The value of log $K_{14}$ from reactions 5 and 6 is $<-12.0$. Even though these values of log $K_{1n}$ are not precise, they are several orders of magnitude lower than the values generally accepted[8] (log $K_{12}$ through log $K_{15}$ of −2.6, −5.8, −10.3, and −16.0, respectively), recently reported[2] (log $K_{13}$ and log $K_{14}$ of −1.1 and −5.4, respectively), or used in thermodynamic equilibrium codes such as EQ3NR[23] (log $K_{12}$ through log $K_{15}$ of −2.25, −4.88, −8.53, and −16.5, respectively).

In conclusion, the solubility of amorphous $UO_2 \cdot xH_2O$, especially at pH values >4, was found to be 3–4 orders of magnitude lower than previously reported.[2,10,12] This difference results primarily from the inability of previous workers to maintain reducing conditions. The measured values for solubility product and the U(IV) first hydrolysis constant are consistent with the reliable solubility and spectrophotometric data and with the properties of other tetravalent actinides. The measured upper-limit values for the equilibrium constants for the formation of $U(OH)_2^{2+}$, $U(OH)_3^{+}$, $U(OH)_4^{0}$, and $U(OH)_5^{-}$ are several orders of magnitude lower than those previously reported.[2,8,23]

**Acknowledgment**. This research was conducted for the U.S. Department of Energy's (DOE) Salt Repository Project (SRP) under Contract DE-AC06-76RLO 1830. This paper is being submitted in advance of DOE technical review because of Congressional shutdown of the SRP. Because of project termination, DOE has expedited the report clearance process to ensure availability of project data, waiving the requirement for formal review by the SRP and the Salt Repository Project Office. This report has received internal PNL clearance. We thank Robert Fulton for analytical and Jan Baer for editorial assistance.

**Registry No.** U, 7440-61-1; $UO_2 \cdot xH_2O$, 19961-12-7.

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# Open-Chain Polyamine Ligands with More Rigid Double Connecting Bridges. Study of Their Metal Ion Selectivities by Molecular Mechanics Calculation, Crystallography, and Thermodynamics

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Ligands with two *N*-(2-aminoethyl), *N*-(3-aminopropyl), or *N*-acetate pendant groups on piperazine (PIP), homopiperazine (HPIP), or 1,5-diazacyclooctane (DACO) are described. Protonation and formation constants of some of the complexes of these ligands with Cu(II), Ni(II), Zn(II), Cd(II), Pb(II), Ca(II), Sr(II), and Ba(II) are determined. Electronic spectra of the complexes with Cu(II) and low-spin Ni(II) are reported. It is shown that (A) doubly bridged open-chain polyamines have metal ion size selectivity patterns that resemble those of isomeric tetraaza macrocycles and (B) ligand field (LF) strengths of doubly bridged open-chain polyamines are similar to those of isomeric tetraaza macrocycles. Point A suggests that size selectivity is controlled by chelate ring size rather than macrocyclic ring size, and point B indicates that LF strength is controlled by donor atom basicity along the series primary < secondary < tertiary if there are no large differences in steric distortions of the M–N bonds. log $K_1$ values of complexes of doubly bridged open-chain polyamine ligands are lower than those ot tetraaza macrocycles. This is attributed to low levels of preorganization in the doubly bridged open-chain polyamine free ligand, where there is a large increase in strain energy on altering the ligand from its lowest energy conformer to that required for complex formation. The crystal structure of $[Ni(BAP\text{-}HP)](ClO_4)_2$ is reported (BAP-HP = 1,4-bis(3-aminopropyl)-1,4-diazacycloheptane). Crystal data: $C_{11}H_{26}Cl_2N_4O_8Ni$, monoclinic, space group $P2_1/n$, $a = 9.008$ (8) Å, $b = 14.251$ (3) Å, and $c = 14.490$ (4) Å, $\beta = 98.09$ (5)°, $Z = 4$, $V = 1841.6$ Å$^3$, $d_m = 1.710$ g·cm$^{-3}$, $d_c = 1.702$ g·cm$^{-3}$. The final conventional $R$ factor was 0.0603. Molecular mechanics (MM) calculations showed that the rigidity of doubly bridged open-chain tetraamines in their complexes was slightly less than that of tetraaza macrocycles.

## Introduction

An important idea in the chemistry of more structurally elaborate ligands is *preorganization*,[1] i.e. that the free ligand is already in the correct conformation for complexing a metal ion. With highly preorganized ligands there may even be a drop in strain energy ($U$) on complex formation.[2,3] More sharply defined metal ion size requirements of highly preorganized ligands lead to enhanced metal ion size-match selectivity; i.e., the ligand complexes more strongly with metal ions that better match the ligand size requirements. This is best seen in spherands[2] (Figure 1), which can selectively extract the tiny amounts of $Li^+$ ion present in AR KOH, since the $Li^+$ ion matches the size requirements of the spherand, whereas $K^+$ does not.[2] Recent work[4,5] has shown how higher levels of preorganization may be achieved for tetraaza macrocycles by double bridging a pair of nitrogen donor atoms, giving sharper metal ion size selectivity, in the ligand B-12-ane$N_4$, seen in Figure 1. The high levels of preorganization due to the piperazine bridge between adjacent nitrogens result in very slow rates of metalation and demetalation, as is found with all highly preorganized ligands.

Molecular mechanics (MM) calculations[6,7] show that the size selectivity of tetraaza macrocycles is mainly controlled by the size

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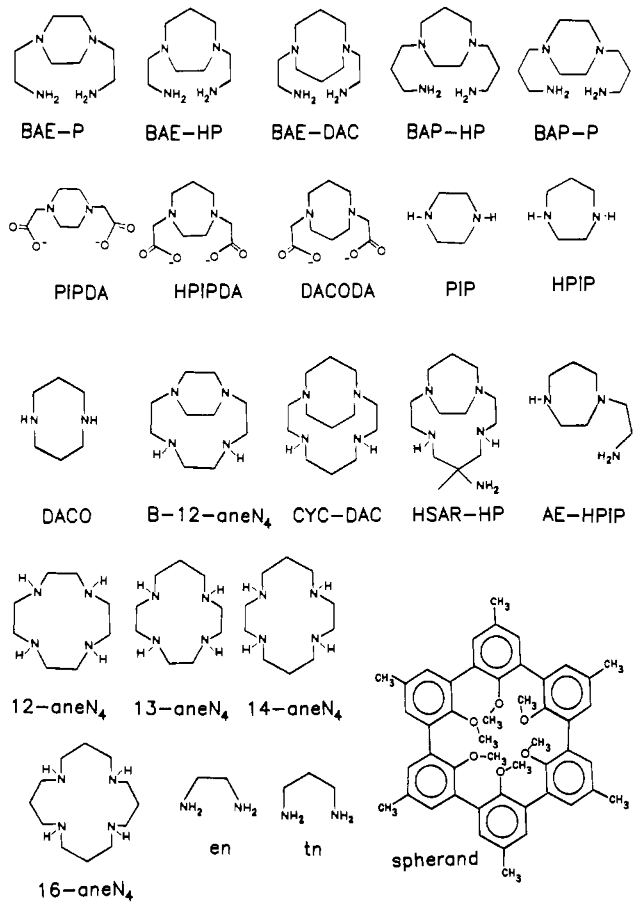
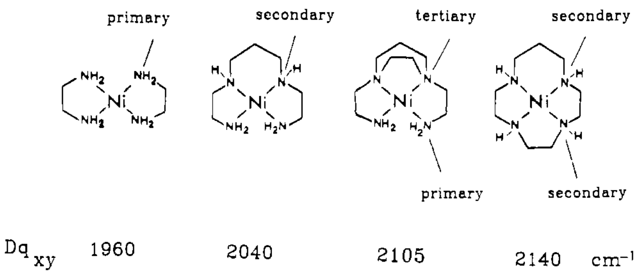


**Figure 1.** Ligands discussed in this paper.

**Chart I**



of the chelate rings rather than of the macrocyclic rings. (The importance of chelate ring size relative to macrocyclic ring size in controlling the selectivity for metal ions is seen in formation constant trends. The macrocyclic ring and chelate ring sizes increase together, but the expected effect of this on formation constants as the size of the metal ion increases *is exactly opposite*[6,7] for the two effects.) Double chelate rings as present in complexes of ligands such as BAE-HP (Figure 1) may thus produce very high size selectivity for metal ions, without the slow rates of metalation associated with the presence of a macrocyclic cavity.

Ligands of the type BAE-P, BAE-HP, BAE-DAC, BAP-P, BAP-HP, DACO, PIPDA, HPIPDA, and DACODA, seen in Figure 1, are of interest in their potential resemblance to tetraaza macrocycles 12-aneN$_4$ through 16-aneN$_4$ (Figure 1). This potential resemblance has a bearing on several areas.

(1) The degree of similarity of the metal ion selectivity patterns of pairs of ligands such as BAE-DAC and 14-aneN$_4$, or BAE-HP and 13-aneN$_4$, which are isomeric, is interesting, since one of the pair of ligands has no macrocyclic cavity (i.e. BAE-DAC and BAE-HPIP), but only chelate rings, to control metal ion size selectivity.

(2) The lack of a macrocyclic cavity may lead to faster rates of metalation than for tetraaza macrocycles, which would be useful in ligand design for selective complexation if the doubly bridged tetraamines such as BAE-DAC showed similar metal ion size selectivity.

(3) Comparison of log $K_1$ values of doubly bridged tetraamines with those of the isomeric tetraaza macrocycles should be enlightening in relation to the nature of the macrocyclic effect.[8]

(4) It has been suggested[9] that a factor in differentiating the coordinating properties of tetraaza macrocycles from those of open-chain tetraamines is the donor power of the nitrogens, which should increase in the order 1° < 2° < 3°. The sum of donor strengths of, for example, BAE-HP (two primary and two tertiary N's) is the same as that of 13-aneN$_4$ (four secondary N's), and this[5] accounts for the high ligand field (LF) strengths of low-spin Ni(II) complexes of tetraaza macrocycles (Chart I).

The above results support the idea that high LF strengths in complexes of tetraaza macrocycles are associated with higher order nitrogens, rather than the presence of a macrocyclic cavity. The effect of nitrogen donor strength on LF strength is observed, however, only if the degrees of steric distortion of the M–N bonds in the complexes compared are similar.

In this paper is reported a formation constant study of metal ion complexes of N-donor ligands (Figure 1) derived from PIP, HPIP, and DACO, by addition of *N*-(2-aminoethyl) pendant groups (BAE-P, BAE-HP, and BAE-DAC), *N*-(2-aminopropyl) pendant groups (BAP-HP, BAP-P), or *N*-acetate groups (DACODA, HPIPDA, PIPDA), plus DACO itself. Billo et al. have reported[10] briefly on the complexing properties of BAE-HP and AE-HP, and studies on DACODA and PIPDA have been reported.[11,12] Musker and Hussain[13] have reported on complexes of DACO with Cu(II) and Ni(II). Recently[4,5] there have been reported macrocyclic ligands that possess double bridges between adjacent pairs of nitrogen donors, such as B-12-aneN$_4$ and B-14-aneN$_4$ (Figure 1), which can be compared with the open-chain analogues discussed here. A crystallographic study of [Ni(BAP-HP)](ClO$_4$)$_2$ was carried out to examine the effect of the double ring on the structure and stability of the complex, and steric properties of doubly bridged chelate rings were investigated by using MM calculations.

## Experimental Section

**Materials.** Metal ion solutions used in the potentiometric study were made up from AR nitrate salts and standardized by the usual procedures. The ligands DACODA and PIPDA were synthesized by the method of Ewin and Hill.[11]

**Syntheses. 1,4-Diazacycloheptane-*N*,*N*′-diacetate (HPIPDA).** The ligand HPIPDA was synthesized by analogy with the method of Ewin and Hill for DACODA and PIPDA. This procedure gave the ligand as the barium salt, which was used to make up a stock solution after precipitation of the barium as sulfate. An elemental analysis was carried out on the barium salt [Ba(HPIPDA)]·2H$_2$O. Anal. Calcd. for $C_9H_{18}BaN_2O_6$: C, 27.90; H, 5.16; N, 7.21. Found: C, 27.61; H, 5.10; N, 6.93.

The ligand BAP-P was obtained from Aldrich, and titration with acid suggested the ligand to be of better than 99% purity.

**1,4-Bis(2-aminoethyl)-1,4-diazacyclohexane (BAE-P).** The ligand BAE-P was sythesized as the tetrahydrobromide: 4.8 g of piperazine hexahydrate was stirred in 25 mL of acetonitrile, and 9.75 g of tosylaziridine in 50 mL of acetonitrile was added. The mixture was refluxed for 24 h. The white solid that separated out was filtered off and washed with methanol. The NMR spectrum, recorded in trifluoroacetic acid, was consistent with the product being the ditosylate of BAE-PIP. The latter compound was detosylated as follows: 5 g of the white solid was heated with stirring at 110 °C for 2 days in a mixture of 113 mL of glacial acetic acid and 163 mL of concentrated HBr. The precipitate that appeared was filtered off, and reduction of the volume of the mother liquor yielded further product. The combined products were recrystallized from water.

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**Table I.** Protonation Constants and Formation Constants of Complexes of Metal Ions with Ligands Studied in This Paper[a]

| | ligand[b] | | | | |
|---|---|---|---|---|---|
| | BAE-P | BAP-P | BAE-HP | BAP-HP | BAE-DAC |
| $pK_1$[c] | 9.64 (2) | 10.2 | 9.65 (2) | 10.05 (2) | 10.78 (2) |
| $pK_2$ | 8.98 (2) | 9.3 | 9.22 (2) | 9.81 (2) | 9.42 (2) |
| $pK_3$ | 5.14 (2) | 6.2 | 6.24 (2) | 8.01 (2) | 6.03 (2) |
| $pK_4$ | | | | 4.84 (2) | |
| log $[K_1(Cu^{II})]$ | 11.91 (3) | 13.42 (3) | 20.3[d] | 18.57 (3) | 21.24 (4) |
| log $[K_1(Ni^{II})]$ | 4.68 (3) | 5.45 (4) | 13.20 (2) | 9.42 (2) | 15.60 (4) |
| log $[K_1(Zn^{II})]$ | 5.81 (3) | 6.32 (3) | 10.18[d] | 8.17 (2) | 12.81 (2) |
| log $[K_1(Cd^{II})]$ | 4.51 (2) | 4.54 (3) | 9.18 (1) | 5.81 (1) | 10.94 (2) |
| log $[K_1(Pb^{II})]$ | *e* | *e* | *e* | *e* | 8.47 (3) |

| | ligand[b] | | | |
|---|---|---|---|---|
| | DACO | PIPDA | HPIPDA | DACODA |
| $pK_1$ | 10.65 (1) | 8.68 (2) | 9.53 (2) | 11.65 (4) |
| $pK_2$ | 7.07 (1) | 4.40 (2) | 5.77 (2) | 4.86 (2) |
| $pK_3$ | | | 1.45 (3) | |
| log $[K_1(Cu^{II})]$ | 10.51 (2) | 7.37[f] | 14.32 (2) | 18.6[g] |
| log $[K_2(Cu^{II})]$ | 7.44 (3) | | | |
| log $[K_1(Ni^{II})]$ | | 3.64[f] | 6.40 (2) | 10.3[g] |
| log $[\beta_2(Ni^{II})]$ | 13.1 (1) | | | |
| log $[K_1(Zn^{II})]$ | *e* | 3.05[f] | 7.98 (2) | 11.07 (2) |
| log $[K_1(Cd^{II})]$ | *e* | *e* | 7.39 (1) | 9.69 (2) |
| log $[K_1(Pb^{II})]$ | *e* | 3.86 (4) | 8.27 (2) | 8.65 (3) |
| log $[K_1(Fe^{III})]$ | | *e* | *e* | 14.43 (2) |

[a] All in 0.1 M $NaNO_3$ at 25 °C. The number in parentheses after a constant indicates the estimated standard deviation in the last figure for the constant. [b] For a key to ligand abbreviations, see Figure 1. [c] For the ligand L, the metal ion M, and the proton H, the constants refer to the following equilibria: $pK_1$, L + H = LH; $pK_2$, LH + H = $LH_2$; $pK_3$, $LH_2$ + H = $LH_3$; $pK_4$, $LH_3$ + H = $LH_4$; log $[K_1(M)]$, M + L = ML; log $[K_2(M)]$, ML + L = $ML_2$. [d] From ref 10. [e] No evidence of complex formation right up to the point of precipitation of the hydroxide. [f] From ref 12. [g] From ref 11.

Anal. Calcd. for $C_8H_{24}N_4Br_4$: C, 19.49; H, 4.91; N, 11.36. Found: C, 19.53; H, 4.70, N, 11.33.

**1,5-Diazacyclooctane (DACO).** The reported[14] synthesis of DACO gives poor yields. An improved synthesis was used here based on the general method of Richman and Atkins,[15] involving the condensation of the ditosylate of 1,3-propanediol with the sodium salt of the ditosylate of 1,3-diaminopropane (yield 50%). The 1,5-ditosylate of DACO was then detosylated by the method of Koyama and Yoshino.[16] The dihydrobromide product was purified by reflux in water with activated charcoal, followed by filtration through Celite and removal of water on a rotary evaporator. The yield of the dihydrobromide salt calculated from weight of cyclic tosylate was 75%; mp 248–249 °C.

**1,5-Bis(2-aminoethyl)-1,5-diazacyclooctane (BAE-DAC).** To a solution of the free base of the ligand DACO (prepared as described above (5.15 g)) in 50 mL of acetonitrile was added a solution of *N*-(2-bromoethyl)phthalimide (25.6 g) in 150 mL of acetonitrile. The mixture was refluxed with effective stirring on an oil bath at 85 °C for 4 h. Acetonitrile was then completely removed on a rotary evaporator, leaving an oily residue. This was then treated with concentrated HCl (100 mL, 12 M) and refluxed for 6 h. Precipitated phthalic acid was filtered off and the pH adjusted to about 12 with 10% NaOH. The solution was then extracted eight times with 100-mL aliquots of $CHCl_3$, and the combined aliquots were dried over $Mg_2SO_4$. After filtration, the chloroform was distilled off to leave a yellow viscous liquid, which was distilled under reduced pressure (0.9 mmHg) at 60–70 °C; final yield 1.80 g (18%). Anal. Calcd for $C_{10}H_{24}N_4$: C, 59.96; H, 12.08; N, 27.97. Found: C, 60.22; H, 11.93; N, 27.60. $^1H$ NMR ($CDCl_3$, TMS): 1.36–2.0 (m, C–C$H_2$–C, 4 H), 2.38–2.48 (s, C–N$H_2$, 4 H), 2.48–3.15 ppm (m, –C$H_2$–N, 16 H).

**1,4-Bis(3-aminopropyl)-1,4-diazacycloheptane (BAP-HP).** To a stirred solution of homopiperazine (5 g) in acetonitrile was added dropwise a solution of *N*-(3-bromopropyl)phthalimide (26.8 g) in acetonitrile (100 mL). After the mixture was refluxed for 6 h, acetonitrile was removed on a rotary evaporator and concentrated HCl (125 mL) added. The mixture was refluxed for a further 2 h and precipitated phthalic acid filtered off. The solution was concentrated on a rotary evaporator and the pH adjusted to 12 with 10% NaOH. Repeated extraction with 100-mL portions of $CHCl_3$, followed by drying of the extracts over $MgSO_4$ and removal of chloroform, gave the crude amine. This was purified by distillation at reduced pressure (0.2 mmHg) at 130–140 °C to yield a clear viscous liquid (yield 41.3%). $^1H$ NMR ($CDCl_3$, TMS): 1.3–2.0 (m, C–C$H_2$–C, 10 H), 2.3–3.1 ppm (m, C$H_2$–N, 16 H).

**Table II.** Crystal Data for $[Ni(BAP\text{-}HP)](ClO_4)_2$

| | | | |
|---|---|---|---|
| chem formula | $NiC_{11}H_{26}N_4O_8CO_2$ | *Z* | 4 |
| fw | 471.96 | *T*, °C | 20 |
| cryst syst | monoclinic | $D_c$, g·cm$^{-3}$ | 1.702 |
| space group | $P2_1/n$ (No. 14) | $D_m$, g·cm$^{-3}$ | 1.710 |
| *a*, Å | 9.008 (8) | abs coeff ($\mu$, cm$^{-1}$) | 13.10 |
| *b*, Å | 14.251 (3) | $\lambda$(Mo K$\alpha$), Å | 0.71073 |
| *c*, Å | 14.490 (4) | transm factor range, % | 82.6–99.97 |
| $\beta$, deg | 98.09 (5) | $R_w(F_o)$ | 0.0603 |
| *V*, Å$^3$ | 1841.6 | final $R(F_o)$ | 0.0603 |

**Table III.** Fractional Coordinates (×10$^4$, Ni × 10$^5$) and Equivalent Isotropic Temperature Factors (Å$^2$ ×10$^3$, Ni ×10$^4$) for $NiC_{11}H_{26}N_4\cdot 2ClO_4$

| | *x/a* | *y/b* | *z/c* | $U_{eq}$[a] |
|---|---|---|---|---|
| Ni | 30563 (7) | −24625 (6) | 41470 (5) | 321 (1) |
| N(1) | 3771 (6) | −1242 (4) | 4537 (4) | 44 (1) |
| N(2) | 1184 (5) | −2229 (4) | 4621 (4) | 46 (1) |
| N(3) | 2219 (6) | −3692 (4) | 3915 (4) | 45 (1) |
| N(4) | 4941 (5) | −2688 (4) | 3697 (4) | 49 (1) |
| C(1) | 2948 (8) | −441 (5) | 4077 (6) | 62 (2) |
| C(2) | 1293 (9) | −628 (5) | 3930 (6) | 64 (2) |
| C(3) | 820 (7) | −1212 (6) | 4724 (5) | 60 (2) |
| C(4) | 1322 (8) | −2695 (6) | 5562 (5) | 65 (2) |
| C(5) | 1330 (10) | −3746 (7) | 5484 (6) | 75 (2) |
| C(6) | 2401 (10) | −4139 (5) | 4872 (5) | 64 (2) |
| C(7) | 2850 (8) | −4324 (5) | 3255 (5) | 57 (2) |
| C(8) | 4542 (9) | −4386 (5) | 3461 (6) | 66 (2) |
| C(9) | 5269 (9) | −3510 (6) | 3151 (6) | 66 (2) |
| C(10) | −5 (7) | −2665 (6) | 3944 (5) | 60 (2) |
| C(11) | 579 (7) | −3550 (5) | 3534 (5) | 58 (2) |
| Cl(1) | 8277 (2) | 2212 (1) | 8798 (1) | 53 (1) |
| O(1) | 7339 (17) | 2024 (10) | 7974 (7) | 92 (5)* |
| O(2) | 7894 (16) | 1645 (9) | 9536 (8) | 82 (5)* |
| O(3) | 9788 (11) | 2006 (14) | 8682 (11) | 133 (8)* |
| O(4) | 8193 (22) | 3153 (5) | 9064 (9) | 99 (6)* |
| O(1′) | 7899 (19) | 1884 (9) | 7882 (6) | 80 (5)* |
| O(2′) | 8203 (21) | 1497 (9) | 9445 (9) | 109 (8)* |
| O(3′) | 9764 (12) | 2578 (15) | 8911 (11) | 127 (8)* |
| O(4′) | 7319 (22) | 2971 (11) | 8945 (11) | 135 (8)* |
| Cl(2) | 8229 (2) | −5372 (1) | 1856 (1) | 53 (1) |
| O(5) | 9533 (5) | −5731 (4) | 2408 (4) | 78 (2) |
| O(6) | 7969 (6) | −5865 (5) | 998 (4) | 95 (2) |
| O(7) | 7013 (6) | −5475 (8) | 2335 (5) | 172 (4) |
| O(8) | 8439 (10) | −4424 (4) | 1650 (6) | 156 (3) |

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*(a_i\cdot a_j)$; the asterisks denote isotropic temperature factors.

**(1,4-Bis(2-aminopropyl)-1,4-diazacycloheptane)nickel(II) Perchlorate ($[Ni(BAP\text{-}HP)](ClO_4)_2$).** BAP-HP (0.1 g) dissolved in 5 mL of water was heated with an equimolar quantity of $Ni(ClO_4)_2\cdot 6H_2O$ for 15 min at 50 °C. When the mixture stood, yellow crystals of the complex were obtained and dried under vacuum. Anal. Calcd for $C_{11}H_{26}Cl_2N_4NiO_4$: C, 27.99; H, 5.55; N, 11.89. Found: C, 28.31; H, 5.86; N, 12.00.

BAE-HP was synthesized by the method of Patel and Billo.[10]

**Stability Constant Determinations.** For most ligands, stability constants could be determined by straightforward glass electrode potentiometric methods, as described previously.[17] For the complex of Ni(II) with DACO, the long equilibration times required made conventional glass electrode potentiometry inconvenient, so that an out-of-cell technique[6] was used. UV–visible spectra of solutions of DACO plus Ni(II) were recorded as a function of pH, and formation constants were calculated from these spectra. Formation constants and protonation constants determined in this work, together with some literature values for comparison, are seen in Table I.

**X-ray Crystallography.** A diffraction-quality crystal was selected by using standard oscillation and Weissenberg techniques. The data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo K$\alpha$ radiation. Cell dimensions were obtained from the least-squares refinement of 25 reflections (16 < $\theta$ <

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**Table IV.** Bond Lengths (Å) and Angles (deg) for Ni(BAP-HP)$(ClO_4)_2$

| | | | |
|---|---|---|---|
| Ni–N(1) | 1.912 (5) | Ni–N(2) | 1.938 (5) |
| Ni–N(3) | 1.919 (5) | Ni–N(4) | 1.930 (5) |
| N(1)–C(1) | 1.469 (9) | N(2)–C(3) | 1.498 (9) |
| N(2)–C(4) | 1.505 (9) | N(2)–C(10) | 1.483 (8) |
| N(3)–C(6) | 1.514 (9) | N(3)–C(7) | 1.483 (8) |
| N(3)–C(11) | 1.516 (8) | N(4)–C(9) | 1.466 (9) |
| C(1)–C(2) | 1.500 (10) | C(2)–C(3) | 1.529 (11) |
| C(4)–C(5) | 1.503 (12) | C(5)–C(6) | 1.507 (11) |
| C(7)–C(8) | 1.514 (10) | C(8)–C(9) | 1.507 (11) |

| | | | |
|---|---|---|---|
| N(1)–Ni–N(2) | 90.7 (2) | Ni(1)–Ni–N(3) | 172.0 (2) |
| N(2)–Ni–N(3) | 83.0 (2) | N(1)–Ni–N(4) | 88.6 (2) |
| N(2)–Ni–N(4) | 178.9 (2) | N(3)–Ni–N(4) | 97.6 (2) |
| Ni–N(2)–C(3) | 114.5 (4) | Ni–N(2)–C(4) | 106.3 (4) |
| C(3)–N(2)–C(4) | 109.2 (6) | Ni–N(2)–C(10) | 106.1 (4) |
| C(3)–N(2)–C(10) | 108.9 (5) | C(4)–N(2)–C(10) | 112.0 (6) |
| Ni–N(3)–C(6) | 103.5 (4) | Ni–N(3)–C(7) | 119.4 (4) |
| C(6)–N(3)–C(7) | 109.5 (6) | Ni–N(3)–C(11) | 106.3 (4) |
| C(6)–N(3)–C(11) | 111.4 (6) | C(7)–N(3)–C(11) | 106.8 (5) |
| N(1)–C(1)–C(2) | 110.8 (6) | C(1)–C(2)–C(3) | 111.5 (6) |
| N(2)–C(3)–C(2) | 111.3 (6) | N(2)–C(4)–C(5) | 111.9 (6) |
| C(4)–C(5)–C(6) | 115.1 (6) | N(3)–C(6)–C(5) | 112.8 (6) |
| N(3)–C(7)–C(8) | 112.0 (6) | C(7)–C(8)–C(9) | 111.1 (6) |
| N(4)–C(9)–C(8) | 111.9 (6) | N(2)–C(10)–C(11) | 110.4 (5) |
| N(3)–C(11)–C(10) | 110.0 (5) | Ni–N(4)–C(9) | 124.6 (5) |
| Ni–N(1)–C(1) | 116.4 (4) | | |

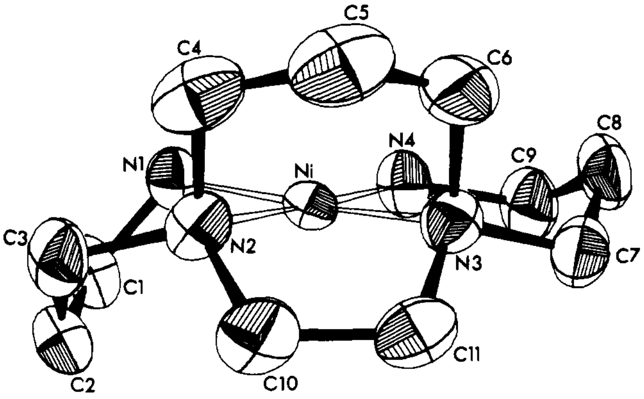

**Figure 2.** Ortep[29] drawing of the complex cation $[Ni(BAP-HPIP)]^{2+}$ showing the numbering scheme and thermal ellipsoids.

18°). Three standard reflections were monitored and showed a 1.6% variation over the data collection. Lorentz, polarization, and absorption corrections (based on a $\psi$ scan of nine reflections) were made by using the method of North et al.[18] The structure was solved and refined with Patterson and Fourier techniques by using the SHELX program.[19] Atomic scattering factors were from ref 20. All non-hydrogen atoms of the cation were refined anisotropically before the hydrogen atoms were located. All hydrogen atoms were placed at geometrically calculated positions with idealized bond lengths (C–H = 1.08 Å, N–H = 0.99 Å). One perchlorate ion was refined anisotropically, but the second perchlorate appeared to be disordered. The oxygen atoms of this perchlorate were fixed to be a pair of regular tetrahedra and then refined isotropically as two rigid bodies pivoting on the chlorine atom, with site occupancy factors of 0.52 (O(1)–O(4)) and 0.48 (O(1′)–O(4′)). Crystal data are given in Table II, fractional atomic coordinates and equivalent isotropic temperature factors are given in Table III, and important bond lengths and angles are given in Table IV. The numbering scheme for the complex cation is shown in Figure 2. Fractional coordinates for hydrogen atoms, anisotropic thermal parameters, and structure factors are given as supplementary material.

**Spectroscopy.** UV–visible spectra were recorded on a Varian/Cary 2300 spectrophotometer, and NMR spectra were recorded on a Bruker 200-MHz spectrometer.

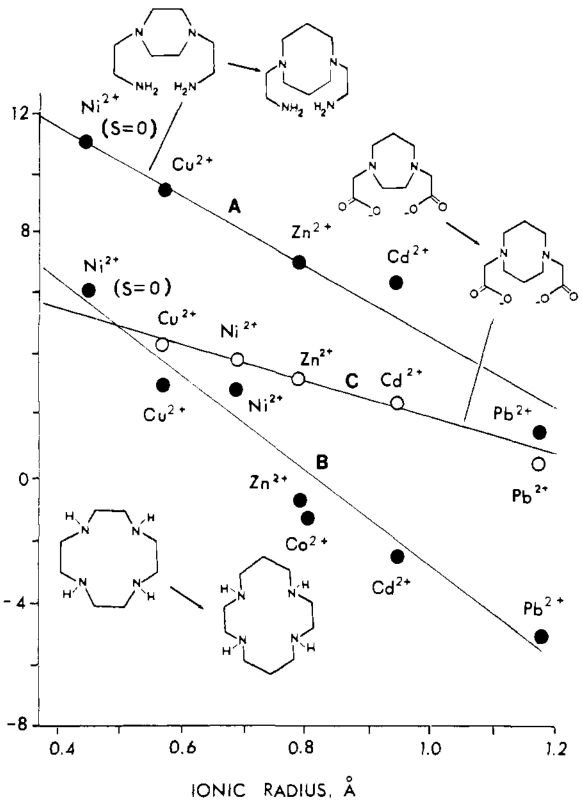

**Figure 3.** Relationship between the change in complex stability on increasing the size of the chelate ring from five-membered to six-membered, $\Delta$ log $K$, and the ionic radius[30] of metal ions, for the pairs of ligands BAE-PIP/BAE-DAC (A), 12-ane$N_4$/14-ane$N_4$ (B), and HPIP-DA/DACODA (C). The similarity of steepness of slope for A to that for B supports the idea[7] that metal ion selectivity of tetraaza macrocycles is controlled by chelate ring size.

**Molecular Mechanics Calculations.** These were carried out on Ni(II) complexes of bridged macrocycles by using the force field described previously.[5] Trial coordinates of complexes for which no crystallographic data were available were generated by using the program ALCHEMY (Tripos Associates, St. Louis, MO). The energy of each complex was calculated as a function of the strain-free M–N length in the range M–N = 1.61–2.41 Å. The minima in such curves represent[21] the best-fit size of the metal ion for coordinating to the ligand. The sharpness of the curve is an indication of the size selectivity[19] of the ligand, with sharper curves indicating sharper size selectivity. We have in this paper attempted to quantify such sharpness of the size selectivity by fitting a polynomial to the energy versus M–N bond length curve and characterizing the sharpness as the second-order derivative of the fitted curve.

## Results and Discussion

Our main aim in studying doubly bridged open-chain tetraamines was to determine how closely these ligands resemble tetraaza macrocycles in their coordination chemistry, as well as to investigate the effect of double bridges on complexing properties. Of primary interest here are (A) selectivity patterns of doubly bridged open-chain polyamines in relation to those of tetraaza macrocycles, (B) LF strengths of the two types of ligands, and (C) relative thermodynamic stabilities of complexes formed by the two types of ligands. Also considered are (D) the crystal structure of [Ni(BAP-HP)]$(ClO_4)_2$ and the origin of the low LF strength of the ligand and (E) the extent to which the double bridges sterically hinder coordination at the axial sites.

**A. Selectivity Patterns of Doubly Bridged Ligands.** In Table I are seen formation constants of ligands studied in this paper. The method developed[7] for analyzing the size selectivity on a change of the ligand structure involves plotting the change in formation constant, $\Delta$ log $K$, that occurs on a change of structure against the metal ion radius ($r^+$). An example is seen in Figure 3, where the structural change involves an increase of macrocyclic

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**Table V.** Energies of d–d Transitions in Electronic Spectra of Complexes of Cu(II) and Ni(II) with Analogous Open-Chain Polyamines, Doubly Bridged Open-Chain Polyamines, and Tetraaza Macrocycles[a]

