The correlation is perhaps surprising. The hydrogen-bonding hypothesis suggests that water should be pulled into the contact solvation shell of Cl⁻ on a preferential basis and that it should remain the dominating solvating species until bulk water activity has been reduced by a factor comparable to the activity change for transfer of the ion from protic aprotic solvent. The results indicate that, in fact, the immediate environment of Cl⁻ is related to the long-range structural aspects of solvent mixtures. We can imagine how this occurs if we look closely at the meaning of our numbers. The advantage of the chemical shift parameter as a solvation probe is that it reflects composition of the solvent layers in contact with Cl⁻. The activities from vapor pressures characterize the solvent in the solution *at a distance far enough from Cl⁻ to be unperturbed by the ions.* Both of these regions are in equilibrium with an intervening region to which we have no experimental access. A reason why water is not strongly preferred over the aprotic solvent in the layer in contact with Cl⁻ might well be that a protic solvent molecule hydrogen

bonded to Cl⁻ is strongly polarized so that it presents a "lyate ion like" aspect to the middle solvent region and this "lyate ion like" species is poorly "solvated" by the aprotic solvent. Conversely, an aprotic molecule solvating Cl⁻ may interact less favorably with the Cl⁻ but much more favorably with the surrounding solvent layer. In this way, the short-range favorable or unfavorable effects are mitigated and the local environment of the ion comes to reflect long-range interactions.

A final point: lines in the mixed solvents were very wide. They imply a residual assymmetry in the field gradient at the nucleus that is not averaged by tumbling.

Cooper H. Langford[12]
Department of Chemistry, Carleton University
Ottawa 1, Ontario, Canada

Thomas R. Stengle
Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01002

Additions and Corrections

The Mechanism of the Aminolysis of Methyl Formate

[*J. Am. Chem. Soc.*, 90, 2638 (1968)]. By G. M. BLACKBURN and W. P. JENCKS, Graduate Department of Biochemistry, Brandeis University, Waltham, Massachusetts 02154.

On page 2639, column 2, line 3, the rate constant for alkaline hydrolysis of methyl formate should read $1.95 \pm 0.1 \times 10^3 \, M^{-1} \, min^{-1}$.

Cyclopropyl Conjugation in Olefinic Esters. Conformational Effects on Ultraviolet Absorption

[*J. Am. Chem. Soc.*, 90, 3769 (1968)]. By MARGARET J. JORGENSON and TERESA LEUNG, Department of Chemistry, University of California, Berkeley, California.

On page 3773, column 1, the second sentence of the third paragraph should read: The values determined for esters 1, 5, and 6, are 9.4, 10.0, and 10.3 cps, respectively.

Biosynthesis of Indole Alkaloids. Vindoline

[*J. Am. Chem. Soc.*, 90, 4144 (1968)] by T. MONEY, 1. G. WRIGHT, F. McCAPRA, E. S. HALL, and A. 1. SCOTT, Chemistry Department, University of British Columbia, Vancouver 8, Canada.

On page 4146, Figure 2, the schematic structure
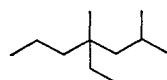
should be replaced by
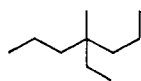
The Interpretation of Porphyrin and Metalloporphyrin Spectra

[*J. Am. Chem. Soc.*, 90, 6577 (1968)]. By ALSOPH H. CORWIN, ARTHUR B. CHIVVIS, ROBERT W. POOR, DAVID G. WHITTEN, and EARL W. BAKER, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland.

In Table I, column 6, the last value should be 24,530 instead of 24,360. On page 6580, Figures 2 and 3 should be interchanged.

The Acid-Catalyzed Hydrolysis of Acyl Phosphates

[*J. Am. Chem. Soc.*, 90, 6803 (1968)]. By DAVID R. PHILLIPS and THOMAS H. FIFE, Department of Biochemistry, University of Southern California, Los Angeles, California 90053.

In the abstract, the legend to Figure 6, and on page 6808 it should read: plots of (log $k_{obsd} + H_0$) *vs.* (log $C_H + H_0$). This expression appeared with the parentheses misplaced.

Spin-Delocalization Mechanisms in Some Paramagnetic Tris-2,2'-bipyridine Complexes of Nickel(II)

[*J. Am. Chem. Soc.*, 90, 6946 (1968)]. By M. WICHOLAS and R. S. DRAGO, William A. Noyes Laboratory, University of Illinois, Urbana, Illinois.

The first compound in Table I should be Ni(bipy)₃-Cl₂·2H₂O. On page 6950, the sentence beginning in column 2, line 37 should read: "The downfield resonance peak is due to either the *ortho* and *para* protons or the *meta* and *para* protons, and the upfield resonance peak is due to either the *ortho* or *meta* protons; however, of these only one assignment is reasonable." The last sentence should read: "If the assignments are correct, the contact shifts are consistent with