Partially Oxidized Bis(squarato)platinum(II) Salts, New Examples of One-dimensional Electric Conductors

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Summary The new complex bis(squarato)platinum(II) and its partially oxidized form have been prepared and characterized.

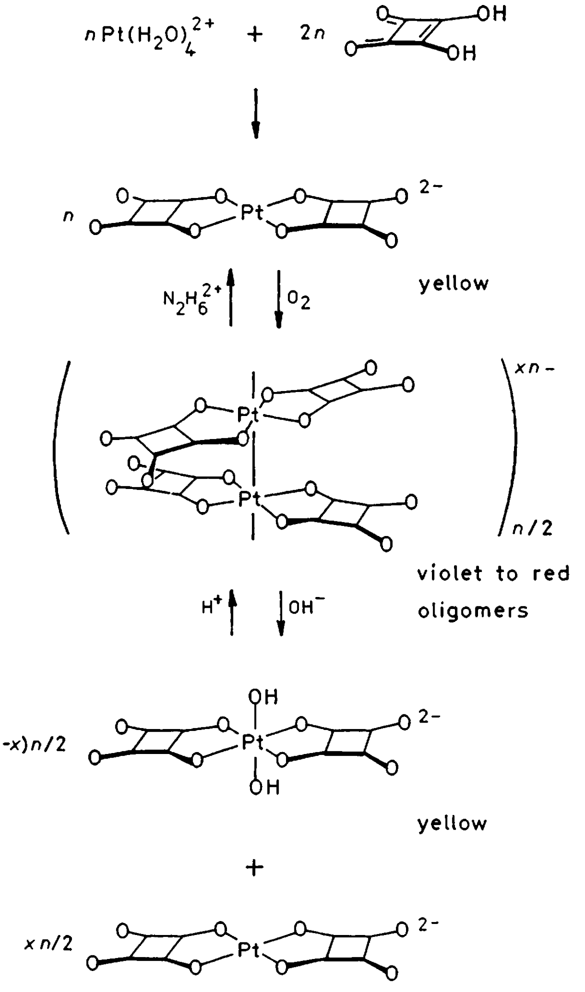
In recent years there has been considerable interest in the chemical and physical properties of highly conducting one-dimensional platinum complexes.[1] However, only three types of such complexes have been characterized in detail; $K_2[Pt(CN)_4X_{0 \cdot 3}] \cdot 3H_2O$ (X = Cl or Br),[1] $(alkali^+)_{1 \cdot 75}$-$[Pt(CN)_4] \cdot 1 \cdot 5H_2O$,[1] and $(alkali^+)_{1 \cdot 64}[Pt(ox)_2] \cdot H_2O$[2] (ox = oxalate), all of which have been known for nearly a hundred years.[3]

In order to prepare new platinum(II) complexes with high conductivity squarate (squa is the anion of 3,4-dihydroxycyclobutenedione) was chosen as the ligand. Chemically the squarate ion is related to the oxalate ion (as a vinyl analogue), although it forms less stable metal complexes.[4] Platinum complexes of squarates do not seem to have been reported, although the bis(dithiosquarato)-platinum(II) complex is known.[5]

Attempts to replace the chloride in tetrachloroplatinate(II) with squarate were not successful, although strongly coloured solutions were formed by treating hexahydroxoplatinum(IV) acid or tetra-aquaplatinum(II)-with squaric acid at 60 °C. From these solutions it was possible to precipitate microcrystalline, black, alkali metal salts. Recrystallization of the lithium or sodium salts, by slow evaporation, gave needle-like crystals which showed pleochroism. The crystals were bluish-black with polarized light having the electric vector along the needle axis and yellow in the direction normal to the needle axis.

The salts gave an intense violet colour in acid to neutral aqueous solution, in analogy to the partially oxidized oxalato complex mentioned above.[6] The absorption, however, does not follow Beer's law, and 10^{-4}—10^{-2} M solutions in polar solvents vary from yellow to deep purple or black (presumably because of oligomerization in solution).

