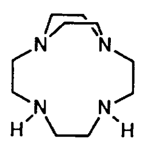
Crystallographic and Molecular Mechanics Study of a Cobalt(III) Complex of a Structurally Reinforced Macrocycle†

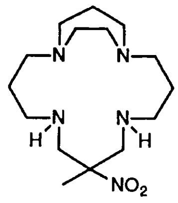
Thembakazi N. Mali, Peter W. Wade and Robert D. Hancock*
Centre for Molecular Design, Department of Chemistry, University of the Witwatersrand, Wits 2050, Johannesburg, South Africa

The complex $[CoL^6(Cl)][CoCl_4]\cdot H_2O$, where L^6 is the reinforced macrocycle 7-amino-7-methyl-1,5,9,13-tetraazabicyclo[11.2.2]heptadecane, has been prepared and its crystal structure determined. The green-black crystals are monoclinic, space group $P2_1/c$, with a = 8.778(2), b = 13.344(4), c = 19.380(8) Å, β = 98.48(2)°, Z = 4, and a final conventional R = 0.0736. The cobalt is co-ordinated in a planar fashion in the cavity of the macrocycle, with one axial co-ordination site occupied by the pendant primary amine group, and the other by a chloride. The Co–N bond lengths to the tertiary nitrogens of the piperazine bridge of the macrocycle are 2.01(1) and 2.02(1) Å, distinctly longer than those [1.97(1) Å] to the secondary amines in the cavity of the macrocycle. The Co–N distance to the pendant primary amine is 2.01(1) Å, and Co–Cl to the axially co-ordinated chloride *trans* to the pendant amine group is 2.26(1) Å. Molecular mechanics calculations are used to analyse the highly distorted co-ordination sphere around the Co^{III}, where the N–Co–N angle involving the nitrogens of the piperazine bridge of the macrocycle is only 73.5(4)°. The calculations reproduce the co-ordination geometry around the Co^{III} well, including the variation in Co–N bond length and the highly distorted N–Co–N angles.

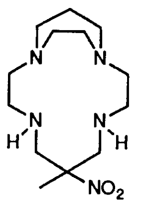
Research on tetraazamacrocycles has led us to the conclusion[1–5] that these ligands, and also other saturated macrocycles, are too flexible to show genuine size-match selectivity. We have accordingly studied a variety of *reinforced* macrocycles.[6–10] These reinforced macrocycles, the first examples of which were synthesised by Wainwright and Ramasubbu,[11,12] show much greater rigidity than do their non-reinforced analogues. This is seen in the considerable compression[6] of the square-planar nickel(II) ion by the ligand L^1, or very considerable stretching of the Cu–N bond in the complex of Cu^{II} with L^2.[10] The ligand-field strengths of the complexes of L^3 and L^4 with low-spin Ni^{II} were[9] higher than any previously reported for low-spin Ni^{II} with four saturated nitrogen donors. This was attributed[9] to the near exact fit of the Ni^{II} into the cavity of the ligand, coupled with the tertiary nature of the nitrogen donors of the bridge. Ligands of the L^5 type have been synthesised by the template method of Lawrance and co-workers.[13] This is a synthetically attractive route to reinforced macrocycles. Reduction of the nitro group on L^5 gives[14] the ligand L^6, which has a pendant amine group which may or may not co-ordinate to the metal ion. In the case of the analogous L^4 with square-planar nickel(II) or copper(II) the pendant amine group is[9] not co-ordinated to the metal ion. In other ligands containing similar pendant amine groups, as in the iron(III) complex of L^7,[15] both pendant amine groups may be co-ordinated to the metal ion. Lawrance and co-workers[14] have reported the synthesis of $[CoL^6(Cl)][ClO_4]_2$, and suggested that the pendant amine group is co-ordinated to the cobalt. The ligand L^6 has a large cavity, as indicated by the long Cu–N bond length of 2.05 Å. We have previously[16] emphasized that the strain-free Co–N bond length for Co^{III} bonded to saturated amines is 1.92 Å, and that in most cases the observed bond lengths, which tend to centre on 1.97 Å, reflect stretching of the Co–N bond in response to steric crowding. It was anticipated that the stretching of the Co–N bond would in this case be quite severe.



