CHAPTER 4

CONCLUSIONS

As a principle of ligand design it seems clear that ligand selectivity for large metal ions can be enhanced by the addition of groups containing alcoholic or ethereal oxygen donor atoms. It is not necessary for the added neutral oxygen donor atom to be part of the macrocyclic ring although the evidence available from this work suggests that addition of oxygen donors into the macrocyclic ring may have a larger effect on metal ion size–selectivity. The ligands THP–15–aneN_3O_2, DHP–15–aneN_2O_3, and DHP–18–aneN_2O_4 indicate that the large 18–membered ring produces larger selectivities for Pb^{2+} over Zn^{2+} than the smaller 15–membered ring. There is thus a discernable effect of macrocyclic ring size on metal ion size–selectivity which must be taken into account.

The addition of neutral oxygen–donor–bearing groups to existing ligands produces metal ion size–selectivity patterns very similar to those of macrocycles. However, addition of only a few oxygen donors in such a way that not too great an amount of steric crowding is produced leads to a moderate increase in the Pb^{2+} over Zn^{2+} selectivity. When a larger number of oxygen donors is added so that sterically more demanding ligands are formed, a high Pb^{2+} over Zn^{2+} selectivity is observed. Thus, the sterically less hindered ligand BHE–18–aneN_2O_4 has a Pb^{2+} over Zn^{2+} selectivity of 5.6 log units whereas the sterically more demanding ligand BHEE–18–aneN_2O_4 has a Pb^{2+} over Zn^{2+} selectivity of 7.2 log units. A marked destabilization of the complexes of small metal ions relative to large metal ions has been achieved by using ligands that are structurally more complex. The destabilization produced for the complexes of small metal ions is due to steric crowding around these ions which lead to bond deformation and an overall decrease in complex stability. Larger metal ions do not adopt rigid geometries and are thus not very susceptible to steric strain. The origin of the size–selectivity pattern was rationalized in terms of the strain free cyclohexane conformation. Thus, for oxygen–donor containing five–membered chelate rings, ideal geometry is retained when large metals coordinate whereas for six–membered chelate rings, the ideal geometry is retained with coordination to small metal ions. That is, larger metal ions are better suited geometrically to coordinating to the five–membered chelate ring and do so with less strain energy.

The crystal structure of $[K(BHE-18-aneNO_2O_4)]^+$ and $[K(BHEE-18-aneN_2O_4)]^+$ shows the metal ion to be eight and nine (major conformer) coordinate respectively. The macrocyclic donors are arranged in the boat and chair conformation and the pendent arms in a cis– and trans–arrangement respectively. The structure of the $[Ba(BHEE-18-aneN_2O_4)(H_2O)]^{2+}$ shows the metal ion to be eleven coordinate because of the participation of a water molecule in coordination. The macrocyclic donors are arranged in a boat conformation and the pendent arms in a cis–arrangement. The charge of the metal ion as well as the effective ionic radii of the metal ion are thought to contribute to the conformation of the ligand.

For the series of open–chain polyamine analogues of bridged macrocycles studied, it has been shown that the presence of the nine–membered macrocyclic ring enhances the complexation of small metal ions such as Ni^{2+}. The ligands which formed five–membered chelate rings favour the complexation of large metal ions whereas those which form six–membered chelate rings favour the complexation of small metal ions. Incorporation of these smaller rigid units into larger macrocycles is expected to display size–selectivity based on the match between cavity size and metal ion size.

CHAPTER 5

DIRECTIONS OF FUTURE RESEARCH

The ligand BHEE–18–aneN_2O_4 may be a highly satisfactory reagent for treating Pb^{2+} intoxication in terms of the required Pb^{2+} over Zn^{2+} selectivity. However, when the complex stability of the Pb^{2+} ion is compared to that of cryptand–2,2,2, the ligand BHEE–18–aneN_2O_4 appears to be on the low side in complexing strength with Pb^{2+}, since cryptand–2,2,2 has a log K_1 of 12.0, compared to 7.2 log units of BHEE–18–aneN_2O_4. Although the addition of sufficient oxygen donors, as in BHEE–18–aneN_2O_4, produces the level of steric crowding required for the destabilization of the complexes of small metal ions, there is still the need for improvement of the binding strength of Pb^{2+}. This can be achieved by simple modification of ligands which already have high affinity for Pb^{2+}. As shown in Section 3.3, by incorporating the structural parameters of BHEE–18–aneN_2O_4 and DAK–2,2, a high affinity for Pb^{2+} can be achieved, while maintaining the selectivity of Pb^{2+} over Zn^{2+} to be ~7 log units.

As discussed in Section 1.4 non–bridged macrocycles are too flexible to display any marked "hole–size–selectivity". For the tetraazamacrocycles, the trans–I conformer of the macrocycle allows the metal ion to coordinate in an out–of–plane mode. It is because these macrocycles are able to fold that geniune "hole–size–selectivity" is not observed. This type of behaviour may be observed if the macrocycles are made more rigid. The need for the synthesis of the bridged macrocycles described in Section 3.6 is therefore required. Also needed are rigid macrocycles having cavity sizes best suited for the metal ion Pb^{2+}.

APPENDIX 1

Data For The Stability Constant Determination Using NMR Of The Alkali Nuclei

Table 1 ^{23}Na NMR study of ligand–Na$^+$ complexes in methanol at 23°C

$^L/Na^+$ mole ratio	^{23}Na chemical shift/ppm	Line width /Hz	$^L/Na^+$ mole ratio	^{23}Na chemical shift/ppm	Line width /Hz
$[Na(15\text{–}aneN_2O_3)]^+$			$[Na(15\text{–}aneN_3O_2)]^+$		
0.00	–2.83	20	0.00	–2.83	20
0.146	–2.80	20	0.335	–2.77	10
0.388	–2.78	15	0.592	–2.76	20
0.827	–2.72	10	1.204	–2.72	25
1.517	–2.62	15	1.518	–2.70	25
$[Na(DHP\text{–}15\text{–}aneN_2O_3)]^+$			$[Na(THP\text{–}15\text{–}aneN_3O_2)^+]$		
0.00	–2.83	20	0.00	–2.83	20
0.146	–2.63	20	0.146	–2.68	30
0.274	–2.45	50	0.276	–2.44	40
0.388	–2.26	40	0.392	–2.31	50
0.446	–2.20	50	0.496	–2.17	40
0.545	–2.02	60	0.592	–2.01	40
0.635	–1.93	70	0.678	–1.90	50
0.718	–1.80	60	0.829	–1.16	40
0.895	–1.42		0.895	–1.15	50
1.040	–1.30	130	0.956	–1.50	60
5.040	(–1)		1.518	–0.57	110
			3.110	(1.2)	

Values indicated in brackets are an approximation. Line broadening at high mole ratio made the determination of chemical shifts difficult.

Table 2 ^{87}Rb NMR study of ligand–Rb$^+$ complexes in methanol at 23°C

^{L}/Rb$^+$ mole ratio	Rb chemical shift/ppm	Line width /Hz	^{L}/Rb$^+$ mole ratio	Rb chemical shift/ppm	Line width /Hz
[Rb(15–aneN_2O_3)]$^+$			[Rb(15–aneN_3O_2)]$^+$		
0.00	–30.92	400	0.00	–30.28	400
0.142	–30.85	420	0.142	–30.24	450
0.267	–30.91	390	0.267	–30.24	450
0.477	–30.87	395	0.719	–30.23	450
1.085	–30.74	400	1.192	–30.07	450
1.378	–30.78	400	1.400	–30.05	450
[Rb(DHP–15–aneN_2O_3)]$^+$			[Rb(THP–15–aneN_3O_2)]$^+$		
0.00	–30.92		0.00	–30.92	
0.142	–28.59		0.142	–30.81	500
0.267	–25.8		0.268	–30.63	500
0.378	–23.3		0.477	–30.31	500
0.477	–18.7		0.719	–29.30	500
0.719	–12.8		1.001	–28.82	500
2.390	(7)		1.193	–28.64	530
			1.400	–27.89	600

Value in bracket is an approximation. Line broadening at high mole ratio made the determination of chemical shift difficult.

