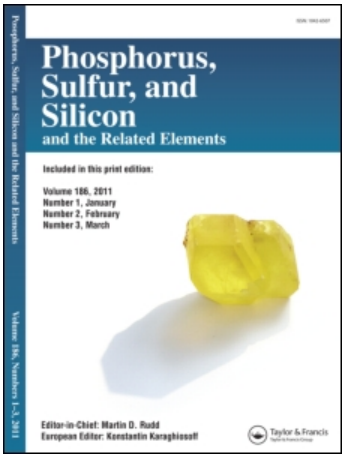

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New Carboxylate Functionalized Phosphodi- and Trihydrazones as Versatile Chelating Agents of Metallic Ions in Organic Solvents and in Water

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Phosphodihydrazones and phosphotrihydrazones having two or three carboxylic acids as substituents are synthesized, and their complexation ability towards various divalent and trivalent metal acetates ($Co(OAc)_2,4H_2O$, $Ni(OAc)_24H_2O$, and $Er(OAc)_3,4H_2O$) in organic solvents is described. The metal/phosphorhydrazone ratio is measured and the results discussed. All these complexes are insoluble in organic solvents and in water. Analogous experiments are carried out in water with sodium salts issued from these phosphodi- or tri-hydrazones, and $NiSO_4$ as a model of industrial waste waters.

Keywords Chelating agents; metal acetates; phosphorhydrazones; waste waters

INTRODUCTION

The removal of metallic contaminants from industrial waste-waters becomes a crucial necessity with the advent of more stringent environmental legislations concerning the quality of the final disposal stream.[1] Some classical means for such removal consists in precipitating hydrated metallic oxides by adjusting the pH with lime or caustic soda,[2] or in using biosorbents.[3] In the latter case, it is known that the functional groups acting in the complexation of metals are generally carboxylate groups (or eventually sulfate groups), and that the density of

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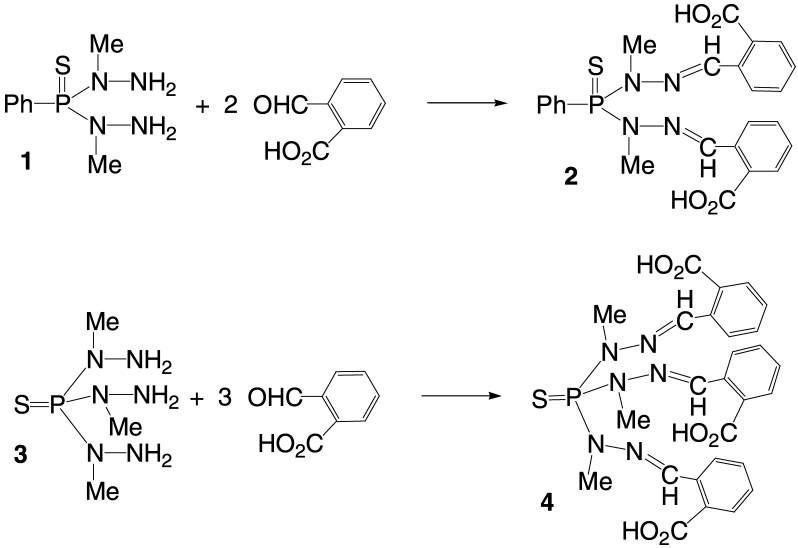
these functions plays a role in the efficiency of the metal sequestration, as shown for instance by the success of ethylenediamine tetraacetic acid (EDTA) as complexing agent.[4] Furthermore, many chemically synthesized chelating agents used in very diversified fields such as catalysis or radiopharmaceuticals[5] also possess carboxylate groups.

