Polymers for Selective Chelation of Transition Metal Ions

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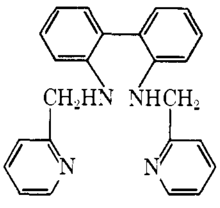
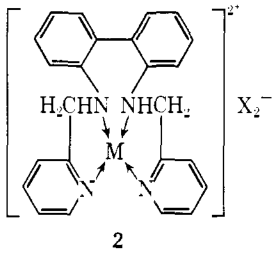
Abstract: Cu(II) and Ag(I) or Ni(II) are selectively removed from acidic aqueous transition metal ion mixtures by polymers containing chelating ligands based on derivatives of *N,N'*-bis(2-pyridylmethyl)-2,2'-diaminobiphenyl (**1**) and *N*-(2-pyridylmethyl)-2,2'-diaminobiphenyl (**6**). Chelated ions are recovered by stripping with 6 *N* mineral acid. Polymer chelating capacities depend on the ligand structure but range up to 1.7 mmol of metal ion per gram of polymer, corresponding to over 90% utilization of chelating sites.

Recovery of Cu(II) from aqueous solutions containing other transition metal ions is an important industrial endeavor which can be accomplished with conventional ion exchange or chelating resins, but such processes are inefficient because of inadequate ion selectivity provided by such resins. Liquid–liquid extraction with certain organo-soluble ligands affords superior selectivity[1] but lacks the mechanical convenience and operational flexibility inherent in solid–liquid systems. Thus, we chose to search for new chelating resins which would combine the advantages of both solid–liquid and liquid–liquid systems, particularly with respect to recovering Cu(II) from aqueous solutions containing soluble Fe(III).

Cu(II) can commonly be 4- or 6-coordinate and exist in any of several geometries, while Fe(III) is most commonly 6-coordinate octahedral. Thus, a ligand with a maximum of four donor atoms and a structure which restricts the donor lone pairs to tetrahedral disposition (obligatory tetrahedral),[2] or which is flexible enough to permit tetrahedral disposition (facultative)[2] might be expected to favor chelation of Cu(II) over Fe(III). In their extensive work on multidentate ligands, Goodwin and Lions prepared *N,N'*-bis(2-pyridylmethyl)-2,2'-diaminobiphenyl (**1**) and, although they did not study its coordination with iron, they did prepare chelates of type **2** with Cu(II) and Pd(II). They concluded that the ligand should be capable of acting as a square or tetrahedral tetradentate even though it can also accommodate to octahedral stereochemistry such as in the Ru(II) chelate **3**.[2]



1



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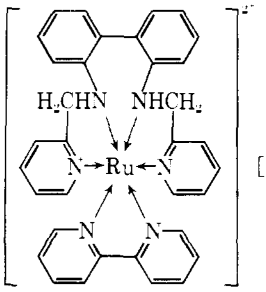
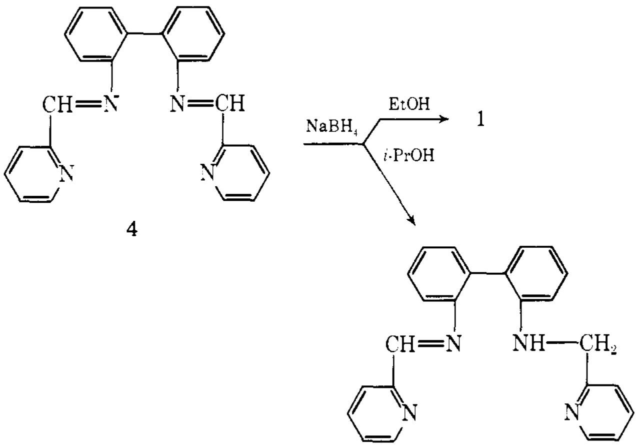


3

The ligand **1** potentially meets the criteria discussed above, and we report here further investigations of it and of analogs immobilized on insoluble supports for use in selective chelation.

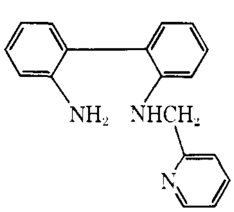
Results and Discussion

Ligand Syntheses. The synthesis of **1** by zinc–acetic acid reduction of a mixture of 2,2'-diaminobiphenyl and pyridine-2-aldehyde in ethanol as described by Goodwin and Lions[2] failed in our hands. We therefore resorted to sodium borohydride reduction of the diimine **4**.[3] Reduction in ethanol gave **1** in over 50% yield but, in isopropyl alcohol, the half-reduced imine **5** was obtained in ~60% yield.[4] By modifying these conditions, the previously unknown tridentate compound **6** was obtained in 80% yield. This compound is a pivotal intermediate to substituted ligands for binding to polymers. The methyl homologs **7** were prepared in a similar way.[3]



4

5



6

The triamine **6** was condensed with the isomeric monohydroxybenzaldehydes, and the intermediate monoimines (**8**) were reduced to the corresponding phenolic tridentate ligands **9**. The latter thus contain a hydroxyl group through which they can be anchored to a suitable polymer.

Table I. Imines from 2,2'-Diaminobiphenyl[a]

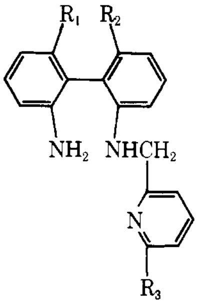
Structure No.	Formula	Formula weight	Anal. % C Calcd	Anal. % C Found	Anal. % H Calcd	Anal. % H Found	Anal. % N Calcd	Anal. % N Found	Yield, %	Mp, °C
5	$C_{24}H_{20}N_4$	364.4	79.1	79.0	5.5	5.7	15.4	15.2	57	180–183
8a	$C_{25}H_{21}N_3O$	379.4	79.2	79.4	5.5	5.7	11.1	11.3	90	108–112
8b	$C_{25}H_{21}N_3O\cdot\frac{1}{2}C_2H_5OH$	402.5	77.5	77.2	6.0	6.3	10.4	10.4	71	69–72
11a	$C_{24}H_{20}N_4O$	380.5	75.8	75.8	5.6	5.3	14.5	14.7	81	148–151
11b	$C_{25}H_{22}N_4O$	394.5	76.1	76.4	5.6	5.7	14.2	14.2	80	148–151
11c	$C_{25}H_{22}N_4O$	394.5	76.1	76.5	5.6	5.7	14.2	14.0	85	148–151
11d	$C_{26}H_{24}N_4O$	408.5	74.4	76.7	5.9	6.1	13.7	13.6	36	64
11e	$C_{26}H_{24}N_4O$	408.5					13.7	13.7	30	140–142
11f	$C_{27}H_{26}N_4O$	422.5	76.8	76.7	6.2	6.1	13.3	13.1	31	153–156

[a] Imines not included in this table were sirups unsuitable for analysis.

