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The Preparation and Characterization of $CdIr(OH)_6$ and $ZnIr(OH)_6$

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$CdIr(OH)_6$ and $ZnIr(OH)_6$ were isolated and characterized in the process of synthesizing new ternary oxides of the platinum-group metals by means of thermal decomposition of hydroxide intermediates. Both compounds crystallize with an ordered ReO_3-type structure. $CdIr(OH)_6$ is tetragonal with $a = 7.86$ Å and $c = 7.91$ Å. It is a magnetically dilute insulator. $ZnIr(OH)_6$ is cubic with $a = 7.64$ Å. It is an insulator with anomalous magnetic behavior. The cadmium and zinc iridium hexahydroxides decompose at 180 and 170°C, respectively.

Introduction

The synthesis of ABO_3 oxides utilizing thermal decomposition of the appropriate $AB(OH)_6$ hydroxide has, in the past, proven to be a technique worthy of further investigation. In 1963, Badarau, Poix and Michel (*1*) were able to isolate two $CdSnO_3$ derivatives using this method. In addition, they obtained a crystalline sample of $CdSn(OH)_6$ in the following year (*2*) and were able to confirm its structure as an ordered ReO_3-type derivative. This was consistent with earlier work by Strunz and Contag (*3*) which dealt with a series of ordered ReO_3-type $ASn(OH)_6$ hydroxides, where A = Fe, Mn, Co, Mg and Ca. Further work with the preparation of $ASn(OH)_6$ hydroxides appeared in 1965, by Badarau, Billiet, Poix, and Michel (*4*).

Last year, Clement, Badarau, and Michel (*5*) published an account of the preparation of the ilmenites $CdPbO_3$ and $CaPbO_3$ by means of the thermal decomposition of $CdPb(OH)_6$ and $CaPb(OH)_6$. Later, Perez, Badarau, and Michel (*6*) studied the strontium lead hydroxide system.

The present work is concerned with the preparation and characterization of $ZnIr(OH)_6$ and $CdIr(OH)_6$, which were isolated in the process of synthesizing new ternary oxides of the platinum-group metals using complex hydroxide intermediates.

Experimental

Reagents

K_2IrCl_6 was obtained from the Matthey Bishop Co. and used directly as received. Reagent-grade zinc metal and $CdCl_2$ were obtained from Baker and Adamson, and U.S.P. grade KOH from Mallinckrodt.

Apparatus

Complex hydroxides were precipitated in polyethylene containers and were investigated with a DuPont 990 thermal analyzer equipped with D.S.C., T.G.A., and D.T.A. modules.

The X-ray data were obtained at room temperature with a 114-mm Debye–Scherrer camera with Ni-filtered Cu*Kα* radiation. Cell dimensions were refined by a least-squares procedure.

The approximate resistances of cold-pressed pellets were measured with a Heathkit vacuum tube voltmeter at various temperatures.

Magnetic susceptibility measurements were obtained from powders by the Faraday method, using a Cahn microbalance, with the samples suspended in a helium atmosphere.

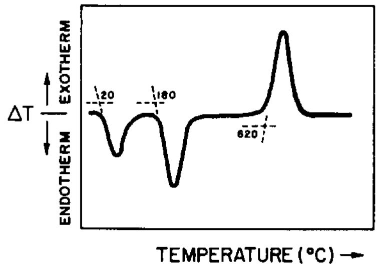

FIG. 1. Schematic of a D.T.A. plot for $CdIr(OH)_6$. The corresponding transition temperatures for the $ZnIr(OH)_6$ derivative are given in the text.

The system was calibrated with $HgCo(SCN)_4$, and diamagnetic corrections used in the calculations were obtained from Selwood (*7*).

Preparations

ZnIr(OH)$_6$

Precipitation from solution was accomplished by first dissolving a sample of K_2IrCl_6 in water and adjusting the pH to approximately 12 with a KOH solution. Twenty-four hours later [allowing full conversion to the $Ir(OH)_6^{2-}$ species (*8–11*)], a stoichiometric amount of Zn^{2+} solution was added, and the resulting flocculant precipitate allowed to digest for three days at room temperature. Filtration, washing with water and then acetone, followed by suction drying and grinding in an agate mortar yielded a fine golden-brown product.

