Binuclear, Nitrogen-bridged Complexes of Disulphurdinitride, $[M(S_2N_2)(PPh_3)]_2{\cdot}CH_2Cl_2$ (M = Pd, Pt)

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Reaction of tetrasulphurtetranitride with tris(triphenylphosphine)platinum(0) or tetrakis(triphenylphosphine)palladium(0) gives $[M(S_2N_2)(PPh_3)]_2{\cdot}CH_2Cl_2$; the *X*-ray structure of the platinum compound shows the $[Pt(S_2N_2)]_2$ unit to be planar: the $S_2N_2^{2-}$ group acts as a bidentate and bridging ligand with the platinum atoms bring bridged by nitrogen to form a four membered Pt_2N_2 ring.

Since the discovery of the unusual electrical behaviour of polymeric sulphur nitride, $(SN)_x$, there has been renewed interest in sulphur–nitrogen compounds,[1] particularly in regard to their potential as 1-D conductors. We are investigating routes to metalla-sulphur–nitrogen complexes[2—4] and clearly an important area is the preparation of binuclear compounds as precursors to extended structures. Although several mononuclear disulphurdinitrido complexes have been described[5—7] there is currently only one example[8] of a binuclear complex and this was prepared from $Ni(S_2N_2H)_2$. The analogous mononuclear $M(S_2N_2H)_2$ palladium and platinum complexes are not as readily available[2] and thus generalisation of the previous route is difficult. Herein we report that reaction of tetrasulphurtetranitride with $M(PPh_3)_n$ (M = Pd, n = 4; M = Pt, n = 3) yields directly $[M(S_2N_2)(PPh_3)]_2{\cdot}CH_2Cl_2$ [M = Pt (**1**); M = Pd, (**2**)].

$$[M(S_2N_2)(PPh_3)]_2{\cdot}CH_2Cl_2$$

(**1**) M = Pt
(**2**) M = Pd

A mixture of $Pt(PPh_3)_3$ (0.3 mmol) and S_4N_4 (0.3 mmol) was stirred in toluene (15 cm³) for 10 min whereupon the dark green solution was reduced to *ca.* 3 cm³ and CH_2Cl_2 added to redissolve the precipitate. On standing overnight red crystals of (**1**) (0.05 mmol) suitable for *X*-ray analysis† were obtained. Compound (**2**) was obtained in a similar fashion as a precipitate from reaction in CH_2Cl_2. Satisfactory microanalyses were obtained for both compounds whilst i.r. (KBr disc) clearly shows the presence of the $S_2N_2^{2-}$ ligand and the similarity of the two compounds [ν(NS) 1032vs (1042vs), 910m (933m), 636s (620m), δ(NS) 379m (363m), ν(MS) 333w (320m), frequencies in cm^{-1}, numbers in parentheses are for the palladium compound].

The *X*-ray structure of (**1**) (Figure 1) reveals a novel structure which is the first example of a binuclear platinum complex containing inorganic sulphur–nitrogen ligands, in this case $S_2N_2^{2-}$. The $[Pt(S_2N_2)]_2$ unit is almost planar with a maximum deviation from the least squares plane of 0.023 Å; the phosphorus atoms lie 0.097 Å out of this plane. The S–N distances in the $S_2N_2^{2-}$ group appear to be insensitive to the bridging nature of the ligand; the distances in (**1**) [S(1)–N(2) 1.687(14), N(2)–S(3) 1.528(13), S(3)–N(4) 1.552(12) Å] being closely comparable to those reported for mononuclear $S_2N_2^{2-}$ and $S_2N_2H^-$ complexes.[6—8] It is notable that there are two short and one long S–N bonds as observed previously.[6] The Pt–S bond length [2.219(4) Å] is significantly shorter than in $Pt(S_2N_2)(PPh_3)_2$ [2.285(5) Å] reflecting the difference in *trans* influence of PPh_3 relative to N^- in $S_2N_2^{2-}$. Finally it is of interest to note that (**1**) provides a rare example of a fully characterised nitrogen bridged Pt_2N_2 ring. The Pt–N distances are comparable with those previously reported.[9—11] The Pt · · · Pt′ and N(4)· · ·N(4′) distances are 3.21 and 2.56 Å respectively.

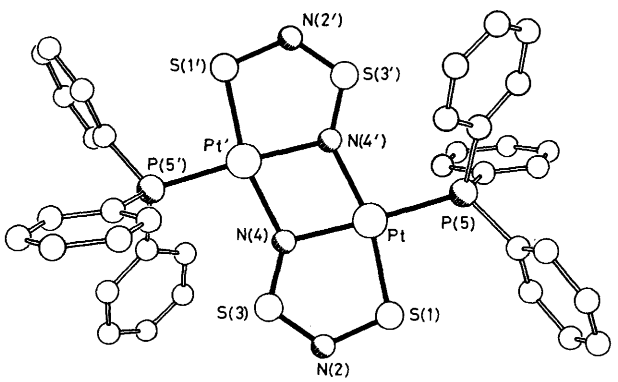

Figure 1. The molecular structure of $[Pt(S_2N_2)(PPh_3)]_2 \cdot CH_2Cl_2$, (**1**). Selected bond distances and angles (e.s.d.s in parentheses): Pt–P(5) 2.255(4), Pt–S(1) 2.219(4), S(1)–N(2) 1.687(14), N(2)–S(3) 1.528(13), S(3)–N(4) 1.552(12), Pt–N(4) 2.042(12), Pt–N(4′) 2.062(11) Å; N(4)–Pt–N(4′) 77.1(5), Pt–N(4)–Pt′ 102.9(5), Pt–S(1)–N(2) 103.1(4), S(1)–N(2)–S(3) 119.7(8), N(2)–S(3)–N(4) 112.7(7), S(3)–N(4)–Pt 116.3(6), N(4)–Pt–S(1) 88.0(3), S(1)–Pt–P(5) 94.8(1), P(5)–Pt–N(4′) 100.1(3)°.

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† *Crystal Data:* $C_{36}H_{30}N_4S_4Pt_2 \cdot CH_2Cl_2$, monoclinic, space group $P2_1/n$ $a = 9.270(3)$, $b = 14.809(4)$, $c = 14.679(4)$ Å, $\beta = 99.59(2)°$, $U = 1987$ Å^3, $Z = 2$, $M = 1122.0$, $D_c = 1.88$ g cm^{-3}, μ(Cu-K_α) = 174 cm^{-1}. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K_α radiation using ω-scans. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give $R = 0.049$, $R_w = 0.042$ for 1638 independent observed reflections $[|F_0|>3\sigma(|F_0|), \theta\leqslant 50°]$. The hydrogen atom positions were included in fixed positions. The CH_2Cl_2 molecule is disordered about a crystallographic centre of symmetry. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.