DALTON
FULL PAPER

# Low-spin iron(II) in a small unsymmetrical $N_6$ macrocycle

**Sally Brooker** *† **and Timothy J. Simpson**

*Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand*

A small unsymmetrical $N_6$ macrocycle has been prepared by template methods, from 2,6-di[*N*-(3-aminopropyl)-aminomethyl]pyridine **I** and 2,6-diacetylpyridine, as $[BaL^1][ClO_4]_2$ **1**. Transmetallation with iron(II) perchlorate, in air, yielded an intense dark purple complex, $[FeL^1][ClO_4]_2$ **2**. A single-crystal structure determination of **2** revealed that the iron(II) ion has a distorted $N_6$ octahedral geometry. Wrapping of this small, fairly inflexible macrocycle around the octahedral sites on the iron atom is facilitated by the presence of the two amine bonds. The iron(II) is low spin and the $^1H$ and $^{13}C$ NMR spectra are correspondingly sharp and unshifted.

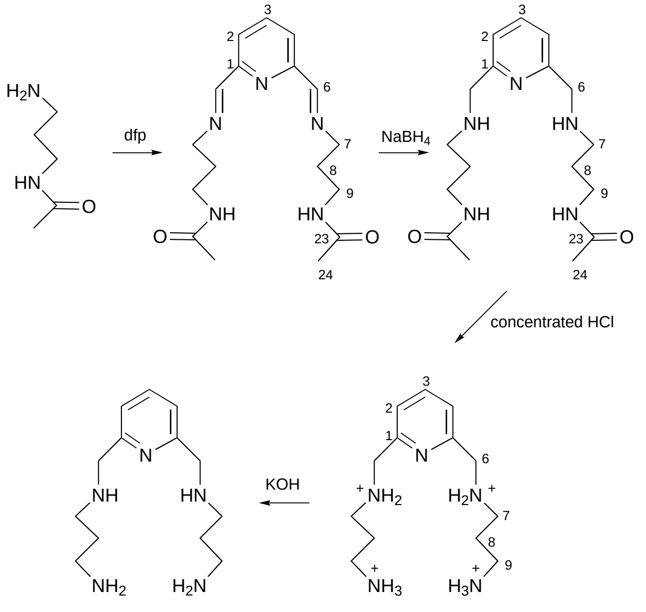
We have recently developed a general route to 'unsymmetrical' macrocycles, that is macrocycles which provide two distinct types of metal-binding sites.[1–3] Such ligands are of considerable interest as they open up the possibility of isolating mixed co-ordination geometry, mixed valence and/or mixed metal complexes.[1–4] In this paper we report the multistep synthesis (Scheme 1) of a suitable precursor, 2,6-di[*N*-(3-aminopropyl)aminomethyl]pyridine **I**, and the results of our investigation into the preparation of barium(II) and iron(II) complexes of the small, unsymmetrical $N_6$ macrocycle $L^1$ derived from **I** (Fig. 1).

In the case of the related, much larger, symmetrical, 30-membered macrocycle $L^2$ (Fig. 1) a mononuclear, low-spin iron(II) complex is formed: a structure determination showed that the iron(II) atom has a distorted $N_6$ octahedral geometry.[5] It was therefore of interest to determine whether the less flexible 20-membered macrocycle $L^1$ could provide a similar '$N_6$ octahedral wrap' around a single iron(II) ion or, as it is large enough to accommodate two transition-metal ions in differing sites,[3,6] yield a diiron complex. Busch[7] has commented that [18]ane$N_6$ (1,4,7,10,13,16-hexaazacyclooctadecane) is the smallest ligand theoretically capable of providing an '$N_6$ octahedral wrap', and octahedral complexes of other 18-membered macrocycles are known,[8] however in all of these examples the rings contain at least four relatively flexible amine links which aid in twisting the cyclic ligand around the octahedral sites. Here we investigate whether or not the small, relatively inflexible macrocycle $L^1$ is able to provide such a geometry for $Fe^{II}$.

