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An Oxo-Bridged Ruthenium(III) Dimer. Structural Characterization of μ-Oxo-bis[nitrobis(2,2'-bipyridine)ruthenium(III)] Perchlorate Dihydrate, $[(bpy)_2(NO_2)Ru-O-Ru(NO_2)(bpy)_2](ClO_4)_2 \cdot 2H_2O$

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The crystal and molecular structure of the complex μ-oxo-bis[nitrobis(2,2'-bipyridine)ruthenium(III)] perchlorate dihydrate, $[(bpy)_2(NO_2)Ru-O-Ru(NO_2)(bpy)_2](ClO_4)_2 \cdot 2H_2O$, has been determined from three-dimensional counter X-ray data. The material crystallizes in the monoclinic space group $P2_1/c$ with four dimeric formula units in a cell of dimensions a = 13.953 (3) Å, b = 22.553 (6) Å, c = 17.916 (4) Å, and β = 52.57 (2)°. The observed and calculated densities are 1.74 (2) and 1.735 g cm^{-3}, respectively. The structure has been refined by full-matrix least-squares procedures to a conventional R factor of 0.066 for 5701 independent observations. The complex cation consists of pairs of approximately octahedrally coordinated ruthenium atoms which are linked by a single oxide bridge. The bridging Ru–O distances are 1.876 (6) and 1.890 (7) Å, the Ru–O–Ru bridging angle is 157.2 (3)°, and the Ru–Ru separation is 3.692 (1) Å. The observed geometry of the complex is consistent with the bonding scheme proposed by earlier workers.

Introduction

The nature and extent of spin–spin interactions in transition metal dimers have received considerable experimental and theoretical study.[2,3] While most of the recently reported structural and magnetic work has centered on the study of complexes of first-row transition metals, there are a number of reports which suggest that dimers of second- and third-row transition metals can give rise to more complex magnetic behavior as a result of the greater radial extension of the 4d and 5d orbitals.[4,5]

Oxo-bridged dimers of ruthenium(III) with 1,10-phenanthroline and 2,2'-bipyridine have recently been reported and studied extensively by Meyer and coworkers.[6] These complexes exhibit antiferromagnetic interactions with $2J$ values in the range −119 to −173 cm^{-1}, and the magnetic exchange has been attributed to a strong Ru–Ru interaction which occurs via the oxide bridge through delocalized molecular orbitals rather than via a direct through-space interaction. On the basis of vibrational spectra and molecular models, Meyer and coworkers concluded that, while the Ru–O–Ru linkage may not be linear, it cannot deviate markedly from linearity.[6] Hence, the Ru–Ru interaction in those complexes is proposed to be entirely different from that in the di-μ-amido complex $[(NH_3)_4Ru(NH_2)_2Ru(NH_3)_4]Cl_4 \cdot 4H_2O$.[5]

In order to further our understanding of magnetic interactions of this type and also to examine the validity of the exchange mechanism proposed, we have undertaken a complete three-dimensional structural analysis of the complex μ-oxo-bis[nitrobis(2,2'-bipyridine)ruthenium(III)] perchlorate dihydrate, $[(bpy)_2(NO_2)Ru-O-Ru(NO_2)(bpy)_2](ClO_4)_2 \cdot 2H_2O$; the results of this analysis are presented herein.

Experimental Section

A sample of the title complex was prepared by Dr. T. R. Weaver and generously donated by Professor T. J. Meyer. Suitable deep purple, rectangular single crystals were obtained with difficulty from aqueous solution. On the basis of precession and Weissenberg photography the crystals were assigned to the monoclinic system. The systematic absences of $0k0$ for k odd and $h0l$ for l odd are consistent with the centrosymmetric space group $P2_1/c$ (C_{2h}^5). The cell constants, obtained by least-squares procedures,[7] are a = 13.953 (3) Å, b = 22.553 (6) Å, c = 17.916 (4) Å, and β = 52.57 (2)°. A density of 1.735 g cm^{-3} calculated for four dimeric formula units in the cell is in good agreement with the value of 1.74 (2) g cm^{-3} obtained by flotation in carbon tetrachloride–bromoform mixtures. Thus, in space group $P2_1/c$, no crystallographic symmetry is imposed on the dimers.

An irregularly shaped crystal bounded by faces of the forms {121}, {010}, {100}, and {102} was chosen for data collection. The separations between opposite faces were as follows: (121) to $(\bar{1}\bar{2}\bar{1})$, 0.495 mm; $(1\bar{2}1)$ to $(\bar{1}2\bar{1})$, 0.472 mm; (010) to $(0\bar{1}0)$, 0.300 mm; (100) to $(\bar{1}00)$, 0.306 mm; (102) to $(\bar{1}0\bar{2})$, 0.691 mm. Intensity data were collected with the crystal mounted on a glass fiber roughly normal to the (102) face. Examination of a number of low-order ω scans suggested that the crystal was single and of moderate quality.

