

Heteropoly Compounds in Chemical Analysis¹

E. R. WRIGHT² with M. G. MELLON, Purdue University

The word "heteropoly" was coined by Rosenheim (36) to designate the class of compounds of which ammonium molybdiphosphate is the most familiar member. Many of them have very useful analytical properties (2, 10), ranging in application from the separation of phosphorus as the insoluble ammonium molybdiphosphate to the action of molybdiphosphoric acid as an oxidation-reduction indicator. These applications have resulted in an extensive literature, as evidence of which the authors have compiled a bibliography of nearly 1,000 references dealing in some way with analytical uses. In spite of their individual applications, however, heteropoly compounds as a class have received little attention in this country. It is the purpose of the present paper to review briefly the status of heteropoly compounds and to indicate the properties and applications which are of analytical interest.

Extent of the Field. As long ago as 1826 Berzelius described the compound now known as ammonium molybdiphosphate (4), although its use in analysis was not suggested until some years later (41). Subsequent investigation disclosed other members of a class of fairly well defined complex compounds characterized by the coordination in the molecule of certain acid anhydride molecules about a central atom or group. As central atom were found most commonly phosphorus, silicon, arsenic, and boron, although titanium, manganese, zirconium, thorium, tin, lead, germanium, iodine, hafnium, and others have been listed as central atoms (10, 14, 35). Coordinating groups are most often oxides of molybdenum, tungsten, and vanadium. In summarizing the general field to 1920 Rosenheim listed 36 elements (35) in addition to oxygen which may take part in forming heteropoly anions.

The extent of the field is not limited by the number of elements which may combine to form complex anions, since variations may occur also in two other respects: (a) by variation in the ratio of coordinated groups to central atoms, and (b) by the state of oxidation of the constituent atoms. In addition, mixed crystals may be formed containing two or more coordinating groups, resulting in the formation of such compounds as the molybditungstophosphates. Two compounds closely related may also differ through isomerism or different crystal structure.

Perhaps the most important of these variations in heteropoly compounds composed of the same elements is the ratio of coordinated atoms (W, Mo, V) to central atoms (P, Si, As). This ratio is never more than 12, although it may be less, a series of well-defined 9- and 6-compounds being known. Other ratios have been reported, however, and the number

¹ Abstracted from a thesis presented by E. R. Wright in 1934 to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Master of Science.

² Present address, Dow Chemical Company, Freeport, Texas.

of postulated compounds of various ratios less than 12 is very large. Wu (45) prefers to speak of the ratio of coordinated atoms or oxide groups to central oxide groups, such as P_2O_5 ; consequently, the nomenclature 24- and 18-acids, often found in biochemical literature, corresponds to that of the older 12- and 9-acids.

It should be mentioned that many of the compounds reported may not be true chemical individuals but mixtures of two or more compounds. Furthermore, the analytical results reported have not always been trustworthy, especially in distinguishing between water of crystallization and water of "constitution". Fortunately for analysts, the 12- and 9-series are the best defined as well as the most important analytically.

The names used now are intended to show that these compounds are derivatives of the central atom acid. This conforms to inorganic nomenclature for such compounds as fluoroborates and chloroplatinates.

Structure of the Compounds. For many years it was customary to report the formula of such compounds in the form of the presumed constituent oxides, such as $3(NH_4)_2O \cdot P_2O_5 \cdot 24MoO_3 \cdot xH_2O$, for ammonium molybdiphosphate. Since this formulation reveals so little about the properties of the compound, and since more satisfactory proposals have been made, it seems time for analysts to abandon the old ideas. The present theories are not yet settled (28), but they seem sufficiently useful in interpreting the analytical behavior of various systems to warrant adoption until something better is available. A knowledge of the structure is of direct interest to the analyst, of course, only insofar as he may understand the necessity and method of controlling variable factors which may affect the results obtained.

Miolati (27) was probably the first to do much toward systematizing this field. His formulation, based upon Werner's coordination theory, was extended by Rosenheim (35), who assumed hypothetical parent aquo-acids, $H_{12-n}(XO_6)$, in which X is the central atom, of valence n , and the oxygen atoms may be replaced by acid radicles, such as MoO_4 or Mo_2O_7 . Complete substitution of Mo_2O_7 groups, with phosphorus as the central atom, would give the formula $H_7[P(Mo_2O_7)_6]$ which becomes $(NH_4)_3H_4[P(Mo_2O_7)_6]$ for ammonium molybdiphosphate. This formulation for the 12-molybdenum compounds seemed satisfactory for interpreting the high basicity, formation in acidic solution, and ready solubility in alkalis. Table I shows other examples of Rosenheim formulations, the last two examples being 6-acids.

