of 0.96 (3) and 1.05 (3) Å in a and b, respectively. These values are in agreement with those found for covalent N–H bonds in similar compounds.[7] An efficient hydrogen bond is set up with one nitrogen atom of the opposite ligand [N(1)···N(15) distance of 3.00 (3) and 3.01 (3) Å, N(1)–H···N(15) angle of 166 (1) and 158 (1)° in a and b, respectively].[8] Two more interactions take place between the two phenanthrolines of each complex. One ortho hydrogen of each phenanthroline (that adjacent to the nitrogen atom interacting with the acidic proton) comes close to the free nitrogen atom of the counter ligand giving rise to the formation of a hydrogen bond [C(2)···N(24), 3.07 (2) and 3.07 (3) Å; C(2)–H···N(24), 122 (1) and 118 (1)°; C(16)···N(10), 3.13 (3) and 3.19 (2) Å; C(16)–H···N(10) 118 (1) and 119 (1)° in a and b, respectively].[9,10] The resulting dihedral angle between the two phenanthrolines is 41°, and one phenanthroline is translated with respect to the other of ca. 2.4 Å.

The key role of the additional C–H···N hydrogen bonds in stabilizing the Hphen$_2^+$ complex is supported by the observation that analogous species are not formed in the case of phenanthrolines in which both ortho hydrogens have been substituted by alkyl or aryl groups. If a self-stacking association was operating in the Hphen$_2^+$ species,[4] one would expect this to be favored by the presence of hydrophobic substituents.[11] However, 2,9-dimethyl-1,10-phenanthroline dissolves in water only in the presence of at least 1 equiv of acid, and partial neutralization of this solution causes the immediate precipitation of the free base. Moreover in a recent study it has been shown that the catenand, formed by two interlocked 2,9-diphenyl-1,10-phenanthroline moieties, gives the monoprotonated species in which the two phenyl substituents of one link are located one on either side of the phenanthroline plane of the other link and the resulting internal stacking was estimated to increase the basicity by several orders of magnitude.[8] The 2,9-bis(*p*-methoxyphenyl)-1,10-phenanthroline would be able to give the same molecular arrangement found in the proton catenate, but it does not appear to form the two to one adduct.[8] Finally, since the formation of Hphen$_2^+$ species appears to occur only in the case of phenanthrolines bearing ortho hydrogens, the pK_A evaluation of protonated phenanthrolines, which does not take into account the presence of dimeric cations, leads to correct values only in the case of 2,9-disubstituted phenanthrolines.[12]

The NMR spectra of phen, (Hphen$_2$)I, and (Hphen)I were recorded.[13] All C–H protons experience a downfield shift going from left to right in the above series; however, only for the ortho protons is this shift smaller going from phen to Hphen$_2^+$ (0.20 ppm) than going from Hphen$_2^+$ to Hphen$^+$ (0.35 ppm). The acidic protons exchange very rapidly even with moisture present in the solvent. In our experimental conditions they fell at 16.0 and 14.7 ppm downfield from TMS, for Hphen$_2^+$ and Hphen$^+$, respectively, and are in very good agreement with those found for the mono- and bis-protonated catenand.[8]

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Registry No. (Hphen$_2$)(ClO$_4$), 21532-75-2.

Supplementary Material Available: Final atomic coordinates and thermal parameters (Tables I and II) and bond distances (Tables III and IV) and angles (Table V) (6 pages). Ordering information is given on any current masthead page.

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(7) Thevenet, G.; Toffoli, P.; Rodier, N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 2599–2602. Thevenet, G.; Rodier, N.; Khodadad, P. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 2594–2599. Thevenet, G.; Toffoli, P.; Rodier, N.; Ceolin, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B33*, 2526–2529.

(8) Cesario, M.; Dietrich, C. O.; Edel, A.; Guilhem, J.; Kintzinger, J. P.; Pascard, C.; Sauvage, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 6250–6254.

(9) Taylor, R.; Kenhard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063–5070.

(10) The distance between the acidic proton and the second nitrogen atom of the same phen is rather short [N(1)–H···N(10) distance of 2.43 (2) and 2.35 (2) Å in a and b, respectively], but it appears to be geometrically determined.

