Crystal and Molecular Structure of *cis*-Bis-(2-methoxyphenyl)bis-(2,2′-bipyridyl)chromium(III) Iodide Monohydrate

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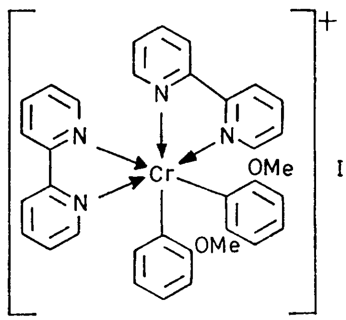
Crystals of the title compound, are triclinic, space group $P\bar{1}$, with cell dimensions a = 12·486, b = 16·657, c = 12·953 Å, α = 129° 41′, β = 51° 28′, γ = 120° 7′, Z = 2. The final R for 3168 counter data refined by least-squares is 0·07. The organometallic cation, which has the *cis*-octahedral configuration, possesses an approximate two-fold axis bisecting the C–Cr–C bond angle. Cr–C is 2·101(12), and Cr–N *trans* to carbon 2·156(10), and *trans* to nitrogen 2·071(10) Å.

AIR- and water-stable organo-chromium(III) compounds have recently become available.[1,2] We have therefore determined the structure of one of them, *cis*-bis-(2-methoxyphenyl)bis-(2,2′-bipyridyl)chromium(III)iodide



(I)

(I), to compare the geometry of the anion with that of the unstable (p-tolyl)$CrCl_2$,(tetrahydrofuran)$_3$.[3] A short communication describing the structure of (I) has already appeared.[1]

EXPERIMENTAL

Recrystallisation of (I) from nitromethane or from methanol gives well formed crystals which become opaque a few minutes after removal from the solution, a behaviour typical of crystals losing solvent of crystallisation. Recrystallisation from commercial ethanol gives red crystals which do not alter with time. The i.r. spectrum of a solution of these crystals suggested that hydroxy-groups were present.

Crystal Data.—$C_{34}H_{30}CrIN_4O_2,H_2O$, M = 723·5, Triclinic a = 12·486(8), b = 16·657(9), c = 12·953(8) Å,† α = 129° 41′, β = 51° 28′ (5), γ = 120° 7′ (4), U = 1597·3 Å^3, Z = 2, D_c = 1505, D_m = 1497, Mo-K_α radiation, λ = 0·71069 Å, μ(Mo-K_α) = 14·22 cm^{-1}. Space group $P\bar{1}$.

The following cell dimensions, also not in a reduced form, were obtained from precession photographs a' = 12·491, b' = 11·048, c' = 18·937 Å, α' = 138° 1′, β' = 104° 22′, γ' = 66° 27′, the two cells are related by the transformation (abc) = (1,0,0, −1,2,1, 1,1,0) ($a'b'c'$). The intensities were collected round b on a Hilger and Watts linear diffractometer equipped with $SrCO_3$–ZrO_2 balanced filters. The intensities of 3168 reflections with $I > 2\sigma$ were used to carry out the structure analysis. No allowance was made for absorption.

Structure Determination and Refinement.—One of three possible solutions of the three-dimensional Patterson function for the positions of the iodine and chromium atoms was found to be satisfactory. A three-dimensional difference-Fourier synthesis based on the phases from these heavy atoms revealed the positions of the remaining atoms in the cation except for the hydrogen atoms.

