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Metal-binding by Mixed Hard–Soft Donor Ligands; the Crystal and Molecular Structure of Bromo(2,10-diaza-6-thiaundecane)palladium(II) Bromide

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The stability of transition metal complexes frequently follows the Irving–Williams series, with copper(II) forming the most stable complexes with a given ligand or set of ligands [1]. In an attempt to design ligands possessing high selectivity for metal ions other than copper(II), we have investigated the coordination behaviour of a range of aminothioethers possessing both hard amino and soft thioether donor functionalities [2]. The ligand $MeHN(CH_2)_3S(CH_2)_3NHMe$ has proved to be of particular interest in this respect, and we describe herein the palladium(II) complex [PdLBr]Br.

The thioether was obtained in 54% yield by the reaction of $MeHN(CH_2)_3SH$ with $[MeH_2N(CH_2)_3Cl]Cl$ in the presence of sodium methoxide. Reaction of L with palladium acetate in methanol resulted in the formation of a pale yellow solution, from which the yellow complex [PdLBr]Br was obtained by the addition of lithium bromide. Recrystallisation from methanol–diethyl ether gave golden yellow needles of X-ray quality.

Crystal data: $C_8H_{20}Br_2N_2PdS$, $M = 442.6$, orthorhombic, space group *Pnam* (No. 62), $a = 10.275(9)$, $b = 13.884(9)$, $c = 9.535(9)$ Å, $U = 1360.2$ Å^3, $Z = 4$, $D_m = 2.12(3)$ g cm^{-3}, $D_c = 2.16$ g cm^{-3}, μ(Mo Kα) = 76.6 cm^{-1}. The structure was solved by heavy atom methods and refined to an R factor of 0.050 (R_w = 0.057) using 889 independent reflections with $I > 2\sigma(I)$ measured on a Stoe Stadi 2 diffractometer (Mo Kα radiation, $\lambda = 0.7107$ Å). The hydrogen atoms were refined isotropically; all non-hydrogen atoms were refined non-isotropically.

All new compounds were characterised by microanalysis, ^{1}H and ^{13}C NMR, IR and mass spectroscopy. See also 'Supplementary Material'.

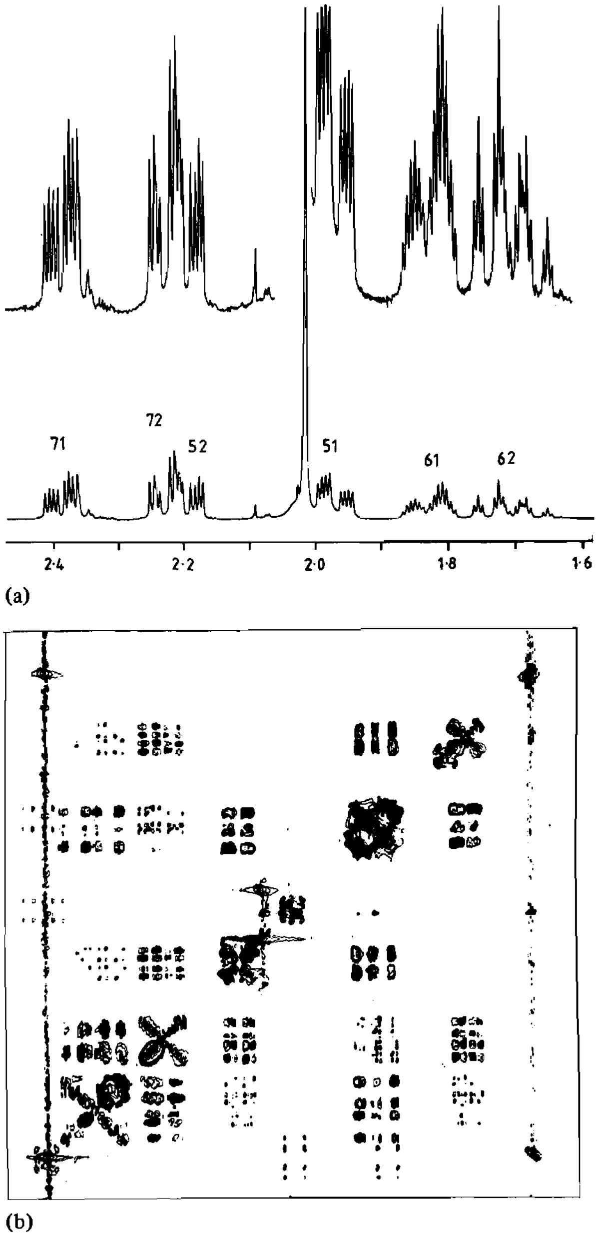

Fig. 1. (a) 400 MHz ^{1}H NMR spectrum of a CD_3SOCD_3 solution of [PdLBr]Br (numbering as in Fig. 2); (b) 250 MHz double-quantum filtered phase-sensitive COSY spectrum of a CD_3OD solution of [PdLBr]Br.

