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Relationship between Lewis Acid-Base Behavior in the Gas Phase and in Aqueous Solution. 1. Role of Inductive, Polarizability, and Steric Effects in Amine Ligands

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Titration calorimetry is used to measure $\Delta H^\ominus$ for the formation of the Ag(I) complexes of primary amines (L) in 0.1 M $\mathrm{LHNO_3}$ at 25 °C. For the addition of the first and second ligand $\Delta H^\ominus$ was found to be 5.72 and 8.58 (isopropylamine), 5.51 and 8.22 (*tert*-butylamine), 6.35 and 9.30 (cyclopentylamine), and 7.22 and 7.64 (cyclohexylamine) kcal mol^{-1}. The pK_a of (cyanomethyl)amine was determined to be 5.15, and log K_1 and log K_2 with Ag(I) were 1.90 and 1.31, in 0.1 M $\mathrm{LHNO_3}$ at 25 °C; the pK_a of (cyanomethyl)amine was determined to be 5.17, and log K_1 and log K_2 with Hg(II) were 5.69 and 10.60, in 0.5 M $\mathrm{LHNO_3}$ at 25 °C. log K_1 and log K_2 values for Hg(II) with primary amines $\mathrm{RNH_2}$, with R = ethyl, isopropyl, *tert*-butyl, cyclopentyl, neopentyl, and benzyl, are also reported. It was found that there was a balance between steric and inductive effects in the formation of the above complexes, which could be correlated well with enthalpies of complex formation determined in the gas phase. For the proton, the steric effects tended to mask the inductive effects, so that, since the proton is often used as an indication of inductive effects in aqueous solution, these are referred to as "hidden" inductive effects. For Lewis acids such as Ag(I) in aqueous solution, which have a low susceptibility to steric hindrance, and Cu(II) and square-planar Ni(II) with C-methylated ethylenediamines, the inductive effects predominate, and good correlations of formation constants with Taft's (1957) σ^* parameter as an indicator of inductive effect are found.

The fact that the pK_a values of primary amines hardly change at all as we change the alkyl substituent from methyl to ethyl, isopropyl, or *tert*-butyl gives the impression that the inductive effects produced by these different substituents are identical. Gas-phase studies of proton basicity[1-4] indicate that this is not so, but even so, it is with some surprise that we find that log K_1 (the formation constant) of the $\mathrm{Ag^+}$ complexes with the same set of amines increases[5] along the series methyl < ethyl < isopropyl < *tert*-butyl as we change the substituent. Similarly, the increase in stability[6] of ethylenediamine (en) complexes of metal ions such as Cu(II), Ni(II), and Zn(II) as the degree of C-methylation of the ligand increases in passing from en to $\mathrm{Me_4en}$ (*C,C,C′,C′*-tetramethylethylenediamine) has been regarded with some bafflement, since the pK_a values of the ligands remain virtually constant. Thus, Rasmussen et al.[7] have not been able to rationalize the increase in stability as a simple steric effect using empirical force-field calculations. Since the pK_a values do not respond to the changes in inductive effect, which can be shown[4] to be present for the gas-phase proton basicities of the above amines, and pK_a values are so often used as a guide to inductive effects, we feel that these should be called "hidden" inductive effects. Possibly the most important example of a hidden inductive effect is the macrocyclic effect in N-donor macrocycles, which is proposed[8] to have a large contribution from the inductive effects of the secondary nitrogens formed on cyclization. These are hidden inductive effects, in that the pK_a values of primary and secondary amines are hardly different.

A considerable amount of data on the binding of amines, alcohols, and other bases to metal ions in the gas phase[9-18] has recently become available, which should allow a better analysis of such inductive effects, which we report in this paper. At the same time, we report here a calorimetric study of the above Ag(I) complexes with primary amines, aimed at using the separate enthalpy and entropy contributions to indicate possible desolvation or steric effects. Also included is a study of the formation constants of a range of primary amines with Hg(II), for comparison with Ag(I), plus an extension of the formation constants for amines with Ag(I) by including the more electron-withdrawing cyanomethyl group and also some secondary amines.