TABLE I.—Heteropoly Compounds

Central Atom	Valence	Parent Acid	Heteropoly Acid
B	3	$H_6(BO_6)$	$H_6[B(Mo_2O_7)_6]$
Si	4	$H_8(SiO_6)$	$H_8[Si(Mo_2O_7)_6]$
P	5	$H_7(PO_6)$	$H_7[P(Mo_2O_7)_6]$
Te	6	$H_6(TeO_6)$	$H_6[Te(MoO_4)_6]$
I	7	$H_5(IO_6)$	$H_5[I(MoO_4)_6]$

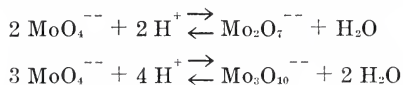
Ratios of coordinated to central atoms of less than 12 are explained by (a) assuming some unsubstituted oxygen atoms, resulting in a formula-

tion such as $H_7[PO(Mo_2O_7)_3]$, called an unsaturated compound, and (b) by the use of MoO_4 or similar groups instead of Mo_2O_7 units, resulting in a formulation such as $H_3[I(MoO_4)_6]$, called a saturated compound.

The importance of hydrogen ion concentration in the formation and stability of the compounds led Jander and his students (18) and Brintzinger (6) to study the aggregation and degradation processes involved in the formation and decomposition of the compounds. It is known, for example, that there is an optimum acidity for the successful formation of precipitates of heteropoly compounds, or of certain colored complexes of this class. This seems to indicate that more or less definite complexes persist in certain ranges of acidity. Thus, all of them are decomposed by strong alkalis, and excess strong acid seems to hinder the formation of the complexes. Middleton (26) summarized the general contributions of Rosenheim and of Jander. The variable states of aggregation postulated by Jander are a little difficult to harmonize with the definiteness of the formulations of Rosenheim or of those mentioned later (10).

Following theoretical work by Pfeiffer (32) and by Pauling (30), a recent series of X-ray studies on crystalline salts and acids by Keggin (19, 20), Illingworth and Keggin (16), Signer and Gross (38), Santos (37), Bradley and Illingworth (5), and Kraus (21) has thrown much light on the structure of the 12-compounds. Many of them have been shown to contain anions such as $[P(W_3O_{10})_4]^{--}$ and to have similar crystal structures. Attempts to prepare compounds with elements other than molybdenum or tungsten in the outer shell failed. No X-ray study of the 9- or 6-series has been made to date (1). This work has aroused considerable discussion (1, 9, 22), and it may provide the final clue to the true nature of the compounds.

Reviews of the general structural problem have been made recently by Elstner (9) and by Riesenfeld and Tobiank (34). As stated in these two papers, Rosenheim's ideas still have merit. Thus, salts of his postulated basicity, such as $(NH_4)_7[P(V_2O_6)_6]$, have been prepared. His formula for ammonium molybdiphosphate, $(NH_4)_3H_4[P(Mo_2O_7)_6]$, becomes Keggin's formula, $(NH_4)_3[P(Mo_3O_{10})_4]$, on the loss of two molecules of water. As Riesenfeld and Tobiank suggested (34), the two equilibria



indicate that the prevailing hydrogen ion concentration may determine whether the compound formed has the formula $H_3[P(Mo_3O_{10})_4]$ or $H_7[P(Mo_2O_7)_6]$. In all such compounds water of crystallization may be expected in the interstices between the anions.

Properties of Analytical Value. The properties of the heteropoly compounds which make them analytically useful are (a) insolubility of certain salts, such as potassium, cesium, rubidium, and many organic bases, (b) instability of these precipitates toward strong bases, (c) ease of reduction, (d) color of the soluble 12- and 9-series and their reduced compounds, and (e) solubility in organic solvents.

Applications. Many applications of the heteropoly compounds have been made by analysts. Complete references to all the individual uses are too numerous to be included, although a few typical or general references are cited below. The outline of kinds of applications follows the classification developed by the senior author for general quantitative methods (24).