The easy synthesis of phosphorhydrazides issued from methylhydrazine, and their quantitative condensation reactions with benzaldehyde derivatives already allowed us to isolate numerous phosphodi- and trihydrazones functionalized by two or three functional groups, including carboxylic acid groups and sulfate groups.[6] This type of reaction was even extended to some dendrimers having hydrazide end groups, and leading to 48 carboxylic acid end groups.[7] However, the complexing ability of these compounds was never tested. In this paper, we report the synthesis of two new phosphorhydrazone derivatives of carboxylic acid and some tests concerning their complexation properties toward M(II) and M(III) metals.

RESULTS AND DISCUSSION

Difunctional (**2**) and trifunctional (**4**) phosphorhydrazone derivatives are easily obtained using our previously reported method,[6] from phosphodi-(**1**) and tri(**3**) hydrazides (Scheme 1). In order to take



SCHEME 1 Synthesis of phosphodi- and phosphotri-hydrazones.

advantage of the presence of sp^2 nitrogen atoms as potential complexing sites, the ortho position was chosen for the location of the carboxylic acid function. The condensation reactions induce as usual a shielding effect in phosphorus NMR, from $\delta = 85.7$ (for **1**) or 84.3 (for **3**) to $\delta = 78.8$ (for **2**) or 72.7 (for **4**).

These compounds are not soluble in water, thus we decided first to study their sequestering properties toward metallic ions in an organic solvent, with the aim of establishing if our initial strategy was right. Methanol is chosen because it solubilizes both the phosphorhydrazones **2** and **4**, as well as various acetate metallic salts. We selected $Co(OAc)_2,4H_2O$, $Ni(OAc)_2,4H_2O$, and $Er(OAc)_3,4H_2O$ as models of M(II) and M(III), expecting that the acetates will be replaced by carboxylic acids as ligands of the metals. A solution of one or two equivalents of the metallic salt in methanol is added at room temperature to a solution of compounds **2** or **4** in methanol (Table I). Two stoichiometries were used to determine the sequestering performance of both compounds. In all cases, a precipitate immediately begins to appear, and after three hours, the color of the solution, due to metallic salts, has faded, an abundant precipitate is formed, and a strong odor of acetic acid emanates from the solution. Separation of the precipitate from the solution followed by evaporation to dryness of the solution affords only traces of matter when a stoichiometric amount of each compound is used, or a higher quantity when 2 equivalents of metals are used.

All the precipitates are insoluble in all the organic solvents we tested (8 different solvents) and in water. This fact precludes any analysis of the precipitates in solution, but it is a very interesting phenomenon, regarding our initial goal to remove metallic ions from waste-waters. The precipitates are examined by IR spectroscopy, which gives an important information: in practically all cases (excepted case d, Table I), the broad band corresponding to asymmetric vibration of the carboxylic

TABLE I Stoichiometry Used for the Complexation of P-Hydrazones by Metal Acetates, and Metal/Phosphorus Ratio Obtained by Elemental Analyses of the Precipitates

Experiment	**a**	**b**	**c**	**d**	**e**	**f**	**g**
P-hydrazone	**2**	**2**	**2**	**4**	**4**	**4**	**4**
$M(OAc)_x$	$Co(OAc)_2$	$Co(OAc)_2$	$Ni(OAc)_2$	$Co(OAc)_2$	$Co(OAc)_2$	$Er(OAc)_3$	$Er(OAc)_3$
M/P initial	1	2	1	1	2	1	2
M/P in precipitate	1.0*	1.3*	1.1*	1.2*	1.5*	1.0*	1.1*

*These values are the average of at least two experiments.

