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Molecular structure of binuclear complex $Fe_2(CO)_6(\mu\text{-}PhNC(O)C_6H_4NH)$, synthesized from $Fe(CO)_5$ and azobenzene

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Abstract

$Fe_2(CO)_6(\mu\text{-}PhNC(O)C_6H_4NH)$ (I) has been synthesized in a low yield by photochemical reaction of $Fe(CO)_5$ with azobenzene in toluene under reflux. The complex has been characterized by an X-ray diffraction study. The Fe–Fe bond (2.401 Å) of the $Fe_2(CO)_6$ binuclear fragment is bridged by the anthranilic acid anilide fragment coordinated to each of the Fe atoms by its PhN (Fe–N 2.047(1) and 2.061(1) Å) or NH (1.982(1) and 1.984(1) Å) groups, respectively.

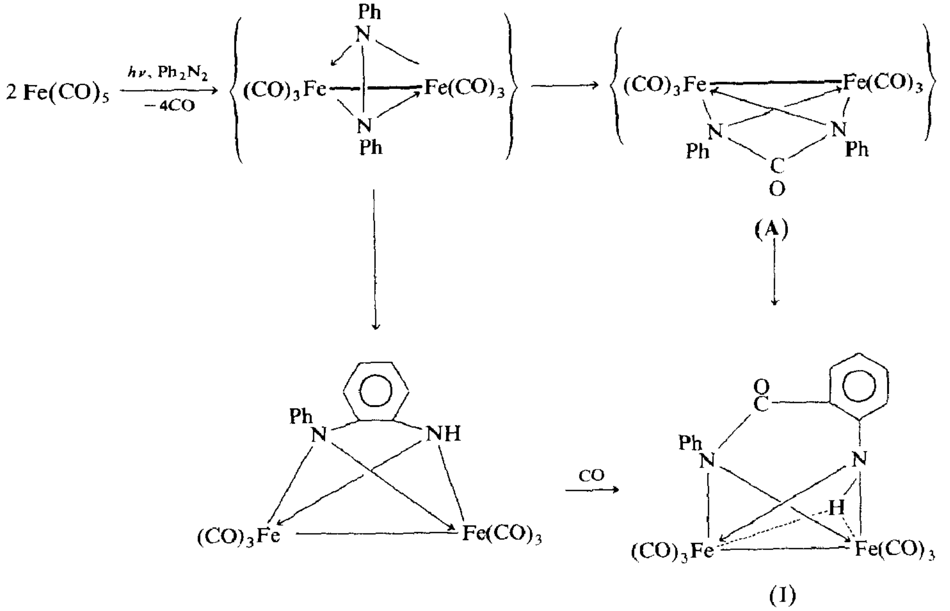
Introduction

Several examples illustrating the analogy between isoelectronic coordination of metal complexes by S_2 and azobenzene PhN=NPh molecules as well as by sulfur atoms and phenylimide (nitrene) fragments have been reported. For instance the following pairs of complexes $(C_5H_4Pr^i)_2V_2(\mu,\eta^1\text{-}S_2)(\mu\text{-}S)_2$ [1] and $(C_5H_5)_2V_2(\mu,\eta^1\text{-}Ph_2N_2)(\mu\text{-}NPh)_2$ [2], $Fe_3(CO)_9(\mu_3\text{-}S)_2$ [3] and $Fe_3(CO)_9(\mu_3\text{-}NMe)_2$ [4] have similar geometries. Since the insertion of CO into the S–S bond proceeds readily for the well known complex $Fe_2(CO)_6(\mu,\eta^2\text{-}S_2)$ to give the μ-dithiocarbonate complex [5], we expected the formation of the analogous complex $Fe_2(CO)_6(\mu\text{-}PhNC(O)NPh)$ (A) in the reaction of $Fe(CO)_5$ with azobenzene under UV-irradiation in toluene under reflex, but the outcome was very different.

