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Interligand Pockets in Polypyridyl Complexes. Crystal and Molecular Structure of the Bis(terpyridyl)chromium(III) Cation

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The crystal and molecular structure of $[Cr(terpy)_2](ClO_4)_3 \cdot H_2O$ (terpy = 2,2′,2″-terpyridine) has been determined by single-crystal X-ray diffraction techniques. Crystals are monoclinic, space group *Cc*, with $Z = 4$ in a unit cell having dimensions $a = 12.94$ (1) Å, $b = 13.61$ (2) Å, $c = 19.44$ (2) Å, and $\beta = 100.63$ (7)°. The structure was solved by conventional Patterson and Fourier methods and refined by "full"-matrix, least-squares refinement techniques to a discrepancy index R of 0.052 for 2150 observed reflections with $I > 3\sigma(I)$. The complex adopts a distorted meridional configuration about chromium(III). Mean Cr–terminal N and Cr–central N distances are 2.06 (1) and 1.97 (1) Å, respectively; the mean intraligand N–Cr–N bond angle is 78.7 (4)°. There are eight ClO_4^- anions about the $Cr(terpy)_2^{3+}$ cation, three of which have oxygens wedged inside the interligand pockets. The three pyridyl rings constituting the terpyridyl ligands are not coplanar; the angle of twist for the terminal rings with respect to the central ring ranges from ~1 to ~8°. There is no evidence of a covalent hydrate; the water of crystallization is hydrogen bonded to ClO_4^- oxygens and does not occupy a site between the ligands.

Introduction

Polypyridyl complexes of chromium(III) continue to provide the inorganic photochemist with some very interesting and novel information on the behavior[1] and reactivity[2,3] of the excited states under various conditions, particularly of solution medium.[4] Recent work from our laboratories on $Cr(NN)_3^{3+}$ species [NN = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or their substituted derivatives] has demonstrated that the lowest excited states ($^2T_1/^2E$) are phosphorescent,[1] are remarkably long-lived (>50 μs) in O_2-free aqueous solutions at room temperature,[1] and are highly reactive toward redox quenchers.[3,5-7] By contrast, the metal-centered, spin-forbidden ^2E state of $Cr(terpy)_2^{3+}$ [terpy = 2,2′,2″-terpyridine] is very short-lived (τ 0.05 μs[8]) compared to the ^2E state of $Cr(bpy)_3^{3+}$ ($\tau = 63$ μs[1]) and this is despite its structural similarity with $Cr(bpy)_3^{3+}$. Interestingly, the metal-to-ligand charge-transfer excited state of $Ru(terpy)_2^{2+}$ is also shorter lived ($\tau \leq 0.005$ μs,[9] $\tau \sim 0.012$ μs[10]) than the bpy analogue ($\tau = 0.60$ μs[6,11]). Such variations in the lifetimes of the $(^2E)Cr(NN)_3^{3+}$ have been rationalized in terms of a model which considers, among others, solvent molecules in the interligand pockets of the cations.[1,12,13]

Pertinent to this notion are the recent thorough studies by Neumann and VanMeter[14,15] on the racemization and dissociation kinetics and solvation of the related $Fe(phen)_3^{2+}$ cation. The solvent affects the racemization rate by solvating the aromatic phen ligands in the transition state and by the solvent's viscous resistance to reorganization in the vicinity of the complex ion when the ion undergoes inversion. The effect on the dissociation rate arises from solvation of the ligand in the transition state and from the solvent's ability to act as a replacing ligand. These solvent effects were understood in terms of a solvation model based on the structure of the complex. Two types of pockets were identified:[14] (i) three large V-shaped pockets between the polypyridyl ligands, each large enough to accommodate two small molecules (e.g., water) or anions, and (ii) two smaller pockets corresponding to the two remaining octahedral faces perpendicular to the threefold axis of the propeller-shaped $Fe(phen)_3^{2+}$ cation. Small molecules in the large pockets can approach the central metal atom to as close as 3 Å.[14] Nmr line width measurements led LaMar and VanHecke[16] to conclude that in aqueous solutions of the $Cr(phen)_3^{2+}$ complex water molecules penetrate about 2 Å into the interligand pockets.

