THESIS

ON

SPECTROPHOTOMETRIC STUDY OF THE MOLYBDENUM BLUE FORMED BY THE REDUCTION OF PHOSPHOMOLYBDATE

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By

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N O T E

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GENERAL INTRODUCTION

CHAPTER I

INTRODUCTION

An important and characteristic feature of the chemistry of molybdenum and tungsten is the formation of a large number of polymolybdate (VI) and polytungstate (VI) acids and their salts in addition to the simple molybdates (VI) and tungstates (VI). Although some analogies exist between these polymolybdates and polytungstates and the poly acids or anions of elements such as silicon, phosphorus, boron... etc., yet they are of only a very general nature and hence of little help in developing detailed knowledge of the molybdenum and tungsten compounds. Indeed these compounds must be regarded as practically unique. Of the other transition elements only vanadium (v) shows somewhat similar behaviour. There are also some fragmentary data suggesting that niobium and tantalum have some ability to form poly acids, but very little is known about them.

The poly acids of molybdenum and tungsten are of two types :

a) The isopoly acids and their related anions, which contains only molybdenum or tungsten along with oxygen and hydrogen.

b) The heteropoly acids and anions which contain one or two atoms of another element in addition to molybdenum or tungsten, oxygen and hydrogen.

The isopoly acids are generally referred to merely as "polyacids". They can also be defind as compounds derived from a simple acid by the elimination of water between two or more molecules of the acid. The heteropoly acids on the other hand are formed by the introduction of radicals of a different acid in the molecule.

Heteropoly acids

Although ammonium phosphomolybdate and silicotungstates were described in the early literature, the first careful determination of the composition of a silicotungstate was not carried out until Marignace.(1) Klein(2) attempted to explain the structure of the paratungstic acid prepared by Laurent(3), but his ideas were met with little success after the discovery of many other more complex acids. Blomstrand(4) attempted to explain the structure of the poly acids by assuming a chain or ring configuration. However the hypotheses set forth by those and other early investigators were unsatisfactory. Copaux(5) attempted a classification of these complex acids based upon their isomorphism,

and concluded that the isopoly acids were quite similar in structure to the heteropoly acids.

Werner[6] applied his ideas on coordination compounds to the nature of silicotungstic acid and its salts. He assumed that the central group is an SiO_4^{4-} ion surrounded by four $(RW_2O_6)^*$ groups (R = a unipositive ion) which are linked to the central group by primary valencies. In addition, he postulated that two R_2 W_2 O_7 groups are linked by secondary valencies to this same central group, and felt that this would result in an octahedral configuration for the poly acids. Although this structure accounted for the behaviour of some of the limiting poly acids containing a tetravalent central ion, difficulties were encountered with those acids having a central ion with a valence other than four, and with those containing metal anhydride aggregations which are not multiples of six.

Miolati[7] and Rosenheim[8] extended Werner's ideas to include those poly acids which do not belong to a limiting acid series and attempted to explain the large number of replaceable hydrogens in many of these acids. Rosenheim and Miolati postulated an entire series of hypothetical parent oxyacids showing six-coordination

and having oxygen atoms at the corners of the octahedral containing the central metal atoms. Each oxygen was then considered to be coordinated to a metal anhydride molecule.

The structures of the unsaturated heteropoly acids (i.e., those which do not belong to the six or twelve limiting acid series) can be explained, according to Rosenheim, by assuming that not all of the six oxygens are displaced by acid anion groups.

Keggin[9] suggested that the structure of a 12-acid anion could be represented as a tetrahedron round the central metal atom surrounded by twelve MoO_3 or WO_3 octahedra, every one of which shares an oxygen with its neighbours. The four resulting Mo_3O_{13} groups share corners to give $\left[XMo_{12}O_{40}\right]^{8-n}$ ions, where n = charge number of x. The large open spaces in this type of anion allow the inclusion of water molecules.

Anderson[9] proposed an analogous scheme for the 6-acids. Six MoO_6 octahedra are joined by sharing edges to form a hexagonal annulus, in the center of which is an octahedral arrangement of bonds round the heteroatom. The central atoms of the known 6-acids all show octahedral stereochemistry.