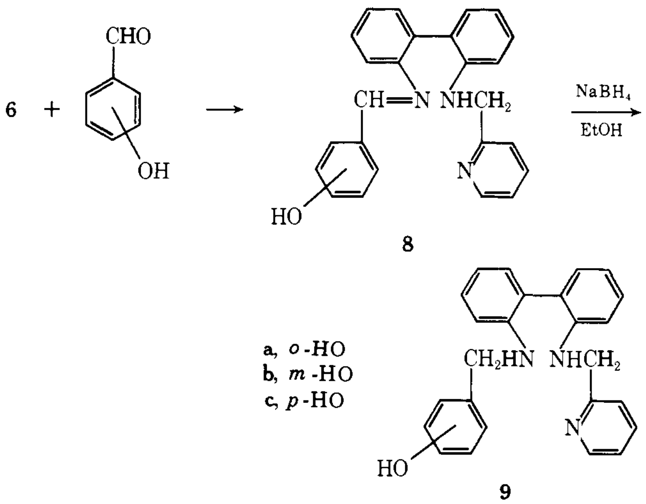
Table II. Amines from Biphenylimines

Structure No.	Formula	Formula weight	Anal. % C Calcd	Anal. % C Found	Anal. % H Calcd	Anal. % H Found	Anal. % N Calcd	Anal. % N Found	Yield,[a] %	Mp, °C
6	$C_{18}H_{17}N_3$	275.3	78.5	78.2	6.2	6.3	15.3	15.0	82	93–94
1	$C_{24}H_{22}N_4$	366.4					15.3	15.4	60	137–138[b]
9a	$C_{25}H_{23}N_3O$	381.4	78.8	78.9	6.1	6.2	11.0	11.0	80	154–156
9b	$C_{25}H_{23}N_3O$	381.4	78.8	78.6	6.1	6.3	11.0	11.1	66	148–150
9c	$C_{25}H_{23}N_3O\cdot H_2O$	399.5	75.2	74.9	6.3	6.4	10.5	10.4	56	110–112
9c	$C_{25}H_{23}N_3O$	381.4	78.8	78.7	6.1	6.3	11.0	11.2	100	132–135
12a	$C_{24}H_{22}N_4O$	382.5	75.4	75.5	5.8	5.7	14.7	14.9	69	187–189
12b	$C_{25}H_{24}N_4O$	396.5	75.7	75.7	6.1	6.3	14.1	14.2	76	160–162
12c	$C_{25}H_{24}N_4O$	396.5	75.7	75.7	6.1	6.1	14.1	14.0	67	170–172
12d	$C_{26}H_{26}N_4O$	410.5					13.7	13.7	77	93–99
12e	$C_{26}H_{26}N_4O$	410.5	76.1	75.9	6.4	6.8	13.7	13.4	44	172–174
12f	$C_{27}H_{28}N_4O$	424.5	76.5	76.5	6.7	7.0	13.2	13.3	78	194–195

[a] Based on imine. [b] Reference 2 cites mp 137°.



7a, $R_1 = R_2 = H$; $R_3 = CH_3$
b, $R_1 = R_2 = CH_3$; $R_3 = H$
c, $R_1 = R_2 = R_3 = CH_3$

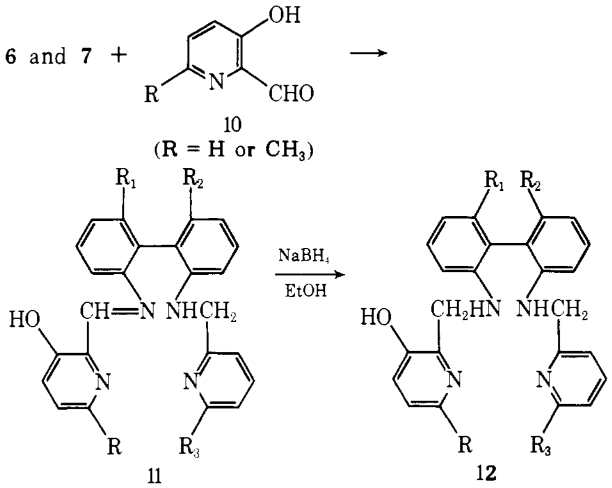


8

a, *o*-HO
b, *m*-HO
c, *p*-HO

9

Similarly, condensation of the amines **6** and **7** with the hydroxypyridine aldehydes **10** gave analogous imines (**11**) which were then reduced to the corresponding tetradentate amines (**12**).[5]



10
(R = H or CH_3)

11

12

a, $R = R_1 = R_2 = R_3 = H$
b, $R = R_1 = R_2 = H$; $R_3 = CH_3$
c, $R = CH_3$; $R_1 = R_2 = R_3 = H$
d, $R = R_3 = CH_3$; $R_1 = R_2 = H$
e, $R = R_3 = H$; $R_1 = R_2 = CH_3$
f, $R = R_1 = R_2 = CH_3$; $R_3 = H$

Yields and analytical data for the imines are compiled in Table I and for the amines in Table II; representative NMR data are given in Table III.

Solution Chelation Studies. As background to polymer chelation studies, it was desirable to examine the ability of the prototype ligands **6** (tridentate) and **1** (tetradentate) to discriminate between Cu(II) and Fe(III) in solution. Thus,

Table III. NMR of Imines and Amines[a]

	Assignments, δ, and multiplicity						
Cmpd	HO	Methine ═CH	Pyridine α	Aromatic and pyridine β, γ	$-CH_2-$	NH	$-CH_3$
6			8.50 (d, $J = 4$)	7.8–6.5 (m)	4.42 (s)	4.16 (s)	
1			8.53 (d, $J = 4$)	7.8–6.5 (m)	4.50 (s)	4.72 (s)	
8a		8.42 (s)	8.4–8.2 (m)	7.4–6.4 (m)		4.35 (s)	
9b[b]			8.7–8.4 (m)	8.0–6.3 (m)	4.50 s	4.28 (s)	
9b[c]			8.4–8.2 (m)	7.8–6.4 (m)	4.41 s	4.22 (s)	
11a		8.89 (s)	8.7–8.1 (m)	7.7–6.5 (m)	4.50 s	4.42 (s)	
11b	12.5 (s)	8.74 (s)	8.2–8.0 (m)	7.5–6.5 (m)	4.5–4.2 (m)	4.7 (s)	2.35 (s)
11c	12.2 (s)	8.80 (s)	8.5–8.3 (m)	7.5–6.5 (m)		4.40 (s)	2.42 (s)
11d	12.2 (s)	8.83 (s)		7.5–6.5 (m)		4.41 (s)	2.46 (s); 2.40 (s)
11e	12.4 (s)	8.99 (s)	8.6–8.4 (m) 8.28 (t, $J = 3$)	7.5–6.5 (m)	4.44 (s)	4.51 (s)	2.16 (s); 1.94 (s)
11f	12.0 (s)	8.79 (s)	8.47–8.27 (m)	7.5–6.4 (m)	4.47–4.27 (m)	4.45–3.97	2.44 (s); 2.09 (s); 1.86 (s)

[a] $CDCl_3$, Me_4Si as reference. [b] Anhydrous. [c] Monohydrate, H_2O δ 3.0.

