The Synthesis of Complexes of Novel Structurally Reinforced Tetraaza-macrocyclic Ligands of High Ligand Field Strength. A Structural and Molecular Mechanics Study

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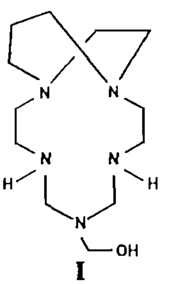
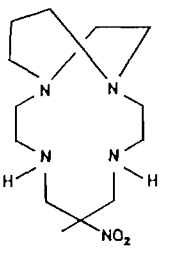
Abstract

The synthesis of the complexes of low-spin Ni(II) with the three novel ligands shown below is described. Molecular structures of these complexes have been determined by single-crystal analysis. Crystal data are as follows. Complex **I**, monoclinic, space group $P2_1/n$, with cell dimensions $a = 8.692(1)$, $b = 10.867(2)$ and $c = 21.618(4)$ Å and $\beta = 93.00(1)°$, $Z = 4$; final conventional $R = 0.081$. Complex **II**, orthorhombic, space group *Pmcn*, with cell constants $a = 9.178(1)$, $b = 14.936(2)$, $c = 30.317(5)$ Å and angles $\alpha = 90.00(1)°$, $\beta = 90.00(7)°$, $\gamma = 90.00(8)°$, $Z = 8$; final $R = 0.060$. Complex **III**, monoclinic, space group $C2/c$, with cell dimensions $a = 18.723(5)$, $b = 10.710(2)$ and $c = 21.162(7)$ Å and $\beta = 94.92°$, $Z = 8$; final conventional $R = 0.047$. The complexes of low-spin Ni(II) have average Ni–N bond lengths of 1.91 (**I**), 1.89 (**II**), and 1.89 (**III**) Å, which are very close to the strain-free Ni–N bond length of 1.91 Å.

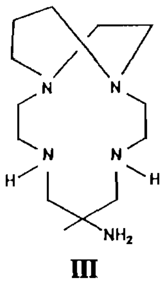
The Ni(II) complex of **III** exhibits the highest ligand field (LF) strength reported to date for a complex of low-spin Ni(II) with saturated nitrogen donor groups. The crystallographic study on the complex shows that there is no significant shortening of the Ni–N bond, which supports the idea that it is the presence of the high donor-strength tertiary and secondary nitrogens in a system of low steric strain which leads to the high LF strength. Ways of designing tetraaza-macrocycles of even higher LF strengths are discussed. Molecular mechanics calculations are used to predict the steric strain in these target complexes and to explain why these macrocycles could not be synthesized.



I



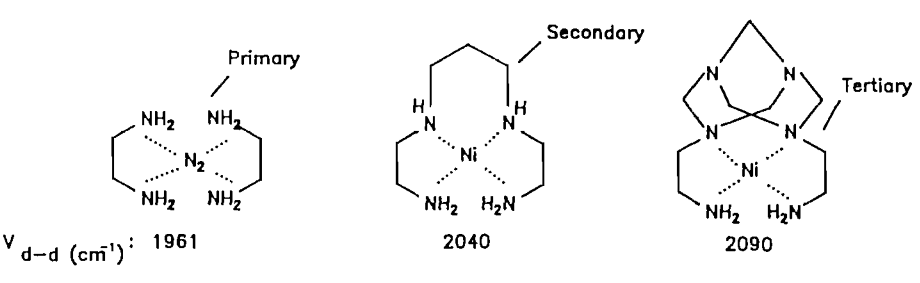
II



III

Introduction

The ability to control the ligand field (LF) strength of complexes is of importance in several areas, such as the control of rates of electron exchange [1], the ability to stabilize high oxidation states [2], and possibly in the development of novel catalysts [3]. The tetraaza-macrocycles are of interest in this regard in relation to the high LF which they produce. It has been an aim of our research program to understand the factors controlling LF strength, and to use this knowledge to design ligands of extremely high LF strength with the aim of stabilizing novel high oxidation states. An important factor involved appears to be [4, 5] the donor strength of the nitrogens along the series primary < secondary < tertiary. Thus, LF strength is increased by having the donor order of the nitrogens as high as possible, as seen in the LF strengths along the series of complexes of low-spin nickel(II) (Scheme 1).



Scheme 1.

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One assumes here that the energy of the d–d band in the spectra of low-spin Ni(II) complexes is proportional to the value of the in-plane LF splitting parameter, $D_q(xy)$, in line with the work of Bossu and Margerum [5]. The second important factor is the steric strain situation in the complexes, or what one might refer to as the steric efficiency of the ligand [4]. Thus, in general, raising the order of the nitrogen donors by adding N-methyl groups leads to a drop in LF strength because the adverse steric effects outweigh the effects of increased donor strength. Similarly, it is important to produce cavity sizes in the ligand appropriate to the size of the metal ion so as to obtain maximum overlap in the M–L bond.

A further factor which might be important in producing high LF strengths is compression of the metal ion by the ligand [6], although molecular mechanics (MM) calculations [4] have shown that this is not important for usual tetraaza-macrocycles. The ligand B-12-aneN$_4$ (see Fig. 1 for structures of ligands discussed here) has a very small cavity, and crystallographic and MM studies [7] of the complex of low-spin Ni(II) with B-12-aneN$_4$ support the idea that the Ni(II) ion has been compressed from its normal Ni–N bond length of 1.91 Å down to a value of 1.86 Å. Accompanying this compression is [8] a LF of unprecedented strength for low-spin Ni(II) with four saturated nitrogen donors.

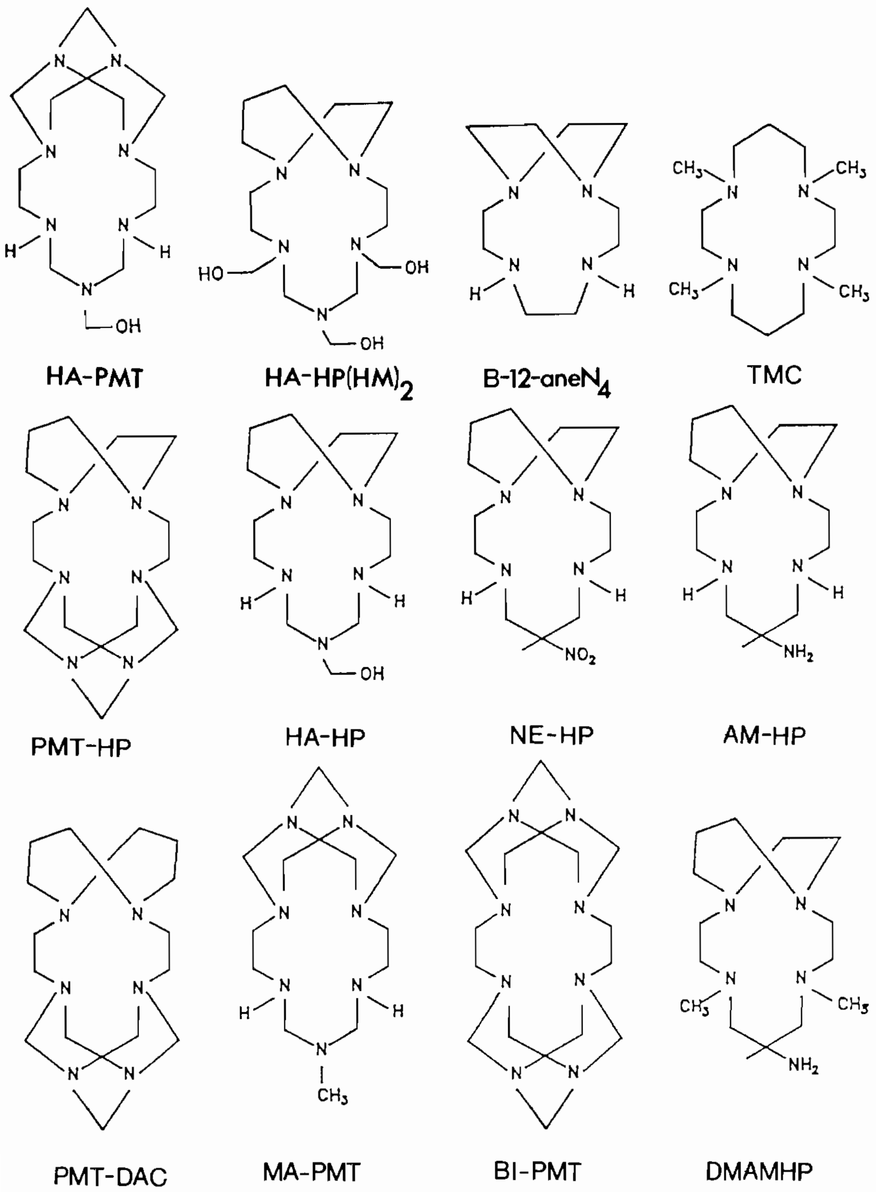
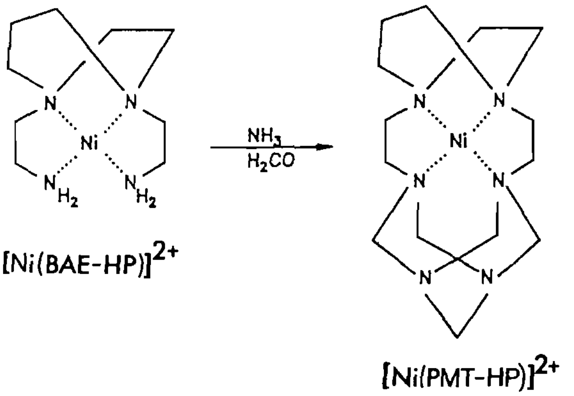
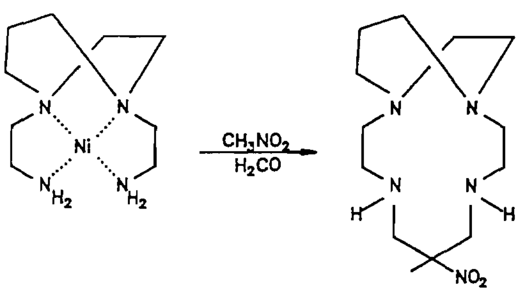


Fig. 1. Ligands discussed in this paper.

Our interest here is to synthesize novel ligands which have even higher LF strength than the tetraaza-macrocycles currently known, by means of increasing the donor strength of the nitrogens. Ideally one would like to carry out a synthesis to produce a ligand such as PMT-HP below using template syntheses of the type reported by Suh *et al.* [9]. The ligand PMT-HP would have four tertiary nitrogen donors in a sterically efficient arrangement with a cavity of about the right size for a metal ion such as Cu(III).



Other possibilities for building up ligands of high donor strength might involve template syntheses of the type recorded by Sargeson *et al.* [10].



In this paper the synthesis and structure of the complexes of low-spin Ni(II) with HA-HP, NE-HP, and AM-HP are reported. The ligand field strengths of these complexes are reported, and found to be amongst the highest to date with four saturated nitrogen donors. The attempt to synthesize the ligand PMT-HP by a template synthesis on the Ni(II) complex of BAE-HP failed, and the reasons for this were explored by molecular mechanics (MM) calculation.

Experimental

Synthesis of [Ni(HA-HP)](ClO$_4$)$_2$ (9-hydroxymethyl-1,4,7,9,11-pentaazabicyclo[2.3.9]hexadecanenickel-(II) perchlorate

To a stirred methanolic/water solution (50% vol./vol.) of nickel chloride hexahydrate (1.276 g, 5.368 mmol) were added *N,N'*-bis(2-aminoethyl)-1,4-diazacycloheptane (0.998 g, 5.368 mmol), prepared by the method of Patel and Billo [11], and an excess of formaldehyde and ammonia. The reaction mixture was then refluxed for 48 h after which a brown solution was obtained. The mixture was left to cool and then centrifuged to remove the nickel hydroxide. Lithium perchlorate (0.35 g, 2.18 mmol) was added to induce crystallization and the solution left to stand overnight. A minute quantity of pale yellowish crude crystals was found. Further crystallization was induced by addition of perchloric acid upon which a second crop of crystals was obtained. The crystals were collected and recrystallized from hot water to develop crystals suitable for X-ray structural determination. *Anal.* Calc. for $C_{12}H_{29}N_5O \cdot (ClO_4)_2$: C, 27.04; H, 5.48; N, 13.14. Found: C, 26.95; H, 5.33; N, 13.11%.

Synthesis of [Ni(NE-HP)](ClO$_4$)$_2$ (6-methyl-6-nitro-1,4,8,11-tetraazabicyclo[2.3.9]hexadecanenickel-(II) perchlorate

The synthetic route followed is based on one described by Comba *et al.* [10b]. A solution of [Ni(BAE-HP)]·$(ClO_4)_2$ was prepared by dissolving the solid (5.75 g, 0.013 mol) in a 1:3 mixture of water and methanol (200 cm^3). The above solution was then treated with nitroethane and triethylamine (5 cm^3). Whilst the solution was being stirred under reflux, a solution of 37% aqueous formaldehyde (5 cm^3) in methanol (20 cm^3) was added dropwise to the mixture. After complete addition, the mixture was left under reflux for a further 4 h after which the solution was cooled in an ice bath and later left to stand under refrigeration. The product was collected by filtration, washed in ethanol and oven dried at 60 °C. Recrystallization from hot water gave crystals suitable for X-ray structural analysis. The final product weighed 3.4 g. *Anal.* Calc. for $C_{13}H_{27}N_5O_2 \cdot (ClO_4)_2$: C, 28.76; H, 5.01; N, 12.90. Found: C, 28.94; H, 5.03; N, 13.05%.

