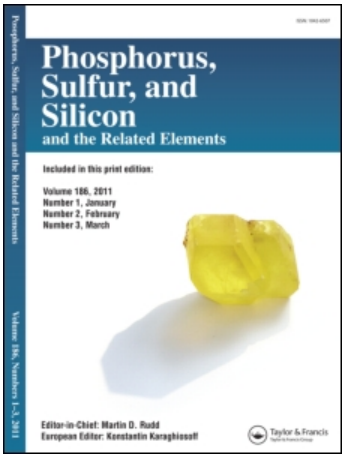


## Phosphorus, Sulfur, and Silicon and the Related Elements

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# Metalla-Sulphur-Nitrogen Chemistry

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# METALLA-SULPHUR-NITROGEN CHEMISTRY

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Abstract The formation of metalla-sulphur-nitrogen complexes containing $RNSN^-$, $OSN^-$, $S_2N_2H^-$, $S_4N_4^{2-}$ and $[S_2N_3(SO_2(NH_2)]^{2-}$ ligands is reported. The new compounds have been characterised by NMR, IR and X-Ray crystallography.



The study of metalla-sulphur-nitrogen[1] compounds is of interest for a number of reasons. Apart from the ability of metal centres to stabilise otherwise very reactive sulphur-nitrogen anions new complexes may possess interesting solid state properties (e.g. as in "stacking compounds") or be useful reagents. We have been involved over the past few years in developing new synthetic routes to metalla-sulphur-nitrogen complexes. Clearly, an important goal must be the development of rational, high yield routes which whenever possible do not involve explosive sulphur-nitrogen precursors. Here, we survey a cross section of our recent work from small anions such as $OSN^-$ through to the tridentate ligand $S_4N_4^{2-}$.

Sulphur dioxide, $OSN^-$ and $NSN^-$ are isoelectronic and it is interesting to investigate whether they form similar compounds. Our starting point in this area was to attempt reactions with $Me_3SiNSNSiMe_3$, (1), which is readily prepared in multi-gram quantities as a distillable slightly air sensitive

liquid. Previously (1) had been used in the synthesis of heterocycles *via* reactions which involve the elimination of $Me_3SiCl$; the thermodynamic driving force for these reactions being the formation of a Si-Cl bond. We have attempted reactions between (1) and *cis*-$PtCl_2(PR_3)_2$ to no effect. However, if $Pt(C_2H_4)(PPh_3)_2$ is used the new complex *cis*-$Pt(NSNSiMe_3)_2(PPh_3)_2$, (2), is obtained[2]. The sulphur diimide ligands are σ-bonded *via* their nitrogen atoms. We have prepared a substituted derivative of (1) *p*-$O_2NC_6H_4SNSNSiMe_3$ (3) by reaction of (1) with *p*-$O_2NC_6H_4SCl$. Reaction of (3) with $PtCl_2$(dppe) proceeds smoothly with the formation of the bis complex $Pt(NSNSC_6H_4NO_2)_2$(dppe) (4) which has the structure shown below[3].



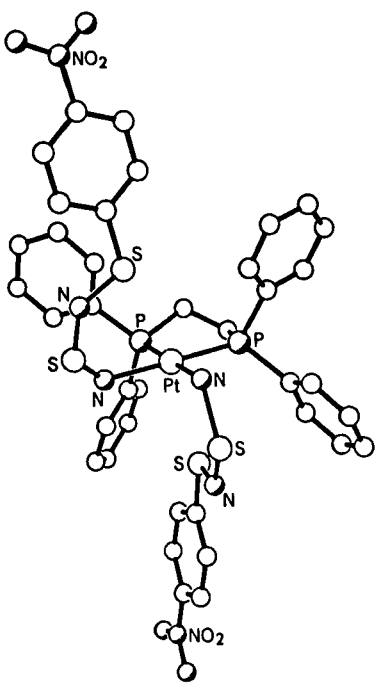


FIGURE 1 The X-ray crystal structure of (4).