The data were collected on an automatic Picker four-circle diffractometer equipped with Cu Kα radiation and a 0.5-mil Ni filter at a takeoff angle of 2.1°; the counter aperture was 5.0 × 5.0 mm and was placed 32 cm from the crystal. The data were collected using the θ–2θ scan technique at a scan rate of 1.0°/min, the peaks being scanned from 0.75° in 2θ below the calculated Kα_1 peak position to 0.75° above the calculated Kα_2 peak position. Stationary-counter, stationary-crystal backgrounds of 10-sec duration were recorded at each end of the scan.

A unique data set having 2θ(Cu Kα_1) $\leq$ 123° was collected. After every 100 reflections, the intensities of three standard reflections were monitored; these standards showed no significant decline in intensity during the data collection period. The total number of data (including space group extinct reflections and standards) which were collected was 7855.

Data processing was carried out in the manner described elsewhere.[8,9] The intensities and their estimated standard deviations were corrected for Lorentz–polarization effects and for absorption. The absorption coefficient for these atoms and Cu Kα radiation is 75.0 cm^{-1}, and for the sample chosen the transmission coefficients ranged from 0.12 [for (8,3,17)] to 0.24 [for (2,25,2)]. Of the data gathered, 5701 exceeded 3 times their estimated standard deviations; only these reflections were used in the refinement of the structure.

Solution and Refinement of the Structure

All least-squares refinements in this analysis were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$; the weights w were taken as $4F_o^2/\sigma^2(F_o)^2$. In all calculations on F_c, the atomic scattering factors for Ru and Cl were from Cromer and Waber,[10] those for O, N, and C were from ref 11, and those for H were from Stewart, Davidson, and Simpson.[12] The effects of the anomalous dispersion of Ru and Cl were included in the calculation of F_c, the values for $\Delta f'$ and $\Delta f''$ being from the tabulation of Cromer and Liberman.[13]

The positions of the two independent ruthenium atoms were deduced from a three-dimensional Patterson function.[14] The locations of the remaining nonhydrogen atoms were determined from subsequent difference Fourier maps and were refined by least-squares calculations. The 2,2'-bipyridine ligands were treated as being comprised of two planar six-membered rings of fixed geometry,[15] with no constraint imposed on the length of or torsion around the C(1)–C(1)' bonds. The C–C and C–N bond lengths in the rings were assigned as the averages of the values determined in these laboratories for a variety of substituted pyridine moieties.[16–23] The hydrogen atoms associated with the bipyridine ligands were included in the calculation of F_c, their positions being assigned on the basis of planar geometry with C–H bond lengths of 0.95 Å[24] and their isotropic thermal parameters being