Synthesis of [Ni(AM-HP)]·(ClO$_4$)$_2$ (6-amino-6-methyl-1,4,8,11-tetraazabicyclo[2.3.9]hexadecanenickel-(II) perchlorate by Catalytic Reduction of [Ni(NE-HP)]·(ClO$_4$)$_2$

Three g of [Ni(NE-HP)]·$(ClO_4)_2$ were reduced with 0.03 g of 5% palladium–carbon catalyst in an autoclave in 100 cm^3 water at 100 °C under hydrogen pressure (25 bar) for 50 h. On cooling, the solution was filtered to remove the catalyst. The volume of solution was thereafter reduced and solid sodium perchlorate added to induce crystallization. On standing, yellow–green crystals were obtained (2.15 g). *Anal.* Calc. for $NiC_{13}H_{29}N_5 \cdot (ClO_4)_2 \cdot \frac{1}{2}H_2O$: C, 29.91; H, 5.70; N, 13.42. Found: C, 29.71; H, 5.73; N, 13.45%.

Crystallography

Data collection and reduction

All intensity data were collected in the $\omega-2\theta$ mode at room temperature on an Enraf-Nonius CAD-4 diffractometer with incident beam graphite monochromated Mo Kα radiation. The cell dimensions were obtained from full-matrix least-squares refinement of 25 reflections. No significant change was noted on the reference intensities which were measured at regular intervals to monitor crystal decomposition. The intensity data were corrected for Lorentz polarization and absorption but not decay. The crystal data and details of the data collection for all the complexes are given in Table 1.

Structure solution and refinement

All structures were solved by Patterson methods using the SHELX 86 program [12]. The structure was then refined by full-matrix least-squares using the program SHELX 76 [12]. All the non-hydrogen atoms of the cation were located in successive difference Fourier maps and refined anisotropically before the hydrogen atoms were located. The positions of the hydrogen atoms were either identified on the difference Fourier map or, if the positions were not apparent, placed at geometrically calculated positions with idealized bond lengths of 1.08 Å. All the hydrogen atoms were refined with a common isotropic temperature factor. When there was no disorder, the perchlorate anions were refined with anisotropic thermal parameters. However if disorder was present, then the components of the disorder were refined as rigid bodies with the Cl–O and O–––O distances fixed at 1.44 and 2.35 Å respectively. All the atomic scattering factors for the heavy metal atoms were obtained from the 'International Tables for Crystallography' [13]. See also 'Supplementary Material'.

Structure solution of Ni[HA-HP](ClO$_4$)$_2$

The structure was solved and refined by standard Patterson and Fourier techniques. However both perchlorate ions were clearly seen to be disordered as characterized by large thermal parameters and observed residual electron density in the vicinity of the perchlorate ions. Oxygen atoms on the major sites of Cl(1) were refined anisotropically. Those on

TABLE 1. Crystal data for the nickel(II) complexes of bridged polyaza-macrocycles

	[Ni(HA-HP)](ClO$_4$)$_2$	[Ni(NE-HP)](ClO$_4$)$_2$	[Ni(AM-HP)](ClO$_4$)$_2$
Formula	$NiC_{12}H_{27}N_5O\cdot(ClO_4)_2$	$NiC_{13}H_{27}N_5O_2\cdot(ClO_4)_2$	$NiC_{13}H_{29}N_5\cdot(ClO_4)_2\cdot\frac{1}{2}H_2O$
Molecular weight (g mol^{-1})	533.00	542.98	522.02
Crystal colour	yellow	orange	yellow
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$Pmcn$	$C2/c$
a (Å)	8.692(1)	9.178(1)	18.723(5)
b (Å)	10.867(2)	14.936(2)	10.710(2)
c (Å)	21.618(4)	30.317(5)	21.162(7)
α (°)	90.00(1)	90.00(1)	90.00(3)
β (°)	93.00(1)	90.00(7)	94.92(3)
γ (°)	90.00(1)	90.00(8)	90.00(2)
V (Å^3)	2039.10	4156.02	4227.60
Z	4	8	8
D_{calc} (g cm^{-3})	1.752	1.736	1.642
D_{meas} (g cm^{-3})	1.734	1.729	1.627(2)
Absorption coefficient, μ (cm^{-1})	12.7	11.75	11.48
Radiation, Mo Kα (cm^{-1})	0.71073	0.71073	0.71073
F(000)	1104.00	2240.00	2168.00
Scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Scan speed (° min^{-1})	0.90–5.49	1.30–5.50	1.30–5.50
ω-scan angle (°)	0.60 + 0.35 tan θ	0.60 + 0.35 tan θ	0.60 + 0.35 tan θ
Theta range (°)	$2 < \theta < 27$	$2 < \theta < 27$	$2 < \theta < 27$
Range in h, k, l	+11, 13, 27	11, 19, 38	+23, 13, 27
Transmission factor range (%)	43.9–99.8	81.2–99.8	63.8–99.9
Crystal dimensions (mm)	0.45 × 0.40 × 0.20	1.50 × 0.40 × 0.20	0.70 × 0.25 × 0.20
Reflections measured	4786	5074	4994
Unique reflections	3900	4412	4161
Used reflections	2934	3715	3357
Parameters refined	366	397	355
Final R	0.081	0.060	0.047
Maximum shift/e.s.d.	3.91	0.66	2.36
Residual density (e Å^{-3})	1.5	1.1	0.8

the minor sites were joined together and refined as rigid bodies, using the rotational disorder model, with common isotropic temperature factors. For all oxygen atoms on Cl(2), the positions of the two distinct pairs of the oxygen atoms were assigned site occupancy factors of 0.45 and 0.55 respectively and refined isotropically. The final cycles of refinement resulted in convergence, with an *R* value of 0.081. The fractional atomic coordinates and equivalent isotropic temperature factors for the non-hydrogen atoms are given in Table 2 and the bond lengths and angles in Table 3. The numbering scheme of the atoms is given in Fig. 2.