## Results and Discussion

### Synthesis of 2,6-di[*N*-(3-aminopropyl)aminomethyl]pyridine I

Our stepwise synthesis of the 'two armed' diamine **I** (Scheme 1) is based on the synthesis of a smaller 'two armed' diamine, derived from reaction of *N*-acetylethane-1,2-diamine with 2,6-diacetylpyridine, reported by Martell and co-workers.[9] However, unlike *N*-acetylethane-1,2-diamine, *N*-acetylpropane-1,3-diamine is not commercially available. Recent literature indicated that it may be difficult to monoacetylate diamines,[10] but modification of the 1941 preparation of *N*-acetylethane-1,2-diamine[11] has allowed us to prepare a range of pure monoacetylated amines,[1–3] including *N*-acetylpropane-1,3-diamine. The subsequent steps are straightforward and the material obtained from the reaction sequence, **I**, was used without further purification.



**I** 4Cl⁻

**Scheme 1** Stepwise synthesis of 2,6-di[*N*-(3-aminopropyl)aminomethyl]pyridine **I**

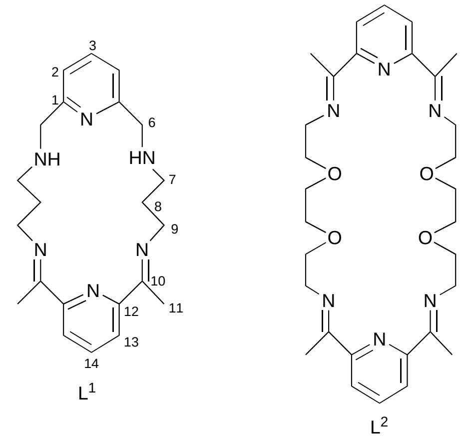


**Fig. 1** Unsymmetrical macrocycle $L^1$ and symmetrical macrocycle $L^2$

### Macrocyclic complexes

As the barium(II) ion was successfully employed to template the formation of related 20-membered symmetrical Schiff-base

---

† E-Mail: sbrooker@alkali.otago.ac.nz

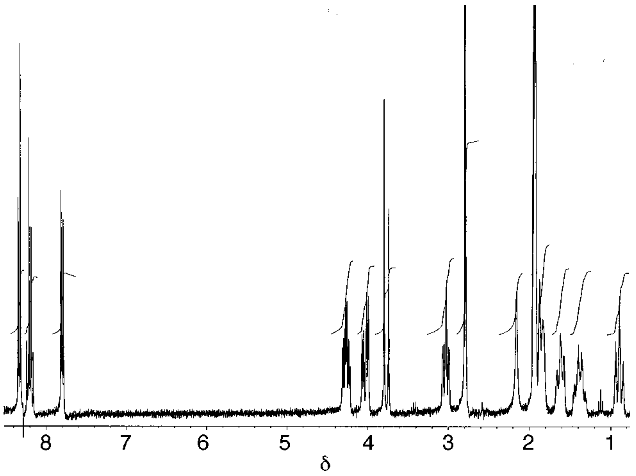


**Fig. 2** Proton NMR spectrum of $[FeL^1][ClO_4]_2$ **2** in $CD_3CN$

macrocycles[6,12] this ion was the logical choice for the template cyclisation of **I** and 2,6-diacetylpyridine to form $L^1$, and resulted in the successful isolation of $[BaL^1][ClO_4]_2$ **1**. The infrared spectrum showed that cyclisation had occurred; a C=N stretch was present at 1626 $cm^{-1}$ and no peaks corresponding to unreacted carbonyl or primary amine were observed. This was confirmed by elemental analysis and FAB mass spectral results. In the solid state the counter ions appear to be co-ordinated to the $[BaL^1]^{2+}$ as the perchlorate peaks at *ca.* 1100 and 620 $cm^{-1}$ in the infrared spectrum are clearly split.

Obtaining sufficiently concentrated representative samples for NMR studies was difficult due to the low solubility of complex **1** in common solvents. The $^1H$ NMR spectrum obtained from a filtered $CD_3CN$ solution showed considerable temperature dependence. At 75 °C the complex picture simplified to a $^1H$ NMR spectrum approximating that initially expected for **1**: a simple $^{13}C$ NMR spectrum was also obtained at this temperature. It was not possible to determine whether this variation with temperature was due to fluxional behaviour or to isomer interconversion, although the former is the more probable cause. Comparison of this macrocyclic complex with the related tetraimine complexes prepared and crystallised by Fenton and co-workers[12] and Nelson and co-workers[6] indicates that either a *syn* or an *anti* arrangement of NH protons is possible. Attempts to grow single crystals to help clarify this point were unsuccessful.