Results and discussion

The only compound which we managed to isolate in a very poor yield (~ 2%) from the reaction of $Fe(CO)_5$ with azobenzene was the binuclear complex

$Fe_2(CO)_6(\mu\text{-}PhNC(O)C_6H_4NH)$ (I) as air-stable bright-red prisms. Complex I probably results from the isomerization of the intermediate (**A**). On the other hand, the well known product of the reaction between $Fe_3(CO)_{12}$ and azobenzene—the binuclear complex $Fe_2(CO)_6(\mu\text{-}PhN\text{-}C_6H_4NH)$ [6]—can also be the intermediate. It is evidently formed from the hypothetical $Fe_2(CO)_6(\mu,\eta^2\text{-}Ph_2N_2)$ and is then converted into I by CO insertion into the N–C bond. As a result a fragment consisting of anthranilic acid anilide coordinated to the $Fe_2(CO)_6$ group is formed which in the IR spectra gives a band at 1625 cm^{-1}, corresponding to the ν_{CO} of the amide group.



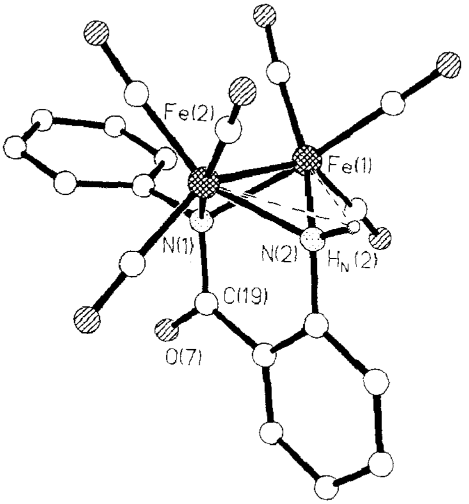


Fig. 1. The structure of $Fe_2(CO)_6(\mu\text{-}PhNC(O)C_6H_4NH)$.

Table 1

Atomic coordinates for $Fe_2(CO)_6(\mu\text{-}PhNC(O)C_6H_4NH)$ (For Fe $\times 10^5$, for O and C $\times 10^4$, for H $\times 10^3$)

Atom	*x*	*y*	*z*
Fe(1)	3103(3)	18166(3)	34075(2)
Fe(2)	3115(3)	37275(3)	35620(2)
O(1)	1151(2)	102(2)	2624(1)
O(2)	−1582(2)	965(2)	3480(1)
O(3)	540(2)	875(2)	4666(1)
O(4)	1030(2)	5772(2)	3038(1)
O(5)	−1519(2)	4610(2)	3850(1)
O(6)	544(2)	3933(2)	4938(1)
O(7)	2770(1)	2910(2)	2788(1)
N(1)	1458(1)	2795(2)	3402(1)
N(2)	−85(1)	2929(2)	2804(1)
C(1)	801(2)	744(2)	2916(1)
C(2)	−847(2)	1294(2)	3455(2)
C(3)	491(2)	1260(2)	4175(1)
C(4)	754(2)	5002(2)	3249(1)
C(5)	−814(2)	4246(3)	3730(1)
C(6)	503(2)	3855(2)	4393(1)
C(7)	2136(2)	2705(2)	3908(1)
C(8)	2470(2)	3624(2)	4206(1)
C(9)	3087(2)	3537(3)	4710(2)
C(10)	3388(2)	2546(3)	4912(1)
C(11)	3094(2)	1636(3)	4597(2)
C(12)	2472(2)	1714(2)	4092(1)
C(13)	398(2)	3019(2)	2231(1)
C(14)	−77(2)	3105(3)	1659(1)
C(15)	403(2)	3165(3)	1088(1)
C(16)	1370(2)	3136(3)	1086(2)
C(17)	1841(2)	3051(3)	1652(1)
C(18)	1373(2)	3000(2)	2223(1)
C(19)	1922(2)	2903(2)	2809(1)
$H_N(2)$	−69(2)	292(2)	273(1)
H(8)	226(2)	427(2)	406(1)
H(9)	323(2)	415(2)	495(1)
H(10)	379(2)	249(3)	538(1)
H(11)	335(2)	97(2)	473(1)
H(12)	229(2)	112(2)	385(1)
H(14)	−76(2)	308(2)	165(1)
H(15)	−6(2)	320(2)	73(1)
H(16)	175(2)	318(2)	70(1)
H(17)	249(2)	310(2)	170(1)