The heteropoly acids are stable only in acid or neutral solutions. In alkaline solutions they undergo hydrolysis. In this it is possible under certain circumstances to note various intermediate stages which contain less than twelve WO_3 or MoO_3 per silicon or phosphorous atom. A stepwise degradation of this sort can be followed with phosphotungstic acid which leads to salts of acids with $P:WO_3$ ratios of 1:11, 2:21 and 2:17[10].

The complex molybdic compounds are in general less stable than the corresponding tungstic complexes. Decomposition into molybdate starts above pH 4.2 and is completed at pH 5.4[11]. Potentiometric experiments show that colourless phospho-1-molybdate and phospho-2.5-molybdate exist; the former is stable only in the pH range 4 to 6. Phospho-12-molybdate is converted to yellow phospho-11-molybdate in the pH range 2.5 to 5 and to the 1:2.5 at higher pH values. In more basic solutions conversion to MoO_4^{-2} and HPO_4^{-2} occurs[12].

It was found that at 20°C and at pH ranges 0.7-1.1, 1.2 - 1.5 and 1.6 - 1.8, the molar ratios of P : Mo in the polyacids were 1:24, 1:20 and 1:16 respectively.

At pH > 2 there exists a known complex with the molar ratio 1:12[13]. The yellow colour of molybdophosphate gradually decreases on standing and tends to approach a constant intensity[14].

It was also found that the stability of heteropoly anion decreases by :

a) Decrease of valence of the central ion.

b) Increase in its atomic weight.

c) Replacement of W by Mo[12].

Analytical uses of the reduced molybdophosphoric acid :

Colorimetric determination of phosphate :

The molybdenum blue reaction has been used for routine colorimetric determination of phosphorus, molybdenum, silicon and other constituents in a wide variety of materials[15]. The reduction of the yellow heteropoly molybdophosphoric acid $H_3P(Mo_3O_{16})_4$ to give the familiar heteropoly blue complex must be conducted under controlled conditions. An excess of molybdate reagent must be present in order to shift the equilibrium to the heteropoly acid side. It is necessary to avoid as far as possible reduction of the excess molybdate added. The heteropoly acid can be separated from essentially the excess of molybdate reagent by extraction[16].

Reduction of molybdophosphates :

The phosphomolybdic acid is very sensitive to reduction remarkably so in comparison with the corresponding simple acid[17]. The complex acids yield, on moderate reduction, highly coloured compounds which resemble the corresponding unreduced compounds in all respects except that of colour.

Phospho-24-molybdic acid and phospho-18-molybdic acid react with a variety of mild reducing agents in acid as well as in alkaline solutions. The sensitivity of reduction runs parallel with the colour of the compound, and this parallelism holds also for the mixed complex acids.

Just as molybdenum and tungsten trioxides yield on reduction a number of lower oxides, the complex acids give rise to new complexes containing different lower oxides. The exact compound forms depend on the nature and the amount of the reducing agent and on whether the solution is acid or alkaline. The phospho-24-molybdic acid gives a lavander-blue colour with excess of the reducing agent and a greenish-blue compound when the complex acid is in excess.

Different reducing agents were used for the reduction of molybdophosphate. These are : $Sn\ cl_2$,[18-24], ascorbic acid[25-30], ferrous sulphate[31,32], benzidine[33], gallic acid[34], hydroiodic acid[17], hydroquinone[35], hydrazine sulphate[28], 1,2,4 aminonaphtholsulfonic acid[36], sodium thiosulphate[37], and compounds possessing conjugated double bond systems[38]. Conde and Pratt[39] found that reduction of molybdophosphate could be attained by using a solution containing Mo^{+6} and Mo^{+5} in a molar ratio of 3:2 and in a mixture of 10 N sulphuric acid and 3 N hydrochloric acid. This solution is stable for more than six months.

The nature of the reducing agent and the reaction condition affect the valence of Mo in the heteropoly blue[40]. With stannous chloride, the maximum absorbance occurs at Mo : Sn 4:1, and the mean valence of the Mo in the complex is 5.5. With thiourea, the maximum absorbance occurs at Mo : thiourea 1:1, and the mean valency is 5. After aging the maximum absorbance occurs at 3:1, where the Mo valence is 5.67, and after further aging the maximum is at 3:2 with a mean Mo valence of 5.3.