On Some Dark-colored Chloroplumbates (II, IV) of the Type $[M^{III}A_6]PbCl_6$

By Masayasu MORI(1)

(Received September 6, 1951)

Introduction

In 1934 Norman Elliott(2) determined the magnetic susceptibility of a violet black compound, $(NH_4)_2SbBr_6$, which had for years been generally believed to be a quadrivalent antimony compound, and found that the substance was diamagnetic and therefore could not contain quadrivalent antimony in an ordinary sense. Three years later K. A. Jensen(3) analysed the crystal structure of three similar compounds, $(NH_4)_2SbBr_6$, Rb_2SbBr_6 and Rb_2SbCl_6, by the x-ray powder method and found scarcely any difference between the lattice structure of these compounds and that of ammonium hexabromostannate (IV) etc. except

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(1) The present address: The Institute of Polytechnics Osaka City University, Minami-Ogi-Machi, Kitaku, Osaka.

(2) N. Elliott, *J. Chem., Phys.*, **2**, 298 (1934).

(3) K. A. Jensen, *Z.anorg. Chem.*, **232**, 193 (1937); *ibid.*, **233**, 295 (1937).

in their lattice dimensions, six halogen atoms being arranged around one antimony atom to make an octahedral structure. It is thus probable that these octahedral ions $SbBr_6$ are a mixture of $Sb\ Br^{-3}_6$ (in which Sb is tervalent) and $Sb\ Br^{-}_6$ (in which Sb is quinquevalent).

Yet another problem remains unsolved: Why do these antimony compounds present a dark violet appearance, which neither tervalent nor quinquevalent antimony compounds do?

While attempting to get some double salts between cobalt(III) or chromium(III) ammine chlorides and chlorides of heavy metals, the present author obtained crystalline compounds of empirical formulas, $[Co(NH_3)_6]PbCl_6$ (violet black), $[Co(NH_3)_5H_2O]PbCl_6$ (puce-colored), $[Cr(NH_3)_6]PbCl_6$ (violet black) and $[Cr(NH_3)_5H_2O]Pb\ Cl_6$ (puce-colored). These compounds, which from their formulas alone might be supposed to have tervalent lead atoms, have shown several points of resemblance to the antimony compounds above mentioned,—for example, in their anomalous coloration and magnetic property. In this paper the methods of preparation and magnetic data pertaining to these compounds will be given.

Experimental

Preparation of Chloroplumbates of the Type $[M^{III}A_6]PbCl_6$.—A solution containing chloroplumbic (IV) acid should first be prepared:

Three and three tenth grams of lead nitrate and 1 g. of potassium chlorate are dissolved in 50 ml. of water and the solution is poured little by little into 50 ml. of concentrated hydrochloric acid containing 1 g. of potassium chlorite. The white precipitate of lead(II) chloride produced at each addition is brought into solution by shaking and mixing, before the next portion is added. The yellow solution thus produced will contain lead(IV) at about 0.1 *M* in concentration.

In order to prepare a chloroplumbate of the type $[M^{III}A_6]PbCl_6$ (where M = Co or Cr), a solution of chloroplumbic acid thus prepared is mixed with a solution of a metal ammine, $[M^{III}A_6]Cl_3$; and the mixture is digested for some time. As starting metal ammine salts, it is recommended that those complex salts should be employed the preparation of which is the easiest. These metal ammines, together with proper solvents and modes of digestion, are given in Table 1.

In each case of preparation a chloroplumbate (IV) of a sallow color is first formed, and this, with liberation of chlorine, is quickly changed into a dark-colored chloroplumbate of the type $[M^{III}A_6]PbCl_6$. It is filtered, and washed with dilute hydrochloric acid and alcohol.

These dark-colored chloroplumbates are hardly soluble in dilute hydrochloric acid but are decomposed by water forming a suspension of lead dioxide. When any of these compounds is warmed with dilute sulfuric acid and iron(II) sulfate, all the lead is precipitated as lead(II) sulfate, and the supernatant liquid shows the color of the complex ions employed as the cation source.

