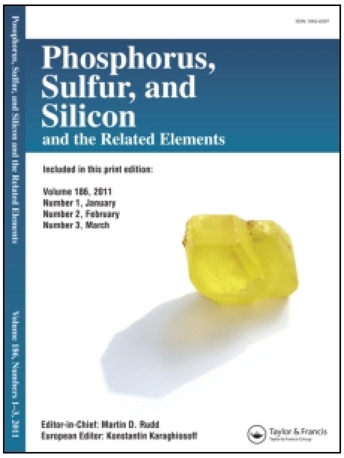

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COORDINATION CHEMISTRY OF PYRIDYLMETHYLAMINO-SUBSTITUTED CYCLO- AND POLYPHOSPHAZENES: SELECTIVITY IN MACROMOLECULE COMPLEX FORMATION AND A LIGAND-STABILISED [$CU_{13}O_9$]-CLUSTER

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Polyphosphazenes with 2-, 3-, and 4-pyridylmethylamino- and phenoxy groups show a rather surprising ion uptake behaviour in reactions with diluted solutions of copper(II)- and cobalt(II)- or nickel(II) salts. Capacity and selectivity for copper of the 2-pyridylmethylamino-substituted polymers are higher than of the other derivatives and are increasing with an increasing number of the functional groups present on the chain. By contrast, polyphosphazenes with more than 50% of 3-pyridylmethylamino substitution and polyphosphazenes with 4-pyridylmethylamino groups show decreasing metal sorption with increasing numbers of functional groups.

A [$Cu_{13}O_9$]-cluster, stabilised by a ligand shell, is formed in the reaction of trans-vic-$N_3P_3(OC_6H_5)_4(NHCH_2C_5H_4N\text{-}2)_2$ with copper(I) iodide and oxygen. The anion is a new iodo cuprate, $[Cu_6I_9]^{3-}$. The molecular structure of the compound was determined by single crystal X-ray structure analysis.

Key Words: Phosphazenes, Copper Cluster, Iodo Cuprate, Ion Uptake

INTRODUCTION

Cyclo- and polyphosphazenes with pyridylalkylamino groups are accessible via reactions of hexachlorocyclotriphosphazene or poly(dichlorophosphazene) with aminoalkylpyridine derivatives.

The attachment of a pyridylalkylamino group to cyclotriphosphazenes introduces two coordination sites in addition to the three nitrogen atoms of the PN system, which also form N-donor complexes. Our studies on the coordination chemistry of cyclotriphosphazenes with one pyridylmethylamino group have shown that 3- and 4-pyridylmethylamino derivatives coordinate exclusively through the pyridyl nitrogen atoms[1] whereas 2-pyridylmethylamino compounds function as bidentate chelating ligands with pyridinic and amino- or PN nitrogen atoms participating in complex formation[2].

The geminal di(2-pyridylmethylamino) substituted species gem-$NP(OC_6H_5)_4(NHCH_2C_5H_4N\text{-}2)_2$ reacts with copper(II) nitrate to form a complex in which the metal is coordinated by two pyridyl-, one amine nitrogen- and three nitrate oxygen atoms.[3]

Studies on the coordination chemistry of the small molecule cyclotriphosphazens provide important information about the complex formation of analogue macromolecules, which are of interest for extraction or ion exchange processes.[4] Our first results from ion uptake studies on polyphosphazens with 2-, 3-, and 4-pyridylmethylamino groups will be discussed here.

Phosphazenes with two pyridylmethylamino groups in vicinal positions are ligands that might form dinuclear metal complexes, which are of significant interest as model compounds for reactive centres of metaloproteins.[5]

Surprisingly the reaction of copper(I) iodide and oxygen with vic-$NP(OC_6H_5)_4(NHCH_2C_5H_4N\text{-}2)_2$ yields a tridecanuclear cationic copper cluster with an iodo cuprate anion. The structure of the compound will be discussed.