This structure was then refined in space group $P\bar{1}$ by a least-squares block-diagonal process, first with isotropic and then with anisotropic temperature factors. The weighting scheme was that proposed by Cruickshank[4] with $w^{-1} = 4{\cdot}26 + |F_o| + 0{\cdot}01475|F_o^2|$. Planes with $3|F_c| < |F_o|$ were omitted from the least-squares totals and from R', and in the last cycle 11 planes were subject to this restriction. The refinement converged with the final values of 0·070 for R for 3168 planes and of 0·0098 for R' ($\Sigma w\Delta^2/\Sigma wF_o^2$) for 3157 planes. At this stage a three-dimensional difference-Fourier map was calculated and this showed 30 peaks in positions which were acceptable as hydrogen atoms. This map also showed two unresolved peaks not far from the centre of symmetry at $(0,\frac{1}{2},\frac{1}{2})$ in the space group $P\bar{1}$, one, X(1) say, had a height *ca.* 5 times that of a hydrogen atom and the second, X(2) say, had a height *ca.* 2 times that of a hydrogen atom. The shortest interatomic distances <3·5 Å involving these peaks were X(1) ··· X(2) 1·309, X(1) ··· X(2′) 2·2, X(2) ··· I 3·4, X(2) ··· C 3·3, X(1) ··· X(1′) 1·2, and X(2) ··· X(2′) 3·4 Å, X(2′) is related to X(2) by a centre of symmetry at $(0,\frac{1}{2},\frac{1}{2})$. If, as the i.r. spectrum and the measured density suggest, there is water present in the structure one would expect these water molecules to be hydrogen bonded to one another or to the oxygen atoms of the methoxyphenyl groups, or to the nitrogen atoms of the bipyridyl groups. There is enough room in the unit cell to accomodate two hydrogen-bonded water molecules at X(1) and X(2′), alternatively the water molecules may be placed at X(1′) and X(2). We attempted to refine a disordered structure with half oxygen atoms at X(1), X(2), X(1′), and X(2′) but there was no significant change in R (0·071). The calculations were carried out on an Elliott 803 B computer with programmes written in this laboratory.[5]

RESULTS AND DISCUSSION

The final values of the structure factors are listed in Supplementary Publication No. 20503 (21 pp., 1 micro-

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† Erroneously given as 12·593 Å in ref. 1.

[1] J. J. Daly, F. Sanz, R. P. A. Sneeden, and H. H. Zeiss, *Chem. Comm.*, 1971, 243.

[2] A. Müller, *Z. Chem.*, 1969, **9**, 311.

[3] J. J. Daly and R. P. A. Sneeden, *J. Chem. Soc.* (*A*), 1967, 736.

[4] D. W. J. Cruickshank, D. E. Pilling, A. Bujosa, F. M. Lovell, and M. R. Truter, 'Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' Pergamon Press, Oxford, 1961.

[5] J. J. Daly, F. S. Stephens, and P. J. Wheatley, unpublished work.

fiche) * and are summarised in Table 1. Tables 2—5 give the positional and thermal parameters and the bond lengths and angles. The positional parameters of the hydrogen atoms were taken from the final difference Fourier synthesis for the two methyl groups and were calculated for the remainder. The standard deviations given in these tables do not take into account any systematic errors. Figure 1 shows the labelling of the atoms in a drawing of the molecule projected on the *bc* plane. Figure 2 shows the packing arrangement.

TABLE 1

R as a function of the layer index and the magnitude of $|F_o|$

k	$\Sigma\lvert F_o\rvert$	$\Sigma\lvert F_c\rvert$	$\Sigma\lvert\Delta\rvert$	N *	R
0	4345·37	4387·41	327·32	139	0·075
1	8901·22	8688·45	692·57	277	0·078
2	8868·88	8709·27	696·89	277	0·079
3	8268·06	8115·01	600·85	257	0·073
4	8331·80	8112·60	599·70	273	0·072
5	6692·98	6607·25	466·41	235	0·070
6	6626·02	6628·66	445·68	246	0·067
7	5980·32	5876·59	350·73	229	0·059
8	5124·60	5051·05	315·43	209	0·062
9	4059·07	4017·61	228·98	179	0·056
10	3639·70	3598·88	245·08	175	0·067
11	3036·77	2993·63	189·10	154	0·062
12	2471·76	2461·45	153·11	137	0·062
13	1965·21	1957·97	124·40	116	0·063
14	1571·55	1578·44	104·71	103	0·067
15	1160·53	1146·47	101·50	84	0·087
16	894·68	897·62	78·54	78	0·088
All	81938·52	80828·36	5721·00	3168	0·070
$4{\cdot}6 < \lvert F_o\rvert \leq 9{\cdot}2$	6·75	6·65	0·10	2	0·015
$9{\cdot}2 < \lvert F_o\rvert \leq 13{\cdot}8$	2043·59	2014·79	377·02	261	0·184
$13{\cdot}8 < \lvert F_o\rvert \leq 18{\cdot}4$	7735·86	7594·96	857·22	679	0·111
$18{\cdot}4 < \lvert F_o\rvert \leq 23{\cdot}0$	8823·67	8770·26	704·67	551	0·080
$23{\cdot}0 < \lvert F_o\rvert \leq 230{\cdot}0$	63328·65	62441·70	4226·50	1675	0·067

* N = No. of planes.

