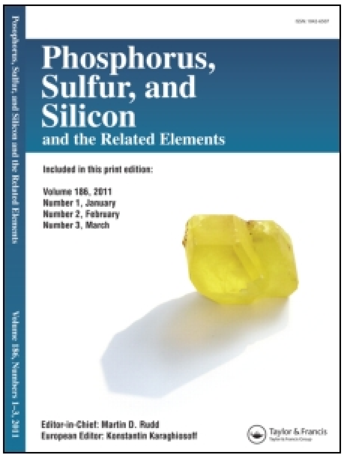

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FOUR- AND SIX-MEMBERED INORGANIC RINGS IN THE "BUTTERFLY"-LIKE $[Mn\{(OPPh_2)_2N\}_2]_2$

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Abstract Manganese(II) compounds of the type $Mn[(XPR_2)(YPR'_2)N]_2$ (X, Y = O, S; R, R' = Me, Ph) were prepared and characterized by IR spectroscopy. The X-ray molecular structure of the $[Mn\{(OPPh_2)_2N\}_2]_2$ is discussed.

Keywords: dicalcogenoimidodiphosphinato ligands, inorganic rings, Mn(II) complexes

INTRODUCTION

The coordination chemistry of tetraorganodichalcogenoimidodiphosphinato ligands, $[(XPR_2)(YPR'_2)N]^-$ (X, Y = O, S, Se; R, R' = alkyl, aryl, alkoxy, aroxy), was extensively investigated in recent years[1]. Most of the research work in this field was concerned to symmetric ligands containing only phenyl groups and same chalcogens attached to phosphorus atoms. Changes in the organic groups or in the chalcogen atoms often resulted in unexpected structures, *e.g.* in $Ni[(SPR_2)(SPR'_2)N]_2$ complexes the NiS_4 core is tetrahedral for R = R' = Me[2], Ph[3], but square-planar when R = Me, R' = Ph[3].

The molecular structure of $Mn[(SPPh_2)_2N]_2$ was previously reported and contains a tetrahedral MnS_4 core[4]. Here we report on the synthesis and IR characterization of various $Mn[(XPR_2)(YPR'_2)N]_2$ and the molecular structure of the dimeric $[Mn\{(OPPh_2)_2N\}_2]_2$.

RESULTS AND DISCUSSION

Manganese(II) compounds of the type $Mn[(XPR_2)(YPR'_2)N]_2$ (X, Y = O, S; R, R' = Me, Ph), were prepared by metathesis reactions between $MnCl_2.4H_2O$ and the alkaline salt of the appropriate ligand, in methanol (Table 1):

$$MnCl_2 + 2\ M[(XPR_2)(YPR'_2)N] \longrightarrow Mn[(XPR_2)(YPR'_2)N]_2 + 2\ MCl$$

The strong infrared absorptions observed for all manganese(II) complexes in the regions 1250-1200, 1150-1110 and 600-550 cm^{-1} were assigned to $\nu_{as}(P_2N)$, $\nu(PO)$, and $\nu(PS)$ stretching vibrations, respectively, by comparison with the spectra of the corresponding free acids and their alkaline salt. The absence of a strong absorption at *ca.* 900 cm^{-1} due to $\nu_{as}(P_2NH)$, is indicative of the presence of the deprotonated form of the ligand and suggests its bidentate coordination through both chalcogens to the metal atom.

The crystal and molecular structure of the tetraphenylimidodiphosphinato derivative was determined by X-ray diffractometry.

The crystal contains distinct $[Mn\{(OPPh_2)_2N\}_2]_2$ dimers, which are separated by normal van der Waals distances. Two of the imidodiphosphinato ligands act as monometallic biconnective units, leading to *six-membered* MnO_2P_2N rings (av. Mn-O 2.071, P-O 1.504, P-N 1.59 Å). The other two ligands act as bimetallic triconnective units, which results in a fused tricyclic $MnO_4P_4N_2$ system as shown in Fig.1 (carbon atoms not shown).

Table 1. Synthesis and IR for $Mn[(XPR_2)(YPR'_2)N]_2$ derivatives.

Compounds	Yield (%)	M.p. (°C)	IR (cm^{-1})[c]
$Mn[(OPPh_2)_2N]_2$[a]	83	302-305	$\nu_{as}(P_2N)$ 1240 $\nu(PO)$ 1150, 1110
$Mn[(SPPh_2)_2N]_2$[b]	85	277-281	$\nu_{as}(P_2N)$ 1240 $\nu(PS)$ 580, 590
$Mn[(OPPh_2)(SPPh_2)N]_2$[b]	98	182-186	$\nu_{as}(P_2N)$ 1250 $\nu(PO)$ 1130 $\nu(PS)$ 570
$Mn[(SPMe_2)(OPPh_2)N_2$[b]	90	192-194	$\nu_{as}(P_2N)$ 1200 $\nu(PO)$ 1135 $\nu(PS)$ 550, 565
$Mn[(OPMe_2)(SPPh_2)N]_2$[a]	82	156-158	$\nu_{as}(P_2N)$ 1200 $\nu(PO)$ 1140 $\nu(PS)$ 600

[a] Using the Na salt of the ligand; [b] Using the K salt of the ligand;
[c] All IR absorptions are very strong.

The coordination geometry at manganese is trigonal bipyramidal $[O(1)_{ax}\text{-}Mn(1)\text{-}O(8)_{ax}$ 171.4(3)°, $O_{eq}\text{-}Mn(1)\text{-}O_{eq}$ (range) 113,9(3) - 124,6(3)°]. The central *four-membered* Mn_2O_2 ring is slightly bent

[Mn(1)O(5)O(8)/Mn(2)O(5)O(8) dihedral angle 23.9°]. The overall conformation of the [Mn{$(OPPh_2)_2N$}$_2$]$_2$ dimer might be described as *cis*, *i.e.* with six-membered MnO_2P_2N rings formed by ligands of the same type placed on the same side of the four-membered Mn_2O_2 ring.

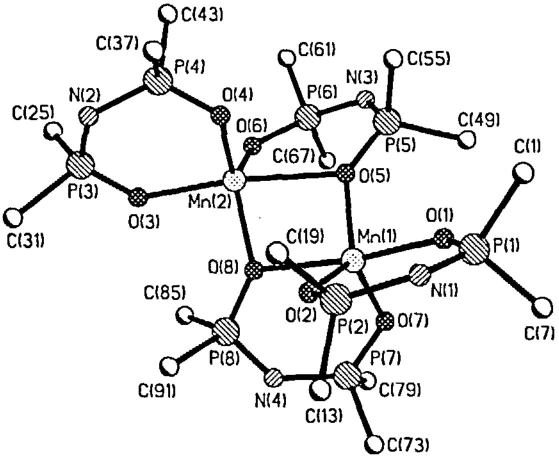

Figure 1. View of the structure of [Mn{$(OPPh_2)_2N$}$_2$]$_2$ dimer (for clarity only *ipso* carbons of the phenyl groups are shown.).

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