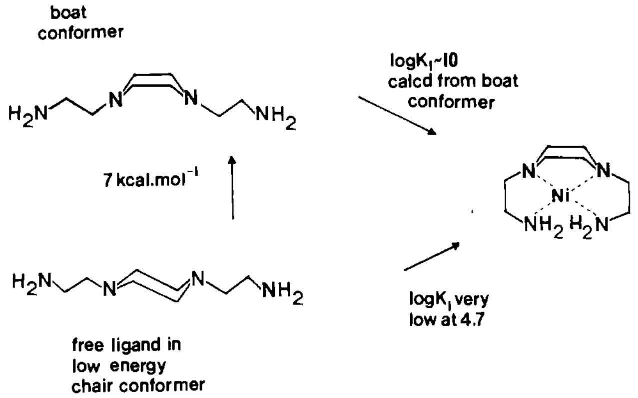
| complex[b] | sum of order of nitrogens[c] | best-fit M–N[d] | d–d[e] Ni(II)[f] | d–d[e] Cu(II) |
|---|---|---|---|---|
| $[M(en)_2]^{2+}$ | 4 | 2.05 | 21 600 | 18 180 |
| $[M(2,2,2\text{-tet})]^{2+}$ | 6 | | | 17 200 |
| $[M(2,3,2\text{-tet})]^{2+}$ | 6 | | 22 440 | 19 000 |
| $[M(TMC)]^{2+}$ | 12 | >2.3 | 19 420 | 16 390 |
| $[M(15\text{-aneN}_4)]^{2+}$ | 8 | 2.22 | 21 500 | 17 610 |
| $[M(DACO)_2]^{2+}$ | 8 | 2.12 | 22 620 | 19 950 |
| $[M(CYCLAM)]^{2+}$ | 8 | 2.07 | 22 470 | 19 900 |
| $[M(BAP\text{-}HP)]^{2+}$ | 8 | 2.06 | 21 600 | 18 000 |
| $[M(BAP\text{-}P)]^{2+}$ | 8 | 2.04 | 21 740 | 17 700 |
| $[M(BAE\text{-}DAC)]^{2+}$ | 8 | 1.98 | 22 220 | 18 500 |
| $[M(13\text{-aneN}_4)]^{2+}$ | 8 | 1.92 | 23 540 | 18 310 |
| $[M(BAE\text{-}HP)]^{2+}$ | 8 | 1.88 | 23 150 | 18 000 |
| $[M(12\text{-aneN}_4)]^{2+}$ | 8 | 1.82 | 23 270 | 16 810 |
| $[M(BAE\text{-}P)]^{2+}$ | 8 | 1.81 | 22 670 | 16 660 |
| $[M(B\text{-}12\text{-aneN}_4)]^{2+}$ | 10 | 1.73 | 23 980 | 17 540 |
| $[M(HSAR\text{-}HP)]^{2+}$ | 10 | 1.90 | 24 020 | |

[a] Units are $cm^{-1}$. Data from this work (BAP-HP, BAE-HP, BAE-DAC), ref 18, or: Ngwenya, M. P.; Hancock, R. D., To be submitted for publication (AM-HP). [b] For ligand abbreviations, see Figure 1, except for TMC, which is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane. [c] Sum of order of nitrogen donors present in ligand, where primary = 1 secondary = 2, and tertiary = 3. [d] Best-fit length of M–N bond required to coordinate with minimum strain energy to ligand, in Å. [e] Units for d–d energies are $cm^{-1}$. [f] Ni(II) is square-planar low-spin Ni(II).

ring size in passing from 12-ane$N_4$ to 14-ane$N_4$. Such plots are linear but *show a decrease in log K with an increase in macrocyclic ring size, as the size of the metal ion increases.* This is not in accord with expectations based on size-match selectivity in the macrocyclic cavity[7] but is typical of the behavior of open-chain ligands when the *chelate ring size* is increased from five-membered to six-membered. Also shown in Figure 3 are the plots of Δ log *K* against $r^+$ in passing from BAE-P to BAE-DAC and from HPIPDA to DACODA. *The bridged open-chain ligands BAE-P/BAE-DAC show in their relationship in Figure 3 a metal ion size selectivity pattern almost identical with that of the pair of macrocycles 12-aneN$_4$/14-aneN$_4$.* The slopes of the Δ log *K* versus $r^+$ relationship are a measure of the sharpness of the size selectivity. The slope for the HPIPDA/DACODA pair of ligands is approximately half of that for the other two pairs of ligands in Figure 3 because here only one five-membered ring has been turned into a six-membered ring instead of two.

An indication of the sharpness of size selectivity of the doubly bridged polyamines relative to that of their macrocyclic analogues can be obtained by MM calculation. The strain energy of these complexes can be calculated as a function of M–N bond length. The minima in these curves represent the best-fit size[19] of the metal ion for complexing the ligand. The steepness of the calculated curves of strain energy versus M–N bond length is a measure of the sharpness of metal ion size selectivity. The steepnesses of the curves have been characterized by their second derivatives. For some doubly bridged polyamines and the isomeric tetraaza macrocycles the best-fit M–N lengths (for square-planar coordination) and second derivatives are as shown in Table VI. The second derivatives for doubly bridged polyamine complexes are somewhat lower than for their macrocyclic analogues. Thus, the second derivative for the BAE-DAC curve at 212 is lower than that for 14-ane$N_4$ at 337. The much lower derivative for the open-chain $(en)_2$ complex is indicative of its greater tolerance to variation in metal ion size, while the very high derivative for the ligand CYC-DAC, a doubly bridged macrocycle, is suggestive of considerable rigidity and sharpness of metal ion size selectivity.

**Scheme I**



Both formation constants, as seen in Figure 3, and MM calculations suggest that doubly bridged open-chain tetraamines do not differ greatly in metal ion size selectivity from tetraaza macrocycles. As with tetraaza macrocycles, the dominant factor in controlling the selectivity for metal ions on the basis of their size is the size of the chelate ring, and it appears that the double chelate ring is roughly twice as effective as controlling metal ion size selectivity as is a single chelate ring.

**B. Ligand Field (LF) Strength of the Doubly Bridged Polyamines.** Table V shows energies of the d–d bands in complexes of Ni(II) and Cu(II) with a variety of tetraamines. The variation in LF strength of the tetraamines may be rationalized in terms of two effects, namely the donor strengths of the nitrogens along the series primary < secondary < tertiary and steric effects on the M–N bond. Thus (see Introduction), the LF strength of Ni(II) complexes can be partly rationalized in terms of the sum of the orders of the nitrogen donor atoms. This overlying trend is apparent for the complexes of Ni(II) in Table V, where the very highest LF strength is found for the complex with AM-HP, which has two tertiary and two secondary N-donors, leading to the highest total order for its donor atoms. The very low LF strength of the $(en)_2$ complex of Ni(II) may, on the other hand, be attributed to its having four primary N-donors only. Modifying the effect of nitrogen donor strength is the effect of steric distortion of the Ni–N bond. Thus, the very low LF strength of $[Ni(TMC)]^{2+}$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacy-

**Table VI**

| | ligand | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $(en)_2$ | $(DACO)_2$ | BAE-P | 12-ane$N_4$ | BAE-HP | 13-ane$N_4$ | BAE-DAC | 14-ane$N_4$ | BAP-HP | CYC-DAC |
| best-fit M–N, Å | 2.05 | 2.12 | 1.82 | 1.82 | 1.89 | 1.92 | 2.01 | 2.07 | 2.05 | 2.05 |
| 2nd deriv | 108 | 127 | 259 | 305 | 244 | 291 | 212 | 337 | 264 | 366 |

**Table VII**

| | log $K_1$[a] | | | | | |
|---|---|---|---|---|---|---|
| | BAE-PIP | 12-ane$N_4$ | BAE-HPIP | 13-ane$N_4$ | BAE-DAC | 14-ane$N_4$ |
| Ni(II) | 4.7 | 16.4 | 13.2 | 18.0 | 15.6 | 20.1 |
| Cu(II) | 11.9 | 23.3 | 20.3 | 24.4 | 21.2 | 26.5 |
| Zn(II) | 5.8 | 16.2 | 10.2 | 15.9 | 12.8 | 15.5 |
| Cd(II) | 4.5 | 14.3 | 9.2 | 12.7 | 10.9 | 11.8 |

[a] Data from ref 6a,b and 25 and this work.

clotetradecane) may be attributed[5,20] to the fact that here the Ni–N bonds have been stretched out from their strain-free value[5] of 1.91 Å to a length of 1.99 Å.[22] The highest LF strengths are observed for complexes that have best-fit M–N lengths, as estimated by MM calculation, close to the strain-free M–N length of the metal ion. In Table V all ligands that have a total nitrogen donor order of 8 have been placed in order of increasing best-fit M–N length as estimated by MM calculation. For low-spin Ni(II), which has a strain-free[5] Ni–N bond length of 1.91 Å, the energies of the d–d transitions peak in the vicinity of a best-fit M–N length for coordinating to the ligand of 1.91 Å, showing that the maximum LF strength is experienced[23] when the metal ion best fits the metal ion size requirements of the ligand. In response to a comment by a reviewer, it is pointed out that best-fit M–N lengths for metal ions are largely independent of force field and have as much meaning as concepts such as ionic radius.[24] For Cu(II) the maximum LF appears to be exerted by ligands with a best-fit M–N length requirement in the vicinity of 2.1 Å. This is a little larger than previously reported[9] strain-free Cu–N lengths for square-planar Cu(II) of about 2.03 Å. However, not only M–N bond length distortion is involved in steric strain, and other factors may be responsible for this being apparently the best-fit situation. This suggestion is illustrated by the BAP-HP complex of Ni(II). The complex $[Ni(BAP\text{-}HP)]^{2+}$ shows a low d–d band energy in spite of not being too far from the required best-fit Ni–N bond length for coordination to low-spin Ni(II). The M–N bond length is only one measure of how well a metal ion fits a ligand. Thus, the strain energy of $[Ni(BAP\text{-}HP)]^{2+}$ is higher than that of other complexes which fit the Ni(II) ion from the bond length point of view. As discussed below, this relates to the distortion of angles involving the Ni(II) ion, such as the Ni–N–C bond angles, which also contributes to a decrease in overlap in the Ni–N bond and therefore a drop in LF strength.

**C. Stability of Complexes of Doubly Bridged Tetraamines Relative to Those of Their Macrocyclic Analogues.** The log $K_1$ values for the doubly bridged open-chain tetraamines, seen in Table I, are considerably lower than for their macrocyclic analogues. This is shown by the examples given in Table VII, grouped together as pairs of isomers.

The stabilities of complexes of the open-chain doubly bridged tetraamine BAE-P are remarkably low. These low complex stabilities do not appear to reflect poor overlap in the M–N bond, since (Table V) the d–d band energies of complexes of doubly bridged polyamines are similar to those of their macrocyclic analogues. The Ni(II) complex of BAE-P has a high d–d band energy but probably the lowest log $K_1$ value for a complex of Ni(II) with a tetraamine. The fairly constant difference in log $K_1$ between complexes of BAE-P and 12-ane$N_4$ probably arises because of the existence of the free ligand of BAE-PIP in the low-energy chair form, which the MM calculations show to be some 7 kcal·mol$^{-1}$ lower in energy than the boat form required for complex formation.

The ligand BAE-P is highly *unpreorganized*, in that the low complex stability reflects the very low energy state of the free ligand as compared to that required for complex formation. The same explanation probably applies to a lesser extent to the free ligands BAE-HP and BAE-DAC. The ligand BAE-P is probably even more unpreorganized than simple tetraamines such as 2,2,2-tet. Possibly also important here is the steric hindrance to solvation of the donor atoms, which Margerum[8] has suggested is a contribution to the macrocyclic effect. The steric difficulty of solvating the donor atoms leaves the free ligand in a high-energy state, leading to greater complex stability, which has been proposed as an important factor in spherands by Cram.[1,2] The level of preorganization of the bridged polyamines is thus probably also low from the point of view that the lack of a macrocyclic cavity leads to much less steric hindrance to solvation of the donor atoms. It is likely that correlations between heats of complex formation and the d–d band energies reported for complexes of Cu(II) and Ni(II)[26] would break down where low complex stability, as is found for BAE-P complexes, is related to ligand effects rather than poor overlap in the M–N bond. Although the rates of complexation were not studied, it was observed that, unlike the case for the tetraaza macrocycles, the rates of equilibration of metal ions with the doubly bridged open-chain ligands were fast in the potentiometric titrations, so that the lower level of preorganization leads to fast metalation and demetalation.

**D. Structure of $[Ni(BAP\text{-}HP)](ClO_4)_2$.** The structure of the complex and the atomic numbering scheme are shown in Figure 2. The Ni–N bond lengths in the complex average 1.925 Å, close to the normal strain-free Ni–N bond length of 1.91 Å[5] for square-planar low-spin Ni(II). The low LF strength of the Ni(II) complex of BAP-HP must thus arise from steric effects other than Ni–N bond length deformation. The drop in LF strength reflects a decrease in overlap in the Ni–N bond. This is possibly caused by the large distortions (Table IV) away from the ideal value of 109.5° observed in some of the Ni–N–C bond angles of the Ni(II) complex of BAP-HP. The angle Ni–N(4)–C(9), at 124.6°, is the largest Ni–N–C angle of which we are aware. Such an opening up of the M–N–C bond angle is usually associated with six-membered chelate rings in polyamines[27] and accompanies flattening of the chelate ring as the M–N bond length increases in length away from the ideal M–N length of 1.6 Å for coordinating to six-membered chelate rings in polyamines. In this case the rigid HPIP bridge in the BAP-HP complex has Ni–N–C bond angles that are close to normal. In contrast, the Ni–N–C bond angles involving terminal nitrogens of the arms have unusually large Ni–N–C values. It would appear that the more rigid Ni–N–C angles which are part of the double bridge have forced the less rigid chelate rings of the arms to absorb most of the steric strain.

The steric strain in $[Ni(BAP\text{-}HP)]^{2+}$ has been analyzed by MM calculation. The MM study predicts large Ni–N–C angles, but Ni–N(4)–C(9) is predicted to be only 117.2°, somewhat smaller than the observed value of 124.6°. The MM calculation shows that a large source of steric strain is H---H nonbonded repulsion in the ligand, particularly between the hydrogens on the terminal nitrogen donors. It seems that the bond angle deformation should be taken up more in the Ni–N–C bond angles and that the Ni–N–C force constants are too large. It is probable that, as suggested,[24] the Ni–N–C ideal bond angle should be about 112°, rather than 109.5°. MM analysis of the structure of $[Ni(BAP\text{-}HP)]^{2+}$ has revealed a minor defect in the force field for square-planar Ni(II), which was not strongly highlighted in the structures analyzed previously.[5]

**E. Steric Hindrance of Coordination at the Axial Sites by Bulky Double Bridges.** Steric hindrance to ligands such as water at the axial coordination site of complexes with doubly bridged chelate rings has been postulated[13,26] as the cause of the square-planar coordination found in $[Ni(DACO)_2]^{2+}$ and the five-coordination found[28] in $[Ni(DACODA)H_2O]$. MM calculations on the complexes of high-spin octahedral Ni(II), with two waters occupying the axial coordination sites, and on the complexes of low-spin Ni(II) with both 14-ane$N_4$ and BAE-DAC are summarized in Figure 4. As found previously,[6c] the Ni–O bonds in the 14-ane$N_4$ complex were stretched by van der Waals repulsion between the coordinated waters and the hydrogens on the macrocyclic ring. For the BAE-DAC complex of high-spin Ni(II), the double bridge clashed sterically with the coordinated waters (Figure 4), producing a very high strain energy. In contrast, the strain energies

