II (20.2%), III (29.7%), and IV (24.2%) were collected as described.[5] Fractionating precipitation, by the given procedure,[5] of a 1.2-g sample of fraction I from benzene solution under Ar in the presence of hexane as the nonsolvent afforded six subfractions, the second, third, fourth, and fifth of which were chosen for further evaluation and are listed in Table I as Ia-d, together with fractions III and IV. All fractions gave IR spectra identical with those obtained in the previous work.[5] Excellent solubility in cold benzene was reaffirmed for Ia-d and IV. Fraction III, practically insoluble in cold benzene, dissolved in hot toluene and chlorobenzene. Anal. Calcd for $C_{50}H_{42}Fe_5$ (1, $\bar{n}$ = 5): C, 65.12; H, 4.59; Fe, 30.28. Found for III: C, 64.98; H, 5.01; Fe, 29.79.

A sample (0.5 mmol) of III was treated with 2,3,5,6-tetracyanoquinodimethane (TCNQ, freshly recrystallized from deoxygenated benzene, 1.0 mmol) in benzonitrile exactly as described by Yamamoto et al.[2] to give a black TCNQ salt (95%). Anal. Calcd for III-TCNQ (TCNQ/Fe = 0.85): C, 67.77; H, 3.32; Fe, 15.60; N, 13.30. Found: C, 67.11; H, 3.53; Fe, 15.11; N, 12.93.

B. By Organohalide-Magnesium Polycoupling. Crude poly(ferrocenylene) was prepared from 1,1′-dibromoferrocene, 1,2-dibromoethane, and magnesium (1:1:2), catalyzed by $NiCl_2$, as described[1] for experiment 2 of that paper. The crude product was separated into fractions I′ (1%), II′ (3%), III′ (26%), and IV′ (19%) and further into Ia′-d′ (from I′) by the same techniques as employed for the isolation of the nonprimed counterparts under A, above. IR spectra were similar to those of corresponding nonprimed fractions but, as noted before,[1] additional impurity bands appeared at 2900-2850 cm^{-1} and near 870 cm^{-1}. NMR spectra ($CDCl_3$) of Ia′-d′ gave the reported[5] monolithic multiplet at δ 3.8-4.4 and weak impurity resonances[1] in the vicinity of δ 2. Fractions Ia′-d′ and IV′ were readily soluble in cold benzene, and III′ showed the same solubility behavior as its counterpart III. Bromine analyses were performed on a Ia′, Id′, and III′: Found: Br, 2.4 (Ia′), 3.9 (Id′), 2.6 (III′).

Samples (0.5 mmol) of both Ib′ and III′ were converted to the TCNQ salts by treatment with TCNQ (1.0 mmol) in benzonitrile by Yamamoto's procedure.[2] Anal. Found for Ib′-TCNQ (TCNQ/Fe = 0.80): N, 12.48; Fe, 15.47; for III′-TCNQ (TCNQ/Fe = 0.83): N, 12.70; Fe, 15.22.

Acknowledgment. Support of this project by Shell South Africa (Pty) Ltd. is gratefully acknowledged. Fathima Khan is thanked for her able assistance with the preparative work.

Registry No. Poly(1,1′-ferrocenylene) (homopolymer), 55884-62-3; poly(1,1′-dibromoferrocene) (homopolymer), 77979-54-5; (1,1′-diiodoferrocene)·(1,1′-dilithioferrocene) (copolymer), 69153-97-5; poly(1,1′-ferrocenylene) (SRU·TCNQ, 55884-67-8.

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(6) The molecular mass was assessed[1] from elemental analytical data on the assumption that each molecule bears two bromoferrocenyl end groups. This premise is invalidated by our observation that polycoupling in the organohalide-magnesium reaction[1] is accompanied by reductive dehalogenation (formation of bromoferrocene and traces of ferrocene identified by GC).

