

Interligand Pockets in Polypyridyl Complexes. The Crystal and Molecular Structure of the $\text{Cr}(2,2',2''\text{-terpyridine})_2^{3+}$ Ion

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Summary A single crystal X-ray study reveals that the title compound possesses a distorted meridional configuration; the interligand pockets are such that, in aqueous solutions, the Cr^{III} core may be considered solvated by water molecules.

POLYPYRIDYL complexes of chromium(III)^{1,2} and ruthenium(II)^{3,4} have been the focus of considerable interest recently because of their potential use in solar energy conversion schemes.⁵ Recent work¹ on the excited state properties of the Cr^{III} complexes has shown that the metal-centred, spin-forbidden 2E state of $\text{Cr}(\text{terpy})_2^{3+}$ ($\text{terpy} = 2,2',2''\text{-terpyridine}$) is very short lived (τ 0.05 μs)² compared to the 2E state of $\text{Cr}(\text{bpy})_3^{3+}$ ($\text{bpy} = 2,2'\text{-bipyridine}$; τ 63 μs)¹ and this despite its structural similarity with $\text{Cr}(\text{bpy})_3^{3+}$. Interestingly, the metal-to-ligand-charge-transfer excited state of $\text{Ru}(\text{terpy})_2^{2+}$ is also shorter lived ($\tau \leq 0.005 \mu\text{s}$;³ τ ca. 0.0012 μs)⁴ than the bpy analogue (0.60 μs).⁵ Variations in the lifetimes of the (2E)- $\text{Cr}(\text{N}-\text{N ligand})_3^{3+}$ transients were rationalized¹ in terms of a model^{6,7} which considers conversion of metal-centred electronic energy into ligand-localized vibrational energy whereby the ligands act as both the oscillating perturbation dipoles and the energy acceptors.

The model further considers the more vibrationally rigid the ligand, the longer the lifetimes of the 2E state. We and others have argued that although the terpy ligand is more rigid than bpy ,^{1,2} $\tau({}^2E)$ of the title compound is not inconsistent with the model. In addition, we have suggested that the ground state structure of $\text{Cr}(\text{terpy})_2^{3+}$ should be highly distorted with the distortion occurring along the direction of the two terpy planes. The Cr^{III} core would then be more exposed (larger interligand pockets) to solvent perturbation¹ such that direct vibrational coupling, between the excited state metal core and the bulk solvent, would shorten $\tau({}^2E)$ through an increase in the rate of non-radiative decay, a major contributor to lifetimes.^{6,7} Meyer and his co-workers⁴ have also referred to the more open structure of $\text{Ru}(\text{terpy})_2^{2+}$ compared to $\text{Ru}(\text{bpy})_3^{3+}$ as a possible cause for the shorter-lived excited state of the terpy complex. These above considerations have led us to examine the nature of the ground state structure of $\text{Cr}(\text{terpy})_2^{3+}$. In addition, we wished to verify whether the one water of hydration and the title compound form the covalent hydrate $[\text{Cr}(\text{terpy})(\text{terpyH}-\text{OH})]^{3+}$, particularly in the light of a recent report⁸ that covalent hydrate formation is an essential step in the dissociation process of the analogous $\text{Fe}(\text{terpy})_2^{3+}$

complex; no dissociation occurs in the absence of water. In a similar study, we have argued that dissociation of a bpy ligand from both the ground state complex, (4A_g)-Cr(bpy) $_3^{3+}$,⁹ and the excited state complex, (2E)-Cr(bpy) $_3^{3+}$,¹⁰ occurs *via* direct attack of the nucleophile (OH⁻ or H₂O) on the Cr^{III} metal core rather than *via* covalent hydrates.¹¹