Table I. Enthalpies of Complex Formation of Ag(I) with Primary Amine Ligands[a]

amine	$\Delta H_a^\ominus$ [b]	$\Delta H_1^\ominus$ [c]	$\Delta H_{\beta_2}^\ominus$ [d]	ref
methylamine	−13.2	−3	−11.7	31
ethylamine	−13.65	−5	−12.5	31
isopropylamine	−13.94	−5.72	−14.30	this work
tert-butylamine	−14.39	−5.51	−13.73	this work
cyclopentylamine	−14.30	−6.35	−15.65	this work
cyclohexylamine	−14.26	−7.22	−14.86	this work

[a] For this work, 25 °C and ionic strength 0.1; from ref 31, ionic strength 0. [b] Heat of protonation of ligand, kcal mol^{-1}. [c] Heat of complex formation to form the AgL complex, $\mathrm{Ag^+ + L = AgL^+}$, kcal mol^{-1}. [d] Enthalpy of complex formation to form the $\mathrm{AgL_2}$ complex, $\mathrm{Ag^+ + 2L = AgL_2{}^+}$, kcal mol^{-1}.

Experimental Section

Materials. $\mathrm{AgNO_3}$ (BDH) and $\mathrm{Hg(NO_3)_2}$ (Hopkins and Williams) were used to make up stock solutions that were standardized as described previously.[19] Benzylamine (BDH), *tert*-butylamine, isopropylamine, and cyclopentylamine (all from Merck) were purified by distillation over zinc dust. Ethylamine (Eastman) as a 70% solution in water, 3-aminopentane, and diisopropylamine (BDH) were used without further purification to prepare stock solutions that were standardized by titration with acid. All amines were found, on the basis of the weight taken, to be more than 99% pure. A stock solution of (cyanomethyl)amine was prepared by treating Holpro Analytics

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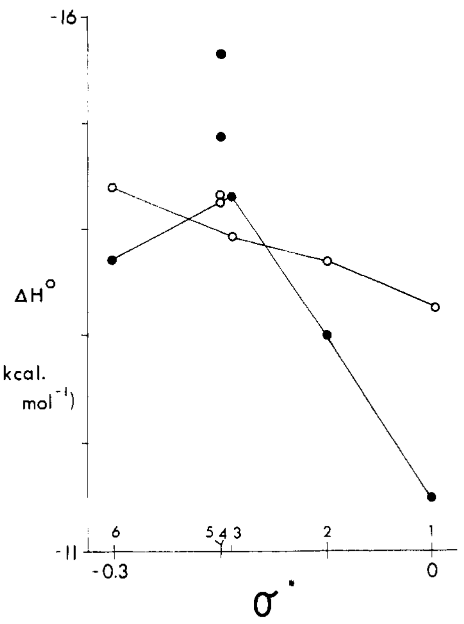

Figure 1. Relationship between $\Delta H^{\ominus}$ for the protonation of primary amines (○) and Taft's[24] inductive effect parameter, σ^*, and between σ^* and ΔH° for formation of the AgL_2^+ complexes (●), where L are the primary amines, indicated on the figure as (1) methylamine, (2) ethylamine, (3) isopropylamine, (4) cyclohexylamine (lower points), (5) cyclopentylamine (upper points), and (6) *tert*-butylamine (data from this work or ref 31).

$[NCCH_2NH_3]HSO_4$ with NaOH to neutrality and then precipitating the sulfate with $Ca(NO_3)_2$.

Potentiometry. The cell and potentiometric apparatus used were as described previously.[5] The study of the Ag(I) systems was carried out at 25 °C at an ionic strength, I, of 0.1 mol dm^{-3}, while the Hg(II) study was carried out at 25 °C and $I = 0.5$ mol dm^{-3}. The background salt making up the ionic strength consisted for both Ag(I) and Hg(II) almost entirely of the nitrate of the amine being studied, which would then suppress any tendency to hydrolysis of the metal ion, particularly the Hg(II), where this is a problem.

