Crystal and Molecular Structure of η-Cyclopentadienyl(diphenylamido)-iodonitrosylchromium

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Crystals of the title complex contain monomeric molecules $[Cr(\eta\text{-}C_5H_5)(NO)(NPh_2)I]$. Crystals are monoclinic, space group $P2_1$, with $a = 10.247(2)$, $b = 8.888(2)$, $c = 9.236(2)$ Å, $\beta = 91° 30(1)'$, and $Z = 2$. Intensities have been measured by diffractometry and least-squares refinement has terminated at R 0.021 over 2 398 independent reflections. The chromium–nitrogen bond lengths are Cr–NO 1.676(3) and Cr–NPh_2 1.894(3) Å. The Cr–I distance is 2.669(1) Å and the Cr–C(cyclopentadienyl) separations are 2.210—2.292(6) (mean 2.250 Å). The angle Cr–N–O is 172.7(3)°. Valency angles of the chromium atom are I–Cr–NO 90.3(1), I–Cr–NPh_2 100.9(1), and ON–Cr–NPh_2 97.2(1)°.

η-CYCLOPENTADIENYL(DIPHENYLAMIDO)IODONITROSYLCHROMIUM can be regarded as a 16-electron complex if it exists in the form of monomeric molecules $[Cr(\eta\text{-}C_5H_5)(NO)(NPh_2)I]$; weak iodine or nitrogen bridges may be present in the solid, however. An X-ray analysis was undertaken to investigate this point and to provide structural comparisons with $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$,[1] $[Cr(\eta\text{-}C_5H_5)(NO)_2(NCO)]$,[2] $[Cr(NPr^i_2)_3]$,[3] and $[\{Cr(\eta\text{-}C_5H_5)(NO)(NMe_2)\}_2]$.[4]

RESULTS AND DISCUSSION

X-Ray measurements on a diffractometer yielded 2 398 significant intensities and least-squares refinement of the atomic co-ordinates and thermal parameters converged at R 0.0211. The atomic numbering scheme is shown in Figure 1 and the crystal structure in Figure 2. The atomic co-ordinates and bond lengths are listed in Tables 1 and 2. Valency angles, intermolecular contacts, thermal parameters, and observed and calculated structure factors are in Supplementary Publication No. SUP 22364 (9 pp.).†

It was not possible to define the correct enantiomorph and correct for anomalous dispersion in the course of the least-squares adjustment of the co-ordinates (see Experimental section) and, accordingly, the standard deviations of the bond lengths involving the chromium atom are underestimated. Nevertheless, the neglected systematic errors are small (≤0.01 Å) and none of our conclusions would be altered if we knew the polarity of the crystal used in the intensity measurements.

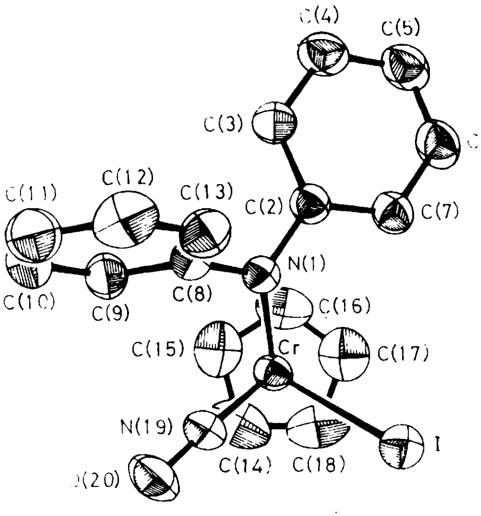

FIGURE 1 The molecular structure of the complex viewed in projection on to the plane of the η-cyclopentadienyl ring. The thermal ellipsoids are bounded by 50% probability surfaces

