$$\mathrm{Rh^{III}(bpy)_3{}^{3+}Fe^{II}(CN)_6{}^{4-}} \xrightarrow{h\nu} \mathrm{Rh^{III}(bpy)_2(bpy^-)^{2+}Fe^{III}(CN)_6{}^{3-}} \quad (1)$$

$$\mathrm{Rh(bpy)_3{}^{2+}Fe(CN)_6{}^{3-}} \rightarrow \mathrm{Rh(bpy)_3{}^{2+}} + \mathrm{Fe(CN)_6{}^{3-}} \quad (2)$$

$$\mathrm{Rh(bpy)_3{}^{2+}} \rightarrow \mathrm{Rh(bpy)_2{}^{2+}} + \mathrm{bpy} \quad (3)$$

$$\mathrm{Rh(bpy)_2{}^{2+}} + \mathrm{Fe(CN)_6{}^{3-}} + 2\mathrm{H_2O} \rightarrow \mathrm{Rh(bpy)_2(H_2O)_2{}^{3+}} + \mathrm{Fe(CN)_6{}^{4-}} \quad (4)$$

The ion pair generated by outer-sphere MLCT excitation (eq 1) may diffuse apart (eq 2). Equation 3 describes only the fact that $\mathrm{Rh(bpy)_3{}^{2+}}$ is known to release a bpy ligand.[14,15] The mechanism of this reaction is not quite clear. Various possibilities, including a disproportionation, are feasible.[15] Finally, electron transfer and subsequent formation of $\mathrm{Rh(bpy)_2(H_2O)_2{}^{3+}}$ (eq 4) is the last step of this mechanism. The low quantum yield of the overall reaction is probably determined by the rapid thermal reversal of the optical CT transition. This back electron transfer competes with the diffusion step (eq 2). The ion pairs $\mathrm{Rh(bpy)_3{}^{3+}M(CN)_6{}^{4-}}$ with M = Ru, Os seem to be also light-sensitive upon outer-sphere MLCT excitation. However, in this case the CT bands occur at shorter wavelength and thus are overlapping with intramolecular absorption bands of the complexes. For this reason a selective outer-sphere MLCT excitation could not be achieved.

It should be mentioned here that related optical outer-sphere CT transitions in ion pairs involving electron transfer between two metals (MMCT) are well-known.[18-20] This type of CT excitation may also induce photochemical reactions of transition-metal complexes.[19] In this context it is also of interest that intramolecular MLCT transitions between remote groups were observed recently.[21] But in this case through-bond as well as through-space interactions between the remote redox centers may cause the appearance of the MLCT band.[21]

Experimental Section

Materials. $\mathrm{[Rh(bpy)_3](ClO_4)_3}$[22] and $\mathrm{K_4[Os(CN)_6]}$[23] were prepared by literature procedures. $\mathrm{K_4[Ru(CN)_6]}$ was commercially (Heraeus) available.

Photolysis. The light source was an Osram HBO 100 W/2 lamp. A Schott PIL 546 interference filter was used for the selection of the mercury line at 546 nm. Photolyses were carried out in 1-cm spectrophotometer cells at room temperature. For quantum yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproducts. Absorbed light intensities were determined by a Polytec pyroelectric radiometer, which was calibrated and equipped with a RKP-345 detector.

Progress of the photolyses was monitored by UV-visible spectrophotometry. The extent of photolysis of $\mathrm{Rh(bpy)_3{}^{3+}}$ in aqueous solution was determined by measuring the decrease of extinction at 320 nm. At this wavelength the extinction coefficients of $\mathrm{Rh(bpy)_3{}^{3+}}$ and the photoproduct $\mathrm{Rh(bpy)_2(H_2O)_2{}^{3+}}$ are $\epsilon = 4.25 \times 10^4$ and $\epsilon = 2.8 \times 10^4$. Free bipyridyl, which was released in the photolysis, has a negligible absorption at 320 nm.