Table I. Positional,[a] Thermal,[b] and Group Parameters for $[(bpy)_2(NO_2)RuORu(NO_2)(bpy)_2](ClO_4)_2 \cdot 2H_2O$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru(1)	12252 (5)	38731 (3)	−37313 (4)	603 (6)	128 (1)	390 (4)	2 (2)	−264 (4)	19 (2)
Ru(2)	29706 (5)	26912 (3)	−36261 (4)	548 (6)	145 (1)	345 (4)	20 (2)	−229 (4)	−4 (2)
Cl(1)	−2597 (2)	1714 (1)	−3205 (2)	104 (2)	24 (6)	57 (2)	−4 (1)	−44 (2)	2 (1)
O(1)	2325 (5)	3292 (2)	−3939 (4)	65 (5)	15 (1)	52 (4)	3 (2)	−38 (4)	0 (2)
N	1034 (7)	3496 (3)	−4685 (5)	93 (7)	17 (2)	42 (4)	−2 (3)	−38 (5)	4 (2)
N′	4511 (6)	3158 (3)	−4167 (4)	74 (6)	20 (2)	49 (3)	1 (3)	−34 (4)	−2 (2)
OA(1)	−1855 (10)	1239 (4)	−3776 (7)	234 (14)	27 (2)	96 (7)	36 (5)	−71 (9)	−8 (3)
OA(2)	−3210 (11)	1933 (6)	−3547 (8)	242 (15)	65 (4)	113 (8)	54 (7)	−114 (10)	−18 (5)
OA(3)	−3427 (10)	1562 (5)	−2280 (7)	203 (13)	56 (4)	67 (6)	17 (6)	−22 (7)	25 (4)
OA(4)	−1890 (11)	2177 (6)	−3323 (10)	195 (14)	65 (4)	148 (11)	−40 (6)	−77 (10)	−30 (6)
OC(1)	24 (6)	3484 (3)	−4508 (5)	81 (6)	27 (2)	60 (4)	0 (3)	−49 (4)	3 (2)
OC(2)	1910 (6)	3308 (3)	−5460 (5)	99 (7)	28 (2)	46 (4)	−1 (3)	−35 (5)	−3 (2)
OD(1)	5490 (6)	2911 (3)	−4572 (7)	84 (7)	22 (2)	132 (7)	3 (3)	−58 (6)	−5 (3)
OD(2)	4518 (6)	3716 (3)	−4121 (6)	110 (7)	15 (2)	108 (6)	−4 (3)	−60 (6)	−3 (2)
OW(1)	−3299 (8)	857 (4)	−913 (7)	134 (9)	34 (2)	103 (7)	10 (4)	−69 (7)	−10 (3)
OW(2)	−2792 (8)	3265 (3)	−4161 (6)	160 (10)	26 (2)	77 (6)	−5 (4)	−54 (6)	7 (3)
Group	x_c[c]	y_c	z_c	ϕ[d]	θ	ρ	B, Å	α[e]	
A	4567 (4)	4629 (3)	−6146 (4)	−0.861 (4)	2.691 (4)	−2.834 (5)			
A′	−1559 (4)	5161 (3)	−3027 (5)	0.548 (4)	2.751 (4)	−0.412 (5)			
B	4076 (6)	1306 (3)	−2582 (3)	−2.669 (4)	2.720 (3)	−1.856 (4)			
B′	4701 (6)	2241 (3)	−6548 (3)	−2.212 (5)	2.367 (3)	1.177 (5)			
C	−1975 (4)	2854 (2)	−1658 (4)	1.972 (4)	−2.670 (3)	1.062 (4)			
C′	1985 (6)	4950 (3)	−2137 (5)	0.127 (7)	−2.040 (4)	2.689 (8)			
D	121 (6)	1449 (3)	−2853 (4)	2.195 (4)	−3.109 (3)	1.086 (4)			
D′	1956 (7)	3446 (3)	−1012 (5)	1.204 (8)	−2.080 (4)	−2.622 (8)			
Cl	2948 (7)	255 (3)	−4967 (5)	−0.482 (11)	−2.540 (10)	1.608 (11)	7.75 (9)[f]	0.469 (6)	
Cl′	2687 (6)	272 (3)	−4803 (4)	2.397 (9)	2.540 (8)	−1.997 (9)	7.75 (9)[f]	0.531 (6)	

[a] Parameters for Ru are $\times 10^5$; those for other atoms are $\times 10^4$. [b] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Coordinates of the group centers, $\times 10^4$. [d] The angles are in radians (see ref 15). [e] α is the occupancy of the disordered ClO_4^- groups. [f] The isotropic thermal parameters of the disordered ClO_4^- groups were constrained to be equal.

assigned as 1.5 Å^2 greater than that of the carbon atom to which they were attached.

Examination of a difference Fourier map in a late stage of the refinement suggested that one of the perchlorate groups was disordered. The two separate ClO_4^- group positions which were observed in the Fourier map were refined as rigid tetrahedral groups with Cl–O bond lengths of 1.397 Å, the weighted average of the values reported in two recent structural reports.[25,26] The two groups were given occupancies of α and $(1 - \alpha)$, the group thermal parameters were constrained to be equal, and the parameter α was varied with the appropriate constraints among the derivatives being taken into account.[27]

Examination of the data at a late stage of refinement suggested that they may be suffering from secondary extinction, and a correction of the type described by Zachiariasen[28,29] was applied. In the final cycle of least-squares refinement, all 16 nongroup atoms were assigned variable anisotropic thermal parameters, the carbon and nitrogen atoms in the bipyridine ligands were assigned variable individual isotropic thermal parameters, and the disordered perchlorate groups were assigned an overall variable group isotropic thermal parameter. The final value of α was 0.468 (6); i.e., we have an approximately 53–47% disorder in this ClO_4^- group. The final values of the conventional agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ were 0.066 and 0.096. The final cycle involved 5701 observations and 256 variables; no atomic or group parameter exhibited a shift greater than 0.1 times its estimated standard deviation, which is evidence that the refinement had converged. The final value of the extinction coefficient c was $(7 \pm 4) \times 10^{-8}$.

A final difference Fourier map showed several large (up to 2 e Å^{-3}) peaks in the vicinity of the disordered perchlorate group. This residual density, which rendered unproductive our effects to locate the hydrogen atoms on the water molecules, suggests that our twofold disorder model is only approximate; since this group is not close to the region of principal interest in the cation, however, no effort was made to improve the model.