CdIr(OH)$_6$

Preparation was analogous to that presented above for the zinc compound.

Results and Discussion

CdIr(OH)$_6$

A drawing depicting the nature of the D.T.A. pattern corresponding to thermal decomposition is shown in Fig. 1. The initial endotherm corresponds to loss of adsorbed surface water, and its size was reduced by increasing the drying time and number of acetone washings after filtration. Decomposition begins at 180°C (second endotherm) as the compound loses 3 moles of water. T.G.A. analysis showed agreement between calculated and measured weight loss to within 5%, less than the lower limit of impurity detection by means of the Debye–Scherrer patterns used for product identification. The product of thermal decomposition was amorphous to X-rays. Diffraction photographs taken after the exotherm (beginning at 620°C) indicated IrO_2, CdO, and possibly Cd_2IrO_4 (identified by its similarity to the diffraction pattern of Ca_2IrO_4).

TABLE I

$CdIr(OH)_6$

d (obs)	*d* (calc)	*h k l*	*I* (obs)
5.725	5.574	1 0 1	20
4.531	4.546	1 1 1	20
3.921	3.927	2 0 0	100
2.771	2.777	2 2 0	90
2.475	2.484	3 1 0	20
2.362	2.370	3 1 1	20
2.267	2.273	2 2 2	60
1.964	1.964	4 0 0	60
1.758	1.759	4 0 2	90
1.605	1.605	4 2 2	90
1.516	1.515	3 3 3	20
1.390	1.389	4 4 0	30
1.313	1.313	4 2 4	60
1.245	1.243	6 0 2	60
1.187	1.185	6 2 2	60
1.136	1.136	4 4 4	20
1.092	1.092	6 0 4	30
1.053	1.052	6 2 4	60
0.9560	0.9562	4 4 6	30
0.9290	0.9290	6 0 6	30
0.9040	0.9041	6 2 6	30
0.8810	0.8795	8 0 4	30
0.8600	0.8618	4 2 8	30
0.8400	0.8398	6 4 6	30

Debye–Scherrer diffraction data are tabulated in Table I, and the refined cell parameters are listed in Table III.

A plot of $1/X_M'$ versus T (Fig. 2), where X_M' represents the molar susceptibility corrected for diamagnetism only, indicates Curie–Weiss behavior from 130° to 390°K. The deviation from linearity below 130°K is attributed to a small amount of paramagnetic impurity. A least-squares best fit gave a

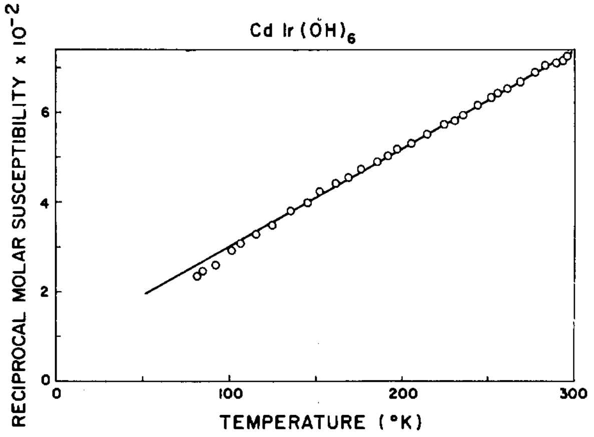

FIG. 2. Reciprocal molar susceptibility versus temperature (°K) for CdIr(OH)$_6$.

