

Registry No. (1,3-COD)Fe(P(OMe)<sub>3</sub>)<sub>3</sub>, 59034-03-6; (1,3-COD)Fe(P(OEt)<sub>3</sub>)<sub>3</sub>, 59034-02-5; (1,3-COD)Fe(P(O-*i*-Pr)<sub>3</sub>)<sub>3</sub>, 59034-04-7; 1,5-COD, 111-78-4; Fe, 7439-89-6; P(OMe)<sub>3</sub>, 121-45-9; Fe(COD)<sub>2</sub>, 55823-33-1.

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- (8) Our calorimetric experiments have shown that excess P(OMe)<sub>3</sub> displaces both COD molecules from Ni(1,5-COD)<sub>2</sub> within the time of mixing at 25 °C (to be published).
- (9) E. L. Muetterties and J. W. Rathke, *J. Chem. Soc., Chem. Commun.*, 850 (1974), have reported the preparation of pure Fe[P(OMe)<sub>3</sub>]<sub>5</sub> by a wet reduction method.
- (10) See ref 1, Figure 2.
- (11) Fe(COD)<sub>2</sub> decomposes above -20 °C.<sup>7</sup>
- (12) A satisfactory elemental analysis was obtained. The compound melted sharply in a sealed, evacuated tube and recrystallized on cooling.
- (13) Chemical shifts are in ppm, positive downfield from internal tetramethylsilane for <sup>1</sup>H and <sup>13</sup>C in C<sub>6</sub>D<sub>6</sub> and negative downfield from external 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P.
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- (15) The lower field -CH<sub>2</sub>- resonance was broader in both <sup>13</sup>C{<sup>1</sup>H} and <sup>1</sup>H spectra, probably reflecting a larger (unresolved) phosphorus coupling.
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### Pentamolybdobis[*cis*-phosphatobis(ethylenediamine)aquacobalt(III)]. A "Neutral" Heteropoly Complex

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We have recently reported some of the first examples of organic derivatives of heteropoly anions.<sup>1,2</sup> Among the new complexes were pentamolybdobisphosphonates, (RP)<sub>2</sub>Mo<sub>5</sub>O<sub>21</sub><sup>4-</sup>, that are structurally analogous<sup>3</sup> to the corresponding molybdophosphate,<sup>4</sup> (OP)<sub>2</sub>Mo<sub>5</sub>O<sub>21</sub><sup>6-</sup>. In these heteropoly complexes the heteroatom, phosphorus, utilizes only three oxygens to bind to the oxometalate structure. The pentamolybdophosph(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., [(H<sub>3</sub>N<sup>+</sup>C<sub>2</sub>H<sub>4</sub>P)<sub>2</sub>Mo<sub>5</sub>O<sub>21</sub><sup>4-</sup>]<sup>2-</sup>. 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.

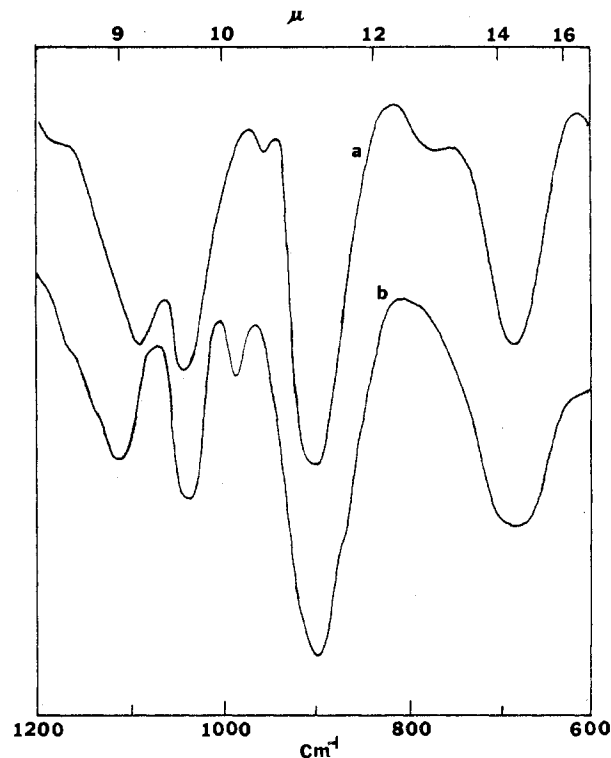


Figure 1. Infrared spectra, in KBr disks, of (a)  $[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{OPO}_3]_2\text{Mo}_5\text{O}_{15}\cdot 8\text{H}_2\text{O}$  and (b)  $\text{Na}_6[\text{P}_2\text{Mo}_5\text{O}_{23}]\cdot 13\text{H}_2\text{O}$ .

