Structural and Thermodynamic Study of the Effect of Sterically Hindering Alkyl Groups on Complex Stability

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The balance between steric and inductive effects on the thermodynamic stability of complexes in aqueous solution has been examined as the bulk of N-alkyl substituents is increased along the series methyl, ethyl, isopropyl, *tert*-butyl. The ligands 7,16-diisopropyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (L^3), and $RN[CH_2CH(CH_3)OH]_2$ (R = Me, L^4; Pr^i, L^5; or Bu^t, L^6) have been prepared. The formation constants of these ligands, and of other ligands with bulky N-alkyl groups, have been determined with the metal ions Cu^{II}, Zn^{II}, Cd^{II}, Pb^{II} and with Ca^{II}, Sr^{II} and Ba^{II} (L^3 only). The N-isopropyl groups of ligand L^3 cause a sharp drop in thermodynamic complex stability for all metal ions, whereas in the series L^2–L^4 lead(II) is unusual in showing a strong increase in complex stability in response to the inductive effects of the larger alkyl groups. In an attempt to understand the lowering of complex stability by the N-isopropyl groups of L^3 the crystal structure of the complex $[KL^3]I$ was determined: monoclinic, space group $P2_1/c$, $a = 12.603(2)$, $b = 14.875(3)$, $c = 13.877(3)$ Å, $\beta = 112.81(1)°$, $Z = 4$, final $R = 0.042$. The structure indicates some stretching of the K–N bond by the presence of the N-isopropyl groups. The parallel between steric hindrance effects by bulky N-alkyl groups and hard and soft acid and base behaviour is discussed.

In 1980 one of the present authors showed[1] that there was an increase in formation constants in aqueous solution for Ag^I along the series of primary amines RNH_2 where R = methyl, ethyl, isopropyl and *tert*-butyl. This result was part of a pattern of growing evidence[2] that amines increase strongly in basicity as N- or C-alkyl substitution proceeds, and that this increased basicity has important effects on complex stability, particularly in such areas[3,4] as the chelate[5] and macrocyclic[6] effects. That this had not been recognised earlier was due to the fact that the protonation constants of these amines respond hardly at all to N- or C-alkyl substitution. Since the protonation constant is generally regarded as an indicator of basicity, it was therefore widely assumed that the alkyl groups had little effect on basicity. That this is not so had been demonstrated as long ago as 1965 by energies of protonation of amines in the gas phase.[7]

Since the observation of the increase in stability of amine complexes of Ag^I with C-methyl substitution no other metal ions have been found to respond as does Ag^I to C-alkyl substitution on monoamines. The reason for this is clear. The increase in basicity along the series methylamine through *tert*-butylamine is accompanied by increasing steric bulk of the alkyl group. The steric hindrance of the larger alkyl groups cancels out their inductive effects, and it is this that accounts for the lack of response of the protonation constant to increase in nitrogen basicity. The steric hindrance responsible for cancelling out the inductive effects of alkyl groups occurs with the waters of solvation on the proton or metal ion. This accounts for the fact that in the gas phase, where there is no water of solvation, the inductive effects become apparent. The linear co-ordination geometry[8] of the silver(I) ion, coupled with rather long Ag–N bonds, keeps the alkyl groups well away from the metal ion, which is only weakly solvated away from its two co-ordination sites. We have always hoped to find examples of this effect with metal ions other than Ag^I. Some preliminary work was done on N-alkyl substituted ligands of the L^1 type. However there was not the hoped for increase in log K_1 on changing the N-alkyl substituent from methyl (L^2) to isopropyl (L^3) with any of the metal ions studied. In order to see what the nature of the steric effect of the added isopropyl group was, the structure of a complex with a large metal ion in the form of the potassium complex $[KL^3]I$ was determined, and is reported here. This structure can be compared with that of the potassium complex[9] of L^1 to determine the effect of bulky N-alkyl groups on structural features such as K–N bond lengths.

