HIGHER OXIDATION STATES OF SILVER

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CONTENTS

I. INTRODUCTION

It is known that silver can appear in three states of oxidation, I, II, and III. The scope of this review is to bring up to date the chemistry of states II and III. Too often this aspect of silver chemistry is superficially treated. With the exception of a few books (5, 100, 125, 127, 170), the whole subject seldom is covered. While the present review was in process of being completed, a monograph by Priyadaranjan Ray and Debabrata Sen (152) appeared. A previous review was published in 1944 (4).

The two higher oxidation states are discussed here separately except for the fluorinated compounds. Particular emphasis has been put in the chapter of AgO since this compound has been studied extensively.

The results of paramagnetic resonance experiments are given in accordance with the notation of the Reports of Progress in Physics (30). The crystallographic notation used throughout has been taken from the International Tables (83). When available, lists of spacings have been given for the purpose of identification. The bibliography covers available references up to December, 1960.

II. ARGENTIC OXIDE, AgO

1. Introduction

AgO is precipitated from the alkaline oxidation of aqueous solutions of silver(I) nonreducing salts. This finely divided, black, crystalline oxide was prepared a century ago (161, 187) but was believed to be a peroxide Ag–O–O–Ag. It was later observed that when dissolved in nitric acid AgO did not reduce lead dioxide, manganese dioxide nor potassium permanganate, nor did it give rise to hydrogen peroxide (10, 13).

Consequently, it was thought to be a silver(II) oxide until it was formulated as a silver(I)–silver(III) oxide (121) on the basis of its magnetic behavior and crystal structure.

AgO also was assumed to be obtained during the oxidation of acid and neutral solutions, but the so-formed products are in fact argentic oxysalts (119, 120). Since 1900, there has been a rising interest in such silver compounds as the oxides, oxysalts, and the silver(II) complexes. The oxide AgO has been used as an oxidizing agent in analytical chemistry (17, 105, 179) and is now commercially available (*e.g.*, Merck Bivasil). It is used in the so-called silver peroxide–zinc alkaline cells (82). During World War II it was used in gas masks for protection against carbon monoxide, based on the reduction which proceeds spontaneously

$$2AgO + CO \rightarrow Ag_2CO_3$$

and completely if AgO is activated with manganese (26).

2. Preparation

As mentioned above, alkaline oxidation of silver solutions yields AgO in the majority of cases. Soluble salts such as nitrate, perchlorate, sulfate, and fluoride yield AgO quantitatively when oxidized with alkaline solutions of sodium or potassium persulfate (43, 73), *i.e.*

$$\begin{aligned} 2Ag^+ + S_2O_8^{=} &\rightarrow 2Ag^{2+} + 2SO_4^{=} \\ 2Ag^{2+} + 4HO^- &\rightarrow 2AgO + 2H_2O \end{aligned}$$

The absence of hydroxyl ions therefore prevents the precipitation of AgO, and generally leads, in the presence of an excess of oxidizing agent, to the precipitation of an argentic oxysalt of the anion present in the solution.

Treatment of argentic oxysalts of the type of $Ag(Ag_3O_4)_2NO_3$ with boiling water also leads to pure AgO (85, 132, 185)

$$Ag(Ag_3O_4)_2NO_3 \rightarrow 6AgO + Ag^+ + NO_3^- + O_2$$

The persulfate oxidation, however, is preferred (73, 132).

A third chemical method for the preparation of AgO consists of treating with boiling water divalent silver complex compounds like the argentic tetrapyridine persulfate (146).

The oxide Ag_2O, suspended in alkaline solutions, is said to be converted into AgO, at least partially, by the action of potassium permanganate, leading to an equilibrium (9).

$$Ag_2O + 2KMnO_4 + 2NaOH \rightleftarrows 2AgO + K_2MnO_4 + Na_2MnO_4 + H_2O$$

The action of alkaline hypochlorites on suspensions of Ag_2O has been reported to yield AgO (55). Presumably, oxidation with ozone and fluorine should lead to the same product.

The electrolytic oxidation of silver anodes in alkaline media has been proved to give AgO at the last stage (67). Although some authors have claimed its production in acid media (94), the assertion that argentic oxysalts are produced under this condition seems more reliable (120). Sometimes the X-ray diffraction pattern of an oxysalt has been attributed to AgO or a higher oxidized oxide (162).

3. Chemical Properties and Thermodynamic Constants

Only recently, in view of its use in alkaline batteries, the stability, solubility, and general behavior of AgO in alkaline solutions have been thoroughly studied (49, 68). Its behavior in acid media, on the other hand, has long been well known. In the latter case, it dissolves at room temperature

$$AgO + 2H^+ \rightleftarrows Ag^{2+} + H_2O$$

This fact, together with the isomorphism with CuO, strongly supported the belief that AgO was a true Ag(II) oxide (118). A rise in temperature leads to evolution of oxygen and reduction of silver(II) to silver(I)

$$4Ag^{2+} + 2H_2O \xrightarrow{\Delta} 4Ag^+ + 4H^+ + O_2$$

The standard free energy for this reaction is (53)

$$\Delta F^0_{298} = -54 \text{ kcal.}$$

AgO is stable in water up to 100°; the reaction

$$4AgO + 2H_2O \rightarrow 4Ag^+ + 4OH^- + O_2$$

is not thermodynamically spontaneous (53).

AgO decomposes slightly in strongly alkaline solutions, a reaction which has been attributed to the presence of local cell actions with a potential of *ca.* 200 mv. (53)

$$\begin{aligned} 2OH^- &\rightarrow H_2O + \tfrac{1}{2}O_2 + 2e^-, E^0 = -0.4 \text{ v.} \\ 2AgO + H_2O + 2e^- &\rightarrow Ag_2O + 2OH^-, E^0 - 0.6 \text{ v.} \end{aligned}$$

The oxide AgO dissolves in dilute alkaline solutions without decomposition, and these reactions have been proposed

$$\begin{aligned} AgO + H_2O &\rightleftarrows Ag(OH)_2 \\ AgO + OH^- + H_2O &\rightleftarrows Ag(OH)_3^- \\ AgO + 2OH^- + H_2O &\rightleftarrows Ag(OH)_4^{=} \end{aligned}$$

Studying the variation of the solubility with pH, the species $Ag(OH)_2$ and $Ag(OH)_3^-$ are found to be the most important. A similar treatment of the data of Ag_2O solubility suggests for this case the species Ag(OH) and $Ag(OH)_2^-$ (53). Calling $K_2 = M_{Ag(OH)_3^-}/M_{OH^-}$, its value at 298°K. leads to a change of free energy for this reaction of 5.150 kcal. Using accepted free energy values for the formation of H_2O and OH^-, and 3.615 kcal./mole for AgO, standard free energies are obtained

$$\begin{aligned} \Delta F^0_{298} \text{ for } Ag(OH)_3^- &= -85.380 \text{ kcal./mole} \\ \Delta F^0_{298} \text{ for } Ag(OH)_2^- &= -57.065 \text{ kcal./mole} \end{aligned}$$

However, the existence of bivalent silver in these solutions is unlikely to occur. A search for paramagnetic resonance in these solutions (122) indicates that there are no paramagnetic ions. The formation of $Ag(OH)_2^-$ and $Ag(OH)_4^-$ in stoichiometric amounts then should be assumed. The coördinations 2 and 4 are suggested on the basis of the tendency of Ag(I) to fill the s- and one p-orbital and of Ag(III) to fill the d-, s-, and two p-orbitals by coördination. This latter fact explains the diamagnetism of all compounds of Ag(III). Consequently, the value for the free energy of $Ag(OH)_3^-$ might be an average, and considering the value for $Ag(OH)_2^-$, the value for $Ag(OH)_4^-$ would be (122)

$$\Delta F^0_{298} \text{ for } Ag(OH)_4^- = -113.7 \text{ kcal./mole}$$

These various thermodynamic constants are assigned by different authors to AgO

$$\begin{aligned} \Delta F^0_{298} &= 3.40\ (144),\ 3.615\ (53),\ 3.463\ (28) \text{ kcal./mole} \\ \Delta F^0_{273} &= 2.88\ (144) \text{ kcal./mole} \\ \Delta H^0 &= -2.73\ (144),\ -2.769\ (28) \text{ kcal./mole} \\ S^0 &= 13.81\ (28) \text{ kcal./(mole deg.)} \end{aligned}$$

The specific heat of AgO has been found to be 0.0869 ± 0.0005 cal./g. at room temperature (87).

The electrical conductivity of AgO at 17° has been found to be 0.07 mho/cm. in powdered samples pressed at 12,000 kg./cm.^{2}, increasing with increasing temperature in the range −40 to 20° (138). AgO exhibits, therefore, the property of semiconductivity. No attempts have been made to measure the Hall effect. Its semiconductivity can be attributed to an excess- or defect-oxygen lattice (121) as in ZnO. There are not, however, experimental results to support this or any other assumption. Recent results show that oxygen defect samples of AgO have paramagnetic centers that can be attributed to Ag(III) coördinated with only three oxygens with a hybridization sp^2 (122), but the correlation of this result with semiconductivity, if any, has not yet been established.