Table 1

Salts to be prepared	Starting metal ammines	Dissolved in	Mixed with H_2PbCl_6 aq. and digested
$Co(NH_3)_6$–$PbCl_6$	4 g. of $Co(NH_3)_6Cl_3$(4)	300 ml. of 3*N* HCl	at 60°C. for 20 min.
$Co(NH_3)_6$ H_2O–$PbCl_6$	5 g. of $Co(NH_3)_5H_2O$–oxalate(5)	100 ml. of *N*/2 HCl	at 40°C. for 5 min.
$Cr(NH_3)_6$–$PbCl_6$	5 g. of $Cr(NH_3)_6$–$(NO_3)_3$	300 ml. of 3*N* HCl	at 60°C. for 20 min.
$Cr(NH_3)_5$ H_2O–$PbCl_6$	5 g. of $Cr(NH_3)_5H_2O$–$(NO_3)_3$	100 ml. of *N* HCl	at 40°C. for 5 min.

Of the starting complex salts mentioned above, hexamminechromium(III) nitrate has been prepared by a method modified from one proposed by S. M. Jörgensen, and aquopentamminechromium(III) nitrate by a new method of the present author's, which will be published shortly.

Analyses:

Calcd. for $Co(NH_3)_6PbCl_6$ or $[Co(NH_3)_6]_2(Pb^{II}Cl_6)$-$(Pb^{IV}Cl_6)$: Pb(total), 35.64 %; Pb(IV), 17.82 %; Co, 10.14 %; Cl, 36.63 %. Found: Pb(total), 35.89 %: Pb(IV) (determined by iodometry), 17.96 %; Co, 9.76 %; Cl, 36.95 %.

Calcd. for $Co(NH_3)_5H_2OPbCl_6$ or $[Co(NH_3)_5H_2O]_2$-$(Pb^{II}Cl_6)(Pb^{IV}Cl_6)$: Pb(total), 35.60 %; Pb(IV), 17.80 %; Co, 10.13 %; Cl, 36.56 %. Found: Pb (total), 35.88 %; Pb (IV), 16.85 %; Co, 9.62 %; Cl, 36.59 %.

Calcd. for $Cr(NH_3)_6PbCl_6$: Pb(total), 36.09 %; Cr, 9.06 %; Cl, 37.05 %. Found: Pb, 36.00 ; Cr, 8.63 %; Cl, 37.46 %.

Calcd. for $Cr(NH_3)_5H_2OPbCl_6$: Pb (total), 36.05 %; Cr, 9.04%; Cl, 37.00 %. Found: Pb, 35.00%; Cr, 9.30 %; Cl, 37.64 %.

Magnetic Susceptibility of the Chloroplumbates of the Type $[M^{III}A_6]PbCl_6$.—In order to test whether the Pb's in such cobalt complex chloroplumbates as $[Co(NH_3)_6]PbCl_6$ have unpaired electrons or not, it is only necessary to determine their magnetic susceptibility; for, in the tervalent cobaltammine complex ions the electrons are known to be all paired.

Measurements by the Gouy's cylinder method have given, as the mass-susceptibility of $[Co(NH_3)_6]PbCl_6$ and $[Co(NH_3)_5H_2O]PbCl_6$, values in the neighborhood of -0.3×10^{-6} E. M. U., thus proving that the Pb's in these compounds have no

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(4) Hexamminecobalt(III) chloride is easily prepared by bubbling air through a solution of cobalt (II) chloride in aqueous ammonia in the presence of ammonium chloride and adsorption charcoal. J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Son, Copenhagen, 1941. See *Chem. Abst.*, **34**, 6534 (1941) and also W. C. Fernelius *et al.*, "Inorganic Syntheses" Vol. II, McGraw Hill Book Co., New York, N. Y., 1946, p. 216.

(5) S. M. Jörgensen, *J. Prak. Chem.*, **31** 89 (1985); *Z. anorg. Chem.*, **17**, 461 (1898).

unpaired electrons and therefore cannot be tervalent in an ordinary sense.

