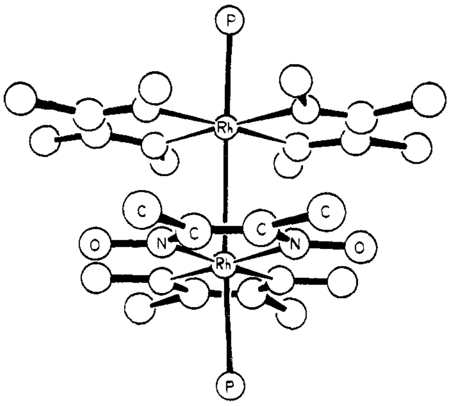

Figure 1. The structure of $Rh_2(DMG)_4(P(C_6H_5)_3)_2$. The phenyl groups are omitted for clarity.

of the usual discrepancy index, $R_1 = \Sigma||F_c| - |F_o||/\Sigma|F_o|$, was 0.085.

The $Rh_2(DMG)_4(P(C_6H_5)_3)_2$ molecule, with the phenyl groups omitted, is depicted in Figure 1. Its most prominent and important structural feature is the Rh–Rh bond, unsupported by bridging groups, with a length of 2.934 (2) Å. The molecule as a whole possesses no rigorous crystallographic symmetry; however, neglecting the phenyl groups, it has very nearly $D_{2d}$ symmetry. The Rh–Rh–P angles are 176.8 (3)°, the two $Rh(DMG)_2$ units are each essentially planar, and the two such planes are virtually parallel to each other and perpendicular to the Rh–Rh axis. One $Rh(DMG)_2$ unit is rotated about the Rh–Rh axis by 92 ± 1° relative to the other. The Rh–N distances range from 1.95 (2) to 2.03 (2) Å with a mean of 1.99 Å, while the Rh–P distances are 2.447 (5) and 2.430 (5) Å.

We believe that this molecule displays an Rh–Rh single bond probably somewhat elongated by repulsive interactions between the parallel pairs of DMG ligands. There are marked similarities to the $Ni(DMG)_2$, $Pd(DMG)_2$, and $Pt(DMG)_2$ structures,[10,11] which consist of parallel infinite chains of planar molecules stacked perpendicular to their planes with each molecule rotated 90° to its chain neighbors. The interplanar spacings in these cases are ~3.24 Å. Even this distance is slightly less than the expected van der Waals contact distance and, together with other evidence, suggests weak M–M attractive forces. The mean interplanar distance of 2.91 Å (essentially equal to the Rh–Rh distance, 2.93 Å) in the dinuclear Rh compound shows that there is a substantial Rh–Rh bond, which would presumably be even shorter were it not opposed by the ligand–ligand repulsions. That the Rh–Rh bond must be essentially a single, two-electron $\sigma$ bond follows from the fact that for Rh(II) the 7 d electrons in the $Rh(DMG)_2(P(C_6H_5)_3)$ moiety can only reasonably be allocated so as to leave one $\sigma$ electron in an orbital directed opposite to the Rh–P bond. Overlap of two such orbitals then forms a single, $\sigma$ Rh–Rh bond, just as a single, $\sigma$ Rh–Cl bond is formed in $ClRh(DMG)_2P(C_6H_5)_3$.

Even allowing for several tenths of an angstrom lengthening of this Rh–Rh bond by repulsions, it seems clear that the Rh–Rh distance, ~2.45 Å, in $Rh_2(O_2CCH_3)_4(H_2O)_2$ is short enough to imply a multiple interaction as previously proposed by us.[12]

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## Preparation and Crystal Structure of a Sterically Unencumbered Tetrahedral Chelate Complex Containing a $NiS_4$ Core, $[SPMe_2NPMe_2S]_2Ni^{II}$

