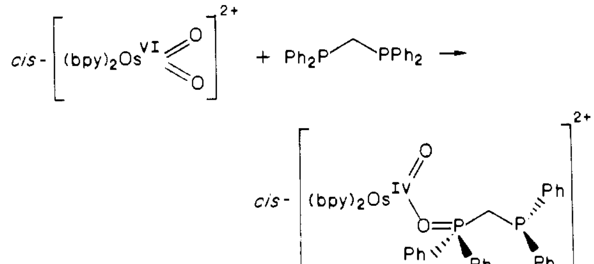
followed by

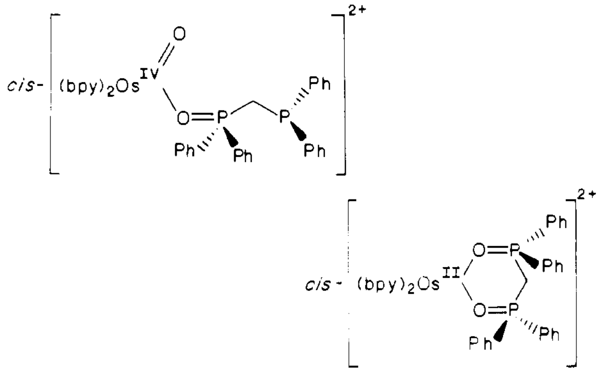
$$\mathrm{Os^{III}(bpy)_2(O)(OPPh_3)^+ + Os^{III}(bpy)_2(OPPh_3)_2^{3+} \rightarrow Os^{IV}(bpy)_2(O)(OPPh_3)^{2+} + Os^{II}(bpy)_2(OPPh_3)_2^{2+}} \quad (11)$$

and reaction 7.

The reactions with the potentially chelating phosphine ligands dppm and *cis*-dppene show that the *cis*-dioxo complex has the capability of carrying out the four-electron oxidation of a single substrate. The reactions presumably occur through an intermediate Os(IV) stage

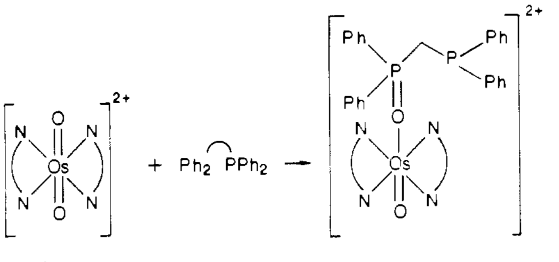

(12)

followed by rapid intramolecular oxidation of the second phosphine site

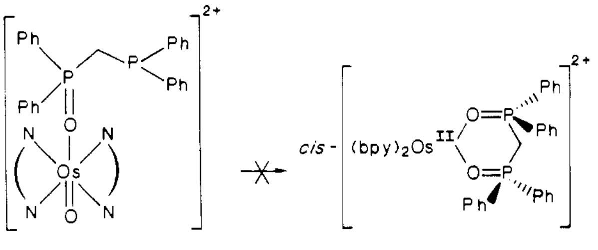

(13)

At diphosphine to dioxo ratios less than 0.5 (Figure 3), Os(III) appears as the initial product by disproportionation as in reaction 6 or by outer-sphere electron transfer as in reaction 8.

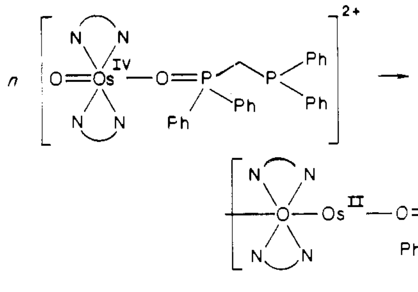
The results of cyclic voltammetry and UV–vis spectra show that the reactions between *trans*-$[\mathrm{Os^{VI}(bpy)_2(O)_2}]^{2+}$ and the diphosphines give trans Os(II) products. These results rule out an initial two-electron oxidation by Os(VI)


(14)

followed by intramolecular oxidation and trans → cis isomerization


(15)

The reactions must occur via initial Os(VI) → Os(IV) reduction (reaction 14) followed by further oxidation of the coordinated ligand to form coordination polymers as in


(16)

We have made no attempt to isolate and characterize the polymers.

Acknowledgment is made to the National Science Foundation under Grant No. CHE-8601604 for support of this research.