Table 3 ^{133}Cs NMR study of ligand–Cs^+ complexes in methanol at 23°C

$^{L}/Cs^+$ mole ratio	Cs chemical shift	$^{L}/Cs^+$ mole ratio	Cs chemical shift
$[Cs(15\text{–}aneN_2O_3)]^+$		$[Cs(15\text{–}aneN_3O_2)]^+$	
0.00	–52.18	0.00	–52.18
0.075	–51.96	0.274	–50.38
0.147	–51.85	0.490	–50.38
0.211	–51.78	0.793	–50.29
0.332	–51.71	1.092	–50.30
0.591	–51.61	1.454	–50.30
1.202	–51.41		
$[Cs(DHP\text{–}15\text{–}aneN_2O_3)]^+$		$[Cs(THP\text{–}15\text{–}aneN_3O_2)]^+$	
0.00	–52.18	0.00	–52.18
0.146	–50.20	0.146	–50.44
0.256	–48.94	0.388	–50.34
0.393	–48.01	0.592	–50.25
0.490	–46.81	0.956	–50.16
0.596	–45.53	1.204	–50.08
0.677	–45.37	1.506	–49.92
0.755	–43.49	3.110	–49.28
0.894	–41.93		
1.013	–40.58		
1.113	–39.67		
1.203	–38.85		
1.298	–37.79		
1.517	–35.21		
5.035	–16.17		

Line widths ranged from 0.6 HZ – 1.1 Hz.

Log K (Na^+–BHP–15–aneN_2O_3)

Metal in cell : mmol = 0.03
Ligand in cell : mmol = 0.00
Cell volume : ml = 3.00
Titrant M : M = 0.009333
Titrant L : M = 0.02326
no = –2.83
n_∞ = –1

Vi/ml	Chemical shift/ppm	$\bar{n}$	log K
0.20	–2.63	0.11	2.5261
0.40	–2.45	0.21	2.5883
0.60	–2.26	0.31	2.7543
0.70	–2.20	0.34	2.7196
0.90	–2.02	0.44	2.8957
1.10	–1.93	0.49	2.8364
1.30	–1.80	0.56	2.9287
1.80	–1.42	0.77	3.4431
2.30	–1.30	0.84	3.4119

mean log K = 2.900
st. dev = 0.326

Log K (Na^+–THP–15–aneN_3O_2)

Metal in cell : mmol = 0.03
Ligand in cell : mmol = 0.00
Cell volume : ml = 3.00
Titrant M : M = 0.009333
Titrant L : M = 0.02326
no = –2.83
n∞ = –1.2

Vi/ml	Chemical shift/ppm	$\bar{n}$	log K
0.20	–2.68	0.04	1.5523
0.40	–2.44	0.10	1.7801
0.60	–2.31	0.13	1.7553
0.80	–2.17	0.16	1.7755
1.00	–2.01	0.20	1.8256
1.20	–1.90	0.23	1.8351
1.60	–1.61	0.30	1.9269
1.80	–1.51	0.33	1.9446
2.00	–1.50	0.33	1.9074
5.00	–0.57	0.56	2.1437

mean log K = 1.845
st. dev = 0.154

log K (Rb^+–BHP–15–aneN_2O_3)

Metal in cell : mmol = 0.05601
Ligand in cell : mmol = 0.00
Cell volume : ml = 3.00
Titrant M : M = 0.01922
Titrant L : M = 0.04257
no = –30.92
n∞ = 7

Vi/Ml	Chemical shift/ppm	$\bar{n}$	log K
0.20	–28.59	0.06	1.6367
0.40	–25.8	0.14	1.7992
0.60	–23.3	0.20	1.8787
0.80	–18.7	0.32	2.2135
1.40	–12.8	0.48	2.3044

mean log K = 1.967
st. dev = 0.283

Log K (Rb^+–THP–15–aneN_3O_2)

Metal in cell : mmol = 0.05601
Ligand in cell : mmol = 0.00
Cell volume : ml = 3.00
Titrant M : M = 0.01922
Titrant L : M = 0.04260
no = –30.92
n∞ = –23.7

Vi/ml	Chemical shift/ppm	$\bar{n}$	log K
0.20	–30.81	0.02	0.8134
0.40	–30.63	0.04	0.9923
0.80	–30.31	0.08	1.0970
1.40	–29.30	0.22	1.4916
2.40	–28.82	0.29	1.4848
3.40	–28.64	0.32	1.4430
5.00	-27.89	0.42	1.5887

mean log K = 1.294
st. dev = 0.285

Log K_1(Cs^+–BHP–15–aneN_2O_3)

Metal in cell : mmol = 0.03
Ligand in cell : mmol = 0.00
Cell volume : ml = 3.00
Titrant M : M = 0.00933
Titrant L : M = 0.02325
no = –52.18
n_∞ = –16.17

Vi/ml	Chemical shift/ppm
0.20	–50.20
0.40	–48.94
0.60	–48.01
0.80	–46.81
1.00	–45.73
1.20	–45.37
1.40	–43.49
1.80	–41.93
2.20	–40.58
2.60	–39.67
3.00	–38.85
3.50	–37.79
5.00	–35.21

$\bar{n}$	log K
0.05	1.8079
0.09	1.7296
0.12	1.6810
0.15	1.7091
0.18	1.7313
0.19	1.6876
0.24	1.8005
0.28	1.8257
0.32	1.8504
0.35	1.8553
0.37	1.8635
0.40	1.8853
0.47	1.9493

mean log K = 1.797
st. dev = 0.081

Log K (Cs^+–THP–15–aneN_3O_2)

Metal in cell : mmol = 0.03
Ligand in cell : mmol = 0.00
Cell volume : ml = 3.00
Titrant M : M = 0.009333
Titrant L : M = 0.02326
no = –52.18
n_∞ = –42.4

Vi/ml	Chemical shift/ppm	$\bar{n}$	log K
0.20	–50.44	0.18	
0.60	–50.34	0.19	2.0601
1.00	–50.25	0.20	1.8022
2.00	–50.16	0.21	1.5523
3.00	–50.08	0.21	1.4564
4.90	–49.92	0.23	1.3909

mean log K = 1.377
st. dev = 0.718

APPENDIX 2

Table 1. Fractional coordinates ($\times 10^4$, Cl and K $\times 10^5$) and equivalent isotropic temperature factors ($\mathring{A}^2$, $\times 10^4$) for $C_{16}H_{34}N_2O_6$.KCl.

$$\underline{U}_{eq} = \frac{1}{3}\sum_i\sum_j \underline{U}_{ij}\underline{a}_i^*\underline{a}_j^*(\underline{a}_i.\underline{a}_j)$$

	x/a	y/b	z/c	$\underline{U}_{eq}$
K(1)	0	29268(3)	25000	350(1)
Cl	50000	47844(4)	25000	437(1)
N(1)	448(1)	2987(1)	99(1)	392(3)
O(1)	2002(1)	3695(1)	2676(1)	493(3)
O(2)	1466(1)	3854(1)	4790(1)	489(3)
O(3)	421(1)	1497(1)	1478(2)	586(4)
C(1)	1615(2)	3265(1)	540(2)	520(5)
C(2)	1970(2)	3987(1)	1492(2)	545(5)
C(3)	2482(2)	4314(1)	3682(2)	572(5)
C(4)	2575(2)	3953(2)	4914(2)	567(5)
C(5)	1516(2)	3547(1)	5971(2)	495(4)
C(6)	347(2)	3585(1)	6854(2)	496(4)
C(7)	278(2)	2129(1)	-458(2)	481(4)
C(8)	810(2)	1438(1)	540(2)	477(4)

