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A Simple High-Yield Preparation of Potassium Tris(oxalato)iridate(III) with a Novel Solvent Extraction Step

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There is currently considerable interest in the photochemical and photophysical properties of Ru(II), Ir(III), and Os(II) with α-diimine ligands [1–11]. Especially with Ir(III), progress has been impeded by the great complexity of the chemistry We have shown that halide free Ir(III) complexes can function as important intermediates in the preparation of α-diimine complexes of Ir(III) [7].

Oxalato complexes of Ru(II) have proven useful in the synthesis of α-diimine ruthenium(II) complexes, and we, thus, considered the tris(oxalato)iridate(III) complex as a synthetic intermediate. Previously published preparations of potassium tris(oxalato)iridate(III), however, exhibited poor product yields [12–15]. For example, a recent sealed-tube reaction (aqueous K_3IrCl_6, $K_2C_2O_4$, 130 °C), was laborious and gave only 30% yield [15]. We attribute the poor yield to difficulty in separating the product from excess $K_2C_2O_4$

We describe a new synthesis of $K_3Ir(C_2O_4)_3$ which uses a novel solvent-extraction step, is simpler than the sealed tube reaction, and gives yields up to 80–85%. This provides a stable, well-defined, readily obtained halide-free iridium complex suitable as a starting material. In preliminary trials we have shown that the reactions of CN^- or α-diimine ligands with $K_3Ir(C_2O_4)_3$ yield mixed oxalato complexes.

Results and Discussion

Potassium hexachloroiridate(IV) (0.48 g, 1.0 mmol) and $K_2C_2O_4$ H_2O (5.5 g, 30 mmol) in 8 ml of water were refluxed five days. Water was added to make the volume 15 ml, and the solution was centrifuged, then slowly stirred into 150 ml of ethanol. The filtrate contained ~4 mmol of liberated Cl^-. The precipitated oxalates were separated (ethanol wash), redissolved in water, evaporated to 10 ml, and refluxed five more days. Then the ethanol precipitation was repeated; the filtrate contained 2 mmol of Cl^-, demonstrating complete reaction.

The redissolved (water, 40 ml) oxalate mixture was treated with $(n\text{-}C_4H_9)_4NHSO_4$ (Aldrich) (1.0 g, 3 mmol); extraction with a few 5 ml portions of CH_3NO_2 separated most of the complex Additional $(n\text{-}C_4H_9)_4NHSO_4$ (0.5–1 mmol) and further extractions removed more complex. The combined extracts were evaporated. The gummy product was dissolved in 20 ml of CH_2Cl_2, was filtered to remove a small amount of white solid, and was evaporated to dryness. Alternatively, the dichloromethane solution may be treated with excess tetramethylammonium chloride in methanol–dichloromethane to precipitate tetra-methylammonium tris(oxalato)iridate(III) which is very soluble in water and in methanol With either method the final product is then dissolved in 25 ml of ethanol and precipitated with KO_2CCH_3 (6 mmol in 30 ml ethanol).

The product (ethanol wash) was dissolved in a minimum amount of water and stored over ethanol; well-formed gold-yellow rods (2–12 mm long) or tablets (typically 2–4 mm on one edge) were obtained Small amounts of colorless impurities could be removed mechanically immediately or after further recrystallization. No other iridium complexes were obtained. Yields of the tris(oxalato)iridate of 0.4–0.45 g (60–70%) were readily obtained; yields up to 85% were possible, especially with further work-up of the reaction solution. The mother liquor may be treated with 30 mmol of oxalic acid, evaporated, the precipitated acid oxalate removed, and the extraction procedure repeated to recover the remaining iridium complex

Using the above procedure but starting with K_2IrBr_6 gave complete reaction in 24 hr and equally good yields of the tris(oxalato)iridate(III). Refluxing $IrO_2 \cdot xH_2O$ with excess oxalic acid in water for 1–2 days gave a yellow solution which, after removal of $H_2C_2O_4$ turned dark. This indicated the presence of polynuclear complexes which are probably analogous to known sulfate species [16].

Our results leave no doubt that our products are $K_3Ir(C_2O_4)_3$ hydrates. Elemental analyses demonstrate absence of N or halide. ^{13}C NMR spectra (25.15 MHz) [7] of the rods and plates in D_2O were obtained on a JEOL PFT-100/EC100 spectrometer. Chemical shifts are reported with respect to TMS and were obtained with an internal dioxane reference. Only a single ^{13}C resonance was obtained for the needles (171.48 ppm) and for the plates (171.43 ppm). This result proves that the two samples contain the same complex ion which has only one magnetically distinguishable carbon.

The rods appear to be a 4.5–5-hydrate. *Anal.* Calcd. for $K_3Ir(C_2O_4)_3 \cdot 4.5H_2O$: C, 11.01; H, 1.39.

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Found: C, 10.92; H, 0.97%. The tablets are perhaps a previously uncharacterized 3.5-hydrate. *Anal.* Calcd. for $K_3Ir(C_2O_4)_3 \cdot 3.5H_2O$: C, 11.32; H, 1.11. Found (two preparations). C, 11.27, H, 0.51, C, 11.32, H, 0.47. Spectral data for both crystals were identical. IR (KBr): 3560 br, 3440 br, 1690, 1660, 1380, 1260, 1242, 900, 817, 551, 466 cm^{-1}, corresponding well with vibrational data for aqueous $Ir(C_2O_4)_3^{3-}$ and solid $K_3Rh(C_2O_4)_3 \cdot nH_2O$ [14].

UV (aq): λ_{max} = 285 nm; ϵ_{max} = 4.6 × 10^3 l mol^{-1} cm^{-1}; lit. [13, 15] 285–290 nm; (4.1–4.5) × 10^3. Density (flotation in CCl_4–$CHBr_3$, 21–22 °C, g cm^{-3}) 2.75 ± 0.02 (rods), 2.62 ± 0.03 (tablets) (lit. 2.500 (4.5-hydrate), 2.759 (optically active 2-hydrate)). Our crystal density data disagreed with results of Herpin [17], which precluded identification of our hydrates with his crystals of racemic 4.5-hydrate and active 2-hydrate.

We attribute our high yields and purity to the solvent extraction step which permits efficient separation of the potassium tris(oxalato)iridate(III) from the $K_2C_2O_4$ reactant which has a similar solubility. There are numerous cationic and anionic counter ions which are suitable for solvent extraction of many bulky high charge ionic products from small low charge reactants. We, therefore, suggest that our procedure is likely to be a general one for improving the yields and purity of products in a variety of inorganic syntheses where a charged complex must be separated from excess ionic reagents.

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