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# Cerium(IV) acetate

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CERIUM(IV) is a useful and desirable oxidant which has many potential applications. However, crystalline compounds are only readily available as double salts of nitrate and sulfate. Although cerous(III) acetate has been known for some years, anhydrous ceric(IV) acetate was not reported until 1956. Patnaik and Panda[1] prepared anhydrous ceric acetate by reacting cerous nitrate with a mixture of acetic anhydride and glacial acetic acid[2]. A crystalline garnet-red, water and light sensitive compound was isolated, but no details of the preparation or composition were given.

We find that reaction of anhydrous cerous nitrate and acetic anhydride (25% v in glacial acetic acid) produced roughly 10-15% Ce(IV) by titration. Variation in the relative amounts of acetic anhydride and acetic acid produced no dramatic changes. In our hands isolation of Ce(IV) acetate from this mixture was laborious and gave impure products.

Ozonation has been employed as an alternative method of converting Ce(III) to Ce(IV)[3] in aqueous solutions. We have adapted this reaction for the preparation of anhydrous crystalline ceric(IV) acetate. Cerous acetate is readily polymerized in solutions of glacial acetic acid-acetic anhydride. Ozonation of this mixture is inconvenient and gave poor yields of inferior product. Small amounts of nitrate have the remarkably beneficial effect of inhibiting polymerization and enhancing solubility of cerous acetate in these media. Homogeneous solutions of cerous acetate under these conditions were readily ozonized at 100° or less. Ceric(IV) acetate was isolated after precipitation from solution as a bright yellow crystalline compound in virtually quantitative yields.

The yield of ceric acetate depends on the amount of nitrate added. Best results were obtained when approximately 3.5 mole per cent of cerous nitrate was added to cerous acetate. In the absence of nitrate, the yield of ceric acetate (85 per cent purity), was 81 per cent. Runs with concentrated nitric acid afforded consistently lower yields (and quality) of product. These effects are listed in Table 1.

Cerous acetate (g)	Cerous nitrate (g)	Yield† (%)	Apparent‡ formula wt.	Purity† (%)	Ce <sup>īv</sup> § (%)
19.5	0	81.0	$443 \pm 2$	84.9	69-0
19-5	0.70	100-0	$373 \pm 3$	<del>99</del> •2	99.0
18.0	2.75	85-0	$405 \pm 8$	92.8	<b>79</b> ∙0
10.0	13.75	52.0	$414 \pm 8$	90.8	47.6
0	20.0	0		—	_
19.5	0·05 <sup>  </sup>	73.0	$444 \pm 9$	84.7	62.5
19-5	2·3"	61.2	$489 \pm 6$	76.9	47.1
19.5	15·0 <sup>#</sup>	0		-	_

Table 1. Purity and yields of ceric(IV) acetate by ozonation of cerous acetate in the presence of nitrate\*

\*In solutions containing 17 ml acetic anhydride and 55 ml glacial acetic acid. †Based on Ce(OAc)<sub>4</sub>. ‡By ferrous titration.

<sup>§</sup>Total Ce(IV) produced. "MI conc. nitric acid.

- 1. D. Patnaik and S. Panda, Curr. Sci. (India) 5, 287 (1956); 26, 355 (1957); J. Indian chem. Soc. 33, 877 (1955).
- Anhydrous Mn(III) acetate has also been prepared from Mn(II) nitrate by a similar procedure. A Chretien and G. Varga, Bull. Soc. chim. Fr. No. 5 3, 2387 (1936); Ceric toluate from the isopropylate has also been reported. H. Baker, et al., J. chem. Engng. Data 7, Pt. 2, 560 (1962).
- 3. A. Job, C.r. hebd. Séanc. Acad. Sci., Paris 136, 45 (1903); C. Lyon and D. Scargill, Rep. U.K. atom. Energy Auth. Rep. No. AERE-R4537 (1964).

