

Iron-^{tert}Butanechalcogenolate Complexes

Synthesis, structural and spectroscopic Investigations

Abstract

Reactions of iron(II)- and iron(III) salts with alkali metal-^{tert}butanechalcogenolates gave to new one- and multi nuclear iron-^{tert}butanechalcogenolate complexes.

The tetraphenylphosphonium salt of $[\text{Fe}(\text{S}^t\text{Bu})_4]^-$ which has never been isolated before was obtained by these reactions. It is a model complex for the oxidised form of rubredoxins. Its molecular structure has been elucidated by X-ray diffraction methods. Contrary to all model complexes isolated so far the novel compound $[(\text{K}\{\text{Benzo-18-crown-6}\}_3)\text{X}][\text{Fe}_2\text{S}_2(\text{S}^t\text{Bu})_4] \cdot \text{MeOH}$, ($\text{X} = \text{Cl}_{4/5}$ and $\text{Br}_{1/5}$) contains the iron in a ligand sphere that models both the monodentate character of the cysteine residues and their coordination behaviour as alkane thiolates in the oxidised form of 2Fe-2S-ferredoxine.

Another isolated complex is the iron-diazene-^{tert}butanechalcogenolate anion $[(\text{Fe}_3(\text{S}^t\text{Bu})_6)_2(\text{CH}_3\text{C}(\text{N})\text{N})_2]^{2-}$. It bears resemblance to a transition state that is important in the reduction of nitrogen by the enzyme nitrogenase. In the course of the investigations reactions with selenolates afforded the anion $[\text{Fe}(\text{Se}^t\text{Bu})_4]^{2-}$ in good yield. It is the first example of a homoleptic metal selenolate complex anion with monodentate alkane selenolate ligands.

Furthermore, salts of the binuclear complex anions $[\text{Fe}_2(\text{E}^t\text{Bu})_5]^-$ ($\text{E} = \text{S}$ and Se) and $[\text{Fe}_2(\text{S}^t\text{Bu})_6]^{2-}$ have been synthesised. The $[\text{Fe}_2(\text{S}^t\text{Bu})_6]^{2-}$ anion shows a remarkable form of isomerism. It exists in both the *anti*-structure which is well known for this type of complex and in a new topology that differs significantly from the first one. The $\text{Fe}_2(\mu\text{-S})_2$ -heterocycle of the new isomer exhibits angles and distances between elements of the same type which are virtually inverted compared to the *anti*-isomer. Therefore it has been labelled *inverse* (*inv*).

The hybridisation of the sulphur atoms differs in both isomers. In *anti*- $[\text{Fe}_2(\text{S}^t\text{Bu})_6]^{2-}$ they are sp^3 - in *inv*- $[\text{Fe}_2(\text{S}^t\text{Bu})_6]^{2-}$ they are sp^2 -hybridised. These complexes are very important with respect to bonding theory of transition metal complexes. Both of them they show due to different hybridisation significant differences in their bond lengths and thus may be classified as bond-stretch-isomers.