Another point of concern in this work is Gillard's view,[17] and his many studies[18] in the last few years, that many anomalies as occur in the aqueous chemistry (kinetics, stabilities, and reactivities) of polypyridyl–metal complexes can be rationalized on the basis of covalent hydrate species participating in equilibria of such complexes in aqueous media. Germane to the present study is a recent report[19] that covalent hydrate formation is an essential step in the dissociation process of the analogous $Fe(terpy)_2^{3+}$ complex; no observable dissociation occurs in the absence of water (i.e., when $a_{H_2O} = 0$). In previous studies, we[20-22] and others[23] have argued that, at least insofar as chromium(III) polypyridyl complexes are concerned, dissociation of a bpy ligand from both the ground-state complex, $(^4A_2)Cr(bpy)_3^{3+}$,[20,21] and the excited state complex, $(^2E)Cr(bpy)_3^{3+}$,[22,23] occurs via direct attack of the nucleophile (OH^- or H_2O) on the chromium(III) metal core rather than via covalent hydrates.[17]

These above considerations have led us to examine the nature of the ground-state structure of the (terpyridyl)chromium(III) cation, $Cr(terpy)_2^{3+}$. In particular, we wished to

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Table I. Experimental Conditions for Intensity Data Collection

a	12.94 (1) Å
b	13.61 (2) Å
c	19.44 (2) Å
β	100.63 (7)°
V	3257 $Å^3$
space group	*Cc*
mol wt	834.9
Z	4
ρ_{calcd}	1.67 g cm^{-3}
ρ_{obsd}	1.65 (1) g cm^{-3} (by flotation)
radiation	Mo Kα (λ = 0.710 69, α_1/α_2 doublet not resolved)
monochromator	highly oriented graphite, $2\theta_{002}$ = 12.1°
cryst-detector dist	25 cm
detector	scintillation counter and pulse height analyzer set for 100% Mo Kα peak
attenuators	Ni foil, when counting rate exceeded 10^4 counts s^{-1}
takeoff angle	3.0°
detector aperture	4 × 4 mm
scan type	coupled θ(cryst)–2θ(detector), 2.0° min^{-1}
scan base width	2.5°
scan length	$\Delta(2\theta)$ = [2.5 + (0.692 [illegible], beginning (1.25°) below the predicted peak
rotation axis	[001]
reflctns measd	$+h, +k, \pm l$
min and max 2θ	4.0 and 45.0°
stds every 50 cycles	600, 040, 0,0,10
variation of stds	±3% (random)
no. of reflctns collected	2307
no. with $I > 3\sigma(I)$	2150

	chosen enantiomer	rejected enantiomer
R	5.2%	5.3%
R_w	5.7%	5.9%
GOF	2.19	2.28

examine the following questions: (1) How large are the pockets? (2) Is the water of hydration in the complex [Cr(terpy)$_2$](ClO$_4$)$_3$·H$_2$O inside the interligand pockets? (3) Does the water molecule form the covalent hydrate? A preliminary communication has appeared[24] and we herein report the details of our findings.

Experimental Section

The complex [Cr(terpy)$_2$](ClO$_4$)$_3$·H$_2$O was available from an earlier study.[1] Crystals were grown from an aqueous solution by slow evaporation methods. The crystal chosen for the X-ray diffraction studies was a parallelepiped with edges about 0.6 × 0.4 × 0.3 mm long. Preliminary Weissenberg and precession photographs showed absences *hkl*, $h + k = 2n + 1$, and *h*0*l*, $l = 2n + 1$, which limited the space groups possible to *Cc* (noncentrosymmetric) and *C*2/*c* (centrosymmetric).

The crystal was aligned on a Picker-Nuclear FACS-1, fully automated diffractometer by using the setting angles of 12 automatically centered reflections, at both positive and negative 2θ values, in a least-squares refinement which also optimized the cell parameters. The 12 reflections were scattered in reciprocal space with 2θ ranging from 20 to 34°. Intensity data were then collected under the conditions listed in Table I. The following expressions were applied during data reduction:

$$I = N - Bt_s/t_b \qquad \sigma(I) = [N + B(t_s/t_b)^2 + (0.02N)^2]^{1/2}$$

$$Lp = \frac{(\sin 2\theta_s)(\cos^2 2\theta_m + 1)}{\cos^2 2\theta_s + \cos^2 2\theta_m}$$

where *I* is the net intensity, *N* is the total count for the scan of duration t_s s, *B* is the total background count accumulated in t_b s, *Lp* is the Lorentz–polarization factor, and $2\theta_s$ and $2\theta_m$ are the diffraction angles at the sample and monochromator crystal, respectively. The linear absorption coefficient for Mo Kα radiation is 6.83 cm^{-1}, and the transmission factors were estimated as ranging from 0.76 to 0.83. No absorption correction was applied.

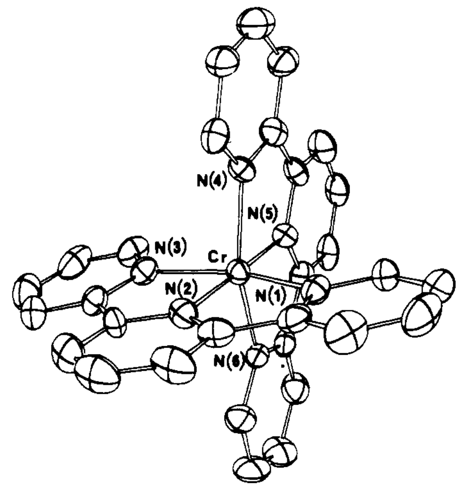

Figure 1. Geometry of the Cr(terpy)$_2^{3+}$ cation about the chromium metal core as viewed about the pseudo-threefold axis.