Table IV. Spectral Determination of Selective Chelation of Cu(II) by Ligands 1 and 6

Composition[a]	Absorbance
1 + Cu(II) + Fe(III)	1.25[b]
Fe(III) only	0.05[b]
1 + Cu(II)	1.22[c]
6 + Cu(II) + Fe(III)	1.15[d]
Fe(III) only	0.17[d]
6 + Cu(II)	0.98[d,e]

[a] Each component 8×10^{-4} *M*, metal as sulfate in 0.01 *N* H_2SO_4, ligand in $CHCl_3$. [b] 385 nm. [c] Calcd 1.26 from ε of prepn 7, Table V. [d] λ 367 nm. [e] Calcd 0.97 from ε of prepn 5, Table V.

chloroform solutions of each ligand were equilibrated by shaking with equimolar aqueous Cu(II) (pH 2) and with similar solutions equimolar in both Cu(II) and Fe(III).[6] Since the extinction coefficients of the isolated Cu(II) chelates had been determined (see Table V), the magnitude of the absorbances of the aqueous phases at the λ_{max} of the chelates gave a direct measure of the extent of chelation in the two-phase system. Correcting the aqueous phase absorbances for absorption by Fe(III) alone (Table IV) shows that both ligands almost quantitatively chelate Cu(II) to the total exclusion of Fe(III). Thus the desired selectivity was established.

Since it was anticipated that extinction coefficients of certain chelates would be needed for calculations such as just described, a series of representative solid chelates was prepared and characterized. These are listed in Table V.

Of particular interest is the Ni(II) chelate derived from the tetradentate ligand **12a** which is a hydroxy-substituted analog of prototype **1**. Concerning the latter, Goodwin and Lions stated that, when it acts as a tetradentate ligand, there is "little doubt" that it is planar.[2] This contention is refuted by our observation that the Ni(II) chelate mentioned (prepn 2, Table V) has a magnetic moment of 3.28 μ_B in solution and thus has two unpaired electrons.[7] The configuration must thus be either tetrahedral or octahedral since, if planar, the chelate would almost certainly be diamagnetic. Furthermore, CPK models of **1** show that planar disposition of the donors is badly distorted, while tetrahedral or octahedral geometries are almost stain free.

As will be discussed below under polymer chelation studies, methyl substitution near the donor sites has a marked effect on coordinating selectivity. How much of this is due to steric influence on ligand geometry and how much simply to shielding of the prospective ion cavity is a moot question. In any case, CPK models show that methyl substitution α to the pyridine nitrogen atoms, such as in ligands of type **12c**, **12d**, and **12f**, exaggerates distortion of the planar and octahedral forms but leaves the tetrahedral relatively unaffected.

Chelating Polymer Preparations. The prototype ligands **1** and **6** were alkylated with chloromethylated cross-linked polystyrene[8] in the presence of triethylamine as the acid acceptor and dioxane solvent. These products are presumed to have structures essentially as depicted in **13** and **14** in which direct N-alkylation has occurred.[9]

Table V. Simple Chelate Preparations

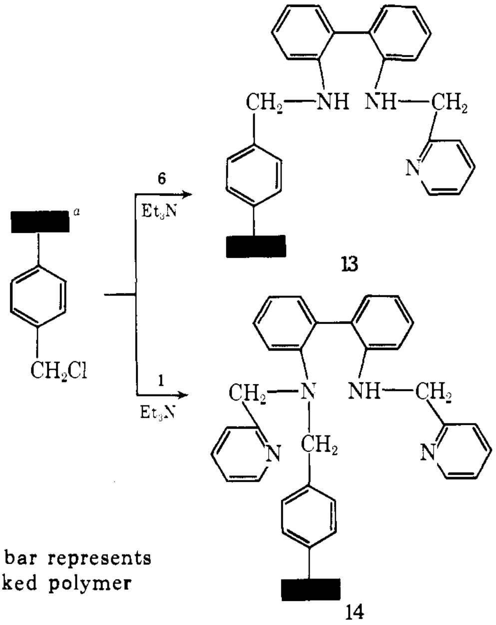
			Anal.							
			% C		% H		% N			
Prepn No.	Ligand	Chelate formula	Calcd	Found	Calcd	Found	Calcd	Found	λ_{max},[a] nm	ε[a]
1	1	$[C_{24}H_{22}N_4Ni]Cl_2 \cdot H_2O$[b,c]	56.0	55.9	4.7	4.9	10.9	11.2		Insol
2	12a	$[C_{24}H_{22}N_4NiO][NO_3]_2$[c,d]	51.0	49.8	3.9	4.3	14.9	14.7		
3	6	$[C_{18}H_{17}N_3Cu]Cl_2 \cdot H_2O$[b,e,f]					9.8	9.4[b]	367	1140[g]
4	6	$[C_{18}H_{17}N_3Cu]SO_4 \cdot 2H_2O$[b,h]	46.0	46.2	4.5	4.7	8.9	8.8	367	1210[i]
5	1	$[C_{24}H_{22}N_4Cu]Cl_2 \cdot H_2O$[b,j,k]					10.8	11.0[l]	385	1560[m]
6	1	$[C_{24}H_{22}N_4Cu]SO_4 \cdot H_2O$[d,h]	53.0	52.8	4.5	4.5	10.3	10.3	388	1580[n]
7	9c	$[C_{25}H_{23}N_3CuO]Cl_2 \cdot H_2O$[b,o]	56.2	56.1	4.7	4.5	7.8	7.8		Insol
8	9c	$[C_{25}H_{23}N_3CuO][NO_3]_2$[h,d,p]	52.8	52.8	4.1	4.3	12.3	12.7		Insol
9	12a	$[C_{24}H_{22}N_4CuO]Cl_2$[d,h]	55.8	55.8	4.3	4.2	10.8	10.8	387	1550[q]
10	12a	$[C_{24}H_{22}N_4CuO][NO_3]_2$[d,r]	50.6	50.8	3.9	4.0	14.7	14.7	387	1500[q]
11	9c	$[C_{25}H_{23}N_3AgO][NO_3] \cdot {}^1/_2H_2O$	53.6	53.3	4.3	4.7	10.0	10.1		
12	5	$[C_{24}H_{20}N_4Ag][BF_4]$	51.5	51.6	3.6	3.7	10.0	10.7		
13	5	$[C_{24}H_{20}N_4Ag][NO_3] \cdot CHCl_3$	45.9	45.9	3.2	3.1	10.7	10.7		

