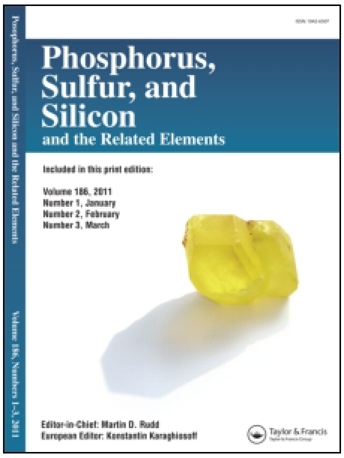


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Metal Ion Uptake of 2-(2-Pyridyl)Ethylamino-Substituted Phosphazenes

Ursula Diefenbach; Marcel Bloy; Brigitte Stromburg

To cite this Article Diefenbach, Ursula , Bloy, Marcel and Stromburg, Brigitte(1999) 'Metal Ion Uptake of 2-(2-Pyridyl)Ethylamino-Substituted Phosphazenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 65 — 68

To link to this Article: DOI: 10.1080/10426509908546183

URL: http://dx.doi.org/10.1080/10426509908546183

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 65-68
Reprints available directly from the publisher
Photocopying permitted by license only

Metal Ion Uptake of 2-(2-Pyridyl)Ethylamino-Substituted Phosphazenes

URSULA DIEFENBACH, MARCEL BLOY and
BRIGITTE STROMBURG

Institut für Anorganische und Analytische Chemie, Freie Universität Berlin,
Fabeckstr. 34–36, 14195 Berlin, Germany

The coordination chemistry of cyclophosphazenes with pyridyl-alkylamino groups is discussed. The structure of a new cobalt(II) complex of the general structure $CoClLCoCl_3$, $L = gem\text{-}N_3P_3(OC_6H_5)_2(NH(CH_2)_2C_5H_4N)_4$, was determined by X-ray crystal structure analysis.

Studies on the ion capacity and selectivity of polyphosphazenes with 2-(2-pyridyl)ethylamino groups show a strong preference for copper(II) uptake from Cu(II)/Co(II) and Cu(II)/Ni(II) mixtures, which increases with an increasing amount of functional groups on the chain.

Keywords: Phosphazenes; Ion uptake; Ion selectivity; Cobalt complex

INTRODUCTION

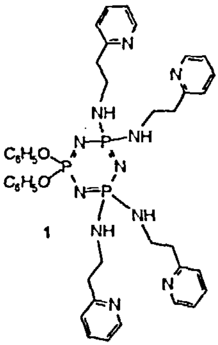
Chelating ion exchangers are highly ion selective materials. Pyridyl-alkylamino groups attached to organic polymeric backbones allow the separation of copper(II) from mixtures with cobalt and nickel at low pH (Dow Chemical, XFS 4195). [1-3] Polyphosphazenes with suitable N-donor groups could possibly show a similar behavior moreover, the physical properties of the material could easily be modified by introducing appropriate cosubstituents. In contrast to organic polymers the coordination chemistry of such materials would be determined by both, the side groups and the nitrogen atoms of the polymeric chain.

We recently reported studies on the ion selectivity and capacity of 2-, 3-, and 4-pyridylmethylamino substituted polyphosphazenes, $[NP(OC_6H_5)_x(NHCH_2C_6H_5N)_y]_n$. [4] To understand the chemistry involved in ion uptake, we systematically investigated the complex formation of cyclotriphosphazenes with pyridylalkylamino groups. [5-9] We reported the syntheses and structure determinations of several copper-, cobalt-, platinum-, and mercury complexes. 3- and 4-pyridylmethylamino substituted derivatives showed metal binding exclusively at the pyridinic nitrogen atoms. [5-7] By contrast, compounds with 2-pyridylmethylamino groups coordinate to copper and platinum by interactions of the amino- and pyridine groups whereas cobalt is bond by PN- and pyridine nitrogen atoms. [8,9] Mercury complexes were not formed with the 2-pyridyl derivatives probably because of sterical hindrance. [5]

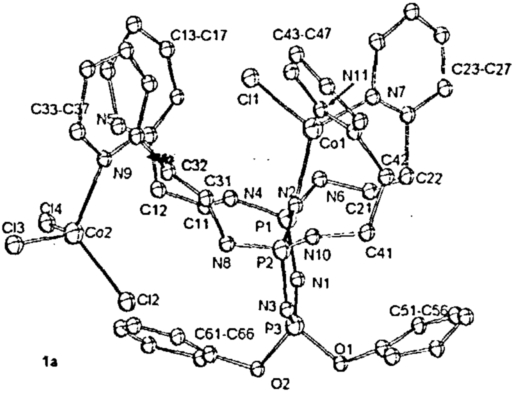
We describe here the structure of a new cobalt coordination compound. We also discuss the ion capacity and selectivity of four polyphosphazenes with different ratios of 2-(2-pyridyl)ethylamino- and trifluorethoxy groups.