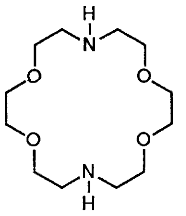
The series of ligands L^4–L^6, where the N-alkyl substituent varies along the series methyl, isopropyl, and *tert*-butyl, was synthesised to see whether in simpler ligands the inductive effect of the N-alkyl group would be reflected in the formation constants. It turned out that this was the case. We have not synthesised the N-ethyl substituted versions of these ligands, but believe the trends are clear enough without it. The synthesis of these ligands, L^4–L^6, as well as of the macrocycle L^3 is reported here. Also reported are the formation constants of these ligands plus L^2 with the metal ions Cu^{II}, Ni^{II}, Zn^{II}, Cd^{II}, Pb^{II}, Ca^{II}, Sr^{II} and Ba^{II}.

Experimental

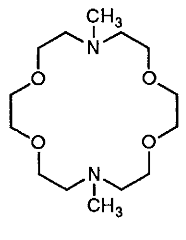
Syntheses.—7,16-*Diisopropyl*-1,4,10,13-*tetraoxa*-7,16-*diazacyclooctadecane* L^3. This ligand was synthesised as the KI complex by the general method of Gatto and Goke.[10] A minor modification was that better yields were obtained with K_2CO_3 than Na_2CO_3. Column chromatography was not required for purification of the ligand. The product KI complex was instead recrystallised from benzene. Yield 43%, m.p. 143–145 °C. NMR ($CDCl_3$): δ 0.9–1.1 (12 H, d, CH_3), 2.6–2.8 (8 H, t, NCH_3), 3.0–3.4 (2 H, m, CH) and 3.5–3.8 (16 H, s + t, CH_2) (Found: C, 42.15; H, 7.55; N, 5.35. Calc. for $C_{18}H_{38}N_2O_4 \cdot KI$: C, 42.15; H, 7.45; N, 5.45%).

7,16-*Dimethyl*-1,4,10,13-*tetraoxa*-7,16-*diazacyclooctadecane* L^2. This was synthesised by the method of Schwing and co-workers.[11]

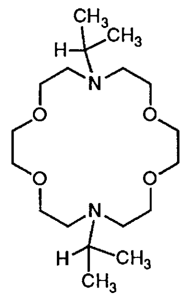
Ligands L^4–L^6. These were made by treating the parent primary amine (methyl-, isopropyl- or *tert*-butyl-amine) with 2 equivalents of propylene oxide in a small volume of ethanol. After standing at room temperature for a few days, the solvent was removed under low pressure. The ligands were obtained as



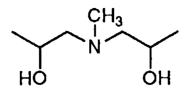
L^1



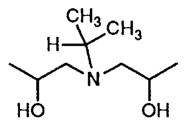
L^2



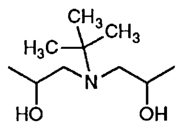
L^3



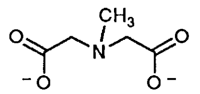
L^4



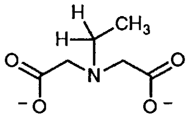
L^5



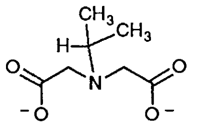
L^6



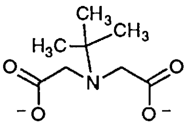
L^7



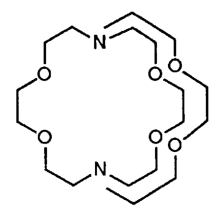
L^8



L^9



L^{10}



L^{11}

Table 1 Details of the crystallographic analysis of [KL^3]I

Formula	$C_{18}H_{38}N_2O_4 \cdot KI$
M	512.51
Crystal dimensions/mm	0.22 × 0.30 × 0.33
Crystal symmetry	Monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	12.603(2)
b/Å	14.875(3)
c/Å	13.877(3)
β/°	112.81(1)
U/Å^3	2398.14
Z	4
D_m, D_c/g cm^{-3}	1.42, 1.41
T/K	298.16
μ/cm^{-1}	14.15
F(000)	1056
θ range/°	3–30
Reflections measured	7499
Unique reflections	6032
Reflections used [$F > 3\sigma(F)$]	4524
Parameters refined	236
Max. residual electron density/e Å^{-3}	1.19
R^{int}	0.045
Final R	0.042