The structure was solved by direct methods. The reflection statistics clearly favored the noncentrosymmetric space group *Cc*, and a successful solution confirmed this space group as appropriate. The initial *E* map revealed all the non-hydrogen atoms of the cation, and the positions of the three perchlorate chlorine atoms. The perchlorate oxygens and the water of crystallization were found on a difference Fourier map phased by the partial structure after two cycles of full-matrix, isotopic least-squares refinement. The refinement was continued to convergence by using isotropic thermal parameters. Anisotropic refinement was performed on both enantiomers. Owing to computer memory restrictions, the structure was blocked into four "full" matrices; furthermore, the terpyridyl groups together and the perchlorate and water oxygen atoms together were refined in alternate cycles. Each of these parts was subjected to four cycles of refinement; the chromium and chlorine atoms were refined in all eight cycles. The hydrogen atoms of the terpyridyl ligands were included in calculated positions but were not refined. The final atomic positions (Table II) correspond to the enantiomer that yielded the lower *R* factors.

For least-squares refinement, the atomic scattering factors were computed from the listings of Cromer and Wager,[25] except for hydrogen where the coefficients computed by Churchill and co-workers[26] were used. Anomalous dispersion corrections were obtained from ref 27. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma(F_o)]^{-2}$, i.e., $[\sigma(I)/2LpF_o)]^{-2}$. The discrepancy indices are $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$. The "goodness of fit" (GOF) is $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ where *m* and *n* are the numbers of observations and variables, respectively. Tables of anisotropic thermal parameters along with the observed and calculated structure amplitudes are available (see the paragraph at the end of the paper regarding supplementary material).

The computer programs used were FORDAP by Zalkin for Patterson and Fourier calculations and SFLS by Prewitt for structure factor and least-squares calculations. Drawings were prepared by Johnson's ORTEP.

Results and Discussion

Figure 1 illustrates the coordination geometry of the Cr(terpy)$_2^{3+}$ cation about the chromium(III) core with the six nitrogen atoms labeled consecutively for each of the terpy ligands. Labeling of the carbon atoms follows a clockwise sequence starting with the C(1), bonded to N(1), and continuing to C(15) which is bonded to N(3). Carbon C(16), bonded to N(4), begins the clockwise sequence in the second terpy ligand. Bond distances and bond angles in the Cr(ter-

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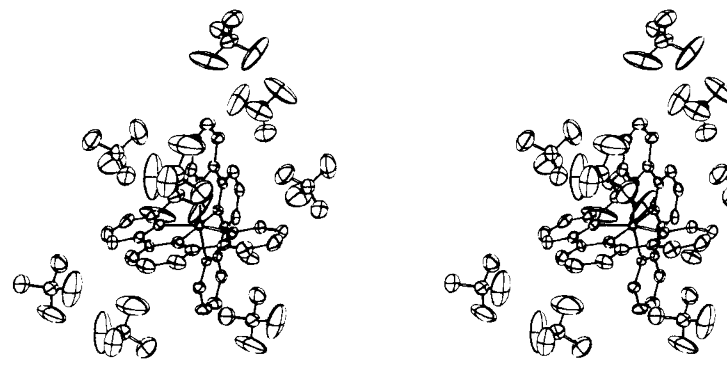

Figure 2. Stereoscopic view of the $[Cr(terpy)_2](ClO_4)_3 \cdot H_2O$ complex.