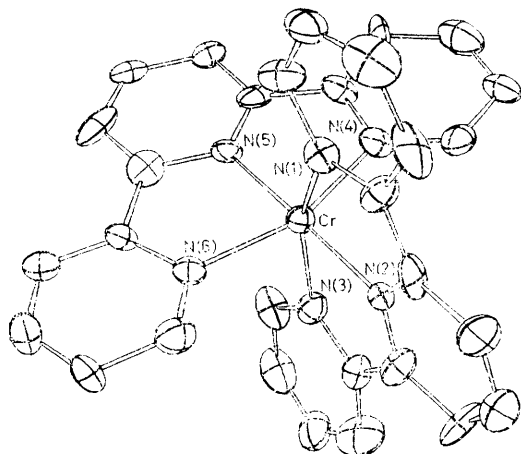


FIGURE 1. Geometry of Cr(terpy) $_2^{3+}$ about the Cr^{III} core.

The title compound was prepared as the perchlorate salt by a procedure described earlier.¹ Recrystallization from aqueous solutions yielded yellow-orange crystals; space group *Cc*; $a = 12.94(1)$, $b = 13.61(2)$, $c = 19.44(2)$ Å,

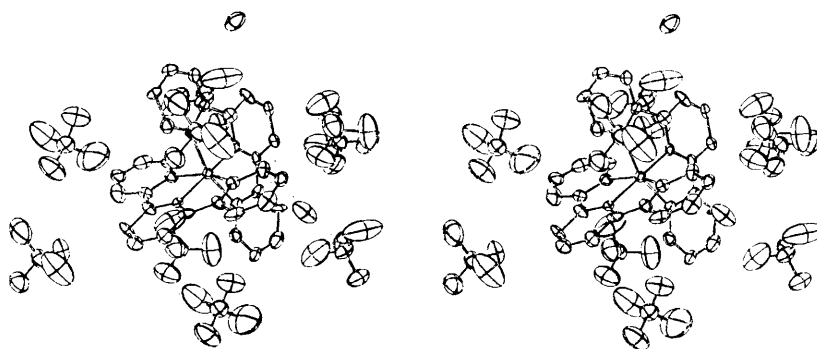


FIGURE 2. Stereoscopic view of the structure of Cr(terpy) $_2^{3+}$.

$\beta = 100.63(7)^\circ$, $Z = 4$ for [Cr(terpy) $_2$](ClO $_4$) $_3 \cdot H_2O$, $D_c = 1.67$ g cm $^{-3}$, $D_m = 1.65$ g cm $^{-3}$ (by flotation). The 2150 reflections with $I > 3\sigma(I)$ were used to solve the structure by statistical methods and Fourier techniques. Full-

matrix, least-squares refinement of all non-hydrogen atoms with anisotropic thermal parameters reduced the final discrepancy index to 5.9%.[†]

The meridional configuration of Cr(terpy) $_2^{3+}$ is depicted in Figure 1; the ClO $_4^-$ anions and H $_2$ O have been omitted for clarity. The structure about Cr^{III} is highly distorted; the mean Cr-N distance is 2.03(4) Å. As noted earlier,¹ the distortion lies along the direction of the two terpy planes with interligand bond angles $> 90^\circ$; $\angle N(1)CrN(5) = 104.2(4)$, $N(3)CrN(5) = N(2)CrN(6) = 99.3(4)$, and $N(2)CrN(4) = 102.5(4)^\circ$. Intraligand NCrN angles range from 77.4 to 80.9°, comparable to bond angles in Cu(bpy) $_3^{2+}$ and Cu(phen) $_3^{2+}$ ¹² (phen = 1,10-phenanthroline), and Cu(terpy) $_2^{2+}$,¹³ but slightly smaller than those in Fe(phen) $_3^{2+}$ (82.9°).¹⁴ Mean distances and bond angles in the ClO $_4^-$ anions are 1.39(4) Å and $109.4 \pm 3.2^\circ$, respectively, and are comparable to values reported by Anderson¹² and to those found for HClO $_4 \cdot H_2O$.¹⁵

