CONTRIBUTION NO. 1616 FROM THE CENTRAL RESEARCH DEPARTMENT,
EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE 19898

Chemistry of Noble Metal Oxides. I. Syntheses and Properties of ABO_2 Delafossite Compounds

BY R. D. SHANNON,* D. B. ROGERS, AND C. T. PREWITT

Received November 21, 1969

Syntheses of the new members of the delafossite-type oxides $PtCoO_2$, $PdCoO_2$, $PdCrO_2$, $PdRhO_2$, $AgCoO_2$, $AgGaO_2$, $AgScO_2$, $AgInO_2$, and $AgTlO_2$ and single-crystal growth of $PtCoO_2$, $PdCoO_2$, $CuCoO_2$, $CuFeO_2$, $AgCoO_2$, $AgGaO_2$, $AgInO_2$, and $AgTlO_2$ are reported. Accurate cell dimensions for 17 members of the delafossite series are given along with thermal stability data for many of the compounds. Palladium and platinum are shown to be formally monovalent in $PdCoO_2$, $PdCrO_2$, $PdRhO_2$, and $PtCoO_2$. The platinum composition appears also to exist over a compositional range $Pt_{1+n}Co_{2-(2n/3)}O_4$ where n = 0.6–0.8. In this latter series, platinum is presumably divalent. Thus, the Pt compound may contain either Pt^+, Pt^{2+}, or a mixture of the monovalent and divalent ions. Closed systems are shown to be effective in preparing ternary noble metal oxides which cannot generally be prepared under autogenous pressure.

Introduction

The occurrence of highly crystalline oxides of the noble metals Pd, Pt, and Ag is not widespread because of the low free energies of formation of the simple oxides of the elements ($\Delta F_f = -14$, -19, and -2.6 kcal/mol, respectively, for PdO, PtO_2, and Ag_2O).[1] These low ΔF_f values result in low decomposition temperatures for PdO, PtO_2, and Ag_2O of 800, 650, and 300°, respectively. Consequently, ternary oxides containing a noble metal and a transition metal are somewhat difficult to prepare because noble metal oxides used as reagents frequently decompose in open systems before reaction occurs. There are many ternary oxides of Ru, Rh, and Ir, but few ternary oxides of the more noble metals Pd, Pt, Ag, and Au. Ternary oxides of Ru, Rh, and Ir include rare earth ruthenates[2] and $PbRuO_3$[3] (pyrochlore), alkaline earth ruthenates (perovskite),[4] rare earth rhodites (perovskite),[5] transition metal rhodites (spinel),[6] $RhVO_4$ and $RhSbO_4$ (rutile),[7] alkali rhodites,[8] rare earth iridates and $PbIrO_3$[3] (pyrochlore),[9] and alkaline earth iridates (perovskite).[10–12] Ternary oxides of Pd and Pt prepared at normal pressures appear to be limited to systems containing alkali and alkaline earth metals. In these systems the oxidized state of the noble metal is apparently stabilized by the high basicity of the companion metal oxide. There are no well characterized oxides of Au.

The difficulties normally encountered in the synthesis of ternary oxides of Pt, Pd, Ag, and Au can be overcome to a certain degree by using closed systems. We have found metathesis, high-pressure, and hydrothermal reactions to be successful in the preparation of ternary noble metal oxides and report in this paper the synthesis of oxides of the type ABO_2 having the delafossite structure where A = Pt, Pd, Ag, and Cu and B = Cr, Fe, Co, Rh, Al, Ga, Sc, In, and Tl.

The most unusual member of the delafossite series, made accidentally in an attempt to prepare a Ba–Co oxide hydrothermally, is $PtCoO_2$. Hexagonal platelike crystals of this compound were found to have a room-temperature metallic resistivity in the basal plane of 3×10^{-6} ohm-cm, a value only slightly greater than that of copper metal. Because of this unusually low resistivity and the fact that $PtCoO_2$ is, to our knowledge, the first ternary oxide of Pt and a first-row transition metal, a detailed study of $PtCoO_2$ and other compounds isotypic with delafossite ($CuFeO_2$) was begun. In part I of this series we report the synthesis and some of the properties of the new compounds $PtCoO_2$, $PdCoO_2$, $PdCrO_2$, $PdRhO_2$, $AgCoO_2$, $AgGaO_2$, $AgScO_2$, $AgInO_2$, and $AgTlO_2$ and the growth of single crystals of $PtCoO_2$, $PdCoO_2$, $CuCoO_2$, $CuFeO_2$, $AgCoO_2$, $AgGaO_2$, $AgInO_2$, and $AgTlO_2$. In part II structure refinements of four compounds in this series—$PtCoO_2$, $PdCoO_2$, $CuFeO_2$, and $AgFeO_2$—are reported and in part III the crystal chemistry and electrical properties of delafossite-type oxides are discussed.