TABLE 2. Fractional coordinates ($\times 10^4$, Ni $\times 10^5$) and equivalent isotropic temperature factors (Å^2, $\times 10^3$, Ni $\times 10^4$) for [Ni(HA-HP)](ClO_4)$_2$

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]
Ni	34999(12)	24428(12)	10791(5)	350(2)
N(1)	4833(8)	1639(8)	1661(3)	38(2)
N(2)	2123(8)	2808(7)	1710(3)	39(2)
N(3)	2021(8)	3266(8)	575(3)	43(2)
N(4)	4713(9)	2164(8)	374(4)	44(2)
N(5)	7036(9)	1574(8)	991(4)	51(2)
O	6013(10)	−372(8)	657(4)	72(2)
C(1)	4373(11)	2008(11)	2293(4)	47(2)
C(2)	2634(12)	2009(11)	2257(5)	50(2)
C(3)	2253(13)	4129(11)	1857(5)	52(3)
C(4)	1593(14)	4926(11)	1351(6)	59(3)
C(5)	2105(15)	4603(12)	701(5)	58(3)
C(6)	2351(12)	3005(12)	−88(5)	54(3)
C(7)	4104(12)	3039(10)	−106(5)	49(2)
C(8)	6415(12)	2368(12)	516(5)	54(3)
C(9)	6534(11)	1835(11)	1603(4)	47(2)
C(10)	574(11)	2475(12)	1438(5)	51(2)
C(11)	492(11)	2761(12)	744(5)	54(3)
C(12)	7338(13)	328(12)	839(6)	65(3)
Cl(1)	11723(3)	−1081(3)	1051(1)	56(1)
Cl(2)	3416(3)	4439(3)	−1743(1)	57(1)
O(1)	11075(14)	−862(13)	1635(4)	121(5)
O(2)	12928(13)	−1997(11)	1132(6)	117(5)
O(3)	12414(16)	50(8)	850(6)	111(5)
O(4)	10626(11)	−1492(15)	594(4)	127(5)
O(1′)	11604(57)	−2224(21)	719(17)	100(13)*
O(2′)	10552(35)	−1058(43)	1504(15)	100(13)*
O(3′)	11460(51)	−72(26)	629(15)	100(13)*
O(4′)	13208(23)	−973(45)	1366(16)	100(13)*
O(5)	4568(17)	4765(16)	−1276(6)	75(6)*
O(6)	3006(24)	3173(9)	−1711(9)	112(8)*
O(7)	2051(17)	5185(18)	−1659(10)	164(12)*
O(8)	3958(21)	4742(17)	−2343(5)	119(7)*
O(5′)	3864(20)	5092(14)	−1189(5)	106(7)*
O(6′)	2158(16)	3617(14)	−1648(8)	115(7)*
O(7′)	3012(21)	5287(13)	−2230(6)	121(7)*
O(8′)	4713(16)	3693(16)	−1916(9)	148(9)*
Ow	4396(16)	1014(10)	8027(7)	131(4)

Starred item = isotropic temperature factor.

[a] $U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a^*_i a^*_j (\mathbf{a}_i \cdot \mathbf{a}_j)$.

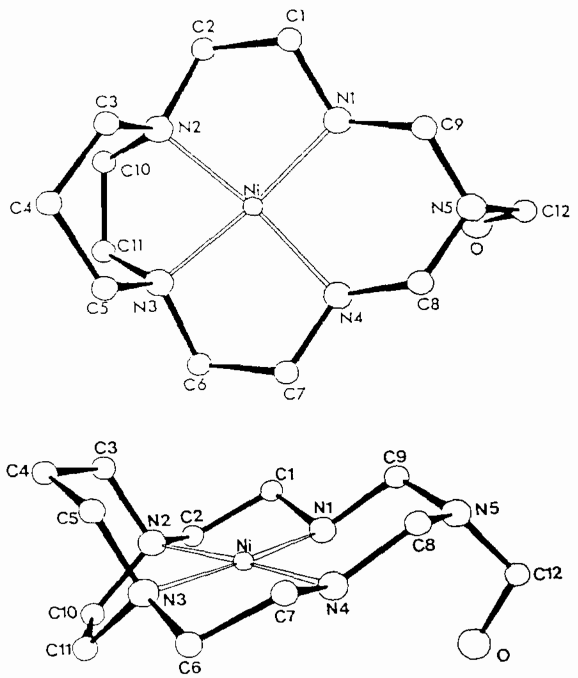


Fig. 2. ORTEP [14] drawings of [Ni(HA-HP)]$^{2+}$ showing the numbering scheme.

Solution and refinement of the structure of Ni[NE-HP](ClO₄)₂

The difference Fourier map revealed the presence of two ligand molecules, each on a mirror plane. These were refined positionally and isotropically to convergence after which they were refined anisotropically. The position of the hydrogen atoms was identified from the difference map. These were tied together and refined with common isotropic temperature factors. The perchlorates were found with their chlorine atoms on the mirror plane as well. Three of the perchlorates were not disordered and the two oxygen atoms on the mirror plane including the one in a general position were refined anisotropically. In the fourth perchlorate, the chlorine atom and one oxygen atom were on the mirror plane and not disordered, and therefore were refined anisotropically. The other two oxygen atoms were disordered with the major to minor component ratio of 3:2. These disordered atoms were refined anisotropically. After a series of refinement cycles, the ultimate refinement value converged to $R = 0.060$. The fractional atomic coordinates and equivalent isotropic temperature factors for the non-hydrogen atoms are given in Table 4 and the bond lengths and angles in Table 5. The numbering scheme of the atoms is given in Fig. 3.

Structure solution of [Ni(AM-HP)](ClO₄)₂

The structure of this complex was solved and refined with the usual standard Patterson and Fourier

TABLE 3. Bond lengths (Å) and angles (°) for [Ni(HA-HP)]$(ClO_4)_2$

Ni–N(1)	1.880(8)	Ni–N(2)	1.902(7)
Ni–N(3)	1.870(8)	Ni–N(4)	1.923(7)
Ni–C(10)	2.697(9)	Ni–C(11)	2.699(10)
N(1)–C(1)	1.499(11)	N(1)–C(9)	1.505(11)
N(2)–C(2)	1.516(12)	N(2)–C(3)	1.473(13)
N(2)–C(10)	1.485(12)	N(3)–C(5)	1.479(14)
N(3)–C(6)	1.501(12)	N(3)–C(11)	1.501(11)
N(4)–C(7)	1.484(12)	N(4)–C(8)	1.511(13)
N(5)–C(8)	1.426(14)	N(5)–C(9)	1.443(12)
N(5)–C(12)	1.421(14)	C(1)–C(2)	1.509(14)
C(3)–C(4)	1.49(2)	C(4)–C(5)	1.54(2)
C(6)–C(7)	1.527(14)	C(10)–C(11)	1.530(14)
N(1)–Ni–N(2)	90.4(3)	N(1)–Ni–N(3)	173.4(3)
N(2)–Ni–N(3)	83.1(3)	N(1)–Ni–N(4)	96.5(3)
N(2)–Ni–N(4)	173.2(3)	N(3)–Ni–N(4)	90.1(3)
N(1)–Ni–C(10)	111.8(3)	N(2)–Ni-C(10)	32.2(3)
N(3)–Ni–C(10)	62.1(3)	N(4)–Ni–C(10)	142.6(3)
N(1)–Ni–C(11)	142.5(3)	N(2)–Ni–C(11)	61.9(3)
N(3)–Ni–C(11)	32.3(3)	N(4)–Ni–C(11)	111.8(3)
C(10)–Ni–C(11)	33.0(3)	Ni–N(1)–C(1)	107.5(6)
Ni–N(1)–C(9)	116.9(6)	C(1)–N(1)–C(9)	110.3(7)
Ni–N(2)–C(2)	105.7(5)	Ni–N(2)–C(3)	108.3(6)
C(2)–N(2)–C(3)	111.9(8)	Ni–N(2)–C(10)	104.9(6)
C(2)–N(2)–C(10)	113.1(7)	C(3)–N(2)–C(10)	112.4(8)
Ni–N(3)–C(5)	109.7(7)	Ni–N(3)–C(6)	107.8(6)
C(5)–N(3)–C(6)	110.6(8)	Ni–N(3)–C(11)	105.9(6)
C(5)–N(3)–C(11)	110.5(8)	C(6)–N(3)–C(11)	112.2(8)
Ni–N(4)–C(7)	105.2(6)	Ni–N(4)–C(8)	112.8(6)
C(7)–N(4)–C(8)	111.0(8)	C(8)–N(5)–C(9)	114.9(8)
C(8)–N(5)–C(12)	118.5(9)	C(9)–N(5)–C(12)	117.9(9)
N(1)–C(1)–C(2)	105.5(8)	N(2)–C(2)–C(1)	107.0(8)
N(2)–C(3)–C(4)	112.8(9)	C(3)–C(4)–C(5)	114.8(9)
N(3)–C(5)–C(4)	112.3(9)	N(3)–C(6)–C(7)	105.1(8)
N(4)–C(7)–C(6)	106.6(8)	N(4)–C(8)–N(5)	112.8(9)
N(1)–C(9)–N(5)	113.1(7)	Ni–C(10)–N(2)	43.0(4)
Ni–C(10)–C(11)	73.6(5)	N(2)–C(10)–C(11)	109.5(8)
Ni–C(11)–N(3)	41.8(4)	Ni–C(11)–C(10)	73.5(5)
N(3)–C(11)–C(10)	108.5(8)		