Transmetallation of complex **1** with iron(II) perchlorate gave $[FeL^1][ClO_4]_2$ **2** in good yield. The C=N stretch observed is weaker and appears as a shoulder on the pyridine ring stretching vibration at 1605 $cm^{-1}$ in the infrared spectrum of this intense purple-black material. This effect has been observed before for low-spin iron(II) diimine species [due to strong $t_{2g}(Fe)–p_{\pi *}(L^1)$ interactions].[5] The conclusion that the iron(II) ion was low spin was reinforced by the facts that the NMR spectra were sharp and unshifted (Fig. 2) and that the Evans method gave a magnetic moment of zero. The low-spin configuration requires the presence of a strong ligand field so we expected the macrocycle would wrap around just one iron(II) ion and that it would be bound by the six macrocycle nitrogen atoms in an approximately octahedral geometry. Elemental analysis, FAB mass and $^1H$ NMR spectral results were consistent with this prediction and comparison of the solution and solid-state UV/VIS spectra indicated that the solid-phase structure is maintained in solution.

Again two diastereoisomers need to be considered due to the possibility of *syn* or *anti* arrangements of the NH protons. To investigate which isomer would be preferred, the structure[5] of the low-spin mononuclear iron(II) complex of the large tetraimine macrocycle $L^2$ was used to derive parameters for a CHARMM minimisation of $[FeL^1]^{2+}$.[13] These calculations reinforced our initial conclusion (based on a comparison of simple Cochrane Minit molecular models of the two isomers) that the *anti* isomer would be hugely preferred over the *syn* isomer. This is because the two pyridine 'head units' need to be at approximately right angles to each other (to form $N_6$ octahedral $Fe^{II}$), and the short $(CH_2)_3$ alkyl chain therefore struggles to connect the two 'head units'. This was not a problem in $L^2$ due to the lengthy $CH_2CH_2OCH_2CH_2OCH_2CH_2$ connector. However, the planarity requirement applying to both tridentate pyridine diimine 'head units' in $L^2$ only applies to one 'head unit' in $L^1$ as the other 'head unit' is a pyridine diamine unit and as such it is much more flexible. In the *anti* isomer full advantage is taken of this flexibility: the amine nitrogen atoms move out of the pyridine ring plane and assist the $(CH_2)_3$ chain to reach around to the approximately planar pyridine diimine 'head unit'.

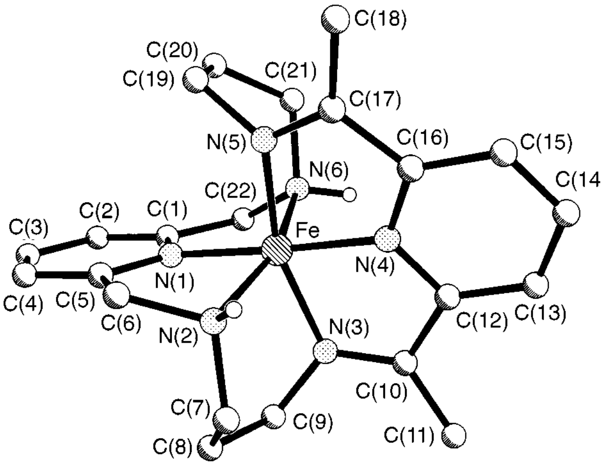


**Fig. 3** Perspective view of $[FeL^1]^{2+}$. Selected bond lengths (Å) and angles (°): Fe–N(1) 1.921(5), Fe–N(2) 2.030(4), Fe–N(3) 1.951(4), Fe–N(4) 1.843(5), Fe–N(5) 1.936(4), Fe–N(6) 2.027(4), N(2)–C(6) 1.497(9), N(3)–C(10) 1.310(9), N(5)–C(17) 1.310(6) and N(6)–C(22) 1.496(6); N(1)–Fe–N(2) 80.6(2), N(1)–Fe–N(3) 100.8(2), N(2)–Fe–N(3) 89.5(2), N(1)–Fe–N(4) 177.2(2), N(2)–Fe–N(4) 101.9(2), N(3)–Fe–N(4) 80.6(2), N(1)–Fe–N(5) 98.5(2), N(2)–Fe–N(5) 92.9(1), N(3)–Fe–N(5) 160.7(2), N(4)–Fe–N(5) 80.2(2), N(1)–Fe–N(6) 80.6(2), N(2)–Fe–N(6) 161.2(2), N(3)–Fe–N(6) 94.1(2), N(4)–Fe–N(6) 96.9(2) and N(5)–Fe–N(6) 89.7(1)