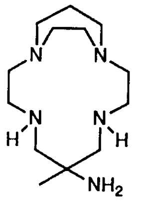
L^1



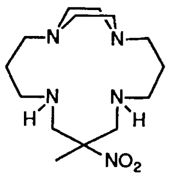
L^2



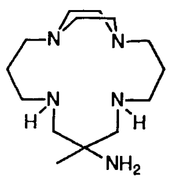
L^3



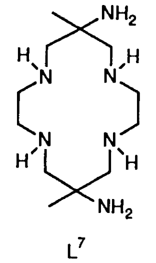
L^4



L^5



L^6



L^7

We report here the synthesis of the complex $[CoL^6(Cl)][CoCl_4]\cdot H_2O$ and a crystallographic study of its structure. The co-ordination sphere around the cobalt(III) in the $[CoL^6(Cl)]^{2+}$ cation turned out to be highly distorted, and it was felt that this would be an excellent test of the ability of molecular mechanics calculations[4] to reproduce structures of co-ordination compounds. Thus, such calculations on the $[CoL^6(Cl)]^{2+}$ cation are also reported.

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non S.I. units employed: dyn = 10^{-5} N, cal = 4.184 J.

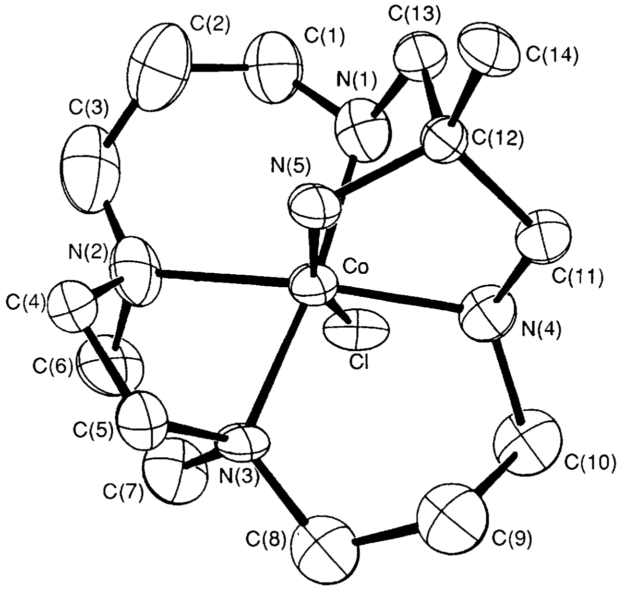


Fig. 1 An ORTEP drawing of the complex cation of $[CoL^6(Cl)][CoCl_4]\cdot H_2O$, showing the numbering scheme

Table 1 Details of the crystallographic analysis of $[CoL^6(Cl)][CoCl_4]\cdot H_2O$

Formula	$C_{14}H_{33}Cl_5Co_2N_5O$
M	583.58
Crystal colour	Black-green
System	Monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	8.778(2)
b/Å	13.344(4)
c/Å	19.380(8)
β/°	98.48(2)
U/Å^3	2245.23
Z	4
D_c/g cm^{-3}	1.72
D_m/g cm^{-3}	1.70
T/K	298
λ (Mo-Kα)/Å	0.710 73
μ/cm^{-1}	11.30
F(000)	1172.0
Transmission coefficients (%)	73.1–99.6
θ range/°	1–25
Reflections measured	3412
Reflections used [$F > 2\sigma(F_o)$]	2636
Parameters refined	257
Maximum shift/e.s.d.	2.68
Residual electron density (maximum, minimum)/e Å^{-3}	1.22, −0.82
R	0.0736
R'	0.0736

