First observation of non-bridging thiolates or tetrahedral geometries within thiolate-containing Schiff-base macrocycles: $[Zn_2L][CF_3SO_3]_2$

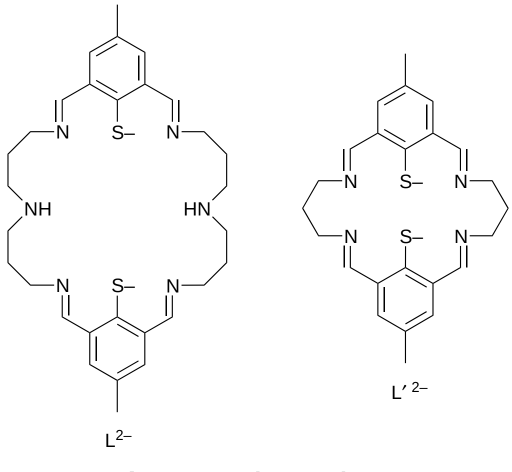
Sally Brooker* and Tony C. Davidson

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

The structure determination of $[Zn_2L][CF_3SO_3]_2$ 1 reveals the first example of non-bridging thiolates within a thiolate-containing Schiff-base macrocyclic complex: the flexibility of such macrocycles is also clearly demonstrated as this is the first example of the provision of distorted tetrahedral metal ion binding sites.

Thiolate-containing complexes are currently of great interest as model complexes for a number of metalloprotein active sites such as Fe–S clusters,[1] Ni–Fe hydrogenase,[2] Cu_A site of cytochrome c oxidase[3] and Zn fingers.[4] The complexes are also of interest in their own right as they exhibit very different properties to those of complexes with other, more common donors such as oxygen or nitrogen. We have therefore incorporated the ‘head unit’ *S*-(2,6-diformyl-4-methylphenyl)dimethylthiocarbamate, which contains a masked thiolate, into a series of Schiff-base macrocycles:[5–7] the thiolate donor is best generated from the masked ‘head unit’ by base hydrolysis prior to the cyclisation reaction.[6] To date, the reported di- and tetra-nuclear Schiff-base macrocyclic complexes formed from this unmasked thiolate have exhibited a wide range of geometries, albeit predominantly square-based ones: from square planar, square pyramidal and octahedral through to one example of trigonal bipyramidal.[5–9] In all of the examples to date the thiolate donors bridge the two metal ions. Here we describe the synthesis and structure of a new dinuclear Schiff-base macrocyclic complex which exhibits very different features.

Hydrolysis of *S*-(2,6-diformyl-4-methylphenyl)dimethylthiocarbamate with NaOH, followed by reaction with *N*-(3-aminopropyl)-1,3-propanediamine in the presence of zinc(II) template ions, yields a yellow powder, $[Zn_2L][CF_3SO_3]_2$ **1**, in 85% yield (Scheme 1).† The IR spectrum of **1** was consistent with the presence of a Schiff-base macrocycle; an imine band was present at 1633 cm^{-1} and there were no primary amine or carbonyl bands. Based on the geometry we observed for the zinc ions in a related macrocyclic complex $[Zn_2L'(H_2O)_2]^{2+}$ **2** (Scheme 1) we expected that the zinc ions in this new complex might also be trigonal bipyramidal, but that now *all* of the donors could be supplied by the macrocycle.[6] To test this proposal a structure determination was carried out on **1**.



Scheme 1 Ligands L^{2-} and L'^{2-}

Yellow single crystals were obtained by diethyl ether diffusion into an acetonitrile solution of **1**.‡ The X-ray structure determination revealed, in contrast to the predicted trigonal-bipyramidal geometry, the first example of a thiolate-containing Schiff-base macrocyclic complex containing metal ions with a distorted tetrahedral geometry (Fig. 1). Each of the two zinc atoms is bound to a single thiolate donor, two imine nitrogen donors and an amine nitrogen donor, and has adopted an approximately tetrahedral geometry. Tetrahedral coordination of zinc ions in mixed thiolate/nitrogen coordination environments is not uncommon[10] and presumably a trigonal-bipyramidal geometry is not observed in this case due to an unfavourable spatial arrangement of the required donors, due to the constraint of them all coming from a single polydentate macrocyclic ligand.[11] Another unique feature of this structure is that the thiolate donors do not bridge the two metal ions. This is in stark contrast with all of the related macrocyclic complexes prepared to date,[5–9,12] and with the well known ability of thiolates to bridge metal ions, a feature of thiolate chemistry which has often resulted in the uncontrolled (and usually undesired) formation of polymers.[13] We have found that the use of thiolate-containing macrocycles has allowed us to control this aspect of thiolate coordination chemistry (as well as a number of other common problems)[6,13] and has thus facilitated the formation of discrete complexes where the thiolate donors only bridge between the metal ions incorporated in the macrocycle.[5–7] However, in this new macrocyclic complex there is no thiolate bridging whatsoever.

