Synthesis and Structural Characterisation of a Novel One-dimensional Polymeric Complex, $[Bu^n_4N][TlWS_4]$

Jian-Ping Lang,*[a] Je Liu,[b] Ming-Qin Chen,[b] Jian-Mei Lu,[a] Guo-Qing Bian[a] and Xin-Quan Xin[c]

[a] *Department of Chemistry, Suzhou University, PO Box 174, Suzhou 215006, PR China*
[b] *Center of Analysis and Measurement, Fudan University, Shanghai 200433, PR China*
[c] *Department of Chemistry, Nanjing University, Nanjing 210008, PR China*

Reaction of $[NH_4]_2[WS_4]$, TlBr and $[Bu^n_4N]Br$ in the solid state produces the mixed-metal sulfur complex $[Bu^n_4N][TlWS_4]$; an X-ray analysis shows that its structure can be described as infinite chains of incomplete double cubane-like $[WTl_3S_7]$ units interconnected *via* face-sharing to form a zigzag arrangement.

It still remains a great challenge to prepare polymeric low-dimensional solids containing different metals. One elegant method is the use of thiometallates as adducts,[1–4] but none have been reported for polymers of low-valent main group elements such as Tl^I and In^I with thiometallates. Here, we report the synthesis and characterisation of $[Bu^n_4N][TlWS_4]$ **I**, the first example of a Tl–W–S complex with a one-dimensional heterometallic polymeric chain structure.

The title compound is obtained by heating $[NH_4]_2[WS_4]$ (0.35 g, 1.0 mmol), TlBr (0.28 g, 1.0 mmol) and $[Bu^n_4N]Br$ (0.96 g, 3.0 mmol) in the solid state at 90 °C for 10 h and extracting the product with DMF (25 ml). The yellow filtrate is left at ambient temperature for 8 d yielding yellow needles of **I** in *ca.* 9% yield.† The IR spectrum of **I** exhibits main bands at 451 and 465 cm^{-1}.

The structure of the polymeric anion is shown in Fig. 1.‡ The anion forms a polymeric zigzag chain parallel to the crystallographic *c* axis which appears to be built up from face-sharing of incomplete double cubane-type $[WTl_3S_7]$ units *via* the [TlS(1a)Tl(2)S(3)] and [TlS(1)Tl(2)S(3a)] planes. The double cubane-like units consist of two incomplete cubane-like $[WTl_2S_4]$ subunits (in each of which one Tl corner is missing) joined by a common [WS(1)TlS(3)] plane.

The X-ray analysis indicates that there are two classes of S atoms in this complex. The S(2) and S(4) atoms are doubly bonded to a W and a Tl atom, the S(1) and S(3) atoms are triply bridged to a W and two Tl atoms. The W atom is unexceptionally tetrahedrally coordinated. Each Tl atom is coordinated by two μ-S and four μ_3-S atoms with a strongly distorted TlS_6 octahedral geometry. The Tl–S lengths in this octahedron, [2.995(3)–3.444(4) Å] are significantly longer than the sum of reasonable estimates of the atomic radii of Tl and S, which shows that there is a large steric demand by the lone electron pairs on the Tl atom in the Tl–S bond. As indicated by the shortest molecular Tl···Tl or Tl···W lengths of 4.839(1) [Tl···Tl(1)], 3.762(1) [Tl···W] and 4.065(1) Å [W···Tl(1)] in **I**, there are no structurally significant bonding metal–metal interactions.