4. *Methods of Analysis*

The stoichiometric valence of silver in AgO suggests the over-all reduction from Ag(II) to Ag(I). Three methods ordinarily have been used for this purpose, namely: (a) oxidation of Fe(II) as Mohr's salt (109, 117, 146) or as ferrous sulfate solutions (56) in CO_2 atmosphere, (b) oxidation of oxalic acid to CO_2 (103, 109, 117), and (c) oxidation of I^- to free iodine (55, 90, 117). Besides these methods, reduction of AgO with H_2O_2 and excess-titration with $KMnO_4$ (18) and oxidation of $Na_2S_2O_3$ (57) also have been used, the latter having been abandoned because of the production of polythionates.

It should be pointed out that methods (a) and (b) may lead to defect-errors due to the evolution of oxygen. This is particularly true in the case of the oxalic acid oxidation, since the resulting CO_2 dilutes the evolving oxygen which retards further reaction with the solution. Method (c) is most advisable as it leads to free iodine when the solution is acidified and at no time is there any evolution of gas. Furthermore, the latter method dissolves silver which by dilution is precipitated as AgI. These facts support the assumption that the dissolution of AgO in concentrated KI solutions probably can be represented by the over-all reaction (117)

$$6AgO + 13I^- + 3H_2O \rightarrow IO_3^- + 6AgI_2^- + 6OH^-$$

and suggests for the analysis of AgO the conditions of standardization of thiosulfate solutions with KIO_3.

5. *Magnetic Behavior and Crystalline Structure*

Early in 1924 (104) AgO was reported to exhibit a characteristic X-ray diffraction pattern, shown in Fig. 1(d). This pattern was attributed by the author (118) to the monoclinic space group C2/c–C_{2h}^6 with four formula units per unit cell of a = 5.79 Å., b = 3.50 Å., c = 5.51 Å., and β = 107°30′ by analogy with its isomorphous copper compound CuO, Tenorite (182), arranging four silvers in (4d), and four oxygens in (4e) (83). Analogous results were reached later (67, 158) though with slightly different values for a, b, and c. Since the first results were obtained by trial and error and the latter derived from Ito's method (158), the latter presumably are more accurate, and equal to a = 5.852, b = 3.478, and c = 5.495 Å. Table I shows the spacings of AgO together with the indices of the reflecting planes. Sometimes the pattern of an oxysalt, Ag_7NO_{11} in most cases, is attributed to AgO (93, 94,

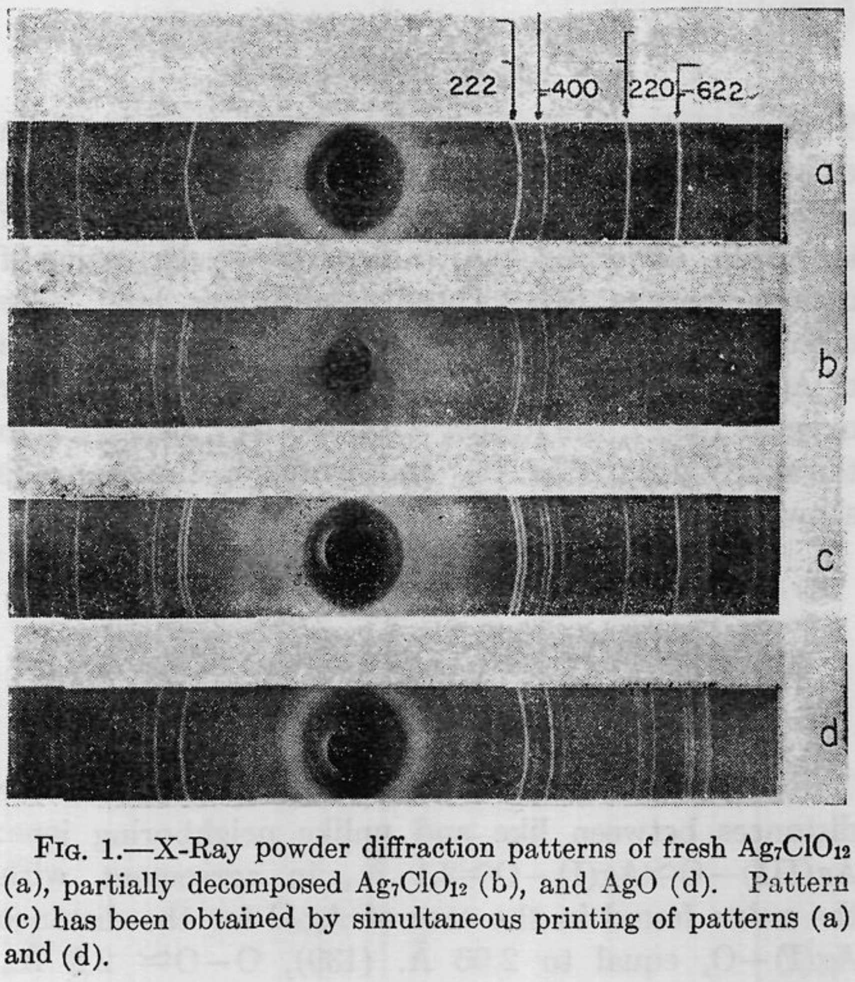


FIG. 1.—X-Ray powder diffraction patterns of fresh Ag_7ClO_{12} (a), partially decomposed Ag_7ClO_{12} (b), and AgO (d). Pattern (c) has been obtained by simultaneous printing of patterns (a) and (d).

TABLE 1
Spacings of AgO

d_{HKL} Å.	*HKL*	d_{HKL} Å.	*HKL*	d_{HKL} Å.	*HKL*
2.956	110	1.450	022	1.097	131
2.790	200	1.422	$40\bar{2}$	1.089	420
2.765	$11\bar{1}$	1.409	113	1.069	$22\bar{4}$
2.620	002	1.389	$31\bar{3}$	1.064	313
2.413	111	1.384	$22\bar{2}$	1.052	$51\bar{3}$
2.282	$20\bar{2}$	1.353	$20\bar{4}$	1.047	024
1.740	020	1.310	004	1.042	$11\bar{5}$
1.699	$31\bar{1}$	1.206	222	1.014	$31\bar{5}$
1.675	202	1.142	$40\bar{4}$	0.997	$33\bar{1}$
1.621	$11\bar{3}$	1.125	$13\bar{1}$	0.988	511
1.477	220	1.118	$51\bar{1}$	0.980	$13\bar{3}$
1.460	311	1.101	$42\bar{2}$	0.974	$60\bar{2}$

The values have been drawn from Scatturin, V., Bellon, P. L., and Zannetti, R., *J. Inorg. Nuclear Chem.*, *8*, 462 (1958).

173, 174). Since the oxysalts are obtained during the anodic oxidation of silver in acid solutions (120) which then yield AgO in alkaline media, some authors also have assumed the existence of either an oxide Ag_2O_3 (31, 67, 173) or an allotropic form of AgO (53). In the author's opinion, however, evidence has not been presented to support either assumption. The hypothesis of an allotropic AgO seems to be, in addition, very improbable. These interpretations will be discussed in greater detail in the chapter on the oxysalts.

The assignment of AgO to the space group $C2/c{-}C_{2h}^6$, however, implies the rather natural assumption of having Ag(II) in the lattice, as it was believed after the work of the Italian chemist Barbieri (10) which proved that AgO was not a peroxide. If it were so, AgO should be paramagnetic since Ag(II) is a $^2D_{5/2}$ ion. Its susceptibility, however, has been found to be (138)

$$\chi = -0.155 \times 10^{-6} \text{ emu./g.}$$

This anomaly was first explained (138) as arising from either metallic bonding or covalent bonding between silvers pairing the unpaired electrons, as in the case of the green, dimerized Cu(II) diamagnetic derivative of diaminobenzene (74). These assumptions later were discussed (121) proposing in consequence a lattice of Ag(I) and Ag(III), the latter coördinated with four oxygens (dsp^2), the former with two (sp), belonging to the space group $P2_1c{-}C_{2h}^5$ and arranging the atoms as shown

Ag(I)	$2d(\bar{1})$	$\frac{1}{2}\frac{1}{2}0$	$\frac{1}{2}0\frac{1}{2}$		
Ag(III)	$2a(\bar{1})$	000	$0\frac{1}{2}\frac{1}{2}$		
O	4e(I)	$\frac{1}{4}\frac{1}{4}\frac{1}{4}$	$\frac{1}{4}\frac{\bar{1}}{4}\frac{\bar{1}}{4}$	$\frac{\bar{1}}{4}\frac{1}{4}\frac{\bar{1}}{4}$	$\frac{\bar{1}}{4}\frac{\bar{1}}{4}\frac{1}{4}$

These arrangements, shown in Fig. 2, lead to these distances between like and unlike neighboring ions: Ag(III) – O ≃ Ag(I) – O ≃ 2.1 Å., in agreement with the value found in the case of Ag_2O for the distance Ag(I) – O, equal to 2.06 Å. (139), O – O ≃ 2.8 Å.,

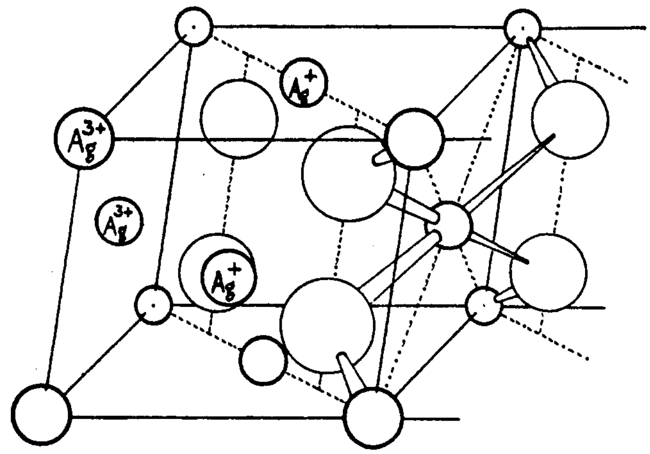


Fig. 2.—Lattice of AgO, showing dsp^2 coördination of one Ag(III) with four oxygens.