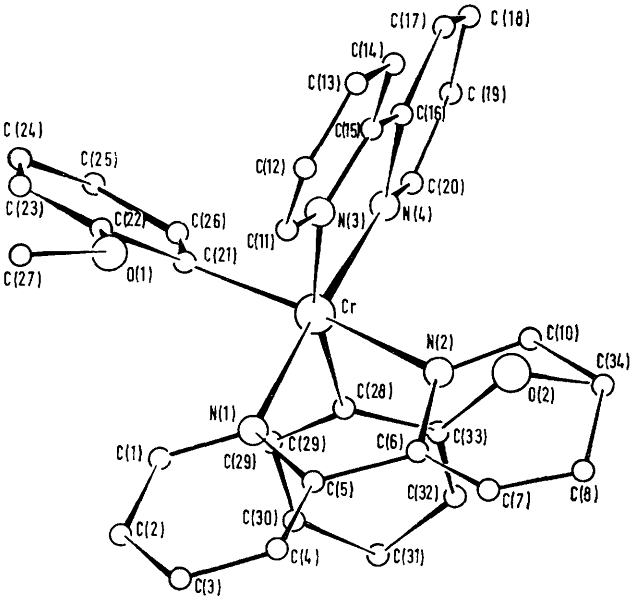

FIGURE 1 The cation and the labelling of the atoms

The analysis shows that the structure is composed of *cis*-bis-(2-methoxyphenyl)bis-(2,2′-bipyridyl)chromium(III)$^+$ ions, iodide ions, and, probably, water molecules. In the complex cation, which possesses an approximate two-fold symmetry axis bisecting the C(21)–Cr–C(28) angle, the co-ordination round the chromium atom is distorted octahedral with the two *o*-methoxyphenyl groups mutually *cis* and the remaining four co-ordination sites occupied by the nitrogen atoms of two bipyridyl molecules (Figure 1).

TABLE 2

Atomic co-ordinates (X Y Z), with standard deviations in parentheses

	X	Y	Z
I	2·3943(13)	3·9934(11)	1·7464(12)
Cr	4·5208(16)	3·6956(16)	7·3724(18)
O(1)	7·804(8)	2·027(9)	3·180(10)
O(2)	1·090(9)	5·145(10)	11·325(10)
N(1)	6·138(8)	5·468(8)	6·300(10)
N(2)	4·795(9)	6·132(9)	9·868(10)
N(3)	6·464(9)	3·265(9)	7·318(10)
N(4)	3·116(9)	2·088(9)	8·639(10)
C(1)	6·767(11)	5·050(12)	4·435(13)
C(2)	7·918(11)	6·265(12)	3·740(14)
C(3)	8·500(12)	7·911(13)	4·954(16)
C(4)	7·870(12)	8·384(12)	6·881(15)
C(5)	6·651(10)	7·134(11)	7·500(12)
C(6)	5·809(11)	7·536(11)	9·557(13)
C(7)	6·040(15)	9·228(13)	11·019(15)
C(8)	5·215(17)	9·478(15)	12·877(17)
C(9)	4·226(16)	8·007(17)	13·207(16)
C(10)	4·057(13)	6·365(14)	11·656(13)
C(11)	8·162(11)	3·995(11)	6·675(13)
C(12)	9·293(13)	3·893(13)	6·981(15)
C(13)	8·671(16)	2·999(15)	7·912(18)
C(14)	6·892(14)	2·227(12)	8·599(14)
C(15)	5·842(12)	2·388(11)	8·251(12)
C(16)	4·000(13)	1·612(11)	8·843(12)
C(17)	3·225(15)	0·465(13)	9·592(14)
C(18)	1·475(16)	−0·274(14)	10·070(16)
C(19)	0·551(14)	0·163(13)	9·816(15)
C(20)	1·394(13)	1·388(13)	9·113(14)
C(21)	4·730(12)	1·429(11)	4·689(13)
C(22)	6·294(13)	0·857(13)	3·011(14)
C(23)	6·391(16)	−0·733)15)	1·295(15)
C(24)	4·823(18)	−1·875(14)	1·255(17)
C(25)	3·271(17)	−1·394(15)	2·802(18)
C(26)	3·202(14)	0·246(12)	4·503(15)
C(27)	9·439(15)	1·718(18)	1·410(17)
C(28)	2·391(11)	4·322(11)	8·024(13)
C(29)	2·266(12)	4·150(12)	6·609(15)
C(30)	0·997(13)	4·735(13)	7·011(17)
C(31)	−0·192(13)	5·530(14)	8·884(19)
C(32)	−0·204(13)	5·735(14)	10·413(17)
C(33)	1·062(11)	5·097(12)	9·941(14)
C(34)	−0·292(16)	5·771(19)	13·305(17)
X(1) water	0·585	8·580	6·666
X′(2) water	−0·780	6·517	4·873