The positional, thermal, and group parameters derived from the final cycle of least-squares are listed in Table I along with their standard deviations as estimated from the inverse matrix. The positional parameters of the bipyridine carbon and nitrogen atoms which may be derived from the data in Table I are given in Table II along with their thermal parameters. The positions of the ligand hydrogen atoms are presented in Table III.[28] A listing of observed and calculated structure amplitudes is available.[28]

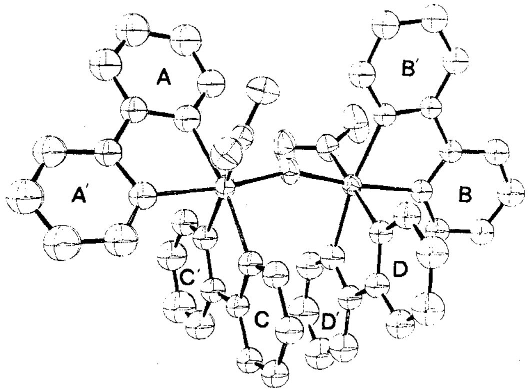

Figure 1. View of the dimeric cation $[(bpy)_2(NO_2)Ru\text{-}O\text{-}Ru(NO_2)(bpy)_2]^{2+}$, with the hydrogen atoms omitted for clarity. A, A′, etc. correspond to pyridine groups A, A′, etc. in the text and tables.

Description of the Structure

The structure consists of dimeric $[(bpy)_2(NO_2)Ru\text{–}O\text{–}Ru(NO_2)(bpy)_2]^{2+}$ cations which are well separated from the perchlorate anions and the water molecules. The geometry of the cation is shown in Figure 1, and the inner coordination sphere around the ruthenium(III) centers is depicted in Figure 2. The complex cation consists of two approximately octahedrally coordinated ruthenium(III) centers which are bridged by the oxide anion; each ruthenium atom is coordinated to two cis 2,2′-bipyridine ligands, the N atom of the nitro group, and the bridging oxide. The bond lengths and angles associated with the cation and anion are listed in Tables IV and V, respectively.

As is apparent from the figures, while the geometry at each ruthenium atom is approximately the same, the pseudooctahedron on one ruthenium atom is rotated by roughly 90°