Table 2 Fractional coordinates (× 10^4) for $[CoL^6(Cl)][CoCl_4]\cdot H_2O$

Atom	X/a	Y/b	Z/c
Co(1)	3 321(2)	7 860(1)	1 395(1)
Cl(3)	4 575(4)	8 990(3)	814(2)
N(1)	5 397(10)	7 432(8)	1 810(5)
N(2)	2 908(10)	6 890(7)	599(5)
N(3)	1 169(12)	18 153(9)	909(5)
N(4)	3 509(12)	8 866(9)	2 147(7)
N(5)	2 650(10)	6 986(8)	2 137(5)
C(1)	6 239(13)	16 753(11)	1 371(7)
C(2)	5 247(14)	15 848(11)	1 092(7)
C(3)	4 118(14)	16 147(11)	456(7)
C(4)	1 475(12)	16 338(10)	736(6)
C(5)	384(13)	17 151(11)	920(6)
C(6)	7 568(16)	2 495(11)	5 038(7)
C(7)	1 312(18)	18 314(12)	148(7)
C(8)	303(17)	9 022(14)	1 124(8)
C(9)	775(16)	19 340(12)	1 848(10)
C(10)	2 296(17)	19 684(12)	2 060(9)
C(11)	3 647(13)	18 384(9)	2 846(6)
C(12)	−3 845(11)	12 738(9)	−2 750(6)
C(13)	−5 362(12)	13 026(9)	−2 527(6)
C(14)	−3 686(13)	13 311(10)	−3 420(6)
O(H_2O)	2 497(25)	1 001(20)	343(14)
Co(2)	1 200(2)	13 646(1)	1 527(1)
Cl(1)	497(3)	12 205(3)	2 026(2)
Cl(2)	2 800(3)	14 496(2)	2 378(2)
Cl(4)	874(3)	9 623(3)	3 813(2)
Cl(5)	2 629(4)	3 349(3)	675(2)

Table 3 Selected bond lengths (Å) and angles (°) for $[CoL^6(Cl)][CoCl_4]\cdot H_2O$ *

Co(1)–N(1)	1.97(1)	Co(1)–N(2)	2.01(1)
Co(1)–N(3)	2.02(1)	Co(1)–N(4)	1.97(1)
Co(1)–N(5)	2.01(1)	Co(1)–Cl(3)	2.26(1)
N(1)–C(1)	1.51(1)	N(2)–C(4)	1.51(1)
C(1)–C(2)	1.54(2)	C(2)–C(3)	1.52(1)
Co(2)–Cl(1)	2.28(1)	Co(2)–Cl(2)	2.30(1)
Co(2)–Cl(5)	2.25(1)	N(3)–C(8)	1.48(2)
N(1)–Co(1)–N(2)	100.3(4)	N(1)–Co(1)–N(3)	173.5(5)
N(1)–Co(1)–N(4)	85.7(4)	N(1)–Co(1)–N(5)	83.7(4)
N(2)–Co(1)–N(3)	73.5(4)	N(2)–Co(1)–N(4)	174.0(4)
N(2)–Co(1)–N(5)	97.9(4)	N(3)–Co(1)–N(4)	100.6(4)
N(3)–Co(1)–N(5)	95.4(3)	N(4)–Co(1)–N(4)	82(1)
N(1)–Co(1)–Cl(3)	84.7(3)	N(2)–Co(1)–Cl(3)	95.4(3)
N(3)–Co(1)–Cl(3)	97.4(4)	N(4)–Co(1)–Cl(3)	85.4(4)
N(5)–Co(1)–Cl(3)	163.8(3)	Co(1)–N(1)–C(1)	117(1)
Co(1)–N(2)–C(3)	120.9(7)	Co(1)–N(3)–C(5)	102.7(7)
Co(1)–N(2)–C(4)	103.9(7)	Co(1)–N(3)–C(7)	106(1)
Co(1)–N(3)–C(8)	120(1)	Co(1)–N(4)–C(11)	111(1)
Co(1)–N(4)–C(10)	116(1)	C(5)–C(4)–C(5)	116(1)
N(2)–C(3)–C(2)	115(1)	N(2)–C(4)–C(5)	105(1)
C(10)–C(9)–C(8)	120(2)	Cl(1)–Co(2)–Cl(2)	106.7(1)
Cl(1)–Co(2)–Cl(2)	112.2(2)	Cl(1)–Co(2)–Cl(2)	105.4(1)

* At the suggestion of a referee, bond lengths have been rounded off to two decimal places, and many angles to the nearest degree, although the TABL routine of SHELX[18] suggested standard deviations somewhat better than this.