(7) The oligomeric nature of this crystalline material is also apparent from the thermogram (under N_2) recorded by Yamamoto's group[1] for their best sample, which indicates weight loss to set in near 300 °C and relative residual weight at 600 °C to approximate 75%. The thermogram obtained by us on our fraction Ib (Du Pont Thermogravimetric Analyzer, Model 951, 15 °C min^{-1}, under Ar), in contrast, shows incipient weight loss for this poly(ferrocenylene) to be some 100 °C higher, the relative residual weight at 600 °C being ca. 85%.

(8) Microanalyses were performed in the Analytical Laboratory of this Department; we are indebted to Mrs. S. Heiss for this analytical service. X-ray powder diffractograms were scanned over the range 2θ = 10-28° on a Rigaku Geigerflex diffractometer, D-Max IIIA, at a scan rate of 10 deg min^{-1}.

Carboranylene-Bridged Poly(benzimidazole)

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The icosahedral *meta*-carborane (1,7-dicarba-*closo*-dodecaborane(12)) cluster lends itself, much like the 1,2- and 1,12-dicarba isomers, as an attractive monomer constituent for the preparation of boron-containing macromolecules for a wide range of potential applications as biomedical, nuclear-shielding, or thermostable materials.[1] Our longstanding interest in heteroaromatic polymers prompted us to utilize the recently described[2] 1,7-diformyl-*meta*-carborane for copolymerization with 3,3′-diaminobenzidine (DAB) and subsequent cyclodehydrogenation of the resulting poly(azomethine) **1** to the carboranylene-bridged poly(benzimidazole) **2**. The low-temperature solution polymerization of aromatic dialdehydes with bis(*o*-diamino)-substituted arenes and subsequent oxidative cycloaromatization of the intermediary poly(azomethines) represent a smooth two-stage synthesis of linear, aromatic poly(benzimidazoles).[3] Using this two-stage approach, we first prepared the open-chain poly(azomethine) **1** by anaerobic copolymerization of 1,7-diformyl-*meta*-carborane and DAB (1:1) in *N*,*N*-dimethylacetamide (DMAC) (6 h at -10 °C, 24 h at 0-25 °C, and then 1 h at 50 °C; Scheme I).

Although a soluble polymeric product was formed under these conditions, the degree of polymerization proved to be unexpectedly low (η_{inh} = 0.08 dL g^{-1}); in addition, the polymer contained sizeable quantities of (unsubstituted) *meta*-carborane. Use of a 5% molar excess of the dialdehyde increased the degree of polymerization only slightly (η_{inh} = 0.09 dL g^{-1}). Extending the reaction time at 50 °C to 6 h did not result in a molecular mass increase as previous experience[3b] would suggest; on the contrary, it caused a dramatic decrease (η_{inh} = 0.02 dL g^{-1}). At the same time, there was enhanced contamination by *meta*-carborane, the latter apparently generated from **1** by cleavage of the C-C bond connecting the azomethine carbon to the carborane carbon atom.[4] In order to suppress this competing backbone fission, it proved necessary to compromise by keeping both the overall reaction time and the upper reaction temperature to a minimum. For example, 6 h at -15 °C and a total of 30 h at 0-25 °C under argon (dialdehyde/DAB = 1.1)[5] gave poly(azomethine) **1** only insignificantly contaminated by *meta*-carborane, although, as would be expected, both the overall polymer yield and the degree of polymerization remained low (first polymer fraction 11% yield, η_{inh} = 0.1 dL g^{-1}; second polymer fraction 56% yield; η_{inh} = 0.07 dL g^{-1}). Surprisingly, even under these mild experimental conditions, electronic absorption spectroscopy indicated that some cyclodehydrogenation (vide infra) had occurred concurrently with polymerization; the spectra (in deoxygenated