The bond angles at the chromium atom show considerable deviations from the ideal octahedral values. Twelve bond angles at the chromium atom close to 90° have a root-mean-square deviation of 7·7° from 90°; the maximum deviation is 13·4° and the minimum 1·5°.

The chromium–carbon bond lengths are essentially equal, mean 2·101(12) Å, which is 0·087 Å (7σ) more than the Cr–C bond[3] in (p-tolyl)CrCl$_2$,3C$_4$H$_8$O and suggests that the air- and moisture-instability of the latter is

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*) 1970, Issue No. 20.

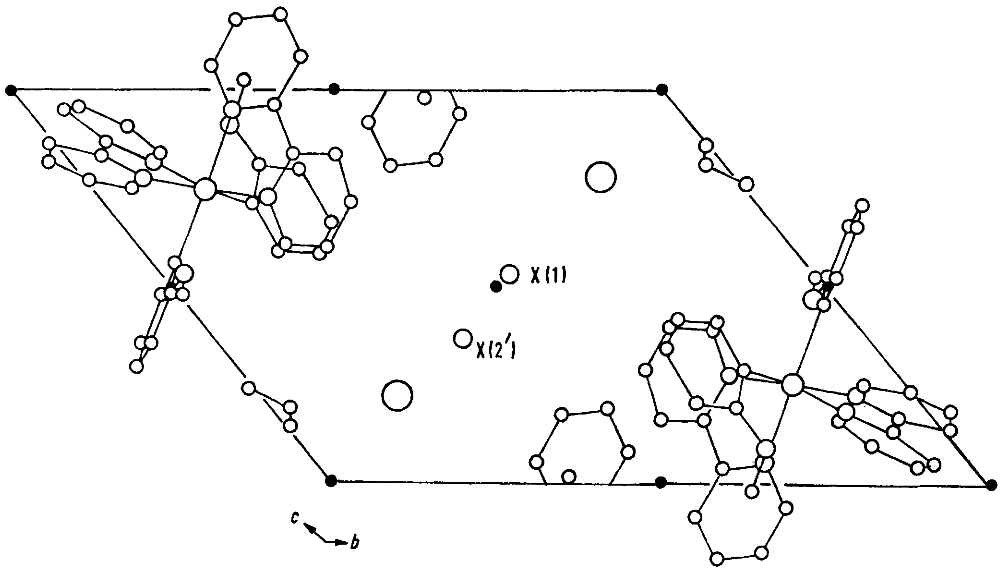

FIGURE 2 The structure projected on the *bc* plane

associated with the long Cr–O rather than with the Cr–C bond.

The chromium–nitrogen bond lengths fall into two classes, those *trans* to nitrogen (mean 2·07 Å) are shorter than those *trans* to carbon (mean 2·16 Å)and within each class the two independent Cr–N bonds are related by the approximate two-fold symmetry axis; this point is discussed further in the following paper. The shorter Cr–N bond length is close to the lengths observed[6] in

TABLE 3

Atomic co-ordinates (Å) of the hydrogen atoms

	X	*Y*	*Z*
H(1)	6·37	3·84	3·56
H(2)	8·38	5·95	2·37
H(3)	9·35	8·78	4·47
H(4)	8·27	9·60	7·77
H(7)	6·76	10·27	10·79
H(8)	5·37	10·68	13·97
H(9)	3·64	8·19	14·55
H(10)	3·34	5·33	11·89
H(11)	8·62	4·64	5·98
H(12)	10·55	4·44	6·52
H(13)	9·47	2·90	8·13
H(14)	6·43	1·59	9·30
H(17)	3·88	0·14	9·76
H(18)	0·89	−1·12	10·58
H(19)	−0·70	−0·36	10·17
H(20)	0·74	1·06	8·94
H(23)	7·53	−1·08	0·15
H(24)	4·86	−3·03	0·05
H(25)	2·18	−2·21	2·73
H(26)	2·06	0·59	5·65
H(29)	3·16	3·58	5·23
H(30)	0·97	4·60	5·95
H(31)	−1·11	5·96	9·19
H(32)	−1·10	6·31	11·79
$H(27)_1$	9·56	1·82	0·61
$H(27)_2$	9·59	0·68	1·01
$H(27)_3$	10·34	0·31	1·86
$H(34)_1$	−0·70	7·02	14·03
$H(34)_2$	0	5·72	12·82
$H(34)_3$	0	5·85	13·94