1. **Separations.** The formation of heteropoly compounds finds considerable use as a means of accomplishing a variety of separations, usually to get the desired constituent itself in a condition susceptible to measurement. In the complex anion the elements molybdenum, tungsten and vanadium will be found in the coordinated groups, while other elements capable of such separation will form the central atom.

a. **Precipitation.** Separation by precipitation rests upon the insolubility of many heteropoly complexes. The precipitation of phosphorus as ammonium molybdiphosphate is well known (15). The separation of potassium similarly has been proposed (25). The precipitation of arsenic as molybdiarsenate is quantitative under proper conditions, while in steel analysis quinquivalent vanadium may be separated as a mixed molybdivanadophosphate. Cesium and rubidium, by virtue of the insolubility of their tungstisilicates and molybdiphosphates, may be separated from the other alkalis (29). Silver, thallous, and mercuric salts are also insoluble (17). Furman and State (13) proposed the precipitation of small amounts of phosphorus as $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{H}[\text{P}(\text{Mo}_3\text{O}_{10})_4]\cdot\text{H}_2\text{O}$.³ Silicon or tungsten may be precipitated as a heteropoly salt of an organic base such as nicotine, this being an example of the formation of quantitative precipitates by the interaction of heteropoly compounds with many organic bases. Methods have been based upon this fact for the determination of alkaloids, nicotine, pyridine, and other basic organic substances, many of which are precipitated as tungstisilicates. Proteins in biological substances are often precipitated with various heteropoly acids, among which have been recommended tungstiphosphoric, molybdiphosphoric, and tungstisilicic acids.

After a precipitation has been made, the precipitate may be treated in a number of different ways provided that the separation has been performed in the proper manner. Several procedures are given below.

b. **Extraction.** Extraction is a much less generally useful method of separation than precipitation. In common with many other complexes, various heteropoly acids are soluble in ether and other selected organic solvents. This property is employed not only in the preparation of the complexes, but it is the basis of the Copaux method of determining phosphorus (7). The procedure consists in shaking ether and ammonium molybdate together with the unknown. The molybdiphosphoric acid extracted in the ethereal layer may then be measured suitably, one method being by colorimetric comparison (33).

2. **Measurement.** Several different chemical characteristics of heteropoly compounds form the basis of the various specific property and

³ More recently Horan, 1939. J. Am. Chem. Soc., **61**, 2022—claims that the formula should be $\text{Co}(\text{NH}_3)_6[\text{P}(\text{Mo}_3\text{O}_{10})_4] \cdot 3\text{H}_2\text{O}$.

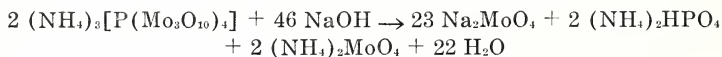
systemic property methods of measurement now being used. The principles of these methods are outlined below, together with appropriate examples of their application.

a. **Gravimetric Methods.** In these methods the separated precipitate is (a) dried and weighed directly, the percentage of desired constituent usually being calculated by means of an empirical factor, or (b) ignited to oxides. There has been much disagreement over the merits of direct weighing. Presumably the discordant results may be attributed to indefiniteness of composition of the heteropoly compound because of failure to achieve the expected ratio of the component groups, due, perhaps, to poor control of the conditions of precipitation with the consequent production of an unsaturated compound. Also such compounds, many of which are stated to be heavily hydrated, may not dry readily to a definite degree of hydration. Still another possibility may be found in ammonium molybdiphosphate, since, according to some writers, each mole holds two moles of nitric acid which are removed with difficulty by washing.

b. **Titrimetric Methods.** The uncertainties associated with the composition of the residues weighed in gravimetric methods has led to rather general use of titrimetric procedures based upon neutralization or oxidation-reduction reactions.

a'. **Neutralimetry.** As would be expected from the fact that heteropoly compounds are composed usually of two weak acids, the complexes are stable only in acidic solution. The stability toward bases differs for individual compounds and decreases in the following order: silicates, phosphates, arsenates (containing a given coordinated group), and tungstates, molybdates, and vanadates (containing a given central atom) (26). Tungstiphosphates, for example, are formed at a higher pH than molybdiphosphates. In a mixture of phosphoric acid and sodium molybdate no proportions of the two constituents will give anything but the 6-compound. As hydrochloric acid is added, first unsaturated members of the 12-series appear and finally the saturated compound. In the case of tungstiphosphates a mixture of one mole of sodium tungstate with four moles of phosphoric acid produces 9-tungstiphosphoric acid, which addition of hydrochloric acid converts to the saturated 12-tungstiphosphoric acid (45).