The single-crystal structure determination carried out on complex **2** shows that the *anti* isomer is indeed observed (Fig. 3). The iron atom has a very distorted octahedral geometry, with angles between *cis* nitrogen donor atoms ranging from 80.2 to 101.9° (N–Fe–N). The pyridine ring planes intersect at 70.8° and the 'head unit' $N_3$ planes at 92.1°, whereas in the $[FeL^2]^{2+}$ complex the planar trimethine units intersect at 81.1°.[5] As expected, bonds to the amine nitrogen donor atoms are longer than those to the imine nitrogen atoms [Fe–N(2) 2.030(4), Fe–N(6) 2.027(4) *vs.* Fe–N(3) 1.951(4), Fe–N(5) 1.936(4) Å], and bonds to the pyridine nitrogen atoms are shorter still [Fe–N(1) 1.921(5), Fe–N(4) 1.843(5) Å]. The latter feature is due to the 2,6 substitution of the pyridine 'head unit'. To ensure that the resulting tridentate co-ordination to the iron atom yields acceptable angles (*i.e.* approaching tetragonal) the iron atom is bound tightly to the pyridine nitrogen atom thus opening out the bite angles of this tridentate unit [N(1)–Fe–N(2)/N(6) 80.6(2), N(4)–Fe–N(3) 80.6(2), N(4)–Fe–N(5) 80.2(2)°]. A related feature is that the N(1)–Fe–N(4) angle is close to straight [177.2(2)°] whereas the other *trans* nitrogen donor atoms make N–Fe–N angles of 161.2(2) and 160.7(2)°.

## Conclusion

Clearly the 20-membered $L^1$ macrocycle is indeed flexible enough to form an octahedral wrap around an iron(II) ion:

co-ordination results in the formation of mononuclear low-spin $Fe^{II}$ in spite of the fact that the alkyl chains linking the two relatively inflexible head units are very short. The fact that one head unit is a pyridine diamine unit gives the small macrocycle increased flexibility which assists in the process of wrapping. To our knowledge the iron(II) complex of the related symmetrical tetraimine macrocycle[6] has not been isolated and characterised: it may be interesting to see whether or not it could form an analogous octahedral complex in spite of the reduced flexibility inherent in the two pyridine diimine 'head units', or whether it would respond to the strain by opening (*via* hydrolysis of an imine bond). However our attention is now directed to extending this successful protecting group approach to the preparation of other, larger 'two armed' diamines in order to access polynuclear macrocycles which provide two distinct types of metal-binding sites.[1–3]

## Experimental

All methanol and ethanol was dried by standard methods before use. 2,6-Diformylpyridine (dfp) was prepared from pyridine-2,6-dimethanol by $SeO_2$ oxidation according to the method of Moore and co-workers.[14] **CAUTION:** *perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with extreme caution.*

### Preparations

**2,6-Di[*N*-(3-aminopropyl)aminomethyl]pyridine I.** *Step* 1. This experimental procedure is a modification of that reported for *N*-acetylethane-1,2-diamine by Aspinall.[11] Ethyl acetate (42 g, 0.48 mol) was added to a threefold excess of diaminopropane (110 g, 1.4 mol) and the resultant solution stirred for 5 d. The ethanol by-product, unchanged ethyl acetate and excess of diaminopropane were removed *in vacuo* leaving *N*-acetylpropane-1,3-diamine as a hygroscopic colourless oil. Yield 35 g, 60% (based on ethyl acetate) (Found: C, 49.8; H, 10.3; N, 22.9. $C_5H_{12}N_2O\cdot0.3H_2O$ requires C, 49.4; H, 10.4; N, 23.0%). IR (smear on KBr plate): 3276s, 3071, 2933, 2865, 1654s and 1637 $cm^{-1}$. NMR spectra ($D_2O$): $\delta_H$(200 MHz) 3.20 [t, H(9)], 2.61 [t, H(7)], 1.97 [s, H(24)] and 1.62 [q, H(8)]; $\delta_C$(50 MHz) 178.4 [C(23)], 42.5 [C(9)], 41.6 [C(7)], 35.8 [C(8)] and 26.3 [C(24)].