The X-ray diffraction study * of I (Fig. 1) shows that the two Fe atoms form a very short single Fe–Fe bond (2.401 Å) and are also linked by the bridging N atoms of the PhN and C_6H_4NH fragments (Fe–N 2.047(1)–2.061(1) and 1.982(1)–1.984(1) Å, respectively). These groups are connected to each other by the CO group (C–O

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* The X-ray diffraction data show that crystals of I are in the space group *Pbca*, *a* 14.454(2), *b* 12.453(2), *c* 21.167(2) Å, *V* 3810.0 A^3, $Z = 8$, T −100 °C, $R = 0.028$, data refined anisotropically by least-squares for all non-hydrogen atoms, all H atoms were located and refined.

Table 2

Bond lengths and bond angles for $Fe_2(CO)_6(\mu\text{-}PhNC(O)C_6H_4NH)$ (I).

Bond	d(Å)	Angle	ω(°)	Angle	ω(°)
Fe(1)–Fe(2)	2.402(1)	Fe(2)Fe(1)N(1)	54.12(6)	Fe(2)N(1)C(19)	118.1(2)
Fe(1)–N(1)	2.058(2)	Fe(2)Fe(1)N(2)	52.52(6)	C(7)N(1)C(19)	109.8(2)
Fe(1)–N(2)	1.969(2)	N(1)Fe(1)N(2)	79.25(9)	N(1)C(7)C(8)	120.3(2)
Fe(1) ··· H_N(2)	2.46(2)	Fe(1)Fe(2)N(1)	54.36(6)	N(1)C(7)C(12)	120.8(2)
Fe(2)–N(1)	2.052(2)	Fe(1)Fe(2)N(2)	52.38(6)	C(8)C(7)C(12)	109.7(2)
Fe(2)–N(2)	1.972(2)	N(1)Fe(2)N(2)	79.31(9)	Fe(1)N(2)Fe(2)	75.11(8)
Fe(2) ··· H_N(2)	2.49(2)	Fe(1)N(1)Fe(2)	71.52(7)	Fe(1)N(2)C(13)	118.2(2)
N(1)–C(7)	1.455(3)	Fe(1)N(1)C(7)	119.5(2)	Fe(1)N(2)H_N(2)	113(1)
N(1)–C(19)	1.429(4)	Fe(1)N(1)C(19)	116.0(2)	Fe(2)N(2)C(13)	121.2(2)
N(2)–C(13)	1.404(3)	Fe(2)N(1)C(7)	117.7(2)	Fe(2)N(2)H_N(2)	116(1)
N(2)–H_N(2)	0.89(2)			C(13)N(2)H_N(2)	109(1)

1.242(3) Å); the C–NPh and C–C_6H_4NH bond lengths are 1.424(3) and 1.479(3) Å, respectively. The interaction of the NH hydrogen atom with both metal atoms is weak (Fe ··· H 2.46(2) and 2.49(2) Å).

Experimental

All synthetic procedures were carried out under pure argon in absolute solvents. IR spectra were recorded with a Specord 75-IR instrument in KBr pellets. X-ray diffraction data were recorded with a Syntex $P2_1$ (λMoK_α, T −100 °C, θ–2θ scan, $2\theta_{max}$ 56 °) automatic diffractometer. Atomic coordinates, and selected bond lengths and angles are listed Tables 1 and 2, respectively.

$Fe_2(CO)_6(\mu\text{-}PhNC(O)C_6H_4NH)$

A solution containing 0.5 g (2.6 mmol) of $Fe(CO)_5$ and 0.23 g (1.3 mmol) of Ph_2N_2 in 30 ml of toluene under reflux was irradiated with UV for 20 h. The mixture was then concentrated to 15 ml, pentane was added and the mixture was kept at room temperature for 7 d. The bright-red prisms precipitated were separated by decantation, washed with pentane and dried in vacuo at 0.1 torr. IR (ν, cm^{-1}): 480 w, 505 w, 530 w, 570 m, 610 w, 620 w, 670–700 br.w, 730 w, 750 w, 930 w, 1015 w, 1050 w, 1100 w, 1260 m, 1590 m, 1625 s, 1980 v.s, 2020 v.s, 2065 s, 3290 br.w.

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