Figure 2. Infrared spectra (Nujol mulls on CsI plates) of the 1350–950 cm^{-1} region for tetraethylammonium ion in the (A) chloride, (B) chloride monohydrate, and (C) hexafluorosilicate.

electronegativity of chlorine relative to fluorine; otherwise the band shapes and splittings are nearly identical. The water–chloride clusters show significant bias toward C_{2v} symmetry; the chloride hydrate-d_2 spectrum at 300 K closely resembles that of the fluoride hydrate-d_2 at 10 K (Table I). Also, in the spectrum of the chloride hydrate at 10 K, the stretching and deformation bands are resolved into their $A_1 + B_1 + B_2$ components (Figure 1 and Table I), which is not true for tetramethylammonium fluoride hydrate. Whether this somewhat greater departure from T_d symmetry arises from lattice effects or from the greater dissimilarity between oxygen and chlorine as compared to oxygen and fluorine cannot be determined at this time.

From extensive cation infrared spectra–crystal structure correlations for tetramethylammonium ion salts,[15] we were able to show[3,4] that tetramethylammonium fluoride hydrate most probably has a unit cell isomorphous with that of the hexafluorosilicate, which contains a dinegative ion with radius equal to that calculated for the proposed $H_4O_2F_2^{2-}$ ion. No such array of structural data is available for tetraethylammonium ion salts; however, we find that the infrared spectrum of the tetraethylammonium cation in the chloride hydrate differs from that in the chloride and again resembles closely that in the hexafluorosilicate (Figure 2). In the 1350–950-cm^{-1} region, the chloride shows two doublets at 1194–1177 and 1073–1057 cm^{-1} and a singlet at 1003 cm^{-1}. The 1003-cm^{-1} band remains unchanged in both the chloride hydrate and the hexafluorosilicate; however, in the chloride hydrate the doublets have collapsed into structured singlets at 1177 and 1077 cm^{-1}, while the hexafluorosilicate shows two singlets at 1185 and 1077 cm^{-1}. More striking is the appearance of two new bands in the spectra of both the chloride hydrate and the hexafluorosilicate at 1316 and 1034 cm^{-1} and 1314 and 1030 cm^{-1}, respectively; these bands are entirely absent in the spectrum of the chloride (Figure 2).

Several weak bands appear in the 2800–2000-cm^{-1} region of the infrared spectrum of tetraethylammonium chloride hydrate, and these can be seen more clearly in the 10 K spectrum of this sample (Figure 1). The two bands at 2205 and 2145 cm^{-1} are reasonably ascribed to combination bands of the XH bend with the two X_4 deformation bands of the water–chloride cluster. The group of bands between 2700 and 2500 cm^{-1} have been identified as the characteristic N–H stretching bands of triethylammonium chloride. In pure triethylammonium chloride, these bands are extremely intense; the N–H band has five times the absorption of the next strongest band, at 1040 cm^{-1}, in the spectrum of triethyl-

ammonium chloride. Neither the 1040-cm^{-1} band nor any other bands ascribable to triethylammonium chloride can be detected in the chloride hydrate spectra at either 300 or 10 K; the presence of this small quantity of the triethylammonium salt does not perturb the spectrum of the hydrate.

Triethylammonium chloride is presumed to arise from β-hydrogen removal from tetraethylammonium ion by chloride ion to yield triethylamine, hydrogen chloride, and ethylene; similar Hofmann elimination has been shown for tetraethyl-[5] and tetrapropylammonium[16] fluorides but has not been previously reported with chloride ion. The commercial tetraethylammonium chloride hydrate starting material is free of triethylammonium chloride, and the amount of the triethylammonium salt increases slowly with time of reflux. The sample of chloride hydrate used for the low-temperature spectrum was ground from a large crystal obtained after several days of reflux; rapid recrystallization yields chloride hydrate free of triethylammonium chloride.