Ag(III) – Ag(III) = Ag(I) – Ag(I) = 3.28 Å., and Ag(I) – Ag(III) = 3.39 Å.

The existence of two kinds of silvers as well as their positions have been confirmed by neutron diffraction (159), providing at the same time accurate figures for the positions of oxygens, namely: xyz, $\bar{x}\bar{y}\bar{z}$, $x \;\; {}^1/_2 - y \;\; z + {}^1/_2$, $\bar{x} \;\; y - {}^1/_2 \;\; {}^1/_2 - z$, with $x = 0.295$, $y = 0.350$, and $z = 0.230$.

The deep blackness of AgO can be attributed to the Ag–O bonding, since the color deepens as the covalent character of the Ag–O bond increases (76).

6. The Argentic Oxide Electrode

Silver and its oxides recently have been incorporated into the field of storage batteries. A hypothetical oxide Ag_4O_3 was assumed to be produced during the anodic oxidation of metallic silver (155, 156) from the analysis of the discharge curves. However, the silver storage batteries were not successful until World War II, when interest in the subject again was aroused. The use of a membrane, first proposed in 1928 (155), again was introduced for overcoming the problem of short shelf life (1). At present, the silver–zinc–alkali system is available both as primary and secondary batteries and has been used as a power supply in some satellites (163). Both components, AgO and ZnO (54), have been studied. This system has a relatively high watt-hour per pound value.

Two oxides are involved in the battery transformations, namely, Ag_2O and AgO. Figure 3 shows a diagram of potential–pH for silver and its oxides. The compound Ag_2O_3, although still questionable, also is included in deference to the original diagrams (45, 47). Recent results show in fact some evidence of either an unstable higher oxide or at least additional oxygen fixed at the electrode in one way or another, after the transformation of Ag_2O into AgO has been completed (36). Line a represents the reduction of H^+ to H_2; line b the reduction of O_2 to H_2O. The areas of Ag^0,

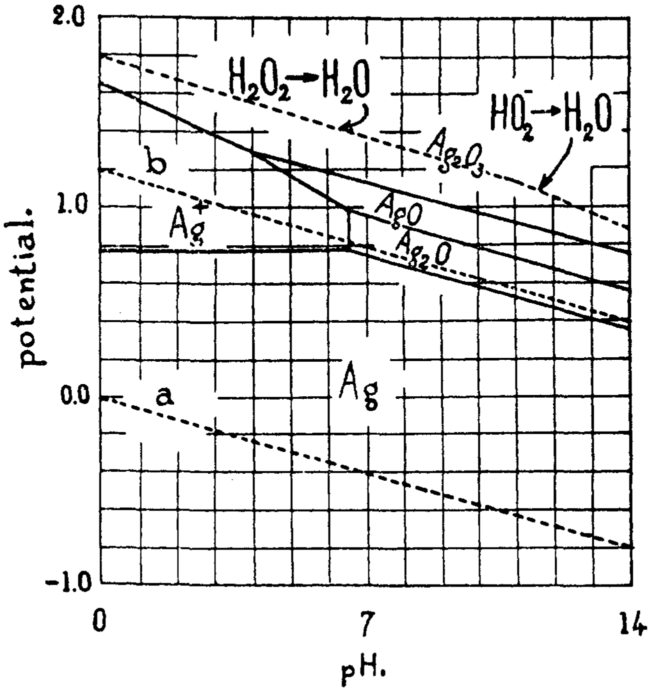


FIG. 3.—Potential-pH diagram of a silver anode (from T. P. Dirkse (47)).

Ag^+, Ag_2O, and AgO, bounded by full lines, are well defined in alkaline media, and fairly reliable in the slightly acid region. It should be noted in this respect that it has been claimed that during the anodic oxidation of Ag to AgO, Ag^0 always is present (46).

The anodic treatment of Ag or Ag_2O in alkaline solutions, as mentioned before, leads to AgO, and the polarization is 100–150 mv. Whether this process is reversible (107) or not (94) is still a matter of discussion. If the reaction is reversible, the equilibrium condition probably is represented by the equation

$$Ag_2O + 2OH^- \rightleftarrows 2AgO + H_2O + 2e^-$$

The variation of the electrode potential with hydroxyl concentration supports the above equation.

The layer of AgO formed in this process is thicker than that of Ag_2O (47, 48). Thus during the oxidation of Ag_2O to AgO, some additional silver is oxidized. At moderate current densities the efficiency of the electrolytic process has been reported to be 100% (51). An excess of charge, in the region of oxygen evolution, has been claimed to yield an oxide of composition approaching Ag_2O_3 (47). Detailed studies made with an a.c. square wave technique (36) lead to the same results, tentatively explained as absorbed oxygen. Further research on this line using X-ray diffraction techniques might well exclude at least one of the possibilities.

The electrolytic transition of Ag_2O to AgO in alkaline solutions recently has been a subject of thorough study, especially dealing with the peak that appears when the higher oxidation process just begins (point X in Fig. 4) (52). Three explanations have been advanced,

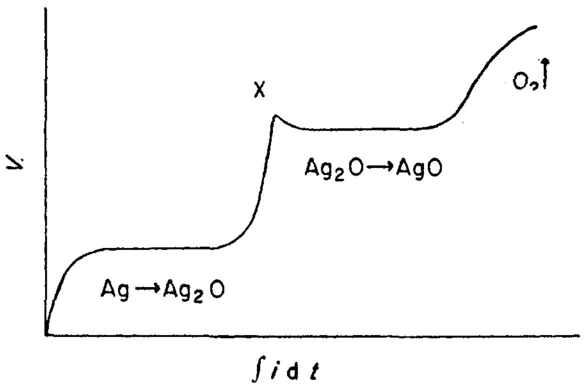


FIG. 4.—Potential as a function of charge of a silver electrode in alkaline solution.

namely: (i) the formation of an unstable oxide Ag_2O_3 according to

$$Ag_2O + 4OH^- \rightarrow Ag_2O_3 + 2H_2O + 4e^-$$

and subsequent decomposition to AgO (77) as

$$Ag_2O + Ag_2O_3 \rightarrow 4AgO$$

(ii) the transition from Ag_2O to AgO proceeds with difficulty, the peak representing the difficulty of forming AgO centers in the lattice of Ag_2O (94), and (iii) the large difference of resistivity between Ag_2O and AgO (24, 52) that leads to a definite over-increase in potential when the film of Ag_2O covers the surface of the anode completely.

The first and second assumptions do not account for the appearance of the same peak during the discharge, as is the case. Therefore, the third assumption should be accepted until a better explanation can be provided. It can be suspected that this effect may not be so trivial since AgO is a semiconductor.

The rather short cell life of these batteries has been attributed to the solubility of Ag_2O in the electrolyte (50).

The normal oxidation potentials reported in the literature are:

$Ag^+ \rightleftarrows Ag^{2+} + e^-$: $E^0 = -1.98$ v. (127), -1.914 ± 0.002 v. (142)

$Ag_2O + 2OH^- \rightleftarrows 2AgO + H_2O + 2e^-$: $E^0 = -0.57$ v. (107) -0.604 v. (28), -0.61 v. (77), -0.60 v. (88, 89)

The action of light on the products of the anodic oxidation of silver in the case of the cell

$$Ag(c),Ag_2O(c)/NaOH(1\ M)/AgO(c)Ag_2O(c),\ Pt$$

has been studied (183). Its electromotive force at 25° is 0.262 v., with a temperature coefficient of 2.20 $\times 10^{-4}$ v./deg. (28).

For more detailed information on the whole subject, the reader is referred to two review articles (47, 82).

