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Preliminary communication

THE MOLECULAR STRUCTURE OF CYCLOPENTADIENYLIRON NITROSYL DIMER; A NOVEL COMPOUND CONTAINING AN Fe—Fe DOUBLE BOND*

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Summary

The molecular structure of cyclopentadienyliron nitrosyl consists of dimeric $[(h^5\text{-}C_5H_5)Fe(\mu\text{-}NO)]_2$ molecules; the bonding parameters indicate the presence of symmetrically-bridged nitrosyl groups, as well as a novel Fe—Fe double bond.

In recent years there has been considerable interest in the stereochemistry and bond properties of systems involving a transition metal to nitrosyl ligand bond. Our previous work on several dimeric transition metal complexes has revealed the symmetrical [1,2] or unsymmetrical [3,4] nature of this ligand when acting as a bridging group. In order to gain insight into this problem we have undertaken the systematic preparation and structural characterization of a large assortment of this kind of complexes. We now report preliminary results of a three-dimensional single-crystal X-ray analysis of $[(C_5H_5)Fe(NO)]_2$ [5]. Crystal data: $[(C_5H_5)Fe(NO)]_2$; dark green crystals (benzene—hexane), monoclinic, space group $P2_1/c$, $a = 7.8257(9)$Å, $b = 5.9998(9)$Å, $c = 11.9875(13)$Å, β 105.548(9)°, $Z = 2$, $D_n = 1.85$, $D_c = 1.848$ g·cm^{-3}.

A set of 1872 independent reflections having $2\theta(\text{Mo-}K_\alpha) < 63.7°$ were collected using Nb-filtered Mo-K_α radiation and θ—2θ scans on a Syntex $P\bar{1}$

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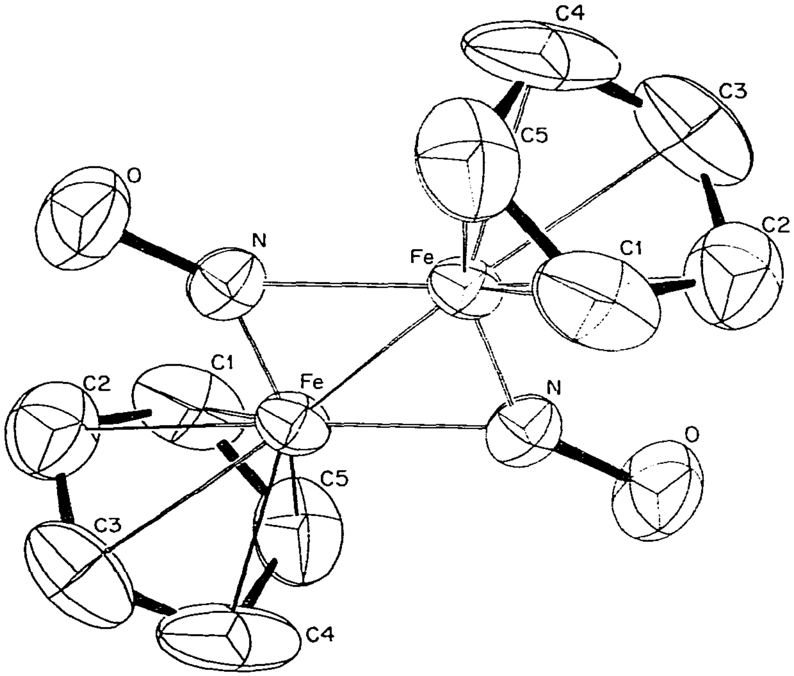

Fig.1. The molecular structure of cyclopentadienyliron nitrosyl dimer.

Autodiffractometer. The 574 independent reflections having 2θ (Mo-K_α) $< 43°$ and $I > \sigma(I)$ were used to solve and refine the structure using the heavy-atom technique and full-matrix least-squares. Unit weighted full-matrix least-squares refinement which employed anisotropic thermal parameters for the eight crystallographically independent non-hydrogen atoms resulted in a conventional R factor of 0.063.

The analysis shows that the crystal contains dimeric $[(h^5\text{-}C_5H_5)Fe(\mu\text{-}NO)]_2$ molecules as shown in Fig. 1. The two iron atoms are bonded to each other symmetrically bridged by two crystallographically equivalent nitrosyl groups; each iron atom is also *pentahapto*-bonded to a cyclopentadienyl ring. The entire $Fe(\mu\text{-}NO)_2Fe$ moiety is virtually coplanar and perpendicular to the planes of the cyclopentadienyl ligands; the five-fold axes of the cyclopentadienyl groups are nearly colinear with the Fe—Fe bond and perpendicular to the vector joining the two bridging nitrosyl groups. While the dimer formally possesses only C_i-$\bar{1}$ symmetry because of the presence of the crystallographic inversion center midway between the two iron atoms, it approximates D_{2h} symmetry.

Average values of 2.09(1)Å and 1.38(2)Å are observed for the Fe—C and C—C bonds, respectively. The two crystallographically independent Fe—N bonds average 1.768(9)Å. The N—O bond length is 1.254(12)Å. Pertinent bond angles are: Fe—N—Fe′, 82.3(4)°; N—Fe—N′, 97.7(4)°; Fe—N—O, 138.8(8)°.

Unlike the structures of $(h^5\text{-}C_5H_5)(NO)Mn(\mu\text{-}NO)_2Mn(h^1\text{-}C_5H_5)(h^5\text{-}C_5H_5)$ [4] and $(h^5\text{-}C_5H_5)(NO)Mn(\mu\text{-}NO)_2Mn(NO_2)(h^5\text{-}C_5H_5)$ [3], which contain highly unsymmetrical nitrosyl bridges, the NO bridges in this compound are of the symmetrical type like those observed in $[(h^5\text{-}C_5H_5)(NO)Cr(\mu\text{-}NO)]_2$ [1], and $(h^5\text{-}C_5H_5)(NO)Cr(\mu\text{-}NO)(\mu\text{-}NH_2)Cr(NO)(h^5\text{-}C_5H_5)$ [6], crystallographic studies on the structure of $[(h^5\text{-}C_5H_5)Co(NO)]_2$ [2] and related systems, which are currently being carried out in our laboratories, will provide data for comparison with the present structure.

If the *pentahapto*-bonded cyclopentadienyl rings and bridging nitrosyl groups are regarded to be 5- and 3-electron donors, respectively, each of the iron atoms in the dimer can achieve a filled valence shell configuration only by forming a (four-electron) double bond between the two metal atoms. The existence of such bond is in good agreement with the observed Fe—Fe bond length of 2.326(4)Å as compared to the 2.50—2.70Å distance usually observed for Fe—Fe single bonds [7].

References

1 J.L. Calderón, S. Fontana, E. Frauendorfer and V.W. Day, J. Organometal. Chem., 64 (1974) C10.
2 J.L. Calderón, S. Fontana, E. Frauendorfer and V.W. Day, work in progress.
3 J.L. Calderón, F.A. Cotton, B.G. de Boer and N. Martinez, J. Chem. Soc., D, (1971) 1476.
4 J.L. Calderón, S. Fontana, E. Frauendorfer, V.W. Day and B.R. Stults, submitted for publication.
5 H. Brunner, J. Organometal. Chem., 14 (1968) 173.
6 L.Y.Y. Chan and F.W. Einstein, Acta Cryst., B, 26 (1970) 1899.
7 M.C. Baird, Progr. Inorg. Chem., 9 (1969) 1.