

# Übergangsmetallkomplexe mit Schwefelliganden, CXXXIII [1]. Synthese, Struktur und Eigenschaften neuer Fe<sup>II</sup>-Komplexe mit [FeN<sub>2</sub>S<sub>2</sub>]-Gerüsten

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

Synthesis, Structure, and Properties of New Fe<sup>II</sup> Complexes with [FeN<sub>2</sub>S<sub>2</sub>] 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(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] fragment was systematically investigated (N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>'<sup>2-</sup> = 1,2-ethanediamine-N,N'-bis(2-benzenethiolate)(2-)). One-pot reactions of FeCl<sub>2</sub>·4H<sub>2</sub>O with the tetradentate amine-thiolate ligand N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>'<sup>2-</sup> and CO, PR<sub>3</sub>, or P(OR)<sub>3</sub> yielded the complexes [Fe(CO)<sub>2</sub>(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] (**1**), [Fe(CO)(PR<sub>3</sub>)(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] (R = Et (**2**), Pr (**3**), Bu (**4**)), [Fe(PMe<sub>3</sub>)<sub>2</sub>(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] (**7**), [Fe(dppe)(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] (**8**, dppe = 1,2-bis(diphenylphosphino)ethane), and [Fe(P(OR)<sub>3</sub>)<sub>2</sub>(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] (R = Me (**9**), Pr (**10**)). Mixed phosphane/phosphite complexes [Fe(PMe<sub>3</sub>)(P(OR)<sub>3</sub>)(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] (R = Me (**11**), Pr (**12**)) were synthesized by PMe<sub>3</sub>/P(OPr)<sub>3</sub> exchange of the labile complexes [Fe(PMe<sub>3</sub>)<sub>2</sub>(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] (**7**) and [Fe(P(OPr)<sub>3</sub>)<sub>2</sub>(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] (**10**). The [Fe(CO)(PR<sub>3</sub>)(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] complexes **3** and **4** also resulted from **1** and PR<sub>3</sub> by photochemical CO substitution. They exhibit characteristic low-frequency ν(CO) bands (≈ 1925 cm<sup>-1</sup>), and their remaining CO ligand proved photolytically inert. Reaction of **3** or **4** with NOBF<sub>4</sub> yielded the dinuclear NO complex [Fe(NO)(N<sub>2</sub>HS<sub>2</sub>')<sub>2</sub>] (**6**) which contains two amide functions.

Contrary to expectations, [Fe(PR<sub>3</sub>)<sub>2</sub>(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] complexes could not be obtained with monodentate phosphanes other than PMe<sub>3</sub>. The corresponding N-methylated ligand N<sub>2</sub>Me<sub>2</sub>S<sub>2</sub>'<sup>2-</sup> yielded only the complexes [Fe(CO)<sub>2</sub>(N<sub>2</sub>Me<sub>2</sub>S<sub>2</sub>')] (**15**) and [Fe(N<sub>2</sub>Me<sub>2</sub>S<sub>2</sub>')] (**16**). X-ray structure analyses of complexes **7**, **8**·MeOH, **3**, [Fe(CO)(dppm)(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')]·0,5THF (**5**·0,5THF, dppm = bis(diphenylphosphino)methane), and **12**·0,5N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>'-H<sub>2</sub> 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(PR<sub>3</sub>)<sub>2</sub>(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] complexes is not caused by steric but by electronic effects. The cyclic voltammograms and the reactivity of the [Fe(L)(L')(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] complexes corroborate this assumption. The oxidation behaviour of the [Fe(L)(L')(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] complexes depends critically on the coligands L and L'. Reaction of **1** with dioxygen leads to oxidative dehydrogenation of the N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>'<sup>2-</sup> ligand and yields the dinuclear Schiff-Base complex [Fe('gma')<sub>2</sub>] ('gma'<sup>2-</sup> = glyoxal-bis(2-mercaptoanil)(2-)). In contrast, oxidation of [Fe(CO)(PR<sub>3</sub>)(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] , [Fe(PR<sub>3</sub>)<sub>2</sub>(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] and [Fe(P(OR)<sub>3</sub>)<sub>2</sub>(N<sub>2</sub>H<sub>2</sub>S<sub>2</sub>')] complexes by dioxygen occurs metal-centered and gives the Fe(IV) complexes [Fe(PR<sub>3</sub>)(N<sub>2</sub>S<sub>2</sub>')] (R = Me, Pr), [Fe(P(OR)<sub>3</sub>)(N<sub>2</sub>S<sub>2</sub>')] (R = Me) and [Fe(N<sub>2</sub>S<sub>2</sub>')<sub>2</sub>] that contain the tetraamionic thiolate-amide ligand N<sub>2</sub>S<sub>2</sub>'<sup>4-</sup>.