Synthesis and Properties of Tris(dithioacetylacetonato)-complexes of Cobalt(III), Rhodium(III), and Iridium(III)

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Summary The isolation of tris(dithioacetylacetonato)-complexes of Co^{III}, Rh^{III}, and Ir^{III} is reported.

ATTEMPTS to prepare the free ligand dithioacetylacetone Me·CS·CH_2·CS·Me (sacsacH) have so far been unsuccessful. Nevertheless, the action of hydrogen sulphide on acetylacetone in the presence of the appropriate bivalent metal ion leads to the isolation of monomeric square-planar complexes, [M sacsac$_2$] where M^{II} = Co, Ni, Pd, or Pt.[1,2] This work has now been extended to achieve the first successful isolation of the monomeric inner complexes [M sacsac$_3$] of the tervalent metals M^{III} = Co, Rh, and Ir.

In the case of rhodium and iridium, the crimson crystalline complexes separate directly from solutions of the tervalent metal ions in the usual reaction medium (acetylacetone and hydrogen sulphide in ethanolic hydrogen chloride[3]). However, we find that dark brown [Co sacsac$_3$] is best prepared by oxidation of [Co sacsac$_2$] with molecular oxygen in the presence of acetylacetone and hydrogen sulphide. A suspension of [Co sacsac$_2$] in ethanolic hydrogen chloride at 0° treated in this way gives an initial product which is largely [Co sacsac$_2$sacac]. Further passage of hydrogen sulphide is required to achieve the complete replacement of oxygen by sulphur. The progress of this reaction may be followed conveniently by repetitive scanning of the i.r. region. The oxidation is accompanied by a clearly defined shift in the strong C–C stretching vibration from 1490 to 1460 cm $^{-1}$. Also the progress of the final oxygen replacement is indicated by the disappearance of the C–O stretching vibration at 1560 cm.$^{-1}$. A substantial byproduct formed during the oxidation step is the tetrachlorocobalt salt of the 3,5-dimethyl-1,2-dithiolylium cation $[C_5H_7S_2{}^+]_2$ $[CoCl_4^{2-}]$ [4] This rather easy ligand oxidation may also be achieved by oxidative addition with halogens.[5] It can be reversed by strong reducing agents, such as sodium borohydride or sodium dithionite, which convert the above dithiolylium salt into a mixture of [Co sacsac$_2$] and [Co sacsac$_3$].[6]

The [M sacsac$_3$] compounds are soluble in organic solvents, although the cobalt(III) complex undergoes slow decomposition in solution at room temperature. The rhodium(III) and iridium(III) complexes crystallise from acetone in nonisomorphous forms, monoclinic (*C*2/*c* or *Cc*) and triclinic, respectively,[7] which are currently being studied by *X*-ray methods in this department. A crystal structure analysis of crystalline [Fe sacsac$_3$][5,6] is also in progress.

The electronic spectra of [Rh sacsac$_3$] and [Ir sacsac$_3$] display intense charge-transfer bands which obscure the region in which *d–d* transitions might be expected Solution spectra of [Co sacsac$_3$] (in benzene, carbon tetrachloride, and cyclohexane) are unsatisfactory due to decomposition. At this stage no inference can be drawn as to whether the stereochemistry of the central ion is octahedral or trigonal prismatic in these sulphur chelates.

These complexes are diamagnetic and their ^1H n.m.r. spectra show only two proton resonances at *ca.* 3·1 (C–H) and *ca.* 7·8 p.p.m. (CH_3) in the expected ratio 1 : 6. The mass spectra are all characterised by a strong peak at *m*/*e* 131 which corresponds to the stable dithiolylium cation $[C_5H_7S_2]^+$ derived by electron loss from the ligand.[1] Well defined peaks are observed for the parent ions [Rh sacsac$_3$]$^{+\cdot}$ and [Ir sacsac$_3$]$^{+\cdot}$. However for the cobalt (III) complex the peak of highest mass corresponds to the fragment [M sacsac$_2$]$^{+\cdot}$; we find a similar situation obtains for [Fe sacsac$_3$].

The tris-chelates have closely similar i.r. spectra to those of the square planar compounds for which a normal coordinate analysis has been published elsewhere.[3] The shift of the C–C stretching vibration noted above is the most marked difference and is general for the tervalent compounds reported here, including [Fe sacsac$_3$].

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