Experimental

Synthesis of the Complex $[CoL^6(Cl)][CoCl_4]$.—The complex $[CuL^5(H_2O)][ClO_4]_2\cdot H_2O$ was synthesised by the method of Lawrance and co-workers.[14] It (6 g) was dissolved in water (100 cm^3) and reduced in an autoclave under 10 atm (*ca.* 10^6 Pa) H_2 for 72 h in the presence of Pd/C catalyst (0.5 g). The solution was filtered and adjusted to pH 12 with NaOH. The free amine L^6 was obtained from the basified solution by repeated extraction with portions (50 cm^3) of chloroform. The combined chloroform extracts were dried over magnesium sulfate overnight, and, after removing the drying agent, the chloroform was removed under vacuum. The final product was an oil (2 g), which was dissolved in methanol (20 cm^3) and $CoCl_2\cdot 6H_2O$ (2.6 g) in methanol (20 cm^3) added. Air was bubbled through this solution for 1 h, concentrated HCl (3 cm^3) was added, and air was bubbled through the solution for 1 h. The solution was filtered and reduced to one third of its initial volume under vacuum. On standing, almost black crystals with a green tinge were deposited. These were recrystallised from hot water and washed with acetone and diethyl ether; yield 0.8 g (Found: C, 28.50; H, 5.55; N, 12.0. Calc. for $C_{14}H_{33}Cl_5Co_2N_5O$: C, 28.85; H, 5.70; N, 12.00%).

X-Ray Crystallography.—Crystals of $[CoL^6(Cl)][CoCl_4]\cdot H_2O$ suitable for crystallography were selected from those obtained as described above. Standard oscillation and Weissenberg techniques were employed. The density was

Table 4 Selected observed bond lengths (Å) and angles (°) in the $[CoL^6(Cl)]^{2+}$ complex cation, together with those calculated by molecular mechanics, as described in the text, for comparison

	Calc.	Obs.		Calc.	Obs.
Co(1)–N(1)	1.97	1.97	Co(1)–N(2)	2.01	2.01
Co(1)–N(3)	2.01	2.02	Co(1)–N(4)	1.98	1.97
Co(1)–N(5)	1.97	2.01	Co(1)–Cl	2.25	2.26
N(1)–Co(1)–N(2)	98.8	100.3	N(1)–Co(1)–N(3)	172.8	173.5
N(1)–Co(1)–N(4)	88.4	85.7	N(1)–Co(1)–N(5)	84.0	83.7
N(1)–Co(1)–Cl(3)	87.7 (85.4)*	84.7	N(2)–Co(1)–N(3)	74.0	73.5
N(2)–Co(1)–N(4)	172.8	174.0	N(2)–Co(1)–N(5)	95.6	97.9
N(2)–Co(1)–Cl(3)	93.8 (97.1)	95.4	N(3)–Co(1)–N(4)	98.8	100.6
N(3)–Co(1)–N(5)	95.6	95.4	N(3)–Co(1)–Cl(3)	93.8 (97.1)	97.4
N(4)–Co(1)–N(5)	83.9	82.4	N(4)–Co(1)–Cl(3)	87.7 (85.7)	85.4
N(5)–Co(1)–Cl(3)	167.5 (165.2)	163.8	Co(1)–N(1)–C(1)	118.2	116.5
Co(1)–N(2)–C(3)	122.0	120.9	Co(1)–N(2)–C(4)	103.6	103.9
Co(1)–N(3)–C(8)	122.0	120.3	Co(1)–N(4)–C(10)	118.2	115.8
C(10)–C(9)–C(8)	109.8	120			

* Values in parentheses calculated with a N–Co–Cl force constant of 0.2 rather than 1.0 mdyn Å^{-1}, as discussed in the text. The other angles are largely unaffected by this alteration.

Table 5 Strain energies (kcal mol^{-1}) for the chair–chair, chair–boat and boat–boat conformers of $[CoL^6(Cl)]^{2+}$, as well as for the complex $[CoL^6Cl(NH_3)]^{2+}$ with the pendant amine group unco-ordinated*

Contribution to strain energy	$[CoL^6(Cl)]^{2+}$ Chair–chair	Chair–boat	Boat–boat	$[CoL^6Cl(NH_3)]^{2+}$ (unco-ordinated pendant amine)
Bond length	4.51	4.80	4.06	7.79
Bond angle	22.27	23.37	23.94	25.85
Torsional	14.50	14.57	16.01	9.91
Non-bonded	8.63	8.34	9.05	13.14
Total	49.91	51.08	53.06	56.71

* Diagrams of the chair–chair and boat–chair conformers, as well as the complex with the pendant amine not co-ordinated, are in Fig. 2.