[a] Solvent 0.01 *N* H_2SO_4 unless noted. [b] Air dried. [c] Light-blue plates. [d] Vacuum dried 80°. [e] Olive-green rosettes. [f] Calcd for Cl: 16.6. Found: 16.5. [g] 1600 in distilled H_2O. [h] Bright-green needles. [i] 1590 in distilled H_2O. [j] Dark-green prisms. [k] Reference 3. [l] Calcd for Cl: 13.7. Found: 14.1. [m] 1630 in distilled H_2O. [n] 1630 in distilled H_2O. [o] Brown-black needles. [p] Prepared in anhydrous ethanol. [q] Solvent distilled H_2O. [r] Olive-black plates.

Table VI. Chelating Polymers

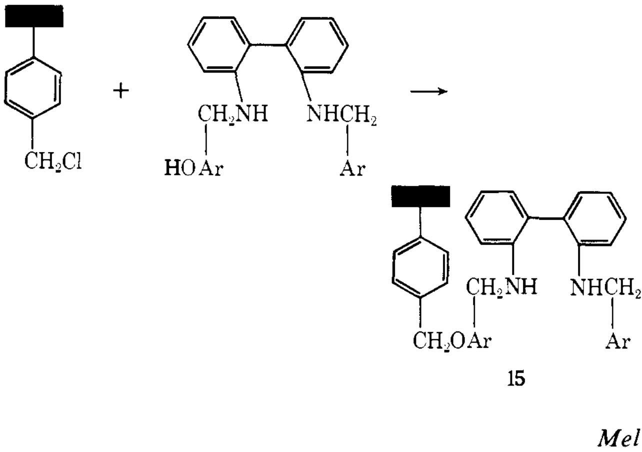
Prepn No.[a]	Ligand structure	Yield, %[b]	% N found[c]	mmol of ligand per g of product[d]	Conversion %[e]
1	9a	83	7.5	1.79	92
2[f]	9a	80	7.4	1.76	91
3	9b	91	7.65	1.82	94
4[f]	9b	79	7.8	1.86	96
5	9c	51	6.55	1.56	80
6[g]	9c	91	7.25	1.73	89
7	12a	78	10.15	1.82	94
8	12b	80	10.0	1.79	95
9	12c	81	9.55	1.71	91
10	12d	65	8.6	1.54	84
11	12e	52	8.55	1.53	84
12	12f	59	8.6	1.53	86

[a] Prepared from anhydrous ligand unless noted. [b] Based on isolated product weights according to the relationship, % yield = $35.5(P - O)/(L - 35.5)/\%\mathrm{Cl}/O \times 100$, where P = product wt, O = original wt of chloromethylpolystyrene, L = ligand molecular wt less 1, and % Cl = % chlorine in original chloromethylpolystryene. These values are affected by mechanical losses. [c] Average of two analyses. [d] Calculated from actual nitrogen content. [e] Based on the ratio of the actual ligand content to the theoretical value calculated from total displacement of chloride by ligand. [f] From anhydrous ligand plus 1 mol equiv of water. [g] From ligand monohydrate.



[a] The heavy bar represents the crosslinked polymer backbone

The phenolic ligands (**9** and **12**) were O-alkylated with the chloromethyl resin in the presence of sodium methoxide and dimethylformamide (DMF) solvent[10] to give products typified by structure **15**. Yields and analytical data for these polymers are given in Table VI.



15

It was discovered quite inadvertently that one pair of polymers prepared from the *p*-hydroxy tridentate ligand **9c** (Table VI, prepn 5 and 6) differed quite markedly in chelating ability depending on whether the anhydrous ligand or the ligand monohydrate was used in the condensation reaction. This will be discussed in the following section.

Polymer Chelation Studies[11] (Table VII). The N-alkylated polymers **13** and **14** showed very low chelation capacities for Cu(II) (2–10% of theory) and little or no ability to discriminate between Cu(II) and Fe(III). Thus, the selectivity and quantitative chelation of Cu(II) by the parent ligands were virtually eliminated by their incorporation into the polymers. This effect is not unreasonable since the *N*-benzyl groups which are part of the strained and rigid polymer backbone are also intimate parts of the coordination sites and would be expected to distort them very badly. On the other hand, the O-alkylated polymers of type **15** (Table VII) have high capacities and selectivities.

The data in Table VII give absolute and competitive chelation capacities. In the absolute capacity measurements, a single transition metal ion solution was applied to the polymer in sufficient amount to theoretically saturate all chelation sites.

In the competitive experiments, mixtures of two or more ions were applied, each individual ion sufficient to saturate all sites.[12]

The tridentate polymers **1–6** have a low to middling Cu(II) capacity depending, among other things, on the polymer attachment site. Thus, when the polymer benzyloxy group is ortho to the ligand methylamino group (as in **1** and **2**), the Cu(II) capacity is quite low (~20% of theory); this probably reflects compression or distortion of ligand sites by the contiguous polymer backbone similar to that discussed above for the direct N-alkylated products **13** and **14**. Nevertheless the Cu/Fe selectivity ratio is high, and the absolute capacity for Ag(I) is substantial. When the polymer attachment site is meta or para (prepns 3, 4 and 6), the constraint is relieved, and the Cu(II) capacity almost doubles (~40% of theory). In this group, the para-attached polymer **5** is exceptional in having an extremely low and apparently erratic affinity for Cu(II); the only preparative difference between it and **6** was that **6** was from chloromethyl polymer condensed with the hydrated ligand **9c**, while **5** was from anhydrous ligand. This drastic effect was not duplicated in either the ortho- or meta-attached pairs (**1** vs. **2** and **3** vs. **4**); the effect remains inexplicable.

With one exception, the tetradentate group of polymers **7–12** have very high Cu(II) affinities ranging up to 90% of theory despite the polymer attachment sites being ortho to the ligand methyl amino groups. The exception is polymer **10** whose drastically reduced Cu(II) and Ni(II) affinities are probably due to the cumulative steric effect of the methyl groups ortho to the pyridine donor atoms. Such steric effects are also reflected in polymers **8** and **9**; in **8** the single methyl substituent distant from the polymer attachment nucleus has no appreciable effect on the Cu(II) affinity (cf. **7**) but, when the single substituent is on the attachment nucleus, it very significantly reduces affinity for both Cu(II) and Ni(II). Apparently the restriction imposed by the polymer-attachment group magnifies the methyl group effect. Whether that effect is on the stereochemistry of the ligand or simply a matter of bulk shielding the ion cavity is open to question.