Table II. Final Positional Coordinates[a] of $[Cr(terpy)_2](ClO_4)_3 \cdot H_2O$

	x	*y*	*z*
Cr	−0.15400	−0.04482 (6)	−0.16000
N(1)	−0.1517 (4)	−0.1580 (4)	−0.22935 (27)
N(2)	−0.2400 (4)	0.0102 (4)	−0.24679 (26)
N(3)	−0.1906 (4)	0.09250 (4)	−0.12526 (27)
C(1)	−0.1003 (6)	−0.2465 (5)	−0.2139 (4)
C(2)	−0.1099 (7)	−0.3198 (5)	−0.2652 (4)
C(3)	−0.1689 (7)	−0.3053 (6)	−0.3303 (4)
C(4)	−0.2192 (6)	−0.2147 (6)	−0.3463 (4)
C(5)	−0.2083 (5)	−0.1421 (5)	−0.2944 (3)
C(6)	−0.2580 (5)	−0.0450 (5)	−0.3036 (3)
C(7)	−0.3211 (7)	−0.0069 (7)	−0.3652 (4)
C(8)	−0.3606 (7)	0.0872 (7)	−0.3634 (4)
C(9)	−0.3394 (6)	0.1443 (6)	−0.3044 (4)
C(10)	−0.2766 (5)	0.1022 (5)	−0.2444 (4)
C(11)	−0.2439 (5)	0.1521 (5)	−0.1761 (4)
C(12)	−0.2611 (7)	0.2494 (6)	−0.1646 (5)
C(13)	−0.2216 (7)	0.2859 (6)	−0.0973 (5)
C(14)	−0.1702 (7)	0.2266 (6)	−0.0448 (5)
C(15)	−0.1548 (6)	0.1279 (5)	−0.0593 (4)
N(4)	−0.2622 (4)	−0.1211 (4)	−0.1158 (3)
N(5)	−0.0676 (4)	−0.0930 (3)	−0.0726 (2)
N(6)	−0.0088 (4)	0.0085 (4)	−0.1694 (3)
C(16)	−0.3654 (5)	−0.1331 (5)	−0.1451 (4)
C(17)	−0.4316 (6)	−0.1898 (5)	−0.1136 (5)
C(18)	−0.3934 (7)	−0.2336 (6)	−0.0502 (4)
C(19)	−0.2853 (6)	−0.2231 (5)	−0.0190 (4)
C(20)	−0.2238 (6)	−0.1651 (5)	−0.0535 (4)
C(21)	−0.1123 (6)	−0.1460 (5)	−0.0276 (3)
C(22)	−0.0561 (6)	−0.1762 (6)	0.0369 (4)
C(23)	0.050512	−0.1494 (5)	0.0527 (4)
C(24)	0.0975 (6)	−0.0959 (5)	0.0056 (4)
C(25)	0.0370 (5)	−0.0677 (5)	−0.0564 (3)
C(26)	0.0697 (5)	−0.0072 (5)	−0.1119 (3)
C(27)	0.1706 (6)	0.0295 (5)	−0.1061 (4)
C(28)	0.1917 (6)	0.0826 (4)	−0.1646 (5)
C(29)	0.1182 (6)	0.1018 (6)	−0.2195 (5)
C(30)	0.0135 (6)	0.0608 (5)	−0.2228 (4)
Cl(1)	−0.0704 (18)	−0.65682 (15)	−0.30839 (10)
Cl(2)	−0.47053 (17)	−0.91219 (15)	−0.06171 (12)
Cl(3)	0.04005 (19)	−0.10264 (16)	−0.37069 (12)
O(1)	0.0312 (6)	−0.6945 (7)	−0.3146 (4)
O(2)	−0.138135 (7)	−0.6497 (7)	−0.3733 (4)
O(3)	−0.1089 (11)	−0.7272 (12)	−0.2711 (8)
O(4)	−0.0610 (10)	−0.5723 (9)	−0.2736 (7)
O(5)	−0.4442 (6)	−0.9225 (5)	−0.1291 (4)
O(6)	−0.5684 (6)	−0.8673 (7)	−0.0645 (4)
O(7)	−0.3934 (8)	−0.8504 (8)	−0.0161 (6)
O(8)	−0.4681 (10)	−1.0032 (6)	−0.0268 (4)
O(9)	0.0294 (11)	−0.1880 (9)	−0.4114 (4)
O(10)	0.0508 (6)	−0.1341 (5)	−0.3002 (3)
O(11)	0.1289 (8)	−0.0470 (10)	−0.3772 (8)
O(12)	−0.0500 (6)	−0.0441 (5)	−0.3870 (4)
O(14)	−0.1515 (5)	−0.4678 (5)	−0.4581 (3)

[a] The estimated standard deviations in parentheses are right justified to the least significant digits of the fractional coordinates.

$py)_2^{3+}$ ion along with those of the ClO_4^- units are collected in Table III. The stereoscopic view of the cation is depicted in Figure 2. Figure 3 summarizes the displacements of the atoms of both terpyridyl ligands, including in each case the chromium atom, about the least-squares plane defined by the four nitrogen atoms N(1),N(2),N(3),N(5) and by N(4),N(5),N(6),N(2); the displacements of the perchlorate chlorines close to these terpyridyl groups are also indicated.

