X-Ray Structure of a Potassium–Sulfur Ladder Polymer with Strong K···Aryl Stabilising Interactions

Alexandra M. Z. Slawin, Joanna Ward, David J. Williams and J. Derek Woollins*

Department of Chemistry, Imperial College, London, UK SW7 2AY

$K[SPPh_2NPPh_2S]$ exhibits a ladder-like polymer structure in which the octahedral geometry about the potassium is achieved *via* K···aryl electrostatic interactions.

The preparation of extended inorganic structures and polymers is currently of considerable interest.[1] Oxygen[2,3] and nitrogen[4] donor systems which coordinate to alkali and alkaline earth metals have been extensively studied, in part at least because of their potential as precursors for metal oxides. Often these systems exist in polymeric ladder type structures. Delocalised 'aromatic' rings containing p-block elements have also been investigated.[5] Surprisingly few structures containing heavier s and p block elements together have been reported. Here we describe the preparation and X-ray structure of $K[SPPh_2NPPh_2S]$ **1**.

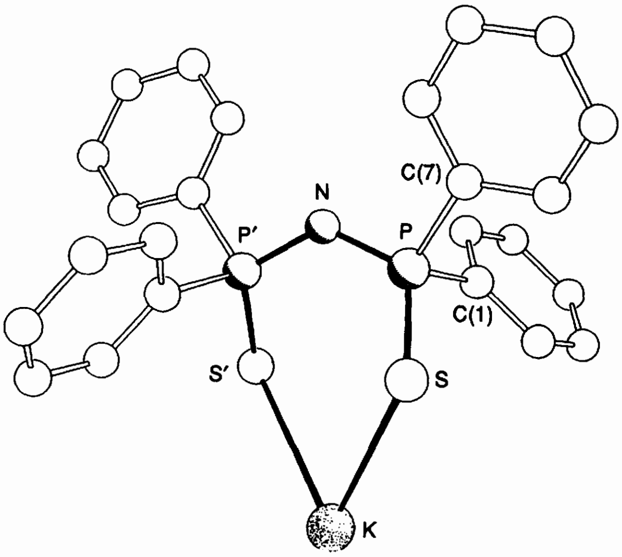

Fig. 1 The X-ray structure of **1** showing the numbering scheme. Selected bond lengths (Å) and angles (°): P–S 1.978(1), P–N 1.592(2), K–S 3.203(1), P–N–P′ 128.6(2), S–P–N 120.7(1), K–S–P 110.7(1), S–K–S′ 80.5(1).

Reaction of $KOBu^t$ with $Ph_2(S)PNHP(S)Ph_2$ **2** in butanol gives **1** in good yield by a modification of the published procedure.[6] Recrystallisation of **1** from methanol gave crystals suitable for X-ray analysis. The X-ray structure reveals (Fig. 1) that upon forming the potassium salt the conformation of the SPNPS chain changes from *anti*[7] to *syn*, with the two sulfur atoms coordinating to potassium. The molecule has crystallographic C_2 symmetry about the N···K vector. Deprotonation of the nitrogen atom leads to a small contraction in the P–N–P angle [128.6(2)° in **1**, 132.6(1)° in **2**], a shortening of the P–N bonds [1.592(2) *cf.* 1.671(2) and 1.684(2) Å] and a lengthening of the P–S bonds [1.978(1) *cf.* 1.950(1), 1.936(1) Å]. There is also an increase in the N–P–S angle in **1** *v.* **2** [120.7(1) *cf.* 114.7(1), 115.3(1)°]. The changes in bond lengths reflect an increase in delocalisation within the SPNPS group in **1** compared with **2**. Comparison of the vibrational spectra of **1** and **2** further supports this conclusion.† Similar effects have been noted in conventional coordination complexes of **2**.[8,9] The six-membered KS_2P_2N ring in **1** is significantly distorted from planar with the PNP plane being twisted (about the C_2 axis) by 31° with respect to the KS_2 plane; the phosphorus atoms lie 0.74 Å above and below the KS_2N plane. The potassium and sulfur atoms in adjacent molecules are linked to form four-membered K_2S_2 rings (Fig. 2) producing an extended ladder like polymer, the potassium atoms being effectively 'spiro' centres. The K···S distances are 3.203(1) and 3.279(1) Å within the six- and four-membered rings, respectively, and the corresponding S···S distances are 4.14 and 4.47 Å [the K···K distance is 4.693(1) Å]. Within the planar four-membered rings the K···S···K and S···K···S angles are 92.8(1) and 87.2(1)°, respectively. The potassium atoms, as shown in Fig. 2, appear to be only four coordinate and asymmetrically disposed. Careful inspection of the environment of each potassium atom reveals close contacts between a potassium atom and one of the C–C bonds within the phenyl rings associated with neighbouring ligands (Fig. 3) [K···C(5)–C(6) bond centroid distance 3.36 Å; K···centroid vector to phenyl ring plane angle 86°]. This compares with