RESULTS AND DISCUSSION

Ion uptake studies on phosphazenes with pyridylmethylamino groups: 12 polymers with different amounts (25%, 50%, 75%, 100%) of 2-, 3-, and 4-pyridylmethylamino groups and phenoxy groups as co-substituents were dissolved in methanol, enclosed in dialysis tubes, and brought in contact with solutions of mixtures of copper(II)- and cobalt(II)- or copper(II)- and nickel(II) nitrate ($c(Cu(NO_3)_2) = c(Co(NO_3)_2)$ or $c(Ni(NO_3)_2) = 0{,}001$ mol/l) for 24 hours.

The macromolecular metal complexes formed were then dried and the metal contents of the samples were determined by AAS. Figures 1-3 show the amount of metal present in the metal complexes of the 12 polymers investigated.

FIGURE 1 clearly shows that

- the capacity (g metal / g polymer) for ion uptake increases with an increasing number of 2-pyridylmethylamino groups on the chain.
- the affinity and selectivity for copper increase with an increasing number of functional groups.
- cobalt and nickel uptake do not depend on the amount of 2-pyridylmethylamino groups.

The complexes of the polymers with 25 and 50% pyridylmethylamino substitution precipitate out of solution, obviously because of cross linking of the monomeric units. The polyphosphazenes with 75 and 100% pyridylmethylamino substitution remain soluble after ion uptake which indicates 1 : 1 complexes of the monomeric units. These observations agree with the coordination chemistry of the small molecule models.

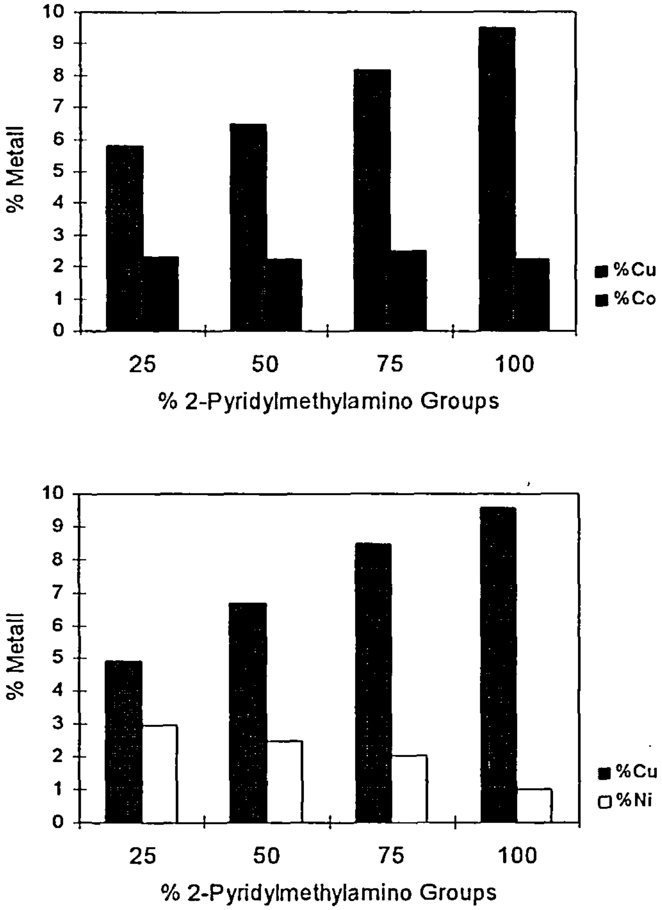

FIGURE 1: Amounts of copper and cobalt (diagram above) and copper and nickel (diagram below) in the metal complexes of the polymers $NP(OC_6H_5)_{1.5}(NHCH_2C_5H_4N\text{-}2)_{0.5}$, $NP(OC_6H_5)(NHCH_2C_5H_4N\text{-}2)$, $NP(OC_6H_5)_{0.5}(NHCH_2C_5H_4N\text{-}2)_{1.5}$, and $NP(NHCH_2C_5H_4N\text{-}2)_2$ with 25%, 50%, 75%, and 100% 2-pyridylmethylamino substitution

Different results were obtained with 3-pyridylmethylamino substituted polyphosphazenes (FIGURE 2).

