Crystal Structure of *mer*-Trichloro(dimethylformamide)(1,10-phenanthroline)chromium(III)

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The crystal structure of the least-soluble isomer of trichloro(dimethylformamide)(1,10-phenanthroline)chromium(III) has been determined from photographic data collected about the *c* crystallographic axis. The monoclinic crystals have space group $P2_1$, with $Z = 2$, unit-cell dimensions $a = 9.77 \pm 0.02$, $b = 13.19 \pm 0.04$, $c = 6.66 \pm 0.02$ Å, $\beta = 104.7 \pm 0.2°$. Parameters for non-hydrogen atoms were refined by least-squares methods to *R* 8.7% for 1 189 reflections.

The chloro-ligands are disposed in a *meridional* configuration about the chromium atom which has essentially octahedral geometry. The equatorial Cr–Cl is markedly shorter (6σ) that the two axial Cr–Cl bonds and the difference is interpreted in terms of π bonding. The dimethylformamide is bound *via* the oxygen atom. The related new complexes [$CrCl_3$(terpy)] (terpy = 2,2',2''-terpyridine) and [$CrCl_3$(phen)] (phen = 1,10-phenanthroline) are reported together with i.r. spectra and other physical measurements.

SOME years ago one of us reported the preparation of [$CrCl_3$(dmf)(phen)] (dmf = *NN'*-dimethylformamide) together with other metal–phenanthroline complexes.[1] However no information concerning their stereochemistry was obtained. A simple octahedral formulation of the chromium complex implies the existence of not only *fac*- and *mer*-forms but also *N*- and *O*-bonded dimethylformamide. We now describe the synthesis of another isomeric form of [$CrCl_3$(dmf)(phen)]. An *X*-ray structure determination and other studies permits elucidation of the stereochemistry of these complexes. The new complexes trichloro(2,2',2''-terpyridine)chromium(III) and trichloro(1,10-phenanthroline)chromium(III) are also reported.

EXPERIMENTAL

Trichloro(dimethylformamide)(1,10-*phenanthroline*)*chromium*(III).—(*a*) *Form insoluble in dimethylformamide.* This complex was prepared as described previously.[1] Far-i.r., ν (cm^{-1}): 311, 341, 364, 390, 403, and 435.

(*b*) *Form soluble in dimethylformamide.* The insoluble form of this complex (0.3 g) was suspended in dimethylformamide (100 cm^3) and the solution allowed to boil for 4 h. The green solution was cooled to room temperature and diethyl ether added to precipitate a pale-green solid. This was washed with diethyl ether and air dried (0.27 g; Found: C, 43.5; H, 3.7; Cl, 25.4; N, 10.2. $C_{15}H_{15}Cl_3CrN_3O$ requires C, 43.8; H, 3.7; Cl, 25.8; N, 10.2%). Far-i.r., ν (cm^{-1}): 294, 313, 352, 388, 416, and 433.

Trichloro(1,10-*phenanthroline*)*chromium*(III).—Both forms of [$CrCl_3$(dmf)(phen)] lose dimethylformamide when heated. This reaction was conveniently studied using a thermogravimetric balance. Loss of ligand occurred at 240 and 280 °C for the soluble and insoluble forms respectively. Both reactions gave green products and these gave identical analyses (Found: C, 42.8; H, 2.3; Cl, 30.9; N, 8.3. $C_{12}H_8Cl_3CrN_2$ requires C, 42.6; H, 2.4; Cl, 31.4; N, 8.3%). For both products the magnetic moment (Gouy method) was 3.85 B.M. at 293 K. Far-i.r., ν (cm^{-1}): 325, 353, 366, and 440.

