The Synthesis and Low-temperature Single Crystal X-Ray Structure of the Charge-transfer Complex ([9]aneS$_3$)$_2$(I$_2$)$_4$ ([9]aneS$_3$ = 1,4,7-trithiacyclononane)

Alexander J. Blake, Robert O. Gould, Christian Radek and Martin Schröder*

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, Scotland EH9 3JJ

Reaction of [9]aneS$_3$ (1,4,7-trithiacyclononane) and I$_2$ in cold CH$_2$Cl$_2$ results in the formation of 1 : 1 and 1 : 2 adducts; the single crystal X-ray structure of the 1 : 2 adduct ([9]aneS$_3$)$_2$(I$_2$)$_4$ shows an unusual polymeric structure with I$_2$ bridging [9]aneS$_3$ thioether units.

The complexation of late transition metals by thioether macrocycles has been studied intensively in the last decade.[1,2] Recently, Willey and coworkers have confirmed the ability of thioether crowns to bind to main group cations such as Sb^{III} and Bi^{III}.[3] Our own work has focused on the chemistry of thioether crowns with transition metal ions,[1] and more recently with Ag^I, Au^I and Tl^I centres.[4] We were interested in whether homoleptic thioether crowns might be capable of binding to halogens and inter-halogens such as I$_2$ and ICl to form charge-transfer complexes. Previous work on iodine-thioether[5] or -thiocarbonyl[6] complexes has shown a wide range of different coordination modes and structures. We report herein the synthesis and structure of an unusual polymeric adduct of I$_2$ with [9]aneS$_3$.

Addition of I$_2$ to one molar equiv. of [9]aneS$_3$ in CH$_2$Cl$_2$ at 0 °C under N$_2$ affords a pale-brown solution; further addition of I$_2$ leads to slight darkening of the solution. The stoichiometry of the I$_2$:[9]aneS$_3$ charge-transfer complex was determined using Job's method[7] of continuous concentration variation. This was carried out by measuring the variation in the absorption band of the charge-transfer complex at 310 nm as a function of I$_2$:[9]aneS$_3$ ratio. Although this method does not eliminate the possibility of formation of higher stoichiometries in solution, it does suggest that the main product in CH$_2$Cl$_2$ solution is the 1 : 1 species ([9]aneS$_3$)(I$_2$). Reaction of [9]aneS$_3$ with ICl in a 1 : 1 molar ratio in CH$_2$Cl$_2$ likewise affords a brown solution; addition of a further equivalent of ICl affords a yellow precipitate which has the stoichiometry ([9]aneS$_3$)(ICl)$_2$. This yellow product is unstable in MeCN and darkens rapidly to give brown solutions. In the solid state, the complex slowly darkens over a period of weeks with the apparent evolution of ICl and/or I$_2$.

