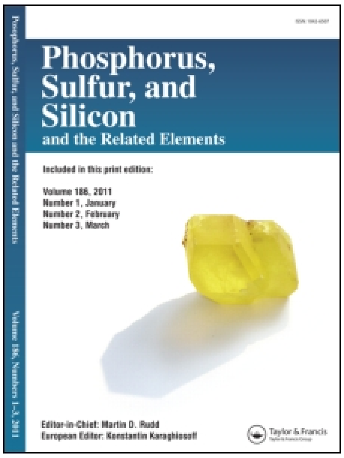

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A Novel Class of Powerful Neutral Chelating Reagents : β-Biphosphoramides

K. Bokolo[a]; J. -J. Delpuech[a]; G. Doucet Ladeveze[a]; Y. Jabbari Azad[a]; L. Rodehuser[a]; P. Rubini[a]; C. Selve[a]
[a] Laboratoire de Chimie Physique Organique, ERA CNRS 222, Université de Nancy I, VANDOEUVRE LES NANCY CEDEX, FRANCE

To cite this Article Bokolo, K. , Delpuech, J. -J. , Ladeveze, G. Doucet , Azad, Y. Jabbari , Rodehuser, L. , Rubini, P. and Selve, C.(1983) 'A Novel Class of Powerful Neutral Chelating Reagents : β-Biphosphoramides', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 315 — 318

To link to this Article: DOI: 10.1080/03086648308076029

URL: http://dx.doi.org/10.1080/03086648308076029

Phosphorus and Sulfur, 1983, Vol. 18 pp. 315-318
0308-664X/83/1801-0315/$18.50/0

A NOVEL CLASS OF POWERFUL NEUTRAL CHELATING REAGENTS : β-BIPHOSPHORAMIDES

K.BOKOLO, J.-J.DELPUECH, G.DOUCET LADEVEZE, Y.JABBARI AZAD,
L.RODEHUSER, P.RUBINI, C.SELVE
Laboratoire de Chimie Physique Organique, ERA CNRS 222, Université de Nancy I, BP 239 54506 VANDOEUVRE LES NANCY CEDEX, FRANCE.

Abstract The structure of β-diphosphoramide chelates and their use as novel extractants are described.

INTRODUCTION

Bidentate phosphate compounds have been used as coordinative extractants which can bind neutral metal salts by completing the coordination requirements of the metal to give neutral adducts. We are reporting investigations on the chelating properties of neutral biphosphorylated ligands which can bind metal ions to yield positively charged metallic complexes. As a consequence of the outstanding solvating properties of hexamethylphosphorotriamide (HMPA), our investigations began using a bidentate analog of HMPA, nonamethylimidodiphosphoramide (NIPA) which proved to have exceptional chelating properties. This prompted us to examine more closely a series of β-diphosphoramides of the general formula $(NMe_2)_2P(O)$-X-$P(O)(NMe_2)_2$ with :

(1) X = NMe (NIPA)
(2) X = O (OMPA)
(3) X = N-*n*-C_6H_{13} (OHIPA)
(4) X = N-n-$C_{12}H_{25}$ (ODIPA)
(5) X = N-CH_2-C_6H_5 (OBIPA)
(6) X = NH (OMIPA)

Our investigations basically aimed at establishing relationships between the extracting properties of the above bidentate phosphoramides and the structure of their chelates in solution and their thermodynamic and kinetic constants (stability constants, partition coefficients, intra and intermolecular ligand exchange rates).

As to the potential applications of these compounds in extraction chemistry, our main field of interest concerned the extraction of the uranyl cation from aqueous solutions. This purpose led us to consider ligands which are less soluble in water than NIPA, and which can be more easily recovered from aqueous media (compounds 3 to 5).

SYNTHESES[1-5]

NIPA was synthesized starting from HMPA and phosphorus oxychloride by reported methods. The syntheses of the NIPA analogs (3) to (6), although using the same scheme, required original variants to obtain the ligands with a high level of purity and in good yield. Another strategy is currently investigated using OMIPA as a starting material and grafting alkyl chains on the bridging imide nitrogen. The metal complexes were prepared in the solid state from their perchlorates, and were then dissolved in a polar inert solvent, e.g. nitromethane.

