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ISOLATION AND INVESTIGATION OF THE COMPLEX $Li_3[FeNp_3N_2] \cdot nEt_2O$ – THE PRODUCT OF INTERACTION OF MOLECULAR NITROGEN WITH A NAPHTHYL DERIVATIVE OF ZERO-VALENT IRON *

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Summary

The complex $Li_3[FeNp_3N_2] \cdot nEt_2O$ produced by the reaction of N_2 with $Li_3FeNp_3 \cdot mEt_2O$ has been isolated and its magnetic properties and IR spectra investigated. The proposed structure of the complex includes the linear fragment FeNNLi.

The reaction of $FeCl_3$ with lithium organic compounds in ether produces low-valent iron complexes âble to reduce dinitrogen [1,2]. In the case of LiPh, the complex active towards N_2 was isolated and found to have the composition $Li_4FePh_4 \cdot 4Et_2O$, and a molecular structure involving the planar fragment FeC_4. Evidently this structure favors coordination of N_2, apparently perpendicular to the plane formed by iron and four carbons. It has been suggested that the reduction of N_2 proceeds with coordination of one of the lithium atoms of nitrogen to form a Fe–N=N–Li fragment [2].

To obtain more evidence for this conclusion and to generalize it to other similar systems the system $FeCl_3$/α-naphthyllithium, which produces the tetrahedral iron(II) complex $Li_2[FeNp_4] \cdot 2Et_2O$ (**A**) was investigated. Complex **A** itself is unable to react with N_2, but it reduces dinitrogen in the presence of other organolithium compounds such as LiPr or LiPh [3,4].

1. Formation of the iron(0) complex in the reaction of $Li_2FeNp_4 \cdot 2Et_2O$ with LiPr and its reaction with N_2

An excess of naphthyllithium does not reduce the iron in $Li_2Fe(II)Np_4 \cdot 2Et_2O$

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* Dedicated to Professor Lamberto Malatesta in recognition of his important contributions to organometallic chemistry.

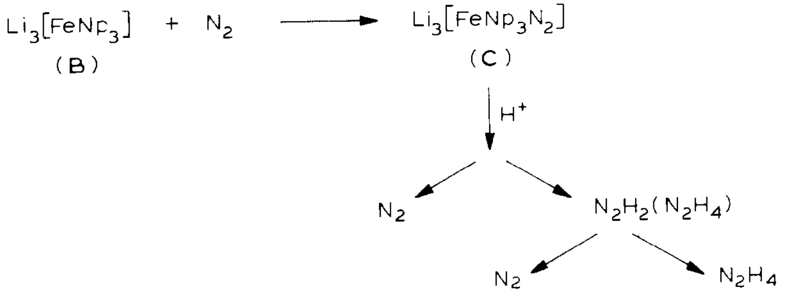
[4]. Presumably involvement of additional aryl or alkyl groups in the iron coordination sphere is needed for the reduction $Fe^{II} \rightarrow Fe^{0}$, but coordination of bulky naphthyl groups is sterically hindered. In the presence of a smaller aryl or alkyl group the reduction of iron(II) proceeds via intramolecular disproportionation or recombination of organic groups in the coordination sphere of the iron; e.g., for LiPr:

$$\underset{(\mathbf{A})}{Li_2FeNp_4} + \text{n-PrLi} \xrightarrow[\text{ether}]{} Li_3FePrNp_4 \rightarrow C_3H_6 + C_{10}H_8 + \underset{(\mathbf{B})}{Li_3FeNp_3}$$

The stoichiometry of this reaction is confirmed by formation of propylene and naphthalene together with the iron(0) complex in the reaction of Li_2FeNp_4 with n-PrLi. The intensely-coloured complex **B** (λ_{max} 547 nm) was isolated from the solution as fine crystals. The elemental analysis corresponds to formulation (**B**).

When kept under dinitrogen, complex **B** reacts with N_2 to form a new complex $Li_3[FeNp_3N_2] \cdot n Et_2O$ (**C**) (λ_{max} 647 nm), containing reduced dinitrogen. The number of naphthyl groups in the complex remains unchanged.