TABLE 4. Fractional coordinates (×10^4, Ni × 10^5) and equivalent isotropic temperature factors (Å^2, ×10^3, Ni × 10^4) for [Ni(NE-HP)]$(ClO_4)_2$

	x/a	*y/b*	*z/c*	U_{eq}[a]
Ni(1)	6756(3)	25000	19247(6)	300(2)
O(1)	73(2)	1339(6)	−607(4)	78(1)
N(11)	258(2)	2500	−522(5)	46(2)
N(12)	651(2)	943(4)	1074(3)	34(1)
N(13)	663(2)	1129(6)	2875(3)	51(1)
C(11)	987(4)	2500	−1193(7)	65(3)
C(12)	753(2)	2500	−293(5)	36(2)
C(13)	865(2)	1100(6)	204(4)	40(1)
C(14)	820(3)	−353(6)	1578(5)	66(2)
C(15)	578(3)	−333(8)	2458(6)	79(2)
C(16)	299(2)	1652(11)	3479(5)	79(2)
C(17)	1096(2)	1120(9)	3358(5)	58(2)
C(18)	1163(4)	2500	3895(7)	72(3)
Ni(2)	68231(3)	75000	81518(6)	266(2)
O(2)	7748(2)	8622(7)	5986(7)	137(3)
N(21)	7556(2)	7500	5990(6)	54(2)
N(22)	6983(2)	9055(4)	7358(3)	32(1)
N(23)	6664(2)	8865(5)	9048(3)	34(1)
C(21)	6919(4)	7500	4975(7)	60(3)
C(22)	7056(3)	7500	5970(5)	37(2)
C(23)	6884(2)	8905(6)	6396(3)	36(1)
C(24)	6764(2)	10378(6)	7740(4)	45(1)
C(25)	6838(3)	10318(6)	8742(4)	47(1)
C(26)	6883(2)	8345(6)	9891(4)	42(1)
C(27)	6178(2)	8896(7)	9143(4)	47(1)
C(28)	6004(3)	7500	9574(7)	57(2)
Cl(1)	9542(1)	7500	3673(2)	52(1)
O(11)	9074(3)	7500	3600(8)	104(3)

(continued)

TABLE 4. *(continued)*

	x/a	*y/b*	*z/c*	U_{eq}[a]
O(12)	9744(3)	7500	2848(6)	105(3)
O(13)	9672(3)	8750(8)	4181(5)	127(2)
Cl(2)	9367(1)	2500	1508(1)	40(1)
O(21)	9149(2)	2500	667(5)	63(2)
O(22)	9821(5)	2500	1410(10)	87(4)*
O(23)	9223(4)	1276(15)	2021(8)	126(4)*
O(22')	9068(6)	2500	2215(13)	71(5)*
O(23')	9669(5)	1259(18)	1547(10)	93(4)*
Cl(3)	1969(1)	2500	1076(2)	54(1)
O(31)	1568(2)	2500	1560(5)	63(2)
O(32)	2331(2)	2500	1620(7)	113(3)
O(33)	1983(2)	1297(9)	485(6)	150(3)
Cl(4)	2907(1)	2500	7666(2)	71(1)
O(41)	2625(3)	2500	8392(5)	116(3)
O(42)	3349(3)	2500	7918(7)	119(3)
O(43)	2817(4)	1372(13)	7119(7)	249(5)

(continued)

Starred item = isotropic temperature factor.

[a] $U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a^*_i a^*_j (\mathbf{a}_i \cdot \mathbf{a}_j)$.

