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# COMMUNICATION

# Synthesis and characterisation of pyro-, tri- and orthophosphato complexes of cobalt(III)

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**Abstract**—The synthesis of complexes of pyro-, tri-, and orthophosphates with bis(ethane-1,2-diamine) cobalt(III) and their characterisation by electronic, infrared and $^{31}P$ NMR spectra, magnetic susceptibility and thermogravimetric measurements are reported. The phosphate groups are found to act as bidentate ligands. © 1997 Elsevier Science Ltd.

*Keywords*: cobalt(III) complex; triphosphate; pyrophosphate; orthophosphate; spectra; characterization.

In this communication, we report the synthesis and characterisation of complexes of pyro-, tri-, and orthophosphato complexes with bis(ethane-1,2-diamine)cobalt(III) species. The syntheses of $[Co(en)_2HP_2O_7]$ and $[Co(en)_2PO_4]$ where en denotes ethane-1,2-diamine, by a different method have been reported but not characterized [1–3].

## EXPERIMENTAL

$[Co(en)_2CO_3]Cl$ was prepared by a known method [4]. Sodium triphosphate hexahydrate was prepared from the commercial anhydrous compound. $Na_4P_2O \cdot 10\,H_2O$, $NaH_2PO_4 \cdot 2H_2O$, $(NH_4)_2HPO_4$ and $H_3PO_4$ of A.R. grade BDH were employed.

About 1.0 g of pyrophosphate was dissolved in 100 cm$^3$ of water and 100 cm$^3$ of propanol was added to it. A solution of 2.4 g of $[Co(en)_2CO_3]Cl$ in 30 cm$^3$ of 1M HCl was then added to it with stirring. The pH of the mixture was maintained at 4.2–4.3 using 1M NaOH with continued stirring. The precipitate obtained was filtered, washed with 1 : 1 ethanol and dried at 110°C. The same procedure was employed for the synthesis of tri-, and orthophosphato complexes but maintaining the pH at 2.0–2.1 and 8.2–8.6, respectively. The precipitates were washed with absolute ethanol and dried at 110°C.

The C,H,N were estimated by microanalysis using Herisu CHN analyser. The phosphate content was estimated by ammonium phosphomolybdate method [5] and cobalt was determined using Perkin–Elmer 2380 atomic absorption spectrophotometer.

The solid state electronic spectra of pyro- and triphosphato complexes were recorded as Nujol mull using U3400 Hitachi spectrometer and that of the orthophosphato complex in aqueous solution. Infrared spectra were measured as KBr pellets using FTS 7 Bio Rad spectrophotometer. Solid state $^{31}P$ NMR spectra were obtained using magic angle spinning technique at 3.2 and 3.8 KHz using Bruker solid state NMR instrument. For the orthophosphato complex, $^{31}P$ NMR was recorded in aqueous solution using Bruker ACF 200 MHz spectrometer. $H_3PO_4$ 85% was used as reference for the solid state and solution NMR spectra. Magnetic susceptibility measurements were made by Gouy method using $Hg[Co(CNS)_4]$ as the calibrant. Complexes were subjected to thermogravimetry between 40–510°C at a heating rate of 10°C per minute using 1500 Stanton Redcroft thermalanalyser. For pH measurements, 361 Systronics pH meter was employed.

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Table 1. Analytical results for phosphato complexes[a] of cobalt(III)

| | Found, (calcd) % | | | | | | Temp. | $^{31}$P NMR | |
|---|---|---|---|---|---|---|---|---|---|
| Complexes | Co | P | C | H | N | Wt Loss | (°C) | σ PPM Ligand | Complex |
| 1 | 13.8 | 14.7 | 11.0 | 6.0 | 12.7 | 16.9 | 220–300 | 1.4 | −5.3 |
| | (13.8) | (14.6) | (11.2) | (5.9) | (13.1) | (16.9) | | | |
| 2 | 12.2 | 20.0 | 9.9 | 4.6 | 11.7 | 8.3 | 240–290 | −7.3 | −4.8 |
| | (12.5) | (19.8) | (10.2) | (4.7) | (11.9) | (7.7) | | −17.0 | −16.6 |
| 3 | 21.3 | 11.1 | 17.4 | 5.9 | 20.3 | — | — | −0.4 | 23.5 |
| | (21.5) | (11.3) | (17.5) | (5.8) | (20.4) | — | — | | |

[a] 1: [Co(en)$_2$HP$_2$O$_7$]4H$_2$O; 2: [Co(en)$_2$H$_2$P$_3$O$_{10}$]2H$_2$O; 3: [Co(en)$_2$PO$_4$].

## RESULTS AND DISCUSSION

The analytical results are presented in Table 1. The magnetic susceptibility measurements have shown the complexes to be diamagnetic. Thermogravimetric analysis of pyro- and triphosphate complexes showed complete loss of water molecules as given in Table 1.

The solid state electronic spectra of the condensed phosphato complexes and [Co(en)$_2$CO$_3$]Cl exhibit two absorption maxima in the region 750–300 nm showing the complexes to be octahedral with the phosphate group acting as a bidentate. The ligand field strength of pyro, and triphosphato ligands is higher than that of carbonate but slightly lower than that of ethane-1,2-diamine as inferred from electronic spectra. The spectrum of Co(en)$_2$PO$_4$] in aqueous solution shows two absorption maxima at 528 and 376 nm as expected [6].

In the infrared spectra of all the three complexes, bands due to coordinated ethane-1,2-diamine are found in the regions expected [7]. The NH$_2$ stretching frequencies of en in the phosphato complexes are somewhat higher than those in the carbonato complex [Co(en)$_2$CO$_3$]Cl. It suggests that the phosphato groups are relatively stronger ligands than the carbonate and consequently the bonding of en to cobalt becomes relatively weaker in the phosphato complexes. The infrared frequencies due to the phosphato group in the sodium salt [8] were compared with those in the complexes. Strong broad bands in the spectra of Na$_4$P$_2$O$_7$ at 1130, 914 and 574 cm$^{-1}$ split and are shifted in the metal complex. These data suggest bidentate coordination of the P$_2$O$_7^{4-}$ moiety to cobalt(III). Intense bands at 1212, 1155 and 1012 cm$^{-1}$ in the spectrum of Na$_5$P$_3$O$_{10}$ are shifted to higher frequencies in the complex. These shifts may be accounted by the increase in the bond order of the uncoordinated P=O linkage on bidentate coordination through oxygen of the other two P=O groups. From the frequency shifts, bidentate bonding of PO$_4^{3-}$ to the metal was inferred.

The solid state $^{31}$P NMR spectra of pyrophosphato and triphosphato complexes show a singlet and doublet signal respectively as expected [9,10]. On complexation, an upfield shift is observed as noted from Table 1. The $^{31}$P NMR shifts on complexation are not large, since the phosphato group is coordinated to cobalt not directly but *via* oxygen. However, the $^{31}$P NMR signal for [Co(en)$_2$PO$_4$] shows a large downfield shift. This trend is opposite to that found for the other two types of phosphato complexes and the magnitude of the shift is also higher. It may be attributed to the fact that the two coordinating oxygens are bonded to the same phosphorus atom in PO$_4^{3-}$ and the chelate ring is a strained four membered ring. In the other two phosphato complexes, the chelate ring is six-membered and only one coordinating oxygen comes from each phosphorous atom.

From the structure of triphosphate, and pyrophosphate, we expect the ligands to coordinate unsymmetrically and orthophosphate may coordinate symmetrically. However, experimental evidences are not available in the present study.

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