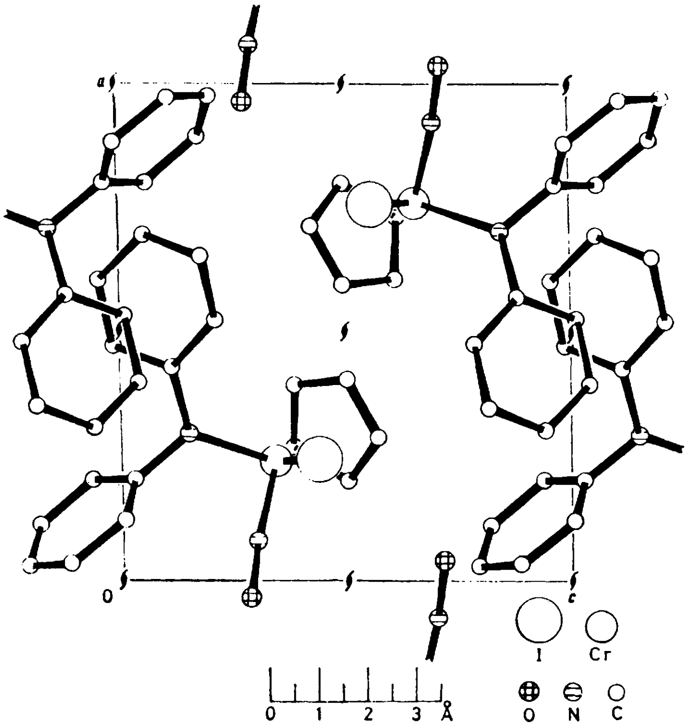

FIGURE 2 The crystal structure, viewed in projection along the b axis

The intermolecular separations are all greater than 3 Å and consistent with the monomeric formulation of the molecule.

The formal oxidation state and number of electrons assigned to the chromium atom can be assessed in two alternative ways. Since the Cr–N–O angle is 172.3(3)°, the metal–nitrosyl fragment is almost linear and the nitrosyl ligand can be regarded as the two-electron donor $[NO]^+$. Cyclopentadienyl and iodide ligands are con-

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

ventionally described as six-electron, $[C_5H_5]^-$, and two-electron, I^-, donors, so that with assignment of the diphenylamide ligand as $[NPh_2]^-$ or $[NPh_2]^+$, $[Cr(\eta\text{-}C_5H_5)(NO)(NPh_2)I]$ can be regarded either as a chromium(II) complex with a 16-electron configuration or a chromium(0) complex with an 18-electron configuration. With the latter choice, the $[NPh_2]^+$ ligand is formally equivalent to $[NO]^+$ and the complex $[Cr(\eta\text{-}C_5H_5)(NO)(NPh_2)I]$ should resemble the 18-electron complexes $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$ and $[Cr(\eta\text{-}C_5H_5)(NO)_2(NCO)]$, as indeed it does.

TABLE 1

Fractional atomic co-ordinates, with standard deviations in parentheses

	x	*y*	*z*
Cr	0.237 79(4)	1.000 00	0.337 00(5)
I	0.243 76(2)	1.282 44(6)	0.435 24(2)
N(1)	0.294 8(2)	1.028 1(3)	0.145 5(3)
C(2)	0.427 8(3)	1.038 0(4)	0.106 6(4)
C(3)	0.470 1(3)	0.978 0(5)	−0.025 3(4)
C(4)	0.602 4(4)	0.985 6(5)	−0.059 0(5)
C(5)	0.692 7(4)	1.049 6(5)	0.039 8(6)
C(6)	0.650 8(3)	1.108 1(5)	0.166 6(6)
C(7)	0.519 4(3)	1.105 5(5)	0.201 4(4)
C(8)	0.203 7(3)	1.028 8(4)	0.024 6(3)
C(9)	0.118 9(4)	0.907 6(5)	0.000 4(4)
C(10)	0.030 2(4)	0.910 3(6)	−0.117 2(5)
C(11)	0.024 3(4)	1.032 4(7)	−0.207 5(5)
C(12)	0.107 5(5)	1.153 3(6)	−0.183 6(5)
C(13)	0.199 0(4)	1.152 1(5)	−0.068 6(4)
C(14)	0.200 2(6)	0.820 4(7)	0.499 1(7)
C(15)	0.265 4(6)	0.757 1(5)	0.378 2(7)
C(16)	0.391 2(5)	0.820 6(6)	0.378 6(6)
C(17)	0.403 1(5)	0.921 5(7)	0.491 0(6)
C(18)	0.285 4(7)	0.923 4(8)	0.565 0(5)
N(19)	0.077 3(3)	1.015 5(4)	0.300 3(3)
O(20)	−0.037 9(3)	1.020 3(5)	0.289 5(4)
H(3)	0.415(5)	0.950(7)	−0.104(6)
H(4)	0.633(6)	0.936(8)	−0.150(7)
H(5)	0.778(5)	1.059(7)	0.025(6)
H(6)	0.708(6)	1.173(8)	0.259(7)
H(7)	0.491(5)	1.165(6)	0.288(5)
H(9)	0.126(5)	0.836(6)	0.057(5)
H(10)	−0.027(7)	0.841(9)	−0.135(8)
H(11)	−0.032(5)	1.034(7)	−0.298(6)
H(12)	0.110(6)	1.239(7)	−0.242(6)
H(13)	0.260(6)	1.228(8)	−0.050(6)
H(14)	0.097(7)	0.786(15)	0.514(8)
H(15)	0.222(10)	0.702(13)	0.294(11)
H(16)	0.449(6)	0.785(13)	0.302(7)
H(17)	0.472(11)	0.971(13)	0.470(11)
H(18)	0.270(5)	0.990(7)	0.620(5)