### Experimental Section

The complexes *cis*-[Co(en)<sub>2</sub>(H<sub>2</sub>O)(HPO<sub>4</sub>)]ClO<sub>4</sub>·0.256H<sub>2</sub>O, [Co(en)<sub>2</sub>PO<sub>4</sub>]<sub>2</sub>·H<sub>2</sub>O, and *cis*-[Co(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub> were prepared as previously described.<sup>5,6</sup> The last named complex was converted to the perchlorate salt by treatment with sodium perchlorate. Optical spectra of these complexes agreed with those reported.<sup>5,7</sup>

**Preparation of [Co<sub>2</sub>(en)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>P<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub>]<sub>2</sub>·8H<sub>2</sub>O.** The complex *cis*-[Co(en)<sub>2</sub>(H<sub>2</sub>O)(HPO<sub>4</sub>)]<sup>+</sup> was prepared by dissolving 0.56 g of [Co(en)<sub>2</sub>PO<sub>4</sub>]<sub>2</sub>·H<sub>2</sub>O (2 mmol) in 100 ml of water and adjusting the pH to 4.7 with dilute sulfuric acid.<sup>5</sup> A solution containing 1.45 g of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (6 mmol) in 20 ml of water was adjusted to pH 4.4 with dilute sulfuric acid. Both solutions were separately filtered to remove dust and the filtrates were chilled to 10–15 °C 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 °C. 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 2 h. The precipitate was collected by filtration, washed successively with large amounts of water acidified to pH 4.5 and acetone, and air-dried. The dried product was red-violet and weighed 1.1 g. Anal. Calcd for Co<sub>2</sub>C<sub>8</sub>N<sub>8</sub>H<sub>32</sub>P<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub>·8H<sub>2</sub>O: C, 6.64; H, 3.62; N, 7.73; P, 4.28; Mo, 33.12; H<sub>2</sub>O, 9.95. Found:<sup>8</sup> C, 6.69; H, 3.63; N, 7.82; P, 4.41; Mo, 33.14; H<sub>2</sub>O (weight loss at 110–115 °C), 11.26.

### Results and Discussion

The complex is insoluble in water at pH 3–5 and in common polar and nonpolar solvents (alcohols, dimethyl sulfoxide, dimethylformamide, propylene carbonate, acetonitrile, nitromethane, benzene, etc.). At pH 6 or above the complex dissolves to give a clear solution of [Co(en)<sub>2</sub>PO<sub>4</sub>] (maximum at 529 nm) and, presumably, MoO<sub>4</sub><sup>2-</sup> ions. If this solution is reacidified to pH ca. 4., the heteropoly complex is re-formed.

The analytical data support the formulation as a neutral zwitterion (or alternatively as a binuclear cobalt complex), [(en)<sub>2</sub>(H<sub>2</sub>O)CoOPO<sub>3</sub>(Mo<sub>5</sub>O<sub>15</sub>)O<sub>3</sub>POCo(H<sub>2</sub>O)(en)<sub>2</sub>]<sub>2</sub>·8H<sub>2</sub>O [I].

The infrared spectrum of the complex in the metal–oxygen stretching region is shown in Figure 1, together with that of sodium pentamolybdodiphosphate, and is characteristic<sup>2</sup> of the

Table I. Visible Absorption Maxima of Some Cobalt Complexes

Complex	Maxima, nm	
	Nujol mull	Soln
$\{[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{OPO}_3]_2\text{Mo}_5\text{O}_{15}\}$	508 ~375 sh <sup>a</sup>	
$[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{OPO}_3\text{H}]\text{ClO}_4 \cdot \text{aq}$	507	507
$[\text{Co}(\text{en})_2\text{PO}_4] \cdot \text{H}_2\text{O}$	360 525	366 529
$\text{cis}-[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]\text{ClO}_4$	370 490	377 492
	~355 sh	359

<sup>a</sup> sh shoulder.

$\text{P}_2\text{Mo}_5$  moiety. Optical absorption data are given in Table I. Energies of the first d-d bands are generally reliable indicators of the constitution of the first coordination sphere of the cobalt(III) ion.<sup>9-11</sup> The data in Table I thus support formula I as  $[\text{CoN}_4(\text{aq})(\text{monodentate phosphate})]$  rather than a salt such as  $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]_2[\text{P}_2\text{Mo}_5\text{O}_{23}]$ . The salt formulation is also ruled out by the hydrolytic dissolution of the complex at pH 6 to give  $[\text{Co}(\text{en})_2(\text{PO}_4)]$ .

We conclude that the complex formed is indeed a neutral zwitterionic species. The interconversion of  $[\text{Co}(\text{en})_2\text{PO}_4]$  to  $\text{cis}-[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{OPO}_3\text{H})]^+$  in aqueous solution occurs rapidly at pH 5,<sup>5</sup> and polymerization of molybdate is also rapid under these conditions. The resulting structure offers a number possibilities for isomerism, since both the  $\text{cis}-[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{O}-)]$  and  $\text{P}_2\text{Mo}_5\text{O}_{23}$  moieties are chiral. It is mildly surprising, and somewhat disappointing, that the resulting zwitterion is insoluble. We presume that the approximately linear charge arrangement,  $2+ \dots 4- \dots 2+$ , leads to a staggered crystal packing with a lattice energy dominated by large electrostatic terms.