Calorimetry. The enthalpy changes for the Ag(I) complexes of isopropylamine, *tert*-butylamine, cyclopentylamine, and cyclohexylamine were determined by titration calorimetry. The calorimeter has been described previously.[20] The way in which the calorimetric data are corrected for heat exchange, for difference in temperature between titrant and titrate, and for "nonchemical" heat effects has been described by Eatough et al.[21] The calorimeter was calibrated with an LKB calibration heater in a constant-current circuit. The overall accuracy of the calorimeter and the corrections applied were checked by measuring the enthalpies of two well-documented reactions.

Calculations. Formation constants were calculated from the potentiometric data with use of program MINIQUAD of Sabatini et al.[22] Enthalpy changes of complex formation were calculated from the calorimetric data, plus the measured stability constants, with use of the KALLE form[23] of the program LETAGROP.

Results and Discussion

Calorimetric Study. The enthalpies of complex formation for the Ag(I) ion with the amines studied are seen in Table I. The heats of complex formation of the bis(amine) complexes are shown in Figure 1 plotted against Taft's σ^* parameter.[24] It can be seen that as σ^* becomes more negative, i.e. the alkyl group becomes more electron releasing, so the enthalpy change on complex formation, $\Delta H^{\ominus}$, also becomes more negative, paralleling fairly closely the behavior of the formation constants. Three points are worthy of comment, which all relate to the way in which the ΔG values for a complex-formation reaction tend to conceal desolvation effects. First, we see that there is a decrease in the enthalpy contribution to the free energy of complex formation of the Ag(I) complex as we pass from isopropyl- to *tert*-butylamine, which is not found in the formation constants. This seems best interpreted as steric hindrance by the *tert*-butyl group leading to desolvation of the complex. The less favorable enthalpy due to displacement of waters is then countered by a more favorable entropy contribution. The second point seems to be the converse of this. The enthalpy contributions to the formation of the Ag(I) complexes of cyclopentylamine and cyclohexylamine are very much more negative than for isopropylamine, which is not found for the free energies. Here the very small steric effect produced by these cyclic alkyl groups[24] leads to less desolvation, with a concomitant increase in the enthalpy and decrease in the entropy contribution.

Table II. Formation Constants of Some Amines with Ag(I)[a]

amine	pK_a	log K_1	log β_2	ref
(cyanomethyl)amine	5.15	1.90	3.21	this work
benzylamine	9.32	3.02	7.04	this work
3-aminopentane	10.41	3.53	7.73	this work
dimethylamine	10.77		5.37	31
diethylamine	10.97	2.98	6.34	31
diisopropylamine	11.09	3.41	6.73	this work

[a] For this work, in 0.1 M $LHNO_3$, where L is the amine being studied, at 25 °C.

Table III. pK_a Values and log K_1 and log β_2 for the Complex Formation Reactions of Amines with Hg(II)[a]

amine	pK_a	log K_1	log β_2	ref
methylamine	10.72	8.66	17.86	31
ethylamine	10.66	8.90	18.44	this work
isopropylamine	10.65	8.75	18.27	this work
tert-butylamine	10.68	8.77	18.00	this work
cyclopentylamine[b]	10.56	8.89	18.51	this work
3-aminopentane	10.52	8.67	18.08	this work
benzylamine[b]	9.40	7.51	16.52	this work
(cyanomethyl)amine	5.17	5.69	10.56	this work

[a] At 25 °C in 0.5 M $LHNO_3$, where L is the amine being studied. [b] Because of solubility problems, these systems were studied in 0.1 M $LHNO_3$.