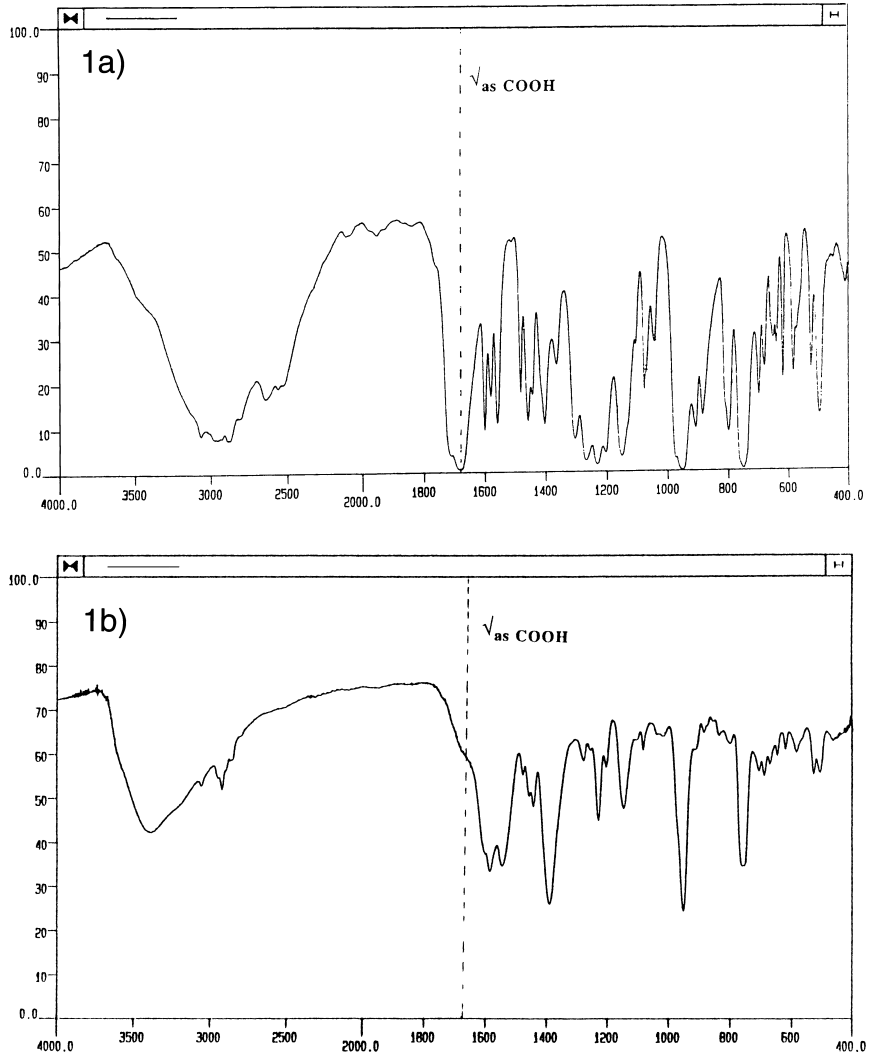


FIGURE 1 IR spectra (KBr) of **4** (a) and of [**4** + $Er(OAc)_3,4H_2O$] (b).

groups at 1700 cm^{-1} has disappeared (compare Figure 1(a) (**4**) and Figure 1(b) (**4** + 1 $Er(OAc)_3$, $4H_2O$)). This means that all the carboxylic acid groups are implied in the complexation. However, the IR data cannot give any information concerning the stoichiometry in the complexes. Indeed, this is not obvious, since we have already shown for complexes issued from phosphorhydrazones having phenols instead of

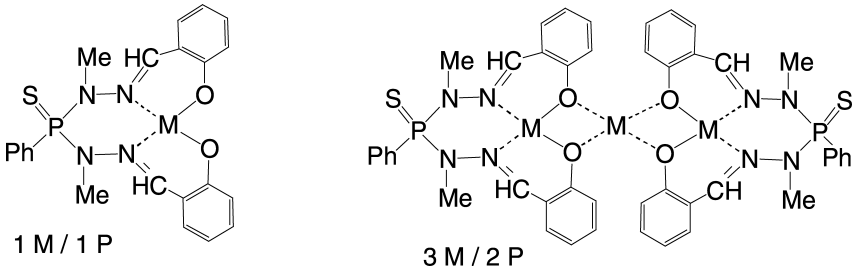
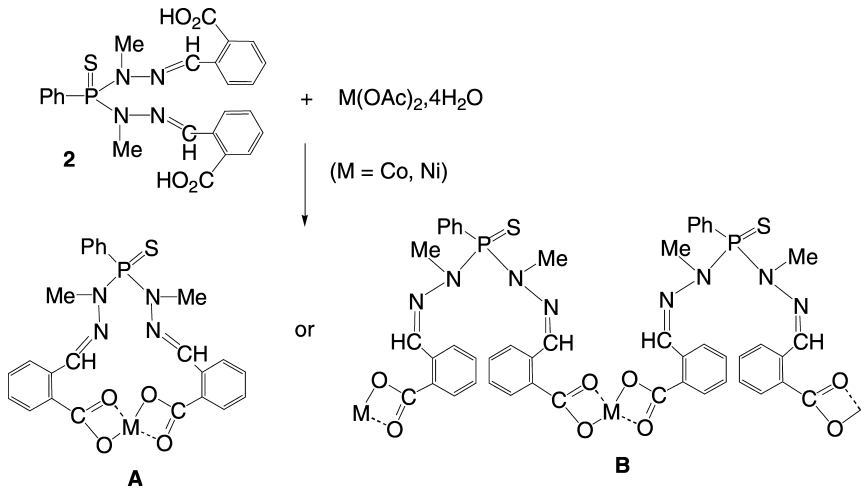


FIGURE 2 Types of complexes previously isolated from phenol functionalized phosphodihydrazones.

carboxylic acid functions that the complexation may afford either 1/1 or 3/2 metal/phosphorhydrazone complexes (see Figure 2).[8]

Elemental analysis of the precipitates obtained here, and more precisely the ratio Metal/P, should give very informative data concerning the stoichiometry of the complexes. Table I displays the M/P ratio obtained for the seven complexation experiments which we carried out. The reaction of one equivalent of divalent metals with compound **2** (cases a and c) and the reaction of one equivalent of a trivalent metal with compound **4** (case f) cleanly affords the expected 1/1 complexes. When a higher number of equivalent of metal per ligand is used (2 equivalents), not all the amount of metal is complexed. The higher percentage of metal retained is when 2 equivalents of Co are added to one equivalent of **4** (case e). The precipitate obtained corresponds to a 3/2 ratio (3 Co/2 **4**), in which all the carboxylic groups have reacted. It must be noted that for an initial 1/1 stoichiometry (case d), the 1/1 complex is not obtained cleanly, and a higher percentage of metal is retained in the precipitate; indeed, the situation in which one carboxylic group will remain unreacted seems unlikely. On the other hand, when 2 equivalents of Er are used with one of **4** (case g), the precipitate obtained has practically the same composition than with the initial 1/1 stoichiometry (case f). Finally, case b corresponds to a mixture of compounds having a 1/1 and a 3/2 stoichiometry. Thus, in most cases, the expected stoichiometries are actually obtained in the complexes, but they are unexpectedly insoluble. In accordance with our previous complexes, we anticipated here the obtaining of the 16-membered macrocyclic structure (**A**) shown in Scheme 2. However, in view of the high insolubility of the complexes, this type of structure seems unlikely. These complexes should be viewed as polymers, in which each metal does not bridge two branches emanating from the same molecule, but two branches of two different molecules (structure **B** in Scheme 2).



SCHEME 2 Complexation of metal acetates by the phosphodihydrazone **2**.