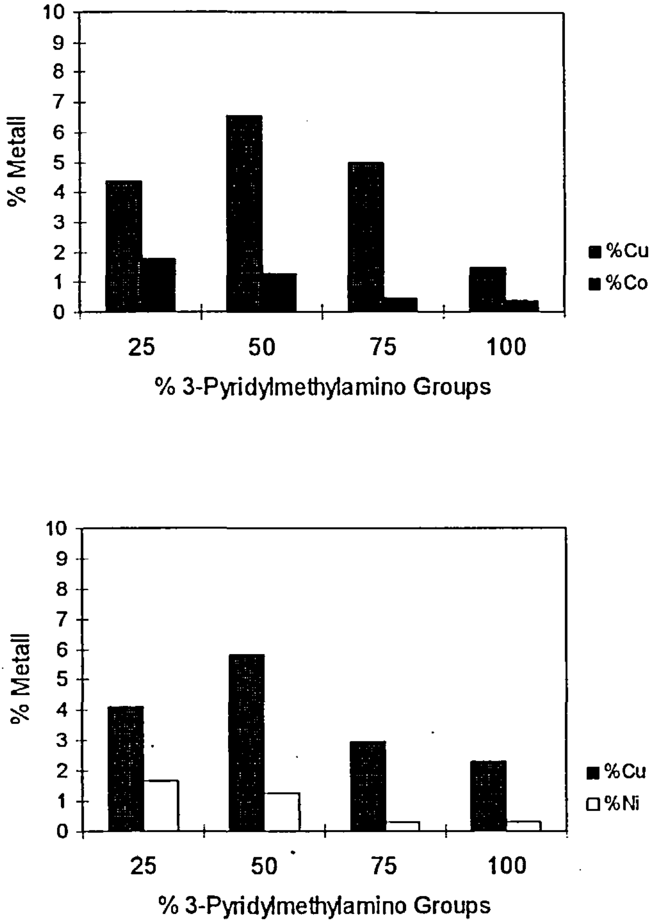

FIGURE 2: Amounts of copper and cobalt (diagram above) and copper and nickel (diagram below) in the metal complexes of the polymers $NP(OC_6H_5)_{1.5}(NHCH_2C_5H_4N\text{-}3)_{0.5}$, $NP(OC_6H_5)(NHCH_2C_5H_4N\text{-}3)$, $NP(OC_6H_5)_{0.5}(NHCH_2C_5H_4N\text{-}3)_{1.5}$, and $NP(NHCH_2C_5H_4N\text{-}3)_2$ with 25%, 50%, 75%, and 100% 2-pyridylmethylamino substitution

- The capacities are significantly lower.
- The amount of metal bound to the polymer decreases, when more than 50% of the substituents are 3-pyridylmethylamino groups.

The ion uptake of the 4-pyridylmethylamino substituted polymers is even more surprising (FIGURE 3).