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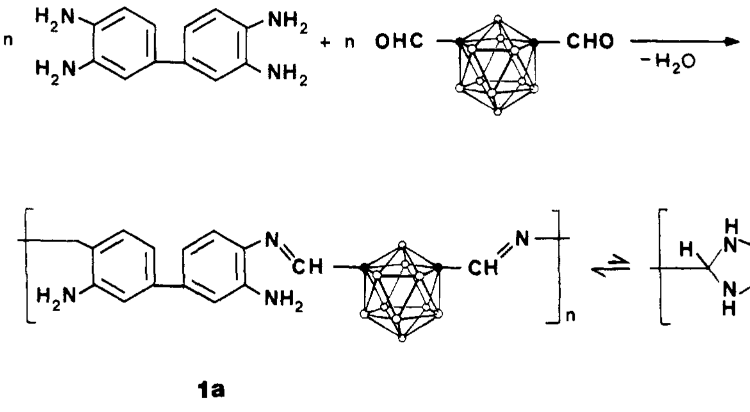
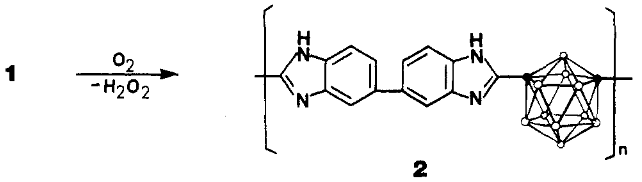
Scheme I



Scheme II



DMAC) of all polymeric products from various repeat runs displayed poly(benzimidazole) bands[3b,c] at 303 nm in addition to poly(azomethine) absorption[3b] near 295 and 440 nm. The IR spectra (KBr) showed the strong BH stretching band at 2590 cm^{-1}, the azomethine C=N stretching band at 1610 cm^{-1} (burying any weak C=C or C=N benzimidazole absorption near this position), and the aromatic out-of-plane CH deformation bands at 865 (w) and 810 (m) cm^{-1}, in addition to the broad (albeit weak) NH stretching feature at 3500–2900 cm^{-1} typical of the benzimidazole system. Weak formyl end-group absorption appeared at 1720 cm^{-1}, and a very faint CH stretching band indicative of simple (i.e., deformylated; vide infra) carboranyl termination emerged at 3110 cm^{-1}. Elemental analytical results were substantially in agreement with the composition of 1 containing minor populations of cyclodehydrogenated units, although there was considerable scattering of data as a consequence of the polymer's combustion resistance.

The second stage of the synthesis involved ferric ion-catalyzed air oxidation of the intermediate 1, dissolved in DMAC, under the previously developed[3a,b] conditions.[6] This resulted in aromatization of azomethine-type units through cyclodehydrogenation, giving rise to the formation of the heteroaromatic polymer 2, poly(*meta*-carborane-1,7-diyl-5,5′-bibenzimidazole-2,2′-diyl) (2)[7] (Scheme II).

Completion of the cyclodehydrogenation process under these conditions was indicated by the disappearance of poly(azomethine) absorption in the electronic spectra, while poly(benzimidazole) absorption at 304 nm attained maximum intensity ($\log \epsilon = 4.08$). The poly(benzimidazole) 2 so obtained in various repeat experiments possessed the same degree of polymerization as the precursor 1 ($\eta_{\mathrm{inh}} \simeq 0.1$ dL g^{-1}) and gave an IR spectrum similar to that of 1 except that the strong 1610-cm^{-1} band was replaced by a broader and less intense one due to the C=C and C=N stretching modes of the benzimidazole ring system at 1618 cm^{-1}, a second characteristic[3c] benzimidazole band emerged in moderate strength at 1445 cm^{-1}, and the broad absorption at 3400–2900 cm^{-1} was enhanced in intensity. Thermogravimetric analysis (He, 5 °C min^{-1}) performed on a sample of 2 with $\eta_{\mathrm{inh}} = 0.1$ dL g^{-1} indicated an incipient weight loss at 550 °C and a relative residual weight of 40% at 800 °C. The thermogram is reproduced in Figure 1, together with that of a "standard" poly(1,3-phenylene-5,5′-bibenzimidazole-2,2′-diyl), $\eta_{\mathrm{inh}} = 0.5$ dL g^{-1}.[3b]