When complex **C** is decomposed by proton-containing reagents, hydrazine is produced together with free dinitrogen and some dihydrogen. The total amount of $N_2 + N_2H_4$ is always equal to a number of molecules of complex decomposed. The maximum yield of hydrazine (22–25% per complex **C**) is obtained when a solution of HCl in dry methanol is used to decompose the complex at −80°C. When pure methanol is used, the yields of N_2H_4 are 10–15%, and for 1 *N* aqueous H_2SO_4 they are only 5–6%. These results suggest that diimide N_2H_2 is initially formed upon decomposition of complex **C**, and disproportionation then gives N_2H_4 and N_2. Some N_2H_2 may give N_2 by reduction of other compounds present in the sytem. Formation of N_2 as well as N_2H_4 could also arise directly from complex **C** in the course of its decomposition:



Differences in the N_2H_4/N_2 ratio when various reagents are used to decompose complex **C** may be explained by changes in the ratio of the rates of these processes.

2. Magnetic measurements.

Magnetic weighing of initial complex **A** of iron(II) has shown that it is paramagnetic (μ_{eff} 5.94 μB) *. This is consistent with crystal field theory, according to which a paramagnetic tetrahedral complex with d^6 electronic configuration has to be high-spin [5].

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* Such a high μ_{eff} value is the result of a 10–15% admixture of supermagnetic iron(0).

Complex **B** (of iron(0)) and the product of its reaction with N_2 (**C**) were shown to be diamagnetic.

3. Infrared spectra.

The IR spectra of complex **C**: (a) $N_2 = {}^{14}N_2$, (b) $N_2 = {}^{15}N_2$, and of complex **B** are shown in Fig. 1. Table 1 lists the observed IR frequencies and tentative band assignments for these complexes.

The most important difference between IR spectra of the dinitrogen-containing **C** complex and its precursor complex **B** is the strong broad (180–200 cm^{-1}) band at 1685 cm^{-1}, which is shifted to ~ 1650 cm^{-1} when ${}^{15}N_2$ is substituted for ${}^{14}N_2$. Thus the band at 1685 cm^{-1} must be attributed to the NN stretching mode. The IR spectrum of complex **C** displays a very weak band at ~ 675 cm^{-1} which is shifted to ~ 655 cm^{-1} upon replacement of ${}^{14}N_2$ by ${}^{15}N_2$, and which may be tentatively assigned to the FeN stretching mode. Other bands in the IR spectrum of complex **C** correspond to the vibrations of naphthyl rings and coordinated ether molecules, and have similar values to those for complex **B**. It is of interest that broad (80–150 cm^{-1}) intense bands in the 1600–1850 cm^{-1} region correspond to the NN stretching mode [7] in the binuclear complex ClL_4ReN_2A (A is a Lewis acid) with a linearly coordinated N_2 bridge; similarly for complex **C** the ν(ReN) frequencies are shifted to 700–900 cm^{-1} [8] compared with 522 cm^{-1} in initial mononuclear complex $Cl(PMe_2Ph)_4ReN_2$ [9].

Discussion

The experimental results and previously reported data [2,3] permit definite conclusions drawn about the coordination of N_2 to the active site of complex **B** and the structure of complex **C** involving reduced dinitrogen.

The diamagnetic complex **B** of iron(0) with electronic configuration d^8 has either a trigonal-pyramidal or planar FeC_3 skeleton. In both cases the structure should favour coordination of the dinitrogen molecule to the iron atom and so linear coordination of a N_2 molecule to iron in complex **B** may be suggested as the first step of the N_2 activation.

Substantial decrease in the NN stretching frequency in complex **C** (to 1685 cm^{-1}) and the significant broadening and increase of the ν(FeN) band compared with those for linear mononuclear complexes (in which the NN stretching frequencies are in the region 1920–2250 cm^{-1}, with narrow bands of about 10–40 cm^{-1}, and metal-nitrogen frequencies not above 530 cm^{-1} *) lead to the conclusion that the coordinated N_2 molecule is bound at the other end to one or several lithium atoms, as we previously postulated for the complex produced in the reaction of N_2 with complex $Li_4[FePh_4] \cdot 4Et_2O$ [2].

Bridging asymmetrical linear coordination of an N_2 molecule to the low valent transition metal atom at the one end and to the acceptor centre at the other is found in several types of dinitrogen complexes, such as the previously mentioned ClL_4ReN_2A (where A is a Lewis acid) [5], L_4MNNH_2, $M = Mo^0$, W^0 [11], $L_3CoN_2Mg(THF)_2$ $L = PPh_3$ [12], *trans*-$[WI(NNSiMe_3)(PMe_2Ph_4)_4]$ [13].