Closely related to (1) is $Me_3SiNSO$, (5). We have carried out reactions between (5) and $Pt(C_2H_4)(PPh_3)_2$ but these give a complex mixture. An alternative route is *via* $Hg(NSO)_2$ (prepared by reaction of (5) with $HgF_2$) as shown below[4].

$$Hg(NSO)_2 + Cp_2TiCl_2 \rightarrow Cp_2Ti(NSO)_2 + HgCl_2$$

$$Hg(NSO)_2 + \textit{cis}\text{-}PtCl_2(PR_3)_2 \rightarrow \textit{cis}\text{-}Pt(NSO)_2(PR_3)_2 + HgCl_2$$

$$Hg(NSO)_2 + Pt(C_2H_4)(PPh_3)_2 \rightarrow \textit{trans}\text{-}Pt(NSO)(PPh_3)_2 + Hg$$

A final, extremely clean route to bis NSO complexes is by reaction of $S(NSO)_2$ in liquid ammonia with the appropriate metal halide. The structure of $Pt(NSO)_2(PMe_3)_2$, (6), obtained by this route is shown below[5].

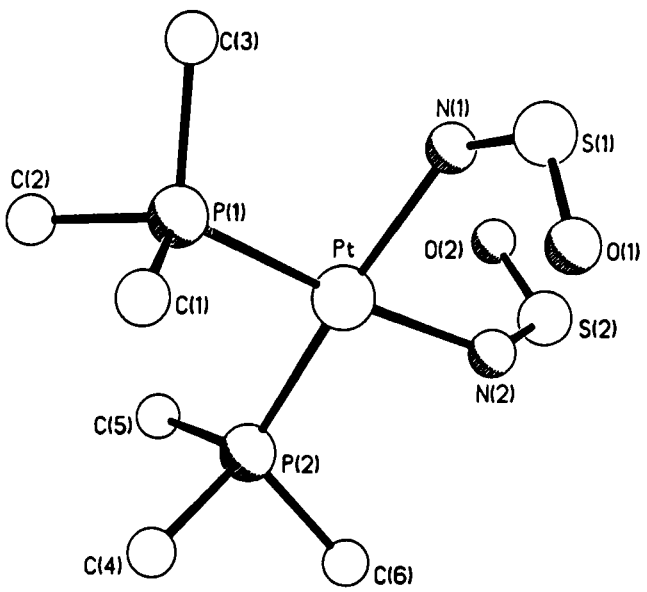


FIGURE 2 The X-ray crystal structure of $Pt(NSO)_2(PMe_3)_2$

We have also developed routes to larger chelate ligands[6-8]. For example, reaction of $Na(S_3N_3)$[6,7] or $S_4N_4H_4$/dbu with *cis*-$PtCl_2(PR_2)_2$ gives $Pt(S_2N_2)(PR_3)_2$, (7) which may be protonated using $HBF_4$ or HCl to give (8), $[Pt(S_2N_2H)(PR_3)_2]X$ (X = $Cl^-$, $BF_4^-$). Alternatively (8) can be obtained by transmetallation reactions using $Me_2SnS_2N_2$ either by reactions with $PtBr_2(COD)$ followed by the phosphine or with the metal chloro-phosphine complex. Treatment of $[S_4N_3]Cl$ with $PtCl_2(PR_3)_2$ in liquid ammonia can also be used to form (7)[5]. We have investigated this latter reaction by $^{14}N$ NMR spectroscopy. Using a high power instrument it is perfectly feasible to obtain spectra of the sulphur-nitrogen species present in liquid ammonia. For example, when $S_4N_4$ is dissolved in liquid ammonia we observe major peaks due to $S_3N_3^-$, $S_4N_5^-$ and and minor peaks (*ca* 0.5%) which we have tentatively assigned to $S_2N_2^{2-}$ [9].

Compounds (8) have interesting crystal structures[7,10]. The cations and anions form stacks with the $PtS_2N_2$ rings laying on top of each other (Figure 3).

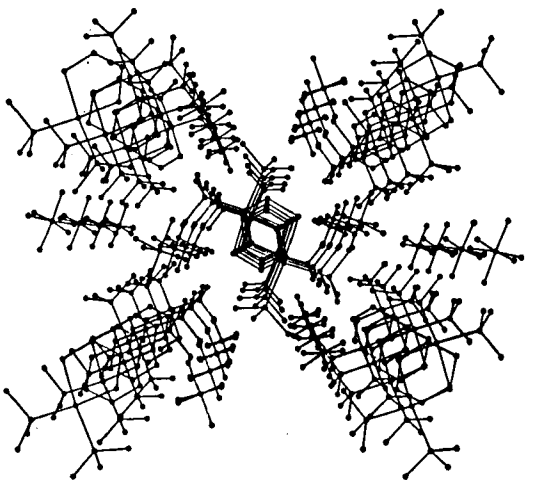

FIGURE 3 The X-ray structure of (8) viewed down the *a* axis.