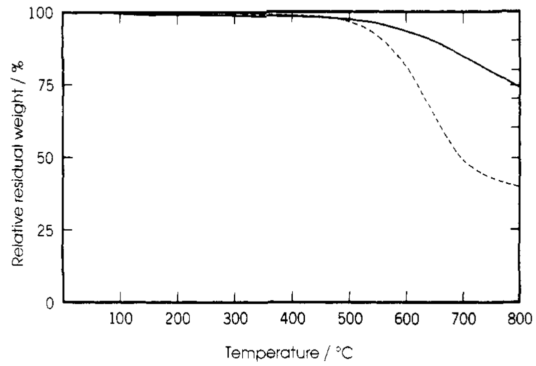
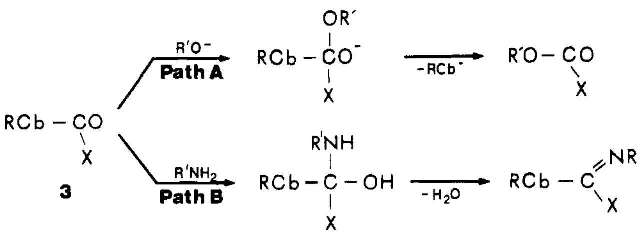


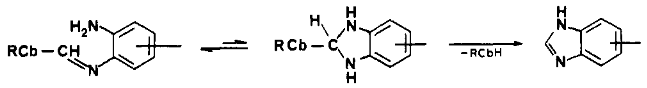
Figure 1. Thermograms (He, 5 °C min^{-1}) of poly(*meta*-carborane-1,7-diyl-5,5′-bibenzimidazole-2,2′-diyl) (2) (dashed line) and poly(1,3-phenylene-5,5′-bibenzimidazole-2,2′-diyl) (solid line). Samples predried for 15 h at 150 °C (0.2 torr).

The observed propensity for C–C bond fission[8] in 1 can be rationalized in terms of the electronic behavior of the carboranyl group as a substituent. The predominance of multicenter, two-electron bonds in the framework structure renders the *meta*-carborane unit a highly electron-deficient cluster system. SCF calculations (NEMO method, one-center 2s–2p zero-overlap elements included)[9] suggest the electronic charge in the framework to be distributed for the greater part over the borane skeleton with the result that the two CH units are even more depleted of electronic charge than are 8 out of the 10 BH units. The powerful resultant electron-withdrawing effect of the carboranyl group substituted at one of the C atoms by a carbonyl (or imino) group has far-reaching consequences in the addition–elimination chemistry at the α-CO (or C=N) double bond in such derivatives. Considering an aldehyde or ketone of type 3 (Cb = *meta*-carborane-1,7-diyl, R = H or other substituents, X = Cl or H, alkyl, aryl, etc.), one predicts inductive electronic charge withdrawal by Cb to cause a partial shift of electron deficiency from the carboranyl to the carbonyl carbon atom. As a result, nucleophilic attack at the latter will be strongly enhanced.[10] At the same time, supported by the steric requirements of the carborane cage, the C_{Cb}–C_{CO} bond polarization toward Cb renders the carbonyl unit an efficacious potential leaving group. As long as the leaving-group character of X in 3 is superior to that of RCb or H_2O, reaction with a nucleophile, NuH, will lead to the expected substitution product RCb–CO–Nu, the primary adduct collapsing with elimination of HX. This reaction sequence is observed, e.g., in polyamide formation from bis(chlorocarbonyl)carboranes with diamines.[11]