Weiss constant of −46.4°K. The average effective moment, calculated for each data point as $\mu_{\mathrm{eff}} = 2.83[X_M'(T - \theta)]^{1/2}$, was 1.94 μ_B. This is slightly higher than the 1.8 μ_B expected for Ir^{4+} (d^5 in a strong octahedral field) if one assumes the free ion value of −5000 cm^{-1} (*12*) for the orbital coupling constant, λ. However, if a reduced coupling constant ($\lambda' = -2500$ cm^{-1}) is used, the calculated moment is 1.91 μ_B, in good agreement with the experimental value. The use of λ' in place of λ is valid (since the Ir^{4+} ions are octahedrally coordinated, and thus may behave differently than would the free ions), but previous work by the authors with Ir^{4+} in similar coordination did not require this substitution. Furthermore, the fact that Curie–Weiss behavior is postulated would lead one to expect the compound to be a semiconductor, while, in fact, electrical resistance measurements indicate a resistance in excess of 5 × 10^6 Ω from liquid nitrogen to 200°C. These factors, coupled with the positions of the Ir^{4+} ions in the ordered ReO_3-type structure, indicate that perhaps the more appropriate interpretation of the magnetic susceptibility data would be to treat the compound as a dilute system of isolated iridium ions. Figure 3 shows a plot of effective moment versus temperature for CdIr(OH)$_6$, calculated as $\mu_{\mathrm{eff}} = 2.83[X_M'(T)]^{1/2}$, along with the theoretical curve of moment versus temperature

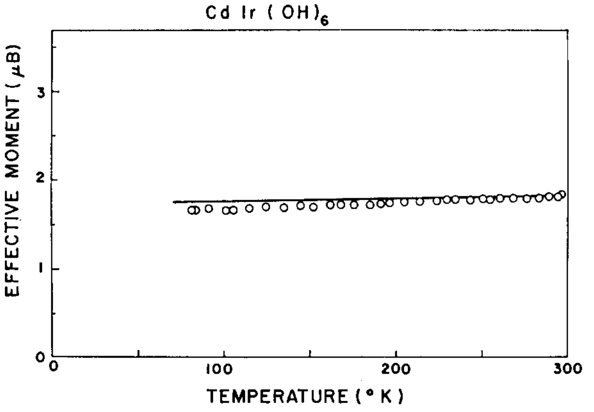

FIG. 3. Effective moment (μ_B) versus temperature (°K) for CdIr(OH)$_6$. Line represents theoretical data from Eq. (1) and circles represent experimental data points.

calculated from Eq. (1) with $\lambda = -5000\ \text{cm}^{-1}$. The good agreement between experiment and theory indicates that indeed this interpretation is probably the more appropriate.

$$\mu_{\text{eff}}^2 = \frac{8 + (3\lambda/kT - 8)\exp(-3\lambda/2kT)}{(\lambda/kT)[2 + \exp(-3\lambda/2kT)]} \qquad (1)$$

$ZnIr(OH)_6$

The D.T.A. patterns obtained for the thermal decomposition of $ZnIr(OH)_6$ were very similar to those for $CdIr(OH)_6$. This hexahydroxide decomposed at 170°C, giving an amorphous product. T.G.A. analysis confirmed the loss of three moles of water upon decomposition. After the exotherm at 566°C, diffraction photographs indicated IrO_2 and ZnO.

Debye–Scherrer diffraction data are tabulated in Table II, and the refined cell parameters are listed in Table III.

TABLE II

$ZnIr(OH)_6$

d (obs)	*d* (calc)	*h k l*	*I* (obs)
4.424	4.412	1 1 1	80
3.814	3.820	2 0 0	100
2.700	2.701	2 2 0	95
2.409	2.416	3 1 0	15
2.299	2.304	3 1 1	70
2.205	2.206	2 2 2	70
1.909	1.910	4 0 0	70
1.751	1.753	3 3 1	60
1.707	1.708	4 2 0	95
1.557	1.560	4 2 2	95
1.470	1.470	5 1 1	60
1.351	1.351	4 4 0	60
1.291	1.291	5 3 1	60
1.273	1.273	6 0 0	70
1.207	1.208	6 2 0	60
1.165	1.165	5 3 3	5
1.152	1.152	6 2 2	60
1.103	1.103	4 4 4	45
1.070	1.070	7 1 1	45
1.060	1.060	6 4 0	45
1.021	1.021	6 4 2	60
0.9950	0.9948	7 3 1	45
0.9270	0.9266	8 2 0	60
0.9010	0.9005	6 6 0	60