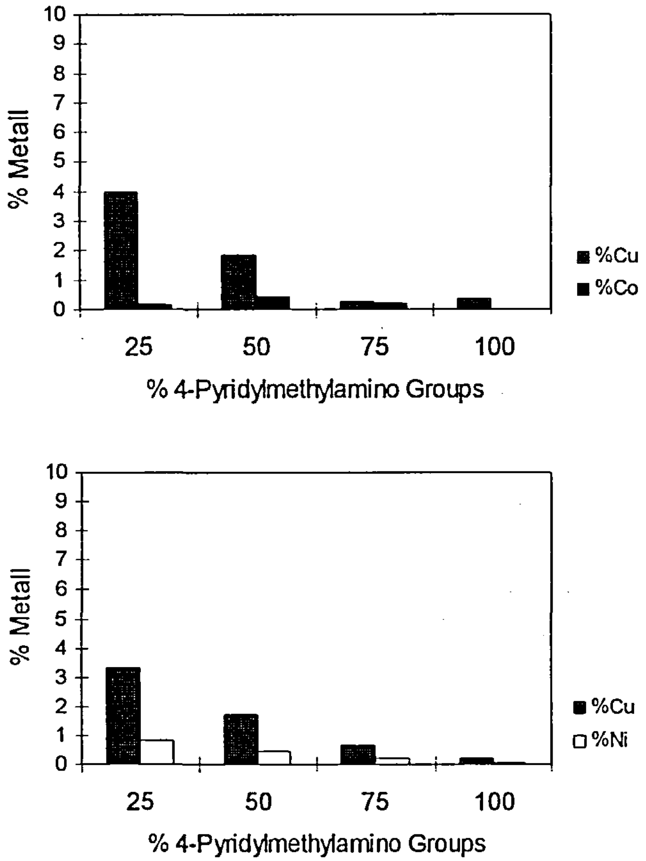

FIGURE 3: Amounts of copper and cobalt (diagram above) and copper and nickel (diagram below) in the metal complexes of the polymers $NP(OC_6H_5)_{1.5}(NHCH_2C_5H_4N\text{-}4)_{0.5}$, $NP(OC_6H_5)(NHCH_2C_5H_4N\text{-}4)$, $NP(OC_6H_5)_{0.5}(NHCH_2C_5H_4N\text{-}4)_{1.5}$, and $NP(NHCH_2C_5H_4N\text{-}4)_2$ with 25%, 50%, 75%, and 100% 2-pyridylmethylamino substitution

All polymers are characterised by

- low capacities,
- decreasing affinity towards copper with increasing amounts of 4-pyridylmethylamino groups.

The contrasterical effect observed can be interpreted as a result of inter- and intramolecular hydrogen bonding, which becomes stronger from 2- to 4-pyridylmethylamino. An increase of the glass transition temperatures of the ligand polymers from 2- to 4-pyridylmethylamino and with an increasing amount of functional groups in the polymers underlines this explanation.

A ligand-stabilised [$Cu_{13}O_9$]-cluster: The trans vicinal di(2-pyridylmethylamino) substituted phosphazene 2,4,6,6-tetraphenoxy-trans-2,4-di(2-pyridylmethylamino)-2λ^5,4λ^5,6λ^5-cyclotriphosphaza-1,3,5-trien reacts with copper(I) iodide and oxygen under formation of a blue crystalline compound in yields of almost 100%.

The single crystal structure analysis allowed the determination of the molecular structure. The cation is formed by four molecules of the ligand which are deprotonated at one of the amine groups (FIGURE 4). Each molecule of the phosphazene acts as a hexadentate chelating ligand with two pyridyl-, the amine-, the amide-, and phosphazene nitrogen atoms participating in complex formation. The ligand shell stabilises a tridecanuclear copper cluster, [$Cu_{13}O_9$]. Twelve copper atoms form four corner-sharing tetrahedra. The geometry around all of them is slightly distorted square planar. The remaining copper atom is square pyramidally coordinated by an iodine- and four oxygen atoms. Each of the oxygen atoms is also connected with a corner of one of the four tetrahedra (FIGURE 4).