Another steric effect is seen in the introduction of hindrance to rotation about the biphenyl central bond as in polymers **11** and **12**. Such substitution, no doubt, restricts the overall flexibility of the ligand but, beyond that, it is not clear what specific steric effects are at work.

Table VII. Polymer Chelation Studies

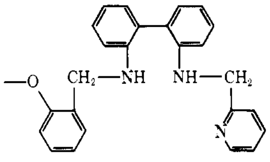
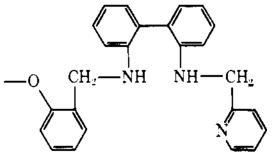
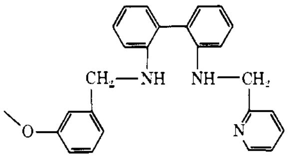
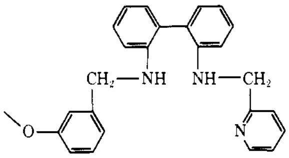
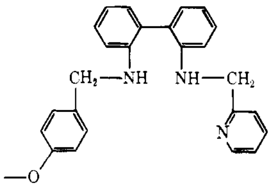
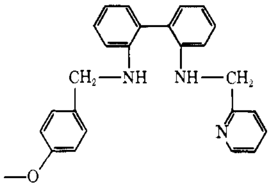
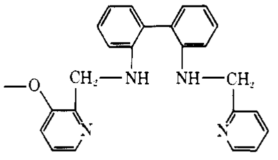
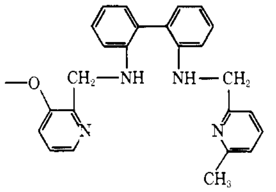
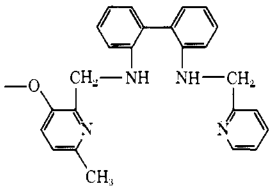
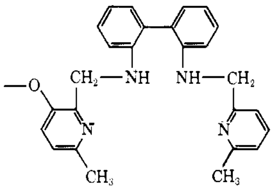
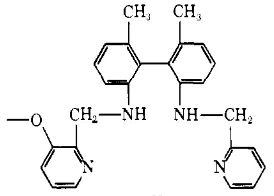
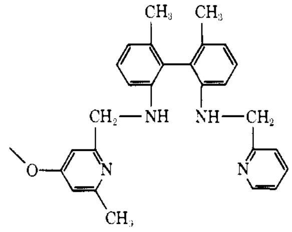
Prepn No.[a]	Polymer ligand structure	Theory capacity, mmol/g	Capacity found, mmol/g[b]				
			Fe[c]	Co(II)	Ni(II)	Cu(II)[d]	Ag(I)
1		1.79	0.002			0.39	
							0.57
			0.001	0.001	0.001	0.13	0.32
2		1.76	0.001			0.38	
							0.53
			0.001	0.001	0.001	0.12	0.31
3		1.82	0.002			0.69	
							0.67
			0.004	0.01	0.003	0.51	0.18
4		1.86	0.001			0.76	
							0.69
			0.003	0.0004	0.002	0.56	0.17
5		1.57	0.006			0.03	
							0.52
			0.03	0.003	0.006	0.15	0.21
6		1.73	0.004			0.75	
							0.60
			0.004	0.0004	0.003	0.55	0.17
7		1.82	0.007			1.70	
					1.15		
					0.44	1.06	
							1.32
			0.004	0.002	0.48	1.16	0.03
8		1.79	0.002			1.62	
					0.50		
					0.03	1.38	
							1.43
			0.003	0.0003	0.23	1.26	0.30
9		1.71	0.001			1.11	
					0.25		
					0.03	1.15	
							1.31
			0.003	0.0002	0.004	0.89	0.34
10		1.54			0.005		
						0.06	
							1.58
			0.003	0.001	0.03	0.07	1.20

Table VII (*Continued*)

Prepn No.[a]	Polymer ligand structure	Theory capacity, mmol/g	Capacity found, mmol/g[b]				
			Fe[c]	Co(II)	Ni(II)	Cu(II)[d]	Ag(I)
11		1.53	0.008			1.14	
					0.50		
					0.08	1.12	
							1.13
			0.008	0.002	0.09	0.91	0.13
12		1.53	0.002			0.98	
					0.06		
					0.002	1.00	
							1.30
			0.002	0.002	0.002	0.61	0.43

[a] Follow the order of polymer preparations in Table VI. [b] A single value in a row means that ion alone was applied, and a multiple value that a mixture of those ions was applied; the former thus gives absolute capacities and the latter relative capacities from which selectivity ratios are determined. [c] Equimolar mixture of Fe(II) and Fe(III). [d] See ref 12.

Experimental Section

Chemicals and Procedures. All chemicals were reagent grade and were used without further purification unless otherwise noted. Melting points are uncorrected. NMR spectra were determined with a Varian A-60 spectrometer.

2,2′-Diaminobiphenyl. 2,2′-Dinitrobiphenyl[13] (50 g) in 500 ml of ethyl acetate was reduced with hydrogen at 7-8 atm absolute, over Raney nickel, at room temperature during 4-5 hr.[14] After removing the catalyst and evaporating to dryness, the crude product was recrystallized from ethanol (3 ml/g) to obtain 80-90% yields of product, mp 77-78°.

***N*,*N*′-Bis(2-pyridylmethyl)-2,2′-diaminobiphenyl (1).** A solution of 9.2 g (0.05 mol) of 2,2′-diaminobiphenyl and 10.7 g (0.1 mol) of redistilled pyridine-2-aldehyde[13] in 1.5 l. of ethanol was slowly distilled until the volume was about 1.2 l. It was cooled to room temperature, 5 g of sodium borohydride was added, and the mixture stirred for 48 hr. The solution was boiled down to a 350 ml volume, treated with Darco and filtered. The filtrate was chilled at −20° overnight to obtain 11 g (60%) of off-white needles, mp 135-137°. It was recrystallized from ethanol [20 ml/g; mp 137-138° (lit.[2] mp 137°)].

***N*-(2-Pyridylmethyl)-*N*′-(2-pyridylmethylene)-2,2′-diaminobiphenyl (5).** A solution of 0.05 mol of 2,2′-diaminobiphenyl and 0.1 mol of pyridine-2-aldehyde in 100 ml of isopropyl alcohol was boiled under reflux for 30 min and then cooled to room temperature. Two grams of sodium borohydride was added, and the solution was stirred overnight. The light-yellow crystalline solid was collected and washed with water and alcohol, yield 10.4 g (57%). It was recrystallized from ethanol (100 ml/g; mp 180-183°).