TABLE 5. Bond lengths (Å) and angles (°) for [Ni(NE-HP)](ClO$_4$)$_2$

Ni(1)–N(12)	1.914(4)	Ni(1)–N(13)	1.898(5)
N(11)–C(12)	1.538(10)	N(12)–C(13)	1.460(7)
N(12)–C(14)	1.498(7)	N(13)–C(15)	1.502(9)
N(13)–C(16)	1.504(9)	N(13)–C(17)	1.498(8)
C(11)–C(12)	1.520(12)	C(12)–C(13)	1.523(7)
C(14)–C(15)	1.506(12)	C(16)–C(16)	1.56(2)
C(17)–C(18)	1.513(9)	Ni(2)–N(22)	1.918(4)
Ni(2)–N(23)	1.895(4)	N(21)–C(22)	1.518(10)
N(22)–C(23)	1.473(6)	N(22)–C(24)	1.497(6)
N(23)–C(25)	1.504(7)	N(23)–C(26)	1.501(6)
N(23)–C(27)	1.483(7)	C(21)–C(22)	1.543(12)
C(22)–C(23)	1.529(6)	C(24)–C(25)	1.515(8)
C(26)–C(26)	1.551(11)	C(27)–C(28)	1.526(8)
N(12)–Ni(1)–N(13)	90.0(2)	Ni(1)–N(12)–C(13)	120.0(3)
Ni(1)–N(12)–C(14)	104.3(4)	C(13)–N(12)–C(14)	111.8(5)
N(12)–Ni(1)–N(12)	96.6(3)	Ni(1)–N(13)–C(15)	106.6(4)
Ni(1)–N(13)–C(16)	104.6(5)	C(15)–N(13)–C(16)	114.1(6)
Ni(1)–N(13)–C(17)	110.3(4)	C(15)–N(13)–C(17)	110.2(6)
C(16)–N(13)–C(17)	110.9(5)	N(13)–Ni(1)–N(13)	83.1(3)
N(11)–C(12)–C(11)	105.0(7)	N(11)–C(12)–C(13)	109.1(4)
C(11)–C(12)–C(13)	109.1(4)	N(12)–C(13)–C(12)	114.7(5)
C(13)–C(12)–C(13)	115.1(6)	N(12)–C(14)–C(15)	105.1(6)
N(13)–C(15)–C(14)	106.9(6)	N(13)–C(17)–C(18)	111.5(7)
C(17)–C(18)–C(17)	113.7(8)	N(22)–Ni(2)–N(23)	90.5(2)
Ni(2)–N(22)–C(23)	118.8(3)	Ni(2)–N(22)–C(24)	104.8(3)
C(23)–N(22)–C(24)	110.9(4)	N(22)–Ni(2)–N(22)	96.1(3)
Ni(2)–N(23)–C(25)	106.5(3)	Ni(2)–N(23)–C(26)	105.6(3)
C(25)–N(23)–C(26)	112.4(4)	Ni(2)–N(23)–C(27)	109.5(3)
C(25)–N(23)–C(27)	111.1(5)	C(26)–N(23)–C(27)	111.4(5)
N(23)–Ni(2)–N(23)	82.8(3)	N(21)–C(22)–C(21)	106.8(7)
N(21)–C(22)–C(23)	109.3(4)	C(21)–C(22)–C(23)	108.0(4)
N(22)–C(23)–C(22)	114.6(5)	C(23)–C(22)–C(23)	115.0(6)
N(22)–C(24)–C(25)	106.4(4)	N(23)–C(25)–C(24)	106.3(5)
N(23)–C(27)–C(28)	111.5(5)	C(27)–C(28)–C(27)	114.1(7)

methods. All atoms were refined with anisotropic thermal parameters. The C–H bond length was constrained to a value of 1.08 Å to facilitate the refinement of the structure. The structure refined readily to converge with a final value of $R = 0.047$. The fractional atomic coordinates and equivalent isotropic temperature factors for the non-hydrogen atoms are given in Table 6 and the bond lengths and angles are seen in Table 7. The numbering scheme of the atoms is given in Fig. 4.

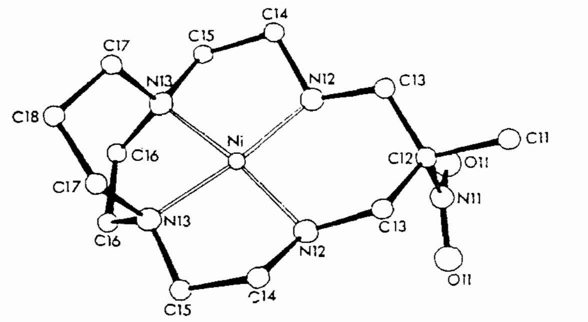


Fig. 3. ORTEP [14] drawing of $[Ni(NE\text{-}HP)]^{2+}$ showing the numbering scheme.

Molecular Mechanics Calculations

Molecular mechanics calculations were carried out using a locally modified version of a program due to Boyd *et al.* [15] and the force field described in ref. 7. All minimizations were terminated when the r.m.s. deviation in coordinates was less than 0.002 Å. The cutoff for non-bonded interactions was set to 7 Å. Trial coordinates were derived from the crystal structures determined above, and manually modified using the graphics program ALCHEMY (TRIPOS Associates, St. Louis, MO). The strain energy of the complexes was determined as a function of the strain-free Ni–N bondlength in the range Ni–N = 1.61 to 2.41 Å. The hole sizes of the ligands were established as the minimum of a fifth order polynomial fitted through this data.

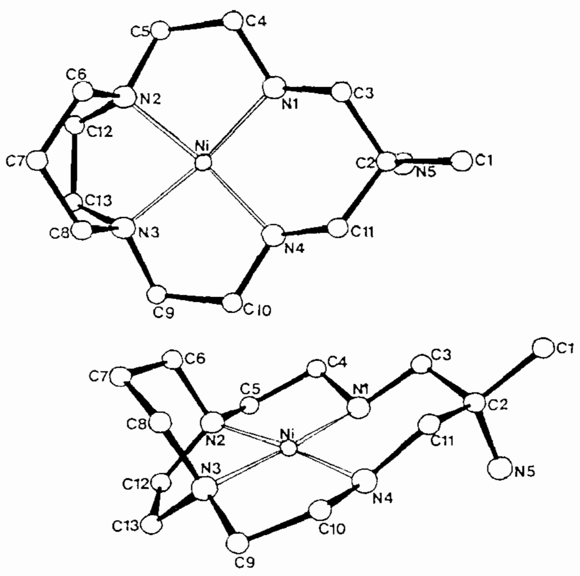
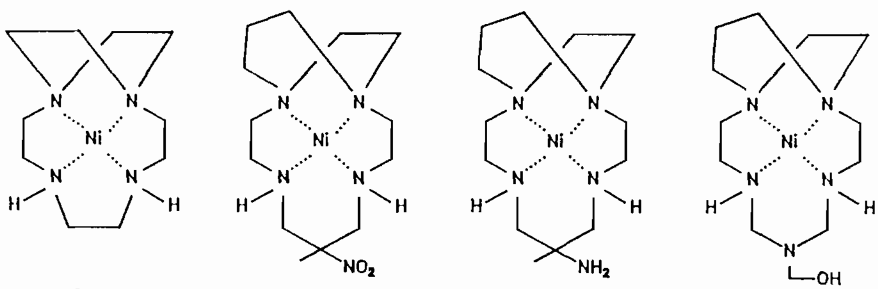


Fig. 4. ORTEP [14] drawings of $[Ni(AM\text{-}HP)]^{2+}$ showing the numbering scheme.



$V_{d-d}(cm^{-1})$	23980	23900	24020	23950
Mean M–N (Å)	1·86	1·91	1·89	1·89

Scheme 2.

Results and Discussion

The energies of the d–d transition in the complexes of low-spin Ni(II) with the ligands studied here are shown in Scheme 2.