Instrumentation. Electronic absorption spectra were obtained on a Kontron Uvikon 810 spectrophotometer. The emission spectrum of free bipyridyl was recorded on a Hitachi 850 fluorescence spectrophotometer.

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Registry No. $\mathrm{Ru(bpy)_3{}^{3+}}$, 18955-01-6; $\mathrm{Fe(CN)_6{}^{4-}}$, 13408-63-4; $\mathrm{Ru(CN)_6{}^{4+}}$, 21029-33-4; $\mathrm{Os(CN)_6{}^{4-}}$, 19356-45-7; $\mathrm{Ru(bpy)_2(H_2O)_2{}^{3+}}$, 47514-50-1.

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Reexamination of the Crystal Structure of [(4-Methylimidazole)pentaamminecobalt(III)] Trichloride Dihydrate

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The structure of the title compound has been described by Henderson, Shepherd, and Abola[1] (hereafter HSA). The space group was reported as $Pna2_1$, with $a = 7.011$ (2), $b = 10.373$ (3), and $c = 21.420$ (3) Å. There are a number of difficulties with their report. First, the unit cell dimensions are wrong. The values of a and c must be interchanged to give even approximate agreement with the reported bond distances, and b must be changed to 10.573 Å to give nearly complete agreement (as well as agreement with the reported volume). Second, the reported z coordinates for the heavy atoms except Nh(2), Nh(3), Nh(4), and Nh(5) are all nearly 0 or $^1/_2$; the x and y coordinates of the pairs Nh(2), Nh(5) and Nh(3), Nh(4) are nearly the same, and their z coordinates average to 0. These observations strongly suggest that the molecule lies in a mirror plane. Accordingly, I have performed refinements in space group $Pnma$ (No. 62), after interchanging the reported y and z coordinates and adding $^1/_4$ to the new y coordinates to give the standard setting. The data were the 1257 reflections reported observed by HSA; the weights were computed according to Hughes,[2] with $4F_{\mathrm{min}} = 18.8$. A refinement of the coordinates and anisotropic thermal parameters of the heavy atoms, minimizing $\sum w(F_o^2 - F_c^2)^2$, with fixed contributions from hydrogen atoms (placed by calculation or from difference maps), converged with an R index of 0.048 ($R = \sum(F_o - |F_c|)/\sum F_o$). There were 104 parameters refined, including a secondary extinction parameter.[3] The results were significantly better than those of HSA, particularly in that the Co-N bond distances, which ranged from 1.930 (16) to 1.992 (10) Å (1.967 (27) Å average) for HSA, now ranged from 1.964 (4) to 1.969 (3) Å (1.966 (3) Å average), and the thermal parameters of the ammine nitrogen atoms were all nearly the same (average of U_{eq} is 0.0352 (4) Å^2, vs. 0.0368 (154) Å^2 for HSA).

The refinement of HSA included some of the hydrogen atoms. The thermal parameters of all the listed hydrogen atoms were refined; the values of U obtained range from 0.000(!)(12) to 1.094 (116) Å^2. The range of numbers is remarkable, and both extreme values have little physical meaning. The range of N-H and C-H distances, where H positional parameters were refined (0.694 (24)-1.095 (48) Å), is also great. The geometry about Nh(5) is far from tetrahedral, with H-N-H angles of 135 (6), 73 (7), and 108 (6)°. A refinement in $Pnma$ including all the hydrogen atoms in one matrix with all the other parameters diverged: the thermal parameters of two of the hydrogen atoms on the solvent water molecules became negative, that of a third exceeded B = 40 Å^2, and the hydrogen atoms bonded to Nh(1) and M(5) shifted to positions up to 3 Å away from the nitrogen atom and the carbon atom. A refinement keeping the coordinates and thermal parameters of the hydrogen atoms on the water molecules and those on Nh(1) and M(5) fixed, but shifting nine hydrogen atoms and their isotropic temperature factors, converged with R = 0.045, marginally better than the refinement of heavy-atom parameters only. The refined hydrogen B values ranged from 2.2 (13) to 8.4 (22) Å^2, and the H-C or H-N distances from 0.79 (5) to 1.17 (8) Å (average 0.90 (12) Å). The refinement of the hydrogen atoms, then, tells us nothing about the hydrogen atom geometry