Scheme III



Scheme IV



A different reaction course will prevail for compounds **3** in which X represents a poor leaving group (H, alkyl, aryl). Attack by a strong nucleophile or base can be expected to lead to carborane elimination, as now the carboranyl anion represents the better leaving group. This has indeed been observed in numerous instances of hydroxide or alkoxide ($R'O^-$) attack on α-carbonyl-substituted *meta*-carborane[10,12,13] (and the respective ortho and para isomers[12–14]), where the liberation of the (R substituted) carborane is accordingly accompanied by acid or ester formation (path A, Scheme III). If the attacking species is a weak nucleophile, e.g., an amine or an orthoformate, retention will be observed of both the RCb and the X groups in the product.[8,10b] Path B illustrates this case for the carbonyl–amine reaction, and it is, of course, this path which underlies the poly(azomethine) formation (Scheme I) of the present work. An additional complication, however, arises in the polycondensation step of Scheme I from the availability of a second amine nucleophile, viz., the *o*-amino group on the adjacent benzene ring. While the "open-chain" azomethine structure (**1a**) is clearly the preferred one as shown by model reactions,[8] it is bound to equilibrate to some extend with the ring tautomer, the imidazoline structure **1b**.[3c] The primary ring closure to **1b** involves an internal nucleophilic attack (addition across the azomethine double bond), and it is at this reaction stage where the ready leaving-group character of the carborane unit is likely to cause competitive RCb elimination with concomitant proton transfer from the imidazoline moiety, resulting in desubstitution of the carborane at the affected C atom and simultaneous heteroring aromatization (Scheme IV). It is, in fact, the stabilization of the heteroring through imidazole formation that provides the major thermodynamic driving force for this reaction and thus brings about the C–C bond cleavage despite the comparatively weak nucleophilicity of the attacking amine.[15] We consider the last-named path to underlie the C_{Cb}–$C_{C=N}$ bond fission observed as a side reaction in the dialdehyde–DAB polycondensation of Scheme I. Since a higher activation energy can be expected for the C–C bond fission (with accompanying intermolecular proton transfer) than for the simple oxidative dehydrogenation (Scheme II), it should stand to reason that lower condensation temperatures should retard the backbone fission process, as indeed observed. However, both the low polymer viscosities measured and the appearance of the faint CH stretching band of the *meta*-carborane system are a clear indication that complete elimination of this bond cleavage has not been achieved in our experiments.

The ultimate poly(benzimidazole) structure **2**, once formed, should, of course, be immune to backbone fission of the observed kind and, hence, should show an appreciable high-temperature stability. The TGA results of Figure 1, while indicating good stability up to 500 °C, reflect a disappointing performance, relative to the phenylene-bridged counterpart, as the temperature is raised beyond 500 °C. This poor stability behavior in the higher temperature region is probably a direct consequence of the comparatively low molecular mass of the sample employed.

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Registry No. 2 (SRU), 57347-15-6; (1,7-diformylmetacarborane)·(3,3'-diaminobenzidine) (copolymer), 70394-27-3.

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(4) Blank reactions involving the heating of a 0.07 M solution of 1,7-diformyl-*meta*-carborane in deoxygenated DMAC for 12 h at 55 °C showed the dialdehyde per se to be sufficiently resistant to deformylation under these conditions.

(5) The procedure typically comprised the dropwise addition, over a period of 45 min, of a rigorously dried and Ar-saturated solution of 1,7-diformyl-*meta*-carborane (1.5 mmol) in DMAC (10 mL) to the stirred and equally well-dried and deoxygenated solution of 3,3'-diaminobenzidine (1.5 mmol; freshly recrystallized[3b]) in the same solvent (2 mL) cooled to −15 °C, followed by stirring for 6 h at −15 °C, 1 h at 0 °C and another 8 h at ambient temperature under Ar. A further portion of the diformylcarborane (0.15 mmol) in DMAC (2 mL) was then added to the solution precooled to −15 °C, and stirred for 8 h at 0–30 °C. Addition of deoxygenated methanol (80 mL) precipitated 1 as a resinous solid, which was washed with methanol and water and was dried for 24 h at 50 °C (0.1 torr); yield 11%. The ground-up pale yellow solid dissolved readily in $CHCl_3$, benzene, and dipolar aprotic solvents: η_{inh} 0.1 dL g^{-1} (30 °C; 0.3% in DMAC). Anal. Calcd for $(C_{16}H_{22}B_{10}N_4)_x$: C, 50.77; H, 5.86; N, 14.80%. Found (average of five determinations): C, 51.98; H, 5.88; N, 13.89. Removal of methanol from the filtrate and addition of water caused slow precipitation of a second portion of 1 (56%), partially soluble in methanol; η_{inh} = 0.07 dL g^{-1}.