Upon the addition of a base, heteropoly compounds break down according to the following type reaction:



Upon this reaction is based the Pemberton method for phosphorus which is widely employed in steel analysis. Usually an excess of standard base is added and back titrated to a definite pH. A similar method is used in the case of tungstisilicates for the determination of alkalooids or nicotine. In general, any element or compound can be determined in this way if a suitable heteropoly compound can be isolated for a neutralimetric titration.

b'. **Redoximetry.** As oxidizing agents heteropoly compounds are much stronger than their individual constituents, the molybdi- and tungsticompounds behaving somewhat as expected from their periodic relationship to the chromates. Wu (45) reported that their sensitivity to reduction increases in the following order: 12-tungstiphosphate, 9-tungstiphosphate (two isomeric forms), 12-molybdiphosphate, and 9-molybdiphosphate. Most sensitive to reduction is a mixed, unsaturated acid corresponding to a mixture of 9-molybdiphosphoric and 9-tungstiphosphoric acids. That this acid is not a mechanical mixture is shown by its increased sensitivity to reduction and by differences in other chemical properties. It is the "phenol reagent" of Folin and Denis. Benedict has used 9-tungstiarsenic acid (3) because of its similar sensitivity to reduction.

When a heteropoly compound is reduced by a mild reducing agent, the product is still a complex form of the same general type, as is evident by its precipitation with ammonia, alkaloids, and other chemical agents. Such an acid is produced by the loss of an atom or two of oxygen from each molecule. Deniges (8) gives the unsatisfying formula $(\text{MoO}_3)_4 \cdot \text{MoO}_2 \cdot \text{H}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ for molybdenum blue. Apparently the term molybdenum blue is used rather loosely to include all blue reduction products of heteropoly molybdenum complexes as well as the blue oxide itself, which supposedly has the formula $(\text{MoO}_2)_2 \cdot \text{MoO}_3$ (23).

Oxidation-reduction reactions have been proposed for the determination of molybdenum, arsenic, phosphorus, and a variety of reducing agents. The determination is carried out by precipitating ammonium molybdiphosphate or molybdiarsenate which is then dissolved and reduced by metallic aluminum, copper, zinc, ferrous iron, stannous tin, or various amalgams (40). Measurements of the reduced heteropoly compound is then made by titration with a standard oxidant. The name molybdomanganimetry has been applied to a form of this process in which potassium permanganate is the titrant (12).

Molybdiphosphoric acid has been proposed as an oxidation-reduction indicator for the titration of hydrazine salts with potassium bromate solution (43).

c. **Volumetric Methods.** With materials producing only a very small amount of the heteropoly precipitate, as in the separation of phosphorus in the form of ammonium molybdiphosphate in steel analysis, attempts have been made (11, 15) to measure the volume of the precipitate after centrifuging it into a graduated capillary tube. Even if the tube is calibrated with known amounts of the desired constituent, the nature of these compounds is such that a rigid control of conditions is likely to be necessary to obtain the specific volumes requisite for reproducible results.

d. **Colorimetric Methods.** Coordinated compounds, such as nickel dimethylglyoxime, often have a color entirely different from that of any of the components. Likewise, the formation of color in the soluble heteropoly compounds may be attributed to a complex structure. Thus with silicon there is formed yellow molybdisilicic acid, $\text{H}_4[\text{Si}(\text{Mo}_2\text{O}_7)_2]$, although none of the reactants alone shows any hue.

Certain colorimetric methods of analysis have been based upon a direct measurement of the color of the heteropoly complex produced. In the procedure for silica, referred to above, the central atom is the desired constituent (42); but in the tungstivanadophosphate method for vanadium (44) the desired constituent presumably constitutes part of the coordinated shell of the complex ion.

On reduction a number of heteropoly compounds give intensely colored reduction products, most of which are blue. This color reaction makes possible the determination of many reducing agents such as uric acid, polyphenols, proteins, adrenaline, cysteine, cystein, ascorbic acid, and reducing sugars (31). Procedures have also been proposed for inorganic reducing agents such as stannous tin, cobalt, mercury, and antimony (39). Indirect determination of many inorganic substances is possible by precipitation of the 8-hydroxyquinolate, filtration, dissolution, and determination of the 8-hydroxyquinolate by reaction with a suitable heteropoly reagent. Phosphorus, arsenic, and silicon are also determined by the blue color of the reduced heteropoly compound. Numerous reducing agents have been studied for this purpose as well as that of determining phosphorus in the presence of arsenic (39).

e. **Nephelometric Methods.** Certain nephelometric determinations are based upon the insolubility of heteropoly compounds (46). Phosphorus, arsenic, alkaloids, and nicotine are among the constituents determined in this way.

f. **Other Methods.** After separation and dissolution of the precipitated heteropoly complex, it is possible, of course, to make some other type of measurement upon the system in order to determine the desired constituent.