Table II. Derived Parameters for Group Atoms

Atom	*x*	*y*	*z*	*B*,[a] Å^2
CA(1)	2167 (4)	4900 (4)	−5003 (4)	3.9 (2)
NA	2542 (4)	4399 (3)	−4845 (4)	4.0 (1)
CA(3)	3722 (5)	4272 (2)	−5412 (4)	4.5 (2)
CA(4)	4567 (4)	4629 (3)	−6146 (4)	5.7 (2)
CA(5)	4188 (6)	5141 (3)	−6310 (4)	6.2 (3)
CA(6)	2985 (6)	5276 (3)	−5736 (4)	5.5 (2)
CA(1)′	867 (4)	5004 (4)	−4342 (4)	3.8 (2)
NA′	228 (5)	4598 (3)	−3660 (4)	3.9 (1)
CA(3)′	−963 (5)	4680 (3)	−3018 (4)	5.2 (2)
CA(4)′	−1559 (4)	5161 (3)	−3027 (5)	5.9 (2)
CA(5)′	−909 (6)	5578 (3)	−3724 (5)	5.9 (3)
CA(6)′	307 (5)	5498 (3)	−4383 (5)	4.9 (2)
CB(1)	4421 (4)	1608 (3)	−4207 (3)	3.5 (2)
NB	3724 (3)	1954 (2)	−3445 (4)	3.4 (1)
CB(3)	3562 (5)	1801 (2)	−2652 (3)	4.0 (2)
CB(4)	4076 (6)	1307 (3)	−2582 (3)	4.4 (2)
CB(5)	4789 (6)	951 (2)	−3360 (5)	5.0 (2)
CB(6)	4961 (6)	1102 (3)	−4173 (4)	4.6 (2)
CB(1)′	4544 (8)	1808 (3)	−5053 (4)	3.2 (1)
NB′	3908 (3)	2293 (1)	−4936 (3)	3.3 (1)
CB(3)′	3993 (5)	2501 (2)	−5676 (4)	4.3 (2)
CB(4)′	4701 (6)	2241 (3)	−6548 (3)	4.5 (2)
CB(5)′	5354 (7)	1744 (3)	−6670 (4)	4.6 (2)
CB(6)′	5274 (10)	1528 (3)	−5920 (5)	4.2 (2)
CC(1)	−529 (7)	3697 (3)	−1713 (4)	3.1 (1)
NC	−243 (5)	3479 (3)	−2524 (3)	3.3 (1)
CC(3)	−960 (4)	3066 (2)	−2487 (3)	3.8 (2)
CC(4)	−1975 (4)	2854 (2)	−1658 (4)	4.0 (2)
CC(5)	−2271 (5)	3075 (2)	−827 (3)	3.9 (2)
CC(6)	−1546 (7)	3498 (3)	−856 (3)	3.6 (2)
CC(1)′	308 (14)	4146 (8)	−1817 (4)	3.5 (2)
NC′	1239 (10)	4281 (4)	−2707 (4)	3.6 (1)
CC(3)′	2055 (4)	4677 (3)	−2854 (3)	4.3 (2)
CC(4)′	1985 (6)	4950 (3)	−2137 (5)	5.3 (2)
CC(5)′	1034 (8)	4813 (5)	−1226 (4)	6.4 (3)
CC(6)′	195 (12)	4410 (9)	−1067 (3)	5.2 (2)
CD(1)	674 (6)	2232 (2)	−2004 (4)	3.7 (2)
ND	1406 (4)	2191 (2)	−2946 (4)	3.4 (1)
CD(3)	1124 (5)	1804 (3)	−3354 (3)	4.1 (2)
CD(4)	121 (6)	1449 (3)	−2853 (4)	5.2 (2)
CD(5)	−631 (5)	1490 (3)	−1889 (4)	5.8 (2)
CD(6)	−352 (5)	1882 (3)	−1465 (3)	4.6 (2)
CD(1)′	1069 (14)	2662 (6)	−1616 (5)	3.8 (2)
ND′	2094 (9)	2956 (2)	−2254 (3)	4.0 (1)
CD(3)′	2519 (5)	3340 (3)	−1948 (4)	4.7 (2)
CD(4)′	1956 (7)	3446 (3)	−1012 (5)	6.4 (3)
CD(5)′	908 (9)	3146 (6)	−357 (3)	6.5 (3)
CD(6)′	465 (14)	2754 (8)	−662 (4)	5.3 (2)
Cl	2948 (7)	255 (3)	−4967 (5)	
OB(1)	2576 (16)	−46 (7)	−4148 (8)	
OB(2)	4201 (7)	324 (8)	−5548 (9)	
OB(3)	2618 (11)	−73 (6)	−5442 (9)	
OB(4)	2398 (16)	812 (5)	−4733 (13)	
Cl′	2687 (6)	272 (3)	−4803 (5)	
OB(1)′	3509 (10)	333 (7)	−5778 (5)	
OB(2)′	2607 (15)	−326 (3)	−4561 (11)	
OB(3)′	3076 (10)	606 (5)	−4375 (8)	
OB(4)′	1554 (9)	473 (6)	−4496 (10)	

[a] The disordered perchlorate groups were assigned a variable group *B* (see Table I) rather than individual atomic *B*'s.

around the Ru–O vector relative to the coordination polyhedron around the other ruthenium atom so that the Ru(1)–N(nitro) vector is approximately perpendicular to the Ru(2)–N'(nitro) vector. The configurations at the two metals in a given dimer are the same; e.g., for the dimer shown in Figure 1 the configuration at both metals is Δ while for that in Figure 2 (which is related to the dimer in Figure 1 by the *c* glide) the configurations are both Λ. Necessarily, in the centrosymmetric space group *P*2₁/*c*, there are an equal number of Δ and Λ dimers.

The eight Ru–N(bpy) distances are in the range 2.061

Table III. Calculated Positions of the Hydrogen Atoms on the Bipyridine Rings.

Atom	*x*	*y*	*z*
HA(3)	0.400	0.393	−0.529
HA(4)	0.540	0.454	−0.652
HA(5)	0.475	0.540	−0.681
HA(6)	0.270	0.562	−0.585
HA(3)′	−0.145	0.439	−0.255
HA(4)′	−0.241	0.522	−0.258
HA(5)′	−0.127	0.594	−0.375
HA(6)′	0.802	0.580	−0.485
HB(3)	0.307	0.205	−0.217
HB(4)	0.395	0.122	−0.201
HB(5)	0.518	0.613	−0.333
HB(6)	0.547	0.860	−0.471
HB(3)′	0.355	0.285	−0.561
HB(4)′	0.472	0.239	−0.706
HB(5)′	0.583	0.154	−0.726
HB(6)′	0.572	0.118	−0.600
HC(3)	−0.075	0.291	−0.306
HC(4)	−0.245	0.255	−0.165
HC(5)	−0.295	0.294	−0.024
HC(6)	−0.173	0.366	−0.290
HC(3)′	0.270	0.477	−0.349
HC(4)′	0.261	0.521	−0.228
HC(5)′	0.101	0.497	−0.073
HC(6)′	−0.043	0.429	−0.044
HD(3)	0.164	0.179	−0.402
HD(4)	−0.006	0.120	−0.316
HD(5)	−0.133	0.126	−0.152
HD(6)	−0.085	0.192	−0.080
HD(3)′	0.327	0.353	−0.241
HD(4)′	0.232	0.371	−0.083
HD(5)′	0.053	0.321	−0.029
HD(6)′	−0.026	0.255	−0.021

