the assignment of the quadrupole splittings for perdeuterated amphiphiles since constraints placed upon the orientation of the C—D bond axes by anchoring of the head group at the interface may predominate. In addition, these effects may be pH dependent.

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B. J. Forrest, L. Hecker, L. W. Reeves*

Department of Chemistry, University of Waterloo
Waterloo, Ontario, Canada N2L 3G1

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A Proton Nuclear Magnetic Resonance Study of "$\mathrm{H(phen)_2}^+$": Self-Stacking of Protonated Phenanthroline

Sir:

Both potentiometric[1,2] and calorimetric[3] studies on 1,10-phenanthroline in acidic solutions have suggested the presence of $\mathrm{H(phen)_2}^+$. However, as recent ^{1}H NMR studies[4] showed that phenanthroline itself self-associates strongly in aqueous solution, forming a stack, and that even the charged $\mathrm{Zn(phen)}^{2+}$ also stacks, albeit much more weakly, it seemed likely that self-stacking of phenanthroline would also occur in the acidic solutions used in the earlier studies.[1-3] Measurements of the concentration dependence of the ^{1}H NMR spectrum of phenanthroline in acidic solution now show that considerable self-stacking occurs, and that this self-stacking accounts better for the earlier results than does the discrete molecular species $\mathrm{H(phen)_2}^+$ alone.

The ^{1}H NMR spectrum of 1,10-phenanthroline at pD 1.8 [corresponding to $\mathrm{H(phen)}^+$][5] and at pD 5.4 [corresponding to the supposed $\mathrm{H(phen)_2}^+$][6] changes considerably as the concentration is increased from 0.01 to 0.1 M: the resonances of H_α, H_β, H_γ, and H_δ shift 0.263, 0.193, 0.324, and 0.415 ppm upfield at pD 1.8, and 0.424, 0.397, 0.603, and 0.744 ppm upfield at pD 5.4, respectively. A computer-calculated least-squares fit[7] of the variation with concentration of the chemical shifts of all four protons and of the differences between the chemical shifts of the individual protons[9] gave the stability and constants which are listed in Table I. The values for unprotonated phenanthroline are also listed for comparison.

Table I. Equilibrium Constants for Stacking, and Chemical Shifts of Monomeric and Stacked Phenanthroline[a]

	H_α	H_β	H_γ	H_δ	av[b] K, M^{-1}
			pD 8		
K	20.8	20.3	21.8	24.5	23.6 ± 1.8
δ_0, ppm	9.087	7.847	8.547	8.021	
δ_∞, ppm	8.23	6.79	6.72	5.67	
$\delta_0 - \delta_\infty$, ppm	0.86	1.06	1.82	2.35	
			pD 5.4		
K	18.7	17.5	20.7	22.5	19.6 ± 2.1
δ_0, ppm	9.112	7.958	8.671	8.039	
δ_∞, ppm	7.93	6.86	6.98	5.93	
$\delta_0 - \delta_\infty$, ppm	1.18	1.10	1.70	2.11	
			pD 1.8		
K	9.0	8.0	11.3	11.0	12.0 ± 2.0
δ_0, ppm	9.223	8.159	8.950	8.242	
δ_∞, ppm	8.38	7.54	7.92	6.91	
$\delta_0 - \delta_\infty$, ppm	0.85	0.62	1.03	1.33	

[a] Measured on a Bruker WH-90 FT spectrometer (90.025 MHz) at 27 °C, $I = 0.1$ ($\mathrm{NaNO_3}$ in $\mathrm{D_2O}$), using $\mathrm{(CH_3)_4N^+NO_3^-}$ as internal reference at 3.188 ppm. [b] Weighted mean of the values of K given by the chemical shifts of H_α, H_β, H_γ, and H_δ and by the six relative shifts $\delta_\alpha - \delta_\beta$, $\delta_\alpha - \delta_\gamma$, ... $\delta_\gamma - \delta_\delta$ (see text and note 9).

The stability constant for self-stacking is lower for $\mathrm{H(phen)}^+$ (pD 1.8) than for phenanthroline itself, owing to Coulombic repulsion; this repulsion is however much smaller than in $\mathrm{Zn(phen)}^{2+}$ for which the stability constant[4] is only 1.1 M^{-1}. It is noticeable that the stability constant at pD 5.4 is not much lower than that for unprotonated phenanthroline (at pD ~8); at pD 5.4, on an average, alternate molecules in the stack are protonated, and, owing to the increased distance between the charges, the Coulombic repulsion is only small. All of the resonances of monomeric phenanthroline shift downfield on protonation as expected. The same is true for the calculated positions of the resonances of H_β, H_γ, and H_δ in fully stacked phenanthroline; however the calculated position of the resonance of H_α is shifted slightly upfield as the pD is decreased from ~8 to 5.4, presumably due to a slight change in the orientation of the molecules in the stack; on further acidification the expected downfield shift occurs.