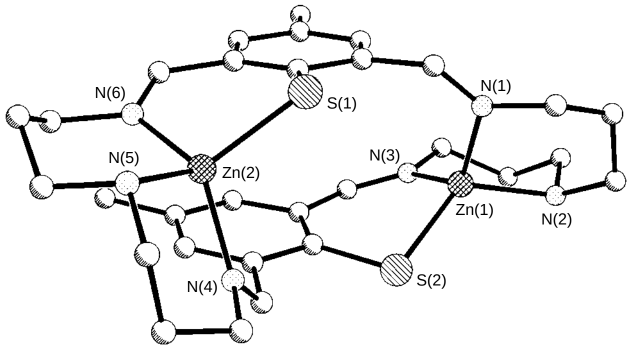


Fig. 1 Perspective diagram of the cation of **1**, $[Zn_2L]^{2+}$. Selected bond lengths (Å) and angles (°): Zn(1)–N(3) 2.007(7), Zn(1)–N(1) 2.024(8), Zn(1)–N(2) 2.031(8), Zn(1)–S(2) 2.254(3), Zn(2)–N(6) 2.001(7), Zn(2)–N(4) 2.032(7), Zn(2)–N(5) 2.036(8), Zn(2)–S(1) 2.253(2), S(1)···S(2) 4.516(3), Zn(1)···Zn(2) 6.077(2); N(3)–Zn(1)–N(1) 126.1(3), N(3)–Zn(1)–N(2) 100.3(3), N(1)–Zn(1)–N(2) 98.6(3), N(3)–Zn(1)–S(2) 100.2(2), N(1)–Zn(1)–S(2) 108.5(2), N(2)–Zn(1)–S(2) 125.5(3), N(6)–Zn(2)–N(4) 123.9(3), N(6)–Zn(2)–N(5) 100.6(3), N(4)–Zn(2)–N(5) 98.6(3), N(6)–Zn(2)–S(1) 100.3(2), N(4)–Zn(2)–S(1) 110.5(2), N(5)–Zn(2)–S(1) 124.7(2), C(1)–S(1)–Zn(2) 99.7(3), C(16)–S(2)–Zn(1) 99.6(3).

The macrocycle has clearly adopted a very different conformation to those observed previously and in so doing reveals considerable flexibility. The use of an aromatic thiolate 'head unit' has allowed the formation of π–π interactions to influence the overall structure.[14] Specifically, favorable π–π interactions exist between the two aromatic rings within the macrocyclic unit: the two aromatic ring planes intersect at 6.8° and are 3.32–3.62 Å apart. Intermolecular π–π interactions are also observed and lead to the molecules packing together in chains. The two monodentate thiolate donors are relatively exposed but intermolecular bridging does not occur. The two triflate anions hydrogen bond to the two secondary amines (O···N 2.85, 2.89 Å), and destroy the otherwise approximate twofold symmetry of the complex.

Molar conductance measurements show that **1** is a 2 : 1 electrolyte in dimethylformamide (dmf) indicating that the cation $[Zn_2L]^{2+}$ is present in solution. ^1H and ^{13}C NMR spectra were obtained in both $[^2H_7]$dmf and CD_3CN. In each case the imine, aromatic and methylene resonances are chemically inequivalent which is consistent with the maintenance of the solid-state structure in solution. Preliminary cyclic voltammetry studies in MeCN show that **1** undergoes an irreversible, approximately two-electron, oxidation at E_{pa} = +1.03 V *vs.* 0.01 M $AgNO_3$/Ag. This behaviour is very similar to that of complex **2** and is currently under further investigation.[6,7]

In summary, we have prepared a new thiolate-containing macrocyclic ligand, as a dizinc(II) complex, and it has very different characteristics from previous thiolate-containing Schiff-base macrocycles. Transmetallations and attempts to induce the thiolates to bridge to introduced metal ion complexes are underway. Further development of this and related systems will provide excellent opportunities to manipulate both the bridging tendency of the incorporated thiolates and the geometries adopted by the incorporated metal ions, giving us, in a controlled way, access to complexes of our own design.[7]

This work was supported by grants from the University of Otago. We thank Professor W. T. Robinson (University of Canterbury) for the X-ray data collection. S. B. thanks the University of Otago for the granting of study leave which has facilitated the writing of this paper, and gratefully acknowledges her host Professor K. Wieghardt and the financial support of the Alexander von Humboldt Stiftung.

Footnotes and References

* sbrooker@alkali.otago.ac.nz

† Satisfactory C,H,N,S analysis was obtained for **1**.