Table IV. Internuclear Separations in $[(bpy)_2NO_2Ru\text{–}O\text{–}Ru(NO_2)(bpy)_2](ClO_4)_2 \cdot 2H_2O$

Atoms	Distance, Å	Atoms	Distance, Å
Ru(1)–Ru(2)	3.692 (1)	Cl(1)–OA(1)	1.407 (9)
Ru(1)–O(1)	1.876 (6)	Cl(1)–OA(2)	1.408 (10)
Ru(2)–O(1)	1.890 (7)	Cl(1)–OA(3)	1.370 (9)
Ru(1)–NA	2.078 (5)	Cl(1)–OA(4)	1.362 (10)
Ru(1)–NA′	2.100 (7)	N–OC(1)	1.242 (9)
Ru(1)–NC	2.071 (4)	N–OC(2)	1.243 (9)
Ru(1)–NC′	2.064 (11)	N′–OD(1)	1.224 (9)
Ru(1)–N	2.067 (11)	N′–OD(2)	1.264 (9)
Ru(2)–NB	2.094 (5)	CA(1)–CA(1)′	1.46 (1)
Ru(2)–NB′	2.074 (4)	CB(1)–CB(1)′	1.49 (1)
Ru(2)–ND	2.073 (5)	CC(1)–CC(1)′	1.47 (2)
Ru(2)–ND′	2.061 (5)	CD(1)–CD(1)′	1.48 (2)
Ru(2)–N′	2.034 (8)		
Constrained Distances in the Group Refinement			
C(1)–N	1.343	C(4)–C(5)	1.374
N–C(3)	1.340	C(5)–C(6)	1.368
C(3)–C(4)	1.372	C(6)–C(1)	1.387

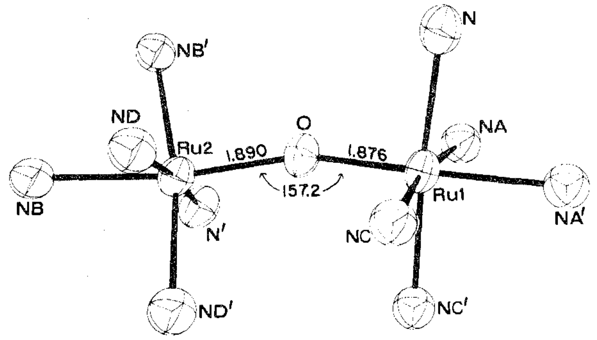

Figure 2. Coordination around the ruthenium(III) atoms in $[(bpy)_2(NO_2)Ru\text{–}O\text{–}Ru(NO_2)(bpy)_2]^{2+}$. Atoms NA and NA′ are the nitrogen atoms of pyridine groups A and A′ and are parts of the same bipyridine ligand, etc. The dimeric cation shown here is enantiomeric to that in Figure 1 (see text).

Table V. Bond Angles in $[(bpy)_2(NO_2)Ru-O-Ru(NO_2)(bpy)_2](ClO_4)_2 \cdot 2H_2O$