TABLE 2

Bond lengths (Å), with standard deviations in parentheses

Cr–I	2.669 4(5)	C(13)–C(8)	1.394(5)
Cr–N(1)	1.894(3)	C(14)–C(15)	1.432(9)
Cr–N(19)	1.676(3)	C(15)–C(16)	1.407(8)
Cr–C(14)	2.229(7)	C(16)–C(17)	1.375(8)
Cr–C(15)	2.210(5)	C(17)–C(18)	1.401(8)
Cr–C(16)	2.265(5)	C(18)–C(14)	1.394(9)
Cr–C(17)	2.292(6)	C(3)–H(3)	0.94(6)
Cr–C(18)	2.254(5)	C(4)–H(4)	1.00(6)
N(19)–O(20)	1.183(4)	C(5)–H(5)	0.89(6)
N(1)–C(2)	1.421(4)	C(6)–H(6)	1.17(7)
N(1)–C(8)	1.436(4)	C(7)–H(7)	1.01(5)
C(2)–C(3)	1.409(5)	C(9)–H(9)	0.83(5)
C(3)–C(4)	1.400(5)	C(10)–H(10)	0.87(8)
C(4)–C(5)	1.403(6)	C(11)–H(11)	1.00(5)
C(5)–C(6)	1.361(7)	C(12)–H(12)	0.93(6)
C(6)–C(7)	1.393(5)	C(13)–H(13)	0.93(7)
C(7)–C(2)	1.402(5)	C(14)–H(14)	1.11(8)
C(8)–C(9)	1.399(5)	C(15)–H(15)	1.01(11)
C(9)–C(10)	1.398(6)	C(16)–H(16)	0.98(7)
C(10)–C(11)	1.369(8)	C(17)–H(17)	0.86(11)
C(11)–C(12)	1.386(8)	C(18)–H(18)	0.80(7)
C(12)–C(13)	1.398(6)		

The Cr–I separation [2.669(1) Å] is larger than the Cr–Cl separation (2.311 Å) in $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$ by 0.38 Å. This may be compared with the difference of 0.34 Å between the normal covalent radii of iodine (1.33 Å) and chlorine (0.99 Å).[5] On the other hand, the Cr–I separation in the anion $[Cr(CO)_5I]^-$ is 2.790(2) Å,[6] and it is apparent that it is not possible to define a unique chromium(0) radius that can be transferred between different environments.

The Cr–NO bond length [1.676(3) Å] is a little shorter than the distances of 1.716(3) Å in $[Cr(\eta\text{-}C_5H_5)(NO)_2(NCO)]$ and 1.711(9) Å in $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$, which suggests that there is greater back donation of charge to the π^* orbitals of an individual nitrosyl ligand as the number of these ligands on the metal atom is reduced. A more pronounced effect of this sort is evident in a comparison between the mean Cr–CO bond length (1.915 Å) in hexacarbonylchromium[7] and the mean Cr–CO separation (*ca.* 1.82 Å) in various arenetricarbonylchromium molecules.[8] The expansion of the N–O separation in $[Cr(\eta\text{-}C_5H_5)(NO)(NPh_2)I]$, 1.183(4) Å, when compared with the distances of 1.157(3) Å in $[Cr(\eta\text{-}C_5H_5)(NO)_2(NCO)]$ and 1.140(3) Å in $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$ is consistent with this argument.