TABLE 4

Anisotropic thermal parameters ($10^4 U_{ij}$ for I, Cr; $10^3 U_{ij}$ for remaining atoms) with standard deviations in parentheses (Å^2) in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})]$

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
I	1039(7)	639(5)	665(5)	−303(9)	650(8)	−739(10)
Cr	246(6)	303(6)	344(7)	22(10)	367(11)	−260(11)
O(1)	41(4)	66(4)	52(4)	25(7)	63(7)	−24(6)
O(2)	46(4)	83(5)	46(4)	50(7)	63(7)	−11(6)
N(1)	28(4)	34(3)	43(4)	5(6)	41(6)	−38(6)
N(2)	34(4)	40(4)	44(4)	14(6)	35(7)	−38(7)
N(3)	39(4)	35(4)	44(4)	11(6)	33(6)	−47(7)
N(4)	38(4)	39(4)	41(4)	5(6)	48(7)	−32(7)
C(1)	31(5)	50(5)	41(5)	19(8)	48(8)	−23(8)
C(2)	29(5)	50(5)	55(6)	6(8)	68(9)	−21(8)
C(3)	35(5)	52(5)	73(7)	4(9)	87(10)	−32(10)
C(4)	32(5)	41(5)	65(6)	−8(8)	61(9)	−43(9)
C(5)	24(4)	39(4)	45(5)	19(7)	42(8)	−25(8)
C(6)	35(5)	40(5)	51(5)	10(7)	43(8)	−47(8)
C(7)	62(7)	45(5)	56(6)	24(10)	20(9)	−81(11)
C(8)	78(8)	58(7)	67(7)	6(12)	27(11)	−96(13)
C(9)	71(8)	85(8)	52(6)	39(13)	47(12)	−66(12)
C(10)	49(6)	66(6)	40(5)	28(10)	42(9)	−44(9)
C(11)	33(5)	41(5)	51(5)	−3(8)	42(8)	−46(9)
C(12)	51(7)	48(5)	68(6)	6(9)	46(10)	−81(11)
C(13)	76(8)	59(7)	80(8)	27(12)	36(11)	−113(14)
C(14)	74(7)	46(5)	52(6)	39(10)	30(9)	−71(11)
C(15)	50(6)	32(4)	39(5)	18(8)	24(7)	−46(8)
C(16)	57(6)	39(5)	30(4)	19(8)	33(7)	−33(8)
C(17)	82(8)	43(5)	47(6)	14(10)	49(9)	−52(11)
C(18)	80(8)	51(6)	54(6)	22(11)	67(10)	−23(12)
C(19)	55(6)	38(5)	46(6)	5(9)	41(9)	−7(9)
C(20)	41(5)	49(6)	50(6)	2(9)	58(9)	−11(9)
C(21)	43(5)	34(4)	49(5)	3(8)	46(8)	−47(9)
C(22)	58(6)	50(5)	49(5)	21(9)	57(9)	−44(10)
C(23)	89(9)	63(7)	45(6)	61(12)	28(10)	−65(12)
C(24)	111(10)	52(6)	59(7)	33(13)	26(10)	−107(14)
C(25)	93(9)	51(6)	78(8)	−16(12)	58(12)	−112(15)
C(26)	70(7)	37(5)	64(6)	−11(9)	45(9)	−93(11)
C(27)	58(7)	104(7)	59(7)	79(13)	110(13)	17(11)
C(28)	34(5)	36(4)	45(5)	−5(7)	38(8)	−45(8)
C(29)	40(5)	43(5)	69(6)	−13(8)	60(9)	−69(10)
C(30)	45(6)	54(6)	84(8)	−2(9)	70(11)	−83(11)
C(31)	39(6)	59(6)	102(9)	−11(10)	85(13)	−86(12)
C(32)	37(5)	54(6)	86(8)	−4(9)	67(11)	−66(11)
C(33)	33(5)	45(5)	61(6)	−20(8)	68(9)	−55(9)
C(34)	59(7)	102(10)	55(7)	45(14)	87(14)	2(12)

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[6] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1363; K. N. Raymond and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2333.

