DALTON
COMMUNICATION

The first co-ordination complex of a bis(triazacyclododecane) ligand; structure of a binuclear nickel complex†

Michael D. Snodin,[a] **Paul D. Beer***,[a] **and Michael G. B. Drew**[b]

[a] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR*
[b] *Department of Chemistry, University of Reading, Whiteknights, Reading, UK RG6 6AD*

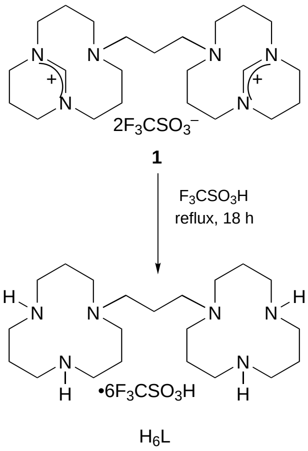
The crystal structure of $[Ni_2L(O_2CCH_3)_2(H_2O)_2][ClO_4]_2$ has been determined and the observed metal-centred chirality analysed; L is a binucleating ligand based on 1,5,9-triazacyclododecane for which a convenient, high yielding synthesis is also presented.

Recent years have seen a considerable number of reports on ligands capable of binding two metal ions.[1] Complexes of such ligands are interesting not only for the electronic interactions that take place between the metal ions, but also for their reactivity towards small molecules. Extra interest has been spurred by the discovery of enzymes containing interacting metal ions at their active sites.[2] In attempts to mimic the co-ordination environment of such active sites, as well as other work more directed towards the activation of small molecules, bis(1,4,7-triazacyclononane) (9[ane]N_3) ligands have featured prominently.[2a,3] This reflects the well known, and excellent co-ordinating properties of 9[ane]N_3 ligands. Recent studies using 1,5,9-triazacyclododecane (12[ane]N_3), however, have shown that this larger macrocyclic ligand imparts interesting biomimetic properties on some of its complexes,[4] quite different from their 9[ane]N_3 analogues.[5] Although their synthesis was first reported a decade ago,[6] the co-ordination properties of bis(12[ane]N_3) ligands are still completely unknown. We therefore report the synthesis, characterisation and structure of the first ever metal complex of a bis(12[ane]N_3) ligand.

To obtain the ligand, a synthetic procedure derived from that developed by Weisman and co-workers[6a,7] was used. By refluxing bis(amidinium)trifluoromethanesulfonate salt, **1** [prepared by the reaction of propane-1,3-diyl bis(trifluoromethanesulfonate) with 2 equivalents of 1,5,9-triazatricyclo[7.3.1.0^{5,13}]-tridecane in dichloromethane], with 20 equivalents of 0.7 M trifluoromethanesulfonic acid for 18 h, a quantitative yield of the hexaprotonated ligand, H_6L, [1,3-bis(1,5,9-triazacyclododecyl)propane hexa(hydrotrifluoromethanesulfonate)] was isolated by precipitation from ethanol–diethyl ether (Scheme 1). Aquamarine crystals of dinickel complex $[Ni_2L(O_2CCH_3)_2(H_2O)_2][ClO_4]_2$ **2** were then isolated from an aqueous mixture of H_6L, nickel perchlorate, sodium acetate and sodium perchlorate, adjusted to near-neutral pH using sodium hydroxide.

The crystal structure of **2** shows that both triazamacrocycles of the ligand bind a nickel ion in a facial, tridentate fashion. Bidentate acetate and water complete the two pseudo-octahedral co-ordination environments. The cation is disordered, with imposed C_2 symmetry. The disorder, however, only affects the atoms bonded to N(25). This has been analysed as 50% of cations containing the atoms C(24A), C(26A), C(90A) around N(25), and C(24B*), C(26B*), C(90B*) around N(25*) (where * is the symmetry element $1 - x, y, \frac{3}{2} - z$). The other 50% of cations contain the atoms C(24B), C(26B), C(90B), C(24A*), C(26A*) and C(90A*). The conformations of individual cations are therefore unequivocal, and are such as pictured in Fig. 1. The disorder can be explained by equal numbers of the 180° rotamers of the C_s-symmetric macrocycle [reflection plane passing through C(91)] being present in the crystal (Fig. 2).