In conclusion, we believe that the water–chloride species in tetraethylammonium chloride hydrate is closely related structurally to the water–fluoride cluster in tetraalkylammonium fluoride hydrates. Since crystalline material can be prepared easily by recrystallization from acetone, we suggest that diffraction studies on this hydrate would be highly desirable. We do not have facilities for such studies ourselves but would be pleased to furnish crystals to persons interested in this material.

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Electrochemistry of Main-Group Phthalocyanines

A. B. P. Lever* and P. C. Minor

Metallophthalocyanines have been the subject of several electrochemical investigations,[1-9] but no systematic study as a function of central metal ion has been published. We have recently completed a study of the electrochemistry of main-

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Table I. Main-Group Phthalocyanine Reduction and Oxidation Couples (mV vs. SCE)

metal	radius, pm	ze/r	E°_{Ox},[a] mV	E°_{Red},[a] mV	E_{Ox} − E_{Red}, mV
$(O\text{-}^tAm)_2Si^{IV}$	54	0.074		−540	
$ClAl^{III}$	67.5	0.044	915	−655	1570
$ClGa^{III}$	76	0.040	865	−735	1600
$ClIn^{III}$	94	0.032	830	−715	1545
Mg^{II}	86	0.023	650	−930	1580
Zn^{II}	88	0.023	685	−900	1585
Cd^{II}	109	0.018	540	−1170[b]	1710
Hg^{II} [b]	110	0.018	250	−1305	1555
Pb^{II} [b]	133	0.015	670	−720	1390

[a] Potentials quoted to nearest 5 mV.   [b] These data were not included in the derivation of the equation of the line. Where previous data exist, agreement is satisfactory.[1,9]

group phthalocyanines with a view of providing a basis for the design of photoredox catalysts. Differential-pulse polarography and cyclic voltammetry were employed to identify the energies of the various redox couplex. We are concerned here with the first ring reduction and first ring oxidation. For most couples, these processes were reversible or quasi-reversible in the medium (DMF/TEAP) employed.

A well-defined relationship was observed between the first ring reduction, or oxidation, and the size and charge of the central metal ion. This information is of special value of those interested in the potential use of phthalocyanines as photocatalysts.

Experimental Section

The main-group metallophthalocyanines were prepared and purified by well-established literature methods.[10] Electrochemical data were recorded with Princeton Applied Research Models 173, 174A, 175, a Houston Model 9002A XY recorder, and Tektronix 5103N storage oscilloscope. A standard calomel electrode was used as a reference (with Luggin capillary) and platinum wire used as working and counterelectrodes. Dimethylformamide (Fisher, "Spectranalysed"), and tetraethylammonium perchlorate (Eastman, recrystallized several times) were used as solvent and supporting electrolyte, respectively. Details of our electrochemical procedures have been previously published.[5]

Discussion

Redox couples for a range of main-group metallophthalocyanines are shown in Table I. A well-defined pattern is readily apparent. (i) The metal phthalocyanines with the more positive central metal ions are more difficult to oxidize. (ii) The phthalocyanine anions with the more positive central metal ions are more difficult to oxidize, i.e., their neutral species are easier to reduce. (iii) From comparison of the dipositive or tripositive ions, the smaller the ion, the easier is the species to reduce, and the more difficult to oxidize. (iv) Elements with especially large radii, specifically lead and mercury, have anomalous redox energies; these ions presumably sit outside the phthalocyanine ring and do not then fit into the well-behaved series of complexes.

Observations i–iii lead to the supposition that these redox energies are functions of the polarizing power of the central metal ion, expressable as charge/radius (ze/r). Increasing polarizing power of the central metal ion causes an increase in the potential at which the phthalocyanine or phthalocyanine anion is oxidized.

