Thionitrosyl Ligand; *X*-Ray Molecular Structure of Dicarbonyl(η^5-cyclopentadienyl)thionitrosylchromium

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Summary An *X*-ray crystallographic analysis of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ shows that the thionitrosyl group co-ordinates essentially linearly to the chromium atom *via* the nitrogen atom.

THE organometallic thionitrosyl complex, $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$, was recently synthesized by the reaction of $Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$ with $S_3N_3Cl_3$.[1] Even though some physical properties of this complex were determined,[1] the mode of linkage of the NS group to the chromium atom remained uncertain. We have determined the molecular structure of the compound and now report our results which constitute the first fully documented *X*-ray structural analysis of a metal–thionitrosyl bond.†

Crystals of the title compound, suitable for *X*-ray work, were grown by sublimation at 35 °C in a static vacuum onto a water-cooled probe. *Crystal data:* $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$, $M = 219{\cdot}2$, monoclinic, space group $P2_1/m$, $a = 6{\cdot}5281(10)$, $b = 9{\cdot}6410(11)$, $c = 7{\cdot}0962(11)$ Å, $\beta = 99{\cdot}22(1)°$, $U = 440{\cdot}84(4)$ Å^3, $D_c = 1{\cdot}65$ g cm^{-3}, $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 14{\cdot}50$ cm^{-1}. The final *R*-index is 0·025 for 848 independent observed $[3\sigma(I)]$ reflections collected on a Nonius CAD4 diffractometer. The molecule has crystallographic *m*-symmetry with a disordered $\eta^5\text{-}C_5H_5$ ring in the ratio 2:1. All non-hydrogen atoms were refined with anisotropic temperature factors. The 2/3 H atoms were refined isotropically and the 1/3 H atoms were held at positions indicated by a difference Fourier synthesis with assigned isotropic thermal parameters.‡

The molecular structure is shown in the Figure which also gives important bond lengths and bond angles. Generally, the molecular geometry is similar to that exhibited by other 'piano stool' molecules [*e.g.*, $(\eta^5\text{-}C_5H_5)Mn(CO)_3$[2] and $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$[3]]. The Cr–C–O linkages are inherently linear, and the Cr–C(cp), Cr–C(O), and C–O bond lengths are comparable to those found in other cyclopentadienylchromium carbonyls.[3,4]

The most chemically interesting feature of the structure is the fact that the thionitrosyl ligand co-ordinates essentially linearly to the metal *via* the nitrogen atom. The Cr–N bond length of 1·694(3) Å falls in the range of values (*i.e.*, 1·630–1·717 Å)[4] reported for Cr–N bonds formed by linear, terminal nitrosyl ligands. Hence, in a formal

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† It has been reported (J. Chatt, *Pure Appl. Chem.*, 1977, **49**, 815) that the molecular structure of $Mo(NS)(S_2CNMe_2)_3$ contains an Mo–N distance of 1·74(1) Å and an Mo–N–S angle of 172·1(7)°. However, no other details of this structure have yet been published.

‡ The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

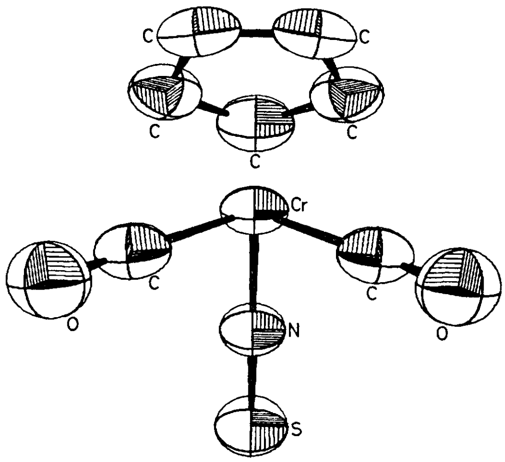

FIGURE. Molecular structure of $(\eta^5\text{–C}_5\text{H}_5)\text{Cr(CO)}_2\text{(NS)}$ as viewed down the crystallographic mirror plane. Only the 2/3 cyclopentadienyl ring is shown, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°), with e.s.d.s. in parentheses are: Cr–N, 1·694(3); Cr–C(O), 1·883(3); C–O, 1·131(3); and N–S, 1·551(3); ∠Cr–N–S, 176·8(2); ∠Cr–C–O, 178·1(2); ∠C(O)–Cr–C(O), 92·4(2); and ∠C(O)–Cr–N, 94·8(1). Cr–C(cp, 2/3), 2·13(1), 2 × 2·19(2), 2 × 2·22(1); Cr–C(cp, 1/3), 2·23(2), 2 × 2·18(2), 2 × 2·23(3).

sense, the thionitrosyl group (an overall three-electron donor in this bonding configuration) can be considered to be bonded as NS^+, a mode of co-ordination that is directly analogous to metal–thiocarbonyl bonding and involves synergistic coupling of σ- and π-bonding components.[5] Consistent with this view of back-donation from Cr π-orbitals to NS π^*-orbitals is the fact that the N–S distance of 1·551(3) Å in the complex is longer than the NS^+ equilibrium bond length of 1·440 ± 0·005 Å determined spectroscopically in the vapour state.[6]

A comparison of the spectroscopic properties of the compounds $(\eta^5\text{–C}_5\text{H}_5)\text{Cr(CO)}_2\text{(NX)}$ (X = O or S) suggests that the NS ligand is more effective in removing electron density from the central metal atom than is the NO ligand.[1] Consequently, it would be expected that the Cr–N(S) bond length would be shorter than the Cr–N(O) bond length in the respective molecules. Regrettably, an effective comparison of these distances is precluded by crystallographic disorder among the CO and NO groups in the solid state structure of $(\eta^5\text{–C}_5\text{H}_5)\text{Cr(CO)}_2\text{(NO)}$.[3]

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