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Ceric acetate obtained in this manner had an empirical formula consistent with  $Ce(O_2CCH_3)_4$ , i.e. formula weight, 376.3. Ferrous titration in aqueous sulfuric acid indicated an equivalent weight of 373 ± 3. Acetate as ligands were determined directly by gas liquid chromatographic analysis of the hydrolysate. The formula weight per acetate was 91 ± 1 compared to a calculated value of 94. Magnetic susceptibility studies, depending on the method, varied between a specific susceptibility of 19-0 × 10<sup>-6</sup> cgs (Gouy method) and  $8.732 \times 10^{-6}$  cgs (Faraday method) at 20°, or effective magnetic moments of 0.575 and 0.555 BM, respectively, after diamagnetic correction. Values as high as  $22 \times 10^{-6}$  cgs have been reported for the susceptibility of other Ce<sup>IV</sup> compounds[4]. Thus, Ce<sup>IV</sup> appears to be paramagnetic although formally it contains no unpaired electrons[5].

The reflectance spectrum of crystalline ceric acetate showed a broad asymmetric absorption band whose principal maximum is at 400 m $\mu$  and extended to 310 m $\mu$ . The spectrum was essentially the same as that obtained from ceric ammonium sulfate. In acetic acid solutions the maximum is centered at 344 m $\mu$ [6].

Ceric acetate is soluble in aqueous solutions of strong acids but slightly soluble in acetic acid and benzene. It is hygroscopic and readily converted to the oxide. A variety of other Ce(IV) carboxylates can be made from the acetate by metathesis using a procedure similar to that employed for Pb(IV) and Tl(III)[7]. Ceric acetate prepared in a less crystalline form as a solvate with acetic acid is more soluble in organic solvents than is the tetraacetate. The latter is probably polymeric, much like ceric tetraalkoxides[8]. Further studies on the thermal and photochemical decarboxylation of ceric carboxylates are in progress.

# EXPERIMENTAL

#### Materials

Cerous acetate (99-9 per cent) from Lindsay Div., American Potash and Chemical Corp. Cerous nitrate hexahydrate from G. F. Smith Co., dehydrated at 1 mm and 100° for 24 hr. Acetic acid, glacial and acetic anhydride, reagent grade, from Baker and Adamson, Allied Chemicals.

#### Preparation of ceric acetate

Cerous acetate (19.5 g, 0.06 moles) and anhydrous cerous nitrate (0.7 g, 0.002 moles) were added to a solution of 17 ml acetic anhydride and 55 ml glacial acetic acid, which had been previously refluxed for 1 hr and then allowed to cool to room temperature. Upon heating to reflux temperature these mixtures evolved NO<sub>2</sub>. Vigorous refluxing was continued until NO<sub>2</sub> evolution was complete and much of the cerous acetate was in solution.

With cerous nitrate it was especially important to heat the system very slowly because the evolution of  $NO_2$  became quite vigorous. This system had the advantage that complete dissolution was effected when  $NO_2$  evolution ceased. Like the nitrate, cerous carbonate had the disadvantage of evolving large volumes of gas (CO<sub>2</sub>) and care had to be taken to prevent ebullition. With cerous acetate no such precautions were necessary when only small amounts of nitrate were added.

The hot solutions of cerous acetate were ozonized immediately, and the slight exotherm of the reaction was enough to maintain the temperature at 70° or greater. Ozone (Welsbach Ozonator, model T-816) was bubbled through the flask through a gas dispersion tube until slightly more than a quantitative amount of ozone was absorbed. The undissolved cerous acetate was taken up during ozonation and when

$$2Ce(OAc)_3 + O_3 + 2HOAc \rightarrow 2Ce(OAc)_4 + O_2 + H_2O$$

the cerous concentration was greater than about 0.4 M, precipitation of the yellow solid became heavy enough to clog the apparatus. The bright yellow solid was collected by vacuum filtration and

- 4. G. Foex, C.r. hebd. Séanc. Acad. Sci., Paris 208, 738 (1939); Int. Crit. Tab. p. 359. McGraw-Hill, New York (1926); Z. anorg. Chem. 190, 143 (1930).
- 5. We were unable to examine induced susceptibilities by temperature dependent studies.
- 6. cf. With ceric acetate made in situ by oxidation with Pb(IV). D. Benson and L. Sutcliffe, Trans. Faraday Soc. 56, 246 (1960).
- 7. W. Mosher and C. Kehr, J. Am. chem. Soc. 75, 3172 (1953); T. Bethea and J. Kochi, to be published.
- 8. D. Bradley, A. Chaterjee and W. Wardlaw, J. chem. Soc. 2260 (1960).