Trichloro(2,2',2''-*terpyridine*)*chromium*(III).— Anhydrous chromium(III) chloride (0.15 g) and 2,2',2''-terpyridine (0.10 g) were dissolved in hexamethylphosphoramide (5 cm^3) a piece of clean granulated zinc being added to catalyse dissolution of the chromium(III) chloride. The mixture was heated to boiling and then allowed to cool. The dark-green crystalline solid which precipitated was filtered, the zinc removed, and washed with hexamethylphosphoramide (3 × 5 cm^3) and then diethyl ether (0.14 g, 83%) (Found: C, 45.8; H, 2.85; Cl, 27.3; N, 10.7. $C_{15}H_{11}Cl_3CrN_3$ requires C, 46.0; H, 2.83; Cl, 27.2; N, 10.7%). The product had the conductance of a non-electrolyte in dimethyl sulphoxide. Far-i.r., ν (cm^{-1}): 314, 346, 395, 428, and 452.

I.r. Spectra.—A Grubb–Parsons DM_4 spectrophotometer calibrated with water vapour was used (500—200 cm^{-1}) for samples in Nujol between polyethylene plates, and a Unicam SP 200G instrument (4 000—650 cm^{-1}) by the KBr disc technique.

Mass Spectrum Measurements.—These were made on an AEI MS 902 mass spectrometer and resulted from electron impact on pyrolysis at 465 °C.

X-Ray Data for mer-[$CrCl_3$(dmf)(phen)] (*Insoluble Form*).—*Crystal data.* $C_{15}H_{15}Cl_3CrN_3O$, Monoclinic, $M = 411.7$, $a = 9.77 \pm 0.02$, $b = 13.19 \pm 0.04$, $c = 6.66 \pm 0.02$ Å, $\beta = 104.7 \pm 0.2°$, $U = 830$ Å^3, $D_c = 1.65$, $Z = 2$, $D_m = 1.61 \pm 0.04$, $F(000) = 418$. Space group from systematic absences ($0k0$ with k odd) $P2_1$ (No. 4) or $P2_1/m$ (No. 11); shown to be the former. Cu-K_α radiation, $\lambda = 1.541\ 8$ Å; μ(Cu-K_α) = 103 cm^{-1}.

Crystals were small needles or prisms elongated parallel to the *c* axis. Unit-cell dimensions were determined from Weissenberg photographs. Intensity data were collected by the multiple-film Weissenberg technique with Cu-K_α

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[1] J. A. Broomhead and F. P. Dwyer, *Austral. J. Chem.*, 1961, **14**, 250.

radiation from a crystal of dimensions *ca.* 0.05 × 0.07 × 0.15 mm, mounted about the *c* axis (longest crystal dimension). Six layers *hk*0—5 were recorded. Intensities were estimated visually by comparisons with a scale of timed exposures of a reflection from the same crystal. Equivalent reflections hkl and $\bar{h}kl$ were averaged but because of the possible non-equivalence of hkl and $h\bar{k}l$ reflections in space group $P2_1$, only reflections with positive *k* were measured. The intensities of 1 189 independent reflections measured (*ca.* 60% of those possible) were corrected for Lorentz and polarization effects and for variation of spot shape on upper-layer photographs.[2] Absorption corrections were not applied, the minimum and maximum values of μr for the crystal used being *ca.* 0.26 and 0.36. The $|F_o|$ values for the various layers were cross-correlated by reference to *h*0*l* data from another crystal (cut to *ca.* 0.05 × 0.05 × 0.05 mm). Approximate values of an overall temperature factor and a scale factor for placing the data on an absolute scale were derived from a Wilson analysis.[3]

Determination and refinement of the structure. Since a statistical analysis of the intensity data indicated no centre of symmetry, space group $P2_1$ was assumed. The chromium atom and two of the three chlorine atoms in the asymmetric unit [Cl(1) and Cl(2)] were located from a three-dimensional Patterson synthesis, with the F^2 values modified by a factor exp $(2B \sin^2\theta/\lambda^2)$ where *B* is the overall isotropic temperature factor. Since there is no unique origin point along the *b* axis in space group $P2_1$, the chromium atom was placed arbitrarily at $y = \frac{1}{4}$. The co-ordinates of the third chlorine atom and the other 19 non-hydrogen atoms were derived from subsequent Fourier and difference-Fourier syntheses. Structure factors calculated at this stage, using scattering factors for neutral atoms [4] and an overall isotropic temperature factor (*B* 2.5 Å^2) gave *R* 0.13.

