

## Crown Thioether Chemistry. The Nickel(II) Complex of Hexathia-24-crown-6

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Hexathia-24-crown-6 wraps around Ni<sup>II</sup> to yield an octahedral cation with meridional stereochemistry in the first reported complex of this ligand.

The co-ordination chemistry of thioethers has come under increasing scrutiny as a result of its potential parallel to that of phosphines, as well as its occurrence in the blue copper proteins. Both contexts raise the question of the electronic consequences of thioether co-ordination, a question that is best addressed in homoleptic hexakis(thioether) complexes. At present few homoleptic thioether complexes are known, however, and still fewer structurally characterised.<sup>1</sup>

Our approach to synthesis of such complexes has focused on the use of crown thioethers such as hexathia-18-crown-6 (18S6), the efficacy of which as a ligand for first-row metal ions has been demonstrated.<sup>2</sup> This work made it clear that the future extension of crown thioether chemistry to second- and third-row transition elements will require a ligand with a larger cavity size than that provided by 18S6. Therefore we have prepared hexathia-24-crown-6 (24S6),<sup>3</sup> the all propyl-linked analogue of 18S6, and its nickel(II) complex in order to permit a direct comparison of the two ligands with a common metal ion. We report here the synthesis, crystal structure, and optical spectrum of [Ni·(24S6)](BF<sub>4</sub>)<sub>2</sub>, the first reported complex of 24S6.

Addition of 24S6 (44 mg, 0.1 mmol) to nickel(II) hexakis(ethanol) tetrafluoroborate (51 mg, 0.1 mmol) in acetic anhydride (3 ml) under nitrogen gives a deep blue-green solution, which upon vapour diffusion with diethyl ether affords [Ni·(24S6)](BF<sub>4</sub>)<sub>2</sub> as turquoise needles.<sup>3</sup> Vapour diffusion of hexane into a solution of [Ni·(24S6)](BF<sub>4</sub>)<sub>2</sub> in dichloromethane gave diffraction-quality crystals, on which an X-ray diffraction data set was collected.<sup>†</sup>

X-Ray diffraction reveals that 24S6, like 18S6, envelops Ni<sup>II</sup> to yield an essentially octahedral complex with (in this case) crystallographically-imposed twofold symmetry (Figure 1). The six thioether sulphur atoms co-ordinate to Ni<sup>II</sup> at distances that range from 2.415(1) to 2.445(1) Å; these distances accord well with the sum of the ionic radii of Ni<sup>2+</sup> and S<sup>2-</sup> (2.44 Å),<sup>4</sup> and with those observed previously in Ni(thiodiglycol)<sub>2</sub>(Br)<sub>2</sub><sup>5</sup> and Ni(1,5-dithiacyclo-octane)<sub>2</sub>Cl<sub>2</sub>.<sup>6</sup>

Comparison of the nickel(II) complex of 24S6 with that of the analogous ethyl-linked macrocycle 18S6<sup>7</sup> is of particular interest. Unlike 18S6, which forms complexes with a variety of transition metal ions<sup>2</sup> to give the centrosymmetric *meso* isomer (in which each loop of three adjacent sulphur atoms co-ordinates facially), 24S6 co-ordinates to Ni<sup>II</sup> to give the chiral (±)-racemic isomer (in which two loops of adjacent sulphur atoms co-ordinate meridionally). Furthermore, because of this meridional stereochemistry in [Ni·(24S6)]<sup>2+</sup>, only eight of the 12 C–S bonds adopt *gauche* placement. This is in contrast with the structurally-characterised [M·(18S6)]<sup>2+</sup> complexes<sup>2</sup> where all C–S bonds adopt *gauche* placement. In addition to these stereochemical differences, [Ni·(24S6)]<sup>2+</sup> has much longer Ni–S bond lengths than [Ni·(18S6)]<sup>2+</sup>;<sup>7</sup> average Ni–S distances are 2.43 and 2.39 Å, respectively. (Short Ni–S bond distances are also found in [Ni·(9S3)<sub>2</sub>]<sup>2+</sup>, for which the average Ni–S length is 2.39 Å.<sup>8</sup>) The crystallographic results therefore indicate that 24S6, in contrast with 18S6, provides a cavity large enough to accommodate Ni<sup>II</sup> without significant compression of Ni–S bond lengths.