III. ARGENTIC OXYSALTS

1. Introduction

There is evidence to support the existence of a series of compounds $Ag(Ag_3O_4)_2X$, where $X = NO_3$ (3, 33, 60, 61, 84, 131, 136), ClO_4 (171), or F (95, 180). A similar compound with $X = HSO_4$ (2, 26, 61, 79, 86, 133, 134) or Ag(II) $(Ag_3O_4)_2SO_4$ (26) also has been reported. The preparation of mixed crystals of the composition $Ag_xCd_{1-x}\,(Ag_3O_4)_2SO_4$ supports the latter formulation (26). $Ag(Ag_3O_4)_2NO_3 = Ag_7NO_{11}$, in particular, has received especial attention since it is fairly stable and very well crystallized. It is the first highly oxidized silver compound ever prepared (153) and was considered for almost a century to be a peroxide, Ag_2O_2. In 1896 it was realized that the primary product of the electrolysis of neutral solutions of $AgNO_3$ with platinum electrodes (153) was not a silver oxide but rather a complex compound with stoichiometric amounts of nitrate (176). Several previous attempts to determine its chemical composition led to different formulas (135, 177, 180). Similar experiments with perchloric, hydrofluoric, and sulfuric acids led to similar products, whose high electrical conductivity was pointed out early in 1852 (108) on the basis of the growth of the crystals at the anode. The similarity of these compounds erroneously led to the assumption of their being an oxide Ag_2O_3, on the basis of X-ray diffraction studies (31). Although there is no doubt that they exist, the question still stands as to whether or not they are daltonides.

2. Preparation and Chemical Properties

The electrolysis of aqueous solutions of $AgNO_3$ with a platinum anode leads to the formation of Ag_7NO_{11} as crystals with a metallic luster, while metallic silver is deposited at the cathode. At the same time, the electrolyte becomes acidic. The over-all reaction is

$$17Ag^+ + NO_3^- + 8H_2O = Ag_7NO_{11} + 10Ag^0 + 16H^+$$

High current densities yield prismatic needles; low density currents yield nearly perfect cubic octahedra (122). Neutralization of argentic acidic solutions also has been claimed to produce precipitation of the same compound, as also does equilibration of solid AgO with the corresponding acid (144). In a similar way the compound $Ag(Ag_3O_4)_2ClO_4 = Ag_7ClO_{12}$ also can be prepared. It is much less stable, however (171).

The spontaneous decomposition of these compounds may be represented by

$$Ag(Ag_3O_4)_2X \rightarrow AgX + 6AgO + O_2$$

This reaction is accelerated in boiling water. The so-produced AgO is fairly pure (185).

3. Crystal Structure and Magnetic Behavior of Ag_7NO_{11}

The compound Ag_7NO_{11} crystallizes in the cubic space group Fm3m (83, 194) with four Ag_7NO_{11} formulas per unit cell of $a = 9.87$ Å. (194). The positions of the atoms are

4 NO_3	(4a)	0	0	0
4 Ag(I)	(4b)	1/2	1/2	1/2
24 Ag(II, III)	(24d)	0	1/2	1/4
32 O	(32f)	x	x	x

with $x = {}^3/_8$, and the general translations

$$(0\,0\,0);\ (1/2\ 1/2\ 0);\ (1/2\ 0\ 1/2);\ (0\ 1/2\ 1/2)$$

Essentially, the structure may be described as a supporting Ag_3O_4 structure with a unit cell of edge one-half and the positions

$$\text{Ag:}\quad \tfrac{1}{2}\,\tfrac{1}{2}\,0 \qquad \tfrac{1}{2}\,0\,\tfrac{1}{2} \qquad 0\,\tfrac{1}{2}\,\tfrac{1}{2}$$

$$\text{O:}\quad \tfrac{1}{4}\,\tfrac{1}{4}\,\tfrac{1}{4} \qquad \tfrac{\bar{1}}{4}\,\tfrac{\bar{1}}{4}\,\tfrac{1}{4} \qquad \tfrac{\bar{1}}{4}\,\tfrac{1}{4}\,\tfrac{\bar{1}}{4} \qquad \tfrac{1}{4}\,\tfrac{\bar{1}}{4}\,\tfrac{\bar{1}}{4}$$

as shown in Fig. 5. The nitrates and silver(I) atoms occupy alternate corners. Each Ag_3O_4-silver is coordinated with four oxygens, in a planar square configuration.

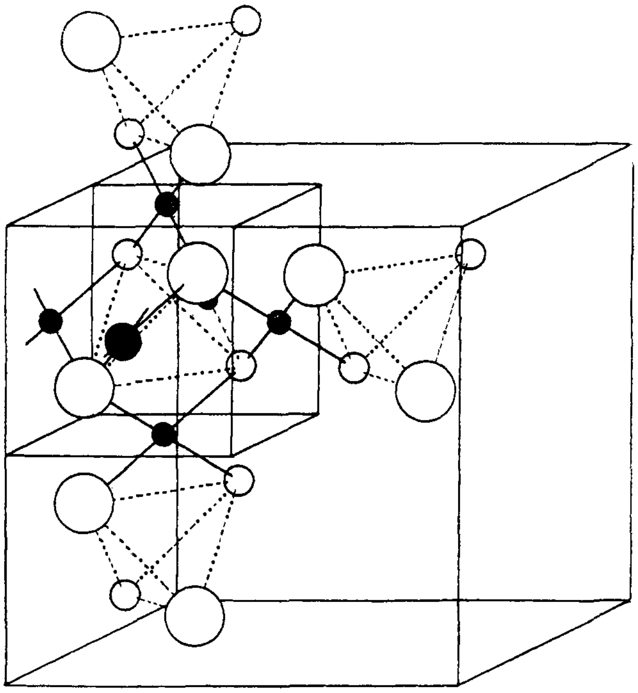


FIG. 5.—Supporting lattice of Ag_3O_4 in argentic oxysalts. Planar square coördination of silver (black circles) with oxygens (white circles) is shown.

Standard patterns and an accurate list of spacings have been prepared by the National Bureau of Standards (178). The value given for the unit cell edge is $a = 9.893$ Å. (178) in good agreement with $a = 9.890 \pm 0.006$ Å. (67). The list of spacings is: argentic oxynitrate (178): 5.73, 4.96, 3.498, 2.980, 2.856, 2.474, 2.270, 2.213, 2.019, 1.903, 1.749, 1.672, 1.649, 1.564, 1.508, 1.491, 1.428, 1.385, 1.372, 1.322, 1.288, 1.237, 1.209, 1.1425, 1.1348, 1.1062. The strongest reflections are: (222): 2.855 Å., (400): 2.474 Å., (220): 1.749 Å., (622): 1.491 Å., and (444): 1.428 A. Fig. (1a) shows the pattern of the isomorphous compound Ag_7ClO_{12}.

Although it has been suggested that the space group should rather be $F\bar{4}3m$ (27, 117, 119, 120) in view of the trigonal symmetry of the NO_3 group (and also ClO_4 and SO_4) there is little doubt, if any, that the actual space group is Fm3m. The interesting feature of such a structure—either Fm3m or $F\bar{4}3m$—is that all silvers of the Ag_3O_4 supporting structure are equivalent, *i.e.*, occupy positions belonging to the same set (24d) in the lattice. On the basis of the known valences of silver, I, II, and III, one might expect the entity Ag_3O_4 to be considered a stoichiometric mixture of AgO and Ag_2O_3, and, therefore, the existence of Ag(II) and Ag(III) occupying two sets of equivalent positions in the lattice and not only one. However, the experimental results show, quite conclusively, that both Ag(II) and Ag(III) occupy the same set (24d). The property of semiconductivity observed in this compound (122) and a feeble paramagnetism that varies with temperature (122), together with the rather high value of the electrical conductivity, *ca.* 100 mho/cm. at room temperature (122), suggest that there is double exchange between Ag(II) and Ag(III) through the oxygen bridge (69, 192, 193) and that the exchange electron of the configuration

$$\text{-Ag(II)-O-Ag(III)-} \rightleftarrows \text{-Ag(III)-O-Ag(II)-}$$

can be picked up to a conduction band by a rise in temperature. Since the ions Ag(III) are planar square coördinated with four oxygens (dsp^2) the sole contribution to the observed paramagnetism should be due to the Ag(II) ions. Both the high electrical conductivity and the low temperature-dependent paramagnetism are not in disagreement with such an assumption. However, further study of these substances should be needed to clarify the situation and try to find a correlation between electric and magnetic properties.

The highest stability of this series of compounds is found in the nitrate. The perchlorate compound decomposes within hours into AgO, at room temperature. Successive X-ray diffraction patterns, shown in Fig. 1, give support to the decomposition reaction

$$Ag(Ag_3O_4)_2ClO_4 \rightarrow 6AgO + AgClO_4 + O_2$$

The pattern of $AgClO_4$ could not be observed due to its deliquescent character. Partial substitution of the anions has not been studied. This substitution, however, should proceed without difficulty, since the values for the unit cell edge are very close. A value of $a = 9.834 \pm 0.009$ Å., for example, has been reported in the case of the oxyfluoride $Ag(Ag_3O_4)_2F$ (67).