Ru(1)-O(1)-Ru(2)	157.2 (3)	O(1)-Ru(2)-N′	92.5 (3)
N-Ru(1)-NA	85.6 (3)	O(1)-Ru(2)-NB	171.4 (3)
N-Ru(1)-NA′	87.6 (3)	O(1)-Ru(2)-NB′	93.5 (2)
N-Ru(1)-NC	98.3 (3)	O(1)-Ru(2)-ND	92.5 (3)
N-Ru(1)-NC′	174.2 (4)	O(1)-Ru(2)-ND′	95.8 (3)
NA-Ru(1)-NA′	77.4 (2)	N′-Ru(2)-NB	90.0 (3)
NA-Ru(1)-NC	170.5 (2)	N′-Ru(2)-NB′	85.8 (2)
NA-Ru(1)-NC′	96.9 (3)	N′-Ru(2)-ND	173.3 (4)
NA′-Ru(1)-NC	94.1 (2)	N′-Ru(2)-ND′	96.3 (4)
NA′-Ru(1)-NC′	87.8 (4)	NB-Ru(2)-NB′	78.5 (2)
NC-Ru(1)-NC′	78.4 (3)	NB-Ru(2)-ND	85.7 (2)
O(1)-Ru(1)-N	92.8 (3)	NB-Ru(2)-ND′	92.1 (3)
O(1)-Ru(1)-NA	93.9 (2)	NB′-Ru(2)-ND	98.4 (2)
O(1)-Ru(1)-NA′	171.2 (2)	NB′-Ru(2)-ND′	170.3 (2)
O(1)-Ru(1)-NC	94.5 (2)	ND-Ru(2)-ND′	78.8 (3)
O(1)-Ru(1)-NC′	92.3 (4)	OA(1)-Cl(1)-OA(2)	108.9 (7)
OC(1)-N-OC(2)	118.2 (8)	OA(1)-Cl(1)-OA(3)	113.4 (6)
OC(1)-N-Ru(1)	122.2 (6)	OA(1)-Cl(1)-OA(4)	109.0 (7)
OC(2)-N-Ru(1)	119.5 (6)	OA(2)-Cl(1)-OA(3)	108.8 (7)
OD(1)-N′-OD(2)	116.2 (7)	OA(2)-Cl(1)-OA(4)	103.8 (9)
OD(1)-N′-Ru(2)	121.6 (6)	OA(3)-Cl(1)-OA(4)	112.4 (9)
OD(2)-N′-Ru(2)	122.2 (6)		

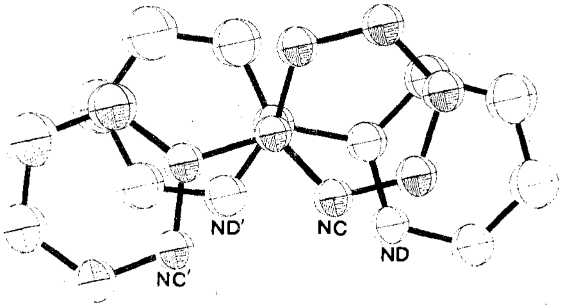

Figure 3. Overlap between the C and D bpy rings on the ruthenium atoms of a single dimer, as viewed normal to the C ring. The shaded ellipsoids are the C and C′ ring atoms.

(5)–2.100 (7) Å, with an average value of 2.077 (14) Å; this distance is probably not significantly different from the two Ru–NO_2 distances of 2.034 (8) and 2.067 (11) Å and is similar to the value of 2.104 (4) Å found[29] in the hexaammineruthenium(III) cation. The absence of any significant shortening of the Ru–N(bpy) bonds relative to these other distances suggests that there is very little multiple bonding between the metal atoms and the aromatic ligand; a similar observation has been made for chromium(III) complexes of the related 1,10-phenanthroline (phen) ligand.[30,31]

The Ru–O distances of 1.876 (6) and 1.890 (7) Å are indicative of considerable multiple bonding between the metal atoms and the bridging oxygen atom. While there are no Ru^{III}–O–Ru^{III} systems known to us with which we may make a comparison, the Fe^{III}–O–Fe^{III} distance in a variety of oxo-bridged iron(III) dimers[32–36] is in the range 1.76–1.8 Å, which is comparable to the present value when allowance is made for the greater covalent radius[37] of Ru(III) (1.30 Å) than of Fe(III) (1.21 Å). The Ru–O separations are also comparable with those in linear Re^{IV}–O–Re^{IV}, Ru^{IV}–O–Ru^{IV}, and Cr^{III}–O–Cr^{III} systems[38–41] and are much shorter than the values reported for Cr^{III}–O bonds involving hydroxide bridges in which there is no multiple bonding.[30,31,40–43] Evidently, there is no structural evidence for a direct, through-space metal–metal interaction, since the Ru–Ru separation is 3.692 (1) Å. The shortness and associated strength of the Ru–O bonds, which are in contrast to the bonding found[2] in dimers with localized spins as in systems of the type $[LCu(OH)]_2^{2+}$ and $[L_2Cr(OH)]_2$, are also consistent with the suggestion of Meyer and coworkers[6] that this complex consists of strongly coupled ruthenium ions in which the spin is in delocalized molecular orbitals. Hence, the general delocalized molecular orbital scheme presented by Meyer and coworkers[6] is probably valid, although the nonlinearity of the Ru–O–Ru linkage removes some of the degeneracies which they have assumed.