viscous oils which were purified by distillation at 1 mmHg (*ca.* 133 Pa) (Found: C, 61.80; H, 12.10; N, 7.85. Calc. for $C_9H_{19}NO_2$: C, 61.70; H, 12.10; N, 8.00. Found: C, 63.80; H, 12.10; N, 7.25. Calc. for $C_{10}H_{20}NO_2$: C, 63.45; H, 12.25; N, 7.40%).

Table 2 Fractional atomic coordinates (× 10^4, × 10^5 for I and K) for [KL^3]I

Atom	X/a	Y/b	Z/c
I	77 163(3)	− 10 282(3)	76 597(3)
K	72 796(10)	13 053(8)	73 521(8)
O(1)	6 416(3)	1 100(3)	5 289(3)
O(2)	8 795(3)	1 404(3)	6 315(3)
O(3)	8 083(3)	1 260(3)	9 407(3)
O(4)	5 721(3)	1 437(2)	8 386(3)
N(1)	4 910(3)	1 960(3)	6 155(3)
N(2)	9 621(3)	1 985(3)	8 522(3)
C(1)	4 542(5)	1 314(4)	5 275(4)
C(2)	5 266(5)	1 322(4)	4 633(4)
C(3)	7 177(5)	1 055(4)	4 763(4)
C(4)	8 313(5)	730(4)	5 516(4)
C(5)	9 871(5)	1 119(4)	7 095(4)
C(6)	10 332(5)	1 866(4)	7 905(4)
C(7)	9 941(5)	1 308(4)	9 367(4)
C(8)	9 264(5)	1 352(4)	10 048(4)
C(9)	7 351(5)	1 135(4)	9 952(4)
C(10)	6 228(5)	772(4)	9 187(4)
C(11)	4 672(4)	1 109(4)	7 605(4)
C(12)	4 192(5)	1 837(4)	6 774(4)
C(13)	4 918(4)	2 889(4)	5 810(4)
C(14)	3 730(5)	3 253(4)	5 091(5)
C(15)	5 486(5)	3 511(4)	6 742(5)
C(16)	9 664(5)	2 900(4)	8 912(4)
C(17)	9 129(6)	3 560(5)	8 010(5)
C(18)	10 872(5)	3 216(4)	9 645(5)

Table 3 Selected bond lengths (Å) and angles (°) for the complex cation [KL^3]$^+$

K–I	3.514(1)	K–O(1)	2.657(3)
K–O(2)	2.806(4)	K–O(3)	2.631(3)
K–O(4)	2.853(4)	K–N(1)	2.963(4)
K–N(2)	2.941(4)	O(1)–C(2)	1.420(6)
N(1)–C(1)	1.480(6)	C(1)–C(2)	1.502(7)
I–K–O(1)	89.8(1)	I–K–O(2)	90.5(1)
O(1)–K–O(2)	61.9(1)	I–K–O(3)	82.3(1)
O(1)–K–O(3)	171.8(1)	O(2)–K–O(3)	120.3(1)
I–K–O(4)	96.5(1)	O(1)–K–O(4)	118.4(1)
O(2)–K–O(4)	173.0(1)	O(3)–K–O(4)	60.5(1)
I–K–N(1)	118.0(1)	O(1)–K–N(1)	62.0(1)
O(2)–K–N(1)	115.7(1)	O(3)–K–N(1)	119.8(1)
O(4)–K–N(1)	61.2(1)	I–K–N(2)	101.3(1)
O(1)–K–N(2)	122.6(1)	O(2)–K–N(2)	61.9(1)
O(3)–K–N(2)	61.8(1)	O(4)–K–N(2)	116.0(1)
N(1)–K–N(2)	140.7(1)	K–O(1)–C(2)	123.7(3)
K–O(1)–C(3)	119.0(1)	K–O(2)–C(4)	100.9(1)
K–O(2)–C(5)	103.3(1)	K–N(1)–C(1)	100.0(3)
C(2)–O(1)–C(3)	114.1(4)	C(6)–N(2)–C(7)	109.9(4)