On addition of base the violet solution immediately turned yellow as it did with reducing agents such as hydrazinium sulphate. From a reduced concentrated solution it was possible to precipitate the yellow potassium bis(squarato)platinum(II) salt. The salt is stable when dry, but it is easily oxidized to the coloured, partially oxidized form by atmospheric oxygen when wet or in solution. The preparative reactions and some of the equilibria in solution are shown in the Scheme.



SCHEME

The reduced yellow salt analysed for $K_2[Pt(C_4O_4)_2]\cdot2H_2O$ and the partially oxidized black salt analysed for $K_{1\cdot6}[Pt(C_4O_4)_2]\cdot2H_2O$, with a Pt^{IV}/Pt^{II} value of 0·202 corresponding to a formal oxidation state of 2·4 for platinum.† The i.r. spectra of $K_2[Pt(squa)_2]$ and $K_{1\cdot6}[Pt(squa)_2]$ are similar, but the Pt–O frequency is shifted from 508 to 532 cm^{-1} on partial oxidation, suggesting stabilisation of the complex.

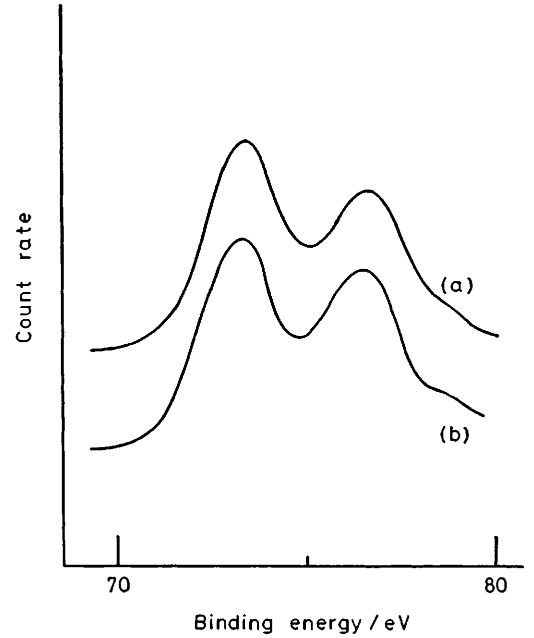


FIGURE. Pt 4*f* region of ESCA spectra of $K_2[Pt(squa)_2]$ (a) and $K_{1\cdot6}[Pt(squa)_2]$ (b).

It has been shown that ESCA can be used to distinguish between a mixed valence compound and a single valence partially oxidized material.[7] The ESCA spectra of $K_2[Pt(squa)_2]$ and $K_{1\cdot6}[Pt(squa)_2]$ are shown in the Figure. The binding energies of $4f_{7/2}$ and $4f_{5/2}$ of the partially oxidized complex are shifted to slightly lower values compared to the platinum(II) compound, but the spectrum shows all the platinum ions to be equivalent, which strongly supports the assumption that $K_{1\cdot6}[Pt(squa)_2]$ is in a metallic state similar to $K_{1\cdot6}[Pt(ox)_2]$. The electrical conductivity of a tablet of the partially oxidized potassium compound was measured using a microwave technique. The conductivity at 25 °C was $5 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$ suggesting a metallic state.[1,8]

Since the crystals show a very large optical anisotropy, a large anisotropy in the conductivity and therefore a considerably larger conductivity in the conducting direction is expected.

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† To determine alkali metal and platinum content a weighed sample was ignited with conc. H_2SO_4. The residue was weighed before and after dissolution of the alkali metal sulphate in water. Quantitative reductions to the platinum(II) complexes were performed under N_2 by potentiometric titration with 0·01 M hydrazinium sulphate. Analytical figures were as follows: for the yellow reduction product $K_2[Pt(C_4O_4)_2]\cdot2H_2O$: C 17·70, H 0·57, K 14·80, Pt 36·44% (calc. C 18·01, H 0·75, K 14·66, Pt 36·57%); for the black, partially oxidized, potassium salt $K_{1\cdot6}[Pt(C_4O_4)_2]\cdot2H_2O$: C 18·23, H 0·51, K 11·71, Pt 37·80% (calc. C 18·56, H 0·78, K 12·08, Pt 37·68%).

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