The Ru–O–Ru bridging angle of 157.2 (3)° is substantially reduced from linearity but is in the range of 139–180° found for other M–O–M systems. McPhail and coworkers[32c] have suggested that, in the oxo-bridged Fe(III) dimers, the value of this bridging angle is determined largely by the stereochemical requirements of the ligands attached to the metal centers. In the present case, the reduction of the bridging angle from 180° may be due to ligand–ligand electronic effects. As is depicted in Figure 3, the observed bridging geometry allows one of the bpy ligands on each ruthenium atom to lie approximately parallel to one on the other ruthenium atom, with an interplanar separation of approximately 3.4 Å and an interplanar angle of less than 2°; the shortest interatomic distances are as follows: CC(6)′–CD(4)′, 3.29 Å; CC(1)–CD(1)′, 3.31 Å; CC(4)–CD(6), 3.32 Å. This observed interplanar separation is similar to that observed in the solid-state structures of a wide variety of purines[44] and aromatic molecular complexes[45] and may be indicative of some attractive π–π interaction between the C and D bpy groups. It is apparent from an examination of Figure 3, however, that the overlap observed here is far from maximized, and in the absence of solid-state spectral data we are unable to state with certainty whether this postulated ligand–ligand interaction is strong enough to dominate the molecular stereochemistry and, hence, to bring about the observed Ru–O–Ru angle.

Since the geometries of the pyridine rings were constrained (Table IV) during the refinement, the individual C–C and C–N bond lengths within the rings reflect only our estimate of their values. The C(1)–C(1)′ distances, which were not constrained, lie in the range 1.46 (1)–1.49 (1) Å, and the dihedral angles

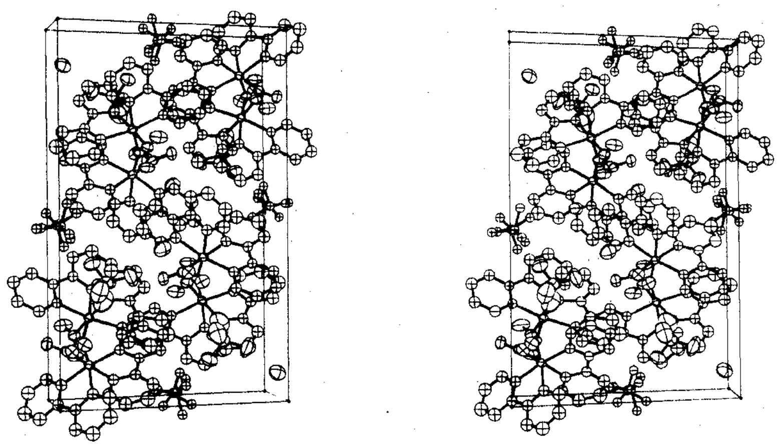

Figure 4. View of the whole cell in $[(bpy)_2(NO_2)Ru-O-Ru(NO_2)(bpy)_2](ClO_4)_2 \cdot 2H_2O$ showing the packing in the crystal.

between pairs of planar groups in the bpy ligands are in the range 2.13–3.16°. The four independent N–Ru–N chelating angles range from 77.4 (2) to 78.8 (3)° with an average value of 78.3 (6)°. These values are similar to those reported for a variety of bpy and phen complexes.[30,31,46–49] Similarly, the N···N "bites" of the bpy rings, which range from 2.61 to 2.64 Å with an average of 2.62 (1) Å, are similar to those in other systems.

The undisordered perchlorate anion may be involved in hydrogen bonding to a water molecule, with an OW(1)···OA(3) distance of 3.01 Å. Our inability to locate the hydrogen atoms on the water molecules makes it difficult for us to assign with confidence this interaction as a hydrogen bond, but there are two pieces of corroborative evidence: the proposed interaction involves the undisordered perchlorate group, which would explain why this anion is ordered while the other is disordered, and the Cl–OA(3) bond is observed to be the longest of the four Cl–O bonds in this group. The bond angles in the ordered anion are in the range observed in a variety of perchlorate structures.[25,26]

To a first approximation, the disordered perchlorate groups are oriented such that the oxygen atoms on the second group (i.e., OB(1)', OB(2'), etc.) are located roughly at the centers of the faces of the tetrahedron formed by the oxygen atoms of the first group (OB(1), OB(2), etc.). Thus, for example, atom OB(4)' lies near the center of the face formed by atoms OB(1), OB(3), and OB(4). The chlorine atoms of the two groups are separated by 0.30 Å, however, and so this approximation is very inexact.

In addition to the possible hydrogen bond discussed above, there may be an interaction involving the nitrite group on Ru(2) and a water molecule, with an OW(2)···OD(1) separation of 3.02 Å.

There is no evidence, however, for any hydrogen bonding involving the bridge, presumably in part because the bulky bpy ligands prevent approach of the solvent or anions to this site. A packing diagram for the whole complex is shown in Figure 4.

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Registry No. $[(bpy)_2(NO_2)RuORu(NO_2)(bpy)_2](ClO_4)_2\cdot 2H_2O$, 55925-17-2.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50214J-10-75.

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