*Step* 2. 2,6-Diformylpyridine (dfp, 23.16 g, 0.17 mol) was dissolved in methanol (120 $cm^3$). *N*-Acetylpropanediamine (39.21 g, 0.34 mol) in methanol (50 $cm^3$) was added dropwise to the stirred, gold-coloured solution over *ca.* 2 h. The mixture was stirred for 2 h, filtered, and evaporated under reduced pressure to leave a brown oil. $^1H$ NMR spectrum (200 MHz, $CDCl_3$): δ 8.42 [s, H(6)], 8.00 [d, H(2)], 7.83 [t, H(3)], 6.17 (br, NH), 3.77 [t, H(7)], 3.42 [q, H(9)] and 1.98 [m, H(8), H(24)].

*Step* 3. The above brown oil was dissolved in methanol (300 $cm^3$) and the solution cooled in an ice-bath. Sodium tetrahydridoborate (25.9 g, 0.68 mol) was added to the stirred, gold-coloured solution in five portions over 15 min. The ice-bath was removed and the mixture stirred for 3 d, refluxed for 1 h and cooled before NaOH (54.8 g, 1.37 mol) dissolved in distilled water (200 $cm^3$) was added. The mixture was stirred for 3 d, filtered and extracted with $CHCl_3$ (4 × 200 $cm^3$). The $CHCl_3$ was removed *in vacuo* to leave a brown oil. $^1H$ NMR spectrum (200 MHz, $CDCl_3$): δ 7.61 [t. H(3)], 7.17 [d, H(2)], 7.05 (br, $NH_B$), 3.87 [s, H(6)], 3.32 [q, H(9)], 2.70 [t, H(7)], 1.93 [s, H(24)] and 1.71 [m, H(8)].

*Step* 4. The above brown oil was dissolved in concentrated HCl (300 g) yielding a dark brown solution. The mixture was refluxed overnight, cooled, and the solvent removed *in vacuo*. Three times the mixture was dissolved in methanol (150 $cm^3$) and the methanol removed *in vacuo*. The resulting fawn powder was dried *in vacuo*, then stored over phosphorus pentaoxide until required: it was used without further purification. Yield 46.13 g (70% based on 2,6-diformylpyridine). The crude product could be recrystallised from ethanol by vapour diffusion of diethyl ether to yield an analytically clean white powder (Found: C, 39.0; H, 7.0; N, 17.4. $C_{13}H_{29}Cl_4N_5$ requires C, 39.3; H, 7.3; N, 17.6%). NMR spectra ($D_2O$, referenced to external 1,4-dioxane): $\delta_H$ 7.62 [t, H(3)], 7.16 [d, H(2)], 4.15 [s, H(6)], 2.97 [t, H(7)], 2.80 [t, H(9)] and 1.86 [m. H(8)]; $\delta_C$ 140.1 [C(3)], 123.9 [C(4)], 51.4 [C(6)], 45.2 [C(7)], 37.3 [C(9)] and 24.4 [C(8)] ppm.

*Step* 5. A portion of the above solid (1.49 g, 3.75 mol) was suspended in ethanol (100 $cm^3$), KOH (0.87 g, 15.66 mmol) dissolved in ethanol (10 $cm^3$) was added and the mixture stirred for 2 h. The volume was reduced *in vacuo* to *ca.* 5 $cm^3$, the mixture cooled in an ice-bath and the KCl filtered off. The reaction flask and the KCl on the frit were washed with ice-cold ethanol (3 × 10 $cm^3$). The brown ethanol filtrates, containing compound **I**, were combined and promptly used in further reactions.

**$[BaL^1][ClO_4]_2$ 1.** To a pale gold, refluxing, ethanol (150 $cm^3$) solution of 2,6-diacetylpyridine (0.61 g, 3.75 mmol) was added barium perchlorate (1.54 g, 3.94 mmol), followed by dropwise addition of compound **I** (3.75 mmol) in ethanol (*ca.* 35 $cm^3$) causing the clear solution to become cloudy. After refluxing for 1.5 h, the off-white precipitate, **1**, was collected, washed with ethanol (2 × 5 $cm^3$), and dried *in vacuo*. A further crop was obtained on cooling and evaporation of solvent (1.55 g, 58%) (Found: C, 36.6; H, 4.2; N, 11.8. $C_{22}H_{30}BaCl_2N_6O_8$ requires C, 37.0; H, 4.2; N, 11.8%). IR (KBr disc): 3295m, 1626m, 1575s, 1133s, 1107s, 1049s, 631s and 619s $cm^{-1}$. FAB mass spectrum: *m*/*z* 615, $[^{138}BaL^1(^{35}ClO_4)]^+$. NMR spectra ($CD_3CN$, referenced to external 1,4-dioxane, 75 °C): $\delta_H$(300 MHz) 8.61 [t, H(14)], 8.43 [d, H(13)], 8.19 [t, H(3)], 7.68 [d, H(2)], 4.47 [d, H(6)], 4.30 [t, H(9)], 3.35 [q, H(7)], 2.88 [s, H(11)], 2.74 (br, NH) and 2.62 [m, H(8)]; $\delta_C$(50 MHz) 170.6, 160.4, 157.4 [C(1), C(10), C(12)], 141.4 [C(14)], 139.8 [C(3)], 126.3 [C(13)], 122.7 [C(2)], 56.8 [C(6)], 50.8 [C(9)], 49.3 [C(7)], 29.6 [C(8)] and 17.3 [C(11)].