Experimental Section

Reagents.—Co_3O_4 used in this study was reagent grade obtained from the Mallinckrodt Co. X-Ray diffraction analysis showed only the presence of Co_3O_4. CoO was prepared from reagent grade $CoCO_3$ by decomposition under vacuum at 400°. The PtO_2 was prepared hydrothermally from commercial PtO_2 by a method already described.[13] $PtCl_2$ was obtained from J. Bishop and Co., whereas $PdCl_2$ was obtained from Fisher Scientific Co. Amorphous PdO from the City Chemical Co. was heated in flowing O_2 at 800° to remove water. Cu_2O, CuO, and CuCl were B & A reagent grade chemicals. The Ag_2O used for hydrothermal experiments was obtained from K & K Laboratories. X-Ray analysis showed very weak diffraction lines attributable to Ag_2CO_3. The sesquioxides of Al, Cr, Fe, Ga, In, and Tl were obtained from Spex Industries, Inc., and were of at

---

[1] A. Glassner, Report ANL-5750, Argonne National Laboratory, Argonne, Ill., 1957.

[2] F. Bertaut, F. Forrat, and M. Montmory, *C. R. Acad. Sci.*, **249**, 829 (1959).

[3] J. M. Longo, P. M. Raccah, and J. B. Goodenough, *Mater. Res. Bull.*, **4**, 191 (1969).

[4] J. J. Randall and R. Ward, *J. Amer. Chem. Soc.*, **81**, 2629 (1959).

[5] (a) R. Chazalon, F. F. Bertaut, and T. Duc, *Bull. Soc. Fr. Mineral. Cristallogr.*, **87**, 98 (1964); (b) R. D. Shannon, *Acta Crystallogr., Sect. B*, **26**, 447 (1970).

[6] G. Blasse, *Philips Res. Rep., Suppl.*, No. 3 (1964).

[7] G. Bayer, *Ber. Deut. Keram. Ges.*, **39**, 535 (1962).

[8] F. F. Bertaut and J. Dulac, *J. Phys. Chem. Solids*, **21**, 118 (1961).

[9] M. Montmory and F. Bertaut, *C. R. Acad. Sci.*, **252**, 4171 (1961).

[10] P. C. Donohue, L. Katz, and R. Ward, *Inorg. Chem.*, **5**, 535 (1966).

[11] J. M. Longo and J. A. Kafalas, to be submitted for publication.

[12] F. Rodi and D. Babel, *Z. Anorg. Allg. Chem.*, **336**, 18 (1965).

[13] R. D. Shannon, *Solid State Commun.*, **6**, 139 (1968).

TABLE I
SYNTHESIS AND THERMAL STABILITY OF ABO_2 DELAFOSSITE-TYPE COMPOUNDS

Compound	Synthesis		Description of Product	Thermal Stability	Comments
$PtCoO_2$	$Pt + Co_3O_4$-H (HCl)	700°	hex. metallic platelets	$PtCoO_2 \xrightarrow{850°} Pt + CoO + 1/2\ O_2$	dta, tga, x-ray
$PdCoO_2$	$PdCl_2 + CoO$-M	700°	hex. metallic platelets	$PdCoO_2 \xrightarrow{900°} Pd + CoO + 1/2\ O_2$	dta, tga, x-ray
$PdCrO_2$	$Pd + PdCl_2 + 2LiCrO_2$-M	800°	black powder	925°	wt. loss and endotherm
$PdRhO_2$	$Pd + PdCl_2 + 2LiRhO_2$-M	800°	black powder	$PdRhO_2 \xrightarrow{800°} Pd$ + unident. phase	dta, tga, x-ray
$CuCoO_2$	$CuCoO_2$-H(Na_2CO_3)	700°	black hex. platelets	-----	
$CuAlO_2$	$Cu_2O + Al_2O_3$-H (NaOH)	500°	black powder	$4CuAlO_2 + 1/2\ O_2 \xrightarrow{650°} Cu_2O + 2CuAl_2O_4$	dta, tga, x-ray
$CuGaO_2$	$Cu_2O + Ga_2O_3$-H (NaOH)	500°	grey powder	500°	wt. gain
$CuFeO_2$	$CuFeO_2$-H (NaOH)	700°	black hex. platelets	$4CuFeO_2 + 1/2\ O_2 \xrightarrow{550°} Cu_2O + 2\ CuFe_2O_4$	dta, tga, x-ray
$CuRhO_2$	$Cu_2O + Rh_2O_3$-H (NaOH)	700°	brown powder	-----	
$AgCoO_2$	$3Ag_2O + 2Co_3O_4$-H (NaOH)	500°	black hex. platelets	600°	endotherm
$AgCrO_2$	$AgNO_3 + LiCrO_2$-F (KNO_3)	350°	black powder	-----	
$AgFeO_2$	$Ag_2O + Fe_2O_3$-H (NaOH)	500°	red transparent hex. platelets	$2AgFeO_2 \xrightarrow{700°} 2Ag + Fe_2O_3 + 1/2\ O_2$	Ref. 16
$AgRhO_2$	$AgNO_3(l) + LiCoO_2$-F (KNO_3)	350°	black powder	$AgRhO_2 \xrightarrow{1000°} Ag$ + unident. phase	dta, tga, x-ray
$AgGaO_2$	$Ag_2O + Ga_2O_3$-H (NaOH)	700°	grey transparent hex. platelets	$AgGaO_2 \xrightarrow{700°} Ag$ + unident. phase	dta, tga, x-ray
$AgInO_2$	$Ag_2O + In_2O_3$-H (NaOH)	500°	orange hex. plates	675°	endotherm
$AgScO_2$	$Ag_2O + Sc_2O_3$-H (NaOH)	500°	white powder	770°	endotherm
$AgTlO_2$	$Ag_2O + Tl_2O_3$-H (NaOH)	500°	black crystals	475°	wt. loss and endotherm

H = hydrothermal
M = metathesis
F = flux

least 99.99% purity. Rh_2O_3 was produced by heating hydrated $RhCl_3$ in air at 800°.