(11) Barbet, J.; Roques, B. P.; Combrisson, S.; Le Pecq, J. B. *Biochemistry* **1976**, *15*, 2642–2650. Delbarre, A.; Roques, B. P.; Le Pecq, J. B.; Lallemand, J. Y.; Nguyen-Dat-Xuong *Biophys. Chem.* **1976**, *4*, 275–279. Schimmack, W.; Sapper, H.; Lohmann, W. *Biophys. Struct. Mechanism* **1975**, *1*, 113–120.

(12) Schilt, A. A.; Dunbar, W. E. *Tetrahedron* **1974**, *30*, 401–403.

(13) NMR spectra (20 °C, Varian XL200 instrument) were recorded for equimolar solutions (10^{-2} M) of phen, (Hphen$_2$)I, and (Hphen)I in anhydrous CD$_2$Cl$_2$. Chemical shifts (δ, ppm, downfield TMS) of H(2), H(3), H(4), and H(5) were as follows: phen, 9.13, 7.64, 8.28, and 7.82; Hphen$_2^+$, 9.34, 7.89, 8.57, and 8.02, Hphen$^+$, 9.69, 8.11, 8.78, and 8.16.

A Note on Some Reported C and N Isotope Effects

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Stevenson and co-workers[1] recently measured values of isotopic exchange equilibrium constants K_1 involving a neutral organic molecule A and its anion radical A$^-$

$$A^* + A^- \rightleftharpoons A^{*-} + A \qquad (1)$$

Here, * refers to substitution by heavier isotope (D/H, ^{13}C/^{12}C, ^{15}N/^{14}N). Some of the systems studied are indicated in Table I. The focus of the study was the large C and N isotope effects (ie's) in the condensed phase (large deviations of K_1 from unity). Stevenson and co-workers suggested that these K_1's be used as the basis of isotope separation processes economically more feasible than those presently employed. We point out here that the reported magnitudes of the carbon and nitrogen ie's are at variance with conclusions based on the statistical mechanical theory of equilibrium ie's.

The theory of equilibrium ie's is well understood.[2] Usually the Born–Oppenheimer approximation is employed, with the additional assumption of the harmonic oscillator-rigid rotor approximation. Quantitative theory requires corrections for these assumptions; however, semiquantitative arguments of the type used here are valid without these corrections.[3] Much work has demonstrated that the heavier isotope in eq 1 will concentrate in that species in which the force constants (fc's) at the position of isotopic substitution are larger and that the magnitude of the ie reflects the difference in the fc's at this position between the species A$^-$ and A. Thus, $K_1 > 1$ if the fc's in A$^-$ are larger.

Table II gives theoretically calculated values of K_1 with nitrobenzene or fluorenone the neutral molecule. The calculations were made by using the well-tested cut-off procedure—only portions of the molecules were included which are no more than two bonds removed from the position of isotopic substitution.[4] The fc's for A were estimated from compilations of fc's.[5] Specific solvation or ion pairing effects were not taken into account for A. The column headings I, II, ... in Table II refer to different

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(1) (a) Stevenson, G. R.; Espe, M. P.; Reiter, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 532. (b) Stevenson, G. R.; Espe, M. P.; Reiter, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 5760. (c) Stevenson, G. R.; Espe, M. P.; Reiter, R. C.; Lovett, D. J. *Nature* **1986**, *323*, 522. (d) Stevenson, G. R.; Reiter, R. C.; Espe, M. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 3847. (e) Stevenson, G. R.; Reiter, R. C.; Au-Yeuno, W.; Pescatove, J. A., Jr.; Stevenson, R. D. *J. Org. Chem.* **1987**, *52*, 5064.

(2) Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, *15*, 261.

(3) Chen, C.-L.; Wolfsberg, M. *Isotopenpraxis* **1987**, *23*, 205. Bron, J.; Chang, C. F.; Wolfsberg, M. *Z. Naturforsch.* **1973**, *28A*, 129.

(4) Stern, M. J.; Wolfsberg, M. *J. Chem. Phys.* **1966**, *45*, 4105.

(5) Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand: New York, 1945. Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; McGraw Hill: New York, 1955. Hartshorn, S. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1974**, *94*, 9002.

