

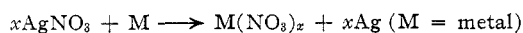
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Reactions of Some Elements with Silver Nitrate in Methanol¹

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Although the reactions of silver salts with elements in aqueous solution are well known, very little work has been done with the corresponding reactions in non-aqueous media. A reaction of the type



will produce an anhydrous nitrate *in situ* in a non-aqueous solvent unless destruction of the solvent produces water as a by-product. The solution of the nitrate would then find obvious application in the preparation of derivatives.

No systematic study of such reactions has been attempted since N. W. Fischer studied them in 1830,³ although Guntz and Martin⁴ studied the reactions of silver nitrate with copper and manganese in acetone and benzonitrile, and Morgan prepared $\text{Cu}(\text{CH}_3\text{CN})_4\text{NO}_3$ from acetonitrile.⁵ Morgan demonstrated that the stoichiometry of the reaction could be determined by weighing the reactants and the product silver. Reactions of silver salts with halogens have been studied⁶ and appear to be forced to completion by the formation of insoluble silver halide.

Ammonium fluoride forms insoluble fluorometallates when allowed to react with methanolic metal bromides.⁷ A similar reaction occurs with the nitrate solutions.

Qualitative Testing

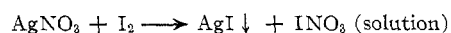
A sample (0.05 g.) of the element was added to 2 ml. of 2% (by weight) silver nitrate in methanol.⁸ Samples were shaken periodically for 24 hr. and the clear solutions tested with ammonium fluoride. Some samples evolved gas so the procedure was modified to detect this. Silver nitrate (0.1 g.) and the element were covered with 10 ml. of methanol in a sealed volumetric flask. Gas formation caused breakage of the seal. Antimony, arsenic, bismuth, cadmium, cobalt, copper, iodine, lead, manganese, nickel, selenium, sulfur, thallium, tin, tungsten, and zinc gave clear evidence of

reaction. Boron, lanthanum, magnesium, molybdenum, niobium, titanium, and vanadium reacted with gas evolution. Aluminum, indium, and iron showed no apparent activity. All elements except antimony, arsenic, boron, iodine, selenium, sulfur, and thallium gave solid derivatives with ammonium fluoride.

The activity of silver nitrate was tested in acetone, acetonitrile, nitromethane, ethyl acetate, and carbon tetrachloride. With the exception of acetonitrile, which often formed insoluble complexes, reactions were slower than in methanol.

Reactions with Nonmetals

The reaction of silver nitrate with iodine occurs rapidly. The stoichiometry was determined by titration of a dilute standard solution of silver nitrate with iodine (both in methanol). A Sargent "Chemical Oscillometer" was used to detect changes in slope of a plot of capacitance *vs.* volume of iodine solution added. The end point occurred at $\text{AgNO}_3/\text{I}_2 = 1.02$, corresponding to the reaction as formulated by Birckenbach.^{6a,b}



The solid formed was identified by X-ray diffraction as $\gamma\text{-AgI}$. Solutions of silver nitrate containing excess suspended sulfur or selenium reacted more slowly than iodine. After several weeks of contact $\beta\text{-Ag}_2\text{S}$ or Ag_2Se could be separated by washing with carbon disulfide. The stoichiometry of the latter reaction is not known as yet.

Simple "Displacement" Reactions

Simple "displacement" reactions were observed with bismuth, cobalt, lead, and zinc. Cadmium, copper, manganese, nickel, and tin are also considered to belong to this group, but are characterized by complications. Lanthanum, magnesium, and thallium are thought to belong to this group, but solvent reaction occurs.

Weighed amounts of dry metal and an estimated twofold excess of silver nitrate were sealed in glass-stoppered flasks with sufficient methanol to make an approximately saturated solution of silver nitrate (*ca.* 2% by weight). The mixtures were allowed to react for a predetermined time and then tested for silver ion. If free of this, the solution and residue were separated. Ammonium fluoride (saturated solution in methanol) was added to the solution and the fluoride precipitate aged for 24 hr. before washing, drying, and X-ray analysis. The residue was weighed and the stoichiometry calculated.⁵ The simple reaction was assumed if the stoichiometry calculated indicated the metal to be present in the same oxidation state as that observed in the fluoride derivative.

Data for some of the reactions are given in Table I.

Cadmium and tin reacted superficially with silver nitrate but reacted vigorously with bismuth nitrate solutions from the action of bismuth on silver nitrate. Cadmium nitrate formed cadmium fluoride and tin gave solid fluoride derivatives which were amorphous to

(1) Taken from the Ph.D. thesis of W. G. Bottjer; supported in part by the U. S. Atomic Energy Commission.