Red lustrous crystals of the [9]aneS$_3$: I$_2$ adduct suitable for X-ray diffraction studies were obtained by sublimation. The structure determination† shows (Fig. 1) two [9]aneS$_3$ mol-
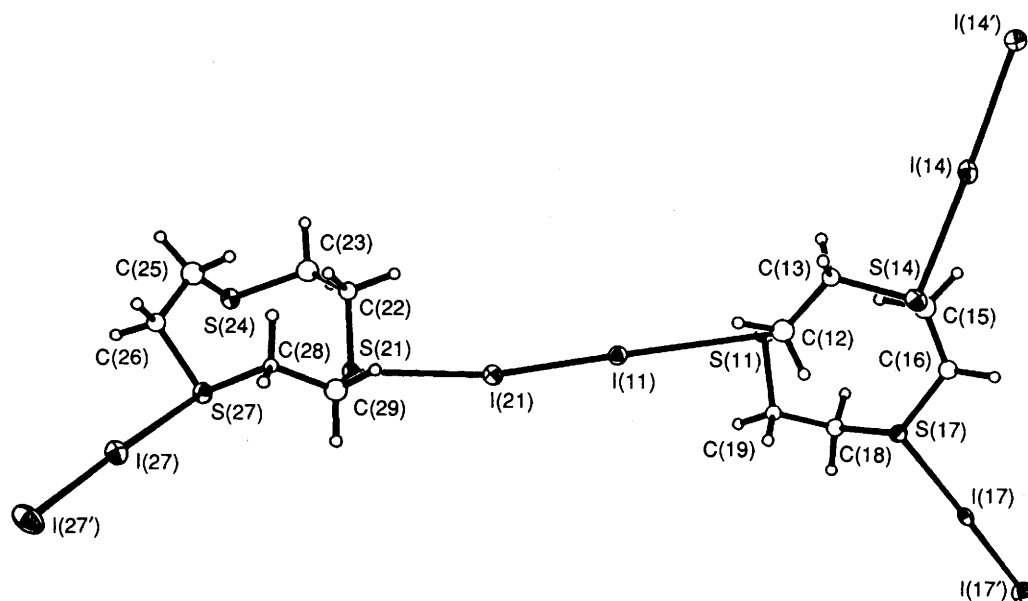
Fig. 1 View of the structure of ([9]aneS$_3$)$_2$(I$_2$)$_4$ with numbering scheme adopted
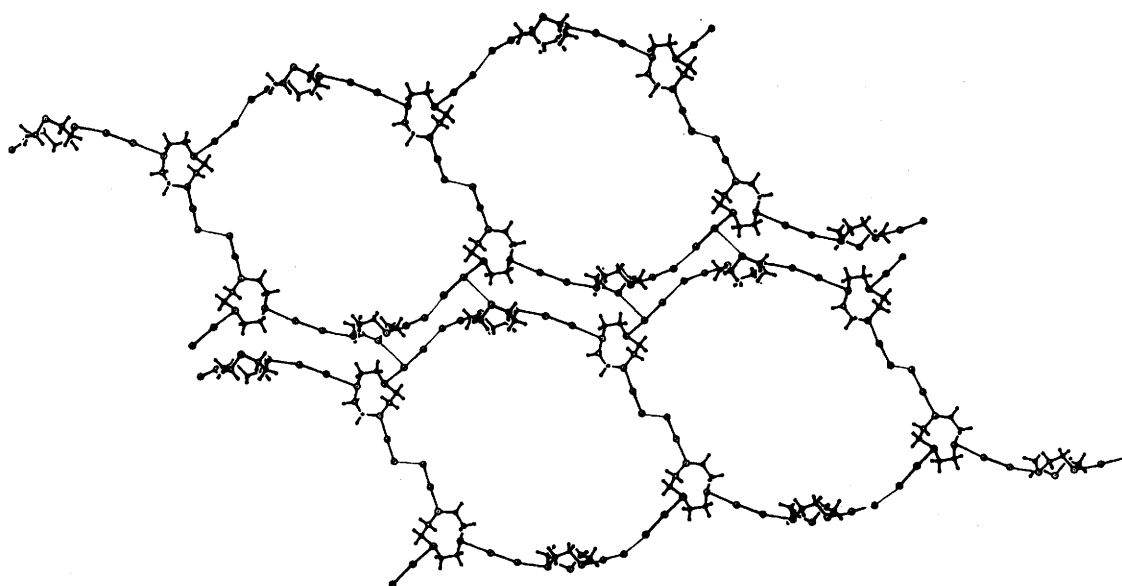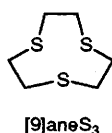

Fig. 2 Packing diagram for ([9]aneS$_3$)$_2$(I$_2$)$_4$

[9]aneS$_3$

ecules linked by a bridging diiodine molecule. The structure is asymmetric: the first macrocycle [S(11)–C(19)] interacts with two terminal I$_2$ molecules in addition to the bridging molecule; the second [S(21)–C(29)] carries only one terminal I$_2$ molecule. The two [9]aneS$_3$ moieties also differ markedly in conformation, with the second adopting one similar to the [333] endo conformation observed for free [9]aneS$_3$ in the crystal and in the vapour phase:[8] the first ring adopts a different conformation for the region around S(11).