The C_s symmetry of the macrocycle is not maintained throughout the cation, however, because of the inclusion of the C_2-related acetate and water ligands. With no overall element of symmetry in individual cations, both nickel ions are therefore chiral centres. Metal-centred chirality is known for octahedral complexes of 12[ane]N_3,[8] and in **2** relies on the fact that one of the two, previously equivalent, secondary nitrogen atoms of each triazamacrocycle is made unique by being co-ordinated



Scheme 1 Synthesis of 1,3-bis(1,5,9-triazacyclododecyl)propane hexa(hydrotrifluoromethanesulfonate)

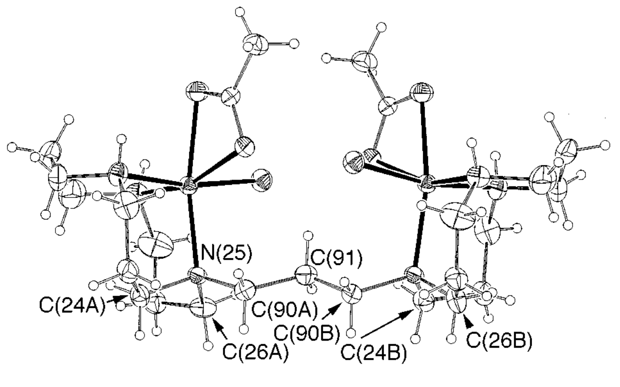


Fig. 1 Structure of an ordered model of $[Ni_2L(O_2CCH_3)_2(H_2O)_2]$ **2**, with ellipsoids at 30% occupancy, together with the atomic numbering scheme

---

† *Non-SI unit employed*: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

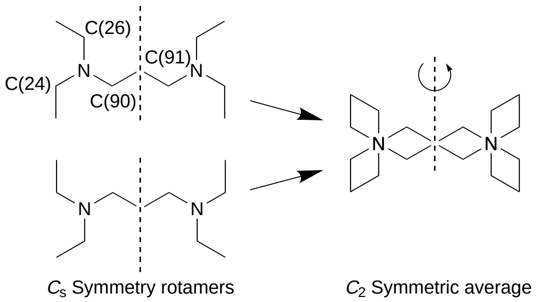


Fig. 2 Effect of rotational disorder on the average molecular geometry

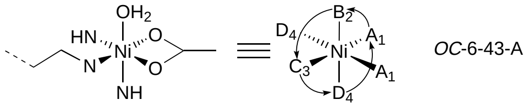


Fig. 3 Designation of the stereochemistry at nickel (numbers refer to the donor atom priority)

trans to a water ligand. Both nickel centres have, superficially, the same chirality, which can be designated as *OC*-6-43-A (abbreviated to 'A' hereon) using IUPAC rules (Fig. 3).[9] The complex pictured can therefore be described as an 'AA' enantiomer. However, slight differences in the conformations of the triazamacrocyclic rings relative to the other ligands provides a differentiation between the nickel ions in individual cations.

The conformation of **2** pictured in Fig. 1 does not, admittedly, represent the whole truth. The complex's centrosymmetric space group (*Pcba*)‡ means that there are equal numbers of 'CC' (here, 'C' is an abbreviation for the configuration *OC*-6-43-C) as well as 'AA' enantiomers in the unit cell (two of each), related by glide planes.

No evidence was found, however, for the non-equivalent 'AC' and 'CA' enantiomers. Careful examination of the bonding within the complex reveals a plausible explanation for this observation. A close approach between the water ligand of one nickel ion and an acetate oxygen bound to the other [O(100) to O(12*) separation of 2.77 Å] indicates an intramolecular H bond. These atoms will therefore have reduced ability to form H bonds to solvent molecules. The postulated mesomeric forms of the complex cannot form such intramolecular H bonds (on geometric grounds), and will therefore possess greater solubility in water.

Magnetic (SQUID) measurements have been also performed on **2** between 10 and 300 K. A straight line is obtained when the inverse of molar susceptibility is plotted against temperature ($1/\chi_m = 1.9001 + 0.529\,14\ T$, $R = 0.999\,98$), indicating that the Curie–Weiss law is obeyed. This implies minimal coupling between the nickel ions. The room-temperature magnetic moment of the complex (3.87 μ_β at 300 K) is correspondingly close to the spin-only value calculated for two, uncoupled, $S = 1$ metal ions (4.0 μ_β).

Acknowledgements

We would like to thank EPSRC, Unilever and the University of Reading for funds towards this research.

References

1 M. W. Gobel, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1141; M. Wall, R. C. Hynes and J. Chin, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1633; R. Breslow and S. Singh, *Bioorg. Chem.*, 1988, **16**, 408; D. H. Vance and A. W. Czarnik, *J. Am. Chem. Soc.*, 1993, **115**, 12165; W. H. Chapman and R. Breslow, *J. Am. Chem. Soc.*, 1995, **117**, 5462; Y. Gultneh, Allwar, B. Ahvazi, D. Blaise, R. J. Butcher, J. Jasinski and J. Jasinski, *Inorg. Chim. Acta*, 1996, **241**, 31; E. A. Kesicki, M. A. DeRosch, L. H. Freeman, C. L. Walton, D. F. Harvey and W. C. Trogler, *Inorg. Chem.*, 1993, **32**, 5851.

