Pentamolybdobis[cis-phosphatobisethylenediamineaquocobalt(III)].
A 'Neutral' Heteropoly Complex

by

Wonsuk Kwak and Michael T. Pope
Department of Chemistry, Georgetown University
Washington, D.C.

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We have recently reported some of the first examples of organic derivatives of heteropoly anions. Among the new complexes were pentamolybdobisphosphonates, (RP)₅Mo₆O₂₇⁻, that are structurally analogous to the corresponding molybdophosphate, (OP)₅Mo₆O₂₇⁻. In these heteropoly complexes the heteroatom, phosphorus, utilizes only three oxygens to bind to the oxometallate structure. The pentamolybdobisphosph(on)ate anions form rapidly and are hydrolytically stable at pH 4-5. Under these conditions, complexes where R contains an amino group are protonated, and the resulting heteropoly anions are zwitterionic, e.g. [(H₃N⁺C₆H₄P)₂Mo₆O₂₇⁻]. In this paper we describe the synthesis of an electrically neutral zwitterion of the same type in which the hetero group is a monodentate phosphate ligand of an inert coordination complex.

Experimental
The complexes cis-[Co(en)₂(H₂O)(HPO₄)]ClO₄·0.256H₂O, [Co(en)₂(H₂O)₂(HPO₄)]·H₂O and cis-[Co(en)₃(H₂O)₃(NO₃)] were prepared as previously described. The last named complex was converted to the perchlorate salt by treatment with sodium perchlorate. Optical spectra of these complexes agreed with those reported. The complex cis-[Co(en)₃(H₂O)(HPO₄)] was prepared by dissolving 0.50 g of [Co(en)₃PO₄]·H₂O (2 mmol) in 100 ml of water and adjusting the pH to 4.7 with dilute sulfuric acid. A solution containing 1.45 g of Na₂Mo₆O₁₃·2H₂O (6 mmol) in 20 ml water was adjusted to pH 4.4 with dilute sulfuric acid. Both solutions were separately filtered to remove dust and the filtrates chilled to 10–15° in an ice-bath. The molybdate solution was added dropwise to the cobalt solution, keeping the pH of the mixture at 4.4–4.7 by the addition of sulfuric acid, and keeping the temperature at 10–15°. A brick red precipitate began to form when ca 2 ml of the molybdate solution had been added. After the final addition of the molybdate solution, the suspension was kept in a refrigerator for two hours. The precipitate was collected by filtration, washed successively with a large amount of water acidified to pH 4.5, and acetone, and air-dried. The dried product was red-violet and weighed 1.3 g. Anal. Calcd. for Co₅C₆H₄N₃F₂P₂Mo₆O₃₂·8H₂O: C, 6.64; H, 3.62; N, 7.73; P, 4.28; Mo, 33.12; H₂O, 9.95. Found: C, 6.69; H, 3.63; N, 7.82; P, 4.41; Mo, 33.14; H₂O (wt. loss 110–115°), 11.26.

Results and Discussion
The complex is insoluble in water at pH 3-5, and in common polar and non-polar solvents (alcohols, dimethylsulfoxide, dimethylformamide, propylene carbonate, acetonitrile, nitromethane, benzene, etc.). At pH 6 or above the complex dissolves to give a clear solution of [Co(en)₃PO₄] (maximum at 529 nm) and, presumably, MoO₄²⁻ ions. If this solution is reacidified to pH ca 4, the heteropoly complex is reformed.
The analytical data support the formulation as a neutral
switterion (or alternatively as a binuclear cobalt complex):
\[ \{\text{en}\}_2(H_2O)\text{CoOPO}_4\text{[Mo}_3\text{O}_8\text{]}_2\text{POCo(H}_2\text{O})\{\text{en}\}_2\cdot 8\text{H}_2\text{O} \] (1)