Atomic parameters were initially refined by full-matrix least squares, minimizing the function $\Sigma w(k|F_o| - |F_c|)^2$. Four cycles, varying the co-ordinates of all atoms (except the *y* co-ordinate of chromium), individual isotropic temperature factors, and the overall scale factor *k*, reduced *R* to 0.105 for the observed reflections. At first, unit weights were used, reflections with $|F_c| < 0.5k|F_o|$ and $(|F_o| - |F_c|/k) > 20$ being given zero weight. Before the fourth refinement cycle, unit weights were replaced by a weighting factor $w = (4F_{\text{min.}}/|F_o|)^2$ for $|F_o| > 4F_{\text{min.}}$ and $w = 1$ for $|F_o| < 4F_{\text{min.}}$ where $F_{\text{min.}}$ is the average minimum observable structure factor ($4F_{\text{min.}} = 25$). Anisotropic temperature factors were next introduced for all atoms and the refinement was continued using a block-diagonal least-squares program. The refinement converged to *R* 0.087 in four cycles, shifts of all parameters in the final cycle being $< 0.5\sigma$. No positional parameters changed by more than σ as a result of the change to anisotropic refinement. The assumption of an anisotropic model could be justified at the 0.005 significance level [5] although, with data not corrected for absorption, not much physical significance can be attached to the anisotropic thermal parameters of the light atoms. A difference-Fourier map, calculated after the final least-squares cycle, failed to reveal clearly the positions of the hydrogen atoms. Inclusion of the nine hydrogen atoms on the sp^2 carbon atoms in the structure-factor calculation, in calculated positions 1.02 Å from the corresponding carbon atoms, resulted in a very slight decrease in *R* to 0.086.

Final positional and thermal parameters of the non-hydrogen atoms, with the corresponding standard deviations are listed in Table 1. Observed and calculated structure amplitudes and anisotropic thermal parameters are deposited in Supplementary Publication No. SUP 21910 (3 pp., 1 microfiche).*

Calculations were done on IBM 360/50 and UNIVAC 1108 computers at the Australian National University Computer Centre, using the following programs, modified where necessary: DATPR2 [3] for Wilson analysis and intensity statistics, MUFR3 [6] for Patterson and Fourier syntheses, ORFLS [7] and SFLS [8] for structure-factor and least-squares calculations, DISTAN [9] for interatomic distances and angles, MEANPLANE [10] and some local ancillary programs.

TABLE 1

Fractional co-ordinates, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cr	0.159 0(3)	$\frac{1}{4}$	0.039 7(4)
Cl(1)	0.021 7(5)	0.339 7(3)	0.204 2(7)
Cl(2)	0.370 9(5)	0.286 9(3)	0.285 9(7)
Cl(3)	−0.035 5(4)	0.186 2(3)	−0.213 1(7)
O	0.191 5(12)	0.358 1(8)	0.866 0(18)
N(1)	0.157 6(12)	0.114 1(8)	0.204 9(19)
N(2)	0.280 4(14)	0.151 9(9)	−0.091 3(21)
N(3)	0.250 1(14)	0.519 3(10)	−0.209 5(21)
C(1)	0.094 0(17)	0.100 2(12)	0.362 3(27)
C(2)	0.099 3(19)	0.003 6(15)	0.460 6(28)
C(3)	0.165 9(20)	−0.073 8(14)	0.399 0(29)
C(4)	0.243 2(16)	−0.060 5(10)	0.237 3(26)
C(5)	0.229 3(17)	0.037 0(12)	0.150 1(25)
C(6)	0.347 2(15)	0.176 2(14)	−0.237 8(25)
C(7)	0.434 1(19)	0.100 5(14)	−0.307 6(30)
C(8)	0.451 0(18)	0.004 2(14)	−0.225 5(29)
C(9)	0.381 1(18)	−0.017 7(11)	−0.073 9(24)
C(10)	0.299 6(17)	0.057 2(12)	−0.010 5(26)
C(11)	0.390 0(20)	−0.114 2(12)	0.020 0(30)
C(12)	0.327 7(20)	−0.135 5(13)	0.172 1(29)
C(13)	0.202 0(18)	0.452 9(12)	−0.091 9(28)
C(14)	0.284 3(20)	0.487 3(13)	−0.401 1(31)
C(15)	0.264 9(21)	0.626 1(11)	−0.158 7(32)