determined by flotation on mixtures of dichloroethane and dibromomethane. The data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (λ 0.710 03 Å). The cell dimensions were obtained from least-squares refinement of 25 high θ reflections. An ω–2θ scan mode was used with a scan width of 0.6 + 0.35 tan θ and a variable scan speed. Three standard reflections were monitored and showed no significant variation over the data collection. Lorentz polarization and absorption corrections were applied to the data according to the method of North *et al.*[17] Crystal data and data collection parameters are given in Table 1. The structure was determined by using Patterson and Fourier techniques with the program SHELX.[18] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at geometrically calculated positions, and included in the refinement with a common isotropic thermal parameter. The presence of a water molecule was indicated by the microanalysis, and this water was found during the course of refinement. Full-matrix least-squares refinement with unit weights converged to $R = 0.0736$. Fractional atomic coordinates for the structure are given in Table 2, and a selection of bond lengths and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Molecular Mechanics Calculations.—These were carried out using the program ALCHEMY[19] for model building and graphics display, and MOLBLD[20] for energy minimization. The force constants were as used by Snow and co-workers[21] in their calculations on complexes of Co^{III} with polyamines. The trial coordinates for the $[CoL^6(Cl)]^{2+}$ cation were generated on ALCHEMY, and the energy minimization of these carried out using MOLBLD.

Results and Discussion

An ORTEP[22] drawing of the complex $[CoL^6(Cl)]^{2+}$ is shown in Fig. 1, with the numbering scheme used. In Table 3 is given a selection of bond angles and lengths. The cobalt lies in the plane of the nitrogen donors of the macrocyclic ring, with the pendant nitrogen on one ring occupying the other co-ordination site. The co-ordination geometry around the cobalt is extremely distorted, with the N–Co–N angle involving the tertiary nitrogens from the piperazine bridge being only 73.5 instead of the 90° expected for a regular octahedron. The Co–N bonds to these bridging nitrogens are 2.01 and 2.02 Å, considerably stretched from the usual bond length of 1.96 Å observed in low-strain complexes of cobalt(III). The cobalt(III) is ill suited to co-ordinate to a piperazine group as is present in L^6, since such a group has minimum strain when co-ordinated to a large metal ion with M–N of 3.8 Å and N–M–N angle of 39°. The Co^{III} has a strain-free M–N length of 1.925 Å,[4] and an ideal N–Co–N angle of 90°, so that the extent of mismatch is extreme. The compromise one observes is that the Co–N lengths to the piperazine nitrogens are stretched to 2.01–2.02 Å, and the N–Co–N angle is compressed to 73.5(4)°.

The structure of the $[CoL^6(Cl)]^{2+}$ cation is the most distorted we have come across in complexes of Co^{III} with saturated polyamine ligands. It was therefore of considerable interest to see how well the molecular mechanics calculations would reproduce this distorted structure. Using the parameters of Snow and co-workers[21] the structure is seen in Table 4 to be reproduced with reasonable accuracy. The only feature of the predicted structure, as far as the co-ordination sphere of the Co^{III} is concerned, that could be signifcantly improved is the Cl–Co–N angles, which are not predicted to be as distorted as observed. This relates to the value of the Cl–Co–N force constant, which was developed[21] using a largely undistorted complex, which did not provide a sensitive indication of its correct value. Lowering the Cl–Co–N force constant from 1.00 to 0.2 mdyn Å^{-1} improves the level of agreement (figures in parentheses in Table 4). The N–Co–N force constant is[21] for comparison 0.68 mdyn Å^{-1}. It is felt that this constant may be more reasonable, since the Co–Cl bond should be weaker than the Co–N bond, and hence more easily distorted.

A second feature of the complex not well reproduced by the calculations is the C–C–C angles of the six-membered chelate rings of the macrocycle. The calculation predicts that these angles should have close to normal values of about 109°, whereas the crystal structure suggests that they should be about 120°. The structure shows, as can be seen in the thermal ellipsoids of Fig. 1, large thermal motion for the central carbon atoms of these trimethylene bridges, with (Table 3) large uncertainties attached to the C–C–C angles. It may be, as suggested by a referee, that this reflects the thermal motion of these atoms, or, which we feel is more likely, some disorder in this structure. The type of disorder that would account for the probably only apparent large thermal motion would involve a percentage of the complex cations present having boat–boat or boat–chair conformations of the six-membered chelate rings, in addition to the chair–chair conformer observed. To test the possibility of conformers involving boat conformations as well as chair conformations in the six-membered chelate rings being present, the energy of these conformers was also calculated. It was found (Table 5) that the boat–chair conformer was only slightly higher in strain than the observed chair–chair conformer. A percentage