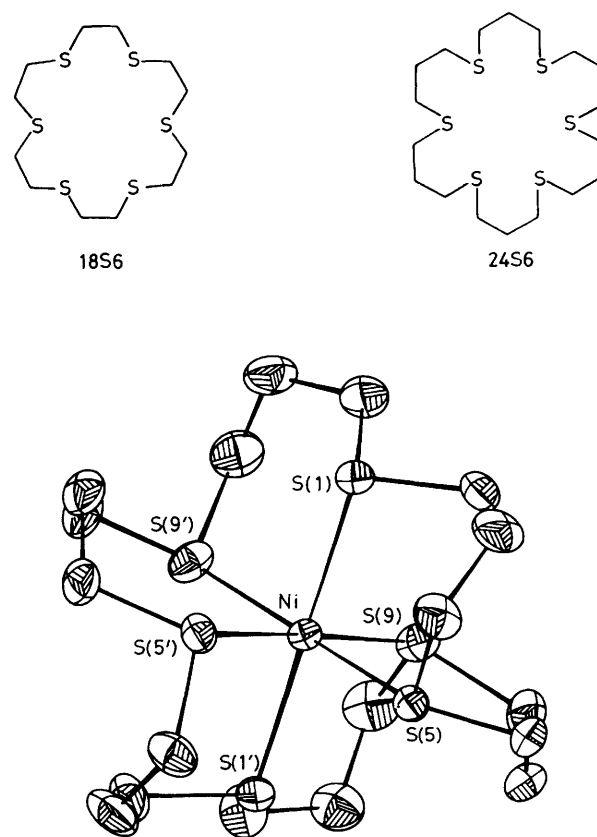


Figure 1. CHEMGRAF drawing of the [Ni·(24S6)]<sup>2+</sup> cation showing thermal ellipsoids at 50% probability level (hydrogen atoms are omitted for clarity).

† Crystal data: C<sub>18</sub>H<sub>36</sub>S<sub>6</sub>NiB<sub>2</sub>F<sub>8</sub>, *M* = 677.2, monoclinic C-centred, space group C2/c, *a* = 13.744(5), *b* = 17.021(5), *c* = 13.801(5) Å, β = 113.25(3)°, *U* = 2966.37 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.52 g cm<sup>-3</sup>. A crystal (0.28 mm × 0.28 mm × 0.34 mm) was sealed in an X-ray capillary under nitrogen for crystallographic studies. An Enraf-Nonius CAD4 diffractometer with Mo-Kα radiation (0.71069 Å) was used for collection of 4353 unique data (excluding systematic absences) with 2θ ≤ 54°. Four standard reflections that were measured every hour showed no decay. Calculations were performed with the CRYSTALS crystallographic programs on a VAX 11/750 computer, with atomic scattering factors from the usual source. The Ni atom was found by Patterson synthesis, and the remaining atoms were found by Fourier difference syntheses and full matrix least-squares refinement based on 2370 data with *I* > 3σ(*I*). At convergence *R* = 5.00% (*R*<sub>w</sub> = 5.32%) for 192 parameters {*R* = Σ(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)/Σ|*F*<sub>o</sub>|, *R*<sub>w</sub> = [Σw(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)<sup>2</sup>/Σw*F*<sub>o</sub><sup>2</sup>]<sup>1/2</sup> with *w* = 1/σ<sup>2</sup>(*F*)}. The highest peak in the difference map was 1.0 e Å<sup>-3</sup>, and was found next to a fluorine atom of the disordered tetrafluoroborate anion.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

The optical spectra of the two complexes support this conclusion. In nitromethane solution  $[\text{Ni} \cdot (18\text{S6})]^{2+}$  exhibits bands at 12 290 and 19 230  $\text{cm}^{-1}$  ( $\epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1} = 24$  and 27, respectively) and  $[\text{Ni} \cdot (24\text{S6})]^{2+}$  has bands at 11 050 and 16 950  $\text{cm}^{-1}$  ( $\epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1} = 100$  and 70, respectively). Thus despite the presence of identical sets of donor atoms, these two complexes differ in  $10Dq$  by over 10%. In addition, probably because of its lack of inversion symmetry, the extinction coefficients of  $[\text{Ni} \cdot (24\text{S6})]^{2+}$  considerably exceed those of the rigorously centrosymmetric complexes  $[\text{Ni} \cdot (18\text{S6})]^{2+}$  and  $[\text{Ni} \cdot (9\text{S3})_2]^{2+}$ .

In conclusion, the present results demonstrate the utility and extend the scope of crown thioethers as ligands for transition metal ions. Moreover, they show that the cavity size of 24S6 just suits a first-row ion. Larger metal ions, in particular those in low oxidation states, those from the second- and third-rows, and main group ions such as Pb, will require ligands with still larger cavity sizes.

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## References

- 1 S. G. Murray and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 365.
- 2 J. R. Hartman and S. R. Cooper, *J. Am. Chem. Soc.*, 1986, **108**, 1202, and references therein.
- 3 L. A. Ochrymowycz, C.-P. Mak, and J. D. Michna, *J. Org. Chem.*, 1974, **39**, 2079. In our laboratory 24S6 was prepared from thiodipropionic acid by a different route that is analogous to that used previously for 18S6: J. R. Hartman, L. A. Ochrymowycz, and S. R. Cooper, *Inorg. Synth.*, submitted for publication.
- 4 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751; L. A. Drummond, K. Henrick, M. J. L. Kanagasundaram, L. F. Lindoy, M. McPartlin, and P. A. Tasker, *Inorg. Chem.*, 1982, **21**, 3923.
- 5 M. R. Udupa and B. Krebs, *Inorg. Chim. Acta*, 1981, **52**, 215.
- 6 N. L. Hill and H. Hope, *Inorg. Chem.*, 1974, **13**, 2079.
- 7 E. J. Hintsa, J. R. Hartman, and S. R. Cooper, *J. Am. Chem. Soc.*, 1983, **105**, 3738.
- 8 W. N. Setzer, C. A. Ogle, G. S. Wilson, and R. S. Glass, *Inorg. Chem.*, 1983, **22**, 266.