DISCUSSION

Structure of mer-[CrCl$_3$(dmf)(phen)].—The *X*-ray structure analysis of the less-soluble form of [CrCl$_3$(dmf)(phen)] has established that the configuration of the chlorine atoms in this compound is *meridional*. Since the analogous complexes [IrCl$_3$(dmf)(phen)] and [RhCl$_3$(dmf)(phen)] are isomorphous with the Cr$^{\text{III}}$ complex, the previously assigned *mer*-labels are confirmed.[11] In addition, a selection between the various isomers already

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[2] D. C. Phillips, *Acta Cryst.*, 1956, **9**, 815.

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[4] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

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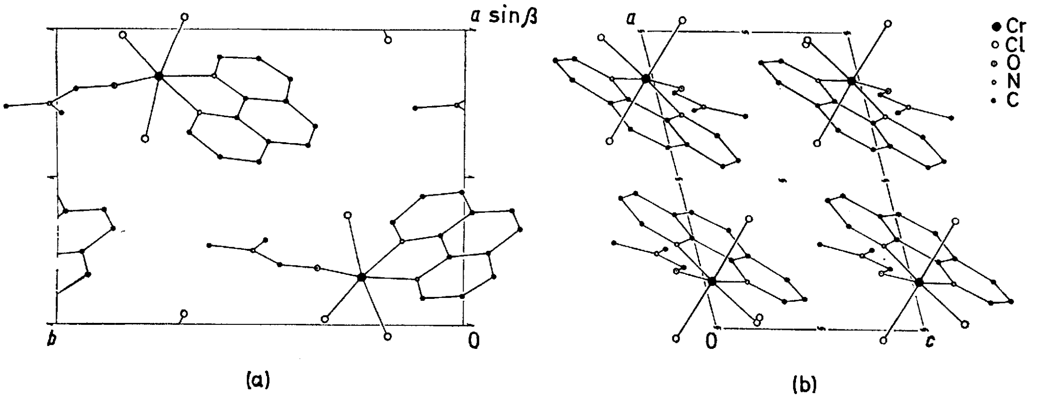

FIGURE 2 Packing of *mer*-[$CrCl_3$(dmf)(phen)] molecules projected (a) down the *c* axis and (b) down the *b* axis

discussed for [{$IrCl_3$(phen)}$_2$] becomes possible and now favours the structure having D_{2h} symmetry.[12] Figure 1 shows the structure of the molecule and the numbering of atoms used. The packing of *mer*-[$CrCl_3$(dmf)(phen)] molecules is shown in Figure 2. The shortest non-bonded distance between adjacent molecules is 3.30 Å and the mean separation of the phenanthroline rings is 3.6 Å, in good agreement with expected van der Waals contacts.

Bond distances and angles with the corresponding standard deviations, calculated from those of the positional parameters, are given in Table 2. The co-ordination of ligands around the chromium atom is approximately octahedral although the geometry is modified by the constraint exerted by the rigid 1,10-phenanthroline system on the N(1)–Cr–N(2) angle. The geometry of the 1,10-phenanthroline ligand is similar to that reported for [$ZnCl_2$(phen)] (ref. 13) and for the phenanthrene molecule.[14] The ligand is approximately planar, the largest deviation from the mean plane being 0.05 Å. The chromium and oxygen atoms and the chlorine atom also lie in this plane, the respective deviations being 0.015, 0.040, and 0.008 Å. Bond distances and angles in the dimethylformamide ligand are as expected.[4] Bond distances involving the chromium atom also agree with expected values but the Cr–Cl(1) bond, in the plane of the 1,10-phenanthroline, is somewhat shorter (by *ca.* 6σ) than the two Cr–Cl bonds approximately perpendicular to this plane. This shortening of the equatorial Cr–Cl bond may be accounted for in terms of π-electronic interactions which are available only in the *mer*-isomer.