In Figure 1 is also shown a plot of the heats of protonation of the same set of ligands vs. the Taft σ^* parameter. Unlike the pK_a values, which are almost insensitive to σ^*, the heats of protonation respond well to a more electron-releasing substituent. This raises the third point about Figure 1. If, as we have proposed, the insensitivity of the pK_a to change of substituent is due to increasing steric hindrance canceling out increasing electron-donating ability as we pass from methylamine to *tert*-butylamine, why is ΔH° so much more negative for the protonation of *tert*-butylamine than for that of methylamine? One would expect increased steric hindrance in the *tert*-butylamine to produce the same result as we see in passing from the Ag(I) complex with isopropylamine to that with *tert*-butylamine, namely, a less favorable enthalpy and more favorable entropy contribution. The best explanation at this stage would seem to be that the alkyl groups produce mainly "steric hindrance of motions" in the protonated amine, which manifests itself as entropy rather than enthalpy.[25,26]

Formation Constants. In Table II are set out the formation constants of Ag(I) and in Table III those of Hg(II), with the amines studied in this work. In Figure 2 are plotted log K_1

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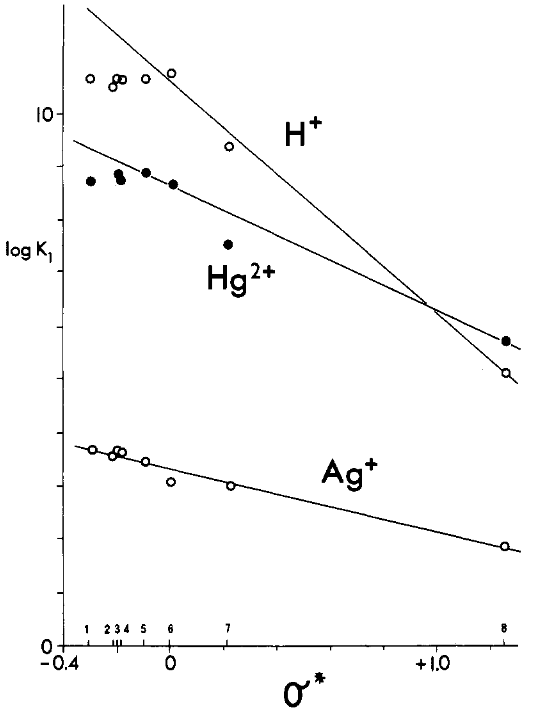

Figure 2. Relationship between log K_1 for the formation of the primary amine complexes of Hg(II), Ag(I), and the proton and Taft's[24] inductive effect parameter σ^*. Key to ligands: 1, *tert*-butylamine; 2, 3-pentylamine; 3, cyclopentylamine; 4, isopropylamine; 5, ethylamine; 6, methylamine; 7, benzylamine; 8, (cyanomethyl)amine (data from this work and ref 5 and 31).

for the formation of the Ag(I) and Hg(II) complexes, plus the pK_a values of the amines, against σ^*. The points for (cyanomethyl)amine allow us, as was hoped, to draw in the slopes of the relationships with considerably greater confidence. The slopes of the relationships decrease in the order H^+ > Hg(II) > Ag(I), which is the order of ability to respond to the electron-donating ability of the substitutent. The amount of deviation from the line increases in the order Ag(I) < Hg(II) < H^+, which is then the increase in susceptibility of the Lewis acid to steric hindrance by the substituent on the amine. These observations can be quantified by using the equation of Taft and Pavelich[27] for the separation of polar (inductive) and steric effects:

$$\log K = \log K^\circ + \rho^*\sigma^* + \delta E_s \qquad (1)$$

log K is the formation constant (or rate constant) for the base with any given substituent and log K° for that with the methyl group as substituent; σ^* is Taft's inductive effect parameter, while ρ^* is analogous to the Hammett ρ constant. E_s is a measure of the ability of the substituent to cause steric hindrance, taken as zero for the methyl substituent, while δ measures the susceptibility of the Lewis acid to steric hindrance. Fitting eq 1 to the data for Ag(I), Hg(II), and the proton, we now obtain values of ρ^* of −1.1, −2.83, and −3.95 and of δ of −0.09, 0.37, and 0.68, respectively. The δ values indicate a very low susceptibility to steric effects on the part of Ag(I).

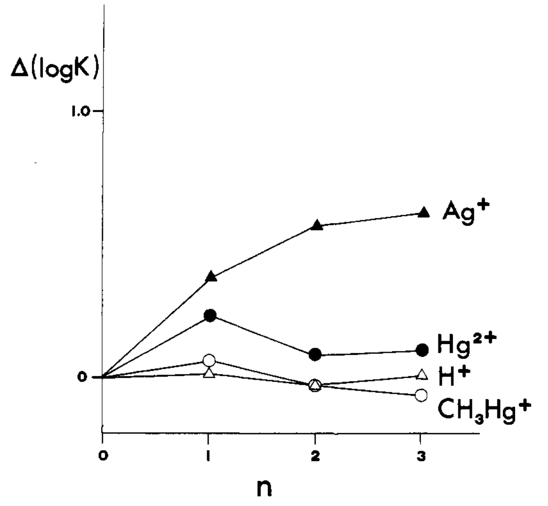

Figure 3. Increase in log K_1, Δ(log K), as a function of n. Δ(log K) is the increase in log K_1 for the ethylamine, isopropylamine, or *tert*-butylamine complex over log K_1 for the methylamine complex, for Ag(I), Hg(II), CH_3Hg^+, or H^+. n is the number of methyl groups added to methylamine in $NH_2C(CH_3)_nH_{3-n}$ in order to generate the above series of primary amines from methylamine through *tert*-butylamine (data for CH_3Hg^+ from ref 33).

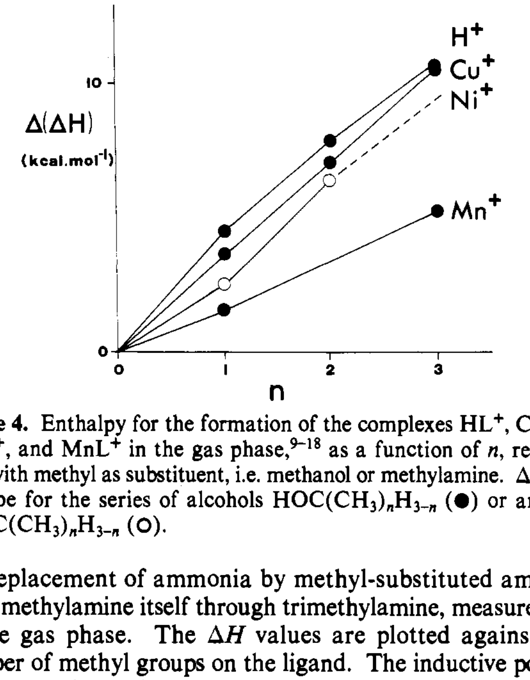

Figure 4. Enthalpy for the formation of the complexes HL^+, CuL_2^+, NiL_2^+, and MnL^+ in the gas phase,[9–18] as a function of n, relative to L with methyl as substituent, i.e. methanol or methylamine. Δ(ΔH) may be for the series of alcohols $HOC(CH_3)_nH_{3-n}$ (●) or amines $NH_2C(CH_3)_nH_{3-n}$ (○).

Comparison with Gas-Phase Results. In Figure 3 is shown the variation in log K, relative to methylamine, for Ag(I), Hg(II), the proton, and CH_3Hg^+, as the substituent is changed from methyl to ethyl, isopropyl, and *tert*-butyl. In Figure 4 are shown similar plots for Lewis acids in the gas phase binding to amines and alcohols where the set of alkyl substituents varies in the same way as in Figure 3. In Figure 5 is shown ΔH for the replacement of ammonia by methyl-substituted amines, from methylamine itself through trimethylamine, measured[9–18] in the gas phase. The ΔH values are plotted against the number of methyl groups on the ligand. The inductive power, as measured by σ^*, varies linearly with increasing methyl-group substitution on methylamine.[24] In addition, Beauchamp and Woodin[9] have shown by electrostatic calculations that the falling off in the stability of the complexes formed as we pass from ammonia to trimethylamine is due to steric interaction between the Li^+ ion and the methyl groups on the ligand. It seems a reasonable assumption at this point that the curvatures seen in Figures 3–5 is due to steric effects. Figure 4 shows that, because of the very slight curvature in the plots, the steric hindrance produced by adding methyl groups to the methyl substituent to end up finally with a *tert*-butyl group produces only very small steric effects. By contrast, Figure 3 shows that, once the Lewis acid has been hydrated, steric hindrance along this sequence becomes rather severe, and Figure 3 has a strong resemblance to Figure 5, where methyl groups are being substituted for the hydrogens on ammonia.