Table 2. Fractional coordinates ($\times 10^3$) and common isotropic temperature factors ($\mathring{A}^2$, $\times 10^3$) for hydrogen atoms in $C_{16}H_{34}N_2O_6$.KCl.

	x/a	y/b	z/c	U
H(1)	37(2)	100(1)	171(2)	64(2)
H(11)	215(2)	277(1)	104(2)	64(2)
H(12)	169(2)	346(1)	-23(2)	64(2)
H(21)	270(2)	422(1)	169(2)	64(2)
H(22)	141(2)	453(1)	113(2)	64(2)
H(31)	194(2)	484(1)	335(2)	64(2)
H(32)	320(2)	453(1)	379(2)	64(2)
H(41)	303(2)	438(1)	565(2)	64(2)
H(42)	299(2)	336(1)	513(2)	64(2)
H(51)	185(2)	293(1)	620(2)	64(2)
H(52)	206(2)	392(1)	673(2)	64(2)
H(61)	2(2)	424(1)	557(2)	64(2)
H(62)	42(2)	344(1)	671(2)	64(2)
H(71)	-52(2)	205(1)	-94(2)	64(2)
H(72)	58(2)	210(1)	-112(2)	64(2)
H(81)	165(2)	151(1)	98(2)	64(2)
H(82)	62(2)	85(1)	11(2)	64(2)

Table 3. Anisotropic temperature factors ($\mathring{A}^2$, $\times 10^4$, C $\times 10^3$) for cation in $C_{16}H_{34}N_2O_6$.KCl.

	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
K(1)	341(2)	361(2)	358(2)	0	171(2)	0
Cl	480(3)	332(3)	490(3)	0	219(3)	0
N(1)	465(8)	382(7)	392(7)	16(6)	251(6)	8(6)
O(1)	521(7)	472(7)	558(7)	-114(6)	311(6)	-188(6)
O(2)	360(6)	654(9)	413(6)	-71(6)	147(5)	-85(6)
O(3)	964(11)	378(7)	690(9)	49(6)	615(9)	31(7)
C(1)	53(1)	62(1)	57(1)	-2(1)	39(1)	-4(1)
C(2)	54(1)	54(1)	67(1)	-1(1)	38(1)	-16(1)
C(3)	50(1)	53(1)	75(1)	-22(1)	34(1)	-23(1)
C(4)	35(1)	69(1)	59(1)	-23(1)	16(8)	-14(1)
C(5)	51(1)	52(1)	36(1)	-7(8)	12(8)	-5(1)
C(6)	66(1)	50(1)	42(1)	-10(8)	32(1)	-6(1)
C(7)	65(1)	44(1)	39(1)	-2(8)	27(1)	3(1)
C(8)	61(1)	43(1)	48(1)	-1(8)	33(1)	7(1)

Table 4. Fractional coordinates ($\times 10^4$, I $\times 10^5$) and equivalent isotropic temperature factors ($Å^2$, $\times 10^3$, I and K $\times 10^4$) for $C_{20}H_{44}N_2O_8$.KI.

$$\underline{U}_{eq} = \frac{1}{3}\sum_i\sum_j \underline{U}_{ij}\underline{a}_i^*\underline{a}_j^*(\underline{a}_i.\underline{a}_j)$$

	x/a	y/b	z/c	$\underline{U}_{eq}$
I	21706(9)	18354(5)	12637(3)	802(2)
K	7534(3)	2190(1)	3869(1)	615(5)
N(1)	7633(8)	2417(5)	2552(3)	52(2)
N(2)	6857(7)	2036(4)	5117(3)	50(2)
O(1)	7548(6)	576(4)	3159(2)	52(1)
O(2)	8267(6)	519(4)	4470(2)	54(1)
O(3)	6528(7)	3741(4)	4402(3)	62(2)
O(4)	5289(6)	3395(4)	3171(3)	64(2)
O(5)	9846(7)	3289(5)	3479(3)	81(2)
O(6)	10620(12)	2988(8)	4692(5)	102(3)*
O(7)	4382(7)	1246(5)	4171(3)	74(2)
O(8)	12088(7)	4381(5)	7685(3)	79(2)
C(1)	7085(11)	1522(6)	2250(4)	59(2)
C(2)	7904(11)	660(6)	2558(4)	62(2)
C(3)	8409(9)	-173(5)	3497(4)	54(2)
C(4)	7834(10)	-292(6)	4101(4)	60(2)
C(5)	7870(10)	418(6)	5069(4)	62(2)
C(6)	8006(11)	1339(6)	5395(4)	65(2)
C(7)	7311(11)	2978(6)	5368(4)	69(2)
C(8)	6354(12)	3762(6)	5037(4)	76(3)
C(9)	5627(11)	4421(6)	4027(5)	70(3)
C(10)	5876(11)	4301(5)	3378(4)	65(2)
C(11)	5134(11)	3251(7)	2522(4)	74(3)
C(12)	6626(11)	3195(7)	2283(4)	67(2)
C(13)	9234(11)	2596(7)	2488(4)	72(3)
C(14)	9988(12)	3393(7)	2858(5)	82(3)
C(15)	10787(19)	3988(12)	3826(8)	88(4)*
C(16)	10529(19)	3897(12)	4477(7)	82(4)*
C(17)	5298(9)	1785(7)	5194(4)	63(2)
C(18)	4110(9)	1912(7)	4622(4)	66(2)
C(19)	3163(12)	1330(9)	3648(5)	95(3)
C(20)	3434(13)	686(9)	3203(5)	108(4)
O(6')	10748(36)	5144(23)	3843(14)	102(3)*
C(15')	11059(55)	3574(33)	4102(24)	88(4)*
C(16')	10302(54)	4433(34)	4281(21)	82(4)*

* isotropic temperature factor.

Table 5. Fractional coordinates ($\times 10^4$) and common isotropic temperature factors($\AA^2$, $\times 10^3$) for hydrogen atoms in $C_{20}H_{44}N_2O_8$.KI.