The $Cr\text{–}NPh_2$ bond [1.894(3) Å], although longer than the Cr–NO bond [1.676(3) Å], is shorter than the Cr–NCO bond (1.982 Å) in $[Cr(\eta\text{-}C_5H_5)(NO)_2(NCO)]$ and the Cr–N bonds (mean 2.185 Å) in tricarbonyl(diethylenetriamine)chromium[9] and it is likely, therefore, that the $Cr\text{–}NPh_2$ bond has some double-bond character. The hybridization of the nitrogen atom of the $Cr(NPh_2)$ fragment approximates to sp^2, since the nitrogen is displaced by only 0.039 Å from the plane defined by the three atoms to which it is bonded. Similar coplanarities are found in $[Cr(NPr^i_2)_3]$,[3] where the Cr–N bonds have a mean length of 1.87 Å.

Although the sum of the valency angles about the nitrogen atom of the diphenylamide ligand is nearly 360° (actually 358.8°), the individual angles deviate significantly from 120°. The difference between the Cr–N–C(2) [124.4(2)°] and Cr–N–C(8) angles [121.2(2)°] is presumably due to a steric effect but the differences between these and the C(2)–N–C(8) angle [114.3(3)°] probably reflect electronegativity differences between the chromium and carbon atoms, the bond from nitrogen to the less electronegative metal atom having more *s* character than the bonds to the carbon atoms.[10]

The phenyl rings are effectively planar and have mean C–C bond lengths of 1.395 and 1.391 Å. The mean C–H bond length (0.96 Å) is contracted from the spectroscopic value for $C(sp^2)$–H but this effect is usual in *X*-ray analyses.[11] The dihedral angle between the planes of the phenyl rings is 78°.

The Cr–C(cyclopentadienyl) distances range from 2.210 to 2.292 (mean 2.250 Å), and the C–C distances in the cyclopentadienyl ring range from 1.375 to 1.432 (mean

1.402 Å). The longest Cr–C distance [Cr–C(17) 2.292(6) Å] is situated approximately *trans* to the nitrosyl ligand (see Figure 1) and the two shortest Cr–C distances [Cr–C(14) 2.229(7) and Cr–C(15) 2.210(5) Å] are associated with the longest C–C bond in the η-C_5H_5 ring [C(14)–C(15) 1.432(9) Å]. Similar effects have been discerned in other complexes.[12]

EXPERIMENTAL

η-Cyclopentadienyl(diphenylamido)iodonitrosylchromium was obtained from chloro(η-cyclopentadienyl)-dinitrosylchromium by reaction with lithium diphenylamide (MeI + Li + NPh_2H). The nitrosyl i.r. absorption is at 1 712 cm^{-1}. The complex was crystallized from diethyl ether and had m.p. 183 °C.

Crystal Data.—$C_{17}H_{15}CrIN_2$, $M = 442.2$, Monoclinic, $a = 10.247(2)$, $b = 8.888(2)$, $c = 9.236(2)$ Å, $\beta = 91° 30(1)'$, $U = 840.9$ Å^3, $D_c = 1.746$, $Z = 2$, $D_m = 1.74$ g cm^{-3} (flotation in aqueous zinc iodide), $F(000) = 432$, μ(Mo-K_α) $= 25.7$ cm^{-1}, space group $P2_1(C_2^2)$.

Crystallographic Measurements.—Cell dimensions were derived from a least-squares treatment of the θ,χ,ϕ setting angles of 12 reflections measured on a Hilger and Watts four-circle diffractometer with Mo-K_α radiation from a graphite monochromator. Intensities were measured by the ω—2θ step-scan procedure, each reflection being scanned in 36 equal steps from 0.72° below to 0.72° above $2\theta_{calc.}$. Counting times were 2 s for each step and 18 s for the background at each end of the scan range. The intensities of two standard reflections were monitored after every 40 intensity measurements and only small random fluctuations detected. Octants *hkl* and *hkl* were surveyed and 2 590 independent intensity measurements obtained for $\theta \leqslant 30°$; of these 192 did not satisfy statistical criteria for significance and were discarded, leaving 2 398 significant intensities for the structure analysis. Absorption corrections were applied by Coppen's DATAP program, modified for use on the Glasgow University KDF9 computer.[13] An 8 × 8 × 8 grid was chosen and transmission factors ranged from 0.37 to 0.58 for the crystal dimensions 0.22 × 0.40 × 0.50 mm.

