squares refinement, the C–H bond distances ranging from 0.94 to 1.19 Å are not unlike others obtained by the X-ray diffraction method.

Calculation of a weighted best plane[18] passing through atoms of the pyrrole–C–NC–Co/2 moiety reveals that the constituent atoms are essentially coplanar. The maximum perpendicular displacement of individual atoms from this best plane is 0.013 Å for C(8), with the deviations of the remaining atoms ranging from −0.000 for Co to −0.008 Å for N(2).

A close conformability of the N–C(CH$_3$)$_3$ moiety to the tetrahedral geometry can be seen by an examination of the N(1)–C(1)–CH$_3$ angles, which vary from 107.5 (7) to 111.1 (9)° only. The *tert*-butyl group conformation may be described in a manner similar to that for peptide chain.[39] Figure 3 shows a view down the N(1)–C(1) bond. As expected, the three methyl carbons are roughly in staggered positions relative to C(5), the deviation from the ideal staggered conformation being a clockwise rotation of the methyl groups by 19° about the N(1)→C(1) axis. The arrangements of the methyl hydrogen atoms viewed down the C(1)–C(2), C(1)–C(3), and C(1)–C(4) bonds are shown in Figure 4. In each case, the three hydrogen atoms are in the expected staggered orientation relative to N(1).

Figure 5 shows the packing in a stereoscopic view down the *c* axis. While the shortest nonbonding intramolecular H···H distance [excluding those for H(methyl)···H(methyl)] is 2.07 Å for H(5)···H(2c), the closest intermolecular H···H contact is 2.38 Å for H(2a) and H(2b) of the adjacent molecule, thus indicating that no abnormal forces are responsible for the crystal packing.

Analogous cobalt and zinc complexes with tetrahedral chelates form isomorphous structures in a number of compounds involving bis(*N*-isopropylsalicylaldiminato)metal(II),[25,30] bis(*N*-butylsalicylaldiminato)metal(II),[23] bis(*N*-*sec*-butylsalicylaldiminato)metal(II),[40] (Et$_4$N)$_2$M^{II}(NCO)$_4$,[26] diethyl 3,3′,5,5′-tetramethyldipyrromethene-4,4′-dicarboxylate,[27] and diethyl 5′-bromo-3,4′,5-trimethyldipyrromethene-3′,4-dicarboxylate.[27] Single-crystal X-ray examination of bis(*N*-*tert*-butylpyrrole-2-carboxaldimino)zinc(II) reveals that the unit cell of the zinc complex is practically isodimensional with that of the analogous cobalt complex.[4] That these two complexes are rigorously isomorphous is further evidenced by their apparently indistinguishable intensity data.[33] Detailed comparison of structural characteristics of the series of (C$_9$H$_{13}$N$_2$)$_2$M^{II} (M = Co, Ni, Cu) will be presented in a future paper.

Acknowledgments.—The author wishes to thank Professor R. H. Holm for furnishing a sample of the compound and for his interest in this work. Collection of the X-ray data was carried out at the University of Wisconsin in the laboratories of Professor L. F. Dahl, to whom the author is indebted for helpful discussions.

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[39] