHELXS 86, A Program for Crystal Structure Solution, University of Göttingen, 1986). Anisotropic thermal parameters were assigned to all non-hydrogen, atoms and hydrogen atoms were inserted at calculated positions except for that on C3, which was located from a difference Fourier map and not refined. Least-squares refinement using SHELX76 (Sheldrick, G. M. SHELX 76, A Program for Crystal Structure Determination, Cambridge University, 1976) and SHELXTL-PC (Sheldrick, G. M., Siemens Analytical X-ray Instruments Inc., Madison, WI 53719, 1990) on 559 reflections with $I > 3\sigma(I)$ converged with $R = 0.023$, $wR = 0.037$, and no residual peaks greater than ± 0.20 e Å⁻³. A blue-green plate with dimensions $0.5 \times 0.4 \times 0.06$ mm was found to be isomorphous with **2**. Reflection data were collected as for **2**. The final atomic coordinates obtained for **2** were used as a starting point and the refinement on 403 reflections with $I > 3\sigma(I)$ converged with $R = 0.040$ and $wR = 0.049$.

(15) This relatively positive potential for Cu(I)/Cu(II) redox reflects the low oxidation state stabilization characteristic of this ligand, originating in the "soft" character of the 6 imino donors, enhanced by the distorted tetrahedral site geometry which favors the Cu(I) rather than the Cu(II) state. Such positive potentials characterize blue Cu proteins such as Pc, Az, where a similar lack of alteration of site geometry on redox change generates fast electron transfer kinetics: Shepard, W. E. B.; Anderson, B. F.; Lewandoski, D. A.; Norris, G. E.; Baker, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 7817–7819. Guss, J. M.; Harrowell, P. R.; Murata, M.; Norris, V. A.; Freeman, H. C. *J. Mol. Biol.* **1986**, *192*, 361–387.

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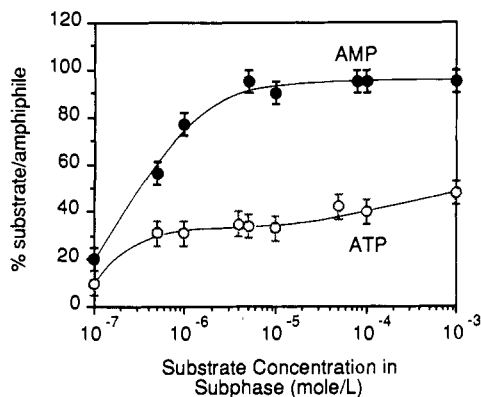


Figure 1. Binding of AMP and ATP to monolayer **1**. Binding efficiencies were determined by applying the Langmuir isotherm. In the case of ATP (20 °C), least-squares fitting (correlation factor 0.998) gave binding constant $K = 1.7 \times 10^7 \text{ M}^{-1}$ and maximum binding $\alpha = 0.34$. AMP (20 °C) substrate gave $K = 3.2 \times 10^6 \text{ M}^{-1}$ and $\alpha = 0.95$ (correlation factor 1.000).

unique combination of cationic⁵ and hydrogen-bonding⁶ properties has led to its investigations in synthetic host-guest systems.⁷ Recent investigations by us and others have focused on host-guest systems at the air-water interface utilizing hydrogen-bonding monolayers.⁸ Some of the advantages of utilizing a monolayer host are the presence of well-characterized interfaces and the orientational control of interacting hosts and guests.

Amphiphile **1** forms a monolayer on pure water at 20 ± 0.2 °C with biphasic behavior and a collapse pressure of ca. 37 mN/m. The liquid expanded region is found at $0.35\text{--}0.6 \text{ nm}^2/\text{molecule}$, and the molecular area is $0.35 \text{ nm}^2/\text{molecule}$ as determined by extrapolation of the solid-like region to zero surface pressure. The monolayer behavior is altered significantly by addition of 1 mM ATP and AMP (Na_2ATP , Na_2AMP , Oriental Yeast Co., enzyme assay 99%) in the pure H_2O subphase.⁹ ATP causes a further condensation of the $\pi\text{-A}$ curve, whereas AMP makes the curve more expanded. This altered $\pi\text{-A}$ behavior suggests unique bindings of ATP and AMP to the guanidinium monolayer.

The extent of substrate binding was then determined by X-ray photoelectron spectroscopy (XPS) of Langmuir-Blodgett (LB) films of the monolayer drawn from substrate-laden aqueous subphases. The films were deposited typically in the z-type orientation on glass plates coated with Au (1000 Å), at a film pressure of 25 mN/m. After deposition of 5–7 layers, the LB films were dried in high vacuum overnight and subjected to XPS analysis. The substrate/amphiphile ratio was determined from the relative area of P_{2p} and N_{1s} peaks after necessary corrections for elemental sensitivity and depth from the surface.^{8a} It is noted that the phosphate incorporation is accompanied by the corresponding loss of the original *p*-toluenesulfonate counterion (as determined by the S/N ratio in XPS data).