Synthesis.—A variety of synthesis techniques have been found applicable for the preparation of noble metal compositions with delafossite structure. In general, they involve either low-temperature reaction, *e.g.*, metathesis with formation of a fused-salt by-product, or reactions under oxidizing conditions, *e.g.*, solid-state reactions at high pressures of internally generated oxygen. In some cases, both oxidizing conditions and low temperatures can be advantageously used together, *e.g.*, in hydrothermal or oxidizing flux reactions.

A summary of some applicable techniques is given in Table I for specific compositions. In addition, a brief description of the various methods is given below.

A. Hydrothermal Reactions.—Typically, hydrothermal syntheses were carried out in sealed, thin-walled platinum or gold tubes, approximately 5 in. long and 3/8-in. diameter, with an externally applied pressure of 3000 atm and at a temperature of 500–700°. Length of time at reaction temperatures was about 24 hr in all cases; subsequently, the tubes and their contents were cooled at a rate of 100°/hr to room temperature.

In the case of $PtCoO_2$, thin hexagonal plates about 1 mm across an edge (see Figure 1a) could be grown on the walls of a Pt reaction tube that had been charged with 2 g of Co_3O_4 in a 20% aqueous solution of HCl occupying 50% of the container volume. Alternatively, the material can be prepared as a fine powder by charging a Pt tube with Co_3O_4, PtO_2, and H_2O followed by hydrothermal reaction. However, the latter method generally results in moderate amounts of Co_3O_4 and Pt as impurity phases. The habit of crystals can be changed from hexagonal platelets to elongated rhombohedra by the addition of 10–15 wt % MnO_2 to the reaction charge (see Figure 1b). Altered cell dimensions and spectrographic analyses of the rhombohedral crystals indicated that Mn had been substituted for Co up to approximately 2%.

Single crystals of $CuMO_2$ (M = Co and Fe) and of $AgMO_2$ (M = Co, Cr, Fe, Ga, In, and Tl) and powder samples of $CuMO_2$ (M = Al, Ga, and Rh) could be prepared hydrothermally in basic solutions by a method similar to that employed by Croft, Tombs, and England[14] in their synthesis of $AgFeO_2$. In the case of

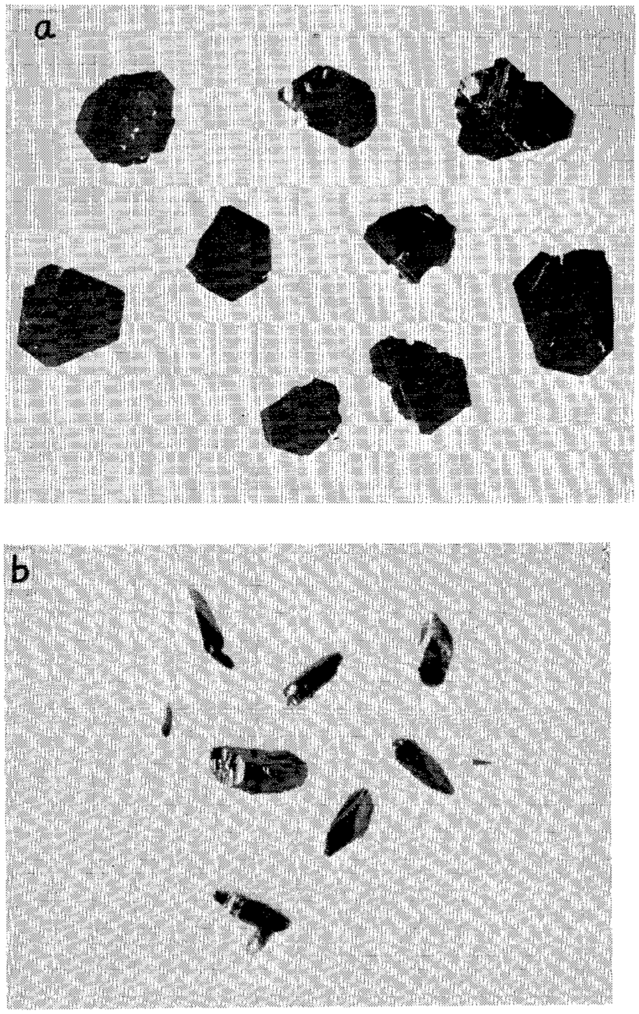

Figure 1.—(a) $PtCoO_2$ plates at 15× magnification. (b) $PtCoO_2$ rhombohedra at 60× magnification.

---

[14] W. J. Croft, N. C. Tombs, and R. E. England, *Acta Crystallogr.*, **17**, 313 (1964).