In view of the insolubility of the complexes, these results in methanol look very promising, thus we decided to try the same experiments in water. A solution of $NiSO_4$ in water (1 g in 200 mL) is used as model of waste water. This salt was chosen because changes of color, easily detectable by colorimetry that are typical for the complexation. In a first approach, compounds **2** and **4** are added to the green solution of $NiSO_4$, but as noted previously, they are insoluble in water; thus no reaction occurs, as shown by the fact that the precipitate of **2** or **4** remains white, while the solution remains colored in green with no modification of the intensity as indicated by colorimetry at 600 nm. Since it is known for biosorbents that the sodium salts of carboxylic acids have much higher binding capacity of metallic ions than the carboxylic acids,[9] we decided to add 2 equivalents of NaOH to **2** to obtain the corresponding sodium salt **5** (Figure 3). Furthermore, compound **5** is soluble in water.

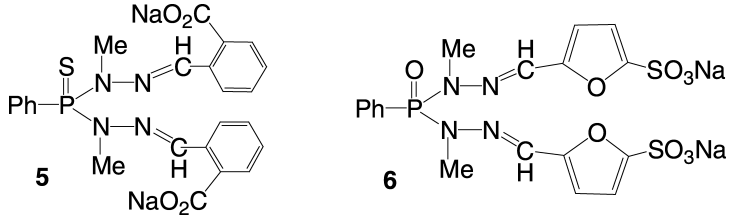


FIGURE 3 Phosphodihydrazone sodium salts.

When compound **5** is added to the solution of $NiSO_4$ in water, in a theoretical 1/1 stoichiometry, the observed behavior depends on the pH of the solution. Tests were carried out between $5 \leq pH \leq 10$ because at a lower pH compound **5** precipitates alone. At acidic pH (5–7), only solutions are observed but a change in color is detected from green for the initial solution to green-blue in the presence of **5**. On the other hand, at basic pH (7–10), a green-blue precipitate is observed, which is more abundant when the pH becomes more and more basic and the solutions become less and less colored. The change of color is indicative of the occurrence of a complexation reaction, as well as the noticeable diminishing of the amount of **5** in solution (after concentration) shown by ^{31}P NMR, in conditions in which it is soluble. A similar test was carried out also with the sodium sulfate derivative **6** and gave exactly the same results as the sodium carboxylate derivative **5**. These results seem promising, but as indicated previously it is well known that caustic soda is used to precipitate hydrated metal oxides in waste waters. It appears that even if compounds **5** and **6** are an efficient complexing agent of nickel in water, they do not offer a real improvement compared to this very simple and inexpensive method, thus no more experiments were carried out in this field.

CONCLUSION

We have demonstrated the complexing ability of carboxylic acid derivatives of phosphodi- and tri-hydrazones towards M(II) and M(III) metals in organic solvents. In most cases, the stoichiometry of the complexes are as expected 1 M(II)/2 CO_2^- and 1 M(III)/3 CO_2^-. The insolubility of these complexes in organic solvents and in water strongly indicates that their structure should be polymeric. Interestingly, the sodium salts of the same carboxylic acid derivatives and a related sulphate derivative also possess complexing properties in water, as illustrated by the sequestration of nickel in basic conditions as a model of industrial wastewaters.

EXPERIMENTAL SECTION

General

All manipulations were carried out with standard high vacuum and dry-argon techniques. The solvents were freshly dried and distilled. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker AC 200, AC 250, or DPX 300 spectrometers. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR and $SiMe_4$ for ^1H and ^{13}C NMR. The attribution

of ^{13}C NMR signals was done using J_{mod} experiments when necessary. Infra-red spectra have been recorded with Perkin Elmer FT 1725x. Elemental analysis were carried out by the Service Central d'Analyses du CNRS in Vernaison (France). Compound **6** was synthesized as described previously.[6]

Synthesis and Characterization of 2

Powdered 2-carboxybenzaldehyde (1.50 g, 10 mmol) and the phosphodihydrazide **1** (1.15 g, 5 mmol) were dissolved simultaneously in tetrahydrofuran (7 mL). The resulting solution was stirred for 3 h at room temperature, then evaporated to dryness to afford a lacquer. This residue was dissolved in acetonitrile, filtered, and evaporated to dryness to afford compound **2** as a white powder in 97% yield.