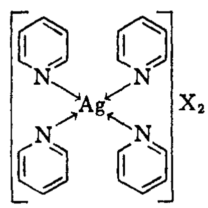
IV. Organic Complexes of Bivalent Silver

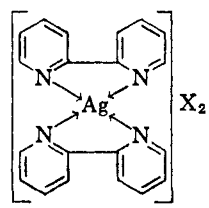
1. Introduction

Bivalent silver is stabilized by coördination with some nitrogen-containing heterocycles. In most cases the coördination occurs through formation of four hybrid dsp^2 bonds (145) as in the case of copper (75, 126), although compounds with higher coördination numbers are known (130). The oxidation potential of Ag(II)/Ag(I) is strongly reduced from 1.914 volts in nitric solution (142) to 1.453 volts in the case of dipyridyl compounds (165). The stability of some of these compounds is very great. The pyridine complex $Agpy_4S_2O_8$ (12, 146), isomorphous with the similar cupric compound (12), is typical of this series. Compounds with dipyridyl (128) and tripyridyl (129) also have been prepared. Coördination with ortho-phenanthroline (*o*-phn) also stabilizes bivalent silver (78). Inner metallic complexes of several pyridine-monocarboxylic (6, 16) dicarboxylic (7), and tricarboxylic acids (8) are known.

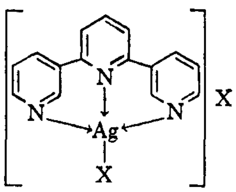
2. Preparation and Properties

These compounds are obtained by a general procedure. Solutions of Ag(I) in the presence of an excess of the ligand molecule are oxidized by means of $K_2S_2O_8$ or $(NH_4)_2S_2O_8$. The persulfates then are precipitated, as yellow to dark red crystalline powders, sparingly soluble in water. By further double decomposition, different salts can be obtained. A series of complex argentic(II) salts having the formula Ag o-phn_2X_2, with $X = {}^1/_2\ S_2O_8$, HSO_4, NO_3, ClO_3, and ClO_4 have been prepared (78). Several dipyridyl complexes, as well as pyridine compounds, have been obtained by anodic oxidation in a divided cell (15). In most cases, their structure is planar.

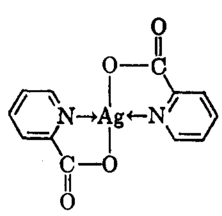




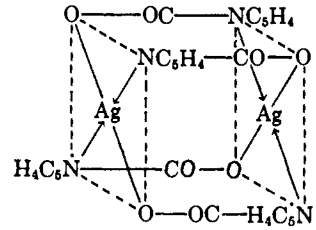
These various dipyridyl compounds have been obtained by oxidation with $K_2S_2O_8$ and double decomposition (128): Ag $dipy_2S_2O_8$, Ag $dipy_2(HSO_4)_2$, $Ag_2dipy_5(S_2O_8)_2$, Ag $dipy_3(NO_3)_2$, Ag $dipy_3(ClO_3)_2$, and Ag $dipy_3(ClO_4)_2$. A complex compound Ag $dipy_2(NO_3)_2 \cdot AgNO_3 \cdot HNO_3$ also has been reported (128). Because of the decrease in oxidation-reduction potential caused by coördination Ag(I) can be oxidized to Ag(II) in the presence of dipyridyl and *o*-phenanthroline by PbO_2, BaO_2, and CeO_2 (109). Ozone also can be used to obtain most of the complex compounds, provided it does not oxidize the ligand molecule (110). In the presence of dilute nitric acid, the tripyridine argentous nitrate $AgtripyNO_3$ is oxidized readily at the anode of an electrolytic cell with the formation of the corresponding argentic(II) nitrate $(AgtripyNO_3)NO_3$. Aqueous solutions of this compound react by double decomposition with the corresponding anions, yielding the compounds (Agtripy-$ClO_3)ClO_3$, (Agtripy$ClO_4)ClO_4$, and AgtripyS_2O_8 (129). Direct oxidation of AgtripyNO_3 with $K_2S_2O_8$ gives AgtripyS_2O_8 (129). There is no evidence of the formation of an argentic (II) derivative coördinated with more than one molecule of tripyridyl (129). The structure of the argentic (II) tripyridyl complexes is



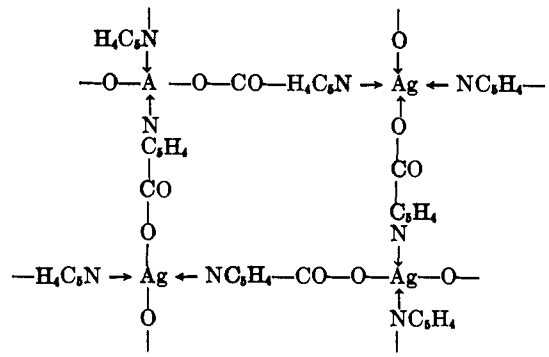
A hypothetical compound of Ag(II) with 8-hydroxyquinoline arising from disproportionation of Ag(I) into metallic silver and Ag(II) in boiling aqueous solutions of silver acetate and the ligand molecule has been reported (137). This compound, however, is diamagnetic (122) and there is no evidence for silver in the bivalent state (25). An important series of compounds is the series of inner metallic complexes of Ag(II) with the pyridine mono-, di-, and tricarboxylic acids, of general formula $Ag(BH_{n-1})_2$ where $n = 1, 2, 3$ for mono-, di-, and tri-carboxylic acids, respectively. The argentic picolinate (pyridine 2-carboxylate) is typical of this series (16). It can be prepared by oxidizing a solution of $AgNO_3$ with $K_2S_2O_8$ in the presence of picolinic acid. According to X-ray diffraction analysis (41), it is isomorphous with the analogous cupric compound. Although its X-ray diffraction pattern could not be elucidated, the isomorphism with the corresponding cupric compound, whose structure has been studied on single crystals of its dihydrate (41), suggests the structural formula



with a planar square dsp^2-hybridization (41). The spacings observed in the X-ray powder diffraction pattern are, in Å.: 8.57, 6.73, 4.28, 3.96, 3.70, 3.29, 3.20, 3.09, 2.86, 2.73, 2.57, 2.43, 2.32, 2.23, 2.08, 1.97, 1.86, 1.75, 1.68, 1.60, 1.54, 1.49 (41). The refractive indices are $\alpha \leq 1.50$ and $\gamma \geq 1.76$ (41). The nicotinate and isonicotinate also are known (6). They are isomorphous with the cupric compounds (39). The structure of these compounds is not known. Two models, one dimeric and the other polymeric, have been suggested (6)



Dimeric Arrangement



Polymeric arrangement

Further work is needed in this field.

Five compounds of the pyridine dicarboxylic acids have been prepared (7), namely: quinolinate (2,3-), cinchomeronate (3,4-), isocinchomeronate (2,5-), lutidinate (2,4-), and dipicolinate (2,6-). The dipicolinate appears in two modifications, dark red and green, according to the number of water molecules of hydration. Although these compounds can be prepared starting from the corresponding acids, the argentic(II) quinolinate is said to be produced as a result of the oxidation of the argentous bis-quinoline nitrate with $(NH_4)_2S_2O_8$ (35). Complex compounds of three pyridine tricarboxylic acids (2,3,6-, 2,4,5-, and 2,4,6-tricarboxylic) have been prepared (8). Two modifications of the pyridine 2,4,6-tricarboxylate (collidinate) are known, also differing in the amount of hydration water. Some of these inner complexes have been studied by means of X-ray diffraction (6, 7, 8), although the samples were polycrystalline. As yet, no interpretation of the structures has been made. The spacings reported in the literature, in Å. are:

Argentic isonicotinate (6): 8.10, 6.17, 4.49, 4.08, 3.69, 3.18, 2.97, 2.79, 2.69, 2.58, 2.39, 2.16, 2.04, 1.91.

Argentic quinolinate, $2H_2O$ (7): 9.400, 7.019, 6.035, 5.478, 4.897, 4.528, 4.247, 3.863, 3.630, 3.601, 3.241, 3.155, 3.002, 2.922, 2.775, 2.655, 2.574, 2.466, 2.378, 2.253, 2.250, 2.199, 2.106, 2.082, 2.036, 1.967, 1.857, 1.763, 1.735, 1.697, 1.674, 1.648, 1.621.

Argentic dipicolinate, $4H_2O$ (green) (7): 10.157, 7.190, 6.146, 5.456, 4.879, 4.301, 3.931, 3.741, 3.620, 3.328, 3.080, 2.898, 2.717, 2.495, 2.317, 2.189, 2.052, 2.000, 1.958, 1.849, 1.808, 1.747.

Argentic dipicolinate, $2H_2O$ (dark red) (7): 10.273, 7.893, 7.289, 5.863, 5.434, 4.915, 4.556, 4.149, 3.767, 3.508, 3.276, 3.029, 2.891, 2.733, 2.615, 2.479, 2.390, 2.236, 2.094, 2.009, 1.946, 1.901, 1.833, 1.788, 1.748.

Argentic collidinate (black) (8): 10.395, 7.579, 6.554, 5.901, 5.221, 4.659, 4.227, 3.597, 3.455, 3.119, 3.002, 2.838, 2.717, 2.504, 2.421, 2.342, 2.268, 2.210, 2.153, 2.097, 2.013, 1.868, 1.818, 1.756.