MOLECULAR STRUCTURES AND DYNAMICS[1-6]

Ligand exchange rates are slow on the NMR timescale in diphosphoramide complexes. Separate signals are effectively observed for free (excess) and bound ligand molecules in the case of tervalent IIIA (Al^{3+}, Ga^{3+}, In^{3+}), and even of bivalent alkaline-earth (Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}) or of monovalent alkaline (Li^{+}) cations. This shows that the sequestering properties of diphosphoramides approach those of the well-known crown ethers and cryptands. Our observations may be summarized as follows.

(a) Li^{+} and Be^{2+} cations : tetracoordinated D_{2d} structures.

(b) Bivalent main group (Mg^{2+}, Ca^{2+}, Sr^{2+}) or transition metal ions : hexacoordinated D_{3d} tris-chelates. The magnetic non-equivalence of the terminal N-dimethyl groups allowed us to determine, besides the intermolecular exchange mentioned above, the rate of optical inversion between the Δ,Λ enantiomers. The chemical shift difference is particularly large for paramagnetic complexes of cobalt (II), allowing us to determine the geometry of the complex, the paramagnetic susceptibilities, the contact and pseudo-contact contributions and to assign each of the two non-equivalent N-dimethyl substituents. Optical inversion and ligand exchange kinetic parameters have been determined by DNMR (^{1}H and ^{31}P) for a variety of cation/ligand systems. In some favourable instances, kinetic parameters can be obtained for both processes. A parallelism between the facilities of racemization and ligand exchange invites us to consider mechanisms for both processes involving as a common first step the release ofone end of the chelate by a dissociative process.

(c) The uranyl cation UO_2^{2+} : hepta or octacoordination in NIPA or OMPA complexes, respectively ; evidence for (i) mononuclear complexes : $UO_2(NIPA)_2Y^{2+}$, with Y = NIPA (singly bonded), MeOH, EtOH, Me_2CO ; and $UO_2(OMPA)_2Y^{2+}$, with Y = EtOH, H_2O ; and (ii) binuclear complexes : $(NIPA)_2UO_2(NIPA)UO_2(NIPA)_2^{4+}$ and $[(OMPA)_2UO_2(OMPA)_2UO_2(OMPA)_2]^{4+}$. The structure of $UO_2(NIPA)_2EtOH^{2+}$ has been determined by X-ray crystallography, confirming the presence of two NIPA ligands in a puckered cis conformation (while free NIPA molecules are in a trans conformation). Uranyl nitrate, a classical salt in uranium chemistry, gives rise to the associated species $UO_2(NIPA)_2(NO_3)^{+}$ and $UO_2(NIPA)(NO_3)_2$.

DIPHOSPHORAMIDES AS EXTRACTANTS

Partition coefficients, yields of extraction, and ligand to cation ratios have been measured by opposing aqueous solutions of metal perchlorates (Fe^{3+}, Al^{3+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+}) to immiscible organic solvents (CH_3NO_2, CH_2Cl_2) containing variable amounts of diphosphoramides. The ligand OHIPA is shown to have the highest extracting power. OHIPA, ODIPA and NIPA are better extractants than OMPA and OBIPA. ODIPA is completely insoluble in H_2O and thus presents the best characteristics for extraction, but the selectivity is weak among the investigated cations, at least as far as their perchlorate salts are concerned.

Uranium extraction by phosphoramides is excellent in the presence of coordinating nitrate ions in moderate concentration (3M) which can be produced favourably by alkali nitrates rather than by nitric acid. The extraction is not sensitive to the presence of sulphate ions. This is in sharp contrast with the classical extraction by trialkyl phosphates which requires higher nitric acid (up to 15 M) and ligand concentrations and works poorly in the presence of sulphate ions. Finally, the extraction may be made wholly or partially selective towards cations found in uranyl ores.

REFERENCES

1. J.-J.Delpuech, L.Rodehüser, P.R.Rubini, Inorg.Chem., 18, 2962 (1979).
2. K.Bokolo, J.-J.Delpuech, L.Rodehüser, P.R.Rubini, ibid., 20, 992 (1981).
3. L.Rodehüser, P.R.Rubini, K.Bokolo, J.-J.Delpuech, ibid., 21, 1040 (1982).
4. P.R.Rubini, K.Bokolo, L.Rodehüser, J.-J.Delpuech, Nouv.J.Chim., 6, 259 (1982).
5. G. Doucet Ladevèze , L. Rodehüser, P.R.Rubini, C.Selve, J.-J. Delpuech, Tetrahedron Lett., 63, 643 (1982).
6. P.R.Rubini, Z.Poaty, J.-C.Boubel, L.Rodehüser, J.-J.Delpuech, Inorg.Chem., 22, 1295 (1983).