**$[FeL^1][ClO_4]_2$ 2. CAUTION:** *On one occasion a small quantity of an impure sample of this perchlorate salt exploded so extreme caution is necessary*. The complex $[BaL^1][ClO_4]_2$ (0.5 g, 0.7 mmol) was suspended in methanol (30 $cm^3$) and brought to reflux. Iron(II) perchlorate (0.38 g, 1.0 mmol) in methanol (10 $cm^3$) was added and the resulting intense purple suspension refluxed for 1 h. A small amount of dark solid was filtered from the hot reaction mixture and discarded. Upon cooling and evaporation of solvent the resulting purple solid was collected and dried *in vacuo* (0.18 g, 40%) (Found: C, 41.6; H, 4.8; N, 13.3. $C_{22}H_{30}Cl_2FeN_6O_8$ requires C, 41.7; H, 4.8; N, 13.3%). IR (KBr disc): 3250m, 1605m, 1571w, 1090s and 625s $cm^{-1}$. FAB mass spectrum: *m*/*z* 533, $[^{56}FeL^1(^{35}ClO_4)]^+$. UV/VIS (MeCN): λ/nm (ε/$dm^3\ mol^{-1}\ cm^{-1}$): 305 (7220), 380 (2970), 500 (11 000), 580 (sh) (*ca.* 2800), 625 (sh) (*ca.* 2230) and 775 (sh) (*ca.* 420). NMR spectra ($CD_3CN$, referenced to external $SiMe_4$): $\delta_H$(300 MHz) 8.33 [d, H(13)], 8.21 [t, H(14)], 8.18 [t, H(3)], 7.79 [d, H(2)], 4.27 [td, H(9′)], 4.05 [dd, H(6′)], 3.77 [d, H(6″)], 3.03 [td, H(9″)], 2.80 [s, H(11)], 2.16 (br, NH), 1.86 [m, H(7′)], 1.61 [m, H(8′)], 1.39 [m, H(8″)] and 0.89 [tt, H(7″)]; $\delta_C$(50 MHz) 176.0, 164.4, 163.0 [C(1), C(10), C(12)], 139.0 [C(14)], 131.6 [C(3)], 123.9 [C(13)], 119.9 [C(2)], 59.4 [C(6)], 47.8 [C(9)], 45.9 [C(7)], 21.9 [C(8)] and 15.7 [C(11)].

### Crystallography

A single crystal of $[FeL^1][ClO_4]_2$ **2** suitable for X-ray analysis was obtained from MeCN by vapour diffusion of diethyl ether.

**Crystal data.** $C_{22}H_{30}Cl_2FeN_6O_8$, $M = 633.3$, black plate, dimensions 0.68 × 0.34 × 0.08 mm, monoclinic, space group *C*2/*c*, $a = 32.559(11)$, $b = 9.140(3)$, $c = 21.270(9)$ Å, $\beta = 124.52(3)°$, $U = 5215(4)$ Å$^3$, $Z = 8$, $F(000) = 2624$, $\mu$(Mo-K$\alpha$) = 0.843 $mm^{-1}$.