0002-7863/89/1511-1493$01.50/0

Table I. Representative K_1 Values from Ref 1

ref	A	solvent[a]	counterion	isotopic sub.	T (K)	K_1
1b	benzene	THF	K^+	D_6/H_6	173	0.27
	benzene	THF	K^+	$^{13}C_6/^{12}C_6$	173	0.48
1d	nitrobenzene	gas phase		$^{15}N/^{14}N$	305	1.02
	nitrobenzene	NH_3	K^+	$^{15}N/^{14}N$	208	2.1
	nitrobenzene	NH_3	Na^+	$^{15}N/^{14}N$	208	0.4
1e	benzophenone	HMPA	Na^+	carbonyl $^{13}C/^{12}C$	298	0.58
	fluorenone	HMPA	Na^+	carbonyl $^{13}C/^{12}C$	298	2.74

[a] THF = tetrahydrofuran, HMPA = hexamethylphosphoramide.

Table II. Cut-Off Model[a] Calculations for K_1

A	isotope	T (K)	I	II	III	I′	II′	III′
nitrobenzene (Nbz)	$^{15}N/^{14}N$	208	0.98	1.02	1.57	1.09	1.13	1.70
		305	0.99	1.01	1.35	1.06	1.09	1.42
fluorenone (Flu)	carbonyl $^{13}C/^{12}C$	298	1.00	1.02				1.62

[a] Neutral molecule A is unsolvated. I, II, and III refer to different anion models: I (I′), II (II′), and III (III′) correspond to A^- (unsolvated), $(A^-)Y$ (singly solvated), and $(A^-)Y_5$ (5-solvated), respectively. Geometry of A^- moiety is same as A. Y is atom with atomic mass 23.0 amu, but results depend only weakly on this mass. In $(A^-)Y$, the Y atom is symmetrically bonded to both oxygens (Nbz) or to one oxygen (Flu). In $(A^-)Y_5$, the four additional Y's are bonded in square-planar geometry to N (Nbz) or to carbonyl C (Flu). Force constants (fc's) in harmonic valence force field: II, II′, III, and III′—Y–O, Y–N (NBz), and Y–C (Flu) stretching fc's equal 20 md/Å, bending fc's involving Y were given values 2–5 md Å; I, II, and III—all single (multiple) bond stretching fc's in A^- moiety 1.3 (0.7) of corresponding value in A; I′, II′, and III′—all stretching fc's involving N (Nbz) or carbonyl C (Flu) in A^- moiety twice the corresponding value in A.

A^- models. Important aspects of these models are described in the footnote. Relevant differences between valence force constants (fc's) in A and in the anionic species are given. Thus, II (II′), III (III′) correspond to solvated (ion-paired) A^- with II (II′) referring to $(A^-)Y$ and III (III′) to $(A^-)Y_5$. In III (III′), four Y atoms are bonded to the isotopically substituted atom with four Y–N (or Y–C) stretching fc's of very large magnitude (20 md/Å). This magnitude was chosen to calculate upper limits to ie's. In I, II, and III, single-bond stretching fc's in the A^- moiety were increased with respect to fc's in the A species, while multiple bond stretching fc's were decreased, as suggested by Khatkale and Devlin[6] (actual magnitudes of increases and decreases here are somewhat arbitrary). By contrast in I′, II′, III′, the stretching fc's in the A^- moiety which determine the ie were increased to twice their respective values in the A species, a choice again made to obtain upper limits to ie's. As expected, ie's are larger for III (III′) than for I (I′). K_1's for III′ are quite high upper limits.

We compare the K_1 values for nitrobenzene $^{15}N/^{14}N$ in ref 1d with our results in Table II. The reported gas-phase result at 305 K lies within the range one might have expected from calculations I and I′. However, the value 2.1 reported at 208 K in NH_3 with potassium the counterion far exceeds the value obtained in calculation III′, which is a high upper limit. One can equally well focus on the reported K_1 value 0.4 at 208 K when the counterion is sodium. This low value requires the fc's at the nitrogen atom in the A species to be very high compared to those in A^-; without giving details, it is clear that the required fc changes are "unnatural". Considerations on vapor pressure ie's[7] show that anomalously larger effects in the condensed phase nitrobenzene systems cannot be rationalized as an involvement of low-frequency motions of the condensed phase.

A few calculations are presented in Table II on fluorenone, which would equally well apply to benzophenone since the models for the two systems are similar. Clearly the large $^{13}C/^{12}C$ ie's reported in ref 1e for these systems are also problematic. No comment is made here on the D/H effects in ref 1 or on the $^{13}C/^{12}C$ effect in benzene; the reported magnitudes of these probably do not exceed easily set theoretical upper limits.