Figure 5 is a graphic illustration of the effect of the balance between steric and inductive effects. As the inductive effects become weaker in passing down the figure from the proton

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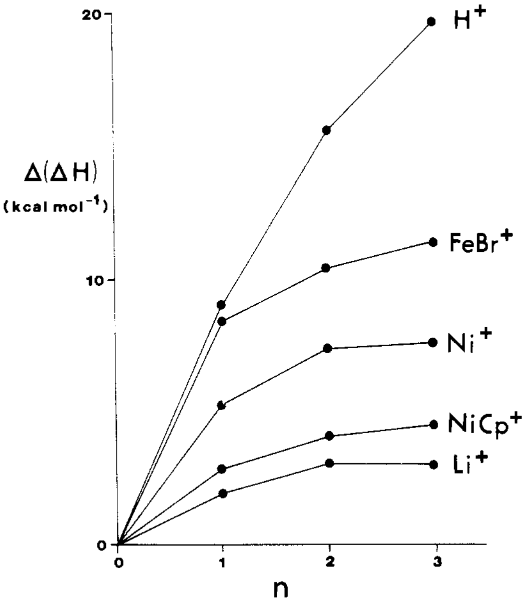

Figure 5. Enthalpy of complex formation in the gas phase relative to the ammonia complex, as methyl groups are added to create the series ammonia, methylamine, dimethylamine, and trimethylamine, as a function of the number of methyl groups on the ligand, *n* (data from ref 9–18). NiCp$^+$ is the cyclopentadienylnickel(II) ion. The increasing curvature, also seen in Figure 3, is attributed to a steady decrease in the contribution of inductive relative to steric effects, as we pass down from the proton to Li$^+$.

to Li$^+$, so the adverse steric effects are able to overpower the inductive effects produced by adding methyl groups to the ligand, until finally in Li$^+$ a reversal of the stability trend is produced. The curve for Ag(I) in Figure 3 is remarkably like that of a metal ion in the gas phase. It is also of interest that in the gas phase,[10–18], the more covalent of the metal ions studied form only complexes with two unidentate ligands bound to them, presumably with linear coordination geometry. These metal ions, namely Co$^+$, Ni$^+$, and perhaps less surprisingly, Cu$^+$, are behaving very much like the more covalent metal ions Ag(I), Hg(II), and Au(I) in aqueous solution. One can see that much of the "soft" behavior of Ag(I) is due to its behaving in solution much like a metal ion in the gas phase. This includes its ability to form strong complexes with ligands with donor atoms from the second and third row of the periodic table, which was proposed[28,29] to be due to its low susceptibility to steric hindrance by these large donor atoms.

A considerable portion of the increase in basicity of amines in adding methyl groups to them[4] is due to the polarizability effect, which stabilizes the ion formed in the gas phase when a Lewis acid combines with a neutral ligand, by delocalizing the charge over the whole molecule. The polarizability effect is largely a function of the size of the substituent and is completely quenched in aqueous solution since the solvent takes over the role of charge dispersal.[4] Taft has shown[4] that the inductive effect is quenched for protonation of amines to an extent of some 50%. Since the increase in the ΔH of complex formation of metal ions such as Cu$^+$ in the gas phase is about the same as that of H$^+$ as we add more methyl groups, it seems reasonable to assume that polarizability effects would account for no more than half of the observed increases and that, were it not for steric effects, we would see increases in log *K* in aqueous solution as more *C*-methyl groups were added.