TABLE 5

Bond lengths (Å) and angles (deg.) with their standard deviations in parentheses

(*a*) Bond lengths

Cr–N(1)	2·073(9)
Cr–N(2)	2·157(10)
Cr–N(3)	2·155(10)
Cr–N(4)	2·069(10)
Mean *trans*	2·071
Mean *cis*	2·156
Cr–C(21)	2·095(12)
Cr–C(28)	2·107(12)
Mean	2·101
N(1)–C(1)	1·362(15)
N(1)–C(5)	1·354(14)
N(2)–C(6)	1·354(15)
N(2)–C(10)	1·340(16)
N(3)–C(11)	1·351(15)
N(3)–C(15)	1·342(15)
N(4)–C(16)	1·349(15)
N(4)–C(20)	1·370(16)
Mean	1·353
C(21)–C(22)	1·412(18)
C(21)–C(26)	1·424(18)
C(22)–C(23)	1·394(20)
C(23)–C(24)	1·409(22)
C(24)–C(25)	1·356(24)
C(25)–C(26)	1·412(22)
C(28)–C(29)	1·392(17)
C(28)–C(33)	1·415(17)
C(29)–C(30)	1·387(20)
C(30)–C(31)	1·351(21)
C(31)–C(32)	1·399(22)
C(32)–C(33)	1·384(20)
Mean	1·395
C(1)–C(2)	1·401(17)
C(2)–C(3)	1·374(18)
C(3)–C(4)	1·399(19)
C(4)–C(5)	1·396(17)
C(6)–C(7)	1·386(18)
C(7)–C(8)	1·378(22)
C(8)–C(9)	1·416(23)
C(9)–C(10)	1·387(21)
C(11)–C(12)	1·405(18)
C(12)–C(13)	1·355(21)
C(13)–C(14)	1·418(21)
C(14)–C(15)	1·395(18)
C(16)–C(17)	1·400(18)
C(17)–C(18)	1·395(21)
C(18)–C(19)	1·396(20)
C(19)–C(20)	1·426(19)
Mean	1·395
C(5)–C(6)	1·493(16)
C(15)–C(16)	1·463(17)
Mean	1·478
O(1)–C(22)	1·403(16)
O(2)–C(33)	1·371(16)
Mean	1·387
O(1)–C(27)	1·451(19)
O(2)–C(34)	1·448(16)
Mean	1·450

(*b*) Angles

N(1)–Cr–N(2)	76·56(36)
N(3)–Cr–N(4)	76·62(36)
N(1)–Cr–N(3)	96·78(35)
N(2)–Cr–N(4)	97·44(37)
N(2)–Cr–N(3)	79·94(36)
C(21)–Cr–N(4)	88·51(42)
C(28)–Cr–N(1)	88·39(40)
C(21)–Cr–N(3)	93·66(41)
C(28)–Cr–N(2)	91·57(41)
C(21)–Cr–N(1)	96·69(41)
C(28)–Cr–N(4)	97·31(41)
C(21)–Cr–C(28)	95·72(45)
N(1)–Cr–N(4)	171·90(37)
N(2)–Cr–C(21)	169·95(42)
N(3)–Cr–C(28)	168·70(41)
Cr–N(1)–C(5)	118·43(71)
Cr–N(2)–C(6)	115·56(75)
Cr–N(3)–C(15)	114·86(74)
Cr–N(4)–C(16)	117·13(76)
N(1)–C(5)–C(6)	114·48(96)
N(2)–C(6)–C(5)	114·64(99)
N(3)–C(5)–C(16)	114·68(100)
N(4)–C(16)–C(15)	115·87(102)
Mean	114·92
C(22)–O(1)–C(27)	117·7(11)
C(33)–O(2)–C(34)	119·8(11)
C(1)–N(1)–C(5)	117·5(10)
C(6)–N(2)–C(10)	118·3(10)
C(11)–N(3)–C(15)	119·1(10)
C(16)–N(4)–C(20)	119·7(10)
Mean	118·6
N(1)–C(1)–C(2)	122·4(11)
N(2)–C(10)–C(9)	122·1(13)
N(3)–C(11)–C(12)	122·1(11)
N(4)–C(20)–C(19)	119·7(11)
Mean	121·6
N(1)–C(5)–C(4)	123·3(10)
N(2)–C(6)–C(7)	123·5(11)
N(3)–C(15)–C(14)	121·9(11)
N(4)–C(16)–C(17)	123·0(11)
Mean	122·9
C(1)–C(2)–C(3)	118·8(12)
C(2)–C(3)–C(4)	120·1(12)
C(3)–C(4)–C(5)	117·7(12)
C(6)–C(7)–C(8)	117·9(13)
C(7)–C(8)–C(9)	119·3(14)
C(8)–C(9)–C(10)	118·7(14)
C(11)–C(12)–C(13)	119·0(13)
C(12)–C(13)–C(14)	119·7(14)
C(13)–C(14)–C(15)	118·3(13)
C(16)–C(17)–C(18)	118·3(13)
C(17)–C(18)–C(19)	119·6(13)
C(18)–C(19)–C(20)	119·7(13)
Mean	118·9
C(26)–C(21)–C(22)	114·4(11)
C(21)–C(22)–C(23)	124·4(12)
C(22)–C(23)–C(24)	117·9(14)
C(23)–C(24)–C(25)	120·8(15)
C(24)–C(25)–C(26)	120·3(15)
C(25)–C(26)–C(21)	122·0(13)
Mean	120·0
C(33)–C(28)–C(29)	114·4(11)
C(28)–C(29)–C(30)	123·9(12)
C(29)–C(30)–C(31)	118·6(14)
C(30)–C(31)–C(32)	122·0(14)
C(31)–C(32)–C(33)	117·4(13)
C(32)–C(33)–C(28)	123·6(12)
Mean	120·0