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washed twice with hot acetic acid-acetic anhydride mixtures. It was dried to constant weight in vacuo at room temperature over potassium hydroxide.

At all stages of the preparation it was important to exclude light. The product is also hygroscopic and exposure to light or air should be as limited as possible. The synthesis can be scaled up and although a small amount of ceric acetate remains in solution close to quantitative yields are attainable. It can be recrystallized from acetic anhydride-acetic acid mixtures but in most cases it was unnecessary.

## Analysis

*Elemental analysis.* Calcd. for CeC<sub>8</sub>H<sub>12</sub>O<sub>8</sub>: C, 25·8; H, 3·22. Found: C, 24·87, 24·54; H, 3·18, 3·19.

Ceric(IV). Ceric acetate was dissolved in concentrated sulphuric acid, diluted with water and an aliquot of a standard solution of ferrous ammonium sulfate added. Phosphoric acid was added and the solution back-titrated with standard Ce(IV) solution to the ferrous phenanthroline end point. Acetic acid did not interfere.

Acetate. Approximately 60 mg ceric acetate was dissolved in trifluoroacetic acid and 2 ml water. An aliquot of a standard aqueous solution of propionic acid was added, and the mixture analyzed by gas liquid chromatography (Varian Aerograph, Model 600 HiFy, hydrogen flame detector, 20 per cent FFAP on acid washed Chromosorb W 60/80), by the internal standard method with calibration curves for acetic acid-propionic acid mixtures. Over a broad range of concentrations, the amount of trifluoroacetic acid used had no effect on the analysis.

Magnetic moments were determined by the Guoy and Faraday methods using  $Co[H_3(SCN)_4]$  as a standard[9, 10]. Reflectance spectra were recorded from 250-2500 m $\mu$  on a Beckman Ratio Recording Reflectance spectrophotometer.

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Department of Chemistry Case Western Reserve University Cleveland, Ohio NELSON E. HAY JAY K. KOCHI

B. Figgis and J. Lewis, *Technique of Inorganic Chemistry* (Edited by H. Jonassen and A. Weissberger), Vol. IV, p. 137ff. Interscience, New York (1965); *Modern Coordination Chemistry* (Edited by J. Lewis and R. Wilkins), Interscience, New York (1960).

10. We wish to thank Professor John Fackler for the use of this apparatus.

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# The exchange of isotopically enriched oxygen with <sup>228</sup>PuO<sub>2</sub>

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THE NEUTRONS emitted from <sup>238</sup>Pu metal which contains no light element impurities are produced by spontaneous fission at the approx rate of  $2.5 \times 10^8$  n/sec per g[1-3]. The neutron generation rate from <sup>238</sup>PuO<sub>2</sub> is much higher than the spontaneous fission value and is principally due to the ( $\alpha$ , n) reaction of <sup>17</sup>O and <sup>18</sup>O, with little or no yield from <sup>16</sup>O[4]. Normal <sup>238</sup>PuO<sub>2</sub> contains 0.037% <sup>17</sup>O and 0.204% <sup>18</sup>O

- 1. A. H. Jaffery and A. Hirsch, A.E.C. Research and Development Report, ANL-4286, Argonne National Laboratory, University of Chicago, Argonne, Illinois (May 12, 1949).
- 2. W. W. T. Crame, G. H. Higgins and H. R. Bowman, Phys. Rev. 101, 1804 (1956).
- 3. D. A. Hicks, J. Ise, Jr. and R. V. Pyle, Phys. Rev. 101, 1016 (1956).
- 4. V. Keshishian and K. M. Broom, Jr. AI-65-190, Vol 9, Atomics International, Canoga Park, Calif. (March 7, 1966).