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Table I. Coordinates and Thermal Parameters for [(4-Methylimidazole)pentaamminecobalt(III)] Trichloride Dihydrate (Numbering As in Ref 1)

atom	*x*	*y*	*z*	U_{eq}, Å$^{2\,a}$
Co	0.1556 (0.4)	$^1/_4$	0.0844 (0.8)	0.0261 (2)
Nh(1)	0.2231 (2)	$^1/_4$	−0.0416 (5)	0.0356 (12)
Nh(25)	0.1127 (2)	0.0485 (5)	−0.0119 (3)	0.0348 (8)
Nh(34)	0.1996 (2)	0.0500 (5)	0.1791 (3)	0.0353 (8)
N(3)	0.0899 (2)	$^1/_4$	0.2108 (5)	0.0309 (11)
C(4)	0.0983 (3)	$^1/_4$	0.3422 (6)	0.0401 (16)
C(5)	0.0413 (3)	$^1/_4$	0.3993 (6)	0.0399 (16)
M(5)	0.0234 (4)	$^1/_4$	0.5342 (7)	0.0609 (22)
N(1)	−0.0017 (2)	$^1/_4$	0.3025 (5)	0.0417 (14)
C(2)	0.0292 (3)	$^1/_4$	0.1923 (6)	0.0351 (15)
Cl(1)	0.2626 (0.8)	$^1/_4$	0.4467 (2)	0.0432 (4)
Cl(2)	0.4828 (0.8)	$^1/_4$	0.6381 (2)	0.0428 (4)
Cl(3)^b	0.3547 (1)	0.2004 (14)	0.1290 (3)	0.0922 (15)
W(1)	0.3684 (2)	$^1/_4$	0.8241 (5)	0.0543 (13)
W(2)^b	0.1643 (4)	0.1717 (24)	0.7102 (7)	0.1300 (47)

$^a U_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(a_i{}^*a_j{}^*)(\vec{a}_i\cdot\vec{a}_j)]$; $\sigma(U_{eq}) = 6^{-1/2}\langle\sigma(U_{ii})/U_{ii}\rangle U_{eq}$. ^{b} Half-occupied sites.

Table II. Selected Distances (Å) and Angles (deg)

Co–Nh(1)	1.966 (5)	C(4)–C(5)	1.362 (9)
Co–Nh(25)	1.969 (3)	C(5)–N(1)	1.376 (8)
Co–Nh(34)	1.964 (4)	N(1)–C(2)	1.341 (8)
Co–N(3)	1.941 (5)	C(2)–N(3)	1.313 (8)
N(3)–C(4)	1.402 (8)	C(5)–M(5)	1.478 (10)
Nh(25)–Co–Nh(1)	89.6 (2)	Co–N(3)–C(4)	126.1 (4)
Nh(34)–Co–Nh(1)	89.6 (2)	Co–N(3)–C(2)	128.0 (4)
N(3)–Co–Nh(1)	179.1 (2)	N(3)–C(4)–C(5)	108.9 (5)
Nh(34)–Co–Nh(25)	88.6 (1)	C(4)–C(5)–N(1)	105.7 (6)
Nh(34)–Co–Nh(25)′	179.1 (1)	C(5)–N(1)–C(2)	108.4 (5)
N(3)–Co–Nh(25)	90.1 (2)	N(1)–C(2)–N(3)	111.1 (5)
N(3)–Co–Nh(34)	89.9 (2)	C(2)–N(3)–N(4)	105.9 (5)
Nh(25)–Co–Nh(25)′	91.7 (1)	C(4)–C(5)–M(5)	131.3 (6)
Nh(34)–Co–Nh(34)′	91.1 (1)	N(1)–C(5)–M(5)	123.0 (6)

but only serves to give a cosmetically better *R* index.