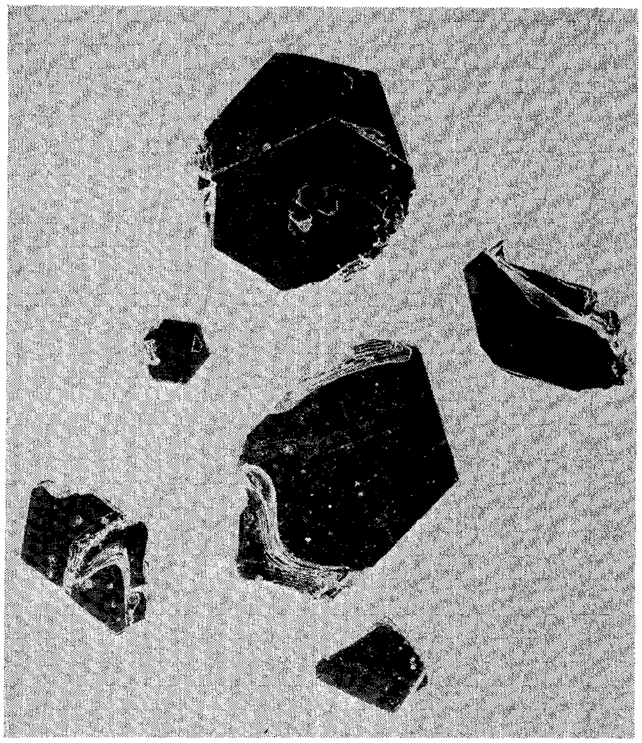

Figure 2.—Hexagonal plates of $CuFeO_2$ at 13× magnification.

$CuFeO_2$, reddish black crystals could be grown as hexagonal plates (see Figure 2) from a charge of 0.5 g of prereacted $CuFeO_2$ in 4 ml of 10 wt % NaOH solution at 700°. The crystals were about 4 mm across an edge. Powder samples of $CuAlO_2$, $CuGaO_2$, and $CuRhO_2$ could be prepared at lower temperatures (~500°) by reaction of Cu_2O with stoichiometric quantities of the appropriate sesquioxides. Growth of the silver-containing analogs was accomplished in more basic solutions (50 wt % NaOH) at 500° by reaction of the sesquioxides with an excess of Ag_2O.

B. Metathetical Reactions.—Reactions involving an exchange of anions between two reagent phases were found to be particularly effective in the synthesis of Pt, Pd, and Cu analogs of the delafossites at low pressures and relatively low temperatures. Typically, these reactions utilized a halide of the noble metal as one reagent and were carried out in sealed, silica ampoules at 500–700° with no application of external pressure. By-product halide salts could be removed after reaction by leaching with H_2O, normally leaving a single-phase, delafossite product. In some cases, residues of other phases, *e.g.*, Pd or $PdCl_2$, remained after the aqueous leach; these could be removed with appropriate solvents, *e.g.*, HBr for $PdCl_2$ or aqua regia for Pd. This method is not applicable to the synthesis of ternary silver oxides because of the high stability of the silver halides.

The following reactions are exemplary for the Pd and Cu oxides

$$PdCl_2 + 2CoO \longrightarrow PdCoO_2 + CoCl_2 \quad (1)$$

$$Pd + PdCl_2 + Co_3O_4 \longrightarrow 2PdCoO_2 + CoCl_2 \quad (2)$$

$$Pd + PdCl_2 + 2LiMO_2 \longrightarrow 2PdMO_2 + 2LiCl \quad (M = Co, Cr, Rh) \quad (3)$$

$$Pd + PdCl_2 + 2LaMO_3 \longrightarrow 2PdMO_2 + 2LaOCl \quad (M = Co, Cr, Rh) \quad (4)$$

$$CuCl + LiFeO_2 \longrightarrow CuFeO_2 + LiCl \quad (5)$$

For the case of platinum cobalt oxide, reaction stoichiometries of the type used for $PdMO_2$ analogs did not lead to single-phase products. However, if nonstoichiometry of the type $Pt_{1+n}Co_{2-(2n/3)}O_4$ ($0.6 \leq n \leq 0.8$) was assumed for the platinum compound, then single-phase products were obtainable from appropriately adjusted reaction stoichiometries

$$(1 + n)PtCl_2 + \left(1 - \frac{n}{3}\right)Co_3O_4 + \frac{4n}{3}CoO \longrightarrow Pt_{1+n}Co_{2-(2n/3)}O_4 + (1 + n)CoCl_2 \quad (6)$$

$$(1 + n)PtCl_2 + 2LiCoO_2 \longrightarrow Pt_{1+n}Co_{2-(2n/3)}O_4 + 2LiCl + \frac{2n}{3}CoCl_3 \quad (7)$$

$$(1 + n)PtCl_2 + \left(2 - \frac{2n}{3}\right)LaCoO_3 \longrightarrow Pt_{1+n}Co_{2-(2n/3)}O_4 + (2 - 2n)LaOCl + \frac{4n}{3}LaCl_3 \quad (8)$$

The products of these reactions, after removal of the soluble chlorides by leaching, consisted of a single phase of platinum cobalt oxide, isostructural with the product from hydrothermal synthesis, in the form of small, hexagonal, platelike crystallites (~0.5 mm on an edge). These results indicate a range of stoichiometry for the platinum cobalt oxide phase.