	x/a	y/b	z/c	U
H(1)	5867(11)	1454(6)	2257(4)	91(5)
H(2)	7263(11)	1544(6)	1776(4)	91(5)
H(3)	9135(11)	737(6)	2589(4)	91(5)
H(4)	7517(11)	40(6)	2291(4)	91(5)
H(5)	8234(9)	-816(5)	3232(4)	91(5)
H(6)	9623(9)	0(5)	3587(4)	91(5)
H(7)	8348(10)	-910(6)	4338(4)	91(5)
H(8)	6593(10)	-363(6)	4012(4)	91(5)
H(9)	6697(10)	167(6)	5021(4)	91(5)
H(10)	8641(10)	-83(6)	5334(4)	91(5)
H(11)	9143(11)	1621(6)	5389(4)	91(5)
H(12)	7866(11)	1223(6)	5868(4)	91(5)
H(13)	7196(11)	2992(6)	5849(4)	91(5)
H(14)	8502(11)	3097(6)	5330(4)	91(5)
H(15)	6750(12)	4430(6)	5241(4)	91(5)
H(16)	5155(12)	3663(6)	5071(4)	91(5)
H(17)	4421(11)	4321(6)	4048(5)	91(5)
H(18)	5978(11)	5119(6)	4189(5)	91(5)
H(19)	7093(11)	4341(5)	3361(4)	91(5)
H(20)	5267(11)	4843(5)	3087(4)	91(5)
H(21)	4517(11)	2599(7)	2409(4)	91(5)
H(22)	4468(11)	3826(7)	2290(4)	91(5)
H(23)	7242(11)	3848(7)	2389(4)	91(5)
H(24)	6363(11)	3101(7)	1787(4)	91(5)
H(25)	9896(11)	1969(7)	2629(4)	91(5)
H(26)	9252(11)	2739(7)	2007(4)	91(5)
H(27)	9446(12)	4043(7)	2680(5)	91(5)
H(28)	11197(12)	3410(7)	2823(5)	91(5)
H(29)	11919(19)	3750(12)	3770(8)	91(5)
H(30)	10583(19)	4684(12)	3633(8)	91(5)
H(29')	11641(55)	3516(33)	4577(24)	91(5)
H(30')	11891(55)	3504(33)	3798(24)	91(5)
H(31)	9485(19)	4183(12)	4597(7)	91(5)
H(32)	11513(19)	4139(12)	4805(7)	91(5)

Table 5. /Cont.

H(31')	11094(54)	4597(34)	4702(21)	91(5)
H(32')	9255(54)	4140(34)	4394(21)	91(5)
H(33)	5297(9)	1055(7)	5330(4)	91(5)
H(34)	4984(9)	2219(7)	5555(4)	91(5)
H(35)	4190(9)	2615(7)	4445(4)	91(5)
H(36)	2974(9)	1804(7)	4730(4)	91(5)
H(37)	3143(12)	2034(9)	3463(5)	91(5)
H(38)	2070(12)	1178(9)	3785(5)	91(5)
H(39)	2826(13)	26(9)	3120(5)	91(5)
H(40)	3898(13)	882(9)	2798(5)	91(5)

Table 6. Anisotropic temperature factors ($\overset{o}{A}^2$, x10^3, I x10^4) for $C_{20}H_{44}N_2O_8$.KI.

	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
I	944(5)	663(4)	744(4)	-43(4)	2(3)	105(4)
K	98(2)	45(1)	48(1)	5(1)	31(1)	14(1)
N(1)	58(4)	56(4)	42(4)	9(3)	10(3)	3(3)
N(2)	57(4)	54(4)	42(3)	-3(3)	15(3)	-7(3)
O(1)	64(4)	47(3)	46(3)	1(2)	14(3)	10(3)
O(2)	61(4)	47(3)	52(3)	4(3)	8(3)	-6(3)
O(3)	70(4)	55(4)	65(4)	-8(3)	24(3)	4(3)
O(4)	65(4)	52(4)	74(4)	-5(3)	7(3)	0(3)
O(5)	64(4)	87(5)	91(5)	-32(4)	13(4)	-27(4)
O(7)	62(4)	96(5)	59(4)	-7(4)	-1(3)	-8(4)
O(8)	75(4)	89(5)	68(4)	12(4)	-6(3)	7(4)
C(1)	81(6)	56(5)	38(4)	-7(4)	9(4)	-4(5)
C(2)	85(7)	59(6)	45(5)	-10(4)	21(5)	-4(5)
C(3)	59(5)	37(4)	65(5)	0(4)	10(4)	7(4)
C(4)	76(6)	47(5)	54(5)	10(4)	6(4)	2(4)
C(5)	72(6)	68(6)	46(5)	15(4)	10(4)	-4(5)
C(6)	73(6)	76(6)	43(5)	9(4)	6(4)	-10(5)
C(7)	90(7)	71(7)	48(5)	-22(4)	19(5)	-20(5)
C(8)	101(8)	57(6)	77(7)	-27(5)	39(6)	-10(6)
C(9)	63(6)	47(5)	102(8)	-4(5)	21(5)	4(4)
C(10)	74(6)	41(5)	77(6)	-2(4)	9(5)	6(4)
C(11)	76(6)	71(6)	68(6)	5(5)	-10(5)	15(6)
C(12)	89(7)	63(5)	46(5)	13(4)	7(4)	6(6)
C(13)	85(7)	71(6)	65(6)	7(5)	26(5)	-4(6)
C(14)	79(7)	76(7)	95(8)	5(6)	26(6)	-8(6)
C(17)	62(6)	71(6)	61(5)	-6(5)	22(4)	6(5)
C(18)	44(5)	72(6)	88(6)	-5(5)	23(5)	-1(5)
C(19)	71(7)	113(9)	95(8)	-13(7)	-5(6)	-19(7)
C(20)	100(9)	136(11)	83(7)	-62(8)	2(7)	-17(8)

Table 7. FRACTIONAL COORDINATES ($X10^4$, I $X10^5$) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS ($\mathring{A}^2$, $X10^3$, I AND BA $X10^4$) FOR $C_{20}H_{48}N_2O_{11}.BAI_2$.

$$\underline{U}_{eq} = \frac{1}{3}\sum_i\sum_j \underline{U}_{ij}\underline{a}_i^*\underline{a}_j^*(\underline{a}_i.\underline{a}_j)$$

	x/a	y/b	z/c	U_{eq}
I	12232(3)	7617(2)	39303(2)	532(1)
BA	5000	10901	7500	289(1)
N	2476(3)	11067(2)	5711(2)	40(1)
O(1)	4566(3)	11685(2)	6103(2)	43(1)
O(2)	6920(3)	11552(2)	6733(2)	44(1)
O(3)	3735(3)	9410(2)	6834(2)	43(1)
O(4)	4052(3)	9808(2)	8534(2)	53(1)
O(5)	5000	12721(4)	7500	65(1)
Hw(1)	4766(70)	12949(44)	7220(36)	137(5)*
C(1)	2489(4)	11779(3)	6174(3)	52(1)
C(2)	3446(4)	11688(4)	5673(3)	51(1)
C(3)	5529(5)	11695(4)	5661(3)	49(1)
C(4)	6574(5)	12080(3)	6098(3)	50(1)
C(5)	7917(5)	11909(4)	7176(3)	56(1)
C(6)	8373(4)	11270(4)	7740(3)	51(1)
C(7)	7936(4)	10282(3)	8695(3)	51(1)
C(8)	2484(4)	9484(3)	6766(3)	53(1)
C(9)	4159(5)	9024(4)	6215(3)	52(1)
C(10)	4486(5)	8958(3)	8618(3)	50(1)
Ow	4076(6)	3644(4)	241(4)	124(2)
Hw(2)	3822(68)	4110(51)	414(43)	137(5)*
Hw(3)	4551(66)	3802(48)	-26(41)	137(5)*

* isotropic temperature factor.