X-Ray Crystallographic Studies.—The data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (0.710 73 Å). The cell dimensions were obtained from least-squares refinement of 25 high θ reflections. An ω–2θ scan mode was used with a scan width of 0.6 + 0.35 tan θ and a variable scan speed. Three standard reflections were monitored and showed no significant variation over the data collection. Lorentz and absorption corrections were applied to the data according to the method of North *et al.*[12] An estimate of the agreement between equivalent reflections was not made. Crystal data and data collection parameters are given in Table 1.

The structure was solved and refined using the Patterson and Fourier techniques of the programs SHELX 86 and 76.[13] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed at geometrically calculated positons and refined with a common isotropic thermal parameter. Fractional atomic coordinates for non-hydrogen atoms in the structure are given in Table 2, and a selection of bond lengths and angles in Table 3. An ORTEP[14] drawing of the complex cation is shown in Fig. 1, showing the numbering scheme.

Additional material available from the Cambridge Crystallo-

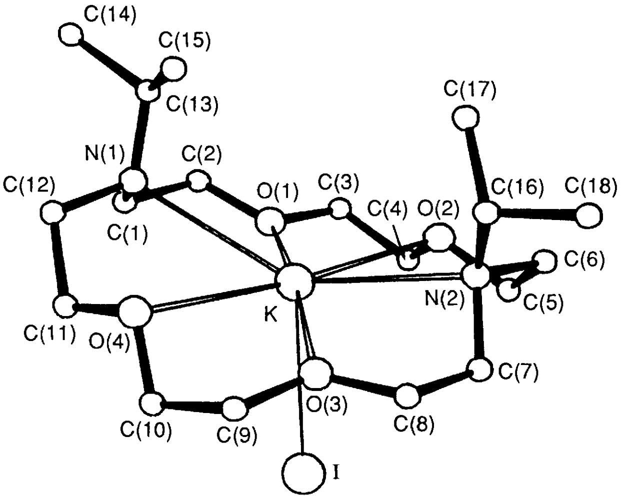


Fig. 1 ORTEP[14] drawing of the complex $[KL^3]I$, showing the numbering scheme

Table 4 A comparison of selected bond lengths (Å) and angles (°) for the $[KL^3]^+$ and $[KL^1]^+$ complex cations

	$[KL^1]^+$ (ref. 9)	$[KL^3]^+$ (this work)
K–O	2.825	2.657
	2.836	2.806
		2.631
		2.853
K–N	2.856	2.963
		2.941
N–K–N	180.0	140.7
N–K–O	60.4	62.0
	60.5	61.2
O–K–O	60.8	60.5
		61.9
N···N	5.712	5.904
Co-ordination number	6	7

Table 5 Protonation and formation constants for the ligands L^1–L^6

	$L^{1\,a}$	L^2	L^3	L^4	L^5	L^6
pK_1 [b]	9.08	9.33(2) (9.58) [c]	9.27(1)	8.81(1)	9.33(1)	9.43(1)
pK_2 [b]	7.94	7.46(2) (7.61) [c]	8.61(1)			
log K_1						
Cu^{II}	6.1	6.80 [c]	n.e.c. [d]	4.88(1)	n.e.c.	n.e.c.
Zn^{II}	3.1	3.77 [c]	n.e.c.	2.87(2)	n.e.c.	n.e.c.
Cd^{II}	5.25	4.04(1) (4.38) [c]	n.e.c.	2.53(2)	1.5(1)	n.e.c.
Ca^{II}	1.8	2.06(2)	n.e.c.	—	—	—
Sr^{II}	2.6	3.89(1)	n.e.c.	—	—	—
Ba^{II}	2.97	3.54(1)	n.e.c.	—	—	—
Pb^{II}	6.8	7.79(1) (8.39) [c]	6.19(1)	3.70(2)	4.14(1)	4.33(2)