*Sir:*

A large body of elegant experimental work has been performed in an effort to ascertain the factors which dictate the stereochemistry of metal(II) chelate complexes. These approaches[1–5] have employed bidentate chelates in which either the donor functions or the degree of crowding can be changed. Monomeric sterically unencumbered[5] chelates of nickel(II) with various permutations of donor sets (NR, S, O) have been found to be planar ($S = 0$), while those which are sterically overcrowded are either fully tetrahedral ($S = 1$) or are involved in a planar $\rightleftharpoons$ tetrahedral equilibrium in solution. Significantly, all known monomeric Ni(II) chelates with four coordinated sulfur atoms are diamagnetic and have been shown to be planar either from crystallographic studies[6] or by inference from magnetic and optical spectral studies.[7]

We now wish to report the preparation and crystallographic characterization of $[SPMe_2NPMe_2S]_2Ni^{II}$, a sterically unencumbered complex in which a Ni(II) ion is coordinated to four sulfur atoms, yet adopts a *tetrahedral* configuration.

The reaction of $Na^+[SPMe_2NPMe_2S^-]$[8,9] with $[Et_4N]_2[NiCl_4]$ in absolute methanol followed by recrystallization from dichloromethane–heptane yields olive

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(8) Ligands of the type $[L'-PR_2NPR_2-L]^-$ (L, L' = O, S, NH; R = Me, Ph) have been synthesized by Schmidpeter,[9] who has demonstrated that certain of them form metal complexes. Names for these ligands may be derived from the generic root "imido-diphosphinate,"[9] since in this way the resulting metal complexes may be named collectively.

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green crystals of bis(imidotetramethyldithiodiphosphino-S,S)nickel(II), $[SPMe_2NPMe_2S]_2Ni^{II}$. *Anal.* Calcd for $C_8H_{24}N_2NiP_4S_4$: C, 20.92; H, 5.28; N, 6.10; mol wt, 459.15. Found: C, 20.80; H, 5.48; N, 5.76; mol wt, 402 ($CHCl_3$). The complex (mp 194–195°) is paramagnetic both in the solid state (3.40 BM) and in solution (3.20 BM: $CHCl_3$) and has an optical spectrum typical of that found for tetrahedral nickel(II) chelate complexes:[1–5] $\lambda_{max}$ ($cm^{-1}$) 14,000, 12,750, 10,700, 8700; $\epsilon$ (l. $mole^{-1}$ $cm^{-1}$) 170.7, 240, 55.9, 34.0 in $CH_2Cl_2$ solution.

The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ ($C_{2h}^5$; no. 14) with $a$ = 15.437, $b$ = 8.796, $c$ = 16.237 Å, $\beta$ = 106.35°, $V$ = 2115.6 Å$^3$, $\rho_{obsd}$ = 1.40 ± 0.02 g $cm^{-3}$, and $\rho_{calcd}$ = 1.44 g $cm^{-3}$ for $M$ = 459.15, $Z$ = 4. A total of 1791 independent reflections, representing complete three-dimensional data ($\sin \theta_{max} = 0.42$; Mo K$\alpha$ radiation) were collected with a Buerger automated diffractometer. The structure was solved by direct methods, Sayre's equation being applied[10] to the 159 reflections with $E \geq 1.5$. Of the eight possible combinations of phase for the three starting reflections, one set achieved internal consistency in three iteration cycles with a consistency index of $C$ = 0.945. An F-map based on these phases clearly showed the $NiS_4P_4$ fragment of the molecule. Subsequent Fourier and least-squares refinement processes have led to the location of all nonhydrogen atoms, the present discrepancy index being

$$R_F = \frac{\sum \left| |F_o| - |F_c| \right|}{\sum |F_o|} = 12.6\%$$

Refinement is continuing.