The ^{1}H NMR spectrum of a $CDCl_3$ solution of the complex is shown in Fig. 1a, together with the double-quantum filtered phase-sensitive COSY spectrum in Fig. 1b [3]. Assignments were made using the COSY experiment, and fitting the coupling constants to a modified Karplus–Conroy equation [4]. In particular, the assignment of H(72) and H(52) was on the basis of the large vicinal couplings to H(62). The spectrum clearly shows that a single isomer of the complex is present, and that the chelate rings are

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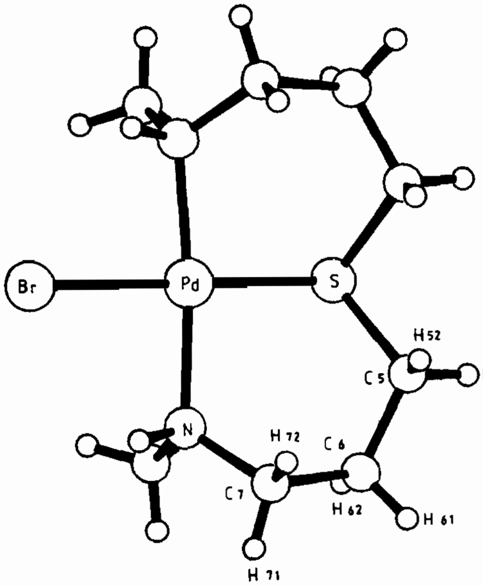

Fig. 2. The crystal and molecular structure of the cation [PdLBr]$^+$ in [PdLBr]Br. Relevant bond distances, Pd–N 2.033(9), Pd–S 2.285(4), Pd–Br 2.449(2) Å; relevant bond angles, Br–Pd–S 176.59(13)°, Br–Pd–N 88.05(24)°, S–Pd–N 91.79(24)°, N–Pd–N′ 173.65(32)°.

equivalent on the NMR time-scale. This is in marked contrast to the macrocyclic complex cation [PdL^1]$^{2+}$ (L^1 = 3,3,7,7,11,11,15,15-octamethyl-1,9-dithia-5,13-diazacyclohexadecane), which exhibits a number of solution conformers [5]. This control by an acyclic ligand is worthy of note, and suggests that it is not necessary to extend to macrocyclic systems to obtain stereochemically non-dynamic complexes with high metal-ion selectivity. The presence of a single methyl resonance indicates the equivalence of the N–Me groups, but this will not distinguish between the *cis* (related by a mirror plane) and *trans* (related by a rotation) isomers. This information was of particular interest to our studies of derivatives incorporating long-chain alkyl substituents upon the nitrogen, and we accordingly performed a single crystal X-ray structure determination of the compound.

The complex consists of discrete [PdLBr]$^+$ cations (Fig. 2) and bromide anions, with L acting as a terdentate NSN donor. The closest contact of the anion to a non-hydrogen atom is 3.55 Å to N(8). The cation has crystallographically imposed mirror symmetry, with unique distances Pd–Br 2.449(2), Pd–S 2.285(4) and Pd–N 2.033(9) Å. The palladium atom is in a slightly distorted square-planar environment; whilst the N_2SBr moiety is planar to within 0.01 Å, the palladium atom is 0.08 Å from this plane. The geometry of the ligand is as expected, with unique torsion angles Pd–N–C–C 68°, N–C–C–C –72.2°, C–C–C–S 69.6° and C–C–S–C –167.5°. Each ring is in a distorted chair conformation. The Pd–S distance is remarkably similar to those of 2.270 and 2.294 Å observed in [$Pd_2(Me_2NCH_2CH_2CH_2S)_2Cl_2$] [6] and in the macrocyclic complexes [PdL^1][PF_6]$_2$ and [PdL^1]$Cl_2\cdot 2H_2O$ [5]. This indicates the strong bonding between the soft thioether and the second row element. It is relevant to note the copper(II) complexes with L are five-coordinate*, and the changes in geometry associated with thioether binding provide a mechanism for circumventing the Irving–Williams order.

Supplementary Material

The atomic coordinates for this work together with Tables of molecular dimensions and thermal parameters are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

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*$CuLX_2$ (X = Cl or Br) are both five-coordinate, with the nitrogens in axial positions of a trigonal bipyramid. The ligand has a very different conformation from that in [PdL]$^{2+}$.