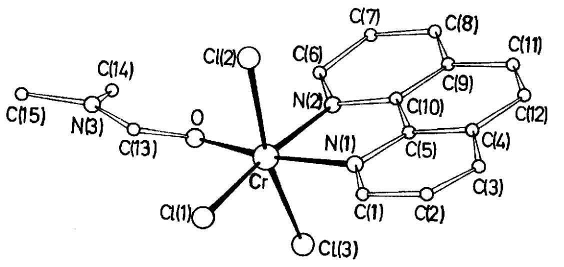

FIGURE 1 Structure of the *mer*-[$CrCl_3$(dmf)(phen)] molecule and numbering of atoms

The $t_{2g}{}^3$ configuration of Cr^{III} could interact with either filled p_π or empty d_π orbitals of the chlorine atoms. Both axial chlorine atoms [Cl(2) and Cl(3) in Figure 2] have to compete for the same pair of metal d_π orbitals whereas Cl(1) can make use of the remaining metal d_π orbital, which is orthogonal to Cl(2) and Cl(3). It also seems unlikely that there is any significant and competitive π interaction in the metal–nitrogen system. Comparison with the

TABLE 2

Bond distances and angles in *mer*-[$CrCl_3$(dmf)(phen)], with estimated standard deviations in parentheses

(*a*) Distances (Å)

Cr–Cl(1)	2.27(1)	C(4)–C(5)	1.40(2)
Cr–Cl(2)	2.34(1)	C(4)–C(12)	1.42(3)
Cr–Cl(3)	2.35(1)	C(5)–C(10)	1.44(2)
Cr–O	1.91(2)	C(6)–C(7)	1.46(3)
Cr–N(1)	2.10(2)	C(7)–C(8)	1.38(3)
Cr–N(2)	2.09(2)	C(8)–C(9)	1.39(3)
N(1)–C(1)	1.36(2)	C(9)–C(10)	1.40(2)
N(1)–C(5)	1.34(2)	C(9)–C(11)	1.41(3)
N(2)–C(6)	1.34(2)	C(11)–C(12)	1.34(3)
N(2)–C(10)	1.35(2)	O–C(13)	1.28(2)
C(1)–C(2)	1.43(3)	N(3)–C(13)	1.34(2)
C(2)–C(3)	1.33(3)	N(3)–C(14)	1.46(3)
C(3)–C(4)	1.47(3)	N(3)–C(15)	1.45(3)

(*b*) Angles (°)

Cl(1)–Cr–Cl(2)	94.6(2)	C(2)–C(3)–C(4)	121(2)
Cl(1)–Cr–Cl(3)	93.6(5)	C(3)–C(4)–C(5)	113(2)
Cl(1)–Cr–O	96.5(6)	C(3)–C(4)–C(12)	126(2)
Cl(2)–Cr–O	90.2(6)	C(5)–C(4)–C(12)	121(2)
Cl(3)–Cr–O	93.5(6)	N(1)–C(5)–C(4)	126(2)
Cl(1)–Cr–N(1)	96.2(6)	N(1)–C(5)–C(10)	116(2)
Cl(2)–Cr–N(1)	86.2(6)	C(4)–C(5)–C(10)	118(2)
Cl(3)–Cr–N(1)	87.6(6)	N(2)–C(6)–C(7)	120(2)
Cl(2)–Cr–N(2)	85.8(6)	C(6)–C(7)–C(8)	122(2)
Cl(3)–Cr–N(2)	85.4(6)	C(7)–C(8)–C(9)	117(2)
O–Cr–N(2)	90.6(6)	C(8)–C(9)–C(10)	120(2)
N(1)–Cr–N(2)	76.7(7)	C(8)–C(9)–C(11)	122(2)
Cl(2)–Cr–Cl(3)	170.2(8)	C(10)–C(9)–C(11)	119(2)
Cl(1)–Cr–N(2)	172.9(8)	N(2)–C(10)–C(5)	115(2)
O–Cr–N(1)	167.2(8)	N(2)–C(10)–C(9)	124(2)
Cr–N(1)–C(1)	126(1)	C(5)–C(10)–C(9)	121(2)
Cr–N(1)–C(5)	116(1)	C(9)–C(11)–C(12)	122(2)
C(1)–N(1)–C(5)	119(1)	C(4)–C(12)–C(11)	120(2)
Cr–N(2)–C(6)	126(1)	Cr–O–C(13)	128(1)
Cr–N(2)–C(10)	116(1)	O–C(13)–N(3)	122(2)
C(6)–N(2)–C(10)	118(1)	C(13)–N(3)–C(14)	121(2)
N(1)–C(1)–C(2)	120(2)	C(13)–N(3)–C(15)	122(2)
C(1)–C(2)–C(3)	120(2)	C(14)–N(3)–C(15)	117(2)