[a] Formation constants from ref. 16. [b] Refers to the equilibria $L + H^+ \rightleftharpoons HL^+$, pK_1, and $HL^+ + H^+ \rightleftharpoons H_2L^{2+}$, pK_2, where L is the free ligand. [c] From ref. 11 in 0.1 mol dm^{-3} $N(CH_2CH_3)_4ClO_4$ as background electrolyte. [d] n.e.c. = No evidence of complex formation right up to the pH at which the metal hydroxide precipitates, or the pH is too high to yield meaningful results.

graphic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Potentiometry.—Potentials were recorded on a Radiometer PHM 84 pH meter using a Radiometer G202B glass electrode, and a jacketed cell thermostatted to 25.0 °C. The glass electrode was standardised from calculated acid concentrations in titrations covering the range pH 2–12. Stock solutions of the ligands were prepared and standardised by titration with acid, and stock solutions of the metal ions were standardised by usual procedures. Three titrations were carried out for each metal ion, and the protonation constants of the ligands were also determined in triplicate. The formation constants were calculated from the potentiometric data using the program MINIQUAD.[15] The formation and protonation constants for ligands L^2–L^7 are in Table 5.

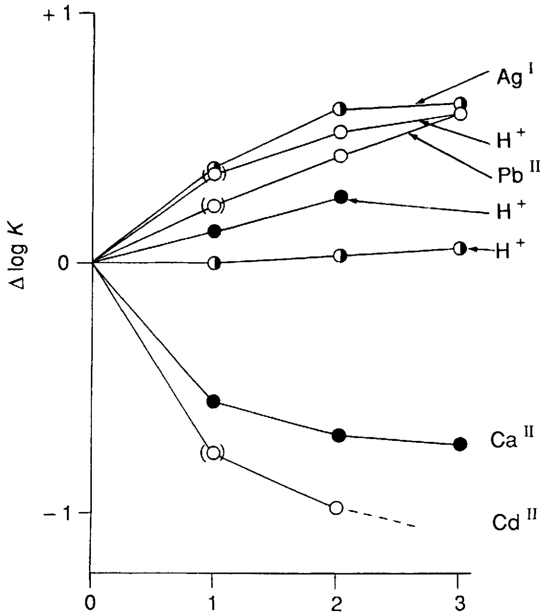


Fig. 2 The change in thermodynamic complex stability, Δ log *K*, produced for complexes of several N-alkyl substituted ligands, as the N-alkyl group is varied along the series methyl ($X = 0$), ethyl ($X = 1$), isopropyl ($X = 2$), *tert*-butyl ($X = 3$); Δ log *K* is log K_1 for the ligand indicated minus log K_1 for its methyl-substituted analogue, and *X* indicates the number of methyl groups attached to the α-carbon atom, in the series $NH_2C(CH_3)_xH_{3-x}$ (◑), $[CH_3CH(OH)CH_2]_2NC(CH_3)_xH_{3-x}$ (○), and $(^-O_2CCH_2)_2NC(CH_3)_xH_{3-x}$ (●). The points indicated in parentheses were estimated by comparison with trends in other similar series

Results and Discussion

The formation constants for L^1–L^3 in Table 5 show that the addition of N-methyl groups to L^1 to give L^2 produces a small increase in log K_1 for all the metal ions studied. This effect of N-methyl substitution is also found to increase log K_1[17] for L^7 relative to iminodiacetate for a wide variety of metal ions. Substitution on the nitrogen of L^1 with an isopropyl group to give L^3 leads to a strong drop in log K_1 for all metal ions. Only Pb^{II} forms a complex with L^3, which is somewhat weaker than the complex with L^2. For all the other metal ions the destabilisation produced by the isopropyl groups on L^3 is such that no complexes can be detected in solution, right up to the point of precipitation of the metal hydroxides, or complete deprotonation of the ligand. This shows that the steric effects of the isopropyl groups on L^3 have completely outweighed the inductive effects, in contrast to L^2 where the inductive effects of the methyl groups outweigh the steric effects.