(6) The procedure involved the introduction of a brisk stream of air (20 h at 25 °C) into a 0.15 M solution of 1 in DMAC containing a catalytic quantity (10^{-3} M) of anhydrous $FeCl_3$, followed by precipitation of 2 with excess H_2O and drying of the yellowish solid at 80–100 °C (0.1 torr): yield, 75%; η_{inh} = 0.1 dL g^{-1}. Anal. Calcd for $(C_{16}H_{18}B_{10}N_4)_x$: C, 51.32; H, 4.85; N, 14.96. Found: C, 52.07; H, 5.58; N, 13.74.

(7) (a) The poly(benzimidazole) 2 was first reported by Green and Mayes.[7b] However, the paper gave no preparative details, and no solubility, viscosity, spectroscopic, or analytical data in support of 2 were presented, nor have any follow-up papers subsequently appeared in print. In light of this dearth of information, the structural assignment given and the reported[7b] excellent performance of their product in thermogravimetric analysis must both be viewed with doubt. (b) Green, J.; Mayes, N., *J. Macromol. Sci., Chem.* **1967**, *A1*, 135.

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EPR Study of Copper(II) Complexes of Poly(L-lysine)

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The interaction of copper(II) ions with poly(L-lysine), $(Lys)_n$, has been the subject of many investigations that have led to considerable confusion and disagreement as to the species which are present in solution. The interaction is of interest because of the observation[1] that $(Lys)_n$, when bound to copper(II), catalyzes the oxidation of 3,4-dihydroxyphenylalanine, DOPA, at high pH. This has been treated as a model for DOPA oxidase, which is utilized in melanin production. The $Cu(Lys)_n$ complex behaves as an asymmetrically selective catalyst,[2] favoring reaction with D-DOPA over L-DOPA, particularly at high pH where $(Lys)_n$ exists in a helical form.[3,4] $Cu(Lys)_n$ has also been reported to model the enzyme catalase[5] and catalyze the decomposition of H_2O_2 at pH between 6 and 7.

The binding of Cu(II) to $(Lys)_n$ has been previously studied by potentiometric titration,[6–8] absorption spectroscopy,[6–9] circular dichroism,[6–9] and NMR spectroscopy.[10,11] The results of these studies have been interpreted in terms of a number of models, summarized in Figure 1, which disagree with one another except for a general agreement that two types of Cu(II) complex form, one at pH <8 and one at pH >8. This paper reports the results of an investigation of the $Cu(Lys)_n$ system using EPR spectroscopy and resolves the discrepancies between the previous interpretations.

Experimental Details

Poly(L-lysine) hydrobromide of molecular mass 4000–15000 and 70000–150000 was purchased from Sigma Chemical Co. and dissolved in deionized water. Copper(II) was added as a concentrated solution of the perchlorate salt, and the pH was adjusted by the addition of small volumes of concentrated $HClO_4$ or NaOH solutions. Replacement of perchlorate by chloride had no effect on the EPR spectra. Some studies were also performed with methanol as a solvent. Methanol promotes α-helix formation[12] in $(Lys)_n$.

EPR spectra were recorded with a Varian E-9 EPR spectrometer operating at 9.1 GHz with 100-kHz modulation. Temperatures between 110 and 300 K were achieved by means of a nitrogen-flow Dewar. The magnetic field was calibrated with a Magnion gaussmeter, and the frequency was measured on a Hewlett-Packard frequency counter. Absorption spectra were recorded on a Cary 219 UV-visible spectrophotometer.