Received, 7th June 1994;§ Com. 4/03453H

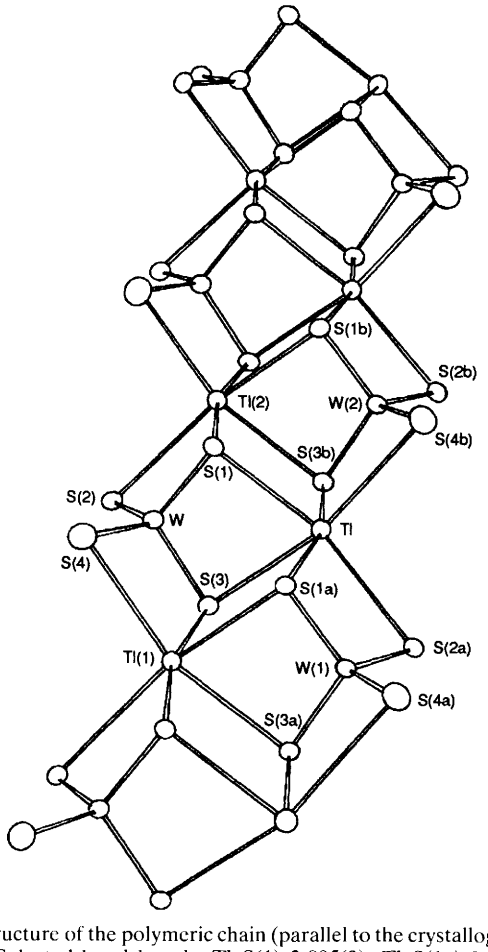

Fig. 1 Structure of the polymeric chain (parallel to the crystallographic *c* axis). Selected bond lengths Tl–S(1) 2.995(3), Tl–S(1a) 3.340(3), Tl–S(2a) 3.444(4), Tl–S(3) 3.100(3), Tl–S(3b) 3.146(3), Tl–S(4b) 3.358(5), W···Tl 3.762(1), W···Tl(1) 4.065(1), Tl···Tl(1) 4.389(1) Å.

Footnotes

† Satisfactory elemental analyses were obtained.

‡ *Crystal data for* **I**: $C_{16}H_{36}NS_4TlW$, M = 758.95, monoclinic, space group Cc, a = 17.127(2), b = 18.313(5), c = 7.838(3) Å, β = 97.11(2)°, V = 2439.3 $Å^3$, Z = 4, D_c = 2.066 g cm^{-3}, μ = 118.1 cm^{-1}, $F(000)$ = 1432; $2\theta \leq 50.0°$ (Mo-Kα, λ = 0.709 30 Å, graphite monochromator, ω–2θ scans, T 293 ± 1 K). The structure was solved by direct methods (SDP/VAX-PLUS)[5] and refined anisotropically using absorption-corrected data to give R = 0.023 and R_w = 0.025 for 2034 independent observed reflections (from a total of 2317 unique reflections) with $I > 3.0\sigma(I)$. H atoms included in calculated positions riding on the parent C atoms. The atomic scattering factors were taken from ref. 6.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Revised version received, 13th September 1994.

References

1 A. Müller, M. Dartman, C. Romer, W. Clegg and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1981, **22**, 178; A. Müller, W. Hellmann, J. Schneider, U. Schimansk, U. Demner, A. Trautwein and U. Bender, *Inorg. Chim. Acta*, 1982, **65**, L41; A. Müller, E. Krickemeyer and M. Penk, *J. Chem. Soc., Chem. Commun.*, 1990, 321; A. Müller, E. Krickemeyer, A. Hildebrand, H. Bogge, K. Schneider and M. Lemke, *J. Chem. Soc., Chem. Commun.*, 1991, 1685; and references cited therein.

2 J. R. Nicholson, A. C. Flood, C. D. Garner and W. Clegg, *J. Chem. Soc., Chem. Commun.*, 1983, 1179.

3 J. M. Manoli, C. Potvin, F. Secheresse and S. Marzark, *Inorg. Chim. Acta*, 1988, **150**, 257; F. Secheresse, S. Bernes, F. Robet and Y. Jeannin, *J. Chem. Soc., Dalton Trans.*, 1991, 2875.

4 J. P. Lang, J. G. Li, S. A. Bao, X. Q. Xin and K. B. Yu, *Polyhedron*, 1993, **12**, 801; J. P. Lang, W. Y. Zhou, X. Q. Xin, J. H. Cai, B. S. Kang and K. B. Yu, *Polyhedron*, 1993, **12**, 1647; J. P. Lang and X. Q. Xin, *J. Solid State Chem.*, 1994, **108**, 118.

5 A. B. Frenz, in *Computing in Crystallography*, ed. H. Schenk, Delft University Press, Delft, 1978, p. 64.

6 D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2B.