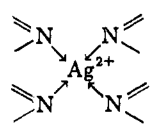
Argentic collidinate, H_2O (chocolate) (8): 9.640, 7.038, 5.232, 4.595, 4.254, 3.825, 3.625, 3.300, 2.935, 2.761, 2.531, 2.398, 2.302, 2.215, 2.149, 2.014, 1.939, 1.819, 1.737, 1.673, 1.593, 1.563, 1.516, 1.478, 1.449, 1.412.

A consideration of the properties of the argentic(II) inner complexes of the pyridine mono-, di-, and tricarboxylic acids indicates that the stability decreases with increasing number of carboxylic groups. In each of the groups, the relative positions of the carboxylic groups has a definite influence upon the stability, with the exception of the monoacids. The stability of nicotinate, isonicotinate, and picolinate is, in fact, more or less the same. The difference in stability observed in the di- and tricarboxylic derivatives has been attributed to the steric effect that could certainly hinder the formation of favorable planar configurations around the metal ion (8). The characteristics and influence of the hybridization dsp^2 in the two groups of compounds have been extensively studied (145, 166). Solutions of some of the compounds have been shown to have a strong absorption at 3500–4000 Å. (172). Exchange of radioactive 110-silver between the monovalent and bivalent states has been studied (34). Total exchange between $AgNO_3$ in aqueous solution and argentic(II) complexes with dipyridyl and with *o*-phenanthroline occurs within two minutes. This fact supports the equilibrium in solution

$$2Ag^{2+} \rightleftarrows Ag^+ + Ag^{3+}$$

3. Magnetic Behavior

The magnetic behavior of these compounds indicates the existence of bivalent silver. The results from bulk magnetic susceptibility determinations can be attributed to paramagnetism of one unpaired electron with the orbital angular momentum almost completely quenched. The compounds $Ag_2dipy_5(S_2O_8)_2$ and $Agdipy_3X_2$, where $X = NO_3$, ClO_3, and ClO_4 have been reported to have values of the susceptibility *ca.* 50% larger than those of the tetracovalent compounds (175). These results, however, have not been confirmed by paramagnetic resonance (123). The tripyridyl compound ($Agtripy$-$ClO_3)ClO_3$ has been reported to be paramagnetic, with a susceptibility of 1434×10^{-6} emu./g.-ion (130). Magnetic studies of mixed crystals $Ag_xCu_{1-x}py_4S_2O_8$ have been made (37), finding the variation of the Curie temperature as a function of the composition. Also, the magnetic behavior of mixed crystals $Ag_xCd_{1-x}py_4S_2O_8$ has been studied (147, 148). The results, however, are questionable (152). The author's own work indicates that argentic(II) compounds, with the exception of AgF_2, are magnetically dilute, differing from the corresponding cupric compounds (124). From magnetic susceptibility measurements, the pyridine mono-, di-, and tricarboxylates have an effective number of magnetons per silver atom of 1.7–1.8 which indicates strong orbital quenching and, therefore, spin-only paramagnetism (6, 7, 8, 37, 101, 175). Former paramagnetic resonance measurements of $Agpy_4S_2O_8$ (64) and of Ag*o*-$phn_2S_2O_8$ (29) have been improved and extended to several other compounds (123). These results point out the existence of two groups of argentic(II) complexes, namely: (i) inorganic salts of complex cation, and (ii) inner complexes. The first group includes those compounds in which the ligand molecules are nitrogen-containing organic bases like pyridine. There are 4 to 6 nitrogen atoms coördinated with each silver ion, and the anion can be $S_2O_8^=$, HSO_4^-, NO_3^-, or ClO_4^-. In these compounds, the unpaired electron is not localized in the silver ion; no hyperfine splitting due to the silver nucleus is observed. The second group includes the derivatives of the pyridine mono-, di-, and tricarboxylic acids. The existence of negative charges (R-COO⁻) localizes the unpaired electron in the silver ion giving rise to a less quenched orbital angular momentum. This group resembles in character the behavior of Ag(II) acidic solutions which, when frozen, also show less quenching. This fact supports the coördination of the argentic(II) ion with the acid's anion. The two magnetic environments of the complex compounds are



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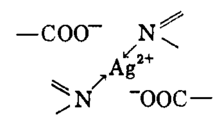


ii

On the basis of what has been suggested in the case of $CuCl_4^=$ and $Cu(H_2O)_4^{++}$ (42), the hybridizations could then be (i) 4d 5s $5p^2$, and (ii) 5s $5p^2$ 5d.

The appearance of a strong hyperfine interaction when Ag(II) is surrounded by negative ions has been noticed after the irradiation of ^{109}Ag-doped KCl single crystals (191). The irradiation leads to the formation of the square planar magnetic complex $AgCl_4^-$. The orbital quenching is almost total in the direction perpendicular to the axis of symmetry and partial in the parallel direction. Table 2 shows the molar magnetic susceptibilities and effective number of magnetons of several compounds. Table 3 shows the magnetic parameters of some complexes, measured by paramagnetic resonance (123).

V. ARGENTIC(II) ION IN SOLUTION

1. Preparation and Chemical Properties

Most highly oxidized silver compounds dissolve in strongly acidified media of nonreducing acids to form

TABLE 2

Magnetic Susceptibilities and Effective Magneton Numbers of Several Argentic(II) Complex Compounds

Ag Compound	$\chi \times 10^6$. emu./g.-ion at room temperature	$P_{eff.}$	Ref.
Ag py$_4$S$_2$O$_8$	1206–1303	1.71–1.78	37, 101, 175
Ag *o*-phn$_2$S$_2$O$_8$	1400	1.84	128
Ag dipy$_2$S$_2$O$_8$	1367	1.82	37, 175
Ag dipy$_2$(NO$_3$)$_2$	1851	2.12	175
Ag dipy$_2$(ClO$_3$)$_2$	1789	2.08	175
Ag dipy$_2$(ClO$_4$)$_2$	2155	2.29	175
Ag$_2$dipy$_5$(S$_2$O$_8$)$_2$	1720	2.04	175
(Ag tripyClO$_3$)ClO$_3$	1434	1.85	130
Ag(II) quinolinate	1247	1.743	7
Ag(II) cinchomeronate	1232	1.742	7
Ag(II) isocinchomeronate	1194	1.712	7
Ag(II) lutidinate	1091	1.644	7
Ag(II) dipicolinate	1252	1.747	7
Ag(II) nicotinate	1240	1.73	6
Ag(II) isonicotinate	1240	1.73	6
Ag(II) pyridine-2,4,6-tricarboxylate, black	1369	1.816	8
Ag(II) pyridine-2,4,6-tricarboxylate, brown	1394	1.832	8
Ag(II) pyridine-2,4,5-tricarboxylate	1225	1.73	8

TABLE 3

Principal Values of the g-Tensor for Several Argentic Complexes

The values have been drawn from McMillan, J. A., and Smaller, B., *J. Chem. Phys.*, *35*, 1698 (1961).

Compound	g_1	g_2	g_3
Ag py$_4$S$_2$O$_8$	2.049	2.098	2.148
Ag *o*-phn$_2$S$_2$O$_8$	2.046*	2.046*	2.168*
Ag dipy$_2$S$_2$O$_8$	2.032*	2.032*	2.164*
Ag$_2$dipy$_5$(S$_2$O$_8$)$_2$	2.040	2.056	2.176
Ag dipy$_2$(NO$_3$)$_2$	2.037	2.047	2.168
Ag dipy$_2$(ClO$_4$)$_2$	2.045*	2.045*	2.169*
Ag dipy$_2$(ClO$_3$)$_2$	2.034	2.065	2.172
Ag(II) picolinate	2.044	2.072	2.244

* Symmetric magnetic complex, $g_1 = g_2 = g_\perp$, $g_3 = g_\parallel$.

Ag^{2+} in solution. Also, Ag^+ acid solutions are readily oxidized by $K_2S_2O_8$, F_2, and O_3 (140, 141, 142, 143, 144). The oxidation of Ag^+ by O_3 in nitric acid solution has been studied extensively (141). From the rate of oxidation the intermediate formation of Ag^{3+} has been postulated as

$$Ag^+ + O_3 \rightarrow AgO^+ + O_2 \quad \text{(slow)}$$
$$AgO^+ + Ag^+ + 2H^+ \rightarrow 2Ag^{2+} + H_2O \quad \text{(fast)}$$

The latter equation should in fact represent an equilibrium to account for the appearance of Ag^{3+} after the precipitation of silver oxysalts such as $Ag(Ag_3O_4)_2NO_3$. The solutions are colored and paramagnetic, this latter fact confirming the existence of bivalent silver in solution. Nitric solutions are brown and sulfuric solutions are greenish black (185); perchloric and phosphoric solutions are pink (122). The paramagnetism of the nitric solutions has been reported to be due to 1.98 (143) and 1.74 (138) effective magnetons per ion. The former value is in very good agreement with the results from paramagnetic resonance experiments (123) which give 1.97 effective magnetons.