***N*-(2-Pyridylmethyl)-2,2′-diaminobiphenyl (6).** To a stirred, refluxing solution of 9.2 g (0.05 mol) of 2,2′-diaminobiphenyl in 200 ml of ethanol was added dropwise, during 2 hr, a solution of 5.3 g (0.05 mol) of redistilled pyridine-2-aldehyde in 100 ml of ethanol. When addition was complete, the mixture was refluxed for an additional 30 min and was then cooled to room temperature. Three grams of sodium borohydride was added, and the solution was stirred overnight (16-20 hr). Another 3 g of sodium borohydride was added and stirring continued for 24 hr more. The solution was transferred to a large erlenmeyer flask and evaporated to dryness on a steam bath. Water (~500 ml) and 300 ml of ether were added, and the mixture was stirred until both layers were clear. The ether was separated, washed with 100 ml of water, dried briefly with sodium sulfate, and evaporated to 50 ml on a steam bath. It was cooled to room temperature and magnetically stirred overnight. A finely divided crystalline white product separated. The mixture was stored at −10° overnight, and the product was collected and washed with a small amount of cold ether, yield 9.2 g (67%), mp 85-95°. Another 2.0 g was obtained from the concentrated mother liquor (total yield, 82%). This material is pure enough for most purposes but, for analysis, it was recrystallized from benzene-hexane, mp 93-94°.

***N*-(6-Methyl-2-pyridylmethyl)-2,2′-diaminobiphenyl (7a).** Reaction of diaminobiphenyl with 1 mol equiv of 6-methylpyridine-2-aldehyde and reduction of the intermediate with sodium borohydride were carried out as described above. Since the product would not crystallize, it was used as a crude sirup obtained by evaporating the ether extract.

***N*-(2-Pyridylmethyl)-2,2′-diamino-6,6-dimethylbiphenyl (7b) and the *N*-(6-Methyl-2-pyridylmethyl) Analog (7c).** The precursor 2,2′-diamino-6,6′-dimethylbiphenyl was prepared from 2-amino-3-nitrotoluene[13] by the method of Carlin and Foltz.[15] It was condensed with pyridine-2-aldehyde and with 6-methylpyridine-2-aldehyde and reduced with sodium borohydride as described above to obtain the products as crude sirups.

3-Hydroxy-2-hydroxymethylpyridine. A boiling solution of 100 g of the hydrochloride salt (85% pure)[13] in 200 ml of water was treated with Darco and filtered. The filtrate was kept hot and stirred gently, while 56 g of solid sodium bicarbonate was added in portions. When addition was complete, the solution was rapidly cooled with vigorous stirring to obtain the free base as a finely divided white solid. After stirring and cooling in an ice bath for 3 hr, it was collected, washed with a little cold water, and dried in a vacuum oven at 80-90°, yield ~50 g (75%), mp 137-141°.

Anal. Calcd for $C_6H_7NO_2$: C, 57.6; H, 5.6; N, 11.2. Found: C, 57.7; H, 5.5; N, 11.0.

3-Hydroxypyridine-2-aldehyde Hydrochloride (10a).[16] Into a 2-l. one-necked flask equipped with heating mantle and magnetic stirrer was placed 20 g of 3-hydroxy-2-hydroxymethylpyridine and 1 l. of benzene. With continuous vigorous stirring, 100 g of finely divided, activated manganese dioxide[17] was added in portions to ensure uniform suspension. The flask was equipped with a Soxhlet extractor head with a cup capacity of about 75 ml, the cup containing 20 g of 4 Å molecular sieves. The mixture was stirred and heated under reflux for 5 hr, cooled to room temperature, filtered, and the filter cake washed with 200 ml of benzene. The combined filtrate and wash was saturated with dry hydrogen chloride, the precipitated salt collected, dried and vacuum sublimed at ~160° (1 mm), yield 17-20 g (65-75%), mp 214-216° dec.

Anal. Calcd for $C_6H_6ClNO_2$: C, 45.2; H, 3.8; N, 8.8. Found: C, 45.1; H, 3.8; N, 8.8.

3-Hydroxy-6-methylpyridine-2-aldehyde Hydrochloride (10b). This compound was prepared from the free base 3-hydroxy-2-hydroxymethyl-6-methylpyridine[13] as described above; yields of sublimed product were 50-65%, mp 215-217° dec.

Anal. Calcd for $C_7H_8ClNO_2$: C, 48.4; H, 4.7; N, 8.1. Found: C, 48.1; H, 4.5; N, 8.0.

Imine Preparations. General Procedures. (Table I). A. From Free Aldehydes. A mixture of 50 mmol each of aldehyde and amine in 100 ml of absolute or 95% ethanol was heated gently on a steam bath for ½ hr and the solution was stored at −10 to −20° for 1 or 2 days to allow the imine to crystallize. In some instances it was necessary to reduce the solution volume to 50 ml or less before chilling and/or to induce crystallization by vigorously scratching the sides of the flask. The products were recrystallized from ethanol.

B. From Hydroxypyridinealdehyde Hydrochlorides. The pyridinealdehyde hydrochlorides (50 mmol) were dissolved in absolute or 95% ethanol (50 ml for the 6-methyl compound and 150 ml for unmethylated homolog). The sublimed salts dissolved slowly so the mixtures were heated on a steam bath with occasional stirring until dissolved. The aldehyde solution was added to a solution of 50 mmol of the amine in 50–100 ml of ethanol, and 50 mmol of sodium methoxide was added immediately. The mixture was heated gently on a steam bath for ½ hr and then either chilled directly or reduced to a 50-ml volume before chilling.

In some cases crystallization was very slow, requiring that the solutions be cooled for 1–2 days. The mixture of yellow imine and by-product sodium chloride was collected on a filter and washed with cold ethanol and then liberally with water to remove sodium chloride. The imine was then recrystallized from ethanol.

Since the purity of the sirupy amines (7) was unknown, they were used in half-fold excess to ensure that enough was present to consume all the aldehyde.

Reduction of the Imines. General Procedure (Table II). To a magnetically stirred suspension or solution of 30 mmol of monoimine in 250 ml of EtOH was added 20 mmol of sodium borohydride. Within 30 min, the imine had dissolved, and the yellow color was discharged. Stirring was continued overnight and, in some cases, a first crop of product had separated. Otherwise the mixture was evaporated to dryness, the residue dissolved in a small amount of 1 *N* sodium hydroxide, and the solution acidified to pH 6 with acetic acid to reprecipitate the product which was then recrystallized from ethanol. In the case of the hydrate of **13c**, the recrystallization solvent was 95% ethanol, and the product was dried in a stream of moist air.