Registry No. dppm, 2071-20-7; dppene, 983-80-2; *cis*-$[\mathrm{Os^{VI}(bpy)_2(O)_2}](\mathrm{ClO_4})_2$, 101980-20-5; *trans*-$[\mathrm{Os^{VI}(bpy)_2(O)_2}](\mathrm{ClO_4})_2$, 102045-51-2; *cis*-$[\mathrm{Os^{II}(bpy)_2(OPPh_3)_2}](\mathrm{ClO_4})_2$, 120022-10-8; $\mathrm{PPh_3}$, 603-35-0; $\mathrm{O^{2-}}$, 16833-27-5; *trans*-$[\mathrm{Os^{II}(bpy)_2(OPPh_3)_2}](\mathrm{ClO_4})_2$, 120056-97-5; *cis*-$[\mathrm{Os^{II}(bpy)_2(O{=}PPh_2CH_2Ph_2P{=}O)}](\mathrm{ClO_4})_2$, 120032-85-1; *cis*-$[\mathrm{Os^{II}(bpy)_2(O{=}PPh_2CH{=}CHPh_2P{=}O)}](\mathrm{ClO_4})_2$, 120022-12-0; *cis*-$[\mathrm{Os(bpy)_2(O{=}PPh_3)_2}]^{3+}$, 120022-13-1; *cis*-$[\mathrm{Os^{II}(bpy)_2(MeCN)_2}]^{2+}$, 116946-87-3; *cis*-$[\mathrm{Os^{II}(bpy)_2(CH_3CN)(OPPh_3)}]^{2+}$, 120022-14-2; *trans*-$[\mathrm{Os(bpy)_2(OPPh_3)_2}]^{3+}$, 120056-98-6; *cis*-$[\mathrm{Os(bpy)_2(O)_2}]^+$, 101980-22-7.

Contribution from the Department of Chemistry,
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Redetermination of the Crystal and Molecular Structure of Tris(bipyridine)chromium(III) Hexafluorophosphate

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Received November 2, 1988

The structure of $[\mathrm{Cr(bpy)_3}](\mathrm{PF_6})_3$ (where bpy = 2,2′-bipyridine) has been previously described in space group *R*32,[1] with an asymmetric unit containing two independent cations, each possessing crystallographic 32 (*D*3) symmetry, and two independent anions, each possessing crystallographic 2-fold (*C*2) symmetry. The two cations, which alternate along a 3-fold axis coincident with the *c* axis of the unit cell, were found to have "opposite chirality". Wide variations in the bonding parameters of chemically equivalent groups were observed, which included[2] N–Cr–N bite angles of 74.8 and 84.7°, N(1)–C(2) distances ranging from 1.33 to 1.40 Å, N(1)–C(6) distances ranging from 1.31 to 1.41 Å, C(2)–C(2a) distances of 1.39 and 1.55 Å, C–C distances within pyridine rings ranging from 1.20 to 1.53 Å, P–F distances ranging from 1.38 to 1.63 Å, and $\mathrm{F{-}P{-}F_{cis}}$ angles ranging from 78.5 to 101.5°.

We became interested in the structure of $\mathrm{Cr(bpy)_3}^{3+}$ because of our work with the related complexes $\mathrm{Cr(bpm)_2Cl_2}^+$, $\mathrm{Cr(bpm)_3}^{3+}$, and $\mathrm{Cr(dpp)_3}^{3+}$ (where bpm = 2,2′-bipyrimidine and dpp = 2,3-bis(2-pyridyl)pyrazine) as building blocks of polymetallic complexes. We were comparing the structures of our systems to those of $[\mathrm{Cr(bpy)_3}](\mathrm{PF_6})_3$ and could not rationalize the differences observed. The large distortions from idealized geometries for $\mathrm{Cr(bpy)_3}^{3+}$ coupled with the "approximate" inversion symmetry relating the two cations led us to reinvestigate the structure of this compound.

Experimental Section

(i) Preparation. $[\mathrm{Cr(bpy)_3}](\mathrm{PF_6})_3$ was prepared directly from the perchlorate salt.

$[\mathrm{Cr(bpy)_3}](\mathrm{ClO_4})_3$ was prepared by using the procedure of Baker and Mehta[3] with the exception that $\mathrm{Cr(aq)}^{2+}$ was generated by using zinc

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(1) Hauser, A.; Mäder, M.; Robinson, W. T.; Murugesan, R.; Ferguson, J. *Inorg. Chem.* **1987**, *26*, 1331–1338.