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**Registry No.**  $\{[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{OPO}_3]_2\text{Mo}_5\text{O}_{15}\}$ , 58933-78-1;  $\text{Na}_6[\text{P}_2\text{Mo}_5\text{O}_{23}]$ , 39475-33-7;  $[\text{Co}(\text{en})_2\text{PO}_4]$ , 19169-67-6;  $\text{Na}_2\text{MoO}_4$ , 14666-91-2.

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## Extension of Rate Correlations between Electrochemical and Chemical Electron-Transfer Processes to Heteronuclear Reactions

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Using an adiabatic theory of electron transfer that is expected to be applicable to outer-sphere reactions, Marcus<sup>1</sup> has shown that two relationships are expected to hold between the

rates of such redox reactions in homogeneous solution and the corresponding reactions at inert-metal electrodes.

(a) The rate constants for an electrochemical exchange reaction  $k^{\text{el}}$  (measured at the standard potential  $E^\circ$ ) and the corresponding homogeneous self-exchange reaction  $k_{\text{ex}}$  are related by

$$\left(\frac{k_{\text{ex}}}{Z_{\text{chem}}}\right)^{1/2} \approx \left(\frac{k^{\text{el}}}{Z_{\text{el}}}\right)$$

where  $Z_{\text{chem}}$  and  $Z_{\text{el}}$  are the homogeneous and heterogeneous collision frequencies, respectively.

(b) When a series of reactants is reduced (or oxidized) electrochemically and chemically, the ratio of the rate constants for these two pathways will be constant for the conditions of a constant metal-solution potential difference and a given coreactant, respectively.

In deriving the above relations, it is assumed that the work terms associated with the approach of the reactants (and products) are negligible or constant. Correlation between electrochemical and chemical electron-transfer rates has chiefly been made using (a).<sup>1-4</sup> Comparison (b) has been used only on a limited basis to compare the electrochemical and chemical reduction rates of some cobalt(III)-pentaammine complexes.<sup>5</sup>

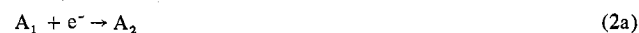
A practical limitation on the application of (a) is the relative scarcity of rate data for homogeneous self-exchange reactions which is apparently due to the difficulties of obtaining data for such reactions. Further, for many electron-transfer reactions followed by rapid chemical steps (e.g., aquation), self-exchange data cannot be obtained and standard potentials for the reactions are unknown or can only be estimated with insufficient precision. Comparison (b) can still be employed for such reactions, although the rate comparisons are relative rather than absolute and require the acquisition of kinetic data for a series of reactions with a common reductant or oxidant.

However, a correlation similar in form to (a) can also be derived enabling a comparison to be made of the absolute rates of outer-sphere electrochemical processes with those for the corresponding heteronuclear<sup>6</sup> homogeneous reactions (i.e., where a net chemical change occurs) as follows.

Consider the heteronuclear homogeneous reaction



and the corresponding electrochemical reactions



For reactions 2a and 2b, respectively, the following equations may be written according to Marcus theory<sup>1</sup> at overpotentials where the quadratic potential term can be neglected and under conditions where the double-layer work terms are negligible

$$\ln k_{\text{A}} = \ln k^{\text{s}}_{\text{A}} - 0.5f(E - E^\circ_{\text{A}}) \quad (3a)$$

$$\ln k_{\text{B}} = \ln k^{\text{s}}_{\text{B}} + 0.5f(E - E^\circ_{\text{B}}) \quad (3b)$$

$k_{\text{A}}$  and  $k_{\text{B}}$  are the rate constants for reactions 2a and 2b at potential  $E$ ,  $k^{\text{s}}_{\text{A}}$  and  $k^{\text{s}}_{\text{B}}$  are the corresponding quantities measured at the standard potentials  $E^\circ_{\text{A}}$  and  $E^\circ_{\text{B}}$  for these reactions, and  $f = F/RT$ .

At an electrode potential where  $\ln k_{\text{A}} = \ln k_{\text{B}} = \ln k^{\text{el}}_{\text{AB}}$ , (3a) and (3b) may be combined to yield

$$\ln k^{\text{el}}_{\text{AB}} = 0.5(\ln k^{\text{s}}_{\text{A}} + \ln k^{\text{s}}_{\text{B}} + 0.5 \ln K_{\text{AB}}) \quad (4)$$

as  $\ln K_{\text{AB}} = f(E^\circ_{\text{A}} - E^\circ_{\text{B}})$ , where  $K_{\text{AB}}$  is the equilibrium constant for reaction 1. However, Marcus has shown that the relation

$$\ln k^{\text{chem}}_{\text{AB}} = 0.5(\ln k_{\text{AA}} + \ln k_{\text{BB}} + \ln K_{\text{AB}}) \quad (5)$$