(2) To whom inquiries should be addressed.

(3) In J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1923, Vol. 3, pp. 319-322.

(4) A. Guntz and F. Martin, *Bull. soc. chim. France*, [4] **7**, 313 (1910).

(5) H. H. Morgan, *J. Chem. Soc.*, **123**, 2901 (1923).

(6) (a) L. Birckenbach, J. Goubeau, and E. Berninger, *Ber.*, **65B**, 1330 (1932); (b) L. Birckenbach and J. Goubeau, *ibid.*, **66B**, 1280 (1933); *ibid.*, **67B**, 1420 (1934); (c) M. I. Ushakov, V. O. Christov, and N. D. Zelinskii, *ibid.*, **68B**, 824 (1935).

(7) H. M. Haendler, F. A. Johnson, and D. S. Crockett, *J. Am. Chem. Soc.*, **80**, 2662 (1958); D. S. Crockett and H. M. Haendler, *ibid.*, **82**, 4158 (1960).

(8) Methanol was redistilled from magnesium activated with iodine.

TABLE I

SIMPLE "DISPLACEMENT" REACTIONS (25°)			
Metal	Initial ratio M/AgNO ₃ , moles	Calcd. oxidation state	Fluoride derivative
Bi ^a	4.07	3.3-3.7	NH ₄ BiF ₄
Co ^b	1.00-0.33	1.97-2.13	NH ₄ CoF ₃
Cu	19.9-1.00	1.81-1.86	NH ₄ CuF ₃ + (NH ₄) ₂ CuF ₄
Mn	15.6-1.00	2.06-2.22	NH ₄ MnF ₃
Pb	4.12	1.94	β-PbF ₂
Zn	2.00-0.25	1.99-2.03	NH ₄ ZnF ₃

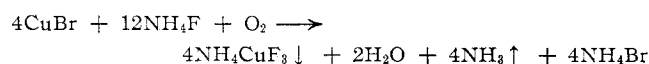
^a Bismuth samples were very sensitive to hydrolysis, the products formed giving excessive and variable weights of residue resulting in high apparent values of oxidation state. ^b Excess cobalt, at 65°, under reflux in a closed system, gave Co(NO₃)₂. Excess AgNO₃ caused the solvent to be attacked. A gaseous mixture of CH₃ONO, HCO₂H, CO₂, and N₂O was evolved and the methanol solution appeared to contain water.

X-rays but which formed tin(IV) sulfide when treated with hydrogen sulfide.

The reaction of copper with silver nitrate was complex, and the results were dependent upon the conditions employed. With the above procedure all ratios of Cu/AgNO₃ greater than 0.5 yielded a blue-green solution in which the calculated oxidation state was 1.84 ± 0.03 . The fluoride product was essentially NH₄CuF₃ contaminated with (NH₄)₂CuF₄. Evaporation of the nitrate solutions resulted in blue oils, suggesting methanol solvation, and ebullioscopic measurements gave molecular weights of 130 ± 2 for the dissolved species, for solutions with up to a twofold change in concentration.

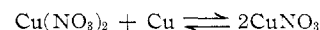
In a second experimental method, silver nitrate was allowed to react with excess copper dust kept in suspension by continuous shaking. In this case the calculated apparent oxidation state approached a limiting value of 1. If the copper was allowed to settle the solutions reverted to the stable form previously described. Very dilute solutions produced by this method reacted vigorously with ammonium fluoride in methanol to give a deep blue solution, ammonia, and pure (NH₄)₂CuF₄. The X-ray diffraction pattern of the latter compound indicates it to be isomorphous with K₂CuF₄.⁹

To support the postulate that reaction with ammonium fluoride involved oxidation-reduction, copper(I) bromide (3 g.) and ammonium fluoride (5 g.) were suspended in dry methanol and allowed free access to dry air through a gas buret connected to a sealed reactor. About 16% of the admitted air (by volume) was absorbed, and the blue coloration and liberation of ammonia occurred. Ammonium trifluorocuprate, NH₄CuF₃, was formed. The reaction is thus assumed to be



These observations with copper suggest an equilib-

rium between copper(I) and copper(II) of the general type



At equilibrium in methanol at 25° the equilibrium composition would appear to lie near 5Cu(NO₃)₂ per CuNO₃. The apparent molecular weight would be consistent with the formulation



or with the assumption that undissociated Cu(NO₃)₂ is present.