The solutions are unstable at room temperature, although the phosphoric solution is fairly stable at 0° (122), and are reduced to monovalent silver after a few hours. They are powerful oxidizing agents. They oxidize in the cold almost instantaneously hydrogen peroxide to oxygen (141), manganous salts to permanganate (141), chromic salts to chromate (188), cerous to ceric salts (9, 11), thallous to thallic salts (141), vanadyl salts to vanadate (190), iodate to periodate (13), and ammonia to nitrogen and its oxides (38, 96, 97, 98, 99, 115, 116). Kinetic studies (143) suggest that the ion Ag^{2+} is coördinated with the anion. The dependence of the color of the solutions upon the anion also supports the assumption of coördination, as well as the fact that during the electrolysis of these solutions some silver migrates to the anode (186). The optical absorption of the nitric solution shows a maximum at 3900 Å. (123). The brown color of the solution is, therefore, accounted for by a tail of the ultraviolet absorption. Neutralization of these solutions leads to the precipitation of AgO with variable amounts of the corresponding oxysalt.

Thermodynamic parameters for the argentic(II) ion have been established by studying the cells

$$\text{(i)} \quad Pt(H_2,H^+)||(Ag^{2+},Ag^+\ (4M\ HNO_3))$$
$$\text{(ii)} \quad Pt(H_2,H^+)||(Ag^{2+},Ag^+\ (4M\ HClO_4))$$

The values of the standard free energy ΔF^0 and the heat of formation ΔH^0 so-obtained are (144):

$$\text{(i)} \quad \Delta F^0 = -44.49 \text{ kcal.}; \quad \Delta H^0 = -41.0 \text{ kcal.}$$
$$\text{(ii)} \quad \Delta F^0 = -46.13 \text{ kcal.}; \quad \Delta H^0 = -41.1 \text{ kcal.}$$

The rate of reduction of the over-all reaction

$$4Ag^{2+} + 2H_2O \rightarrow 4Ag^+ + 4H^+ + O_2$$

also has been studied. Two independent reactions involving the intermediate formation of Ag^{3+} have been postulated to account for the observed facts (140).

It has been suggested (14) that during the dissolution of AgO in HNO_3 disproportionation occurs giving rise to Ag^{3+} through the mechanism

$$2AgO + 4HNO_3 \rightarrow AgNO_3 + Ag(NO_3)_3 + 2H_2O$$

but there is no doubt that silver is mainly in the paramagnetic bivalent state (123, 138, 143). An equilibrium

$$2Ag^{2+} \rightleftarrows Ag^{3+} + Ag^+$$

strongly displaced toward the left side in acid solution, however, has been postulated to account for the fast isotopic exchange of ^{110}Ag in perchloric solutions (66). The isotopic exchange rate increases with decreasing pH. This fact can be explained by means of the equilibrium

$$Ag^{3+} + H_2O \leftrightarrows AgO^+ + 2H^+$$

since a faster exchange with Ag^{3+} than with AgO^+ should be expected (122).

Ag^{2+} in solution is said to occur during the charge of lead storage batteries when small amounts of argentous ion are added. This addition is claimed to decrease the oxygen overvoltage through the formation of Ag^{2+} although it increases at the same time the rate of corrosion (103, 160).

2. Magnetic Behavior

Electron paramagnetic resonance of Ag^{2+} in solution at room temperature (123) shows a broad line at $g = 2.124 \pm 0.005$ and no resolvable hyperfine structure. This fact has been attributed to a very short spin-lattice relaxation time (123). Frozen solutions observed at 77°K. disclose a strong symmetric g-anisotropy that permits the evaluation of the principal components of the hyperfine interaction between the unpaired electron and the silver nuclei ^{107}Ag and ^{109}Ag, which have spin $^1/_2$ and nuclear magnetic moments differing by less than 20%. The observed paramagnetic parameters are (123):

$$g_{\parallel} = 2.265 \pm 0.001; \quad g_{\perp} = 2.065 \pm 0.001$$
$$A_{\parallel} = 51 \times 10^{-4}\ \text{cm.}^{-1}; \quad A_{\perp} = 30.5 \times 10^{-4}\ \text{cm.}^{-1}$$

Measurements of the hyperfine splitting with pure ^{107}Ag and ^{109}Ag samples also have been made, confirming the above results (123). From spectroscopic data of the Ag^{2+} $^2D_{5/2}$ state (62, 63, 65) and the magnetic parameters, the splittings of the ^2D levels by the ion environment have also been calculated (123). The tetragonal character of the hybridization dsp^2 explains the axial symmetry of the magnetic complex.

3. Silver as a Catalyst

Oxidation by persulfates in acid solution is strongly accelerated by argentous ions. Detailed studies of the oxidation rate have been made in the case of Cr^{3+} and NH_4^+. The rate of oxidation has been shown to vary with $S_2O_8^=$ concentration (115, 116, 188, 189). Many other papers have appeared in the field of catalysis using Ag^+ but this review will only cover those that have included statements regarding to the mechanism of the catalysis itself. In the case of Cr^{3+}, an intermediate compound was postulated (115, 116)

$$S_2O_8^= + Ag^+ \rightarrow 2SO_4^= + \text{intermediate compound (slow)}$$
$$\text{intermediate compound} + Cr^{3+} + H_2O \rightarrow Cr_2O_7^= + Ag^+ \text{(fast)}$$

The effect of pH is small. The effect of Ag^+ concentration, on the contrary, is significant. The rate of decomposition of $S_2O_8^=$ has been found to be (188, 189)

$$-\frac{d}{dt}[S_2O_8^=] = k[S_2O_8^=][Ag^+]$$

In 0.1 N $HClO_4$, k = 0.333 liter mole^{-1} min.$^{-1}$ at 25°, and 0.765 at 35°.

The intermediate compound has been assumed to be Ag^{3+} (188, 189) and the oxidation reactions for Cr^{3+} therefore should be

$$S_2O_8^= + Ag^+ \rightarrow 2SO_4^= + Ag^{3+}$$
$$3Ag^{3+} + 2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^= + 3Ag^+ + 14H^+$$

A similar study of the rate of oxidation of oxalic acid by $S_2O_8^=$ in the presence of Ag^+ (23) supports the same mechanism. In this case, however, the intermediate formation of Ag^{2+} has been assumed, according to the rate-determining partial reaction

$$S_2O_8^= + Ag^+ \rightarrow SO_4^= + SO_4^-Ag^{2+}$$

The formation of an intermediate species Ag_3O_4 also has been claimed (79), although this assumption does not seem to be justified. The formation of Ag^{3+} has been proposed repeatedly by several authors (21, 22, 44, 71, 72, 188, 189, 190). The supporters of Ag^{2+} (20, 109) base their assertion upon the fact that the bis-dipyridyl argentous ion, which is oxidized to the corresponding argentic(II) complex, is as effective a catalyst as the argentous ion itself. These facts, however, do not necessarily rule out an intermediate step of trivalent silver (14). If, at any time, the concentration of the intermediate silver ion is high enough, the equilibrium

$$Ag^{3+} + H_2O \rightleftarrows AgO^+ + Ag^+ + 2H^+$$

would support the preferential formation of Ag^{2+} since the oxidation processes take place in acid media. However, during the oxidation of 8-hydroxyquinoline by $K_2S_2O_8$ in the presence of rather high concentrations of $AgNO_3$, the author has failed to observe any paramagnetic resonance that could be attributed to Ag^{2+}, after freezing the solutions at 77°K. Curiously enough, in all cases a strong absorption characteristic of an unidentified free radical could be observed (122). These results might well support the assumption that Ag^{3+} is the main intermediate product, although the absence of observable resonance always could be accounted for by a concentration of Ag^{2+} lower than 10^{13} ions per cubic centimeter of solution. Further work should be done to give a distinct explanation to this state of affairs.

VI. FLUORINATED COMPOUNDS

1. Introduction

The behavior of silver with respect to fluorine is unusual. Besides the semimetallic compound Ag_2F, whose structure has been fully investigated (181), several compounds of Ag(II) and Ag(III) are known. Among them, AgF_2 presents the interesting property of being ferromagnetic below 163°K. and the sole magnetically dense argentic compound known so far.

A. Bivalent Silver Fluoride

1. Preparation and Chemical Properties

Finely divided fresh AgCl dried at 110° is treated with

F_2 at 200° (58, 149, 157). The so-obtained compound, having the formula AgF_2, is an amorphous, black solid, which is very hygroscopic and reacts vigorously with water. It is decomposed by the action of atmospheric moisture, and may be used as a fluorinating compound. It melts at 690° and is stable up to 700° under one atmosphere of fluorine (184). The heat of formation of AgF_2 by direct synthesis has been found to be 84.5 $\pm$ 1.2 kcal./mole (184). Fluorination of metallic silver (91) with F_2 and of AgCl with ClF_3 (154) led to the formation of a yellow modification of AgF_2. Although no crystalline modifications are known, it has been anticipated that AgF_2 should have the structure of rutile (40) as does CuF_2. A similar argument, however, based on CdF_2, would rather suggest a fluorite structure (122).

