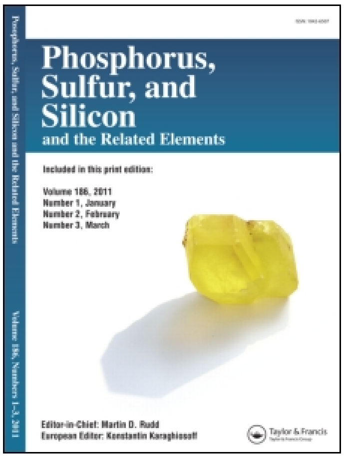

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Synthesis, Complexes and Metal Extraction Ability of $R^1R^2NC(X)NHP(Y)(0Ph)_2$

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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 corresponding 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 reactions 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 isolated: CuA, NiA_2, CoA_2 and ZnA_2. Spectroscopic investigations (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 extractants 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 results 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).