The ligands L^4–L^6 show for Pb^{II} a strong increase in log K_1 as the inductive effect of the N-alkyl groups increases from methyl through to *tert*-butyl. This is summarised in Fig. 2, where Δ log *K*, the increase in log K_1 in changing the N-alkyl substituent from N-methyl, is plotted as a function of *X*. Here *X* is the number of methyls attached to the α-carbon of the N-alkyl substituent (*i.e.* $X = 0$ for methyl, 1 for ethyl, 2 for isopropyl and 3 for *tert*-butyl). Thus, Δ log *K* is simply log K_1 for the particular N-alkyl substituent minus log K_1 for the N-methyl substituent. Fig. 2 illustrates the various types of response found in the thermodynamic stability of complexes as the N-alkyl substituents on ligands are changed from methyl through to *tert*-butyl. The thermodynamic stability of the complexes of Pb^{II} along the series L^4–L^6 increases strongly as the N-substituent is changed from methyl to *tert*-butyl. There is a similar response in protonation constant along this series of ligands. One notes that the curvature of the relationship is greater for the proton than for Pb^{II}. This indicates a different mix in the contributing factors to the increase in thermodynamic stability of the complex formed. The almost linear response of the lead(II) relationship suggests that steric effects are minimal. The inductive effects along the methyl to *tert*-butyl series increase linearly, while the steric effects increase geometrically,[18] so that a strong contribution from steric effects leads to curvature in relationships such as those in Fig. 2. By contrast, and somewhat surprisingly in view of the suggested role of the linear co-ordination geometry of Ag^I in allowing the inductive effects to manifest themselves, the relationship for Ag^I with the series of ligands methylamine to *tert*-butylamine is considerably more curved than that for Pb^{II} with L^4–L^6. All results to date for this type of relationship confirm, however, the suggestion[19] that it is only large metal ions, preferably with low co-ordination number, that can tolerate severely sterically hindering N-alkyl substituents such as the *tert*-butyl group. With small metal ions, the N-alkyl substituent is drawn in too close to the hydration sphere, or other co-ordinated ligands, or parts of the same ligand, and severe steric hindrance results.

Fig. 2 also shows that Ca^{II} with L^7–L^{10}, or Cd^{II} with L^4–L^6, responds to increasing bulk of the N-alkyl substituent with a drop in log K_1. The tailing off of this drop with increasing substituent bulk, evident for Ca^{II} in Fig. 2, is not what would be expected from the rapid increase in steric effects in passing along the series from methyl to *tert*-butyl. One would suggest here that a special steric situation exists where there may be a change of structure after the initial increase in steric bulk has occurred, so that the presence of the *tert*-butyl group is not as detrimental to complex stability as might have been anticipated. The calcium(II) ion is much 'harder' than Pb^{II}, or Ag^I,[20] so that the Ca–N bonds should be considerably more ionic than the Pb–N or Ag–N bonds. Thus, the stability of the complexes of Ca^{II} drops, even though Ca^{II} has a fairly large ionic radius,[21] with increasing bulk of the N-alkyl substituent, because the Ca^{II} cannot respond to the increasing covalence in the M–N bond implied by the increasing inductive effect of the larger N-alkyl substituent.