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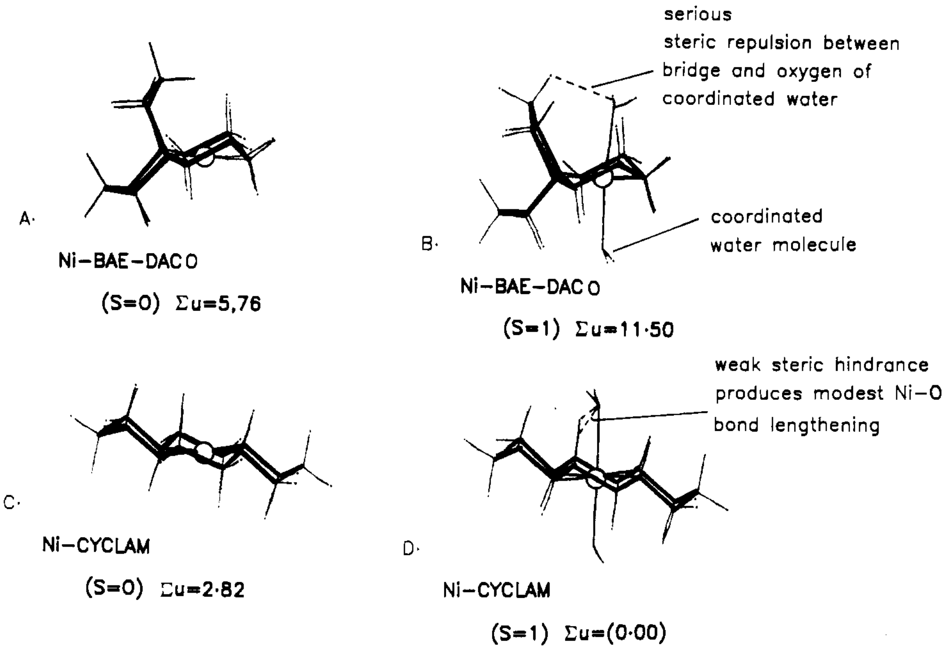

**Figure 4.** Energy-minimized structures of complexes of high-spin and low-spin Ni(II) with 14-ane$N_4$ and BAE-DAC (see Figure 1 for key to abbreviations). Strain energies (*U*) are quoted relative to that of the high-spin Ni(II) complex of 14-ane$N_4$ in kcal·mol$^{-1}$. A depicts the low-energy conformer of the complex of low-spin Ni(II) with BAE-DAC, showing the central methylene bridge of the boat form of the chelate ring blocking off the axial coordination site. For B added axial waters of octahedral high-spin Ni(II) are severely sterically hindered by hydrogens on the boat-form ring of the bridge, resulting in relatively high steric strain. 14-ane$N_4$ complexes of low-spin Ni(II) (C) and high-spin Ni(II) (D) show low steric strain. As discussed in the text, a high *U* value for the BAE-DAC complex of high-spin Ni(II) likely accounts for it not existing in appreciable concentrations compared to the amount of BAE-DAC complex with low-spin Ni(II).

of the BAE-DAC and 14-ane$N_4$ complexes of low-spin Ni(II) are much closer together in energy (Figure 4), indicating that the low-spin complex of BAE-DAC with Ni(II) does not suffer steric destabilization in the same way as occurs for the high-spin complex.

**F. Stability of the $(DACO)_2$ Complex of Ni(II).** In their study Musker and Hussain[13] found log $\beta_2$ = 18.3 for the $(DACO)_2$ complex of Ni(II). This determination was repeated because of the unusual fact that this log $\beta_2$ value is higher than that reported[13] for Cu(II). However, both potentiometrically and spectroscopically we have obtained log $\beta_2$ = 13.1 for the Ni(II) $(DACO)_2$ complex, which is more in line with the usual relative stability of Ni(II) and Cu(II) complexes. Musker and Hussain do not give extensive experimental details and results, so it is not clear why the discrepancy has arisen. However, one finds no evidence from the MM calculations, or the LF strength of the complexes, that the $(DACO)_2$ complex of Ni(II) has any different features that would lead to unusual complex stability.

## Conclusions

(1) Doubly bridged tetraaza polyamines resemble their macrocyclic isomers very closely in patterns of metal ion selectivity, demonstrating further the dominant role of the size of the chelate ring in controlling metal ion size-based selectivity.

(2) Both types of ligands are similar in their ability to produce high ligand field strengths, which is based primarily on the total donor strength of the nitrogens along the series primary < secondary < tertiary. The effect of the order of the nitrogen donor on LF strength may be modified by steric distortion of the M−N bond.

(3) Tetraaza macrocycles form complexes with most metal ions that have log $K_1$ values higher than those of their doubly bridged analogues, which arises because of the low levels of preorganization of the doubly bridged polyamines. Doubly bridged open-chain tetraamines as free ligands have low-energy conformers that are unsuitable for complex formation. More powerfully coordinating ligands may be produced in the future by combining double bridges into macrocyclic structures. An indication of this is seen in that Ni(II) complexes of HSAR-HP (Figure 1) are resistant to demetalation[31] even after refluxing in cyanide or sulfide for 1 week.

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**Registry No.** BAE-P, 6531-38-0; BAP-P, 7209-38-3; BAE-HP, 22217-18-1; BAP-HP, 124099-97-4; BAE-DAC, 91135-29-4; DACO, 5687-07-0; PIPDA, 124099-98-5; HPIPDA, 124099-99-6; DACODA, 124125-60-6; DACO·2HBr, 40422-46-6; $[Cu(BAP-HP)]^{2+}$, 124100-00-1; $[Ni(BAE-DAC)]^{2+}$, 124100-01-2; Zn, 7440-66-6; Cd, 7440-43-9; Pb, 7439-92-1; $[Ni(BAP-HP)](ClO_4)_2$, 70212-12-3; $[Cu(BAE-DAC)]^{2+}$, 124100-02-3; $[Ni(BAE-HP)]^{2+}$, 63949-66-6; $[Cu(BAE-HP)]^{2+}$, 46241-45-6; Cu, 7440-50-8; Ni, 7440-02-0; $[Ba(HPIPDA)]\cdot 2H_2O$, 124125-61-7; $[Ni(CYCLAM)]^{2+}$, 46365-93-9; $[Ni(CYCLAM)(H_2O)_2]^{2+}$, 104485-30-5; $[Ni(BAE-DAC)(H_2O)_2]^{2+}$, 124100-03-4; Fe, 7439-89-6; piperazine, 110-85-0; tosylaziridine, 3634-89-7; 1,3-bis[[(4-methylphenyl)-sulfonyl]oxy]propane, 5469-66-9; 1,3-bis[[(4-methylphenyl)sulfonyl]-amino]propane disodium salt, 53118-69-7; 1,5-bis[(4-methylphenyl)-sulfonyl]-1,5-diazacyclooctane, 67761-04-0; *N*-(2-bromoethyl)phthalimide, 574-98-1; homopiperazine, 505-66-8; *N*-(3-bromopropyl)phthalimide, 5460-29-7.

**Supplementary Material Available:** Tables SI and SII, listing anisotropic temperature factors and derived hydrogen positions, and a table giving all crystal data and refinement details (4 pages); a table of observed and calculated structure factors for $[Ni(BAP-HP)](ClO_4)_2$ (19 pages). Ordering information is given on any current masthead page.

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(31) Hancock, R. D.; Ngwenya, M. P.; Wade, P. W.; Boeyens, J. C. A.; Dobson, S. M. *Inorg. Chim. Acta*, in press.