Unit-cell parameters were determined by least-squares refinement of 25 accurately centred reflections in the range $7 < 2\theta < 31°$. Using 1.4° ω scans, 4974 reflections were collected with $5 < 2\theta < 50°$ at 180 K on a Nicolet R3m four-circle diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å). Crystal stability was monitored by recording three check reflections every 97; no significant variations were observed. The data set was corrected for Lorentz-polarisation effects and an empirical absorption correction applied, based on ψ-scan data ($T_{max} = 0.91$, $T_{min} = 0.84$). 4580 Reflections were independent, and the 3560 having $F > 4\sigma(F)$ were ultimately used in the structure refinement. Direct methods (SHELXS 86[15]) revealed most of the structure and the few remaining non-hydrogen atoms were located from Fourier-difference maps. Hydrogen atoms, other than those on the two amine nitrogen atoms, were inserted at calculated positions using a riding model. The two amine hydrogen atoms were located from difference maps, then allowed to ride on their respective nitrogen atoms. Hydrogen atoms were constrained to have a common refined thermal parameter. One of the half-occupancy perchlorate ions was restrained to have an approximately tetrahedral geometry. Anisotropic thermal parameters were assigned to all non-hydrogen atoms, and the refinement of 392 parameters (in two blocks of 266) converged with $R = 0.054$, $wR = 0.066$, $g = 0.0007$, goodness of fit = 1.79. The final difference map showed no features greater than ±1.5 e Å$^{-3}$. The function minimised in the refinement was $\Sigma w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + gF_o^2]^{-1}$.

CCDC reference number 186/881.

## Acknowledgements

This work was supported by grants from the University of Otago. We are grateful to P. D. Croucher for his help and we thank Drs. D. S. Larsen and C. Clark (University of Otago) for helpful discussions, Professor W. T. Robinson (University of Canterbury) for the X-ray data collection and Mr. B. M. Clark (University of Canterbury) for the FAB mass spectra.

## References

1 S. Brooker and P. D. Croucher, *J. Chem. Soc., Chem. Commun.*, 1993, 1278.
2 S. Brooker and P. D. Croucher, *J. Chem. Soc., Chem. Commun.*, 1995, 2075; 1997, 459.
3 S. Brooker, P. D. Croucher, T. C. Davidson and P. D. Smith, unpublished work.
4 For example, F. C. J. M. van Veggel, M. Bos, S. Harkema, H. Van de Bovenkamp, W. Verboom, J. Reedijk and D. N. Reinhoudt, *J. Org. Chem.*, 1991, **56**, 225; J. de Mendoza, E. Mesa, J. C. Rodriguez-Ubis, P. Vázquez, F. Vögtle, P. M. Windscheif, K. Rissanen, L. M. Lehn, D. Lilienbaum and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1331; K. K. Nanda, R. Das, K. Venkatsubramanian, P. Paul and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1993, 2515.
5 S. M. Nelson, M. McCann, C. Stevenson and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1979, 1477; M. G. B. Drew, M. McCann and S. M. Nelson, *Inorg. Chim. Acta*, 1980, **41**, 213.
6 See, for example, M. G. B. Drew, J. Nelson, F. Esho, V. McKee and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1982, 1837; C. Harding, D. McDowell, J. Nelson, S. Raghunathan, C. Stevenson, M. G. B. Drew and P. C. Yates, *J. Chem. Soc., Dalton Trans.*, 1990, 2521.
7 D. H. Busch, *Rec. Chem. Prog.*, 1964, **25**, 107.
8 See, for example, G. R. Newkome, V. K. Majestic and F. R. Fronczek, *Inorg. Chim. Acta*, 1983, **77**, L47; G. H. Searle, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 4021; G. L. Rothermel, L. Miao, A. L. Hill and S. C. Jackels, *Inorg. Chem.*, 1992, **31**, 4854; S. W. A. Bligh, N. Choi, E. G. Evagorou, W.-S. Li and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 1994, 2399.
9 W. R. Harris, I. Murase, J. H. Timmons and A. E. Martell, *Inorg. Chem.*, 1978, **17**, 889.
10 A. R. Jacobson, A. N. Makris and L. M. Sayre, *J. Org. Chem.*, 1987, **52**, 2592.
11 S. R. Aspinall, *J. Am. Chem. Soc.*, 1941, 852.
12 H. Adams, N. A. Bailey, D. E. Fenton, R. J. Good, R. Moody and C. O. Rodriguez de Barbarin, *J. Chem. Soc., Dalton Trans.*, 1987, 207.
13 T. J. Simpson, B.Sc. (Hons) Report, University of Otago, 1992.
14 N. W. Alcock, R. G. Kingston, P. Moore and C. Pierpoint, *J. Chem. Soc., Dalton Trans.*, 1984, 1937.
15 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, 467.

*Received* 10*th November* 1997; *Paper* 7/08061A