Complications often arose from variations in the ratio of starting materials. The most striking of these occurred in the cobalt system. Mixtures of cobalt and silver nitrate, with excess cobalt, yielded only cobalt(II) nitrate solutions at room temperature and at 65° (under total reflux). With excess silver nitrate, however, the solvent was vigorously attacked at 65°, the nitrate being reduced and the solvent oxidized to formic acid. Since there is no reaction between silver nitrate and methanol, alone or with powdered glass present, it would appear that the cobalt acts catalytically, perhaps through the formation of cobalt(III). The detection of formic acid in the evolved gas is puzzling, since its evolution at 65° indicates azeotrope formation with methanol rather than reaction to methyl formate. Although the infrared spectrum of the evolved gas was relatively complex, all reported bands and intensities for formic acid were found.

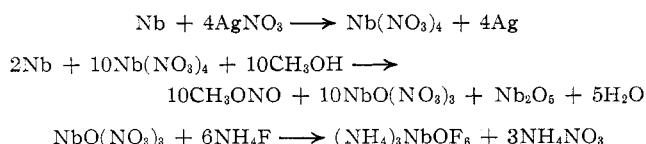
A large excess of metallic lead, in the presence of silver nitrate, produced yellow incrustations on the metallic surface. The solid evolved nitrogen dioxide during drying, decomposed to lead(II) oxide at 110°, and was very insoluble in methanol. The material is probably similar to the nitrate oxynitrite described by Senderens¹⁰ but must be investigated in greater detail.

Some Complex Reactions

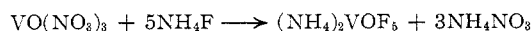
Titanium, vanadium, and niobium react vigorously to give clear solutions and gas evolution. All of the evolved gas could be trapped at -10°, and infrared analysis showed the gas to be pure methyl nitrite. Reaction of the clear solutions with ammonium fluoride gave excellent yields of (NH₄)₂TiF₆, (NH₄)₂VOF₃, and (NH₄)₃NbOF₆. It was unsafe to heat the solutions for long periods because a secondary reaction produced methyl nitrate in substantial quantity.

The precise course of the reaction is open to question and must account for these observations: (1) methyl nitrite is the only gaseous product; (2) no oxidized solvent fragment was found in the solvent or in the solid residues; (3) the reactions were run with excess metal, but the residue always contained an oxygen-containing phase as well; (4) gas evolution appeared to occur on the metal surface. On the basis of these requirements, and the assumption of an oxidation state

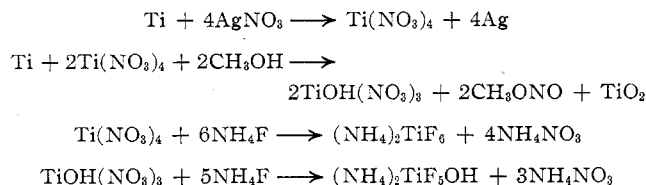
characteristic of the precipitated fluoride, the following sequence of reactions is proposed: For niobium



For vanadium, the first two steps are as for niobium, followed by



For titanium



The postulation of $\text{NbO}(\text{NO}_3)_3$ as an intermediate is reasonable. A recent paper¹¹ indicates that the compound has been prepared and that it reacts with potassium fluoride to give K_3NbOF_6 . We have also shown¹² that a bromide, prepared in methanol but not isolated, reacts with methanolic ammonium fluoride to give $(\text{NH}_4)_3\text{NbOF}_6$. A similar argument can be applied to the case of vanadium, although the corresponding $\text{VO}(\text{NO}_3)_3$ has not yet been isolated.

The existence of titanium(IV) nitrate in solution is less definite, and the evidence for the formation of the hydroxy nitrate is inferential. The formation of methyl nitrite must be accompanied by solvent oxidation or the introduction of oxygen into the titanium species by some oxidative mechanism. It does not seem reasonable, however, to assume that oxide ion can be present in the fluoride derivative without substantially altering the X-ray diffraction pattern from the $(\text{NH}_4)_2\text{TiF}_6$ type. Hydroxyl can substitute isomorphously for fluoride without an alteration in the observed powder pattern.

(11) B. O. Field and C. J. Hardy, *Proc. Chem. Soc.*, 11 (1963).

(12) A. E. Baker and H. M. Haendler, *Inorg. Chem.*, 1, 127 (1962).

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Charge-Transfer Spectra Involving Anions Outside the Coordination Sphere

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The existence of charge-transfer bands in the electronic spectra of coordination compounds is now well established. Depending upon the formal charge on

the metal and the nature of the ligands, such bands may involve either the "oxidation" or the "reduction" of the metal ion.¹ In most known cases of charge-transfer bands in coordination compounds, the group involved in the transfer is coordinated to the metal.