C. Solid-State Reactions.—Except for Cu analogs, direct reaction of oxide reagents to form delafossite is precluded at ambient pressures because of the high temperatures necessary for solid-state diffusion, coupled with the inherent instability of the binary oxide reagents. Application of pressure, however, permits synthesis of essentially all of the delafossite phases by this method. The following reactions are typical

$$Cu_2O + Fe_2O_3 \xrightarrow[1000°]{\text{sealed silica tubes, ambient pressure}} 2CuFeO_2 \quad (9)$$

$$PdO + CoO \xrightarrow[800°]{\text{sealed Pt tubes, 3 kbars pressure}} PdCoO_2 \quad (10)$$

$$3PtO_2 + Co_3O_4 \xrightarrow[700-950°]{\text{sealed Au tubes, 3 kbars pressure}} 3PtCoO_2 + 2O_2 \quad (11)$$

D. Oxidizing Flux Reactions.—An unusual method for low-temperature synthesis under oxidizing conditions, which involved the use of a low-melting, oxidizing flux, was employed in the synthesis of $AgCrO_2$, $AgRhO_2$, and $AgCoO_2$. In these preparations, use was made of $AgNO_3$–KNO_3 fluxes in which $AgNO_3$ was also a reagent in reactions of the type

$$AgNO_3(l) + LiMO_2(s) \xrightarrow[350°]{} LiNO_3(l) + AgMO_2(s) \quad (M = Co, Rh, Cr) \quad (12)$$

In a typical example, 0.64 g of $LiCrO_2$, 4.05 g of $AgNO_3$, and 2.5 g of KNO_3 were sealed in an evacuated silica tube and heated at 350° for ~4 days. The product $AgCrO_2$ was recovered as a fine black powder by leaching the nitrate mixture with water. In the case of $AgCrO_2$ synthesis, $Ag_2Cr_2O_7$ was also present as a residue from the aqueous leach but was removable by subsequent leaching with a dilute solution of NH_4OH.

Methods.—The density of several crystals of $PtCoO_2$ was determined by the displacement method in bromoform. The densities of several powder samples of $PtCoO_2$ were determined pycnometrically.

Decomposition temperatures of certain delafossite phases were determined by dta, tga, and high-temperature X-ray diffraction. Dta and tga runs were made using the Du Pont Series 900 dta and Du Pont Series 950 tga units. High-temperature X-ray patterns were obtained on a powder camera designed by Central Research Laboratories in Red Wing, Minn.

X-Ray powder diffraction data were obtained at 25° on a de Wolff–Guinier camera; *d* values were calculated using $\lambda(Cu\ K\alpha_1)$ 1.54051 Å with a KCl internal standard ($a = 6.2931$ Å).

Magnetic susceptibility measurements were made on samples of $PdCoO_2$ and $PtCoO_2$ using a Faraday balance. These measurements covered the temperature range 4.2–300°K.

Chemical analyses of the palladium cobalt oxide and platinum cobalt oxide compositions, for which stoichiometries were questionable, employed standard techniques for determining Pt and Co content of solutions obtained by dissolving in aqua regia metallic residues from a hydrogen reduction of the oxides. Oxygen contents of the oxides were determined using a Leco "Nitrox 6" oxygen analyzer, which incorporates inert-gas fusion and a gas chromatographic readout.

Results

Table II lists cell dimensions of the Pt-, Pd-, Cu-, and Ag-containing delafossite phases. Of these compounds, nine have been prepared for the first time. These include $PtCoO_2$, $PdCoO_2$, $PdCrO_2$, and $PdRhO_2$. The X-ray diffraction patterns of these compounds are given in Table III. These compounds are the first known examples of ternary oxides of the noble metals Pt and Pd with first-row transition metals and provide the first examples of two-coordinated Pt and Pd atoms. In addition, $PtCoO_2$, $PdCoO_2$, $PdCrO_2$, and $PdRhO_2$ are unusual in that Pt and Pd appear to be formally monovalent.

TABLE II

CELL DIMENSIONS OF ABO_2 DELAFOSSITE-TYPE COMPOUNDS

Compound	a, Å	c, Å	Unit Cell Volume, Å3
$PtCoO_2$ - hydroth.	2.8300 ± 4	17.837 ± 2	123.80
- metath.	2.8230 ± 4	17.815 ± 3	
$PdCoO_2$	2.8300 ± 3	17.743 ± 2	123.04
$PdCrO_2$	2.9230 ± 3	18.087 ± 3	133.83
$PdRhO_2$	3.0209 ± 2	18.083 ± 2	142.91
$CuCoO_2$	2.8488 ± 1	16.920 ± 2	118.92
$CuAlO_2$	2.8571 ± 2	16.940 ± 2	119.76
$CuCrO_2$(20)	2.975	17.096	131.04
$CuGaO_2$	2.9750 ± 2	17.154 ± 2	131.48
$CuFeO_2$	3.0351 ± 1	17.166 ± 2	136.94
$CuRhO_2$	3.074 ± 1	17.094 ± 9	139.93
$AgCoO_2$	2.8729 ± 2	18.336 ± 2	131.07
$AgAlO_2$(18)	2.890 ± 2	18.27 ± 2	132.1
$AgCrO_2$	2.9843 ± 4	18.511 ± 4	142.77
$AgGaO_2$	2.9889 ± 2	18.534 ± 2	143.39
$AgFeO_2$	3.0391 ± 2	18.590 ± 2	148.69
$AgRhO_2$	3.0684 ± 4	18.579 ± 4	151.48
$AgScO_2$	3.2112 ± 2	18.538 ± 2	165.55
$AgInO_2$	3.2772 ± 3	18.881 ± 3	175.62
$AgTlO_2$	3.568 ± 2	18.818 ± 6	207.5

Five new compounds in the $AgMO_2$ series were prepared (M = Co, Ga, Sc, In, and Tl). Their X-ray diffraction patterns have been sent to ASTM. Although no new Cu-containing members of the series were found, growth of single crystals of $CuCoO_2$ and $CuFeO_2$ is reported for the first time. Single crystals of $AgCoO_2$, $AgGaO_2$, $AgInO_2$, and $AgTlO_2$ were also grown.