Effect of Adding *C*-Methyl Groups to Ethylenediamines. Although Leussing[30] suggested many years ago that the increased stability of the complexes of metal ions such as Cu(II) and Ni(II) was due to the inductive effect produced as *C*-methyl groups were added to en, this has largely been ignored, presumably because the proposed inductive effects are not evidenced in the pK_a values of the ligands. We thus find pK_a values for the addition of the first and second proton to substituted en ligands of[31] 9.89 and 7.08 (en) 9.85 and 6.76 (DL-bn), 9.98 and 6.41 (Me$_4$en), and 10.41 and 5.62 (bcen), whereas log K_1 for the Cu(II) complexes of the same ligands are respectively 10.48, 10.87, 11.63, and 12.20. (DL-bn is DL-2,3-butylenediamine, and bcen is bicyclohexane-1,1′-diamine.) In view of the gas-phase results and the results with Ag(I) in aqueous solution, with the series of ligands methylamine to *tert*-butylamine, it seems most reasonable that the original suggestion by Leussing is correct. We are seeing with en ligands as C-methylation is increased is an increase in the inductive effect and the nonresponse of the pK_a values to C-methylation is irrelevant.

We do not have appropriate E_s values to describe the steric effects of the C-methylated ethylene bridges of the above ligands, but we can approximate these quite well by assuming that each ligand is made of two halves generated by cutting the ligand at the C–C bond and replacing the cut with a hydrogen atom. Thus, en is regarded as being two methylamines, Me$_4$en as two isopropylamines, bcen as two cyclohexylamines, and pn as a methylamine plus an ethylamine (pn

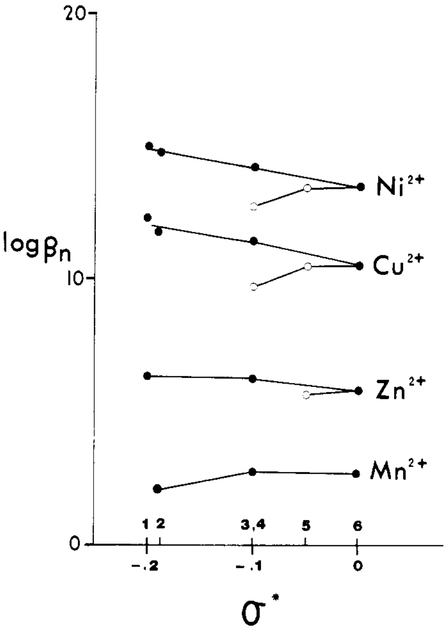

Figure 6. Formation constant, log β_n, of the C-substituted ethylenediamine ligands as a function of the Taft σ^* parameter.[24] For all except Ni(II), which is log β_2 for the formation of the bis complex, the constants are log K_1 for the monocomplexes. The σ^* values for the chelating en ligands are derived by summing the σ^* values for the two halves of the chelate as described in the text. For the symmetrically substituted en ligands (●), we see that inductive effects outweigh steric but that for the unsymmetrically substituted (○) the reverse is true. Key to ligands: 1, bicyclohexane-1,1′-diamine; 2, 1,1,2,2-tetramethylethylenediamine; 3, DL-2,3-butylenediamine; 4, 1,1-dimethylethylenediamine; 5, 1,2-propylenediamine; 6, en (data from ref 6 and 31). One should note the usual decrease in inductive effects as we pass from the top to the bottom of the figure, so that with Mn(II) we see the strong curvature produced by the now predominating steric effects.

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is 1,2-propylenediamine). We thus find that (Figure 6) there is a strong increase in log K for a variety of metal ions as the σ^* values for these ligands increase, provided that they are symmetrically substituted. This at first sight seems inexplicable, unless we note that, while the σ^* values increase linearly from methylamine to *tert*-butylamine as more methyl groups are added, the E_s values "telescope", so that they are for methyl 0.00, ethyl 0.07, isopropyl 0.47, and *tert*-butyl 1.54. Thus, the symmetrical ligand DL-bn produces the same inductive strength as Me_2en (1,1-dimethylethylenediamine), because DL-bn is in our model composed of two ethyl groups, while Me_2en is composed of one methyl and one isopropyl. The latter ligand has, however, a much larger combined E_s value of 0.47, as against only 0.14 for the two ethyl groups of DL-bn. Figure 6 shows how finely balanced are the contributions of inductive and steric effects, in that such a seemingly small change as placing both methyl groups on the same C atom of the bridge of Me_2en can destabilize the complex relative to that of en, whereas placing them on separate C atoms as in DL-bn can stabilize the complex.