Cr$^{\mathrm{III}}$(en)$_3$ ions (2·08 Å) or in [7] Cr$^{\mathrm{O}}$(bipy)$_3$ (2·08 Å) while the longer bond is a little shorter than that found [8] in Cr$^{\mathrm{O}}$(CO)$_3$(dien), 2·18 Å.

The heterocyclic organometallic rings are not planar; the torsion angles (deg.) round one are: 6·3(5) N(1)–C(5), −6·2(6) C(5)–C(6), 3·3(5) C(6)–N(2), −0·1(7) N(2)–Cr, and −3·5(7) Cr–N(1); for the other ring they are: −3·7(5) N(4)–C(16), 9·3(6) C(16)–C(15), −10·2(5) C(15)–N(3), 6·4(7) N(3)–Cr, and −1·2(7)° Cr–N(4). Thus in each of the rings, corresponding to a torsion angle of zero, there are four atoms coplanar, and the overall planarity is destroyed in the first case by C(5) and in the second case by C(15).

No anomalous bond lengths or angles were found in the two bipyridyl groups nor are they significantly different from those found in the bipyridyl molecule,[9] which, however, is centrosymmetric in the solid state. The individual pyridine rings are planar, the maximum deviation from the corresponding least-squares (*w* atomic number) plane being −0·028 Å for C(5). The angles between the pyridine rings is 8° 23′ for those containing N(1) and N(2) and 9° 8′ for those containing N(3) and N(4). The chromium atom is displaced from the pyridine rings by 0·15, −0·15, 0·32, and −0·14 Å from the rings containing N(1), N(2), N(3), and N(4).

The bond lengths in the methoxyphenyl group are normal [10] and the benzenoid rings are planar, maximum deviation 0·019 Å for C(23). The bond angles at the carbon atoms bonded to chromium, both 114·4°, show a large contraction from the 120° angle which may be assumed for anisole. This angular contraction is commonly observed in a number of σ bonded transition-metal–aryl compounds.[11]

The torsion angles C(26)–C(21)–Cr–C(28) (41·3) and C(29)–C(28)–Cr–C(21) (40·4°) are measures of the twists of the methoxyphenyl groups about the Cr–C bonds and would be equal if the cation had a two-fold symmetry axis. The magnitude of these angles is controlled mainly by non-bonded repulsions H(26) · · · H(29), O(1) · · · H(1), and O(2) · · · H(20). The van der Waals' and non-bonded intramolecular contacts show no unusual features.

This structure analysis, when compared with that [3] of (*p*-tolyl)CrCl$_2$,3THF, shows that a Cr$^{\mathrm{III}}$–C(aryl) σ bond length changes when the environment at the chromium atom alters. The following paper describes the effect on this bond length of changes within the aryl group.

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