Figure 4 shows a plot of $1/X_M'$ versus T. A Curie–Weiss interpretation is inappropriate, since extrapolation by least squares gives a Weiss constant of −11°K and an average effective moment, calculated as $\mu_{\text{eff}} = 2.83\,[X_M'(T - \theta)]^{1/2}$, of 1.46 μ_B. This is significantly low, even less than the spin-only value of 1.73 μ_B. Treating the compound as a dilute system of iridium ions is also unsuccessful, since the calculated effective moment, as $\mu_{\text{eff}} = 2.83[X_M'(T)]^{1/2}$, ranges between 1.38 to 1.43 μ_B from 100 to 300°K, compared to the expected range of 1.77 to 1.83 μ_B obtained from Eq. (1) with $\lambda = -5000\ \text{cm}^{-1}$. Magnetic susceptibility measurements taken from a second sample of $ZnIr(OH)_6$, prepared 3 months after the sample used for the initial

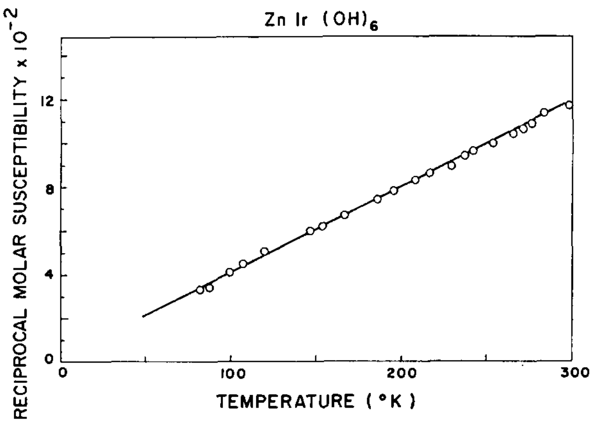

FIG. 4. Reciprocal molar susceptibility versus temperature (°K) for $ZnIr(OH)_6$.

TABLE III

Compound	Decomposition	Crystal system and cell parameters	Electrical properties	Magnetic properties
$CdIr(OH)_6$	180°	tetragonal (ordered ReO_3-Type) $a = 7.86$ Å $c = 7.91$ Å	insulator	dilute system of Ir^{4+} $\mu_{eff} = 1.83\ \mu_B$ at 296°K
$ZnIr(OH)_6$	170°	cubic (ordered ReO_3-Type) $a = 7.64$ Å	insulator	inconclusive

magnetic studies, agreed to within 2% over the temperature range of liquid nitrogen to room temperature. Thus no conclusive interpretation of the magnetic susceptibility data was obtained.

Two-probe electrical resistivity measurements on a cold-pressed pellet indicated a resistance in excess of $20 \times 10^6\ \Omega$ from liquid nitrogen to 200°C.

Several other $AIr(OH)_6$ precipitates were prepared, but none was sufficiently crystalline for crystallographic characterization. However, the one-to-one ratio between the A cation and Ir was confirmed by thermal decomposition, which yielded several one-to-one ABO_3 oxides identical to those previously prepared by conventional solid state reaction. Thus $CaIrO_3$ (ortho. perovskite) (*13*, *14*), $BaIrO_3$ (18R)(*15*, *16*), $SrIrO_3$ (monoclinic distortion of 6H) (*17*), as well as a new $BaIrO_3$ (4H) were isolated as pure phases.

Similarly, $BaRuO_3$ (9R) (*18*), the orthorhombic perovskites $CaRuO_3$ and $SrRuO_3$ (*19*), and $Pb_2Os_2O_{7-x}$ (defect pyrochlore) (*20*, *21*) were all isolated, as well as several new ternary oxides of osmium. The preparation and characterization of these derivatives will be published shortly.

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