AD-A032 544 GEORGETOWN UNIV WASHINGTON D C DEPT OF CHEMISTRY F/G 7/2
PENTAMOLYBDOBIS (CIS-PHOSPHATOBISETHYLENEDIAMINEAQUOCOBALT(III)--ETC(U)
NOV 76 W KWAK, M T POPE N00014-75-C-0945
UNCLASSIFIED TR-5 NL

| OF |
AD
A032544

END
DATE
FILMED
1-77

FC.

12

Office of Naval Research

Contract No. N00014-75-C-0945

Task No. NR 053-576

Technical Report No.5

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

by

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

Prepared for Publication

in

Inorganic Chemistry

Contribution from the Department of Chemistry, Georgetown University, Washington, D.C. 20057

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

Wonsuk Kwak and Michael T. Pope

We have recently reported some of the first examples of organic derivatives of heteropoly anions[1,2]. Among the new complexes were pentamolybdobisphosphonates, $(RP)_2Mo_5O_{21}^{6-}$, that are structurally analogous[3] to the corresponding molybdophosphate[4], $(OP)_2Mo_5O_{21}^{6-}$. In these heteropoly complexes the heteroatom, phosphorus, utilizes only three oxygens to bind to the oxometallate 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. $[(H_3N^+C_2H_4P)_2Mo_5O_{21}^{6-}]^{2-}$. 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.

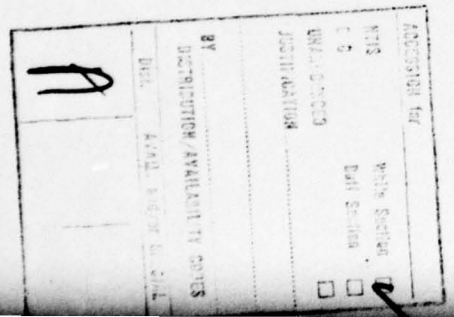
Experimental

The complexes cis-$[Co(en)_2(H_2O)(HPO_4)]ClO_4\cdot 0.256H_2O$, $[Co(en)_2PO_4]\cdot H_2O$ and cis-$[Co(en)_2(H_2O)_2](NO_3)_3$ were prepared as previously described[5,6]. The last named complex was converted to the perchlorate salt by treatment with sodium perchlorate. Optical spectra of these complexes agreed with those reported[5,7].

Preparation of $[Co_2(en)_4(H_2O)_2P_2Mo_5O_{23}]\cdot 8H_2O$.- The complex cis-$[Co(en)_2(H_2O)(HPO_4)]^+$ was prepared by dissolving 0.56 g of $[Co(en)_2PO_4]\cdot H_2O$ (2 mmol) in 100 ml of water and adjusting the pH to 4.7 with dilute sulfuric acid[5]. A solution containing 1.45 g of $Na_2MoO_4\cdot 2H_2O$ (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 1.1 g. Anal. Calcd. for $Co_2C_8N_8H_{32}P_2Mo_5O_{31}\cdot 8H_2O$: C, 6.64; H, 3.62; N, 7.73; P, 4.28; Mo, 33.12; H_2O, 9.95. Found[8]: C, 6.69; H, 3.63; N, 7.82; P, 4.41; Mo, 33.14; H_2O (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 $[Co(en)_2PO_4]$ (maximum at 529 nm) and, presumably, $MoO_4^{=}$ ions. If this solution is reacidified to pH ca 4, the heteropoly complex is reformed.



The analytical data support the formulation as a neutral zwitterion (or alternatively as a binuclear cobalt complex):

$$[(en)_2(H_2O)CoOPO_3(Mo_5O_{15})O_3POCo(H_2O)(en)_2]\cdot 8H_2O \qquad (I)$$

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[2] of the P_2Mo_5 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[9,10,11]. The data in Table 1 thus support formula I with [CoN_4(aq)(monodentate phosphate)] rather than a salt such as $[Co(en)_2(H_2O)_2]_2[P_2Mo_5O_{23}]$. The salt formulation is also ruled out by the hydrolytic dissolution of the complex at pH 6 to give $[Co(en)_2(PO_4)]$.