Table 8. FRACTIONAL COORDINATES ($\times 10^4$) AND COMMON ISOTROPIC TEMPERATURE FACTORS(Å^2, X10^3) FOR HYDROGEN ATOMS IN $C_{20}H_{48}N_2O_{11}$.BaI_2.

	x/a	y/b	z/c	U
H(21)	3444(66)	9790(48)	8618(41)	137(5)
H(1)	1646(4)	11798(3)	5839(3)	137(5)
H(2)	2625(4)	12370(3)	6476(3)	137(5)
H(3)	3403(4)	12216(4)	5290(3)	137(5)
H(4)	3328(4)	11097(4)	5370(3)	137(5)
H(5)	5733(5)	11052(4)	5505(3)	137(5)
H(6)	5293(5)	12071(4)	5171(3)	137(5)
H(7)	6351(5)	12710(3)	6278(3)	137(5)
H(8)	7297(5)	12124(3)	5762(3)	137(5)
H(9)	8600(5)	12063(4)	6830(3)	137(5)
H(10)	7652(5)	12480(4)	7445(3)	137(5)
H(11)	9147(4)	10883(4)	7696(3)	137(5)
H(12)	8199(4)	11299(4)	8311(3)	137(5)
H(13)	7762(4)	9610(3)	8614(3)	137(5)
H(14)	7999(4)	10428(3)	9278(3)	137(5)
H(15)	1915(4)	9056(3)	7029(3)	137(5)
H(16)	2017(4)	10071(3)	6623(3)	137(5)
H(17)	4537(5)	9381(4)	5791(3)	137(5)
H(18)	4435(5)	8366(4)	6198(3)	137(5)
H(19)	4744(5)	8581(3)	8166(3)	137(5)
H(20)	4853(5)	8682(3)	9135(3)	137(5)

Table 9. ANISOTROPIC TEMPERATURE FACTORS ($\mathring{A}^2$, X10^3, X10^4) FOR $C_{20}H_{48}N_2O_{11}$.BAI$_2$.

	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
I	442(2)	568(2)	586(2)	50(2)	59(2)	-28(2)
BA	29(1)	28(1)	29(1)	0	-2(1)	0
N	30(2)	41(2)	46(2)	2(2)	-3(2)	-2(1)
O(1)	40(2)	55(2)	32(2)	5(1)	-3(1)	-3(1)
O(2)	38(2)	45(2)	48(2)	5(1)	0(1)	-9(1)
O(3)	41(2)	45(2)	44(2)	-7(1)	2(1)	-4(1)
O(4)	48(2)	44(2)	70(2)	10(2)	16(2)	5(2)
O(5)	106(5)	41(3)	45(3)	0	-10(3)	0
C(1)	41(3)	53(3)	59(3)	16(2)	-9(2)	0(2)
C(2)	48(3)	63(3)	38(2)	13(2)	-13(2)	-9(2)
C(3)	52(3)	59(3)	35(2)	5(2)	6(2)	-9(2)
C(4)	50(3)	54(3)	47(3)	12(2)	4(2)	-11(2)
C(5)	43(3)	63(3)	61(3)	9(3)	-5(2)	-19(2)
C(6)	30(2)	66(3)	57(3)	5(3)	5(2)	-1(2)
C(7)	48(3)	45(3)	55(3)	4(2)	-10(2)	10(2)
C(8)	43(3)	46(3)	69(3)	1(2)	3(2)	-11(2)
C(9)	54(3)	51(3)	54(3)	-14(3)	13(2)	-7(3)
C(10)	57(3)	39(3)	55(3)	11(2)	9(2)	2(2)
Ow	152(5)	81(4)	153(5)	-41(4)	82(4)	-39(4)

APPENDIX 3

The following supplementary material can be found on the microfiche inside the back cover of this thesis.

Data for protonation and stability constant determinations

Microfiche 1

Microfiche 2

Page

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Microfiche 3

Observed and Calculated Structure Factors

Microfiche 4

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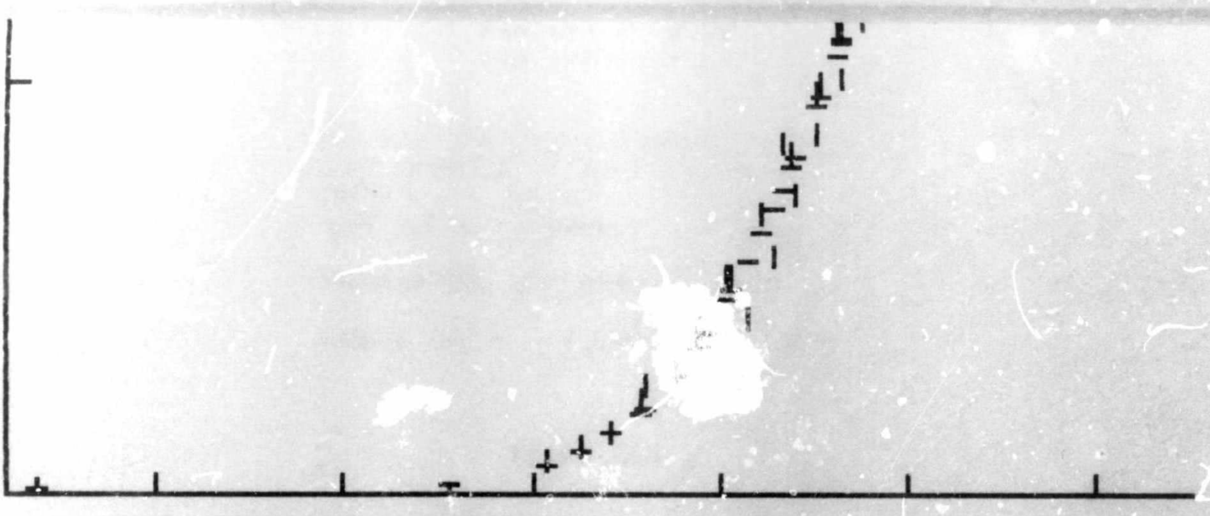

X - AXIS STARTS AT -10.8 UNITS = 1.0
Y - AXIS STARTS AT 0 UNITS = 0.5

¦ = EXPERIMENTAL NBARS
_ = THEORETICAL NBARS

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1.80          -6.8         -6.95        0.26        0.24        -0.02
2.00         -12.4         -6.79        0.34        0.32        -0.02
2.20         -17.9         -6.64        0.41        0.39        -0.02
2.40         -23.1         -6.50        0.49        0.47        -0.02
2.60         -28.3         -6.37        0.57        0.55        -0.02
2.80         -33.7         -6.23        0.64        0.62        -0.02
3.00         -39.1         -6.10        0.72        0.69        -0.02
3.20         -46.2         -5.92        0.79        0.78        -0.02
3.40         -54.4         -5.70        0.86        0.85        -0.01
3.60         -6[illegible]3         -5.47        0.94        0.91        -0.03
```

```
                          TITRATION 3

                EO          /MV    =    416.1
                INIT VOL    /ML    =     21.00
                H+  IN CELL/MMOL   =      0.25100
                LIG IN CELL/MMOL   =      0.09700
                M IN CELL   /MMOL  =      0.03330
                TITRANT B- /M      =      0.05150


V/ML          E/MV           LG          NBAR          TH        TH-NBAR

1.30          84.0         -7.08        0.14        0.19          0.05
1.40          77.0         -6.86        0.21        0.28          0.07
1.50          72.7         -6.73        0.28        0.35          0.06
1.60          68.8         -6.62        0.36        0.41          0.05
1.70          65.2         -6.51        0.43        0.47          0.03
1.80          60.1         -6.35        0.51        0.56          0.05
1.90          56.2         -6.24        0.58        0.62          0.04
2.04          48.9         -6.02        0.68        0.73          0.05
2.20          40.3         -5.76        0.79        0.83          0.04
2.42          22.1         -5.20        0.91        0.95          0.04
2.60           2.8         -4.60        0.95        0.99          0.03
```

Log K1(ZnII)-DHP-15-ane-N2O3

Log K1(ZnII)-DHP-15-ane-N2O3

```
                         ACID CONSTANTS:

                         PKA (1) =  8.30
                         PKA (2) =  7.62


                  MATRIX CONDITION NUMBER =    1.0000
                  CONVERGENCE IN *2* CYCLES
                  RMSD =     .0318
                  SUM DELTA SQUARED =     .04