One of the important features of the macrocyclic effect is[8] that with N-donor macrocycles, provided that the metal ion fits reasonably well into the macrocycle, there is a strong increase in the ligand field parameter $10Dq$. We find that for *C*-methyl-substituted en ligands the same effect is found. Thus, in the square-planar form of the Ni(II) complex with en, the single intense transition occurs at 22 200 cm^{-1}, while in the analogous complex[6] with Me_4en the transition occurs at 23 000 cm^{-1}. Similarly, for the square-planar Ni(II) complexes of triethylenetetramine, this transition occurs at 22 300 cm^{-1}, while for the macrocycle 13-aneN_4 (1,4,7,10-tetraazacyclotridecane) it occurs[34] at 23 530 cm^{-1}. The similar response of the above ligand field transitions, and the "hidden" nature of the inductive effects, whether we are dealing with the effects of C-methylation on en type ligands, or the macrocyclic effect, suggests that the extra stabilizations observed for both these effects are in many ways similar in origin.

Conclusions. The binding of the proton to ligands in water is not always a good indicator of inductive effects, which therefore may be "hidden". Gas-phase results show up these hidden inductive effects very strongly, for both the proton and other Lewis acids. For both the proton and other Lewis acids, these inductive effects may be masked in aqueous solution by steric hindrance. For metal ions with low susceptibility to steric hindrance such as Ag(I) with primary amines or square-planar Cu(II) and Ni(II) with C-methylated en ligands, the inductive effects may be able to overcome steric effects and manifest themselves as increasing complex stability and stronger ligand fields.

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Registry No. (Cyanomethyl)amine, 540-61-4; benzylamine, 100-46-9; 3-aminopentane, 616-24-0; diisopropylamine, 108-18-9; ethylamine, 75-04-7; isopropylamine, 75-31-0; *tert*-butylamine, 75-64-9; cyclopentylamine, 1003-03-8.

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Metal Effects on Metalloporphyrins and on Their π–π Charge-Transfer Complexes with Aromatic Acceptors: Urohemin Complexes[†]

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Metallouroporphyrins containing Cu(II), Ni(II), Fe(III), and Co(II) were investigated with absorption and resonance Raman spectroscopy. Systematic spectral changes are observed as the metal is varied. The spectral changes associated with metal substitution were found to be similar to changes observed for π–π complexation of the metalloporphyrins with phenanthrolines. Further, metal substitution systematically alters spectral changes that accompany π–π complexation of the metalloporphyrin with neutral aromatic acceptors. The spectral changes can be traced to the effects of the metal ion and the π–π interaction on the highest occupied $a_{2u}(\pi)$ orbital of the porphyrin. An interpretation based on arguments concerning the $a_{2u}(\pi)$ orbital leads to an explanation of the core-size dependence of several Raman marker lines of metalloporphyrins and also of the spin-state marker lines in hemes. Iron(III) uroporphyrin and its complexes with derivatives of phenanthroline are examined in detail. The binding constants for these complexes and the resulting spectral changes are strikingly similar to those for complexes with other metal porphyrins. Both copper uroporphyrin and iron(III) uroporphyrin complexes show a proportionality between the shifts in the core-size marker lines and the acceptor properties of a series of phenanthroline derivatives. Comparisons of other spectroscopic and equilibrium binding data suggest that urohemin, like copper uroporphyrin, forms charge-transfer complexes with the phenanthroline ring parallel to the porphyrin macrocycle.

Introduction

Metalloporphyrin complexes, as intermediates in reactions catalyzed by the metalloporphyrins, are central to the phenomenon of catalytic activation, and, in particular, the coordination chemistry of the metal ion has been extensively studied in this regard. The porphyrin ring too plays an essential role in the catalytic process. For example, the macrocycle provides a "surface" with specific steric properties that influence catalytic reactions. In addition, cis and trans effects on axial coordination at the metal affect ligand reactivity and have received considerable attention.[1-4] Among the cis effects

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