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molecular structure of *fac*-[CrCl$_3$(dien)] (ref. 15) {dien = H$_2$N·[CH$_2$]$_2$·NH·[CH$_2$]$_2$·NH$_2$} shows almost identical Cr–N bond distances as found for the phenanthroline complex, yet here metal–nitrogen ligand π bonding is not possible. A further point of interest is that the three Cr–Cl distances in *fac*-[CrCl$_3$(dien)] are almost identical (mean 2.32 Å) and only slightly shorter than the axial Cr–Cl distances in *mer*-[CrCl$_3$(dmf)(phen)] (mean 2.35 Å). Since there are no symmetry restrictions concerning the π interactions available to all three Cr–Cl bonds in the *fac*-isomer, three equal bond lengths are expected. It follows that *mer*-[CrCl$_3$(dien)] should display a similar shortening of the axial Cr–Cl bond as found here but unfortunately *X*-ray structural information for this isomer is not available. It would also be interesting to have detailed structural information for *mer*-isomers of the type MCl$_3$L$_3$ in which the metal has a $t_{2g}{}^6$ configuration. For complexes of this type metal–chlorine π interaction is possible only in the direction from metal to ligand. Thus information as to the acceptor properties of chlorine d_π orbitals should follow. The structure of *mer*-[CrCl$_3$(dmf)(phen)] (Figure 1) shows co-ordination of dimethylformamide *via* oxygen. This is consistent with the interpretation of the i.r. spectral shift of the carbonyl band. Dimethylformamide has a strong ν(CO) at 1 673 and 1 635 cm^{-1} respectively for the soluble and insoluble forms of [CrCl$_3$(dmf)(phen)]. Similar evidence for the co-ordination of dimethylformamide *via* oxygen has been used elsewhere.[16] Far-i.r. spectra were measured originally in the hope of distinguishing between the *fac*- and *mer*-isomers. However, unambiguous assignments of bands in the 311—395 cm^{-1} range are not possible since this metal–chlorine region is overlapped at either end by other metal–ligand and ligand vibrational modes.

Although conclusive evidence for the formula of the amorphous thermal decomposition product, [CrCl$_3$(phen)], has not been obtained, a five-co-ordinate structure would appear most consistent with both mass-spectral and i.r. results. In the i.r. spectrum there are three strong bands (probably Cr–Cl stretching vibrations) at 366, 353, and 325 cm^{-1}. We have been unable to prepare pure samples of the analogous bromo-complexes to verify these tentative assignments. Both square-pyramidal and trigonal-bipyramidal geometries lead to the prediction of three metal–chlorine bands whereas bridged dimeric structures require at least four.[12] No evidence for a dimeric [{CrCl$_3$(phen)}$_2$] species or for a monomeric molecular ion could be obtained from mass-spectral measurements. Instead peaks corresponding to *m*/*e* values for [CrCl$_2$(phen)]$^+$, [CrCl(phen)]$^+$, and [Cr(phen-H)]$^+$ were found (phen-H = 1,10-phenanthrolinyl). Other examples of five-co-ordinate chromium(III) complexes are known.[17]

[6/571 *Received, 25th March,* 1976]

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