There are a variety of metal ion radii available in the literature. We have chosen to use the effective ionic radii of Shannon and Prewitt[11] because their list contains a fairly
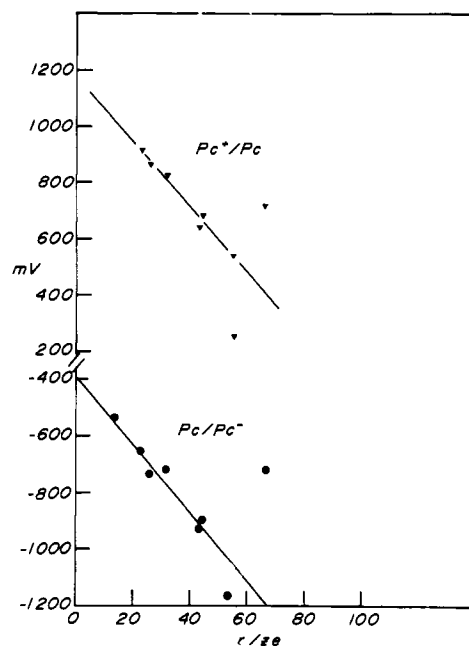

Figure 1. Main-group phthalocyanine oxidation and reduction potentials plotted as a function of r/ze. Points lying off the lines are for the large ions Pb(II), Hg(II), and Cd(II) (reduction only) which do not lie within the phthalocyanine ring.

complete set of radii shown as a function both of valency and coordination number.

The coordination numbers of these species are not unambiguously known, but it is likely that most of the complexes will be solvated to form six-coordinate derivatives in solution in DMF.

Since these main-group species are all closed-shell ions, we have used the formal charge (2+ or 3+ etc.) to generate (ze/r) values shown in Table I.

A plot of these quantities, E° vs. ze/r, is curved. A linear plot is conveniently obtained by plotting E° against (r/ze) and is shown in Figure 1 for both phthalocyanine reduction and oxidation. The linearity of both plots is striking. The equations of the lines are as follows: oxidation, $(ze/r)(E^\circ - 1170) = -11.7$; reduction, $(ze/r)(E^\circ + 385) = -12.0$. E° is relative to the standard calomel electrode.

Although the least-squares plots do not show that the lines are strictly parallel, the deviation therefrom is small. For most species the difference in potential between ring reduction and oxidation is close to 1570 mV.

Provided that the metal ion sits inside the phthalocyanine ring, these correlations provide a method of estimating main-group phthalocyanine redox potentials. Interestingly, the limit of phthalocyanine oxidation and reduction appears to be +1170 and −385 mV (vs. SCE), respectively, as (r/ze) approaches 0. All main-group phthalocyanines should fall within these confines, provided the metal lies inside the phthalocyanine ring.

Successive oxidation and reduction potentials (e.g., second and third reductions) can be estimated from the established intervals between these various processes.[4]

Transition-metal phthalocyanines follow a similar trend.[5,8,12] For a given valency where, within the first-row transition series the size of the metal ion does not change greatly, the reduction potential depends upon the valency. Thus Cr(II), Mn(II), Ni(II), and Cu(II) phthalocyanines all reduce at essentially the same potential (ca. −0.84 vs. SCE) anodic of M(I) species

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such as Fe(I) and Co(I) and cathodic of M(IV) species such as TiO and VO.[12]

The use of these data in the design of photoredox catalysts will be the subject of a future communication.[13]

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Intramolecular Redox Decomposition of [(en)₂Co(SCH₂CH₂NH₂)]²⁺ and Related Complexes

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Intramolecular electron-transfer (IET) rates are not affected by precursor complex formation[1] and therefore directly reflect the extent of coupling between the electron-donor and -acceptor portions of the molecule. Recent strategies employed to measure IET rates include (1) formation of metastable coordinated ligand radicals (often by pulse radiolytic techniques) which subsequently decay by IET,[2–4] (2) formation of metastable binuclear complexes which then decay by IET,[5–7] and (3) evaluation of intervalence electron transfer between metals of stable binuclear complexes.[8–10] Another approach to measuring IET rates has appeared sporadically in the literature[11–14] but has not been systematically exploited since it depends on the availability of complexes with very specific properties. These complexes must contain a potentially reducing ligand coordinated to a metal ion that can function as a one-equiv oxidant (usually cobalt(III)) in an array that is kinetically inert but thermodynamically unstable. In addition, upon thermal activation these complexes must undergo IET to yield the one-equiv reduced metal center and a ligand free radical rather than suffering the usual metal–ligand bond fission. This type of IET reaction is of interest not only because it allows the intrinsic rate of inner-sphere ligand-to-metal electron transfer to be probed but also because it is the

thermally induced analogue to photochemically induced ligand-to-metal charge-transfer excitation.[15,16]