(2) Atom labels refer to Figure 1 of this paper.

Table I. Crystal Data

formula: $C_{30}H_{24}N_6F_{18}P_3Cr$	$V = 5591$ (2) Å^3
fw: 955.51	$Z = 6$
space group: rhombohedral, $R\bar{3}c$ (No. 167), hexagonal axes, obverse setting	$D_{calc} = 1.70$ g/cm^3
$a = 17.9842$ (23) Å	$R = 0.0624$
$c = 19.9617$ (37) Å	$R_w = 0.0837$

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å$^2 \times 10^3$) for $[Cr(C_{10}H_8N_2)_3](PF_6)_3$

	x	y	z	U(eq)[a]
Cr(1)	0	0	2500	35 (1)
P(1)	4772 (2)	0	2500	64 (1)
F(1)	3949 (4)	0	2500	212 (9)
F(2)	5630 (5)	0	2500	238 (10)
F(3)	4360 (5)	−912 (3)	2195 (3)	157 (4)
F(4)	5015 (4)	448 (3)	1796 (3)	120 (3)
N(1)	1108 (3)	465 (3)	1959 (2)	42 (2)
C(2)	1670 (3)	231 (3)	2179 (3)	41 (3)
C(3)	2387 (4)	400 (4)	1820 (4)	56 (3)
C(4)	2542 (5)	824 (5)	1215 (4)	63 (4)
C(5)	1992 (5)	1086 (5)	1004 (4)	63 (4)
C(6)	1287 (5)	907 (4)	1372 (3)	55 (3)
H(3)	2803 (40)	259 (41)	1979 (31)	61 (20)
H(4)	2999 (44)	902 (39)	974 (35)	59 (20)
H(5)	2051 (32)	1340 (34)	600 (29)	36 (15)
H(6)	862 (41)	1068 (39)	1208 (34)	62 (19)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

amalgam. The perchlorate salt was dissolved in water (deionized and then distilled over alkaline permanganate in an all-glass apparatus) and reprecipitated by the addition of a saturated aqueous solution of KPF_6. The metathesized product was collected by vacuum filtration and redissolved in acetone, and the solvent was allowed to evaporate slowly to induce crystal formation.

(ii) X-ray Structure Analysis. A yellow parallelepiped crystal with approximate dimensions of 0.20 × 0.20 × 0.30 mm was mounted on the end of a glass fiber. All measurements were made at 21 ± 1 °C on a Nicolet R3m/V diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Cell dimensions were obtained from 41 reflections with $14.98° < 2\theta < 35.30°$. One hemisphere of data ($\pm h,+k,\pm l$), totaling 5273 reflections, was measured to $2\theta = 45.0°$, by using ω–2θ scans at speeds ranging from 2.09 to 14.65°/min (in ω). Equivalent data were merged ($R_{int} = 0.038$) to give 824 unique reflections. An empirical absorption correction ($\mu = 5.46$ cm^{-1}), based on azimuthal scans of 10 moderately intense reflections with $47° < \pm\chi < 71°$, resulted in normalized transmission factors ranging from 0.72 to 1.00; corrections for Lorentz and polarization effects were also applied. Periodic measurement of three representative reflections over the course of data collection (45.5 h) indicated crystal and electronic stability. Other relevant crystallographic information is given in Table I.

As the systematic absences ($hkil$, $-h + k + l = 3n + 1, 3n + 2$; $h\bar{h}0l$, $l = 2n + 1$) indicate either the acentric space group $R3c$ or the centric space group $R\bar{3}c$, structure solution using direct methods was carried out for both possibilities.

Refinement of the acentric solution was difficult, requiring heavy damping to reach convergence, and resulted in a model that was very distorted. The problems encountered in this refinement indicate the presence of missed inversion symmetry;[4] therefore, the centrosymmetric space group $R\bar{3}c$ was assumed to be the correct choice. The rapid convergence of the refinement in this space group to a chemically reasonable model verifies this decision.