Rund and Keller measured[10] the variation of the ^{1}H NMR spectrum of phenanthroline with added acid[11] and concluded that, as the solubility of unprotonated phenanthroline is low (0.015 M at 25 °C), unprotonated phenanthroline could not account for the strong solutions possible,[13] but that $\mathrm{H(phen)_2}^+$ must be present in solutions with H^+:phen ratios of 1:2. However the formation of a stack in which some molecules are protonated completely accounts for the variation of the NMR spectrum with pH[10] and with phenanthroline concentration as observed here and for the variations of the solubility with pH observed earlier.[1,10]

A preliminary X-ray measurement[14] of the unit cell size of the solid "$\mathrm{H(phen)_2ClO_4}$" isolated from weakly acidic solutions indicated insufficient space for a regular tetrahedral arrangement of nitrogen atoms about the hydrogen ion in the proposed $\mathrm{H(phen)_2}^+$ cation: the structural measurements have never been completed. Presumably the crystals contain a stack of phenanthroline molecules, for which there is sufficient space in the unit cell.

In the earliest report[1] of potentiometric evidence for the existence of $\mathrm{H(phen)_2}^+$ and $\mathrm{H(phen)_3}^+$, 0.015 M solutions of phenanthroline were used. Owing to the similarity between the stability constants for stacking in neutral solution and at pD 5.4, the proportions of the variously sized stacks changes little

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with pH: 64, 26, 8, and 2% for monomer, dimer, trimer, and tetramer in 0.015 M solution. Indeed the average number of molecules in each stack decreases from 2.28 at pD 8, 2.24 at pD 5.4, to 2.16 at pD 1.8 for a 0.015 M solution. Thus it is understandable that the original results fitted the presence of $H(phen)_2^+$ with some suggestion of the presence of $H(phen)_3^+$. More recent measurements[2,3] have used 0.01 M solutions and found only evidence for $H(phen)_2^+$: the average number of molecules in each stack is nearer 2.0 under these conditions. Likewise the variation of the pK_a with pH found in the potentiometric determination of the pK_a by Krumholz[15] and the similar anomalies found in potentiometric titrations in 0.01 M solution observed earlier[16] can also be explained by the presence of short stacks. However, in the much stronger solutions (0.6 M) used by Rund,[10] stacking proceeds further: at the pK_a the average length of stack is 5.0 and at pD 1.8 it is still 4.2, despite the lower stability constant. In the strongest solution obtainable at the pK_a, 3.5 M, there are on an average ten molecules in each stack and 64% of the phenanthroline is present in stacks containing more than ten molecules: only 1.3% is present as the monomer.

Thus the experimental results which led to the suggestion of $H(phen)_2^+$ and $H(phen)_3^+$ are explained better by the stacking of phenanthroline under the conditions used.

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(7) Analysis of second-order NMR spectra and calculation of the stability constants for self-stacking were performed using a Hewlett-Packard 9821A calculator. The variation of chemical shift with concentration was fitted using the isodesmic[8] model of indefinite noncooperative stacking to the relationship $\delta_{obsd} = \delta_\infty + (\delta_\infty - \delta_0)[1 - (4KC + 1)^{1/2}]/2KC$ between the observed chemical shift δ_{obsd} in a solution of total phenanthroline concentration C, the chemical shifts at infinite dilution δ_0 and of a molecule within a stack δ_∞ and the stability constant K.
(8) The isodesmic model of indefinite noncooperative stacking (Schimmack, W.; Sapper, H.; Lohmann, W. *Biophys. Struct. Mechanism* **1975,** *1*, 113–120) assumes that the equilibrium constants for the equilibria

$$(A)_n + A \rightleftharpoons (A)_{n+1}$$

$$K = [(A)_{n+1}]/[(A)_n][A]$$

are all equal [A = phenanthroline, half-protonated phenanthroline (pD 5.4), or monoprotonated phenanthroline (pD 1.8)].
(9) Effectively using one resonance of phenanthroline as a reference for another which is shifted more, to exclude the possibility of any interaction with the internal reference which was $(CH_3)_4N^+$. Use of an external reference, together with an estimated susceptibility correction, for the strongest solutions of phenanthroline at pD 5.4 (0.6–3.5 M) showed that, with [phen] $\geqslant$ 2 M, no internal reference could be reliable.
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Paul R. Mitchell
Institute of Inorganic Chemistry, University of Basel
Spitalstrasse 51, CH-4056 Basel, Switzerland

