X-Ray Molecular Structure of μ-(Isopropylamino)-μ-(propanone oximato-*O*,*N*)-bis(tricarbonyliron) (*Fe–Fe*): a New Unsymmetrical Nitroso Binuclear Compound

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Summary *X*-Ray analysis of μ-(isopropylamino)-μ-(propanone oximato)-bis(tricarbonyliron)(*Fe–Fe*), the main product of the reaction between [$Fe_3(CO)_{12}$] and 2-nitropropane, shows an unusual structure with an Fe–N–O–Fe ring, which can be related to the nature of novel intermediates in the reduction of nitro-compounds by iron carbonyls.

CONSIDERABLE attention has been recently devoted to the products and mechanism of the reduction of organic nitro-compounds by iron carbonyls[1].

We have investigated the reactions of [$Fe_3(CO)_{12}$] with nitroethane and 2-nitropropane,[2] and we now report the *X*-ray structure analysis of the main product of the second reaction.

[$Fe_3(CO)_{12}$] reacts with an equimolar quantity of 2-nitropropane in toluene at 80 °C to give several products, from which the title compound was isolated by t.l.c. as orange crystals (m.p. 94·5 °C, yield *ca.* 5%); elemental analysis indicates the formula $Fe_2(CO)_6(C_6H_{14}N_2O)$.

This complex crystallizes (from n-heptane solution at −20 °C) in the triclinic system, space group $P\bar{1}$, with cell dimensions a = 12·008(5), b = 9·827(4), c = 8·580(4) Å, α = 120·53(4), β = 99·29(1), γ = 96·80(1)°, M = 409·95, U = 836·4 Å^3, D_m = 1·64 g cm^{-3}, D_c = 1·63 g cm^{-3}, Z = 2.

A total of 2945 reflections were collected on an automatic Philips PW 1100 four-circle diffractometer to $2\theta \leqslant 50°$ (Mo-K_α radiation, λ = 0·7107 Å, graphite monochromator). The structure was solved with an initial Patterson map and all the light non-hydrogen atoms were located with subsequent difference-Fourier syntheses. Isotropic refinement, using least-squares methods, led to the present R = 0·090 for 2536 reflections with $I > 2\sigma(I)$.

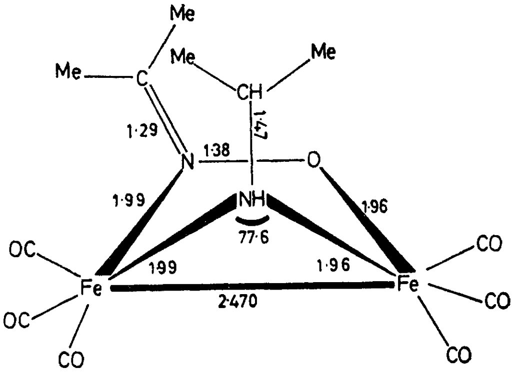

FIGURE. A schematic molecular view showing the more important distances (Å) and angles (°). Average e.s.d. of Fe–Fe = 0·002 Å; average e.s.d. of Fe–N, Fe–O, N–O, and C–N 0·01 Å; average e.s.d. of Fe–N–Fe angle 0·3°.

The structure (see Figure) shows an isopropylamino-group and a propanone oximato group both bridging an $Fe_2(CO)_6$ unit; the N · · · N distance has the non-bonding value of 2·66(1) Å.

The large value of the Fe–N–Fe angle involving the bridging nitrogen atom of the isopropylamino-ligand is a consequence of the greater length of the Fe–Fe bond, with respect to similar complexes[3] with non-bonding N · · · N distances. A novel feature of the structure is the presence of the Fe–N–O–Fe ring with an sp^2 hybridized nitrogen atom of the propanone oximato ligand.

The i.r. spectrum shows six carbonyl bands at 2072(s), 2031(vs), 1995(vs), 1986(vs), 1973(s), and 1965(m) cm^{-1}, consistent with the asymmetrical structure; other significant absorptions are at 3262 (ν_{N-H}), 1737 (ν_{N-O}), and 1601 ($\nu_{C=N}$) cm^{-1}. In the mass spectrum the fragmentation of the parent ion peak (m/e 410) proceeds *via* successive loss of the 6 CO groups, together with the loss of the *N*-bonded oxygen atom.

The 100 MHz ^{1}H n.m.r. spectrum ($CDCl_3$) is in accord with the solid-state structure showing resonances at τ 6·75br (NH), 7·25 (septet) and 8·37 (d) (Pr^i), and 8·05 and 8·25, (each s, propanone oxime-Me).

This is the first reported example of an unsymmetrical binuclear nitroso-complex of an iron carbonyl. In the reduction of alkyl nitro-compounds by iron carbonyls a pathway involving nitrene radicals is commonly accepted;[4] this structure gives evidence of an additional step involving nitroso-intermediates.

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