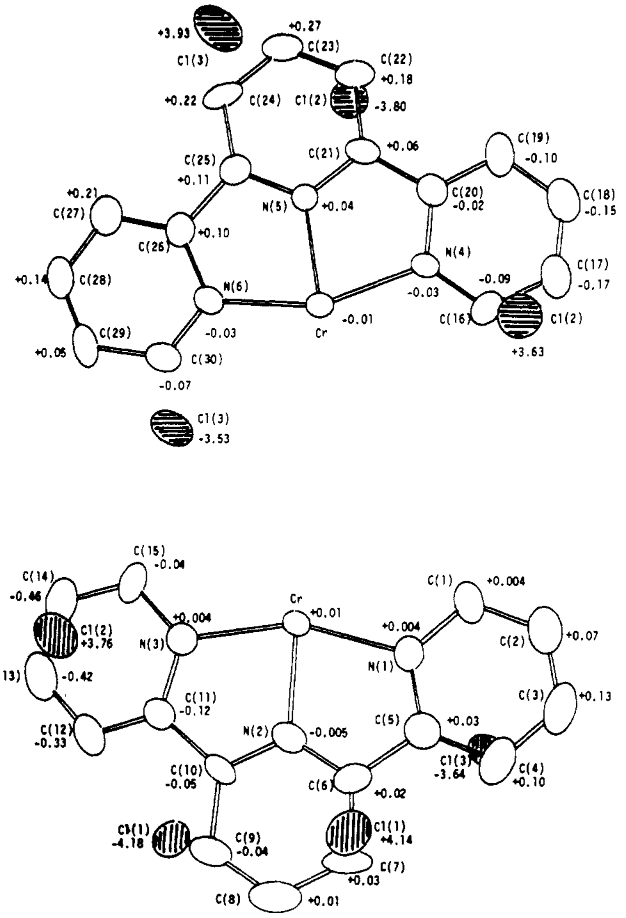

Figure 3. Displacement (Å) of atoms from the least-squares planes defined by (bottom) the N(1),N(2),N(3),N(5) nitrogens and by (top) the N(4),N(5),N(6),N(2) nitrogen atoms. Equations of planes: (bottom) $-0.8842x - 0.3825y + 0.2680z = 0.6607$; (top) $-0.2771x + 0.8277y + 0.4880z = -1.5872$ (where x, y, and z are orthogonal coordinates).

Inasmuch as the terpyridyl ligand is tridentate, complexation with chromium(III) forms the $Cr(terpy)_2^{3+}$ cation, which, in principle, can exist in two diastereomeric configurations: facial and meridional. Of these two forms, the *mer* form is expected (and found) to be the thermodynamically more stable diastereomer. In the fac configuration, one of the pyridyl rings would of necessity be forced sterically to adopt a position perpendicular to the plane of the remaining two pyridyl rings; here the sp^2 nature of inter-ring bonds would have to be

Table III. Bond Distances and Bond Angles in the $[Cr(terpy)_2](ClO_4)_3 \cdot H_2O$ Complex[a]

Distances, Å

Cr-N(1)	2.049 (5)	C(8)-C(9)	1.371 (12)	C(18)-C(19)	1.426 (11)	N(6)-C(26)	1.380 (8)
Cr-N(2)	1.987 (5)	C(9)-C(10)	1.413 (10)	C(19)-C(20)	1.379 (10)	N(6)-C(30)	1.331 (9)
Cr-N(3)	2.070 (5)	N(2)-C(6)	1.318 (8)	C(20)-C(21)	1.461 (10)	Cl(1)-O(1)	1.437 (8)
Cr-N(4)	2.052 (5)	N(2)-C(10)	1.342 (8)	C(21)-C(22)	1.389 (10)	Cl(1)-O(2)	1.400 (8)
Cr-N(5)	1.964 (5)	C(10)-C(11)	1.480 (10)	C(22)-C(23)	1.405 (12)	Cl(1)-O(3)	1.349 (16)
Cr-N(6)	2.052 (5)	C(11)-C(12)	1.367 (10)	C(23)-C(24)	1.392 (10)	Cl(1)-O(4)	1.327 (13)
N(1)-C(1)	1.382 (8)	C(12)-C(13)	1.403 (13)	C(24)-C(25)	1.364 (10)	Cl(2)-O(5)	1.418 (8)
N(1)-C(5)	1.354 (8)	C(13)-C(14)	1.371 (13)	N(5)-C(21)	1.343 (8)	Cl(2)-O(6)	1.398 (8)
C(1)-C(2)	1.398 (10)	C(14)-C(15)	1.395 (11)	N(5)-C(25)	1.375 (9)	Cl(2)-O(7)	1.470 (12)
C(2)-C(3)	1.365 (12)	N(3)-C(11)	1.364 (9)	C(25)-C(26)	1.479 (9)	Cl(2)-O(8)	1.409 (9)
C(3)-C(4)	1.402 (12)	N(3)-C(15)	1.366 (9)	C(26)-C(27)	1.383 (10)	Cl(3)-O(9)	1.397 (12)
C(4)-C(5)	1.399 (10)	N(4)-C(16)	1.362 (9)	C(27)-C(28)	1.413 (12)	Cl(3)-O(10)	1.415 (7)
C(5)-C(6)	1.466 (9)	N(4)-C(20)	1.359 (8)	C(28)-C(29)	1.318 (13)	Cl(3)-O(11)	1.401 (12)
C(6)-C(7)	1.416 (10)	C(16)-C(17)	1.376 (11)	C(29)-C(30)	1.456 (11)	Cl(3)-O(12)	1.399 (8)
C(7)-C(8)	1.381 (14)	C(17)-C(18)	1.376 (12)				