Figure 1 describes the binding behavior of ATP and AMP at a substrate concentration of $10^{-7}\text{--}10^{-3} \text{ M}$. ATP binding becomes

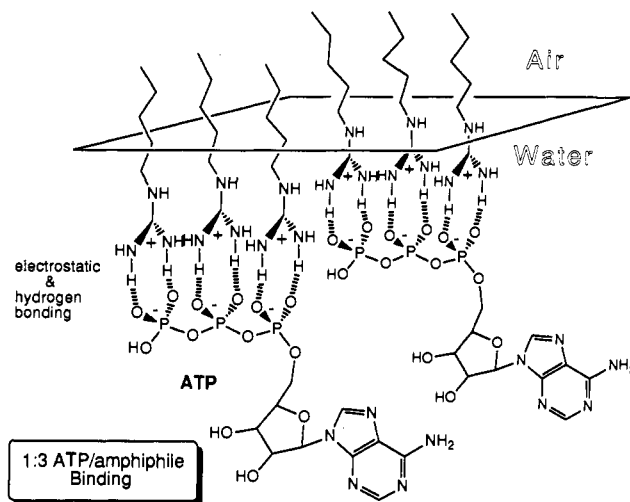


Figure 2. Schematic illustration of the specific binding of ATP to guanidinium monolayer **1** at the air-water interface.

apparently saturated at 10^{-5} M at a 1/3 substrate/amphiphile ratio and then increases slightly at $10^{-4}\text{--}10^{-3} \text{ M}$. On the other hand, AMP is bound in a 1/1 ratio, with saturation binding again at ca. 10^{-5} M . The Langmuir adsorption isotherm¹⁰ was employed to dissect the saturation behavior, to give the binding constants of $1.7 \times 10^7 \text{ M}^{-1}$ ($\Delta G^\circ = 9.7 \text{ kcal/mol}$) and $3.2 \times 10^6 \text{ M}^{-1}$ ($\Delta G^\circ = 8.7 \text{ kcal/mol}$) for ATP and AMP, respectively. The respective site occupancies were 0.34 and 0.95.

The XPS data clearly establish that the substrate binding occurs very effectively via specific formation of the guanidinium-phosphate pair at the air-water interface. FT-IR spectra (ν_{NH} region) of the LB films show that a strong, broad absorption at 3400 cm^{-1} and a shoulder at 3190 cm^{-1} with non-hydrogen-bonding counteranions (e.g., Cl^-) is transformed into a strong broad band at 3180 cm^{-1} with a shoulder at 3350 cm^{-1} for phosphate counteranions. Thus, the hydrogen-bonding interaction must be responsible, in addition to the electrostatic interaction, for the formation of the specific guanidinium-phosphate pair. Supportive evidence for this presumption was obtained by ATP binding experiments against monolayer **2**, which is the trimethylammonium counterpart of **1**. The binding ratio (ATP/amphiphile = 1.8/3.0) was not specific, and the binding constant was smaller ($K_a = \text{ca. } 5 \times 10^6 \text{ M}^{-1}$) at $10^{-7}\text{--}10^{-5} \text{ M}$ ATP.

In conclusion, we demonstrated that ATP and AMP were bound to the guanidinium-functionalized monolayer via specific hydrogen bonding and electrostatic attraction. A conceivable mode of binding is illustrated in the case of ATP in Figure 2. The multiple nature of the binding not only enhances the binding energy but also affects the molecular organization of the monolayer as implied by the $\pi\text{-A}$ isotherm. This was in fact endorsed by UV-vis reflection absorption spectroscopy of the azobenzene moiety of the monolayer.¹¹ The binding constants achieved here are a few orders of magnitude larger than those of polyammonium macrocycles with phosphate substrates.¹²

We have shown recently that the hydrogen-bonding interaction is used effectively for molecular recognition at the air-water interface.^{8a-d} The present results are consistent with this view. Combinations of these individual interacting units would produce more elaborate molecular recognition systems.

Registry No. **1**, 137174-78-8; **2**, 125678-70-8; ATP, 56-65-5; AMP, 61-19-8.

(10) For a description of the Langmuir adsorption isotherm, see: Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; Wiley-Interscience: New York, 1990; p 421.

(11) Results to be presented in an upcoming publication.

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