                  PARAMETERS AND ERRORS

                  LOG K (1) =   6.454 +-     .012


                            TITRATION 1


                    E0          /MV    =    332.5
                    INIT VOL    /ML    =     19.00
                    LIG IN CELL/MMOL =        0.07395
                    M IN CELL   /MMOL =        0.06660
                    TITRANT H+ /M      =        0.05019


V/ML          E/MV          LG          NBAR          TH        TH-NBAR

0.20        -112.0        -4.62         1.01         0.99         -0.02
0.40         -80.2        -5.30         0.94         0.93         -0.01
0.60         -63.8        -5.67         0.87         0.86         -0.01
0.80         -53.0        -5.90         0.80         0.78         -0.02
1.00         -44.5        -6.09         0.72         0.70         -0.03
1.20         -37.4        -6.25         0.65         0.61         -0.04
1.40         -31.4        -6.39         0.57         0.54         -0.04
1.60         -27.1        -6.48         0.50         0.48         -0.02
1.80         -19.6        -6.69         0.43         0.37         -0.06
2.24          -8.7        -6.97         0.26         0.23         -0.03
2.40          -3.5        -7.12         0.20         0.18         -0.02
2.60           5.6        -7.39         0.13         0.10         -0.02
2.80          16.7        -7.74         0.05         0.05          0.00
3.00         102.9       -10.64         0.00         0.00          0.00


                            TITRATION 2

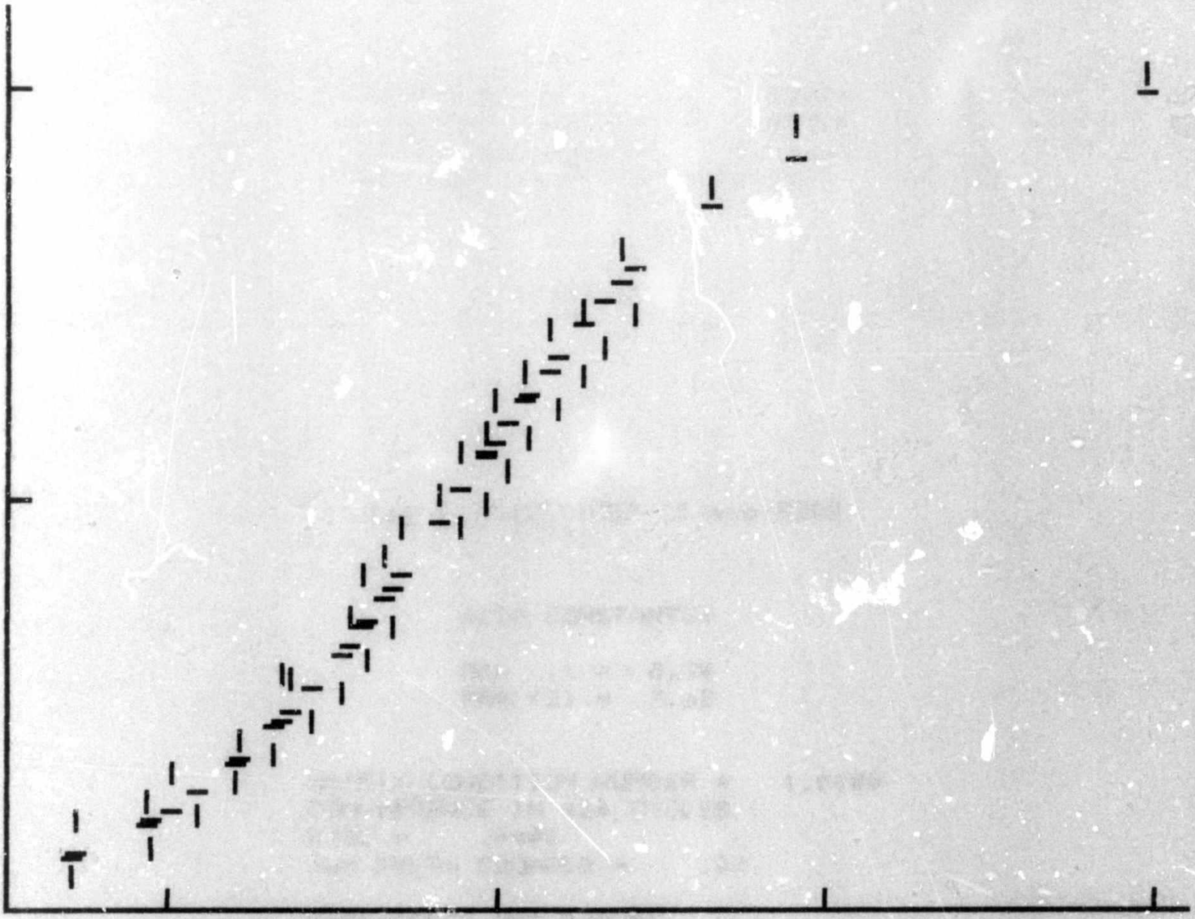

                    E0          /MV    =    331.0
                    INIT VOL    /ML    =     20.00
                    H+  IN CELL/MMOL =        0.25100
                    LIG IN CELL/MMOL =        0.09700
                    M IN CELL   /MMOL =        0.06660
                    TITRANT B- /M      =        0.05150


V/ML          E/MV          LG          NBAR          TH        TH-NBAR

1.10          40.3        -8.43         0.00         0.01          0.01
1.20          25.0        -7.93         0.03         0.03          0.00
1.30          14.0        -7.57         0.07         0.07          0.00
1.40           9.0        -7.42         0.11         0.10         -0.01
1.50           3.5        -7.25         0.15         0.14         -0.01
1.60          -0.6        -7.12         0.18         0.18         -0.01
```

2.00	4.2	-7.45	0.35	0.32	-0.03
2.20	10.7	-7.63	0.28	0.24	-0.04
2.40	16.3	-7.79	0.20	0.18	-0.03
2.60	25.7	-8.07	0.13	0.10	-0.03

Log K1(CdII)-DHP-15-ane-N2O3



X - AXIS STARTS AT -8.5 UNITS = 1.0
Y - AXIS STARTS AT 0 UNITS = 0.5

! = EXPERIMENTAL NBARS
_ = THEORETICAL NBARS

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1.50        105.3       -7.79       0.15        0.18        0.03
1.60        101.3       -7.67       0.19        0.22        0.03
1.70         97.7       -7.57       0.23        0.26        0.04
1.80         94.4       -7.47       0.26        0.31        0.05
1.90         91.8       -7.40       0.30        0.35        0.04
2.00         88.9       -7.32       0.34        0.39        0.05
2.32         81.0       -7.11       0.46        0.51        0.04
2.40         78.4       -7.04       0.49        0.55        0.05
2.50         75.8       -6.97       0.53        0.59        0.05
2.60         73.2       -6.90       0.57        0.62        0.05
2.70         69.8       -6.81       0.61        0.67        0.06
2.80         67.0       -6.74       0.65        0.71        0.06
2.90         64.2       -6.67       0.69        0.74        0.06
3.00         60.8       -6.58       0.72        0.78        0.06


                        TITRATION 2


           E0          /MV    =   332.1
           INIT VOL   /ML     =    20.00
           H+  IN CELL/MMOL   =     0.07530
           LIG IN CELL/MMOL   =     0.02910
           M IN CELL  /MMOL   =     0.01670
           TITRANT B- /M      =     0.05150


V/ML         E/MV         LG         NBAR          TH      TH-NBAR

0.40         21.0       -8.28       0.10        0.07       -0.04
0.44         11.9       -7.99       0.16        0.12       -0.04
0.52          0.7       -7.65       0.28        0.23       -0.05
0.60         -7.8       -7.41       0.41        0.34       -0.06
0.64        -11.8       -7.29       0.47        0.41       -0.06
0.70        -18.3       -7.11       0.56        0.51       -0.05
0.74        -22.0       -7.01       0.62        0.57       -0.05
0.80        -28.0       -6.84       0.71        0.66       -0.05


                        TITRATION 3


           E0          /MV    =   332.5
           INIT VOL   /ML     =    19.00
           LIG IN CELL/MMOL   =     0.07395
           M IN CELL  /MMOL   =     0.06660
           TITRANT H+ /M      =     0.05019


V/ML         E/MV         LG         NBAR          TH      TH-NBAR

0.20        -98.7       -5.02       1.02        0.99       -0.03
0.40        -55.9       -6.10       0.95        0.91       -0.04
0.60        -43.1       -6.35       0.88        0.86       -0.02
0.80        -31.6       -6.62       0.80        0.76       -0.04
1.00        -25.2       -6.74       0.73        0.71       -0.02
1.20        -17.6       -6.92       0.65        0.62       -0.04
1.40        -12.4       -7.03       0.58        0.55       -0.02
1.60         -6.3       -7.18       0.50        0.47       -0.04
1.80         -0.3       -7.34       0.43        0.38       -0.05
```