The final difference map shows maximum excursions of +1.23 and −1.16 e/Å^3, both in the $y = {}^1/_4$ plane, the first near Cl(3) and the second near the cobalt atom. It is clear that the model for Cl(3) and W(2) is unsatisfactory. There is a residual positive density running in a column along **b** where these atoms are located. In an attempt to model this better, I had placed Cl(3) and W(2) off the mirror plane, as disordered pairs of atoms. This led to a decrease in the U_{22}'s by 47% and 61%, respectively. These thermal parameters are still large, though: U_{22} for Cl(3) is 0.174 (11) Å^2 and for W(2) is 0.309 (33) Å^2, corresponding to mean deviations of 0.41 Å for Cl(3) and 0.56 Å for W(2) along **b**. It is possible[4] that in fact there is additional nonstoichiometric water in this column, perhaps one extra molecule every four or five cells. I did not develop a model for this. The remainder of the difference map is featureless but noisy.

In their discussion, HSA note that the plane of the imidazole ring is expected to make an angle of 45° with the Nh(1)–Nh(2)–Nh(4)–Co–N(3) plane. The expectation really is that the imidazole plane bisect the angles Nh(2)–Co–Nh(5) and Nh(3)–Co–Nh(4); because of the increased symmetry in the *Pnma* description, it now exactly does. The Nh(25)–Co–Nh(25)′ angle is 91.7 (1)°, so the angle between the imidazole planes and the Nh(25)–Co–Nh(1)–N(3) plane is 45.9 (1)°; for the Nh(34)–Co–Nh(34)′ angle of 91.1 (1)°, the interplanar angle is 45.6 (1)°.

On the basis of these refinements, I conclude that the structure of this cobalt compound is better described in the centric space group *Pnma*, rather than in *Pna*2$_1$. The addition of the mirror plane makes the molecule exactly planar; it improves the agreement of chemically equivalent distances, and it improves the overall pattern of thermal parameters. It is clear that the data are not good enough to allow refinement of all the hydrogen parameters, and even those that are well-behaved enough not to diverge lead to geometries that are unreasonable. I therefore believe the refinement with fixed hydrogen contributions based on hydrogen positions idealized from difference maps or calculated from known geometry is the best one. The coordinates, distances, and angles given in Tables I and II are from that refinement.

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Supplementary Material Available: Tables of anisotropic thermal parameters and assigned hydrogen parameters (2 pages); a listing of structure factors (7 pages). Ordering information is given on any current masthead page.

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First Structurally Characterized Geometric Isomers of an Eight-Coordinate Complex. Structural Comparison between *cis*- and *trans*-$SmI_2[O(CH_2CH_2OMe)_2]_2$

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Geometrical isomers should exist for eight-coordinate complexes;[4] however, none have been structurally characterized thus far. Indeed, it has been stated that "the preparation, isolation and characterization of such isomers remains an unanswered challenge".[5] Herein, we report the X-ray crystal structure of *cis*-$SmI_2[O(CH_2CH_2OMe)_2]_2$ (**1**). This and the reported[6] structure of the corresponding trans isomer (**2**) constitute the first structural characterizations of a pair of geometrical isomers of an eight-coordinate complex. In addition, these are also the first geometrical isomers of a lanthanide-metal compound. Because of the spherical nature of the lanthanide ions and the absence of significant crystal field effects, the geometrical arrangement of ligands in lanthanide-metal complexes is normally governed by steric rather than bonding requirements.[7]

Results and Discussion

1 was obtained as a byproduct in low yield by the addition of diglyme to a mixture obtained by the reaction of SmI_2[8] with 2 equiv of *t*-BuOK. Interestingly, the addition of diglyme to $SmI_2(THF)_2$ alone resulted in the formation of the trans isomer (**2**).[6]

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