The over-all geometry of the molecule is shown in Figure 1. The central nickel atom is tetrahedrally coordinated by the four sulfur atoms of the two chelate rings. There is a slight flattening of the coordination tetrahedron: the intraligand angles are S(1)–Ni–S(2) = 107.9 (2)° and S(3)–Ni–S(4) = 109.1 (3)°, while other angles at the nickel are S(1)–Ni–S(3) = 106.2 (2)°, S(2)–Ni–S(4) = 105.9 (3)°, S(1)–Ni–S(4) = 111.4 (3)°, and S(2)–Ni–S(3) = 116.3 (3)°. The rings are markedly nonplanar; the dimensions and orientation of the P–N–P backbone are remarkably similar to those found in imidotetraphenyldiphosphinic diamide chloride.[11] The phosphorus atoms are each approximately tetrahedral and the disposition of the methyl groups clearly does not preclude the adoption of a planar $NiS_4$ structure. Nickel–sulfur distances in the present structure range from 2.270 (7) to 2.306 (7) Å, averaging 2.291 Å, slightly longer than the distances found in *planar* $NiS_4$ chelates (2.10–2.24 Å).[6] The average P—S distance of 2.033 Å is intermediate between that expected for P=S (1.94–1.96 Å) and for P—S (2.08–2.19 Å).[12]

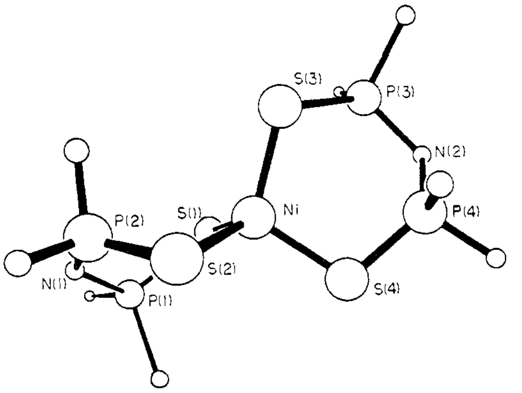

Figure 1. The stereochemistry of $[SPMe_2NPMe_2S]_2Ni^{II}$. Average distances and angles are: Ni–S = 2.291 ± 0.014 Å, S–P = 2.033 ± 0.008 Å, P–N = 1.606 ± 0.035 Å, P–Me = 1.820 ± 0.042 Å; Ni–S–P = 104.2 ± 1.3°, S–P–N = 116.7 ± 1.6°, P–N–P = 127.3 ± 1.5°, S–P–Me = 108.2 ± 1.0°, Me–P–Me = 105.9 ± 1.0°, Me–P–N = 109.6 ± 1.5°.

The single most important feature of the present molecule is undoubtedly the tetrahedral configuration about the nickel atom. The significance of this result and the utility of imidodiphosphinates as ligands is even more apparent when changes in both the donor set and the substituents are made. Thus, the purple complex bis(imidotetraphenyldiiminodiphosphinato-NH,NH)-nickel(II), $[NHPPh_2NPPh_2NH]_2Ni^{II}$, which has a $Ni(-NH)_4$ core and bulky substituents, is diamagnetic and presumably planar. *Anal.* Calcd for $C_{48}H_{44}N_6NiP_4$: C, 64.95; H, 5.01; N, 9.47; mol wt, 887.57. Found: C, 65.67; H, 4.91; N, 9.20; mol wt, 795 ($CHCl_3$); mp 201–203°; $\lambda_{max}$ ($cm^{-1}$) 15,000, 12,120, 11,420, 6570; $\epsilon$ (l. $mole^{-1}$ $cm^{-1}$) 98.9, 3.6, 4.3, 4.7.

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## The Mechanism of a Metal-Catalyzed Cycloaddition Reaction

*Sir:*

Little is known about why transition metals are effective in catalyzing cycloaddition reactions. For example, rhodium on carbon[1] and various coordination complexes of rhodium[2] transform I into II, but whether the carbon–carbon bonds are broken and formed in the same[2,3] or in subsequent[1,4] steps is unclear. For cycloaddition reactions in general, it is difficult to establish

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