The bond lengths for both bridging [I(11)–I(21) 2.754(2) Å] and terminal [I(14)–I(14′) 2.785(2), I(17)–I(17′) 2.816(2),

I(27)–I(27′) 2.799(2) Å] I–I distances are, as expected, significantly longer than the I–I bond length in either the vapour [2.667(2) Å][9] or the solid state at 110 K [2.715(6) Å].[10] The S···I distances involving the I$_2$ bridge are the longest at 3.197(6) Å [for S(11)–I(11)] and 3.054(6) Å [for S(21)–I(21)]; the S–I distances to terminal diiodine molecules are 2.870(6), 2.760(6) and 2.862(6) Å for S(14)–I(14), S(17)–I(17) and S(27)–I(27) respectively. The variation of I–I vs. S–I bond distances fits the curve plotted by Herbstein and Schwotzer[11] in the region of minimum perturbation: that is, long I–I bonds are associated with short S–I bonds and vice versa. The quasi-linear S–I–I angles range from 174.86(14) to 178.35(14)°, with the exception of the I(11)–I(21)–S(21) angle of 168.39(13)°.

As commonly found for structures containing I$_2$, there are extensive intermolecular contacts, here I···I and S···I. It is noteworthy that the closest S···I intermolecular contacts of

3.721 and 3.751 Å involve the unique, uncoordinated sulfur S(24). The closest I···I contact is one of 3.778(3) Å. The greater non-linearity at I(21) compared with I(11) may be linked to the participation of the former in two relatively short contacts of 4.036(3) and 4.204(3) Å (the van der Waals radius for I is 2.10 Å). Fig. 2 illustrates part of an infinite sheet of ([9]aneS$_3$)$_2$(I$_2$)$_4$ molecules formed by these contacts: sheets are cross-linked and offset from one another to form an infinite three-dimensional network of molecules.

Reaction of I$_2$ and ICl with [12]aneS$_4$, [14]aneS$_4$, [16]aneS$_4$, [15]aneS$_5$ and [18]aneS$_6$ all give similar 1 : 1 and 2 : 1 brown or yellow adducts of varying solubility. Future work is aimed at the solid state characterisation of these materials and the investigation of partially charged species derived from them.

We thank the SERC for support and the Royal Society of Edinburgh and Scottish Office Education Department for a Support Research Fellowship to M. S.

Received, 2nd March 1993; Com. 3/01229H

References

1 A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 1990, **35**, 1.
2 S. R. Cooper and S. C. Rawle, *Struct. Bond. (Berlin)*, 1990, **72**, 1.

3 G. R. Willey, M. T. Lakin, M. Ravindran and N. W. Alcock, *J. Chem. Soc., Chem. Commun.*, 1991, 271; G. R. Willey, M. T. Larkin and N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, 1992, 591.
4 *E.g.*: A. J. Blake, D. Collison, R. O. Gould, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1993, 521; A. J. Blake, J. A. Greig, A. J. Holder, T. I. Hyde, A. Taylor and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, 1989, **29**, 197; A. J. Blake, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1992, 2987.
5 G. Y. Chao and J. D. McCullough, *Acta Crystallogr.*, 1960, **13**, 727; C. Rømming, *Acta Chem. Scand.*, 1960, **14**, 2145; F. H. Herbstein, P. Ashkenazi, M. Kaftory, M. Kapon, G. M. Reisner and D. Ginsburg, *Acta Crystallogr. Sect. B*, 1986, **42**, 575; A. L. Tipton, M. C. Lonergan, C. L. Stern and D. F. Shriver, *Inorg. Chim. Acta*, 1992, **201**, 23.
6 E. L. Ahlsen and K. O. Strømme, *Acta Chem. Scand., Ser. A*, 1974, **28**, 175; F. Freeman, J. W. Ziller, H. N. Po and M. C. Keindl, *J. Am. Chem. Soc.*, 1988, **110**, 2586; D. Atzei, P. Deplano, E. F. Trogu, F. Bigoli, M. A. Pellinghelli and A. Vacca, *Can. J. Chem.*, 1988, **66**, 1483.
7 P. Job, *Anal. Chim.*, 1928, **9**, 113; 1936, **17**, 97.
8 R. S. Glass, G. S. Wilson and W. N. Setzer, *J. Am. Chem. Soc.*, 1980, **102**, 5068; R. Blom, D. W. H. Rankin, M. Schröder and A. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1991, 773.
9 I. L. Karle, *J. Chem. Phys.*, 1955, **23**, 1739.
10 F. van Bolhuis, P. B. Koster and T. Migchelsen, *Acta Crystallogr.*, 1967, **23**, 90.
11 E. F. H. Herbstein and W. Schwotzer, *J. Am. Chem. Soc.*, 1984, **106**, 2367.