Several features of the full structure are noteworthy: the title compound adopts the meridional geometry as sterically required by the terpy ligands; no covalent hydrate¹¹ is evident in the ground state structure; the water of hydration does not occupy a site in the interligand pockets, rather it is hydrogen-bonded to a ClO $_4^-$ ion; there are eight ClO $_4^-$ anions about Cr(terpy) $_2^{3+}$ within 3.32 Å of a non-hydrogen atom (Figure 2). Three of these ClO $_4^-$ ions have oxygens wedged in the pockets (Cr-O *ca.* 4.5 Å) so that in the solid state Cr(terpy) $_2^{3+}$ and ClO $_4^-$ form tight ion pairs. This is reminiscent of the strong outer-sphere complexes formed between Fe(bpy) $_3^{2+}$ and ClO $_4^-$ in aqueous solutions.¹⁶ Molecular models and the distortions evident in the structure (Figure 1) indicate that the interligand pockets in

Cr(terpy) $_2^{3+}$ are larger than those in Cr(bpy) $_3^{3+}$; thus, the Cr^{III} core in the former complex is exposed to a greater solvent perturbation in solution. Indeed, molecular models show that up to eight H $_2$ O molecules can be positioned

[†] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

inside the pockets. Under these conditions, the Cr^{III} metal core may be essentially considered as being hydrated in aqueous solutions.

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¹ N. Serpone, M. A. Jamieson, M. S. Henry, M. Z. Hoffman, F. Bolletta, and M. Maestri, *J. Amer. Chem. Soc.*, 1979, **101**, 2907, and references therein.

² B. Brunshwig and N. Sutin, *J. Amer. Chem. Soc.*, 1978, **100**, 7568.

³ C. T. Lin, W. Böttcher, M. Chou, C. Creutz, and N. Sutin, *J. Amer. Chem. Soc.*, 1976, **98**, 6536.

⁴ R. C. Young, J. K. Nagle, T. J. Meyer, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1978, **100**, 4773.

⁵ N. Sutin, *J. Photochem.*, 1979, **10**, 19; V. Balzani, F. Bolletta, M. T. Gandolfi, and M. Maestri, *Topics Current Chem.*, 1978, **75**, 1.

⁶ M. S. Henry, *J. Amer. Chem. Soc.*, 1977, **99**, 6138.

⁷ M. S. Henry and M. Z. Hoffman, *Adv. Chem. Series*, 1978, **168**, 91.

⁸ W. S. Walters, R. D. Gillard, and P. A. Williams, *Austral. J. Chem.*, 1978, **31**, 1959.

⁹ M. A. Jamieson, N. Serpone, and M. Maestri, *Inorg. Chem.*, 1978, **17**, 2432; M. Maestri, F. Bolletta, N. Serpone, V. Balzani, and L. Moggi, *ibid.*, 1976, **15**, 2048.

¹⁰ M. A. Jamieson, N. Serpone, M. S. Henry, and M. Z. Hoffman, *Inorg. Chem.*, 1979, **18**, 214; M. Maestri, F. Bolletta, L. Moggi, V. Balzani, M. S. Henry, and M. S. Hoffman, *J. Amer. Chem. Soc.*, 1978, **100**, 2694.

¹¹ R. D. Gillard, *Co-ordination Chem. Rev.*, 1975, **16**, 67; R. D. Gillard, R. J. Lancashire, and P. A. Williams, *J.C.S. Dalton*, 1979, 190; J. A. A. Sagues, R. D. Gillard, R. J. Lancashire, and P. A. Williams, *ibid.*, p. 193.

¹² O. P. Anderson, *J.C.S. Dalton*, 1972, 2597; 1973, 1237.

¹³ R. Allmann, W. Henke, and D. Reinen, *Inorg. Chem.*, 1978, **17**, 378.

¹⁴ A. Zalkin, D. H. Templeton, and T. Ueki, *Inorg. Chem.*, 1973, **12**, 1641.

¹⁵ 'Tables of Interatomic Distances and Configurations in Molecules and Ions,' Chem. Soc. Special Publ., No. 18, 1965, p. 58s.

¹⁶ L. Johansson, *Chem. Scripta*, 1976, **10**, 72.