We conclude that the complex formed is indeed a neutral zwitterionic species. The interconversion of $[Co(en)_2PO_4]$ to *cis*-$[Co(en)_2(H_2O)(OPO_3H)]^+$ in aqueous solution occurs rapidly at pH 5[5], and polymerization of molybdate is also rapid under these conditions. The resulting structure offers a number possibilities for isomerism, since both the *cis*-$[Co(en)_2(H_2O)(O-)]$ and $P_2Mo_5O_{23}$ 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...-4...+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

Complex	Maxima (nm) Nujol Mull	Solution
$\{[Co(en)_2(H_2O)OPO_3]_2Mo_5O_{15}\}$	508	-
	ca 375 sh[a]	-
$[Co(en)_2(H_2O)OPO_3H]ClO_4\cdot aq$	507	507
	360	366
$[Co(en)_2PO_4]\cdot H_2O$	525	529
	370	377
cis-$[Co(en)_2(H_2O)_2](ClO_4)_3$	490	492
	ca 355 sh	359

[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) $\{[(Co(en)_2(H_2O)OPO_3]_2Mo_5O_{15}\}\cdot 8H_2O$, and

(b) $Na_6[P_2Mo_5O_{23}]\cdot 13H_2O$

References

1. K.M. Barkigia, J.M. Rajković, M.T. Pope and C.O. Quicksall, J.Am.Chem.Soc., 97, 4146 (1975).
2. W. Kwak, M.T. Pope and T.F. Scully, ibid, 97, 5735 (1975).
3. J.K. Stalick and C.O. Quicksall, Inorg.Chem., 15, 0000(1976).
4. R. Strandberg, Acta Chem.Scand., 27, 1004 (1973).
5. S.F. Lincoln and D.R. Stranks, Austr.J.Chem., 21, 37(1968).
6. F.P. Dwyer, A.M. Sargeson and I.K. Reid, J.Am.Chem.Soc., 85 1215 (1963).
7. J. Bjerrum and S.E. Rasmussen, Acta Chem.Scand., 6, 1265 (1952).
8. C,H,N,P analyses by Galbraith Laboratories Inc., Knoxville, Tenn. Molybenum was determined spectrophotometrically (ref. 2).
9. D.S. McClure and P.J. Stephens, Coordination Chemistry, A.E. Martell, ed. Van Nostrand-Reinhold, New York, 1971.
10. H. Yamatera, Bull.Chem.Soc.Japan, 31, 95 (1958).
11. C.I. Lepadatu, Z.Phys.Chem.Neue Folge, 60, 205 (1968).

Infrared Spectra of

(a), $[Co_2(en)_4(H_2O)_2(PO_4)_2(MoO_3)_5]8H_2O$

(b), $Na_6[P_2Mo_5O_{23}]13H_2O$

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
Department of Chemistry
Georgetown University
Washington, D.C. 20057

2a. REPORT SECURITY CLASSIFICATION
unclassified

2b. GROUP

3. REPORT TITLE
(6) Pentamolybdobis(cis-phosphatobisethylenediamineaquocobalt(III)).
A 'Neutral' Heteropoly Complex.

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
(9) Technical Report

5. AUTHOR(S) (First name, middle initial, last name)
(10) Wonsuk Kwak and Michael T. Pope

6. REPORT DATE
(11) November 1976

7a. TOTAL NO. OF PAGES
7 (12) 7p.

7b. NO. OF REFS
11

8a. CONTRACT OR GRANT NO.
(15) N00014-75-C-0945

b. PROJECT NO.

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
Technical Report No.5
(14) TR-5

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT
Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Chemistry Branch
Office of Naval Research
Arlington, Va. 22217

13. ABSTRACT
The synthesis, optical and infrared spectra of the title compound, $\{[Co(en)_2(H_2O)OPO_3]_2Mo_5O_{15}\}$ are described. The complex is an electrically neutral zwitterion.

401 215

DD FORM 1 NOV 65 1473

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Heteropoly complex						
Organic derivative						
Neutral zwitterion						
Cobalt coordination complex						