2. *Magnetic Properties*

The known paramagnetic silver compounds generally are magnetically dilute (124, 167). In fact, argentic(II) compounds exhibit values of the susceptibility near 1200 $\times$ 10^{-6} emu./g.-ion, corresponding to spin contribution only, and hence an almost total quenching of the orbital angular momentum. AgF_2, on the contrary, exhibits a value about one third of that expected for a magnetically dilute compound. The actual value is 440 $\times$ 10^{-6} emu./g.-ion at room temperature (70). Exchange effects occur in this compound giving rise to ferromagnetism (70) below a well defined Curie point of $-110°$. Its density is about 4.57–4.58 g./cm.^{3}. This value probably explains the appearance of ferromagnetism at low temperature, according to Slater's ratio D/r (19) where D is the distance between neighboring atoms and r the radius of the energy shell in which the electron spin is uncompensated. However, since the compound is amorphous, it is doubtful whether the value of D could be sufficiently meaningful, since the condition for the appearance of ferromagnetism states that D/r should be greater than 3, but not much greater.

B. Ag(III) *Fluorides*

1. *Preparation and Chemical Properties*

AgF_3 is not known, but compounds of the type $KAgF_4$ have been prepared and found to be diamagnetic (102). Their diamagnetism can be accounted for by a hybridization involving one d-orbital, presumably dsp^2, as in other argentic(III) compounds. $KAgF_4$ is obtained by treating with fluorine an equimolecular mixture of $AgNO_3$ and KCl or KNO_3 at 200–400°, as a yellow compound that darkens in fluorine atmosphere at higher temperature. $CsAgF_4$ and $BaAgF_5$ also have been prepared (80). These complex fluorides are very unstable, react vigorously with water and decompose with atmospheric moisture. When heated at 200°, $BaAgF_5$ is said to yield the more stable $BaAgF_4$ (80). The magnetic behavior of $BaAgF_4$ has not been studied. The compounds $MAgF_4$ (M = K, Cs) (80) are similar to gold compounds $MAuF_4$ (M = K, Rb, Cs) (81). The X-ray diffraction patterns of both series of compounds are known but they are too complicated to be elucidated (81). Compounds such as Cs_2AgF_6 and $CsAuF_6$ also have been reported. On the basis of their X-ray powder diffraction patterns, very like to those of $MAgF_4$, it has been suggested that a mixture of $MAgF_4$ and MF_2 (80) is present, and that K_2AgF_6, Cs_2AuF_6, and Cs_2AgF_6 are also mixtures containing MF_2.

VII. Trivalent Silver Complex Compounds

Introduction.—Although an oxide Ag_2O_3 has been claimed to be produced during the auto-oxidation of $(NH_4)_2S_2O_8$ in the presence of Ag^+ (38), there is not enough evidence to prove that such an oxide may be prepared under ordinary conditions. The state of oxidation III, however, can be stabilized by coördination with some nitrogen-containing organic bases and three inorganic anions, namely: fluoride, periodate, and tellurate. Compounds of the type $MAgF_4$ with M = K, Cs already have been treated in the chapter of fluorinated compounds.

A. *Inorganic Complexes*

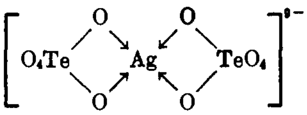
Preparation and Properties.—Periodates of trivalent silver (112) and copper (111) have been obtained as pure, crystalline, diamagnetic substances. The silver compounds have been reported to have the formula $M_7Ag(IO_6)_2$, with M standing for an alkaline metal or hydrogen. The observed diamagnetism has been explained by a hybridization dsp^2 as in the case of the tetracovalent $Ni(CN)_4^{=}$ ion (113). Compounds with the alkaline metal partially substituted by hydrogen and having several molecules of hydration water also have been prepared (113). These compounds have been reported as isolated in the pure state: $K_6HAg(IO_6)_2 \cdot 10H_2O$, $K_7Ag(IO_6)_2 \cdot KOH \cdot 8H_2O$, $KHNa_5Ag(IO_6)_2 \cdot 16H_2O$, $KNa_6Ag(IO_6)_2 \cdot NaOH \cdot H_2O$ (113). The color of these compounds is brown, darker than the auric(III) and lighter than the cupric(III) compounds. Argentic(III) compounds are less stable than auric(III) but more stable than cupric(III) periodates. They are obtained by oxidizing Ag_2O with a boiling solution of KOH or NaOH and KIO_4.

Argentic(III) and cupric(III) tellurates were first obtained during the study of tellurium separation from heavy metals (32). Later studies led to assigning them the general formula (114) $M_{9-m}H_mAg(TeO_6)_2 \cdot nH_2O$, with M as the alkaline metal. These compounds are produced by oxidizing Ag^+ with $S_2O_8^{=}$, in the presence of TeO_2 and an alkaline hydroxide. Oxidation with $K_2S_2O_8$ of a mixture of Ag_2SO_4, TeO_2, and NaOH in boiling water has been reported to yield, for example,

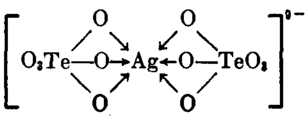
$Na_6H_3Ag(TeO_6)_2 \cdot 18H_2O$ and $Na_7H_2Ag(TeO_6)_2 \cdot 14H_2O$.

However, compounds such as $H_xM_{7-x}Ag(IO_6)_2 \cdot nH_2O$ and $H_xM_{9-x}Ag(TeO_6)_2 \cdot nH_2O$ can be suspected not necessarily to be daltonides. Further work should be undertaken in this field.

The structures of both types of compounds, periodates and tellurates, are not known. In view of their diamagnetism, it is supposed that the silver ion is coordinated with two oxygens of each anion (113, 114). If this were so, the structural formula could be represented as



From steric considerations, however, an octahedral configuration involving a hybridization (4d 5s $5p^3$ 5d) such as

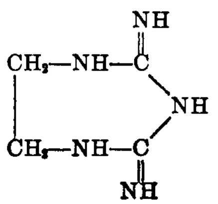


could not be ruled out, at least in the absence of more information.

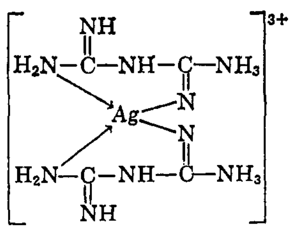
B. *Organic Complexes*

Preparation and Properties.—Silver(III) is very stable when coördinated with ethylenedibiguanide(151). A compound with ethylene biguanide

EnBigH =

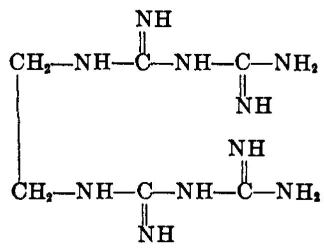


of composition $Ag(EnBigH)_2X_3$ where X = SO_4, NO_3, ClO_4, or OH has been reported (150). However, no further information has appeared on this compound. Attempts to stabilize silver(III) with the simple biguanide, $C_2H_7N_5$, did not succeed until recently (152). The oxidation with $K_2S_2O_8$ of a cold aqueous solution of a mixture of biguanide sulfate and $AgNO_3$ at pH 6.5–7.0 has in fact been claimed to yield sparingly soluble, brown crystals of $Ag(C_2H_7N_5)_2(OH)SO_4 \cdot 7H_2O$. This substance can be converted into $Ag(C_2H_7N_5)_2(NO_3)SO_4 \cdot 6H_2O$ by treating with a solution of 1*N* HNO_3 (152). The suggested structure for the complex cation is

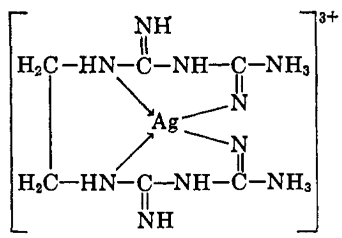


A complex silver(III) ethylene dibiguanide hydroxide and its salts, as mentioned above, have been prepared (151). Their composition is given by $AgEn(BigH)_2X_3$, where X = HSO_4, NO_3, ClO_4, or OH, and

$En(BigH)_2$ =



The structure formula of the complex cation is (152)



The molecular conductivity has been found to be 518 mho at 20° (151), corresponding to that of a tripositive complex cation.

The stability of this complex cation in aqueous nitric solution has been determined from the equilibrium constant of the reaction between the complex and the hydrogen ion, and the acid dissociation constants of ethylene dibiguanide. The equilibrium constant was derived from pH and Ag^{3+} concentrations. The latter were drawn from measurements of the oxidation-reduction potential $E(Ag^{3+}/Ag^+)$. The dissociation

$$[AgEn(BigH)_2]^{3+} \rightleftarrows Ag^{3+} + En(BigH)_2$$

led to a value pK = 52.16 at 32° (168).

The rate of decomposition of silver(III) ethylene dibiguanide nitrate as a function of the pH at 25, 35, and 45° also has been studied (169).

Silver(III) ethylene dibiguanide nitrate and sulfate have been shown to have a wide optical absorption band, in solution, extending from 3000 to 3700 Å. (152).

All these compounds are diamagnetic. No argentic(II) complexes with biguanide as a complexing ligand have been reported so far. The oxidation always goes through the trivalent state.

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