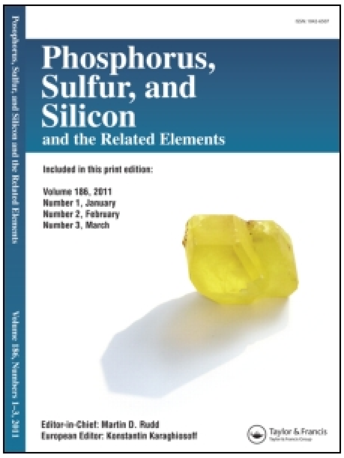

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Strategies for the Synthesis of New Materials Based on Squarate-Substituted Phosphazenes and *d* or *f* Metals

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We report the synthesis of a new organo-inorganic ring system, squarate-substituted cyclophosphazene derivative **3**. The isolated product was characterized by means of elemental analysis, IR and ^{13}C-NMR spectroscopy. Elemental analysis, molar conductivity data, IR and electronic spectra support the general formulae of obtained complexes: $[M_2(3)(OH_2)_4(ClO_4)_2](ClO_4)_4$, ($M=Fe^{3+}$, Cr^{3+}), $[M_2(3)(OH_2)_8Cl_4]Cl_2$, ($M=Eu^{3+}$, Ce^{3+}).

Keywords: cyclophosphazene; transition metal complexes

INTRODUCTION

The versatile coordination chemistry of *squaric acid*[1] and that of *cyclophosphazenes*[2] are well documented.

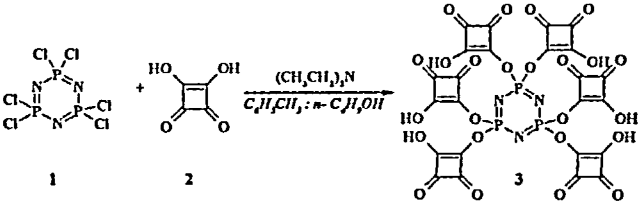
There are three major ways in which *cyclophosphazenes* can act as ligand toward transition metal[3]: a) coordination by skeletal (ring) nitrogen atoms; b) ring phosphorus transition metal covalent bond formation; c) coordination by an exocyclic group substituted on ring phosphorus. Of these the latter is the most versatile method as it offers the advantage of designing and assembling appropriate cyclophosphazene ligands by a proper choice of substituent[4].

On the other hand the most important features presented by squaric acid are the aromaticity and the large value of its bite angle. which explain the behaviour of squaric acid: as bridging ligand (monodentate, μ-1,2- and μ-1,3-bismonodentate, tetrakismonodentate) with 3*d* metals; as chelating ligand with *s* and *f* metals.

EXPERIMENTAL SECTION

Electronic spectra have been recorded at room temperature on a VSU-2G spectrophotometer using MgO as standard sample. *Infrared spectra* were recorded on a Perkin-Elmer spectrophotometer as KBr pellets in the 4000-400 cm^{-1} region. *NMR-spectra* were recorded on a spectrometru AVANCE DX400. *Molar conductance* was measured at room temperature on a Radelkis KFT conductivity meter. *Magnetic susceptibility measurements* were carried out at room temperature on a Faraday-type balance. Hexachlorocyclophosphazene and squaric acid were purchased from *Aldrich Chemical* and were used as received.

A. Ligand synthesis Hexachlorocyclophosphazene **1** was reacted with a molar excess (8 mol) of the squaric acid (3,4-dihydroxy-3-cyclobuten-1,2-dion, **2**) in the presence of triethylamine as a base, in toluene-butanol (1:1) solvent mixture (SCHEME 1).



SCHEME 1 Ligand synthesis

The formation of product **3** was monitored by TLC using silica gel sheets, and as eluent CH_3Cl/MeOH (90:10). The resulted viscous liquid was recrystalized from methanol and yield colourless needle-like crystals (η =67%). The structure of **3** was confirmed by IR and NMR spectra. Characteristic bands in IR spectra of compounds **1** and **3** useful in diagnostic sense are presented in TABLE 1.

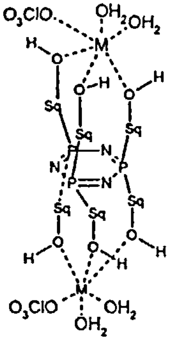
TABLE 1 The main IR bands for **1** and **3** (ν, cm^{-1}, KBr)

Compound	$\nu_{P\text{-}Cl}$	$\nu_{P\text{-}N}$	$\nu_{P\text{-}O}$	$\nu_{C\text{-}O}$	$\nu_{C=O}$
				$\nu_{C\text{-}C}$	
1	620	1190	-	-	-
		1240			
3	-	1214	1315	1465	1710
		1250		1480	