2 (*a*) J. L. Sessler, J. W. Sibert and V. Lynch, *Inorg. Chem.*, 1990, **29**, 4143 and refs. therein; (*b*) B. L. Vallee and D. S. Auld, *Proc. Natl. Acad. Sci. USA*, 1993, **90**, 2715 and refs. therein.

3 K. Wieghardt, I. Tolksdorf and W. Herrmann, *Inorg. Chem.*, 1985, **24**, 1230; J. L. Sessler, J. W. Sibert, V. Lynch, J. T. Markert and C. L. Wooten, *Inorg. Chem.*, 1993, **32**, 621; X. Zhang, W.-Y. Hsieh, T. N. Margulis and L. J. Zompa, *Inorg. Chem.*, 1995, **34**, 2883; H. Diril, H.-R. Chang, M. J. Nilges, X. Zhang, J. A. Potenza, H. J. Schugar, S. S. Isied and D. N. J. Hendrickson, *J. Am. Chem. Soc.*, 1989, **111**, 5102; M. J. Young and J. Chin, *J. Am. Chem. Soc.*, **117**, 10577; L. J. Farrugia, P. A. Lovatt and R. D. Peacock, *J. Chem. Soc., Dalton Trans.*, 1997, 911; P. D. Beer, M. G. B. Drew, P. B. Leeson, K. Lyssenko and M. I. Ogden, *J. Chem. Soc., Chem. Commun.*, 1995, 929.

4 E. Kimura, T. Shiota, T. Koike, M. Shiro and M. Kodama, *J. Am. Chem. Soc.*, 1990, **112**, 5805; T. Koike, E. Kimura, I. Nakamura, Y. Hashimoto and M. Shiro, *J. Am. Chem. Soc.*, 1992, **114**, 7338; E. Kimura, T. Koike, M. Shionoya and M. Shiro, *Chem. Lett.*, 1992, 787.

5 P. Chaudhuri, C. Stockheim, K. Wieghardt, W. Deck, R. Gregorzik, H. Vahrenkamp, B. Nuber and J. Weiss, *Inorg. Chem.*, 1992, **31**, 1451; G. C. Silver, P. Gantzel and W. C. Trogler, *Inorg. Chem.*, 1995, **34**, 2487; G. C. Silver and W. C. Trogler, *J. Am. Chem. Soc.*, 1995, **117**, 3983; L. J. Zompa, *Inorg. Chem.*, 1978, **9**, 2531.

6 (*a*) G. R. Weisman, D. J. Vachon, V. B. Johnson and D. A. Gronbeck, *J. Chem. Soc., Chem. Commun.*, 1987, 886; (*b*) P. Hubsch-Weber and M.-T. Youinou, *Tetrahedron Lett.*, 1997, **38**, 1911.

7 R. W. Alder, R. W. Mowlam, D. J. Vachon and G. R. Weisman, *J. Chem. Soc., Chem. Commun.*, 1992, 507.

8 S. Fujinami, Y. Matsunami and M. Shibata, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2101.

9 J. M. Harrowfield and S. B. Wild, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Wiley-Interscience, New York, 5th edn., 1987, vol. 1, p. 385; T. E. Sloan, *Top. Stereochem.*, 1981, **12**, 1.

10 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

11 G. M. Sheldrick, SHELXL, program for crystal structure refinement, University of Göttingen, 1993.

Received 3rd *July* 1997; *Communication* 7/04692H

---

‡ Crystal data for complex **2** $C_{25}H_{56}Cl_2N_6Ni_2O_{14}$, $M = 853.04$, Mo-Kα radiation, $\lambda = 0.7107$ Å, crystal size 0.30 × 0.35 × 0.25 mm, orthorhombic, space group *Pbca*, $a = 14.472(12)$, $b = 15.542(14)$, $c = 16.56(2)$ Å, $U = 3725$ Å^3, $Z = 4$, $D_c = 1.500$ g cm^{-3}, $\mu = 1.223$ mm^{-1}, $F(000) = 1752$. 9500 Reflections were collected in the range $4 \leqslant 2\theta \leqslant 50°$ at 293 K, using the MARresearch Image Plate System. The 3242 independent reflections with $I > 2\sigma(I)$ were used in the structure determination and refinement. The structure was solved by direct methods using SHELX 86,[10] and then refined on F^2 using SHELXL[11] to a final R value of 0.103. Three of the carbon atoms in the ligand were disordered over two positions, and these were refined with 50% occupancy. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. CCDC reference number 186/702.