Metal–Ligand Synergism in the Chemistry of Macrocyclic Complexes. Base-Induced Reduction of a Cobalt(III) Complex[1]

Sir:

Base-induced, oxidation–reduction reactions of transition metal complexes are reasonably common,[2-6] but almost always mechanistically obscure. In many of these reactions, reduction of the metal in a coordination complex is accompanied by oxidation of a basic species. These reactions may be very roughly classified into two groups depending on whether the base oxidized is a ligand or solvent species. However, it seems unlikely that a similar dichotomous classification will be useful at a mechanistic level since these reactions frequently appear to involve facile electron transfer from a coordinated ligand to the metal. Even the oxidations involving solvent species frequently proceed through intermediates formed from nucleophilic additions of the base to an unsaturated ligand.[3,4,7] Thus, the frequently proposed, but rarely observed, key intermediates in these reactions contain reduced metal centers and coordinated radical ligands. While most of these reactions are very complicated in detail, their potential significance is illustrated in proposals that they mediate base hydrolyses,[8] could be the basis for catalytic oxidations of organic substrates,[9] and could play a key role in the use of transition metal substrates to mediate the light-induced oxidation of water.[4]

We have found a substantial number of base-induced oxidation–reduction reactions of tetraaza macrocyclic complexes of cobalt. These reactions are mechanistically very interesting since the coupling of ligand and metal redox chemistry seems to provide a means for circumventing the very large reorganizational barriers associated with cobalt(III)–(II) couples.[10] Some of these reactions (e.g., with the $Me_4[14]tetraeneN_4$[11] ligand) appear to result in ligand degradation and difficult-to-characterize products.[10c] In contrast we have found the base-induced redox chemistry of $(Me_2[14]1,11\text{-}dieneN_4)$-cobalt[11] complexes to be very extensive, but reasonably straightforward. The key to this system has been the discovery that a major product of the base-induced redox chemistry is a C–C-coupled, bis macrocyclic, binuclear complex.

When rigorously deaerated, aqueous $Co(Me_2[14]1,11\text{-}dieneN_4)Cl_2^+$ (perchlorate media) and NaOH are mixed, a sparingly soluble, yellow precipitate (A) is formed immediately in ~90% yield. The new compound is a low-spin cobalt(II) complex [$\mu_{eff} = 2.12\ \mu_B$/Co; λ_{max} 345 nm (ϵ 5.7×10^2/Co)]. The elemental analysis of this compound is not distinguishable from that of $[Co(Me_2[14]1,11\text{-}dieneN_4)(OH_2)_2](ClO_4)_2$; however, the physical properties differ considerably. The most immediate difference is the very limited solubility of the new compound. Under conditions of high pH (>3) in aerated solutions, we have found that A is formed in competition with the previously reported oxygenation product, $Co(Me_2[14]\text{-}1,11\text{-}dieneN_4\text{-}13\text{-}one)(OH_2)_2^{2+}$.[10c] In acidic chloride solutions A may be air oxidized to a cobalt(III) complex, B. This latter complex is also obtained from the stoichiometric (1:1) $FeCl_3$ oxidation of $Co(Me[14]1,11\text{-}dieneN_4)Cl_2^+$ in deaerated, acidic solutions. The methods of generation (summarized above) and the physical characterization (summarized below) indicate that products A and B are binuclear complexes coupled through the bridgehead carbons of the β-diimine moieties of the macrocyclic ligand.

The infrared spectra of B and $Co(Me_2[14]1,11\text{-}dieneN_4)$-$Cl_2^+$ differ principally in the C=N region, with the strong absorptions at 1667 and 1691 cm^{-1}, respectively. A very similar shift is observed for the analogous monomeric complex methylated at the bridgehead carbon (C-13). In the ^{1}H NMR spectra, the resonance for the bridgehead protons (integrated intensity equivalent to one ^{1}H per macrocycle) of compound B were 5.9 ppm downfield from Me_4Si ($Me_2SO\text{-}d_6$ solvent),

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