Thermal stabilities for some of the delafossite-type phases are listed in Table I. The Pt, Pd, and Ag compounds appear to decompose to the precious metal and a transition metal oxide. The stability of the Cu-containing phases appears to be controlled by the oxidation of the cuprous ion with simultaneous formation of the Cu spinel.

The results of some chemical analyses of $PdCoO_2$ and $PtCoO_2$ are given in Table IV. A sample of $PdCoO_2$ produced by reaction of $PdCl_2$ and CoO (reaction 1) was carefully washed in aqueous HBr and aqua regia to remove $CoCl_2$ and any residual $PdCl_2$ or Pd. Analysis of this sample gave the composition $Pd_{1.00}Co_{1.06}O_{2.00}$, which is in reasonable agreement with the nominal stoichiometry.

Although analysis of several crystals of $PtCoO_2$ prepared hydrothermally agreed reasonably well with the 1:1:2 stoichiometry, metathesis reactions formulated to give the stoichiometric compound failed to yield a single-phase product, as discussed in the Experimental Section of this paper. Further metathesis reactions formulated to give $Pt_{0.8}Co_{0.8}O_2$ (*i.e.*, reactions 6, 7, and 8), however, did yield a single-phase product. Therefore, it would appear that platinum cobalt oxide is capable of existence over a range of stoichiometries and that different compositions within that range are accessible by different synthesis techniques. Several results of chemical analyses on samples of platinum cobalt oxides are listed in Table IV. These results support the conclusion of variable stoichiometry for this phase and suggest considerable variation from the nominal compositions. It should be noted from Table II that there is also a significant variation in cell dimensions between those samples prepared hydrothermally and those prepared by metathesis.

Discussion

A. Stoichiometry and Valency of Pd- and Pt-Containing Delafossite Phases.—The stoichiometry of the delafossite phases $CuAlO_2$,[15,16] $CuCrO_2$,[17] $CuFeO_2$,[18] $AgAlO_2$,[15] and $AgFeO_2$[14,19] has previously been established as 1:1:2 by chemical analyses and density measurements. It has also been established from considerations of interatomic distances,[20] from electrostatic energy calculations,[21] and from Mössbauer[22] studies that iron is present in the trivalent and copper in the monovalent state in $CuFeO_2$. In part II of this series further arguments for $Cu^{I}Fe^{III}O_2$ and $Ag^{I}Fe^{III}O_2$ will be presented based on accurate interatomic distances in these compounds. Because Buist, *et al.*,[23] reported

---

[15] W. Gessner, *Z. Anorg. Allg. Chem.*, **352**, 145 (1966).

[16] H. Hahn and C. de Lorent, *ibid.*, **279**, 281 (1955).

[17] W. Dannhauser and P. A. Vaughn, *J. Amer. Chem. Soc.*, **77**, 896 (1955).

[18] H. Wiedersich, J. W. Savage, A. H. Muir, Jr., and D. G. Swarthout, *Mineral. Mag.*, **36**, 643 (1968).

[19] A. Krause, Z. Ernst, St. Gawrych, and W. Kocay, *Z. Anorg. Allg. Chem.*, **228**, 352 (1936).

[20] A. Pabst, *Amer. Mineral.*, **31**, 539 (1946).

[21] C. Delorme and F. Bertaut, *J. Phys. Radium*, **14**, 129 (1953).

[22] A. H. Muir, Jr., and H. Wiedersich, *J. Phys. Chem. Solids*, **28**, 65 (1967).

[23] D. S. Buist, A. M. M. Gadalla, and J. White, *Mineral. Mag.*, **35**, 731 (1966).