Simple Chelate Preparations (Table V). To a gently boiling solution of 2 mmol of ligand in 15–25 ml of ethanol was added dropwise a warm solution of 2 mmol of metal salt in 5 ml of water. In most cases, the crystalline chelate separated when the mixtures were allowed to stand at room temperature for several hours. In others, the solution was allowed to evaporate to deposit the chelate.

Exceptions to this procedure are the Ag(I) chelates of the aminoimine **5** (Table V, prepns 12 and 13). For the fluoborate, a solution of 0.73 g of **5** in 25 ml of chloroform was shaken with a solution of 0.83 g of 47% silver fluoborate in 5 ml of water. The yellow microcrystalline chelate separated immediately and was collected and washed with chloroform, water, and ethanol. Similar treatment of the ligand in chloroform with equimolar aqueous silver nitrate caused the chloroform layer to become bright yellow. After standing for several days, the crystalline chelate separated as bright-yellow prisms. It was collected and washed with water and then sparingly with chloroform. The air-dried product was the monochloroform solvate; if vacuum dried, it effloresced and gave variable elemental analyses depending on the extent of drying.

Chloromethylated Polystyrene. Polystyrene beads[18] (1% cross-linked, 200–400 mesh) were chloromethylated with chloromethyl methyl ether according to a published procedure.[19] Recovery was quantitative; the chlorine content corresponded to chloromethylation of 89% of the available benzene rings.

Anal. Found: Cl, 20.5, 20.6, equivalent to 5.8 mg-atoms of Cl/gram of polymer.

Polymer–Ligand Condensations (Table VI). A solution of 11.6 mmol of ligand and 0.63 g (11.6 mmol) of sodium methoxide in 50 ml of anhydrous DMF was stirred, under nitrogen, at room temperature for 10 min, and then 2.00 g of the above chloromethylpolystyrene (equiv to 11.6 mg-atoms of Cl) was added. The mixture was stirred under nitrogen and heated at 85–90° for 12 hr. The product was collected on a coarse frit funnel and washed successively with 50 ml of DMF, then DMF-H_2O mixtures (4:1, 3:2, 2:3, 1:4), and finally plain water. Another plain DMF wash was followed by DMF–EtOH mixtures, proportions as above. The polymer was then vacuum dried at 80–90° for 24 hr.

In one experiment (Table VI, prepn 6), ligand monohydrate was used and, in two others (Table VI, prepns 2 and 4), 210 μl of water was added to the anhydrous ligands to simulate their use as monohydrates.

Table VIII

Ion	Salt form	Weight, g/l.
Fe^{3+}	$FeNH_4(SO_4)_2{\cdot}12H_2O$	25.0
Fe^{2+}	$Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$	19.5
Co^{2+}	$CoSO_4{\cdot}7H_2O$	14.0
Ni^{2+}	$NiSO_4{\cdot}6H_2O$	13.1
Cu^{2+}	$CuSO_4{\cdot}5H_2O$	12.5
Ag^{+}	$AgNO_3$	8.5

Alkylation of 1 with Chloromethylated Polystyrene. A mixture of 2.0 g of chloromethylated polystyrene (11.6 mg-atoms of Cl), 4.25 g (11.6 mmol) of **1**, and 1.60 ml (11.6 mmol) of triethylamine in 50 ml of dioxane was boiled under reflux for 16 hr and then filtered while hot. The solid was washed with hot dioxane, then chloroform, then ethanol and vacuum dried, yield 3.0 g (26%).

Anal. Found: N, 4.6, equivalent to 0.82 mmol of ligand *per* gram.

Alkylation of 6 with Chloromethylated Polystyrene. A reaction similar to that above was carried out with 3.2 g of **6**. The initial dioxane filtrate afforded triethylammonium chloride in 59% yield. The polymer was washed and dried as above to obtain 3.3 g (47%) of product.

Anal. Found: N, 6.6, equivalent to 1.57 mmol of ligand *per* g.

Polymer Chelation Procedures (Table VII). The top of a chromatography column, 1-cm i.d., 15-cm long, was equipped with a standard grind ball joint for attachment of a liquid reservoir having a standard socket joint and stopcock. The bottom end of the column had a coarse fritted disk and two-way stopcock outlet. One leg of the two-way outlet was attached through rubber tubing to a separatory funnel containing 0.1 *N* H_2SO_4, the liquid level in the funnel being about 40 cm above the frit to provide an adequate pressure head for backwashing. Some of the wash solution was drawn into the column well above the frit to eliminate bubbles in the dead space between the frit and the takeoff. This dilute acid was drained from the column to a level just barely above the top surface of the frit. Into the column was introduced 1.00 g of dry polymer and sufficient 15% H_2SO_4 to make a mobile slurry; it was gently stirred with a fine glass rod to eliminate bubbles.

The polymer was allowed to settle and was then topwashed with 25 ml of 15% H_2SO_4 at the maximum takeoff rate permitted by the column (i.e., no external pressure applied). This wash was necessary to activate the polymer. When the liquid level had just reached the surface of the resin, topwashing was stopped, and the resin was backwashed with 25 ml of 0.01 *N* H_2SO_4 in portions. After admitting the last portion of backwash, the resin was allowed to settle without simultaneous takeoff, leaving a liquid column about 6–8 cm above the resin surface.

The ion solutions shown in Table VIII were prepared by dissolving the appropriate salts in 1000 ml of 0.01 *N* H_2SO_4 such that all were nominally 0.05 *M*, corresponding to about 3 g of metal ion per liter.

A reservoir was fitted to the top of the column and to it was added ion solution containing about 1 ½ times the amount of metal ion sufficient to theoretically saturate the column, or about 50 ml of 0.05 *M* solution *per* gram of polymer. In competition experiments with ion mixtures, the concentration of each individual ion was 0.05 *M*. The solution was allowed to percolate through the column at a rate determined by the spontaneous takeoff rate. A 6–8 cm liquid column was left on top of the resin, and the reservoir was replaced with one containing 25 ml of distilled water; this was used to topwash the column in the same way that the ion solution had been applied. The exhausted ion solution and water wash were discarded.

Chelated ions were stripped from the resin by topwashing with 15% H_2SO_4 (25 ml/g of polymer), the eluate being collected in a 100-ml volumetric flask and finally diluted to the mark with 15% H_2SO_4.[20] Using a 100-ml eluate volume and dividing the ion concentration in parts per million by ten permits easy conversion to total milligrams of metal in the eluate and thus the resin capacity in milligrams of metal/gram of resin.