Hydrogen atoms were located by using standard difference Fourier techniques and were included in the refinement with isotropic thermal parameters. The final cycle of refinement was based on 670 observed reflections ($F_o^2 > 3\sigma(F_o^2)$) and 106 parameters and converged (maximum shift/σ = 0.01) with residual values[5] of $R = 0.0624$, $R_w = 0.0837$, and goodness of fit = 2.98. The maximum and minimum peaks on the final difference map correspond to 0.63 and −0.72 e/Å^3, respectively, and were located in the vicinity of the PF_6^- ion.

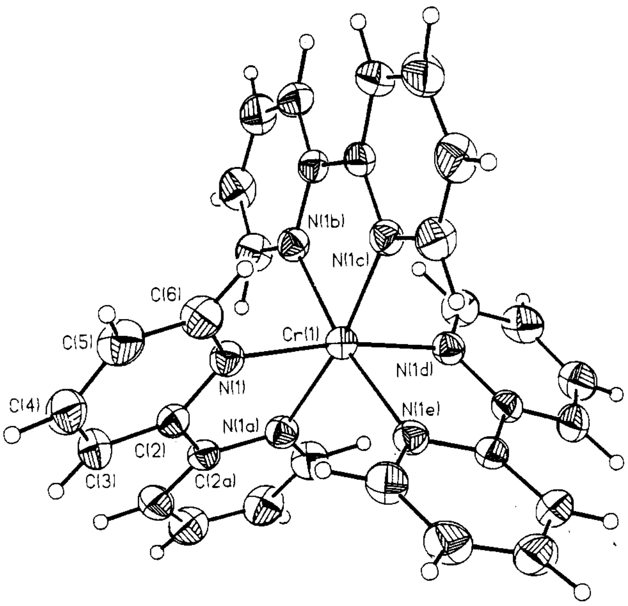

Figure 1. Thermal ellipsoid plot (50% probability) of the $[Cr(bpy)_3]^{3+}$ cation, showing the atom-numbering scheme. Bonding angles about the chromium atom are N(1)–Cr(1)–N(1a) = 79.1 (2)°, N(1)–Cr(1)–N(1b) = 92.3 (2)°, N(1)–Cr(1)–N(1c) = 94.6 (2)°, and N(1)–Cr(1)–N(1d) = 171.0 (2)°.

Table III. Comparison of Bonding Parameters[a] for $[Cr(bpy)_3](PF_6)_3$ (I) and $[Cr(bpy)_3](ClO_4)_3\cdot(bpy)(ClO_4)$ (II)

	I	II
	Distances (Å)	
Cr(1)–N(1)	2.042 (5)	2.032 (6)
N(1)–C(2)	1.35 (1)	1.353 (7)
C(2)–C(2a)	1.47 (1)	1.47 (2)
N(1)–C(6)	1.361 (8)	1.36 (2)
	Angles (deg)	
N(1)–Cr(1)–N(1a)	79.1 (3)	79.9 (4)
Cr(1)–N(1)–C(2)	115.6 (4)	114.9 (9)
Cr(1)–N(1)–C(6)	126.3 (5)	126 (1)
C(2)–N(1)–C(6)	117.8 (6)	118 (1)
N(1)–C(2)–C(2a)	114.5 (4)	114.8 (3)
C(3)–C(2)–C(2a)	123.4 (6)	122 (1)
N(1)–C(2)–C(3)	122.0 (6)	123 (1)

[a] Values given for I are unique (all others equal by 32 symmetry); values in parentheses are esd's. Values for II are averages (except for dihedral angles) of chemically equivalent but crystallographically independent groups; values in parentheses are σ's based on the range of values.

Atomic coordinates are given in Table II. The structure of the $[Cr(bpy)_3]^{3+}$ cation is shown in Figure 1. Figure SI (supplementary material) shows the packing of ions in the crystal as viewed down the unique c axis.

Structure solution and refinement and the calculation of derived results were performed by using the SHELXTL[6] package of computer programs. Neutral-atom scattering factors were those of Cromer and Waber,[7] and the real and imaginary anomalous dispersion corrections were those of Cromer.[8]

Discussion

The distorted geometry of the structure of $[Cr(bpy)_3](PF_6)_3$, resulting from the $R32$ refinement, is the result of a missed center of symmetry.[4] Addition of an inversion center midway between the two cations generates a $\bar{3}$ site at (0, 0, $^1/_4$); a subsequent shift

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(3) Baker, B. R.; Mehta, B. D. *Inorg. Chem.* **1965**, *4*, 848.