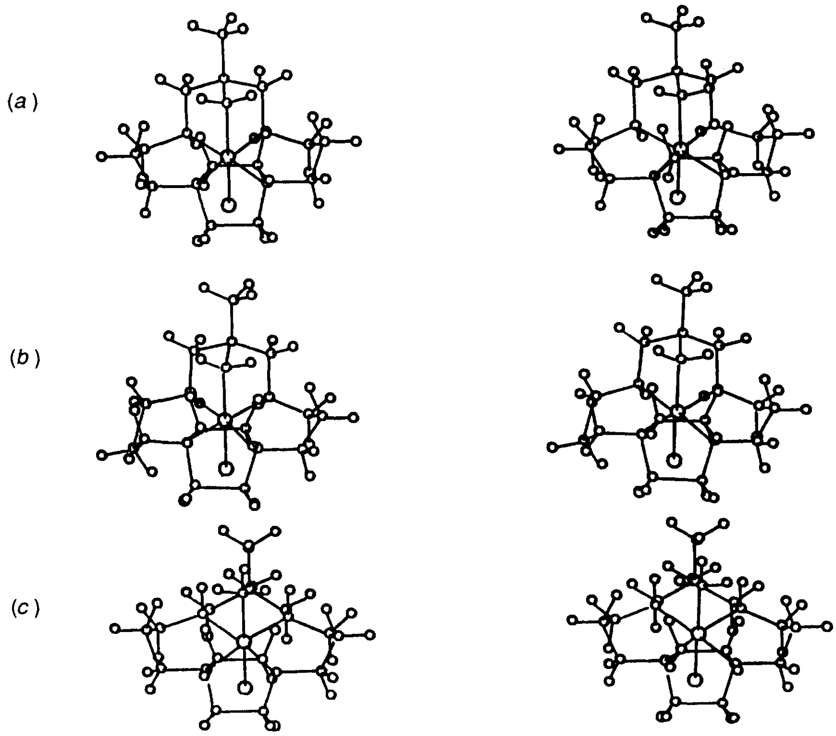


Fig. 2 Stereoviews (ALCHEMY program) of the molecular mechanics generated structures of (*a*) the observed chair–chair conformer of the [CoL^6(Cl)]$^{2+}$ cation, (*b*) the boat–chair conformer of [CoL^6(Cl)]$^{2+}$, and (*c*) the complex [CoL^{6}Cl(NH$_3$)]$^{2+}$, where the pendant amine group on the ligand is not co-ordinated

of the boat–chair conformer present would account for the apparent large thermal motion. In support of this the C–C bond lengths in this bridge at about 1.44 Å are unusually short, a further sign[4] of disorder. The large C–C–C angles of 120(2)° are thus probably not representative of the structure, and the values of 109.8° indicated by the molecular mechanics calculation are to be preferred.

As can be seen in Fig. 1, the Cl–Co–N(5) angle is considerably distorted away from the expected 180°. The molecular mechanics calculations show that this is largely due to repulsive van der Waals interactions between the co-ordinated chloride and the double bridge of the piperazine ring. This suggests, as was hoped would be the case, that co-ordination at the vacant axial site of this complex would be strongly sterically hindered. This should lead to interesting kinetic and thermodynamic effects in the co-ordination of ligands to this site.

The strain energy in [CoL^6(Cl)]$^{2+}$ at 49.9 kcal mol^{-1} is the highest that we have come across, compared with, for example, a value of 35.8 kcal mol^{-1} for the next most highly strained complex [CoL$_2$]$^{3+}$ (L = 4-azaheptane-1,7-diamine), or of 17.1 kcal mol^{-1} for the low-strain complex [Co(dien)$_2$]$^{3+}$ (dien = diethylenetriamine). These energies were all calculated[23] with the same force field, and, although one cannot really directly compare strain energies in molecules with different numbers and types of atoms, the differences are indicative of the relative amounts of strain in these complexes. The high steric strain in [CoL^6(Cl)]$^{2+}$ is in part due to the steric requirements of the piperazine bridge, but also the formation of a boat conformation six-membered ring in order that the pendant nitrogen should co-ordinate to the cobalt. This led us to wonder whether the conformer with the pendant nitrogen not co-ordinated would not be significantly lower in energy, and why the pendant nitrogen did in fact co-ordinate. The program ALCHEMY was therefore used to build up the conformer (Fig. 2) with the pendant amine not co-ordinated to the cobalt, and replaced by an ammonia to simulate a ligand which would have to complete the octahedral co-ordination geometry for the Co^{III}. The parameters for the ammonia were the same as used for the other nitrogens co-ordinated to the cobalt. The molecular mechanics calculation showed that the strain energy (Table 5) of this complex was considerably higher than that with the pendant amine co-ordinated to the cobalt. The increase in strain is greater than would be expected from an increase of only four atoms, the nitrogen and three hydrogens of ammonia. This suggests that the pendant amine co-ordinates to the cobalt, even though this generates very significant amounts of steric strain, because the alternative of having it not co-ordinated would lead to even more steric strain, with the occupation of the axial co-ordination site by a unidentate ligand such as ammonia.

