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Preliminary communication

A DEFINITIVE IDENTIFICATION OF THE STRUCTURES OF DICYCLOPENTADIENYLDICHROMIUM TETRANITROSYL*

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Summary

The molecular structure of dicyclopentadienyldichromium tetranitrosyl consists of dimeric $[(h^5\text{-}C_5H_5)Cr(NO)_2]_2$ molecules in the *trans* configuration; the preliminary results of NMR and IR studies indicate the stereochemically nonrigid behaviour of this molecule in solution.

King et al. [1] recently reported that the reaction of $(h^5\text{-}C_5H_5)Cr(NO)_2Cl$ with $NaBH_4$ in a two-phase water—benzene system, yielded a red-purple crystalline solid, $[(h^5\text{-}C_5H_5)Cr(NO)_2]_2$ (I), bearing a remarkable resemblance to the isoelectronic $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ (II). The reported PMR measurements [2], as well as other evidence [3], strongly supports the three structure model in solution for the iron carbonyl complex, providing strong proof of the bridged—non bridged structure interconversions. Therefore, it seemed relevant to establish wether the isoelectronic chromium nitrosyl complex would behave in a similar fashion in showing this kind of fluxionality [2]. The proton NMR spectrum of the title compound (I) exhibits two single sharp lines at room temperature (τ 5.00 and 5.20 in $CDCl_3$ solution), with an intensity ratio shown of about 20/1. In order to ascertain the effect of an increase in the

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dielectric constant of the medium, small additions of polar solvents were made, resulting in an increase in relative intensity of the high field resonance. By analogy with the iron system, we assign the high and low field singlets to the *cis* and *trans* isomers, respectively; this behaviour and its consistency with infrared correlations (vide infra) are to be expected from the *cis* $\rightleftharpoons$ *trans* equilibrium. The infrared spectrum of (I) in cyclohexane solutions exhibits two bands at 1677 and 1518 cm^{-1}, which can be assigned to the antisymmetrical terminal and bridging nitrosyl stretches, with the intensity of the terminal nitrosyl roughly twice as intense as the bridging nitrosyls [4]; the weak band at 1748 cm^{-1} can be assigned to the symmetric terminal N—O stretch of the *cis* isomer [4]. At this point, these observations strongly suggest the existence of both bridged, *cis* and *trans* structures in solution.

In order to determine the molecular parameters of this complex, a single-crystal X-ray structural study was performed. Crystal data: $[(C_5H_5)Cr(NO)_2]_2$, dark-purple crystals (benzene—hexane), triclinic, space group $P1$, a = 7.174(1), b = 6.069(1), c = 7.927(1)Å, α 106.73(1)°, β 102.52(1)°, γ 85.18(1)°, D_m = 1.80, D_c = 1.823 g·cm^{-3}.

A set of 5900 independent reflections having 2θ(Mo-K_α) < 94.1° were collected using Zr-filtered Mo-K_α radiation and θ—2θ scans on a Systex $P\bar{1}$ autodiffractometer. The 708 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 non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms resulted in a conventional R factor of 0.027.

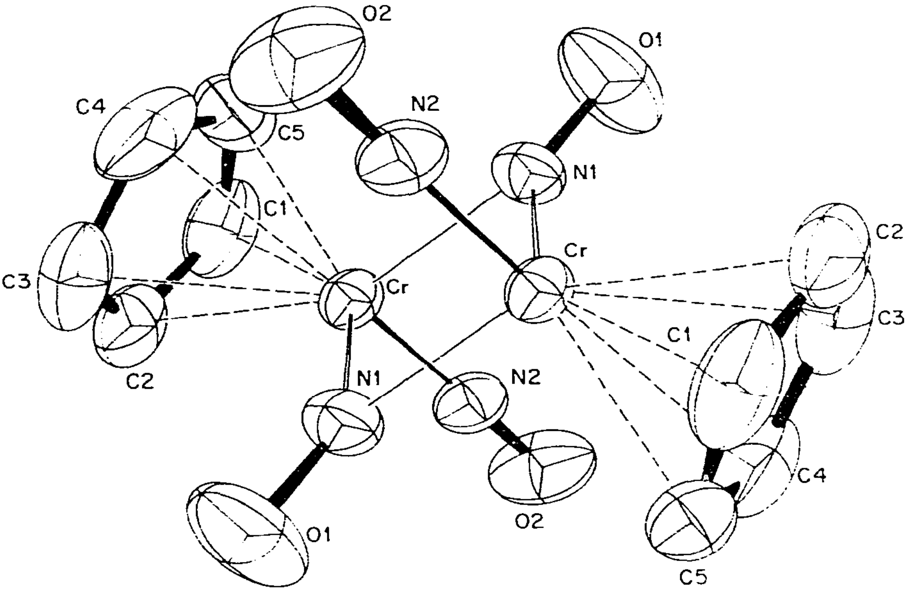

Fig.1. The molecular structure of dicyclopentadienyldichromium tetranitrosyl.

The analysis shows that the crystal consists of discrete dimeric $[(C_5H_5)Cr(NO)_2]_2$ molecules in the *trans* configuration as shown in Fig. 1. The two chromium atoms of the dimer are bonded to each other and are bridged by the two crystallographically equivalent nitrosyl groups, the two halves of the dimer being related to each other by the inversion center at the origin of the unit cell. Each chromium atom is also bonded to a terminal nitrosyl group and *pentahapto*-bonded to a cyclopentadienyl group. The Cr—Cr distance is 2.615(1)Å. The bridging Cr—N distances average 1.960(3)Å, while the terminal Cr—N distance is 1.690(3)Å. The Cr—C, C—C and C—H distances average 2.209(4), 1.377(7) and 0.90(5)Å, respectively. The nitrosyl N—O distances are 1.193(4) and 1.181(4)Å for bridging and terminal ligands respectively. Pertinent angles are: Cr—N—Cr′ (bridging nitrosyl), 86.7(1)°; Cr—N—O average 136.4(3)° for bridging nitrosyl and 175.6(5)° for the terminal group; N′—Cr—N (both bridging nitrosyl groups), 93.3(1)°.

This investigation is the first structural determination of one compound containing two symmetrically bonded bridging nitrosyl groups.

References

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