The corresponding chromium compounds have shown strong paramagnetism, but this may be due to the presence of unpaired electrons in tervalent chromium complex ions. Considering every point of resemblance between these cobalt (III) and chromium(III) ammine chloroplumbates, it seems quite reasonable to think that in the latter, too, the Pb's do not exist in the tervalent state.

It therefore seems adequate to name these compounds as hexamminecobalt(III) chloroplumbate (II, IV) etc.

Considerations

Several series of compounds are known which have a characteristic dark color and contain the same element in different valence states.(6) The chloroplumbates (II, IV) described above appear to be new additions to these series, because:

(i) They are all dark colored which is inexplicable from the colors of the component ions. (Double salts between $[Co(NH_3)_6]Cl_3$ etc. and $Pb Cl_2$ show the color of $Co(NH_3)_6^{+++}$ ions etc.(7) and so do the chloroplumbates (IV) of these complex cations.)

(ii) The magnetic property of $[Co(NH_3)_6]PbCl_6$ and $[Co(NH_3)_5H_2O]PbCl_6$ denies the existence of any unpaired electrons in Pb's; and it is natural to think that the compounds contain $Pb Cl^{-4}_6$ and $PbCl^{-2}_6$.

(iii) Two very similar series:

$$(NH_4)_2SnBr_6, \ (NH_4)_2SbBr_6, \ (NH_4)_2TeBr_6$$

and

$$[Co(NH_3)_6]TlCl_6, \ [Co(NH_3)_6]PbCl_6, \ [Co(NH_3)_6]BiCl_6$$

are obtained where Sn, Sb and Te as well as Tl, Pb and Bi are arranged in the order of atomic numbers.(8)

Some hypotheses have been advanced by different authors as to the reason of the coloration of these mixed valence compounds ("Oscilieren" or "resonance" for example); but the experimental evidence is not sufficient for any of them; and anything like a perfect solution of the problem must depend on the fruits of further researches.

Summary

(1) Compounds ranging from violet black to puce in color, $[Co(NH_3)_6]PbCl_6$, $[Cr(NH_3)_6]PbCl_6$, $[Co(NH_3)_5H_2O]PbCl_6$ and $[Cr(NH_3)_5H_2O]Pb Cl_6$ have been prepared, by mixing a solution of $[Co(NH_3)_6]Cl_3$ etc. (in dil. HCl) and a solution containing H_2PbCl_6 and digesting them at 40° to 60°.

(2) $[Co(NH_3)_6]PbCl_6$ and $[Co(NH_3)_5H_2O]PbCl_6$ are diamagnetic and therefore it seems natural to consider these compounds as hexamminecobalt(III) chloroplumbate (II, IV) and aquopentamminecobalt(III) chloroplumbate (II, IV) respectively.

It is the author's genuine pleasure to acknowledge his indebtedness to Mr. Meitaro Endo without whose wholehearted coöperation in magnetic measurements, these pages could never have been written.

His sincere thanks are also due to Prof. Kenjiro Kimura and Dr. Yukio Murakami of the University of Tokyo for their tutorial advice and offer of laboratory facilities.

Chemical Institute, Faculty of Science,
The University of Tokyo, Tokyo

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(6) L. Pauling, *Chem. Eng. News*, **25**, 2970 (1947).

(7) F. Ephraim and P. Mosimann, *Helv. Chim. Acta*, **6**, 1122 (1923); *ibid.*, **9**, 630 (1926).

(8) In a letter to the author, Prof. Tokunosuké Watanabé and Mr. Masao Atoji of the University of Osaka have kindly informed him that the crystal lattice structure of $Co(NH_3)_6PbCl_6$ or $[Co(NH_3)_6](Pb^{II}Cl_6)(Pb^{IV}Cl_6)$ exhibits a close resemblance with a slight deformation to that of $Co(NH_3)_6TlCl_6$, the latter being composed of $Co(NH_3)_6{}^{+3}$ and $TlCl_6{}^{-3}$ arranged in a NaCl-type. See *Acta Cryst.*, **3**, 405 (1950).