Anionic Hexafluoroacetylacetonate Complexes of Alkali Metals

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Summary Anionic alkali-metal complexes of the type $[M(CF_3COCHCOCF_3)_2]^-$ have been prepared using $[C_{14}H_{19}N_2]^+$ as the counter ion; mixed alkali-metal complexes are also reported.

CATIONIC and neutral complexes of the alkali metals with oxygen and nitrogen donor atoms have been characterised.[1] We now report the synthesis of anionic complexes of these metals with hexafluoroacetylacetone as the donor ligand.

Mono-protonated 1,8-bis(dimethylamino)naphthalene hexafluoroacetylacetonate, $[TMNDH]^+[hfac]^-$, is readily prepared as a crystalline product by stoicheiometric reaction of the components. The reaction makes use of the deprotonating capability of the strong base TMND,[2] and the near total enolisation of hfacH in solution.[3] Addition of this compound in 1:1 mole ratio to metal(II) hexafluoroacetylacetonates yields the complexes $[TMNDH]^+[M(hfac)_3]^-$, (M = Mg, Mn, Cu, Ni). *X*-Ray crystallographic studies show that these complexes are isomorphous, and confirms that co-ordinative saturation of the metal atom is attained through enolate addition of the hfac anion.[4]

An extension of this, and related, reactions to alkali-metal hexafluoroacetylacetonates has led to the isolation of anionic complexes of these metals. $[TMNDH]^+[hfac]^-$ reacts with M(hfac), (M = Li, Na) in benzene–ethanol to give, on removal of the solvent, crystalline samples of $[TMNDH]^+[Li \text{ or } Na,(hfac)_2]^-$. These complexes are 1:1 electrolytes in nitromethane. Khfac and $[TMNDH]^+[hfac]^-$ gave a complex of stoicheiometry 2Khfac:1$[TMNDH]^+[hfac]^-$. The conductivity suggested a 2:1 electrolyte, and so the complex may be formulated as $[K]^+[TMNDH]^+[K(hfac)_3]^{2-}$. The i.r. spectra of the complexes are different from those of each component, and those of physical mixtures of the components. Preliminary *X*-ray crystallographic studies confirm that these are new crystalline phases and not mixtures, and the analyses are satisfactory.

The reaction of K(or Na)(hfac) with M^{II} $(hfac)_2$ gave K^+ (or Na^+)$[M^{II}(hfac)_3]^-$. Similar reactions have been carried out between alkali-metal hexafluoroacetylacetonates and have given the compounds $KLi(hfac)_2$ (as a monohydrate) and $K_2Na(hfac)_3$. The i.r. spectra, analytical data, and preliminary *X*-ray crystallographic studies show that these are new crystalline phases. Previously, m.s. investigation of alkali-metal derivatives of β-diketones had shown peaks at greater *m/e* values than $(ML)^+$, and values corresponding to $M_2L_2^+$ were identified. Exchange reactions between alkali-metal chelates within the ion source of the spectrometer have been shown to yield such species as $M^1M^2L_2^+$. It was not, however, established that such structures existed in the solid phase.[5]

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