RESULTS AND DISCUSSION

The new multifunctional ligand **1** can be obtained from the reaction of hexachlorocyclotriphosphazene with four equivalents of 2-(2-aminoethyl)pyridine in the first and sodium phenoxide in the second step. When **1** is reacted with cobalt(II) chloride the unexpected binuclear coordination compound **1a** is formed. Two cis-vicinal arranged pyridylethylamino substituents coordinate to CoCl by two pyridyl groups. The tetrahedron is completed by a PN nitrogen atom. A second cobalt atom is tetrahedrally surrounded by one of the remaining pyridine groups and three chlorine atoms.



1



1a

Polyphosphazenes with 25, 50, 75 or 100% 2-(2-pyridyl)ethylamino substitution ($[NP(OCH_2CF_3)_x(NH(CH_2)_2C_6H_5N)_y]_n$; x = 1.5, 1, 0.5, 0 and y = 0.5 (25%), 1 (50%), 1.5 (75%), 2 (100%)) and additional trifluorethoxy groups were reacted with mixtures of copper(II) and cobalt(II) or nickel(II) in solutions (c(Cu = Co or Ni) = 0.001 mol/l). Determination of the metal contents of the polymeric metal complexes (Figure 1) shows that

- capacity and selectivity for copper(II) increase with an increasing number of functional groups.
- capacity and selectivity for copper(II) are lower than found for 2-pyridylmethylamino substituted polymers. [4]
- cobalt and nickel uptake are not directly related on the amounts of functional groups.

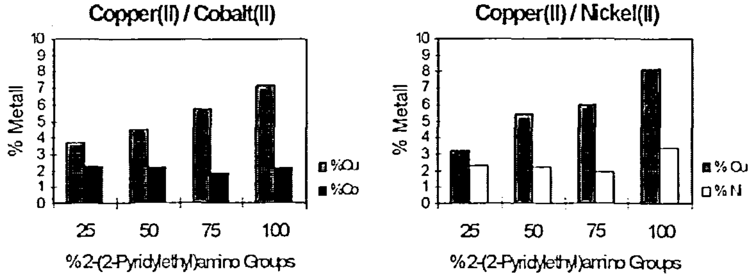


Figure 1. Metal contents of the polymeric complexes after ion uptake

Acknowledgements

U.D. thanks the Deutsche Forschungsgemeinschaft for a habilitation fellowship. We are grateful to the DFG and the Fonds der Chemischen Industrie for financial support. We thank I. Brüdgam for the data collection. We extend our thanks to Prof. Dr. U. Engelhardt and Prof. Dr. Harry R. Allcock for their support.

References

[1] A.K. Sengupta, Y. Zha, *AIChE Journal*, 38, 153, (1992)
[2] R.R. Grinstead, *Ion Exchange Technology*, 509, (1984)
[3] R.R. Grinstead, *Hydrometallurgy*. 12, 387, (1984)
[4] U. Diefenbach, M. Kretschmann, B. Stromburg, *Phosphorus, Sulfur Silicon* in press
[5] U. Diefenbach, P. Adamaszek, M. Bloy, *Heteroatom Chem.* in press
[6] U. Diefenbach, P. Adamaszek, M. Bloy, M. Kretschmann, S. Scholz, *Z. Anorg. Allg. Chem* in press
[7] U. Diefenbach, M. Kretschmann, Ö. Çavdarci, *Monatsh. Chem.*, 127, 989, (1996)
[8] U. Diefenbach, M. Kretschmann, B. Stromburg, *Chem. Ber.*, 129, 1573, (1996)
[9] M. Kretschmann, U. Diefenbach, *Z. Anorg. Allg. Chem.*, 624, 335, (1998)