Results and Discussion

EPR spectra obtained of frozen solutions of $Cu(Lys)_n$ at 110 K were typical of tetragonally elongated octahedrally coordinated Cu(II) with $g_\parallel > g_\perp$. Anisotropic spectra were also obtained for liquid solutions at 300 K and, although of poorer resolution because of partial motional averaging, were identifiable as arising from the same species observed in frozen solutions. Thus there is no temperature dependence of the species present in solution, and the frozen solution results can be correlated with the results obtained by other techniques using liquid solutions. Although methanol promotes α-helix formation[12] in $(Lys)_n$, EPR spectra obtained from frozen methanol solutions of $Cu(Lys)_n$ showed no significant differences from the spectra of frozen aqueous solutions.

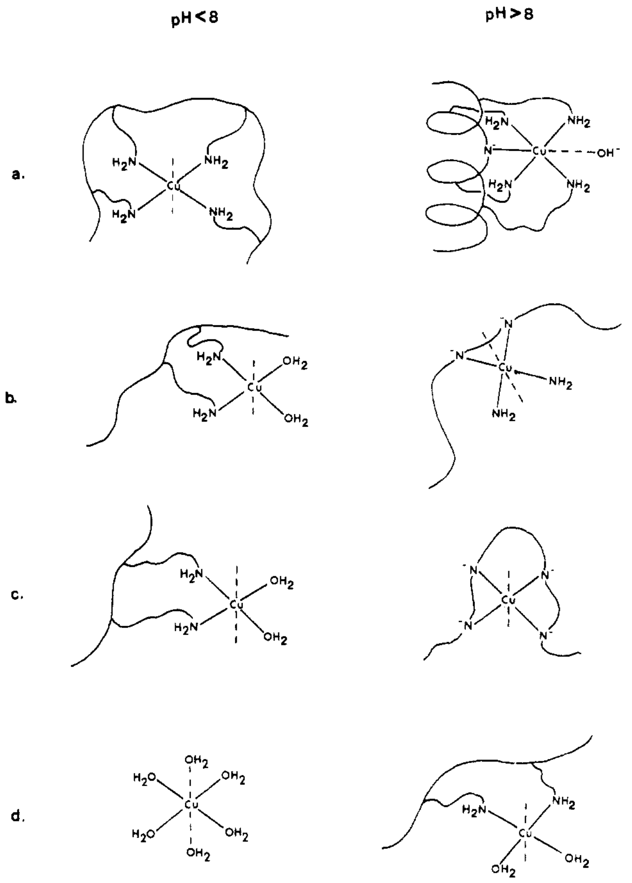

Figure 1. Structures of the copper-binding sites of $(Lys)_n$ as suggested by previous workers for pH < 8 and pH > 8: (a) ref 7; (b) ref 9; (c) ref 6; (d) ref 10 and 11.

EPR studies were performed at a variety of Cu:Lys ratios. At a 1:4 ratio, which is what most previous workers have used, EPR spectra were broad and baselines were poor between pH 6 and 11 owing to $Cu(OH)_2$ precipitation and, above pH 11, because of $Cu(OH)_4{}^{2-}$ formation. Therefore most studies were carried out at a 1:30 Cu:Lys ratio, where the copper hydroxide species did not form. Studies at other ratios were performed on a more limited basis. Although Garnier and Tosi[13] observed terminus binding of $(Lys)_n$ for $n = 25$, our spectra showed no variation with chain length, which indicates that coordination of chain termini to copper(II) is not important for chains where $n > 25$. Minor differences related to chain length were noted (Table I), but these do not suggest any major differences in the structures and probably reflect different degrees of intra- and interchain complexation to copper.

EPR spectra were obtained between pH 2 and 13. When solutions of $(Lys)_n$ and Cu(II) were initially mixed, a pH of about 4 resulted, and the broad EPR spectra indicated aggregation of the Cu(II) species. Slowly increasing the pH did not change the spectra. It was therefore necessary to raise the pH to 13 and reduce the pH by progressive additions of acid to fully observe all species. The same species did form at lower pH but at a much slower rate, equilibrium being attained only after several days. This