Thus, the large magnitudes of heavy atom isotope effects reported in ref 1 for K_1 require unreasonably large changes of force constants between A and A^-; the results cannot be accepted as equilibrium ie's.

Registry No. ^{13}C, 14762-74-4; ^{15}N, 14390-96-6.

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(6) Khatkale, M. S.; Devlin, J. P. *J. Chem. Phys.* **1979**, *70*, 1851; *J. Phys. Chem.* **1979**, *83*, 1636.

(7) Jancso, G.; Van Hook, W. A. *Chem. Rev.* **1974**, *74*, 689 and references therein.

Mixed-Valence Cu(I)Cu(II) Macrocyclic Complex: A Result of a Cu(II)-Promoted Oxidation of Aziridines into Cyanide

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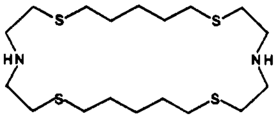
During our investigation on activating properties of the binuclear $[2Cu\subset\mathbf{1}]^{4+}$ system, we have studied its interaction with aziridinum compounds. The *N*-methylaziridine in the presence of $[2Cu\subset\mathbf{1}]^{4+}$ leads to cyanide ions producing a new binuclear mixed-valence copper(I,II) complex, **2**. The two metallic centers, bridged by a cyanide ion, are enclosed in **1**.[1] The X-ray structure and physico-chemical properties of **2** provide a good opportunity to emphasize the expected cyanide binding mode in the mixed-valence derivative of hemocyanin[2,3] depicted for the half-met CN form.[4] It is also a new example of concerted interactions between binuclear complexes, substrates, and solvents in reactions involving multielectronic processes,[5] and could be relevant to the role of the ethylene-forming enzyme (EFE) in the conversion of 1-aminocyclopropane carboxylic acid (ACC).[6,7]



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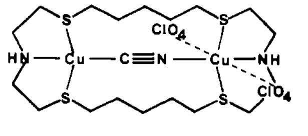

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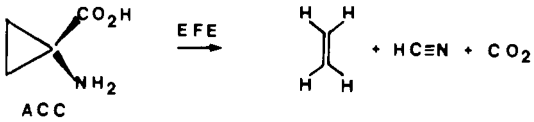

[†] UA405 CNRS: Electrochimie et Physico-chimie des complexes et des systèmes interfaciaux; IBMC CNRS: Laboratoire de Cristallographie Biologique.

(1) (a) Agnus, Y. L. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J. A., Eds.; Adenine Press: New York, 1983; pp 371–393. (b) Agnus, Y.; Louis, R.; Gisselbrecht, J. P.; Weiss, R. *J. Am. Chem. Soc.* **1984**, *106*, 93–102.

(2) (a) Gaykema, W. P. J.; Hol, W. G. J.; Vereijken, J. M.; Soeter, N. M.; Bak, H. J.; Beintema, J. J. *Nature* **1984**, *309*, 23–29. (b) Linzen, B.; Soeter, N. M.; Riggs, A. F.; Schneider, H. J.; Schartau, W.; Moore, M. D.; Yokota, E.; Behrens, P. Q.; Nakashima, H.; Takagi, T.; Nemoto, T.; Vereijken, J. M.; Bak, H. J.; Beintema, J. J.; Volbeda, A.; Gaykema, W. P. J.; Hol, W. G. J. *Science* **1985**, *229*, 519–524. (c) Gaykema, W. P. J.; Volbeda, A.; Hol, W. G. J. *J. Mol. Biol.* **1985**, *187*, 255–275.

(3) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bonding* **1983**, *53*, 1–57.

(4) (a) Himmelwright, R. S.; Eickman, N. C.; Solomon, E. I. *J. Am. Chem. Soc.* **1979**, *101*, 1576–1586. (b) Himmelwright, R. S.; Eickman, N. C.; LuBien, C. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 5378–5388.

(5) (a) Zanello, P.; Tamburini, S.; Vigato, P. A.; Mazzocchin, G. A. *Coord. Chem. Rev.* **1987**, *77*, 165–273. (b) Karlin, K. D.; Gultneh, Y. *Prog. Inorg. Chem.* **1987**, *35*, 219–327.