Angles, Deg

N(1)-Cr-N(2)	78.5 (2)	C(4)-C(5)-C(6)	124.4 (6)	C(22)-C(23)-C(24)	121.5 (7)
N(1)-Cr-N(3)	157.5 (2)	N(1)-C(5)-C(6)	114.1 (5)	C(23)-C(24)-C(25)	118.4 (7)
N(1)-Cr-N(4)	89.2 (2)	C(5)-C(6)-N(2)	113.9 (5)	C(24)-C(25)-N(5)	120.9 (6)
N(1)-Cr-N(5)	104.0 (2)	C(5)-C(6)-C(7)	127.2 (6)	C(21)-N(5)-C(25)	120.5 (6)
N(1)-Cr-N(6)	94.8 (2)	N(2)-C(6)-C(7)	118.9 (6)	C(24)-C(25)-C(26)	127.2 (6)
N(2)-Cr-N(3)	79.0 (2)	C(6)-C(7)-C(8)	118.6 (7)	N(5)-C(25)-C(26)	111.9 (6)
N(2)-Cr-N(4)	103.0 (2)	C(7)-C(8)-C(9)	121.8 (8)	C(25)-C(26)-C(27)	122.2 (6)
N(2)-Cr-N(5)	177.3 (3)	C(8)-C(9)-C(10)	117.1 (7)	C(25)-C(26)-N(6)	114.1 (6)
N(2)-Cr-N(6)	99.9 (2)	C(9)-C(10)-N(2)	120.2 (6)	N(6)-C(26)-C(27)	123.7 (6)
N(3)-Cr-N(4)	96.1 (2)	C(6)-N(2)-C(10)	123.4 (6)	C(26)-C(27)-C(28)	115.9 (7)
N(3)-Cr-N(5)	98.5 (2)	C(9)-C(10)-C(11)	125.3 (6)	C(27)-C(28)-C(29)	122.2 (8)
N(3)-Cr-N(6)	88.7 (2)	N(2)-C(10)-C(11)	114.5 (6)	C(28)-C(29)-C(30)	119.1 (8)
N(4)-Cr-N(5)	78.2 (2)	C(10)-C(11)-C(12)	124.2 (7)	C(29)-C(30)-N(6)	120.3 (7)
N(4)-Cr-N(6)	157.1 (2)	C(10)-C(11)-N(3)	113.5 (6)	C(26)-N(6)-C(30)	118.6 (6)
N(5)-Cr-N(6)	79.0 (2)	N(3)-C(11)-C(12)	122.2 (7)	O(1)-Cl(1)-O(2)	112.4 (5)
Cr-N(1)-C(1)	125.2 (4)	C(11)-C(12)-C(13)	116.9 (8)	O(1)-Cl(1)-O(3)	103.0 (7)
Cr-N(1)-C(5)	114.9 (4)	C(12)-C(13)-C(14)	121.8 (8)	O(1)-Cl(1)-O(4)	110.6 (7)
Cr-N(2)-C(6)	118.6 (4)	C(13)-C(14)-C(15)	119.0 (8)	O(2)-Cl(1)-O(3)	107.4 (8)
Cr-N(2)-C(10)	118.0 (4)	C(14)-C(15)-N(3)	119.5 (7)	O(2)-Cl(1)-O(4)	112.4 (7)
Cr-N(3)-C(11)	143.0 (3)	C(11)-N(3)-C(15)	120.5 (6)	O(3)-Cl(1)-O(4)	110.5 (9)
Cr-N(3)-C(15)	124.4 (4)	C(16)-N(4)-C(20)	119.2 (6)	O(5)-Cl(2)-O(6)	112.1 (5)
Cr-N(4)-C(16)	125.4 (4)	N(4)-C(16)-C(17)	121.7 (7)	O(5)-Cl(2)-O(7)	111.1 (6)
Cr-N(4)-C(20)	116.9 (4)	C(16)-C(17)-C(18)	119.3 (7)	O(5)-Cl(2)-O(8)	111.6 (5)
Cr-N(5)-C(21)	119.7 (4)	C(17)-C(18)-C(19)	120.0 (7)	O(6)-Cl(2)-O(7)	106.5 (6)
Cr-N(5)-C(25)	119.7 (4)	C(18)-C(19)-C(20)	117.4 (7)	O(6)-Cl(2)-O(8)	110.0 (6)
Cr-N(6)-C(26)	115.1 (4)	C(19)-C(20)-N(4)	122.3 (7)	O(7)-Cl(2)-O(8)	105.1 (6)
Cr-N(6)-C(30)	126.2 (5)	C(19)-C(20)-C(21)	123.8 (6)	O(9)-Cl(3)-O(10)	106.1 (5)
C(1)-N(1)-C(5)	119.9 (6)	N(4)-C(20)-C(21)	113.9 (6)	O(9)-Cl(3)-O(11)	113.3 (8)
N(1)-C(1)-C(2)	119.4 (6)	C(20)-C(21)-C(22)	125.3 (6)	O(9)-Cl(3)-O(12)	110.7 (6)
C(1)-C(2)-C(3)	121.1 (7)	C(20)-C(21)-N(5)	112.8 (6)	O(10)-Cl(3)-O(11)	108.2 (7)
C(2)-C(3)-C(4)	119.3 (7)	N(5)-C(21)-C(22)	121.8 (7)	O(10)-Cl(3)-O(12)	108.7 (5)
C(3)-C(4)-C(5)	118.7 (7)	C(21)-C(22)-C(23)	116.8 (7)	O(11)-Cl(3)-O(12)	109.6 (6)
C(4)-C(5)-N(1)	121.5 (6)				