The very sterically crowded situation produced at the axial co-ordination site of [CoL^6(Cl)]$^{2+}$, as evidenced by crystallography and molecular mechanics, suggests that the complex should have interesting ligand-substitution properties with regard to the axial co-ordination site, and this aspect of the chemistry of this complex is currently being studied.

Acknowledgements

The authors thank the University of the Witwatersrand, and the Foundation for Research Development, for generous funding for this work.

References

1 V. J. Thom, G. D. Hosken and R. D. Hancock, *Inorg. Chem.*, 1985, **24**, 3378.
2 V. J. Thom and R. D. Hancock, *J. Chem. Soc., Dalton Trans.*, 1985, 1877.
3 V. J. Thom, C. C. Fox, J. C. A. Boeyens and R. D. Hancock, *J. Am. Chem. Soc.*, 1984, **106**, 5947.
4 R. D. Hancock, *Prog. Inorg. Chem.*, 1989, **37**, 187.
5 R. D. Hancock, *Acc. Chem. Res.*, 1990, **23**, 253.
6 R. D. Hancock, S. M. Dobson, A. Evers, P. W. Wade, M. P. Ngwenya, J. C. A. Boeyens and K. P. Wainwright, *J. Am. Chem. Soc.*, 1988, **110**, 2788.
7 R. D. Hancock, A. Evers, M. P. Ngwenya and P. W. Wade, *J. Chem. Soc., Chem. Commun.*, 1987, 1129.

8 P. W. Wade, R. D. Hancock, J. C. A. Boeyens and S. M. Dobson, *J. Chem. Soc., Dalton Trans.*, 1990, 483.

9 R. D. Hancock, M. P. Ngwenya, P. W. Wade, J. C. A. Boeyens and S. M. Dobson, *Inorg. Chim. Acta*, 1989, **164**, 73.

10 G. Pattrick and R. D. Hancock, *Inorg. Chem.*, 1991, **30**, 1419.

11 K. P. Wainwright, *Inorg. Chem.*, 1980, **19**, 1396.

12 K. P. Wainwright and A. Ramasubbu, *J. Chem. Soc., Chem. Commun.*, 1982, 277.

13 P. Comba, N. F. Curtis, G. A. Lawrance, M. A. O'Leary, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1988, 2145; P. Comba, N. F. Curtis, G. A. Lawrance, A. M. Sargeson, B. W. Skelton and A. H. White, *Inorg. Chem.*, 1986, **25**, 4260.

14 L. M. Engelhardt, G. A. Lawrance, T. M. Manning and A. H. White, *Aust. J. Chem.*, 1989, **42**, 1859.

15 P. V. Bernhardt, T. Hambley and G. A. Lawrance, *J. Chem. Soc., Chem. Commun.*, 1989, 553.

16 V. J. Thom, J. C. A. Boeyens, G. J. McDougall and R. D. Hancock, *J. Am. Chem. Soc.*, 1984, **106**, 3198.

17 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

18 G. M. Sheldrick, in *Crystallographic Computing*, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, 1985.

19 ALCHEMY, Tripos Associates, St. Louis, MO, 1989.

20 R. H. Boyd, S. M. Breitling and M. Mansfield, *Am. Inst. Chem. Eng. J.*, 1973, **19**, 1016.

21 M. R. Snow, *J. Am. Chem. Soc.*, 1970, **92**, 3610; D. A. Buckingham, I. E. Maxwell, A. M. Sargeson and M. R. Snow, *J. Am. Chem. Soc.*, 1970, **92**, 3617.

22 C. K. Johnson, ORTEP, Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

23 T. W. Hambley, G. H. Searle and M. R. Snow, *Aust. J. Chem.*, 1982, **35**, 1285.

Received 21*st June* 1991; *Paper* 1/03144I