During our research into the chemistry of (thiolato)cobalt(III) complexes,[17–19] we noted that while the prototype complex [(en)₂Co(SCH₂CH₂NH₂)]²⁺ has remarkable kinetic stability under ordinary conditions, it does slowly undergo intramolecular redox decomposition upon thermal activation. This thiol-to-metal IET reaction is of special interest in view of the prevalence of thiol–metal interactions in redox enzyme systems[20,2] and in view of the possibility that it is the harbinger for a large number of IET reactions of (thiolato)cobalt(III) complexes, the composition of which can be systematically and extensively varied. In this paper we report on the kinetics of the intramolecular redox decomposition of [(en)₂Co(SCH₂CH₂NH₂)]²⁺ and some of its derivatives.

Experimental Section

Triply distilled, charcoal-filtered water and doubly vacuum distilled perchloric acid (G. F. Smith, 70–72%) were used for all kinetic experiments. Lithium perchlorate solutions were prepared by neutralization of Baker "Ultrex" lithium carbonate. The perchlorate salts of (2-mercaptoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) and ((methyl 2-aminoethyl thioether)-*N,S*)bis(ethylenediamine)cobalt(III) were prepared and purified as previously described.[22] Spectrophotometric determinations were conducted on a Cary 14, Cary 210, or Cary 118B recording spectrophotometer. Temperature was maintained to +0.5 °C (as measured with a National Bureau of Standards certified thermometer) by means of a Neslab constant-temperature bath.

The metal-containing reaction product was quantitatively determined to be cobalt(II) by means of a modified Kitson[23] procedure; the Kitson procedure was also used to monitor the amount of cobalt(II) produced as a function of time. The organic reaction products were qualitatively identified by the following procedures. After reaction of the title complex in 0.1 M HClO₄ at 70 °C for 4 days, the reaction solution was made basic with an excess of 1 M NaOH and the organic products were extracted into chloroform. (1) TLC analysis of the CHCl₃ layer (Eastman 6060 SiO₂ sheets; 1/1 acetone/methanol mobile phase; visualization by either molecular iodine or phosphomolybdic acid) shows only two components. These components have the same respective R_f values as authentic samples of ethylenediamine and cystamine (NH₂CH₂CH₂SSCH₂CH₂NH₂) treated in the same fashion. (2) During visualization with phosphomolybdic acid, the component identified as cystamine behaves in the same fashion as does authentic cystamine and as is typical for disulfides; i.e., no color develops until the chromatogram is heated at 110 °C for about 30 min. Thiols generate color with phosphomolybdic acid immediately at room temperature, while sulfonic acids do not generate color even on heating. (3) The ultraviolet spectrum of the chloroform layer exhibits a broad peak at 247 nm, while a similarly treated sample of authentic cystamine exhibits an analogous peak at 248 nm. Absorption in this region is typical for dialkyl disulfides.[24]

The kinetics of the redox decompositions were monitored at 428 or 278 nm for [(en)₂Co(SCH₂CH₂NH₂)]²⁺, at 482 or 500 nm for the methylmercury adducts,[18] and at 487 nm for the thioether complex; observed reaction rates are not dependent upon the monitoring wavelength. The initial concentration of the cobalt(III) complex ranged from 0.07 to 5.4 mM, and ionic strength was maintained at 1.00 ± 0.01 M with HClO₄ and LiClO₄. In a typical kinetics experiment, 100 mL of a HClO₄/LiClO₄ solution containing the cobalt(III)

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