(4) Marsh, R. E.; Schomaker, V. *Inorg. Chem.* **1979**, *18*, 299.

(5) Residuals: $R = \sum||F_o| - |F_c|| / \sum|F_o|$; $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$, $w = 1/[\sigma^2(F) + 0.0005F^2]$; $S = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, N_o = number of observations; N_v = number of variables.

(6) Sheldrick, G. M. "SHELXTL, Crystallographic Computing System"; Nicolet Instruments Division: Madison, WI, 1986.

(7) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(8) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

of origin by $-^1/_4$th of a cell length along the z axis transforms the space group to $R\bar{3}c$. Our studies have indeed verified that reflections with $l = 2n + 1$ are systematically unobserved for the class $(h\bar{h}0l)$, a required condition for this space group.

The model obtained from the $R\bar{3}c$ refinement has chemically reasonable distances and angles that compare favorably with the geometry observed for the $Cr(bpy)_3^{3+}$ cation of a perchlorate salt, which cocrystallizes with bipyridinium perchlorate.[9] A comparison of pertinent bonding parameters is given in Table III.

The structure of $[Rh(bpy)_3](PF_6)_3$, which was found to be isostructural with the chromium compound,[1] has not been redetermined. However, it seems likely that it too has been incorrectly described in space group $R32$ and that the correct space group should be $R\bar{3}c$.

Acknowledgment. We thank Professor P. E. Hoggard for supplying a preprint of ref 9. After the structure determination reported in this paper was completed, we became aware, through our personal communication with the original author, that the error in space group had also been detected by Dr. Richard E. Marsh. An accurate low-temperature redetermination of the structure of the isomorphous Rh complex, performed by the original author, yielded results fully in accord with those reported herein. J.D.P. acknowledges the Office of Basic Energy Sciences, Department of Energy, for partial support of this work.

Registry No. $[Cr(bpy)_3](PF_6)_3$, 97881-83-9.

Supplementary Material Available: For $[Cr(bpy)_3](PF_6)_3$, tables of crystallographic information, anisotropic thermal parameters, and all distances and angles and Figure SI, showing a packing diagram with a view down the unique axis (3 pages); a listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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(9) Lee, K. W.; Hoggard, P. E. *Inorg. Chem.*, in press. Hoggard, P. E. Personal communication.

Additions and Corrections

1988, Volume 27

R. P. F. Kanters, P. P. J. Schlebos, J. J. Bour, W. P. Bosman, H. J. Behm, and J. J. Steggerda*: Reaction of CO and an Isonitrile with $PtAu_8(PPh_3)_8^{2+}$. Crystal Structure of $Pt(CO)(AuPPh_3)_8(NO_3)_2 \cdot 2C_4H_{10}O \cdot 2CH_2Cl_2$.

Page 4034. The charge of the ion in the title should be 2+, not 3+. The corrected version appears above. Under Preparation of the Compounds, the preparation of $Pt(CO)(AuPPh_3)_8(NO_3)_2$ should begin as follows: A 200-mg (50-μmol) sample.—R. P. F. Kanters

María-José Bermejo, Josê-Ignacio Ruiz, Xavier Solans, and Jordi Vinaixa*: Synthesis and Study of the Fluxional Behavior of Octahedral Manganese(I) Complexes with a Monodentate 1,8-Naphthyridine Ligand. X-ray Crystal Structure of *fac*-$[Mn(\eta^1\text{-}1,8\text{-naph})(\eta^2\text{-phen})(CO)_3]ClO_4 \cdot {}^1/_2CH_2Cl_2$ (naph = 1,8-Naphthyridine, phen = *o*-Phenanthroline).

Page 4389. In column 1, lines 19–21, two errors appear in the order given for ΔG^* values for octahedral complexes of first-row transition metals with an η^1-naph ligand. The corrected order should read as follows: Cr(0) $\{[Cr(\eta^1\text{-naph})(CO)_5]$, 58.7 kJ/mol$\}^{14}$ < Mn(I) $\{[Mn(\eta^1\text{-naph})(\eta^2\text{-chel})(CO)_3]^+$ (chel = phen, bpy), 63 kJ/mol$\}$ < Fe(II) $\{[Fe(\eta^1\text{-naph})(CO)_2Cp]^+$, ≫71 kJ/mol$\}$.[15]—Jordi Vinaixa