The infrared spectrum of the complex in the metal-oxygen
stretching region is shown in Figure 1 together with that of
sodium pantamolybdodiphosphate, and is characteristic of
the P2Mo6+ moiety. Optical absorption data are given in Table 1.
Energies of the first d-d bands are generally reliable indicators
of the constitution of the first coordination sphere of the cobalt(III)
ion. The data in Table 1 thus support formula I with
\[ \{\text{Co(en)}_2\text{(aq)}\} \text{[monodentate phosphate]} \] rather than a salt such as
\[ \{\text{Co(en)}_2(H_2O)_2\}_{2[\text{P}_2\text{Mo}_6\text{O}_{18}]} \]. The salt formulation is also ruled
out by the hydrolytic dissolution of the complex at pH 6 to give
\[ \{\text{Co(en)}_2\text{(PO}_4\text{)}\} \].

We conclude that the complex formed is indeed a neutral switter-
ionic species. The interconversion of \( \{\text{Co(en)}_2\text{PO}_4\} \) to \( \text{cis-[Co(en)}_2\text{(H}_2\text{O)}\text{[PO}_4\text{]}_2\text{]}^+ \) in aqueous solution occurs rapidly at pH 5, and
polymerization of molybdate is also rapid under these conditions.
The resulting structure offers a number of possibilities for isomerism,
since both the \( \text{cis-[Co(en)}_2\text{(H}_2\text{O)}\text{[O]}^- \) and \( \text{P}_2\text{Mo}_6\text{O}_{18}^2+ \) moieties are chiral.
It is mildly surprising, and somewhat disappointing, that the re-
sulting switterion is insoluble. We presume that the approximately
linear charge arrangement, \(+2\ldots-4\ldots+2\), leads to a staggered crystal
packing with a lattice energy dominated by large electrostatic terms.

### Table 1: Visible Absorption Maxima of Some Cobalt Complexes

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<th>Complex</th>
<th>Nujol Mull</th>
<th>Solution</th>
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<tr>
<td>( {\text{Co(en)}_2\text{(H}_2\text{O)}\text{OPO}_4\text{]}_2\text{MoO}_3\text{]}_2)</td>
<td>(ca 375 \text{ sh}^a)</td>
<td>-</td>
</tr>
<tr>
<td>(\text{Co(en)}_2\text{(H}_2\text{O)}\text{OPO}_4\text{]}_2\text{ClO}_4\cdot \text{aq})</td>
<td>507</td>
<td>507</td>
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<tr>
<td>(\text{Co(en)}_2\text{PO}_4\text{]}_2\cdot \text{H}_2\text{O})</td>
<td>525</td>
<td>529</td>
</tr>
<tr>
<td>(\text{cis-[Co(en)}_2\text{(H}_2\text{O)}\text{[ClO}_4\text{]}_2)</td>
<td>490</td>
<td>492</td>
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<tr>
<td>(ca 355 \text{ sh})</td>
<td>359</td>
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\( a \) sh, shoulder
Acknowledgments. - This research has been supported by the Office of Naval Research through Contract No. N00014-75-C-0945.

Figure Caption

Figure 1. - Infrared spectra, in KBr discs, of
(a) $\left\{\left[\left(\text{Co}(en)_2\right)(\text{H}_2\text{O})\text{PO}_4\right]_3\text{Mo}_6\text{O}_{13}\right\}^\cdot8\text{H}_2\text{O}$, and
(b) $\text{Na}_4[\text{P}_2\text{Mo}_9\text{O}_{26}]^\cdot13\text{H}_2\text{O}$

References

8. C,H,N,P analyses by Galbraith Laboratories Inc., Knoxville, Tenn. Molybdenum was determined spectrophotometrically (ref. 2).
Infrared Spectra of
(a), [Co₂(en)₄(H₂O)₂(P₄O₆)₂(MoO₃)₅]₈H₂O
(b), Na₆[P₂Mo₅O₂₃]₃H₂O
The synthesis, optical and infrared spectra of the title compound, \( [(\text{Co(en)})_2(\text{H}_2\text{O})\text{OPO}_4]_2\text{Mo}_3\text{O}_13 \) are described. The complex is an electrically neutral zwitterion.
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