[a] See footnote *a* of Table II.

modified substantively to accommodate the steric distortion. The structure about chromium(III) in the meridional form (Figure 1) is highly distorted; the mean chromium-terminal nitrogen distance is 2.06 ± 0.01 Å while the mean chromium-central nitrogen distance is 1.97 ± 0.01 Å. The difference of ~0.09 Å between these two chromium-nitrogen bond distances has also been noted in $Cu(terpy)_2^{2+}$ (0.123 Å)[28] and in the metallo-mono(terpyridyl) complexes Ga-terpy (0.078 Å),[29] Zn-terpy (0.12 Å),[30] and Sn-terpy (0.08 Å).[31]

As noted earlier,[1] the distortion occurs in the two terpyridyl planes (see Figure 4) with interligand bond angles N(2)-Cr-N(4), 103.0 (2)°, and N(2)-Cr-N(6), 99.9 (2)°; also, the angle N(1)-Cr-N(5) is 104.0 (2)° and N(3)-Cr-N(5) is 98.5 (2)°. The mean intraligand N-Cr-N angle is 78.7 ± 0.4°, comparable to bond angles in $Cu(bpy)_3^{2+}$ and $Cu(phen)_3^{2+}$ ions,[32] $Cu(terpy)_2^{2+}$,[33] and $Co(terpy)_2^{2+}$[34] but slightly smaller than those found in $Fe(phen)_3^{2+}$ (82.9°).[35] Carbon-nitrogen and carbon-carbon distances in the terpy ligands reveal

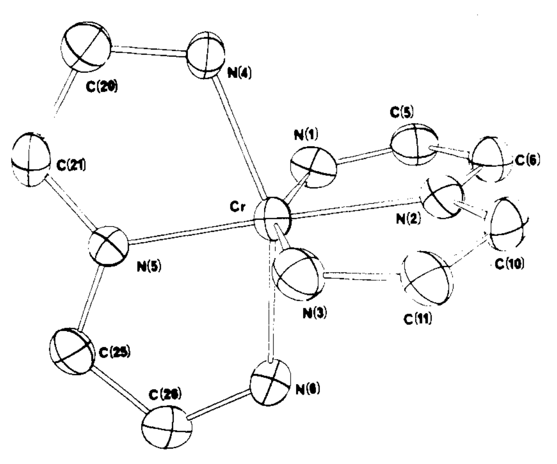

Figure 4. Skeletal view of the $Cr(terpy)_2^{3+}$ cation illustrating the distortion(s) about the chromium core.

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nothing unusual, 1.36 ± 0.02 and 1.39 ± 0.03 Å, respectively; the C–C distances of the bonds joining the pyridyl rings are significantly longer, 1.47 ± 0.01 Å. Mean distances and bond angles in the ClO_4^- anions are 1.40 ± 0.04 Å and 109.4 ± 2.8°, respectively, and agree fairly well with values reported by Anderson[32] and with those found for $HClO_4 \cdot H_2O$.[36]

Certain features of the full structure are worth noting. There are eight perchlorate anions about $Cr(terpy)_2^{3+}$ within 3.32 Å of a non-hydrogen atom (Figure 2). In particular, three of these ClO_4^- anions have oxygen atoms wedged in the interligand pockets ($Cr–O_{ClO_4^-}$ distance ~4.5 Å) such that in the solid state it is not unreasonable to view $Cr(terpy)_2^{3+}$ and ClO_4^- as forming tight ion pairs. This is reminiscent of the strong outer-sphere complexes formed between $Fe(bpy)_3^{2+}$ and ClO_4^-; stability constant $\beta_3 = 60\ M^{-3}$ in aqueous solutions.[37-39] The more opened shallow pockets[37,38] in the $Cr(terpy)_2^{3+}$ complex and its greater charge should lead to stronger outer-sphere complexes.