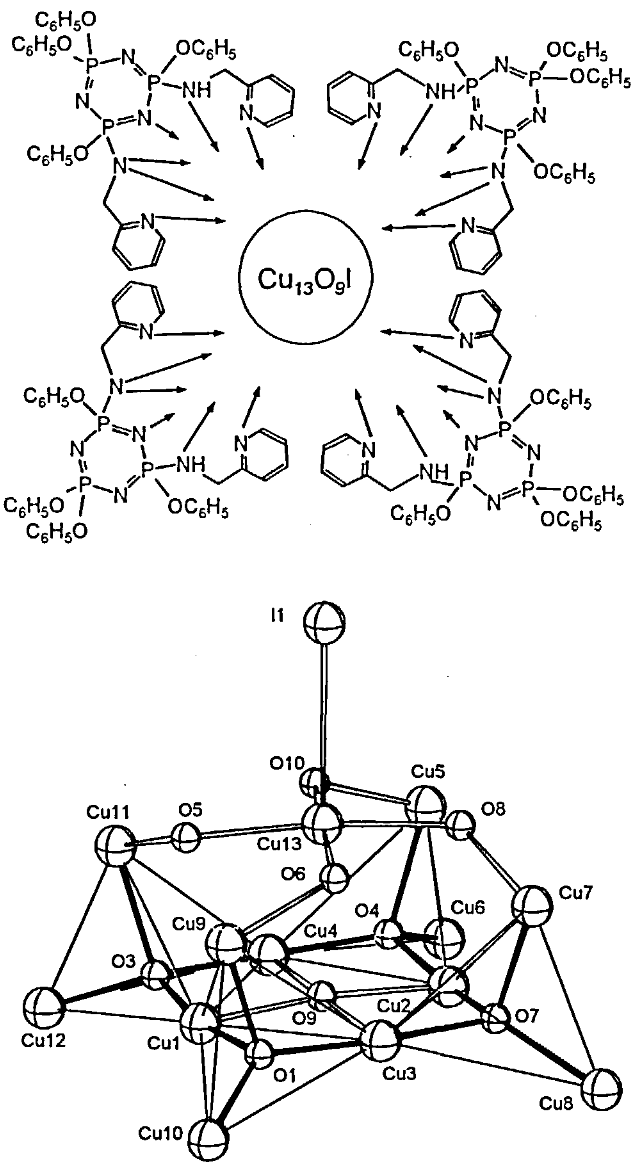

FIGURE 4: Formation of the ligand shell around the $[Cu_{13}O_9]I$-cluster (above) and the structure of the $[Cu_{13}O_9]I$-unit (below)

The cluster is bound to the ligand in the following manner. The shared corners are coordinated by three oxygen atoms of the cluster and a phosphazene nitrogen atom. The upper corners (FIGURE 4) are attached to two oxygen atoms and additionally to a pyridyl- and an amide group. The lower corners are bound to one oxygen atom and one pyridyl-, amine-, and amide group.
Cu-O bond lengths are in a range of 1.85(2) (Cu(3)-O(1)) and 2.01(2) (Cu(3)-O(9)) Å, Cu-N bonds 1.92-2.08 Å; copper copper distances are 2.789(5) (Cu(5)-Cu(6)) to 2.916(5) (Cu(4)-Cu(11)) Å.

The anion is a new iodo cuprate, $[Cu_6I_9]^{3-}$, which is formed by four edge-sharing tetrahedra analogue to the bromocuprate $[Cu_6Br_9]^{3-}$ [6] (FIGURE 5). Cu-I distances are found in a range of 2.369(8) (Cu(39)-I(23)) to 3.072(7) (Cu(25)-I(2)) Å, Cu-Cu bond lenghts between 2.516(9) (Cu(27)-Cu(39)) and 2.93(2) (Cu(14)-Cu(39) Å.

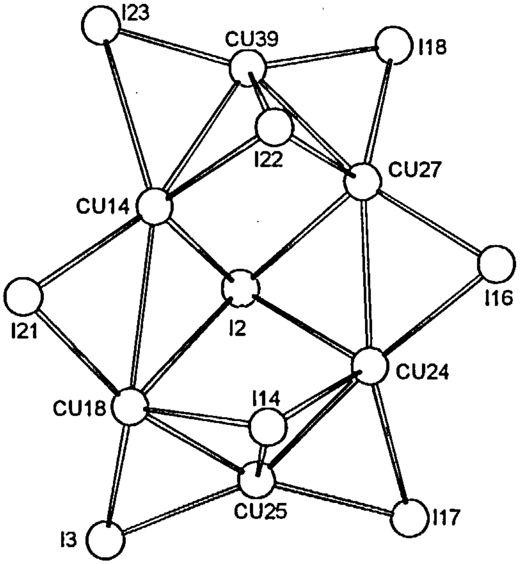

FIGURE 5: Iodo cuprate anion

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