Reaction of $S_4N_4O_2$ with *cis*-$PtCl_2(PR_3)_2$ proceeds smoothly to give an interesting new $PtS_2N_3$ ring system with one substituted nitrogen atom[5]. The crystal structure of a typical example ($PR_3$ = $PMe_2Ph$) is shown below.

Finally, the largest ring system that we have prepared to date is obtained when $S_4N_4$ is reacted with the dimeric $Pt_2Cl_4(PR_3)_2$. The final product contains a Pt(IV) centre with a tridentate $S_4N_4^{2-}$ which adopts a *mer* conformation[11].



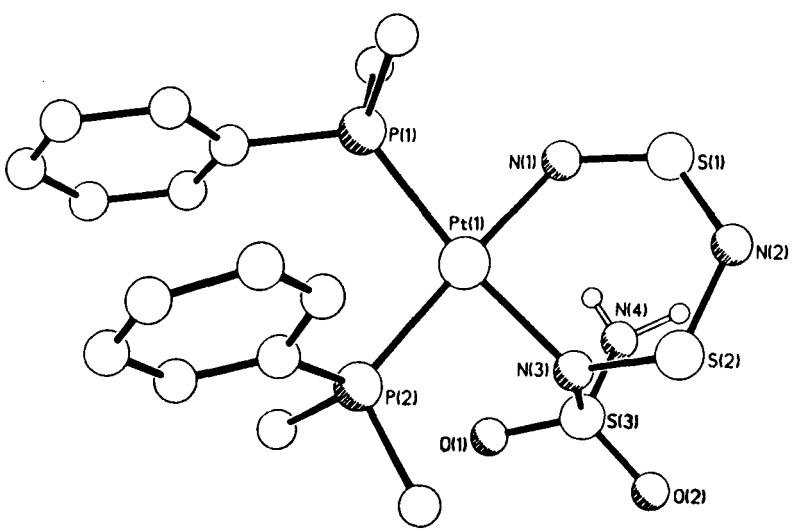


FIGURE 4 The X-ray crystal structure of $Pt(PMe_2Ph)_2\{S_2N_3(SO_2(NH_2))\}$

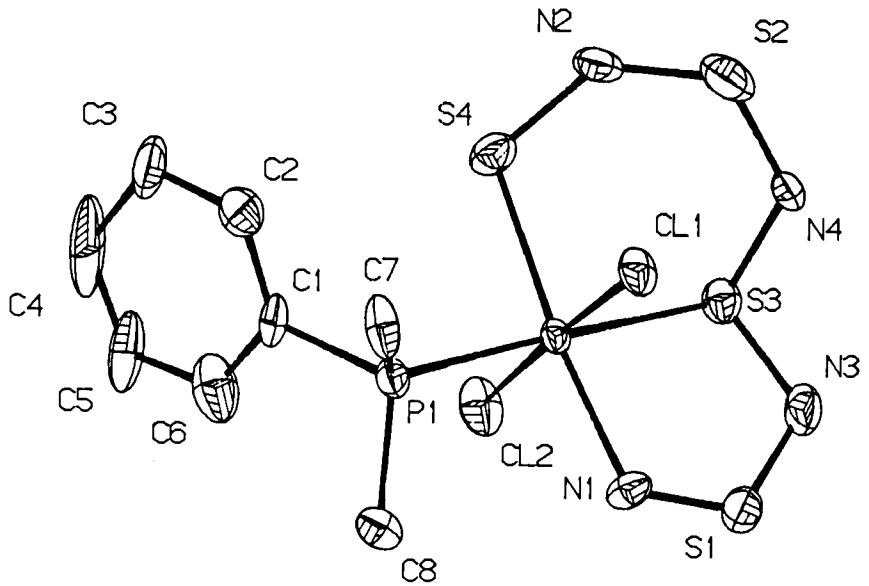


FIGURE 5 The X-ray crystal structure of $PtCl_2(PMe_2Ph)(S_4N_4)$



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