Examples in which the group involved is not coordinated to the metal are less common. Linhard² has observed that a very intense ultraviolet band that appears in solutions of $\text{Co}(\text{NH}_3)_6^{3+}$ shifts to lower energies upon the addition of bromide or iodide ion. He attributes this to charge transfer between the anion and the complex cation. We wish to report here two series of compounds in which charge transfer involving anions outside the coordination sphere may be responsible for the observed spectra of the solids.

Experimental

Materials.—The synthesis of $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ was accomplished by the method of Burstall and Nyholm.³ In this procedure anhydrous chromium(III) chloride and the required amount of bipyridyl are dissolved in hot methanol and a trace of zinc dust is added. Upon cooling, a green substance precipitates, and after recrystallization from water, brown $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ is obtained. *Anal.* Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{Cl}_3\text{Cr}\cdot 2\text{H}_2\text{O}$: C, 47.40; H, 3.95; N, 11.06. Found: C, 47.79; H, 4.18; N, 10.89.

The salts $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{X}\cdot 2\text{H}_2\text{O}$ ($\text{X} = \text{Br}^-$, N_3^-) and $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{X}$ ($\text{X} = \text{I}^-$, SCN^-) were prepared by dissolving $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ in warm water and adding an aqueous solution of the sodium salt of the appropriate anion. The different salts immediately precipitated. *Anal.* Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{Cl}_2\text{BrCr}\cdot 2\text{H}_2\text{O}$: C, 43.55; H, 3.66; N, 10.17. Found: C, 43.75; H, 3.92; N, 10.07. Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_7\text{Cl}_2\text{Cr}\cdot 2\text{H}_2\text{O}$: C, 46.76; H, 3.93; N, 19.10. Found: C, 46.9; H, 3.38; N, 19.4. Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{Cl}_2\text{ICr}$: C, 42.74; H, 2.87; N, 9.97. Found: C, 42.13; H, 2.88; N, 10.06. Calcd. for $\text{C}_{21}\text{H}_{16}\text{N}_6\text{Cl}_2\text{SCr}$: C, 51.1; H, 3.27; N, 14.20. Found: C, 50.91; H, 3.29; N, 14.70.

X-Ray powder data showed the three dihydrates (Cl^- , Br^- , N_3^-) to be isomorphous as were the two anhydrous salts (I^- , SCN^-). The colors of the salts were distinctly different, being for the chloride, bromide, and azide different shades of green, for the iodide yellow, and for the thiocyanate light brown.

The preparation of $[\text{Cr}(\text{phen})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ followed exactly that of the analogous bipyridyl complex with the substitution of 1,10-phenanthroline for the bipyridyl. The product recovered from the methanol, however, was red in color and analysis indicated that the recovered product was approximately the 4-hydrate. *Anal.* Calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{Cl}_2\text{Cr}\cdot 4\text{H}_2\text{O}$: C, 48.79; H, 4.09; N, 9.48. Found: C, 49.42; H, 3.59; N, 9.30.

The salts $[\text{Cr}(\text{phen})_2\text{Cl}_2]\text{X}\cdot 4\text{H}_2\text{O}$ ($\text{X} = \text{Br}^-$, N_3^- , SCN^-) and $[\text{Cr}(\text{phen})_2\text{Cl}_2]\text{I}\cdot 2\text{H}_2\text{O}$ were precipitated from a warm aqueous solution of the chloride by the addition of the appropriate sodium salt. *Anal.* Calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{Cl}_2\text{BrCr}\cdot 4\text{H}_2\text{O}$: C, 45.43; H, 3.78; N, 8.83. Found: C, 45.74; H, 3.63; N, 8.67. Calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_7\text{Cl}_2\text{Cr}\cdot 4\text{H}_2\text{O}$: C, 48.24; H, 4.02; N, 16.42. Found: C, 48.05; H, 3.84; N, 16.36. Calcd. for $\text{C}_{26}\text{H}_{16}\text{N}_6\text{Cl}_2\text{SCr}\cdot 4\text{H}_2\text{O}$: C, 48.94; H, 3.92; N, 11.42. Found: C, 49.54; H, 3.52; N, 12.12. Calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{Cl}_2\text{ICr}\cdot 2\text{H}_2\text{O}$: C, 44.58; H, 3.10; N, 8.67. Found: C, 44.54; H, 3.35; N, 9.37.

Again the X-ray powder data show that all the 4-hydrates (Br^- , N_3^- , SCN^- , red Cl^-) are isomorphous. The colors of the

(1) See, for example, L. E. Orgel, "An Introduction to Transition Metal Chemistry," John Wiley and Sons, New York, N. Y., 1960, Chapter 6.

(2) M. Linhard, *Z. Elektrochem.*, 50, 224 (1944).

(3) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3577 (1952).