It is seen that the energies of these d–d transitions are all very close to that in the complex with B-12-aneN$_4$, the highest known to date, and that the energy of the d–d transition for the complex of low-spin Ni(II) with AM-HP is by a narrow margin higher than that in the B-12-aneN$_4$ complex.' The results in chart 4 reinforce the interpretation [4] of the energy of the d–d transitions in complexes of transition metal ions with polyamine ligands being controlled primarily by the donor strengths

TABLE 6. Fractional coordinates (×10^4, Ni × 10^5) and equivalent isotropic temperature factors (Å^2, ×10^3, Ni × 10^4) for $[Ni(AM\text{-}HP)](ClO_4)_2 \cdot 0.5H_2O$

	x/a	y/b	z/c	U_{eq}^{a}
Ni	38166(3)	25083(6)	37781(2)	308(1)
N(1)	3730(2)	3728(4)	3119(2)	35(1)
N(2)	3803(2)	1228(4)	3165(2)	44(1)
N(3)	3890(2)	1169(4)	4358(2)	45(1)
N(4)	3833(2)	3657(4)	4462(2)	37(1)
N(5)	4123(3)	5930(5)	3842(3)	59(1)

(continued)

TABLE 6. *(continued)*

	x/a	*y/b*	*z/c*	$U_{eq}{}^a$
C(1)	2812(4)	6522(6)	3820(3)	67(2)
C(2)	3374(3)	5492(4)	3811(2)	43(1)
C(3)	3227(3)	4767(5)	3195(2)	42(1)
C(4)	3544(3)	3057(6)	2510(2)	51(1)
C(5)	3934(3)	1837(6)	2543(3)	54(1)
C(6)	3073(3)	643(6)	3134(3)	60(1)
C(7)	2964(3)	−83(6)	3720(4)	79(2)
C(8)	3157(3)	586(6)	4335(4)	67(2)
C(9)	4122(3)	1692(6)	4993(3)	60(1)
C(10)	3770(3)	2936(6)	5056(2)	54(1)
C(11)	3293(3)	4659(5)	4385(2)	39(1)
C(12)	4369(3)	316(5)	3389(3)	55(1)
C(13)	4421(3)	256(6)	4121(3)	59(1)
Cl(1)	5835(1)	3017(2)	4288(1)	55(1)
Cl(2)	1257(1)	2822(1)	3196(1)	56(1)
O(11)	5360(2)	2716(5)	3746(2)	76(1)
O(12)	6460(2)	3624(5)	4122(2)	88(1)
O(13)	6018(3)	1937(6)	4644(3)	126(2)
O(14)	5457(2)	3854(6)	4680(2)	96(2)
O(21)	1860(2)	2782(6)	3640(2)	103(2)
O(22)	1460(3)	2790(6)	2569(2)	114(2)
O(23)	827(5)	1886(10)	3309(3)	254(4)
O(24)	942(5)	3948(8)	3275(4)	216(4)
Ow	5000	4991(6)	2500	70(2)

$^a U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j (\mathbf{a}_i \cdot \mathbf{a}_j)$.

TABLE 7. Bond lengths (Å) and angles (°) for $[Ni(AM\text{-}HP)](ClO_4)_2 \cdot 0.5H_2O$

Ni–N(1)	1.907(4)	Ni–N(2)	1.887(4)
Ni–N(3)	1.884(4)	Ni–N(4)	1.898(4)
N(1)–C(3)	1.475(6)	N(1)–C(4)	1.490(6)
N(2)–C(5)	1.507(7)	N(2)–C(6)	1.500(6)
N(2)–C(12)	1.489(6)	N(3)–C(8)	1.505(7)
N(3)–C(9)	1.486(7)	N(3)–C(13)	1.511(7)
N(4)–C(10)	1.488(6)	N(4)–C(11)	1.473(6)
N(5)–C(2)	1.476(6)	C(1)–C(2)	1.526(7)
C(2)–C(3)	1.521(7)	C(2)–C(11)	1.526(7)
C(4)–C(5)	1.495(8)	C(6)–C(7)	1.493(10)
C(7)–C(8)	1.503(10)	C(9)–C(10)	1.498(8)
C(12)–C(13)	1.543(8)		
N(1)–Ni–N(2)	90.0(2)	N(1)–Ni–N(3)	173.7(2)
N(2)–Ni–N(3)	83.7(2)	N(1)–Ni–N(4)	96.2(2)
N(2)–Ni–N(4)	173.8(2)	N(3)–Ni–N(4)	90.1(2)
Ni–N(1)–C(3)	116.9(3)	Ni–N(1)–C(4)	107.5(3)
C(3)–N(1)–C(4)	110.8(4)	Ni–N(2)–C(5)	107.0(3)
Ni–N(2)–C(6)	106.9(3)	C(5)–N(2)–C(6)	111.0(4)
Ni–N(2)–C(12)	106.9(3)	C(5)–N(2)–C(12)	113.5(4)
C(6)–N(2)–C(12)	111.2(4)	Ni–N(3)–C(8)	106.3(3)
Ni–N(3)–C(9)	107.6(3)	C(8)–N(3)–C(9)	112.3(5)
Ni–N(3)–C(13)	106.9(3)	C(8)–N(3)–C(13)	110.2(5)
C(9)–N(3)–C(13)	113.2(4)	Ni–N(4)–C(10)	108.1(3)
Ni–N(4)–C(11)	115.0(3)	C(10)–N(4)–C(11)	111.5(4)
N(5)–C(2)–C(1)	115.0(5)	N(5)–C(2)–C(3)	107.6(4)
C(1)–C(2)–C(3)	107.8(4)	N(5)–C(2)–C(11)	108.0(4)
C(1)–C(2)–C(11)	107.3(4)	C(3)–C(2)–C(11)	111.1(4)
N(1)–C(3)–C(2)	114.1(4)	N(1)–C(4)–C(5)	107.8(4)
N(2)–C(5)–C(4)	107.7(4)	N(2)–C(6)–C(7)	111.8(5)
C(6)–C(7)–C(8)	115.5(5)	N(3)–C(8)–C(7)	112.1(5)
N(3)–C(9)–C(10)	108.6(4)	N(4)–C(10)–C(9)	108.6(4)
N(4)–C(11)–C(2)	113.5(4)	N(2)–C(12)–C(13)	109.2(4)
N(3)–C(13)–C(12)	108.7(4)		

of the nitrogens along the series primary < secondary < tertiary.

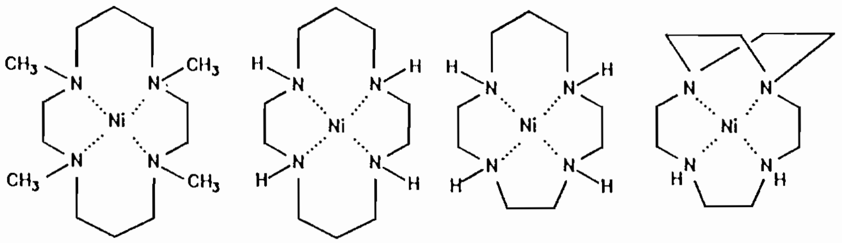
A second important point is the steric situation in the M–N bonds. Any steric effects which lead to distortion of the M–N bond length, or angles involving the M–N bond, lead to a lowering of the LF strength [4]. In other words, the LF strength is a measure of the overlap in the M–N bond, and any distortion which lowers the overlap in the M–N bond leads to a lowering of the LF. The classical example of this is the complex of low-spin Ni(II) with TMC (see Fig. 1), where there are four tertiary nitrogen donors present, which should lead to a LF of the highest possible strength with saturated nitrogen donors. However, the repulsion between the methyl groups on the N-donors leads [16] to a stretching of the Ni–N bond length from the strain-free value [7] of 1.91 Å out to a value of 1.99 Å [16]. This stretching of the Ni–N bond is accompanied by a drop in the energy of the d–d band as shown in Scheme 3.