$^{31}P\{^1H\}$ NMR (CD_3OD): $\delta = 78.8$ (s). ^1H NMR ($DMSOD_6$): $\delta = 3.3$ (d, $^3J_{HP} = 9.4$ Hz, 6H, CH_3), 7.5–8.0 (m, 13H, C_6H_4, C_6H_5), 8.6 (s, 2H, H–C=N). $^{13}C\{^1H\}$ NMR (CD_3OD): $\delta = 32.1$ (d, $^2J_{CP} = 9.6$ Hz, CH_3), 127.9–138.9 (m, C_6H_4, C_6H_5), 134.6 (d, $^3J_{CP} = 10.7$ Hz, H–C=N), 170.6 (s, COOH). IR(KBr): 1683 (ν_{COOH}). M.P. 173°C. Anal. Calcd for $C_{24}H_{23}N_4O_4PS$ (494.5): C, 58.29; H, 4.69; N, 11.33. Found: C, 57.95; H, 4.61; N, 11.21.

Synthesis and Characterization of 4

Powdered 2-carboxybenzaldehyde (1.50 g, 10 mmol) and the phosphotrihydrazide **3** (0.66 g, 3.33 mmol) were dissolved simultaneously in THF (7 mL). The resulting solution was stirred for 3 h at room temperature, then evaporated to dryness to afford a lacquer. This residue was dissolved in acetonitrile, filtered, and evaporated to dryness to afford compound **4** as a white powder in 98% yield.

$^{31}P\{^1H\}$ NMR ($DMSOD_6$): $\delta = 72.7$ (s). ^1H NMR ($DMSOD_6$): $\delta = 3.4$ (d, $^3J_{HP} = 8.8$ Hz, 9H, CH_3), 7.4–8.7 (m, 12H, C_6H_4), 8.7 (s, 3H, H–C=N). $^{13}C\{^1H\}$ NMR (CD_3OD): $\delta = 30.3$ (d, $^2J_{CP} = 9.1$ Hz, CH_3), 128.3–138.2 (m, C_6H_4), 138.4 (d, $^3J_{CP} = 13.1$ Hz, H–C=N), 170.7 (s, COOH). IR(KBr): 1683 (ν_{COOH}). M.P. 165°C. Anal. Calcd for $C_{27}H_{27}N_6O_6PS$ (594.6): C, 54.54; H, 4.58; N, 14.13. Found: C, 54.48; H, 4.61; N, 14.05.

Synthesis and Characterization of 5

A 0.15 M solution of NaOH in water was added to powdered **2**. The precipitate progressively dissolved and was totally dissolved after the

addition of two equivalents of NaOH. After evaporation of water compound **5** was isolated as a white powder in 97% yield. $^{31}P\{^1H\}$ NMR (D_2O): $\delta = 78.0$ (s). ^1H NMR ($DMSOD_6$): $\delta = 3.23$ (d, $^3J_{HP} = 7.0$ Hz, 6H, CH_3), 7.3–9.0 (m, 15H, C_6H_4, C_6H_5, H—C═N). $^{13}C\{^1H\}$ NMR (CD_3OD): $\delta = 32.2$ (d, $^2J_{CP} = 9$ Hz, CH_3), 128–139 (m, C_6H_4, C_6H_5), 134.5 (d, $^3J_{CP} = 10$ Hz, H—C═N), 174.6 (s, COO). Anal. Calcd for $C_{24}H_{21}N_4Na_2O_4PS$ (538.5): C, 53.54; H, 3.93; N, 10.41. Found: C, 53.45; H, 4.05; N, 10.34.