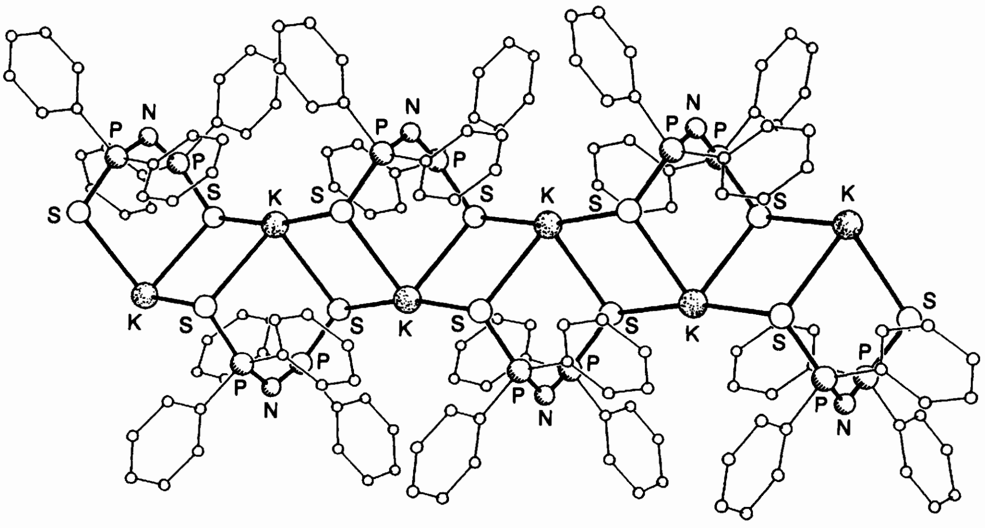

Fig. 2 One of the ladder-like polymer chains in the structure of **1**

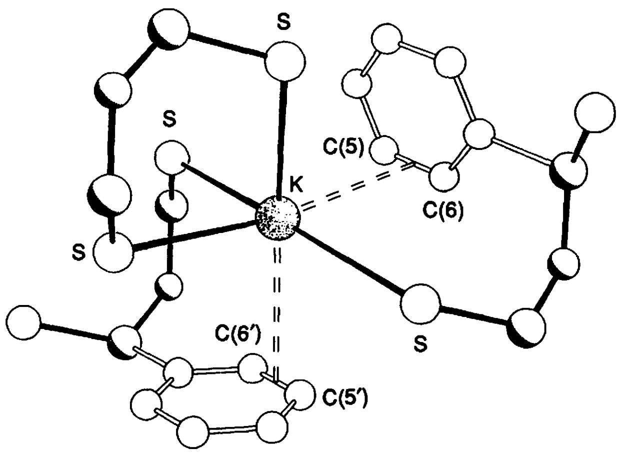

Fig. 3 The coordination geometry about a potassium atom in **1** showing the K···aryl vectors which complete the octahedral coordination of the metal

values in the range 3.0–3.2 Å for formally bonded K–C linkages. These interactions are almost certainly electrostatic in nature and result in a slightly distorted octahedral geometry about each potassium centre [angles at potassium are in the ranges 80.5(1)–101.0(1) and 169.3(1)–170.5(1)°]. It is notable that these K–π interactions exist, particularly since **1** was recrystallised from methanol and thus solvation could have readily satisfied the coordination requirements of the potassium. It is probable that the K···aryl interactions are indeed a significant feature in determining the propagation of the polymer structure. Further studies into the generality of this alkali metal···aryl interaction are in progress.

We are grateful for the SERC for the provision of the diffractometer.

Received, 9th August 1993; Com. 3/04773C

Footnote

† Complex **1** gave satisfactory microanalyses and displayed the expected spectroscopic properties (corresponding values for **2** in parentheses): $^{31}P\{^1H\}$ δ 35.8 (s) [55.7 (s)]; IR ν(PNP)/cm^{-1} 1199 (928), ν(PS)/cm^{-1} 606, 584 (689, 650). *Crystal data* for **1**: $C_{24}H_{20}KNP_2S_2$ (the molecule is disposed about a two-fold axis), M = 487.6, monoclinic, a = 8.355(2), b = 27.639(7), c = 10.221(2) Å, β = 92.87(2)°, U = 2357.1 Å^3, space group $I2/a$ (body-centred lattice chosen because C-faced centred cell has β = 127.54°) Z = 4, D_c = 1.374 g cm^{-3}, μ(Cu-$K\alpha$) = 49.97 cm^{-1}. Crystal dimensions 0.4 × 0.4 × 0.3 mm. Data were measured on a Siemens P3/PC diffractometer with graphite monochromated Cu-$K\alpha$ radiation using ω scans. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give R = 0.035, R_W = 0.036 for 1423 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leq 116°$]. 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.

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