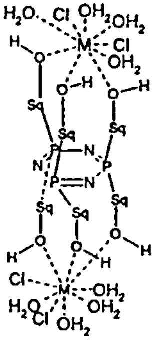
In IR spectrum of **3** $\nu_{P\text{-}N}$ is shifted to higher values than in the starting compound **1** and a new band specific to $\nu_{P\text{-}O}$ appears. The stretching vibrations $\nu_{C\text{-}C}$, $\nu_{C\text{-}O}$, $\nu_{C=O}$ are characteristic to squaric

acid. The disappearance of the peak at 620 cm^{-1} (ν_{P-Cl}) is a major argument that ring phosphorus is no longer bonded to chlorine.
^{13}**C-NMR** (δ, ppm, $CDCl_3$ + DMSO) : 198.52 (P-O-C-C=O), 190.72 (C-C-C=O), 188.2 (P-O-C), 187.6 (C-C-OH); ^{1}**H-NMR** (δ, ppm, DMSO): 5.72 (-OH)

B. Synthesis of complexes Substituted-cyclophosphazene **3** was reacted with $Fe(ClO_4)_3{\cdot}xH_2O$, $Cr(ClO_4)_3{\cdot}6H_2O$, $EuCl_3{\cdot}6H_2O$ or $CeCl_3{\cdot}6H_2O$ in methanol in 1:2 molar ratio. All the reactions are quite facile and the resulting complexes could be isolated in almost quantitative yields (80-90%). Elemental analysis, molar conductivity data, IR and electronic spectra support the general formulae of obtained complexes: $[M_2(3)(OH_2)_4(ClO_4)_2](ClO_4)_4$, (M=$Fe^{3+}$, Cr^{3+}), $[M_2(3)(OH_2)_8Cl_4]Cl_2$, (M=Eu^{3+}, Ce^{3+}).



$[M_2(3)(OH_2)_4(ClO_4)_2](ClO_4)_4$,
(M=Fe^{3+}, Cr^{3+})



$[M_2(3)(OH_2)_8Cl_4]Cl_2$,
(M=Eu^{3+}, Ce^{3+})

Conductivity measurements of complexes in acetonitrile solutions revealed that they exhibit conductivity values within the normal range of 1: 4 and 1:2 electrolytes (TABLE 2).

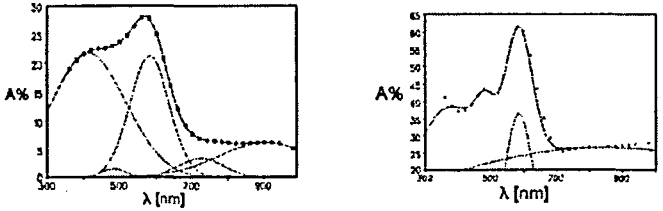
TABLE 2 Conductivity data for complexes (10^{-3}M in acetonitrile)

Compound	Conductivity (μS cm^{-1} mol^{-1})	Electrolyte type
$[Fe_2(3)(OH_2)_4(ClO_4)_2](ClO_4)_4$	460	1:4
$[Cr_2(3)(OH_2)_4(ClO_4)_2](ClO_4)_4$	478	1:4
$[Eu_2(3)(OH_2)_8Cl_4]Cl_2$	257	1:2
$[Ce_2(3)(OH_2)_8Cl_4]Cl_2$	271	1:2

The *infrared spectra* of all synthesised complexes display a broad and intense band located around 3400-2900 cm^{-1}, which points out the presence of strong hydrogen bonds assigned to the OH group of the water molecules. Also iron and chromium complexes have spectral bands characteristic to ClO_4^- ion (ν_{ClO4} = 1086, 626 cm^{-1}). The electronic spectrum of the complex $[Fe_2(3)(OH_2)_4(ClO_4)_2]$-$(ClO_4)_4$, show absorption bands characteristic to Fe^{3+} in distorted octahedral geometry and according to the value of effective Bohr magneton number (μ_{eff} = 4.65 BM) they are low-spin complexes. The electronic spectrum of $[Cr_2(3)(OH_2)_4(ClO_4)_2](ClO_4)_4$ shows three absorption bands which can be assigned to the spin allowed *transitions specific for Cr^{3+} in octahedral distorted geometry* (μ_{eff} = 5.67BM) (TABLE 3 and FIGURE 1)

TABLE 3 Electronic spectra of complexes

$[Fe_2(3)(OH_2)_4(ClO_4)_2](ClO_4)_4$	${}^2T_{2g}\to{}^4T_{1g}$ 21.4kK	*Spin forbidden* 24.7 kK	${}^2T_{2g}\to{}^4T_{2g}$ 27.8 kK
$[Cr_2(3)(OH_2)_4(ClO_4)_2](ClO_4)_4$	${}^4A_{2g}\to{}^4T_{2g}$ 17.1 kK	${}^4A_{2g}\to{}^4T_{1g}$ 21.3 kK	${}^2T_{2g}\to{}^4T_{2g}$ 27.2 kK



$[Fe_2(3)(OH_2)_4(ClO_4)_2](ClO_4)_4$ $[Cr_2(3)(OH_2)_4(ClO_4)_2](ClO_4)_4$

FIGURE 1 Electronic spectra of the complexes

The coordination tendency of the ligand 3 was studied toward *d* (Fe^{3+}, Cr^{3+}) and *f* (Eu^{3+}, Ce^{3+}) metal ions. The luminescence spectra of the europium and cerium complexes will provide further information about their structure and properties.

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