Before proceeding with application of another ion solution, the resin was backwashed with 25 ml of 0.01 *N* H_2SO_4 in portions as previously described. The settled volume of 1% cross-linked resin equilibrated with 15% H_2SO_4 was about twice that when equilibrated with 0.01 *N* H_2SO_4. The increased swelling in the more concentrated acid caused the spontaneous flow rate to slow markedly, but the faster, more convenient rate was restored by the dilute acid wash.

Results are summarized in Table VII.

Acknowledgments. The author thanks Eleanor G. Applegate for expert technical assistance and Joan D. Hogan, Lucretia C. Hovsepian, and Harry C. Hauger for the metal ion analyses. Helpful discussions with Dr. M. Panar are also gratefully acknowledged.

References and Notes

(1) (a) M. J. Slater, *Chem. Ind.* (*London*), 478 (1971); (b) A. W. Fletcher, *ibid.*, 776 (1971).

(2) H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **82**, 5013 (1960).

(3) This compound would not crystallize and was used as a crude sirup.

(4) The difference is apparently a solubility effect; **5** is so insoluble in isopropyl alcohol that it crystallizes immediately on being formed.

(5) Reduction of the nonphenolic imines to **1**, **6**, and **7** required a large excess of sodium borohydride and reaction times of 24–48 hr, whereas the phenolic imines **8** and **11** required only slightly more than the theoretical amount of reducing agent and were reduced in less than an hour. This rate enhancement may reflect the formation of phenoxyboron hydrides in which the reducing residue is restrained near the reducing site and protected from solvolytic decomposition.

(6) The ligands were almost instantaneously sequestered into the aqueous phase.

(7) The magnetic moment was determined by NMR for which I am grateful to Drs. W. D. Phillips and C. C. McDonald and Mr. F. V. Ferrari of this laboratory.

(8) U.S. standard 200–400 mesh, 1% cross-linked with divinylbenzene.

(9) Good yields of triethylammonium chloride were recovered as by-products, thus the reaction was not a simple quaternization.

(10) L. R. Melby and D. R. Strobach, *J. Org. Chem.*, **34**, 421 (1969).

(11) The polymers were used in conventional chromatography columns equipped with an outlet for eluate collection and backwashing. The neutral polymers are hydrophobic and thus ineffective when packed in pure water. They were activated by treatment with 15% sulfuric acid followed by washing and equilibration with 0.01 *N* acid. The metal salt solutions were 0.05 *M* in metal ion in 0.01 *N* sulfuric acid; see Experimental Section.

(12) Since all the polymers virtually totally excluded Fe(II) and Fe(III), the competitive experiments with iron and Cu(II) give values essentially equivalent to absolute capacities for Cu(II).

(13) Aldrich Chemical Co., Milwaukee, Wis.

(14) The reduction proceeded fairly well in ethanol solvent, but ethyl acetate gave better yields of purer product. Contrary to our observations, J. L. Everett and W. J. C. Roos, *J. Chem. Soc.*, 1972 (1949), report that reduction in ethanol produces benzocinnoline.

(15) R. B. Carlin and G. E. Foltz, *J. Am. Chem. Soc.*, **78**, 1997 (1956).

(16) D. Heinert and A. E. Martell, *Tetrahedron*, **3**, 49 (1958), describe an aqueous, acidic manganese dioxide oxidation which was unsatisfactory in our hands. This modification of the anhydrous procedure of E. P. Papadapoulos, A. Jassar, and C. H. Issidorides, *J. Org. Chem.*, **31**, 615 (1966), proved superior.

(17) Shepperd Chemical Co., Cincinnati, Ohio.

(18) Bio-Beads S-XI, Bio-Rad Laboratories, Richmond, Calif.

(19) K. W. Pepper, H. M. Paisley, and M. A. Young, *J. Chem. Soc.*, 4097 (1953).

(20) Ion analyses were done by atomic absorption and expressed in parts per million.

Ethylbenzenium Ions and the Heptaethylbenzenium Ion[1a]

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Abstract: A series of ethyl-substituted benzenium ions has been prepared under stable-ion conditions by protonation or electrophilic ethylation of the corresponding arenes. The series culminates in the heptaethylbenzenium ion (**1**-Et), and the physical and chemical properties of **1**-Et were investigated. The ions were studied by ^1H NMR and ^{13}C NMR spectroscopy, and the ^{13}C NMR spectra were compared with the analogous methyl-substituted benzenium ions. The carbon chemical shifts are interpreted in terms of charge distribution and are consistent with a regional charge distribution model but not the total or π charges calculated by the ab initio method. $^1J_{CH}$ values for C_1 in the benzenium ions indicate a high degree of strain in the hexa-substituted species relative to the less substituted members. The highly crowded ion **1**-Et appears to have several anomalously deshielded carbon resonances in the C_6–C_1–C_2 fragment.

The ability of aromatic compounds to undergo ring protonation in strongly acidic media to form arenium ions is one of the best known aspects of stable-ion chemistry.[2] The structures of these ions have been determined by a variety of spectroscopic methods including uv spectroscopy,[2] ^1H NMR spectroscopy,[2,3] and in recent years ^{13}C NMR spectroscopy.[3c-e,4]

The most intensely studied arenium ions have been the methyl-substituted benzenium ions; ^1H NMR spectra have been reported for all isomeric ions from the *p*-methylbenzenium ion[3c] to Doering and Saunders' heptamethylbenzenium ion (**1**-Me).[3a] The charge distributions in several of these ions have been discussed in relation to the carbon-13 chemical shifts of the ring carbon atoms[3c,4a,b] and, in the earlier literature, to the proton chemical shifts.[2]

We have now extended our studies and prepared a series of ethyl-substituted benzenium ions including the heptaethylbenzenium ion (**1**-Et). The physical and chemical data for **1**-Et are discussed in relation to those for **1**-Me.[3a] The question of steric-induced strain in highly substituted benzenium ions is one of continuing interest; it has been suggested on the basis of ^1H NMR spectral parameters that the hexamethylbenzenium ion (**2**-Me) is distorted, relative to less substituted derivatives, with the C_1–CH_3 group forced pseudo-axial.[2,5] Since one-bond ^{13}C–^1H coupling ($^1J_{CH}$) magnitudes are known to be dependent upon strain,[6] this seemed a logical technique with which to investigate this problem. Steric factors could be more important in ethyl-substituted benzenium ions, and the carbon-13 chemical shifts and $^1J_{CH}$ values are compared with the methyl-substituted analogs and discussed in relation to charge distribution and ring strain.

Ethylbenzenium ions are of particular importance, because the aluminum chloride catalyzed liquid phase ethylation of benzene is one of the largest scale manufacturing processes. The red-oil layer produced in this reaction con-

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