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Synthesis, Complexes and Metal Extraction Ability of $R'R''NC(X)NHP(Y)(OPh)_2$

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SYNTHESIS, COMPLEXES AND METAL EXTRACTION ABILITY OF $R^1R^2NC(X)NHP(Y)(OPh)_2$

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The new 1,1-disubstituted 3-diphenoxy(thio)phosphoryl-
 (thio)ureas, $R^1R^2NC(X)NHP(OPh)_2$, HA, with X,Y = O,S, were
 synthesized by addition of secondary amines to the corre-
 sponding P-iso(thio)cyanates. This reaction is reversible
 if X,Y = S. $(PhO)_2P(Y)Cl$ reacts with $H_2NC(X)NR_2$ in the
 presence of an HCl acceptor only if X,Y = O. Side reac-
 tions are observed. Phosphorylated derivatives of biuret
 were isolated from such a reaction mixture.

The compounds HA are acids forming neutral metal chelates
 MA_n . The following complexes of HA (X,Y = S) were isola-
 ted: CuA , NiA_2 , CoA_2 and ZnA_2 . Spectroscopic investiga-
 tions (IR, UV-VIS, NMR, ESCA) and magnetic measurements
 show that the coordination takes place via the two sulfur
 atoms in the molecule. It was found by means of 1H NMR
 spectroscopy, that the rotation barriers of the terminal
 NR_2 group are about 60 kJ/mol for the free ligand and
 rises by chelation.

The thiophosphorylated thioureas HA are excellent extrac-
 tants for many metal ions. Under equivalent conditions
 the distribution ratios D of metal ions decrease in the
 sequence: Ag^+ , Hg^{2+} , Bi^{3+} , Cd^{2+} , Pb^{2+} , Sc^{3+} , Tm^{3+} , Eu^{3+} ,
 Zn^{2+} , Co^{2+} , Ni^{2+} , Fe^{2+} . D drops with increasing acidity
 of the aqueous phase. The results are compared with re-
 sults of other bidentate ligands like

$(PhO)_2P(X)NHP(Y)(OPh)_2$, $[(PhO)_2P(O)]_nNH[C(O)Ph]_{2-n}$ and
 $[(PhO)_2P(O)]_nCH_2[C(O)Ph]_{2-n}$ (n = 0, 1, 2).