An interesting feature of Fig. 2 is the rather different response of the proton to the series L^4–L^6, as compared with the series of methylamine to *tert*-butylamine. In the L^4–L^6 series the protonation constants rise strongly with increasing inductive effect of the N-alkyl substituent, whereas the protonation constants for the series methylamine to *tert*-butylamine are almost invariant. The explanation[19,22] for this is that, in the series of primary amines, steric effects balance out the inductive effects, and there is no variation in protonation constant. For the tertiary nitrogens of the series L^4–L^6, the other N-alkyl substituents (the 2-hydroxypropyl groups) have already through steric hindrance considerably desolvated the proton attached to the nitrogen in the alkylammonium cation formed. The steric hindrance to the waters of solvation produced by the methyl, isopropyl, or *tert*-butyl groups is thus much lessened, and the inductive effects of these N-alkyl groups become apparent.

The Structure of $[KL^3]I$.—Fig. 1 shows an ORTEP view of the complex. The potassium is co-ordinated to the four oxygens and two nitrogens of the ligand, and appears also to be co-ordinated to the iodide ion with a K–I bond of 3.514 Å. The sum of the ionic radii[21] of K and I is 3.58 Å (octahedral co-ordination), so the K–I distance in the L^3 complex is certainly short enough to indicate a significant bond. A search of the literature for K–I bonds yields a report by Gokel and co-workers[23] on complexes with macrocyclic ligands, involving distances of 3.469 and 3.619 Å. The K–I length obtained in this study is right between these two, supporting the suggestion that this is a K–I bond. The nitrogen donors of the complex are bent away from the site of co-ordination of the iodide ion, with the N–K–N angle being 140.7°. It is most likely that the bending of this angle, in contrast to the 180° found[9] in $[KL^1]^+$, arises because of co-ordination of the iodide ion in the L^3 complex.

The interest in the structure of the potassium complex of L^3 lies in the origin of the destabilisation of the L^3 complex of even the large lead(II) ion by the N-isopropyl groups. Table 4 shows a comparison of structural features relating to the co-ordination geometry around the potassium in the L^1 and L^3 complexes. There is some evidence of steric strain in the stretching of the K–N bonds from 2.856 Å in the L^1 complex to 2.952 Å in the L^3 complex. At the same time, however, the K–O bonds are shortened from a mean value of 2.830 Å in the L^1 complex to 2.737 Å in the L^3 complex. Fig. 1 shows the two N-isopropyl groups of the L^3 complex of K^+ to be quite far apart, and space-filling drawings indicate no strong steric interactions between the N-isopropyl groups. Indeed, they are rotated towards each other, which would not be so if they clashed seriously. Molecular mechanics calculations[24] on the potassium complexes of L^1 and L^3 using the force field of Kollman and co-workers[25] reproduce the lengthening of the K–N bonds in L^3, but not the shortening of the K–O bonds. However, the calculations do show that the isopropyl groups of L^3 do sterically interact with the macrocyclic ring, and that the cause of steric destabilisation of the L^3 complexes is local steric hindrance between the isopropyl groups and adjacent portions of the macrocyclic ring. In all probability, in the lead(II) complex of L^3 a major factor in its destabilisation would be steric hindrance by the isopropyl groups which inhibits higher co-ordination numbers. The crystal structure[26] of the L^1 complex of Pb^{II} shows a co-ordination number of eight, with both counter ions co-ordinated, and with the cryptand L^{11} the co-ordination number[27] is 10. It therefore seems likely that Pb^{II} would prefer to co-ordinate extra water molecules in solution to achieve co-ordination numbers in excess of seven, which would most certainly be hindered by the isopropyl groups.