TABLE III

POWDER DIFFRACTION DATA FOR SOME ABO_2 DELAFOSSITE PHASES

			$PtCO_2$*			$PdCoO_2$			$PdCrO_2$			$PdRhO_2$		
H	*K*	*L*	d_{calcd}	d_{obsd}	*I*	d_{calcd}	d_{obsd}	*I*	d_{calcd}	d_{obsd}	*I*	d_{calcd}	d_{obsd}	*I*
0	0	3	5.9433	5.9450	90	5.9144	5.9072	45	6.0291	6.0229	20	6.0275	6.0209	5
0	0	6	2.9717	2.9728	100	2.9572	2.9559	90	3.0146	3.0137	65	3.0138	3.0130	90
1	0	1	2.4255	2.4260	70	2.4275	2.4272	80	2.5070	2.5065	30	2.5892	2.5884	10
0	1	2	2.3609	2.3609	90	2.3621	2.3616	100	2.4377	2.4375	100	2.5131	2.5141	100
1	0	4	2.1459	2.1460	70	2.1450	2.1448	85	2.2088	2.2088	40	2.2643	2.2644	95
0	1	5	2.0184	2.0185	30	2.0165	2.0165	15	2.0740	2.0753	2	2.1197	2.1198	5
0	0	9	1.9811	1.9814	40	1.9715	1.9713	50	2.0097	2.0089	10	2.0092	2.0088	2
1	0	7	1.7651	1.7655	30	1.7618	1.7616	30	1.8082	1.8084	5			
0	1	8	1.6481	1.6483	60	1.6444	1.6445	85	1.6863	1.6864	30	1.7104	1.7104	85
0	0	12	1.4858	1.4856	20	1.4786	1.4788	35	1.5073	1.5074	5	1.5069	1.5071	15
1	0	10	1.4413	1.4415	40	1.4372	1.4373	70	1.4717	1.4722	15	1.4875	1.4874	70
1	1	0	1.4135	1.4135	30	1.4149	1.4149	65	1.4615	1.4614	20	1.5104	1.5106	85
1	1	3	1.3751	1.3751	15	1.3760	1.3762	15						
0	1	11	1.3515	1.3513	10	1.3473	1.3474	15	1.3789	1.3791	2			
1	1	6	1.2765	1.2764	30	1.2763	1.2762	65	1.3151	1.3151	15	1.3503	1.3503	80
2	0	2										1.2946	1.2945	60

TABLE IV

ANALYTICAL DATA FOR $PdCoO_2$ AND $PtCoO_2$

Nominal compn	Density, g/cm³		% Pd or Pt		% Co		% O	
	d_x	d_m	Calcd	Found	Calcd	Found	Calcd	Found
$PdCoO_2$			53.99	53.29	29.82	30.5		
$PtCoO_2$	11.5	11.5	68.3	68.7	20.6	18.6	11.19	
$Pt_{0.8}Co_{0.8}O_2$	9.5	11.1	66.36	68.2	20.04	18.7	13.60	13.15
$Pt_{0.8}Co_{0.8}O_2$			66.36	66.66	20.04	19.5	13.60	12.45
$Pt_{0.9}Co_{0.73}O_2$			70.2	68.7	17.1	19.8	12.7	11.5

that $CuFeO_2$ does not exist as a stoichiometric phase (therefore, not as $Cu^IFe^{III}O_2$), we attempted to prepare the phase with varying stoichiometry under controlled, sealed-tube conditions by varying the stoichiometry of reaction 9. In all cases in which the stoichiometry varied from that of reaction 9, the product was contaminated with large amounts of secondary and tertiary phases. Specifically, when we attempted to reproduce the stoichiometry reported by Buist, *et al.* (*e.g.*, $3Cu_2O \cdot Fe_3O_4$), we obtained spinel as a major phase. We conclude, consistent with the work of Wiedersich, *et al.*,[18,22] and with our determination of interatomic distances reported in part II, that delafossite copper iron oxide exists only as a stoichiometric or, at least, nearly stoichiometric phase.

By analogy with the known delafossite phases, one would expect monovalent Pd and trivalent Co in $PdCoO_2$. However, because monovalent Pd had never been observed in an oxide and because platinum cobalt oxide apparently exhibits varying stoichiometry, the formulation $Pd^ICo^{III}O_2$ seemed suspect. For example, one might imagine $Pd^{II}Co^{II}O_2$ since Pd is normally divalent and Co^{II} is not uncommon; alternatively, the possibility of $Pd^{II}{}_{0.8}Co^{III}{}_{0.8}O_2$ seemed reasonable on the basis of our experience with the platinum system. However, several attempts to carry out reactions analogous to reaction 6 with $PdCl_2$ in lieu of $PtCl_2$, which for $n = 0.6$ would have given $Pd_{0.8}Co_{0.8}O_2$, were unsuccessful. This result was consistent with chemical analyses, which for the Pd analog always gave reasonable agreement with the stoichiometric formulation. Thus, we conclude that $PdCoO_2$ does not exhibit a broad range of stoichiometry. A refinement of the crystal structure of $PdCoO_2$ (part II) showed Co to be present in the trivalent low-spin state. Furthermore, Cr and Rh could be substituted for Co whereas no normally divalent cation substitution could be made. Since the trivalent state is the most stable for Cr and Rh, there seems little doubt that Pd is present formally as Pd^+. Further evidence for Pd^I-$Co^{III}O_2$ is the very weak non-Curie–Weiss, paramagnetic susceptibility [$\chi_g \approx (94/T + 0.93) \times 10^{-6}$ emu/g] found for $PdCoO_2$. The monovalent palladium sublattice, with delocalized electrons giving rise to a high metallic conductivity (see part III), would normally be expected to contribute only a temperature-independent (Pauli paramagnetic) term, while low-spin, trivalent cobalt would be diamagnetic. The weak, temperature-dependent term is most likely due to a small paramagnetic impurity. For example, a 1% Co impurity would account reasonably well for the observed behavior. Alternatively, a small amount of high-spin Co in thermal equilibrium with low-spin Co^{III}, as found occasionally for other oxides of cobalt,[24] would contribute a temperature-dependent term to the observed susceptibility.

