The Molecular Structure of Cyclopentadienyldinitrosylchromium Chloride

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DESPITE the considerable interest in the bonding in metal nitrosyl complexes[1] very few of these materials have been subjected to three-dimensional *X*-ray analysis. The Fe–N–O angle in $Na_2Fe(CN)_5NO,2H_2O$, 178°, does not differ significantly from 180°,[2] whereas in $(NO)_4Fe_2S_2Et_2$[3] the angles are 167° and 168°, and in $CsFe_4S_3(NO)_7,H_2O$[4] the deviations from linearity extend to 20°. Still greater deviations from linearity have been claimed in some less accurate *X*-ray determinations.[5]

Kettle has recently noted[6] that the two sets of π^*-orbitals of the carbon monoxide molecules in $M(CO)_n$ groups ($n \neq 1$) transform independently and that when there is significant transfer of electrons from metal *d*-orbitals into these π^*-orbitals the M–C–O fragments can then be bent, the extent of bending depending on the difference in occupation of the two π^*-orbitals. The average deviation from linearity in metal carbonyls is about 5°.[6]

The somewhat scanty data available for metal polynitrosyls suggest that the departures from linearity may be more marked for these compounds than for metal carbonyls. To investigate this, and other structural aspects of metal nitrosyl complexes, we are engaged in a number of crystal-structure analyses of suitable crystals.

Cyclopentadienyldinitrosylchromium chloride[7] crystallizes in the orthorhombic system, space group $P2_12_12_1$, with four molecules of $C_5H_5ClCrN_2O_2$ in a cell of dimensions $a = 10{\cdot}79$, $b = 12{\cdot}24$, $c = 5{\cdot}95$ Å. After Fourier and least-squares refinement the final discrepancy factor, *R*, is 9·8% over 744 independent reflexions. The cyclopentadienyl ring is randomly distributed over two orientations in the same plane.[8] The chromium, chlorine, nitrogen, and oxygen atoms are not involved in the crystal disorder and the positional standard deviations of these atoms are small (Cr, 0·002 Å; Cl, 0·004 Å; N, 0, 0·014 Å). The final electron-density distribution is shown in the Figure and the molecular dimensions are listed in the Table.

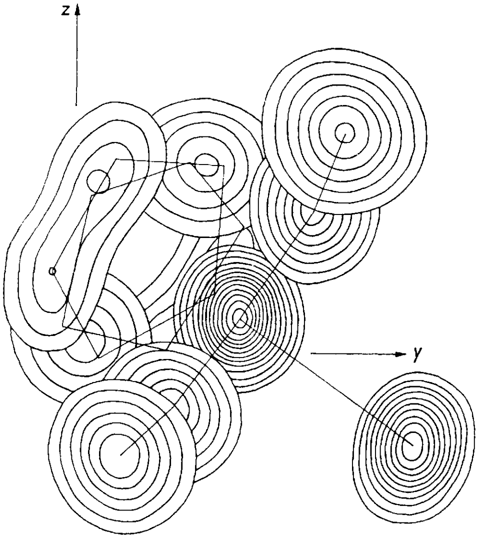
TABLE

Molecular Dimensions

	Cr–N(1)	1·717 Å	Cr–N(1)–O(2)	170·8°
	N(1)–O(2)	1·128	Cr–N(3)–O(4)	166·4
	Cr–N(3)	1·704	N(1)–Cr–N(3)	94·3
	N(3)–O(4)	1·152	Cl–Cr–N(1)	99·1
	Cr–Cl	2·311	Cl–Cr–N(3)	99·1
average	Cr–C	2·199		

If the Cr–NO bond orders were the same as those of the Cr–CO bonds in Cr(CO)$_6$, then we should expect the Cr–N distance to be about 0·06 Å shorter (because of the smaller radius of the nitrogen atom) than the Cr–C distance of 1·92 Å in hexacarbonylchromium,[9] *i.e.*, to be about 1·86 Å. The actual distances are very considerably shorter and there must therefore be appreciable electron donation from the metal *d*-orbitals to the π^*-orbitals of the nitrosyl groups. Both CrNO fragments are significantly bent, and by amounts which are greater than those reported for metal carbonyls.[6] Kettle's mechanism for bending, as distinct from the effect of crystal-packing forces, suggests a relationship between the departure from linearity and the amount of electron donation from the metal *d*-orbitals into the NO π^*-orbitals. It is noteworthy that the amount of bending at N(3), 13·6°, is greater than that at N(1), 9·2°, and that N(3) is associated with a shorter Cr–N bond and a longer N–O bond than is N(1). These bond-length differences are not sufficiently large to be established as significant, but, nevertheless, *both* are in the direction required by the CrNO valency angles.

Since the single-bond covalent radii of chlorine and carbon (*sp*) are 0·99 and 0·69 Å, respectively, we would predict a length of 2·22 Å for a Cr–Cl bond of the same order as the Cr–C bonds in hexacarbonylchromium. The actual length of the Cr–Cl bond, 2·311 Å, is consistent with chlorine having little π-bonding capacity. The average Cr–C distance of 2·20 Å is close to the average Cr–C (aromatic) distance of 2·23 Å in $C_6H_6Cr(CO)_3$,[10] $C_6Me_6Cr(CO)_3$,[11] and C_6H_5OMe-$Cr(CO)_3$.[12]



FIGURE

Final three-dimensional electron-density distribution shown by means of superimposed contour sections drawn parallel to (100). *Contour interval* 3e$Å^{-3}$ *around the chromium atom,* 2e$Å^{-3}$ *around the chlorine atom, and* 1e$Å^{-3}$ *around the others.*

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