An interesting point arising from the rather similar LF strengths of the complexes of AM-HP and B-12-aneN_4 with low-spin Ni(II) is that the factors leading to these high LF strengths are somewhat different in the two cases. Thus, there is definitely considerable compression of the Ni(II) in the B-12-aneN_4 complex, which might be expected to lead to a higher LF strength than in the AM-HP complex, which has the same donor strength (two tertiary and two secondary nitrogens), but normal Ni–N bond lengths. The reason that the compression of the Ni(II) in the B-12-aneN_4 complex does not lead to a higher LF strength than in the AM-HP complex with its normal Ni–N bond lengths lies in the distortion of the angles involving the Ni–N bond in the B-12-aneN_4 complex. The N–Ni–N angles between *trans* nitrogens in the B-12-aneN_4 complex average 169° [7], reflecting the fact that the Ni(II) is squeezed up out of the too-small cavity to lie some 0.2 Å above the plane formed by the four nitrogen donors. In contrast, the Ni(II) lies almost exactly in the plane of the four nitrogen donors of $[Ni(AM\text{-}HP)]^{2+}$. In addition, the Ni–N–C angles in the B-12-aneN_4 complex are [7] all very small, being in the vicinity of 103° instead of the usual 109.5°, further indicating poor overlap in the Ni–N bond, whereas those in the AM-HP complex tend to be in the vicinity of 107°. The slightly lower LF strengths of the NE-HP and HA-HP complexes above most likely reflect the electron withdrawing natures of the nitro and the hydroxymethyl groups respectively.

The fact that in the complex $[Ni(AM\text{-}HP)]^{2+}$ a very high LF has been achieved in a complex with near-normal Ni–N bond lengths, and that this high LF strength appears to be due to the high donor strength of the nitrogens, suggests that ligands such as PMT-HP discussed in the 'Introduction' with their four tertiary nitrogen donors would provide the ultimate LF strength. Hole sizes of the ligands PMT-HP, BI-PMT and PMT-DAC were determined by molecular mechanics calculations to be 1.89, 1.96 and 1.98 Å, respectively. Of these ligands, PMT-HP has the most appropriate hole size for low-spin Ni(II). Were it possible to make these three ligands, an unrivalled opportunity would be presented to test the variation in ligand field strength as a function of Ni–N bond length, with the nickel atom coordinated exclusively to tertiary nitrogen atoms.

It was our hope that the condensation of formaldehyde and ammonia with the Ni(II) BAE-HP complex would lead to the PMT-HP complex, but only HA-HP was obtained. In their study, Suh *et al.* [9] hoped to produce the Ni(II) complex of BI-PMT (Fig. 1) by the same condensation using methylamine in the place of ammonia, but only MA-PMT was obtained. On the basis of our result, it is also predicted that HA-PMT would have been produced using ammonia instead of the target Ni(II) complex of BI-PMT. It is of interest to consider here possible reasons for the failure of the condensation.

It has been suggested that the non-formation of the cap is due to the instability of the methylenediamine linkages containing uncoordinated primary or secondary nitrogens, preventing the formation of the bridging cap by fragmentation of the N–C–N linkage [9, 17]. Since HA-HP and MA-PMT have been prepared, and contain methylenediamine linkages, this was considered unlikely.



ν_{d-d} (cm^{-1})	19420	22470	23540	23980
Ni–N (Å)	1·99	1·93	1·90	1·86

Scheme 3.

Molecular mechanics calculations show that the Ni–N bond lengths in the complex with HA-HP are at the strain-free length of 1.91 Å, and the complex has a strain of 18.1 kcal/mol. When the formation of the cap is completed in the hypothetical PMT-HP complex, the Ni–N bond lengths are slightly shorter at 1.90 Å and the strain in the complex is 19.8 kcal/mol, not much greater than in the HA-HP precursor. Thus any obstacle to preparation of PMT-HP must lie in the formation of an intermediate.

When HA-HP reacts with formaldehyde, the H atoms on the secondary nitrogens are replaced by $-CH_2OH$ groups. Molecular mechanics calculations were performed on this intermediate with different $(H)O-C(H_2)-N-C$ torsion angles. The most stable conformation of HA-HP(PM)$_2$ has a very high strain energy of 30.5 kcal/mol and a Ni–N bond length of 1.93 Å. Similar results were obtained with the product of a hypothetically successful reaction of HA-PMT with formaldehyde. The strain energy of the HA-PMT complex was 13.7 kcal/mol, and the strain energy of the hypothetical *N,N'*-bis(hydroxymethyl) intermediate was calculated to be 29.5 kcal/mol.

To analyze the steric effect of the HPIP unit, the ethylene bridge of the homopiperazine unit of HA-HP(HM)$_2$ was deleted with ALCHEMY, and the resultant structure refined to a strain energy of 24.3 kcal/mol, 6.2 kcal/mol less than that of HA-HP(HM)$_2$. Therefore the bulk and rigidity of the homopiperazine bridge makes a substantial contribution to the strain in the HA-HP(HM)$_2$ intermediate. Thus it can be reasonably inferred that the high thermodynamic penalty of producing this intermediate is responsible for failure to prepare PMT-HP from HA-HP, and that a large contribution to the instability of the intermediate arises from the presence of the homopiperazine unit in the macrocycle. This effect is probably also responsible for the failure of Suh *et al.* to prepare BI-PMT instead of MA-PMT [9].

This work has thus demonstrated that high LF strengths can be achieved by producing nitrogens of high donor strength in sterically efficient situations, without significant compression of the metal ion. The design principle which becomes apparent is that to achieve even higher LF strengths, four tertiary nitrogen donors in a sterically efficient arrangement will be needed. An interesting property of the Ni(II) complex of AM-HP is that it is highly resistant to demetallation, having survived refluxing in cyanide and in sulphide for one week. This suggests that complexes of this type may exhibit the inertness found in the sepulchrates [18], and have potential usefulness in applications such as imaging agents [19], where resistance to demetallation is an important property.

Future Work

Alternative methods of producing ligands with tertiary nitrogen donors are currently being investigated. For example, the synthesis of ligands such as DMAMHP (Fig. 1) will be attempted, and their metal selectivity properties investigated. It is hoped that both structural characterization and stability constant studies of such a ligand will help to explain further the source of the high ligand field strength in macrocyclic complexes and ways of achieving this with minimum steric problems.

Supplementary Material

Tables of the fractional atomic coordinates and common isotropic temperature factors for the hydrogen atoms, anisotropic temperature factors, and calculated and observed structure factors are available from the authors on request.

Acknowledgements

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