Log K1(CdII)-DHP-15-ane-N2O3

```
                    ACID CONSTANTS:

                    PKA (1) =  8.30
                    PKA (2) =  7.62

              MATRIX CONDITION NUMBER =   1.0000
              CONVERGENCE IN *2* CYCLES
              RMSD =     .0443
              SUM DELTA SQUARED =    .07

              PARAMETERS AND ERRORS

              LOG K (1) =   7.126 +-    .016


                      TITRATION 1


               E0          /MV   =   416.6
               INIT VOL   /ML    =    20.00
               H+  IN CELL/MMOL =     0.25100
               LIG IN CELL/MMOL =     0.09700
               M IN CELL  /MMOL =     0.06660
               TITRANT B- /M    =     0.05150


V/ML         E/MV         LG         NBAR         TH       TH-NBAR

1.20         121.6       -8.30       0.04        0.06        0.03
1.30         113.7       -8.05       0.07        0.11        0.03
1.40         109.3       -7.92       0.11        0.14        0.03
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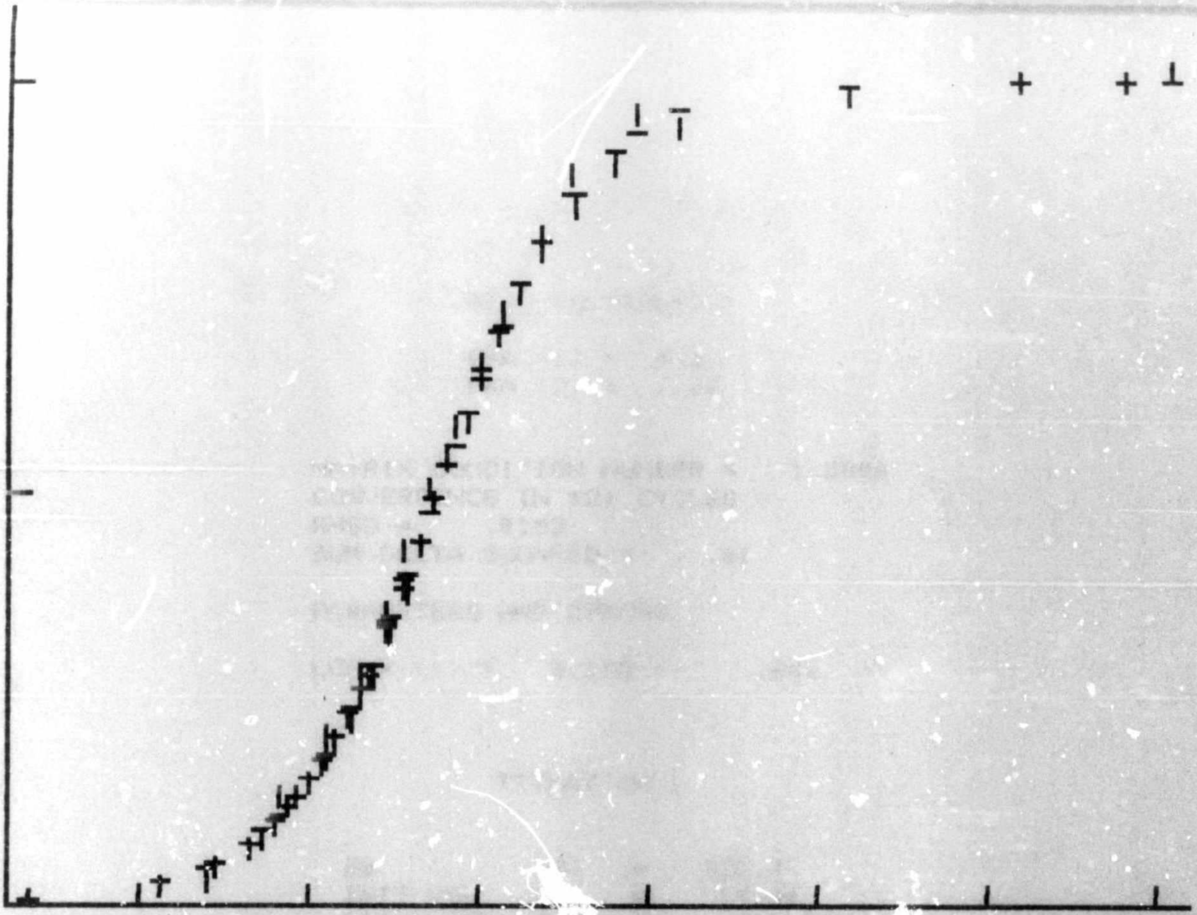


X - AXIS STARTS AT -10.8 UNITS = 1.0
Y - AXIS STARTS AT 0 UNITS = 0.5

| = EXPERIMENTAL NBARS
_ = THEORETICAL NBARS

```
V/ML          E/MV          LG          NBAR          TH          TH-NBAR

3.20          159.3         -9.60        0.03          0.04          0.02
3.40          149.3         -9.28        0.08          0.09          0.01
3.60          142.8         -9.08        0.13          0.13          0.00
3.80          137.0         -8.91        0.18          0.18          0.01
4.00          132.4         -8.77        0.23          0.24          0.01
4.20          128.7         -8.67        0.28          0.28          0.00
4.40          124.5         -8.55        0.33          0.34          0.01
4.60          121.4         -8.46        0.38          0.38          0.00
4.80          117.6         -8.36        0.43          0.44          0.01
5.00          114.3         -8.27        0.48          0.49          0.01
5.20          111.3         -8.20        0.54          0.53          0.00
5.40          107.1         -8.09        0.59          0.60          0.01
5.60          103.6         -8.00        0.64          0.65          0.01
5.80           99.8         -7.9[illegible]        0.69          0.70          0.01
6.00           95.1         -7.77        0.74          0.75          0.01
6.20           90.2         -7.64        0.79          0.80          0.01
6.40           83.7         -7.46        0.84          0.86          0.02
6.60           75.8         -7.24        0.89          0.91          0.02
6.80           62.9         -6.85        0.94          0.96          0.02
7.00           31.5         -5.84        0.98          1.00          0.01
7.20           -1.1         -4.83        1.00          1.00          0.00
7.40          -22.9         -4.22        1.00          1.00          0.00
7.60          -35.3         -3.93        1.01          1.00         -0.01