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* E.g. for mononuclear $H_2Fe(PPh_3)_3N_2$ with linearly coordinated N_2; ν(NN) 2074 cm^{-1}, $\Delta_{1/2}$(NN) 29 cm^{-1} in benzene solution; ν(FeN) 473 cm^{-1}, $\Delta_{1/2}$(FeN) 10 cm^{-1} in the solid state [10].

TABLE 1. IR SPECTRA OF THE COMPLEXES $Li_3[FeNp_3N_2]\cdot nEt_2O$ AND $Li_3FeNp_3\cdot mEt_2O$ (cm^{-1})

$Li_3[FeNp_3N_2]\cdot nEt_2O$ [b]	$Li_3FeNp_3\cdot mEt_2O$	Tentative assignment [a]	$Li_3[FeNp_2N_2]\cdot nEt_2O$ [b]	$Li_3FeNp_3\cdot mEt_2O$	Tentative assignment [a]
475 m	478 w	31	1360 m	1350 m, sh	
510 w			1367 s	1362 s	44
610 w, sh			1389 s	1386 s	36, $\delta_{A_1}(CH_3)_{Et_2O}$
628 m	621 w	48	1415 w		
675(655) vw		$\nu(FeN)$	1443 m	1450 m	$\delta_E(CH_3)_{Et_2O}$
731 m					
748 w, sh	750 m, sh	39	1488 s	1490 vw	$\delta_{A_1}(CH_2)_{Et_2O}$
764 w, sh	758 m, sh				
782 vs	781 vs	30	1502 m	1506 m	43
788 vs	800 vs, sh		1508 m		
	820 w		1522 m	1524 vw	
	843 w	26	1535 m		
882 m	882 vw	$\nu_s(C-O)_{Et_2O}$	1555 w	1550 vw	
	911 vw		1562 m	1568 w	
940 m	944 w	29	1593 m	1593 m	35
	958 m		1608 m		
1010 m	1010 m	47	1685(1650) s, br		$\nu(NN)$
1015 m, sh			2865 m	2865 s	$\nu(A_1)(CH_3)_{Et_2O}$
1060 s	1061 m	$\nu_{as}(CO)_{Et_2O}$		2870 m.	$\nu(A_1)(CH_2)_{Et_2O}$
1091 m	1095 vw			2910 w, sh	$\nu(B_1)(CH_2)_{Et_2O}$
1117 s			2925 m	2930 vs	$\nu(CH)_{Et_2O}$
1126 m, sh	1122 m	38			
1140		46	2955 m	2962 s	$\nu_E(CH_3)_{Et_2O}$
1150 w	1150 w		3000 w	3005 vw	
1180 m	1180 vw		3024 s	3030 m	42
1210 w	1210 w	45	3048 s	3050 s	34
1242 w	1242 w		3060 m, sh	3065	33
1267 m	1269 m	37	3075 w	3070 vw	41
1287 m	1289 m				

[a] The numbers indicate the vibrations of the naphthyl ring according to ref. 6. The symbols ν_E, ν_{A_1}, ν_{B_1}, δ_A, δ_E signify the vibrations of coordinated ether. [b] The frequencies $\nu(NN)$, $\nu(FeN)$ for $Li_3[FeNp_3{}^{15}N_2]\cdot nEt_2O$ are shown in parentheses. vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

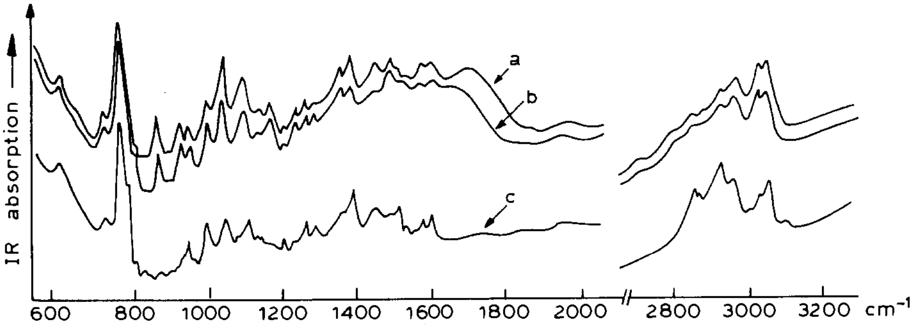

Fig. 1. IR spectra in the region of 500–3300 cm^{-1}. (a) $FeNp_3{}^{14}N_2Li_3 \cdot nEt_2O$; (b) $FeNp_3{}^{15}N_2Li_3 \cdot nEt_2O$; (c) $FeNp_3Li_3 \cdot mEt_2O$.