We have already remarked above that the steric requirements of the terpyridyl ligand force the meridional geometry upon $Cr(terpy)_2^{3+}$. Nevertheless, the three pyridyl rings forming a terpy ligand are not coplanar. The angles of twist (error ~0.5°) between terminal rings 1 and 3 and the central ring 2 are 1.3 and 7.8°, respectively; those for rings 4 and 6 with respect to ring 5 are 4.5 and 1.5°, respectively.[40] The angles of twist found in other terpyridyl complexes range from 4 to 6°.[28-31] Such distortions are also evident from the displacements collected in Figure 3. Clearly, the ring most twisted comprises atoms with the largest displacements. Two factors may be responsible for this noncoplanarity. First, inasmuch as the ClO_4^- anions are strongly attracted by the chromium(III) and penetrate into the pockets, the terpyridyl ligands must distort to accommodate these anions (radius of ClO_4^- 2.92 Å[41]). This is demonstrated by noting that where a perchlorate group is close to a pyridyl ring and lies on one side of the least-squares plane, the terpyridyl atoms are displaced substantially in the opposite direction. Note for example (Figure 3) $ClO_4^-(2)$ at +3.76 Å above the N(1),N(2),N(3),N(5) plane and atoms C(13) and C(14) at –0.42 and –0.46 Å, respectively, below the plane. It is also clear that the C(27) and C(28) carbons, which are displaced to +0.21 and +0.14 Å, respectively, above the plane defined by N(4),N(5),N(6),N(2), are not influenced by any nearby ClO_4^- anion. We view the other factor as originating from the steric nature of the complexed terpyridyl ligand: the two chromium–terminal nitrogen bonds constrain the ligand to "buckle". No doubt, the displacement values in Figure 4 represent equilibrium distances following the various intra- and intermolecular forces in the unit cell.

There is no evidence of covalent hydrate in the ground-state structure of $[Cr(terpy)_2](ClO_4)_3 \cdot H_2O$. The single water of crystallization does not occupy a site in the interligand pockets ($Cr–O_{water}$ distance 6.9 Å); rather, the water molecule is hydrogen bonded to oxygen atoms of two different ClO_4^- ions (2.96 Å; cf. $O–H--O^- = 2.75 \pm 0.13$ Å[42]). In addition, the structures of the $Ir(bpy)_2(Hbpy)^{3+}$[43] and $Cr(bpy)_2(H_2O)Cl^{2+}$[44] complexes reveal no covalent hydrates. A further comment on these covalent hydrates is necessary.

For the analogous iron(III)–terpyridyl cation, the dissociation reaction profile in acid media closely resembles that observed for the dissociation of $Fe(bpy)_3^{2+}$[45] in aqueous H_2SO_4 and parallels that of $Fe(phen)_3^{3+}$[46] in that there is no observable reaction when $a_{H_2O} = 0$.[19] Burgess and Twigg[47] have interpreted their dissociation kinetic data (to ~7 M H_2SO_4) of $Fe(terpy)_2^{2+}$ in terms of successive Fe–N bond rupture. In the corresponding iron(III) species, Gillard and co-workers[19] begin the dissociation process with covalent-hydrate and pseudobase formation at the C(6) position of the terpy ligand followed by bond rupture to explain the dependence of the dissociation rate on the activity of water in H_2SO_4 media (range $0 < a_{H_2O} < 1$ or $0 \le [H_2SO_4] \le 12$ M). That k_{obsd} is 0 when a_{H_2O} is 0 was taken as evidence that water is an essential ingredient in the dissociation kinetics in these iron polypyridyl species. While this is true, we wish to point out, however, that an associative pathway, where the nucleophile H_2O attacks the metal directly, is kinetically indistinguishable from the path involving covalent-hydrate formation. It needs to be emphasized also that the importance of the presence of water proves neither of these two mechanisms. Relevant to this discussion are Neumann's dissociation and racemization studies[15] on $Fe(phen)_3^{2+}$ in various solvents. It was shown that the order of dissociation rates in pure solvents is DMF > formamide > H_2O > CH_3OH > acetone > CH_3CN > CH_3COOH; for DMF, formamide, CH_3OH, and acetone, the rates varied in the same order as the solvent's ability to act as a ligand. Evidently, in the dissociation process, a strongly coordinating ligand must be present to replace the dissociated ligand.[15] Hence, it is not surprising that no observable dissociation reaction occurs when $a_{H_2O} = 0$ for the iron(III)–terpyridyl complex.

Finally, molecular models and the distortions evident in the structure of $Cr(terpy)_2^{3+}$ (Figure 1 and 4) indicate that the interligand pockets in this complex are larger than those in the corresponding $Cr(bpy)_3^{3+}$ cation. Thus, the chromium(III) core in the former terpyridyl species is expected to be influenced by a greater solvent perturbation in solution. Indeed, molecular models reveal that up to eight water molecules can be positioned inside these pockets. Under such conditions, the Cr(III) metal may be regarded as being essentially hydrated in aqueous solutions. Similar conclusions were reached for $Fe(phen)_3^{2+}$ from "apparent molar volume" studies in such solvents as formamide, Me_2SO, and DMF; these solvent molecules can occupy the space between the phenanthroline ligands in much the same way that ClO_4^- ions do in solids.[14]

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Registry No. $[Cr(terpy)_2](ClO_4)_3 \cdot H_2O$, 81447-11-2.

Supplementary Material Available: Listings of anisotropic thermal parameters and structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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