                         TITRATION 3

                E0           /MV     =    331.0
                INIT VOL     /ML     =     21.00
                H+  IN CELL/MMOL     =      0.15060
                LIG IN CELL/MMOL     =      0.04850
                M IN CELL    /MMOL   =      0.09990
                TITRANT B-  /M       =      0.05150


V/ML          E/MV          LG          NBAR          TH          TH-NBAR

1.00           96.9        -10.67        0.00          0.00          0.00
1.10           72.8         -9.87        0.02          0.02          0.00
1.20           62.7         -9.56        0.04          0.05          0.00
1.30           55.9         -9.35        0.07          0.07          0.01
1.40           50.9         -9.21        0.09          0.10          0.01
1.50           47.5         -9.13        0.12          0.12          0.00
1.60           43.0         -9.01        0.15          0.15          0.00
1.70           39.3         -8.92        0.17          0.18          0.01
1.80           35.9         -8.85        0.20          0.21          0.01
1.90           32.3         -8.77        0.22          0.24          0.01
2.00           29.2         -8.71        0.25          0.26          0.01
2.10           25.7         -8.64        0.27          0.29          0.02
2.30           18.8         -8.53        0.32          0.35          0.02
2.50           10.8         -8.44        0.38          0.40          0.02
```

Log K1(PbII)-DHP-15-ane-N2O3

Log K1(PbII)-DHP-15-ane-N2O3

```
                    ACID CONSTANTS:

                    PKA (1) =  8.30
                    PKA (2) =  7.62


              MATRIX CONDITION NUMBER =    1.0000
              CONVERGENCE IN *2* CYCLES
              RMSD =     .0153
              SUM DELTA SQUARED =      .01

              PARAMETERS AND ERRORS

              LOG K (1) =   8.258 +-     .006


                       TITRATION 1


                E0          /MV     =   332.7
                INIT VOL    /ML     =    19.00
                LIG IN CELL/MMOL =      0.07395
                M IN CELL   /MMOL =      0.06660
                TITRANT H+ /M       =      0.05035


V/ML          E/MV          LG          NBAR          TH          TH-NBAR

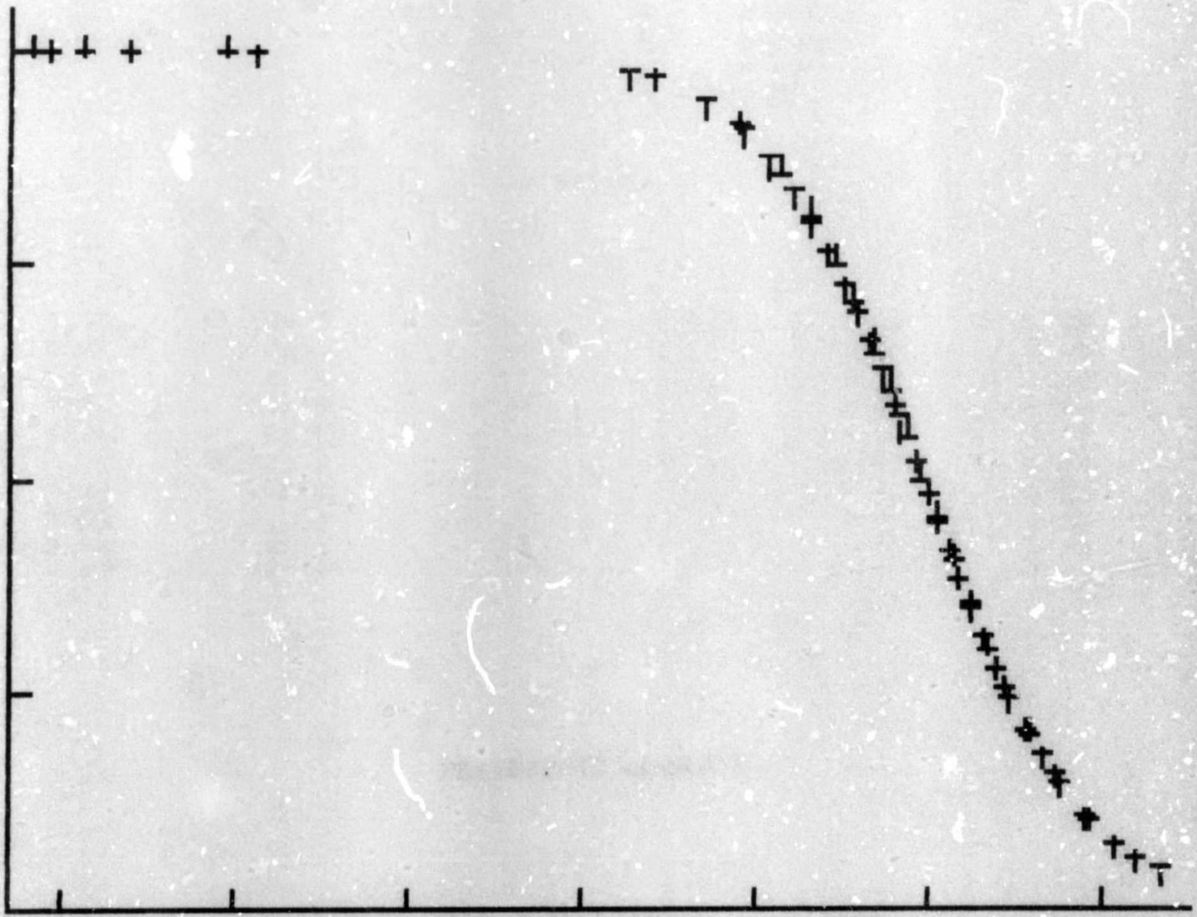
0.40         -25.5        -7.11         0.96         0.93         -0.02
0.60          -9.4        -7.48         0.88         0.86         -0.02
0.80          -0.8        -7.64         0.81         0.80          0.00
1.04           9.6        -7.89         0.72         0.70         -0.01
1.20          15.0        -8.01         0.66         0.64         -0.02
1.40          21.3        -8.16         0.58         0.56         -0.03
1.60          27.1        -8.30         0.51         0.47         -0.03
1.80          32.7        -8.45         0.43         0.39         -0.04
2.00          36.9        -8.55         0.36         0.34         -0.01
2.20          42.9        -8.71         0.28         0.26         -0.02
2.40          49.9        -8.91         0.21         0.18         -0.02
2.60          58.9        -9.19         0.13         0.11         -0.03


                       TITRATION 2


                E0          /MV     =   415.1
                INIT VOL    /ML     =    27.00
                H+  IN CELL/MMOL =      0.45170
                LIG IN CELL/MMOL =      0.14550
                M IN CELL   /MMOL =      0.09990
                TITRANT B- /M       =      0.05150
```

```
2.40     -126.6     7.77     1.22     1.20     -0.02
2.60     -121.4     7.69     1.32     1.29     -0.03
2.80     -114.2     7.56     1.43     1.41     -0.02
3.00     -108.2     7.46     1.53     1.50     -0.03
3.20      -99.5     7.32     1.63     1.61     -0.02
3.40      -89.7     7.15     1.73     1.71     -0.02
3.60      -75.2     6.91     1.83     1.83     -0.01
3.80      -46.6     6.42     1.93     1.94      0.00
4.00      106.0     3.94     2.01     2.00     -0.01
```

PKA-DHP-15-aneN2O3



```
X - AXIS STARTS AT 2.7 UNITS = 1.0
Y - AXIS STARTS AT 0 UNITS = 0.5

   ! = EXPERIMENTAL NBARS
   _ = THEORETICAL NBARS
```

Author Bhavan Rekha
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