The suggestion has been made[20] that the reason for the 'soft' behaviour of many metal ions, in the sense of hard and soft acids and bases of Pearson,[28] relates to steric effects. Thus, the silver(I) ion is not soft only because it can form covalent bonds to, for example, the iodide ion, but also because it is large and has space in its co-ordination sphere for the large iodide ion. The calcium(II) ion by contrast has space for the iodide ion, but has little ability to form a M–N bond of sufficient covalence to bond strongly to iodide. In contrast, a metal ion such as Cu^{II} has considerable ability to form covalent M–L bonds, but has[20] no room in its tightly packed co-ordination sphere for the large iodide ion. The parallel between this suggestion[20] and the response to steric hindrance provided by bulky N-alkyl groups reported in this paper is very strong. The large ions Ag^I and Pb^{II} respond favourably in terms of complex stability to the bulky N-alkyl group, and also complex strongly with the bulky iodide ion. The calcium(II) ion, in spite of being large, has little ability to form covalent M–L bonds, and so does not respond to the inductive effects of N-alkyl groups, and does not bind iodide ion well either. Finally, the small copper(II) ion does not respond well to the inductive effects of bulky N-alkyl groups, nor does it bind well to large donors such as iodide. It is our intention to explore further ligands such as L^{10}, in comparison with L^7. Ligand L^{10} should complex most metal ions in the Periodic Table, and so help to extend the analogy between hard/soft behaviour and the role of steric effects.

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References

1 R. D. Hancock, *J. Chem. Soc., Dalton Trans.*, 1980, 416.
2 R. D. Hancock and A. E. Martell, *Comments Inorg. Chem.*, 1988, **6**, 237.
3 R. D. Hancock and F. Marsicano, *J. Chem. Soc., Dalton Trans.*, 1976, 1096.
4 R. D. Hancock and G. J. McDougall, *J. Am. Chem. Soc.*, 1980, **102**, 6551.
5 G. Schwarzenbach, *Helv. Chim. Acta*, 1952, **35**, 2344.
6 J.-M. Lehn, *Acc. Chem. Res.*, 1978, **11**, 49.
7 M. S. B. Munson, *J. Am. Chem. Soc.*, 1965, **87**, 2332.
8 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley-Interscience, New York, 1988, p. 939.
9 D. Maras, B. Metz, M. Herceg and R. Weiss, *Bull. Soc. Chim. Fr.*, 1972, 551.
10 V. J. Gatto and G. W. Gokel, *J. Org. Chem.*, 1984, **106**, 8240.
11 P. Corbeaux, B. Spiess, F. Arnaud and M. J. Schwing, *Polyhedron*, 1985, **4**, 1471.
12 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
13 G. M. Sheldrick, in *Crystallographic Computing*, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, 1985.
14 C. K. Johnson, ORTEP, Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
15 A. Sabatini, A. Vacca and P. Gans, *Talanta*, 1974, **21**, 53.
16 F. Arnaud-Neu, B. Spiess and M. J. Schwing-Weill, *Helv. Chim. Acta*, 1977, **60**, 2633; G. Anderegg, *Helv. Chim. Acta*, 1975, **58**, 1218.
17 A. E. Martell and R. M. Smith, *Critical Formation Constants*, Plenum, New York, 1974–1977, 1982, 1989, vols. 1–6.
18 J. Shorter, in *Advances in Linear Free Energy Relationships*, eds. N. B. Chapman and J. Shorter, Plenum, London, 1972.
19 R. D. Hancock, B. S. Nakani and F. Marsicano, *Inorg. Chem.*, 1983, **22**, 2531.
20 R. D. Hancock and F. Marsicano, *Inorg. Chem.*, 1980, **19**, 2709.
21 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
22 R. W. Taft, in *Kinetics of Ion-Molecule Reactions*, ed. P. Ausloss, Plenum Press, New York, 1979.
23 R. D. Gandour, F. R. Fronczek, V. J. Gatto, C. Minganti, R. A. Schultz, B. D. White, K. A. Arnold, D. Mazzocchi, S. R. Miller and G. W. Gokel, *J. Am. Chem. Soc.*, 1986, **108**, 4078.
24 R. D. Hancock and P. W. Wade, unpublished work.
25 G. Wipff, P. Weiner and P. A. Kollman, *J. Am. Chem. Soc.*, 1982, **104**, 3249.
26 B. Metz and R. Weiss, *Acta Crystallogr., Sect. B*, 1973, **29**, 1088.
27 B. Metz and R. Weiss, *Inorg. Chem.*, 1974, **13**, 2094.
28 R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533.

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