Summary

A brief review of the significance of heteropoly compounds in analytical chemistry is presented, including the formulations advanced by various investigators, the properties of analytical utility, and the types of applications that have been made in practical procedures.

Bibliography.

1. Anderson, 1937. *Nature*, **140**:850.
2. Bassett, 1925. *Theory of quantitative analysis*, 229-238, Routledge and Sons.
3. Benedict and Franke, 1922. *Journ. Biol. Chem.*, **52**:387.
4. Berzelius, 1826. *Pogg. Ann.*, **6**:369.
5. Bradley and Illingworth, 1936. *Proc. Roy. Soc.*, **A157**:113.
6. Brintzinger and Ratanarat, 1935. *Z. anorg. allgem. Chem.*, **224**:97.
7. Copaux, 1921. *Compt. rend.*, **173**:656.
8. Deniges, 1927. *Bull. soc. pharm. Bordeaux*, **65**:107.
9. Elstner, 1935. *Angew. Chem.*, **48**:343.
10. Emeleus and Anderson, 1938. *Modern aspects of inorganic chemistry*, 180-195, Van Nostrand Co.
11. Fick, M. S., 1938. Thesis, Purdue University.
12. Fontes and Thivolle, Sept. 1925. *Chimie & Industrie*, Special No., 93.
13. Furman and State, 1936. *Ind. Eng. Chem. Anal. Ed.*, **8**:420.
14. Grosseup, 1930. *Journ. Am. Chem. Soc.*, **52**:5154.

15. Hillebrand and Lundell, 1929. Applied inorganic analysis, Wiley and Sons.
16. Illingworth and Keggin, 1935. Journ. Chem. Soc., 575.
17. Illingworth and Santos, 1934. Nature, **134**:971.
18. Jander and Banthien, 1936. Z. anorg. allgem. Chem., **229**:129; See also, 1934, Koll. Beihefte, **41**:297.
19. Keggin, 1933. Nature, **131**:908; **132**:351.
20. Keggin, 1934. Proc. Roy. Soc., **A144**:75.
21. Kraus, 1936. Z. Krist., **94**:257; 1937, **96**:330.
22. Kraus, 1937. Naturw., **25**:250.
23. Latimer and Hildebrand, 1935. Reference book of inorganic chemistry, Macmillan Co.
24. Mellon, 1937. Methods of quantitative chemical analysis, Macmillan Co.
25. Meyer, 1907. Chem. Ztg., **31**:158.
26. Middleton, 1933. Journ. Chem. Ed., **10**:726.
27. Miolati and Pizzighelli, 1908. J. prakt. Chem., **77**:417.
28. Morgan and Burstall, 1937. Inorganic chemistry, 185-186, 300-313, Chemical Publishing Co.
29. O'Leary and Papish, 1934. Ind. Eng. Chem. Anal. Ed., **6**:107.
30. Pauling, 1929. Journ. Am. Chem. Soc., **51**:2868.
31. Peters and Van Slyke, 1932. Quantitative clinical chemistry, Williams and Wilkins Co.
32. Pfeiffer, 1918. Z. anorg. allgem. Chem., **105**:26.
33. Raskin, 1936. Zavodskaya Lab., **5**:267.
34. Riesenfeld and Tobiank, 1935. Z. anorg. allgem. Chem., **221**:287.
35. Rosenheim, in Abegg and Auerbach, 1921. Handbuch der anorganischen Chemie, Band IV, 1 Abt., 2 Halfte, 977-1065.
36. Rosenheim and Kahn, 1911. Z. anorg. Chem., **69**:247.
37. Santos, 1935. Proc. Roy. Soc., **A150**:309.
38. Signer and Gross, 1934. Helv. Chim. Acta, **17**:1076.
39. Snell and Snell, 1936-7. Colorimetric methods of analysis, Van Nostrand Co.
40. Someya, 1928. Z. anorg. allgem. Chem., **175**:347.
41. Svedberg and Struve, 1848. J. prakt. Chem., **44**:257.
42. Swank and Mellon, 1934. Ind. Eng. Chem. Anal. Ed., **6**:348.
43. Szebelledy, 1937. Mikrochim. Acta, **2**:57.
44. Wright and Mellon, 1937. Ind. Eng. Chem. Anal. Ed., **9**:251.
45. Wu, 1920. Journ. Biol. Chem., **43**:187.
46. Yoe, 1929. Photometric chemical analysis, Vol. II, Wiley and Sons.