Synthesis and Elemental Analysis of the Precipitates a, b, c

A solution of 0.60 or 1.20 mmol of $Co(OAc)_2,4H_2O$ or $Ni(OAc)_2,4H_2O$ in methanol (10 mL) was added dropwise to a solution of phosphodihydrazone **2** (0.30 g, 0.60 mmol) in methanol (10 mL). The resulting mixture was stirred for 3 h at room temperature. The abundant precipitate was filtered, recovered, and evaporated to dryness to afford a green-blue powder insoluble in organic solvents and water. The elemental analysis data are the average of at least two experiments.

a) [**2** + 1Co]: Found: C, 47.7; H, 4.4; N, 8.9; P, 4.9; Co, 9.4. Calculated for $[C_{24}H_{21}N_4O_4PS + Co + 4H_2O] = C_{24}H_{29}N_4O_8PSCo$: C, 46.23; H, 4.67; N, 8.98; P, 4.96; Co, 9.45.

b) [**2** + 2Co]: Found: C, 42.7; H, 4.3; N, 7.7; P, 4.1; Co, 10.2. Calculated for $[2C_{24}H_{21}N_4O_4PS + 2Co + Co(CH_3CO_2)_2 + 12H_2O] = C_{52}H_{72}N_8O_{24}P_2S_2Co_3$: C, 41.75; H, 4.85; N, 7.49; P, 4.14; Co, 11.82.

c) [**2** + 1Ni]: Found: C, 45.9; H, 4.5; N, 8.6; P, 4.7; Ni, 9.8. Calculated for $[C_{24}H_{21}N_4O_4PS + Ni + 4H_2O] = C_{24}H_{29}N_4O_8PSNi$: C, 46.25; H, 4.69; N, 8.99; P, 4.97; Ni, 9.42.

Synthesis and Elemental Analysis of the Precipitates d, e, f, g

A solution of 0.50 or 1.00 mmol of $Co(OAc)_2,4H_2O$ or $Er(OAc)_3,4H_2O$ in methanol (10 mL) was added dropwise to a solution of phosphotrihydrazone **4** (0.30 g, 0.50 mmol) in methanol (10 mL). The resulting mixture was stirred for 2 h at room temperature. The abundant precipitate was filtered, recovered, and evaporated to dryness to afford a powder insoluble in organic solvents and water. The elemental analysis data are the average of at least two experiments.

d) [**4** + 1Co]: Found: C, 43.2; H, 4.4; N, 10.5; P, 4.1; Co, 9.8. Calculated for $[C_{27}H_{25}N_6O_6PS + Co + 4H_2O] = C_{27}H_{33}N_6O_{10}PSCo$: C, 44.82; H, 4.60; N, 11.62; P, 4.28; Co, 8.15. Calculated for $[2C_{27}H_{24}N_6O_6PS +$

$3Co + 12H_2O] = C_{54}H_{72}N_{12}O_{24}P_2S_2Co_3$: C, 41.15; H, 4.60; N, 10.66; P, 3.93; Co, 11.22.

e) [**4** + 2Co]: Found: C, 43.4; H, 4.6; N, 10.4; P, 3.9; Co, 11.7. Calculated for $[2C_{27}H_{24}N_6O_6PS + 3Co + 12H_2O] = C_{54}H_{72}N_{12}O_{24}P_2S_2Co_3$: C, 41.15; H, 4.60; N, 10.66; P, 3.93; Co, 11.22.

f) [**4** + 1Er]: Found: C, 38.9; H, 3.8; N, 9.6; P, 3.7; Er, 19.3. Calculated for $[C_{27}H_{24}N_6O_6PS + Er + 4H_2O] = C_{27}H_{32}N_6O_{10}PSEr$: C, 39.77; H, 3.96; N, 10.31; P, 3.80; Er, 18.61.

g) [**4** + 2Er]: Found: C, 36.9; H, 3.7; N, 8.5; P, 3.3; Ni, 19.9. Calculated for $[C_{27}H_{24}N_6O_6PS + Er + 4H_2O] = C_{27}H_{32}N_6O_{10}PSEr$: C, C, 39.77; H, 3.96; N, 10.31; P, 3.80; Er, 18.61.

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