‡ *Crystal data* for **1**: $C_{32}H_{40}F_6N_6O_6S_4Zn_2$, pale yellow block, crystal dimensions 0.80 × 0.26 × 0.18 mm, monoclinic, space group $P2_1/c$, a = 14.830(2), b = 21.422(3), c = 14.148(2) Å, β = 114.723(9)°, U = 4083(1) Å^3, μ = 1.456 mm^{-1}. Data were collected at 170 K on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). 6963 Reflections were collected in the range $4 < 2\theta < 48°$ and the 6336 independent reflections were used in the structural analysis after a semi-empirical absorption correction had been applied. The structure was solved by direct methods (SHELXS-86)[15] and refined against all F^2 data (SHELXL-93)[16] to R_1 = 0.071 [for 4028 $F > 4\sigma(F)$; wR_2 = 0.204 and goodness of fit = 1.04 for all 6336 F^2; 517 parameters; all non-hydrogen atoms anisotropic, CF_3 groups disordered]. CCDC 182/600.

1 See for example: R. H. Holm, S. Ciurli and J. A. Weigel, *Prog. Inorg. Chem.*, 1990, **38**, 1.
2 See for example: A. F. Kolodziej, *Prog. Inorg. Chem.*, 1994, **41**, 493; M. A. Halcrow and G. Christou, *Chem. Rev.*, 1994, **94**, 2421; A. Volbeda, E. Garcin, C. Piras, A. L. De Lacey, V. M. Fernandez, E. C. Hatchikian, M. Frey and J. C. Fontecilla-Camps, *J. Am. Chem. Soc.*, 1996, **118**, 2989.
3 See for example: S. Iwata, C. Ostermeier, B. Ludwig and H. Michel, *Nature*, 1995, **376**, 660; H. Bertagnolli and W. Kaim, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 771.
4 See for example: B. L. Vallee and D. S. Auld, *Acc. Chem. Res.*, 1993, **26**, 543; J. M. Berg, *Science*, 1996, **271**, 1081.
5 S. Brooker and P. D. Croucher, *J. Chem. Soc., Chem. Commun.*, 1995, 1493; 2075; *Chem. Commun.*, 1997, 459.
6 S. Brooker, P. D. Croucher and F. M. Roxburgh, *J. Chem. Soc., Dalton Trans.*, 1996, 3031.
7 S. Brooker, P. D. Croucher, T. C. Davidson, G. S. Dunbar, P. D. Smith, S. P. Cramer, C. Y. Ralston, A. McAuley and S. Subramanian, unpublished work.
8 A. J. Atkins, A. J. Blake and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1993, 1662; A. J. Atkins, D. Black, A. J. Blake, A. Marin-Becerra, S. Parsons, L. Ruiz-Ramirez and M. Schröder, *Chem. Commun.*, 1996, 457; N. D. J. Branscombe, A. J. Blake, A. Marin-Becerra, W-S. Li, S. Parsons, L. Ruiz-Ramirez and M. Schröder, *Chem. Commun.*, 1996, 2573.
9 P. E. Kruger and V. McKee, *Chem. Commun.*, 1997, 1341.
10 See for example: J. Castro, J. Romero, J. A. García-Vázquez, M. L. Durán, A. Castiñeiras, A. Sousa and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, 1990, 3255; C. Zhang, R. Chadha, H. K. Reddy and G. N. Schrauzer, *Inorg. Chem.*, 1991, **30**, 3865; R. Baggio, M. T. Garland and M. Perec, *J. Chem. Soc., Dalton Trans.*, 1993, 3367; J. J. Wilker and S. J. Lippard, *J. Am. Chem. Soc.*, 1995, **117**, 8682; U. Brand, R. Burth and H. Vahrenkamp, *Inorg. Chem.*, 1996, **35**, 1083.
11 V. McKee, *Adv. Inorg. Chem.*, 1993, **40**, 323.
12 G. A. Lawrance, M. Maeda, T. M. Manning, M. A. O'Leary, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1990, 2491.
13 See for example: I. G. Dance, *Polyhedron*, 1986, **5**, 1037; J. R. Dilworth and J. Hu, *Adv. Inorg. Chem.*, 1993, **40**, 411.
14 See for example: C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525; P. R. Ashton, P. T. Glink, M. V. Martinez-Diaz, J. F. Stoddart, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1930; H. Adams, F. J. Carver, C. A. Hunter, J. C. Morales and E. M. Seward, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1542; I. Dance and M. Scudder, *Chem. Eur. J.*, 1996, 481.
15 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
16 G. M. Sheldrick, *J. Appl. Crystallogr.*, 1997, manuscript in preparation.

Received in Cambridge, UK, 28th July 1997; 7/05415G