To our knowledge this is the first time monovalent Pd is reported in an oxide compound. However, it must be emphasized that this is only a *formal* valence state. As discussed in part III of this series, the palladium compounds, as well as $PtCoO_2$, exhibit high electrical conductivity and it is doubtful that the concept of monovalent Pd has much meaning in such systems.

For platinum cobalt oxide, magnetic susceptibility data [$\chi_g \approx (126/T + 0.38) + 10^{-6}$ emu/g] and an accurate Co–O distance obtained from a refinement of the structure also indicated the presence of trivalent low-spin Co. These results implied the presence of Pt^I (d^9) in $PtCoO_2$ with an electron configuration identical with that of Pd^I (d^9). However, as previously described in this paper, the platinum system exists over a relatively broad range of stoichiometry and,

---

(24) G. Blasse, *J. Appl. Phys.*, **36**, 879 (1965).

presumably, contains variable oxidation states of Pt. For $Pt_{0.8}Co_{0.8}O_2$, all of the platinum would be divalent, for $PtCoO_2$, all of the platinum would be monovalent, and for intermediate compositions, mixtures of monovalent and divalent platinum would occur. Our work would suggest that the platinum system is the only one of the known delafossite systems in which wide variations of stoichiometry can occur. In this system, the stoichiometry that does pertain seems to be dependent on synthesis conditions, perhaps on applied pressure. Metathetical reactions at ambient pressures tended to give the larger variations in stoichiometry.

B. Chemistry of Noble Metal Oxides.—The noble metals come from two groups in the periodic table—the platinum metal and coinage metal groups. The binary and ternary oxides of most of these metals have, until recently, been poorly characterized, partly because of their scarcity and partly because of difficulties in preparation. The major difficulty encountered in preparation is the tendency of the more noble metal oxides to dissociate at low temperatures before reaction can occur or before solid-state diffusion becomes rapid enough to allow highly ordered crystalline oxides to form. The tendency to dissociate is accentuated as one proceeds diagonally downward to the right across the "noble metal" group of the periodic table (Table V). The free energies of formation, ΔF_f, a rough measure of their nobility, become less and less negative until at the extreme lower right, $\Delta F_f(Au_2O_3)$ is positive. Since one expects similar free energy of formation trends in the ternary oxides, this behavior is reflected in the number of known ternary oxide compounds of the elements.

TABLE V

FREE ENERGIES OF FORMATION OF SOME NOBLE METAL OXIDES, ΔF_f (KCAL/MOL)

			Cu_2O
			−34.5
RuO_2	Rh_2O_3	PdO	Ag_2O
−39.7	−48.9	−14	−2.6
OsO_2	IrO_2	PtO_2	Au_2O_3
−49.5	−32	−19	+18.8

In this paper we have illustrated several obvious ways to overcome this difficulty in synthesis: (1) increasing the oxygen partial pressure in the system and (2) utilizing low-temperature synthesis methods—metathesis and oxidizing flux reactions. The hydrothermal method in some cases combines these two factors.

In one variation of method 1 a sample is placed in a bomb with internal oxygen pressure. This method was used successfully by Muller and Roy[25] and Shannon[13] to prepare phases in the Pt–O and Rh–O systems; it frequently results in nonequilibrium phases and shows considerable sensitivity to starting materials. Another variation involves placing stoichiometric mixtures of the oxides in a sealed container and externally pressurizing the entire sample. We have utilized pressures of 3 kbars in this method and found the same disadvantages as for internal pressurizing. Frequently the samples are not single phase and large crystal fragments cannot be obtained to provide adequate characterization.

Metathesis reactions were used to prepare the Pt- and Pd-containing samples and $CuFeO_2$ and are particularly advantageous in producing highly crystalline samples that can be easily purified. This method is believed to work well because of the less refractory nature of the reactants and because of the large free energy of formation and fluxing action of the resultant alkali halides. The method is, however, not applicable to the synthesis of $AgMO_2$ delafossite phases because of the stability of AgCl.

In the hydrothermal method used to prepare $PtCoO_2$, HCl apparently reacts with the Pt container to give an intermediate platinum compound which in turn reacts with the Co_3O_4 to give $PtCoO_2$. Similar reactions using HF, HBr, or HI solutions were unsuccessful. Hydrothermal syntheses using concentrated solutions of NaOH were highly effective in crystal growth.

An unusual result is that Co appears to be the only metal capable of reacting with Pt to form an ABO_2 delafossite phase. Similar hydrothermal reactions were attempted with Mn-, Ni-, and Zn-containing oxides without success. Similarly, high-pressure reactions at 65 kbars of PtO_2 and the transition metals Ti, Cr, Mn, Fe, Ni, Cu, Rh, and In did not result in any other $PtMO_2$ phase. Finally, metathesis reactions using $PtCl_2$ and $LiMO_2$ or appropiate metal oxide, where M = Cr, Rh, Mn, Ni, or Fe, were unsuccessful. Although the failure of these methods to produce any other Pt-containing delafossite phases does not rule out their existence, it would appear that for some unexplained reason Co is unique.

Acknowledgments.—We wish to thank J. F. Weiher for magnetic susceptibility data and to acknowledge, posthumously, W. H. Cloud for helpful discussions.

---

(25) O. Muller and R. Roy, *J. Less-Common Metals*, **16**, 129 (1968).