In all cases such a bridging coordination of N_2 results in an effect similar to that observed for our complex C; i.e. decrease of ν(NN) mode frequency and increase in its halfwidth compared with those for mononuclear end-on complexes. Presumably coordination between lithium ion and the dinitrogen molecule promotes additional electron transfer from Fe to N_2, a decrease of the NN bond order leading to approach to the structure Fe–N=N–Li. The decomposition of the complex by protic reagents produces diimide without strong dependence on acidity of the added substance; this feature is also consistent with a structure which already contains a doubly-bonded N=N moiety.

Similar results were obtained for the complex $(Ph_3P)_3CoN_2Mg(THF)_2$ [12]. Its IR spectrum contains a broad band at 1840 cm^{-1} and decomposition by protic species gives hydrazine and dinitrogen, probably arising from initially formed diimide.

Experimental

Reagents. Dry iron(III) chloride was prepared by chlorination of iron powder at 240–260°C. It was purified by sublimation in a stream of chlorine mixed with argon.

Solvents. Diethyl ether, pentane, toluene were dried as specified in ref. 14. n-Propyllithium and α-naphthyllithium were synthesized as previously described [15,16].

Lithium tetranaphthylferrate. $Li_2(FeNp_4) \cdot 2Et_2O$ was prepared by dry iron chloride with α-naphthyllithium in ether at −15°C, as described in ref. 14.

Dinitrogen complex C. A freshly-prepared ether solution of n-propyllithium was added under dinitrogen to a stirred ether solution of lithium tetranaphthylferrate at 0°C. The initial concentration of iron complexes was 1.5×10^{-2} *M* and the final ratio n-PrLi/Fe ≈ 1.5. The mixture was allowed to warm during several hours to room temperature, the colour of the mixture changing during this procedure from bright crimson to dark green. The progress of reaction was monitored by analysis of aliquots for hydrazine content after decomposition by dry HCl; the end of the reaction corresponds to 22–25% N_2H_4/Fe. Subsequently the ether was evaporated in vacuo, and the resulting black powder was washed 4–5 times with small portions of cold pentane, then dried in vacuo and stored under dry dinitrogen or argon.

Analytical procedures. In the analysis for bound nitrogen the solution of the complex was decomposed by condensation of dry HCl into the evacuated and frozen solution of the complex in liquid nitrogen. The non-condensing gases ($N_2 + H_2$) produced in decomposition were transferred by Toepler pump to the calibrated volume and dinitrogen was determined by gas chromatography. Water was added to the decomposed complex and N_2H_4 was analyzed in the water fraction by use of dimethylaminobenzaldehyde [17]. After oxidation of all the iron present in the solution to ferric ions by means of concentrated HNO_3, these ions were determined spectrophotometrically by adding NH_4CNS and measuring the optical density at 20400 cm^{-1}.

The number of naphthyl groups bound to iron after reduction of lithium tetranaphthylferrate by n-propyllithium was assessed from the amount of naphthalene (as revealed by GLC) produced by careful hydrolysis at 0°C of the dinitrogen complex **C** by H_2SO_4 (20%) [18].

Spectral measurement. Infrared spectra (Fig. 1) were recorded on UR20 and Perkin–Elmer 325 spectrometers. The stated frequencies are accurate to ±(1–2) cm^{-1} and ±(2–5) cm^{-1} for narrow and broad bands, respectively. The samples were made up under an inert atmosphere as tablets with KBr or Nujol mulls. Hermetically sealed cells with KBr windows were used. Electronic adsorption spectra were recorded on a Specord UV-VIS spectrophotometer. Solutions of samples of complexes for spectral measurements were prepared under an inert atmosphere in a glass vacuum system.

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