Structure Analysis.—Initial co-ordinates of the Cr and I atoms were deduced from a three-dimensional Patterson synthesis and positions of the C, N, and O atoms then obtained from an electron-density distribution.

The atomic parameters were adjusted by least-squares calculations, using the program devised by Cruickshank, Smith, and Sime for the KDF9 computer. The weighting scheme adopted was $w = [1 - \exp(-p_1\sin^2\theta/\lambda^2)]/(1 + p_2|F_o| + p_3|F_o|^2)$, where p_1, p_2, and p_3 were adjusted at various stages to ensure approximate constancy of $\langle w\Delta^2\rangle$, over various ranges of $|F_o|$ and $\sin\theta$; the final values were 5.0, 0.1, and 0.000 5, respectively. Atomic scattering factors, including dispersion corrections $\Delta f'$ and $\Delta f''$ for chromium and iodine, were those listed in ref. 14. The *y* co-ordinate of the chromium atom was arbitrarily set, and retained, at 1.0 to define the origin.

Two rounds of full-matrix refinement of positional and isotropic thermal parameters gave R 0.053 and $R' = 0.071$. The atoms were then assigned anisotropic thermal parameters and three rounds of block-diagonal calculations gave R 0.0284 and R' 0.0371.

Since $P2_1$ is a polar space group there are two polarities to be considered for the crystal structure and if anomalous dispersion is significant it should be possible to distinguish between the two alternatives by statistical tests[15] based on R or by an assessment of the molecular dimensions around the anomalous scatterers. Accordingly, the anomalous scattering associated with the Cr and I atoms was allowed for in structure-factor calculations and the hydrogen atoms were located in an electron-density difference map. Both possible enantiomorphic structures were refined by five cycles of block-diagonal and two cycles of full-matrix calculations with isotropic thermal parameters for the hydrogen atoms and anisotropic parameters for the other atoms and these calculations converged at R 0.0216, R' 0.0286 for one enantiomorph and R 0.0216, R' 0.0284 for the mirror image. Since these results do not discriminate between the two possibilities we next deleted anomalous dispersion from the calculations and performed five more rounds of block-diagonal least-squares adjustment of the atomic parameters, these calculations giving R 0.0211 and R' 0.0283. For the resulting atomic arrangement and its mirror image we then calculated structure factors incorporating anomalous-dispersion corrections and obtained R 0.0266 and R' 0.0354 for one enantiomorph and R 0.0267 and R' 0.0348 for the other. These differences are not sufficient to define the absolute configuration of the crystal structure.

Unless $\Delta f''$ is included in structure-factor calculations an anomalous scatterer appears to be closer to the *X*-ray source than it actually is. On allowing for anomalous dispersion the other atoms undergo displacements in the polar direction, relative to the anomalous scatterer, and the shifts have the same magnitude but opposite sign for the alternative enantiomorphous structures.[16] Comparison of the results obtained by the earlier least-squares refinements with allowance for anomalous dispersion revealed small differences in the lengths of the bonds radiating from chromium, but not in the other bond lengths, the differences ranging from 0.002 Å for Cr–I to 0.029 Å for Cr–C(15). The Cr–N distances were 1.892 and 1.675 Å in enantiomorph I and 1.896 and 1.678 Å in enantiomorph II, while the Cr–C(cyclopentadienyl) distances were 2.224—2.297 (mean 2.260 Å) in enantiomorph I and 2.195—2.286 (mean 2.239 Å) in II. Consideration of the internal consistency of these results and comparison with other complexes failed to indicate one set of results as preferable. The differences between the two alternatives are small, however, and it is satisfactory to use the results from the final series of least-squares calculations that neglected anomalous dispersion and converged at R 0.0211; these results are given in Tables 1 and 2.

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