

Übergangsmetallkomplexe mit Schwefelliganden, CXXXIII [1]. Synthese, Struktur und Eigenschaften neuer Fe^{II}-Komplexe mit [FeN₂S₂]-Gerüsten

Transition Metal Complexes with Sulfur Ligands, CXXXIII [1].

Synthesis, Structure, and Properties of New Fe^{II} Complexes with [FeN₂S₂] Cores

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In order to obtain suitable precursors for iron complexes that model the reactivity of the active sites of nitrogenases, the coordination chemistry of the [Fe(N₂H₂S₂')] fragment was systematically investigated (N₂H₂S₂'²⁻ = 1,2-ethanediamine-N,N'-bis(2-benzenethiolate)(2-)). One-pot reactions of FeCl₂·4H₂O with the tetradentate amine-thiolate ligand N₂H₂S₂'²⁻ and CO, PR₃, or P(OR)₃ yielded the complexes [Fe(CO)₂(N₂H₂S₂')] (**1**), [Fe(CO)(PR₃)(N₂H₂S₂')] (R = Et (**2**), Pr (**3**), Bu (**4**)), [Fe(PMe₃)₂(N₂H₂S₂')] (**7**), [Fe(dppe)(N₂H₂S₂')] (**8**, dppe = 1,2-bis(diphenylphosphino)ethane), and [Fe(P(OR)₃)₂(N₂H₂S₂')] (R = Me (**9**), Pr (**10**)). Mixed phosphane/phosphite complexes [Fe(PMe₃)(P(OR)₃)(N₂H₂S₂')] (R = Me (**11**), Pr (**12**)) were synthesized by PMe₃/P(OPr)₃ exchange of the labile complexes [Fe(PMe₃)₂(N₂H₂S₂')] (**7**) and [Fe(P(OPr)₃)₂(N₂H₂S₂')] (**10**). The [Fe(CO)(PR₃)(N₂H₂S₂')] complexes **3** and **4** also resulted from **1** and PR₃ by photochemical CO substitution. They exhibit characteristic low-frequency ν(CO) bands (≈ 1925 cm⁻¹), and their remaining CO ligand proved photolytically inert. Reaction of **3** or **4** with NOBF₄ yielded the dinuclear NO complex [Fe(NO)(N₂HS₂')₂] (**6**) which contains two amide functions.

Contrary to expectations, [Fe(PR₃)₂(N₂H₂S₂')] complexes could not be obtained with monodentate phosphanes other than PMe₃. The corresponding N-methylated ligand N₂Me₂S₂'²⁻ yielded only the complexes [Fe(CO)₂(N₂Me₂S₂')] (**15**) and [Fe(N₂Me₂S₂')] (**16**). X-ray structure analyses of complexes **7**, **8**·MeOH, **3**, [Fe(CO)(dppm)(N₂H₂S₂')]·0,5THF (**5**·0,5THF, dppm = bis(diphenylphosphino)methane), and **12**·0,5N₂H₂S₂'-H₂ confirm the pseudo-octahedral coordination of the Fe centers by two *trans*-S and two *cis*-N donors and two *cis*-coligands. The structural data further suggest that the unexpected instability of the [Fe(PR₃)₂(N₂H₂S₂')] complexes is not caused by steric but by electronic effects. The cyclic voltammograms and the reactivity of the [Fe(L)(L')(N₂H₂S₂')] complexes corroborate this assumption. The oxidation behaviour of the [Fe(L)(L')(N₂H₂S₂')] complexes depends critically on the coligands L and L'. Reaction of **1** with dioxygen leads to oxidative dehydrogenation of the N₂H₂S₂'²⁻ ligand and yields the dinuclear Schiff-Base complex [Fe('gma')₂] ('gma'²⁻ = glyoxal-bis(2-mercaptoanil)(2-)). In contrast, oxidation of [Fe(CO)(PR₃)(N₂H₂S₂')] , [Fe(PR₃)₂(N₂H₂S₂')] and [Fe(P(OR)₃)₂(N₂H₂S₂')] complexes by dioxygen occurs metal-centered and gives the Fe(IV) complexes [Fe(PR₃)(N₂S₂')] (R = Me, Pr), [Fe(P(OR)₃)(N₂S₂')] (R = Me) and [Fe(N₂S₂')₂] that contain the tetraamionic thiolate-amide ligand N₂S₂'⁴⁻.

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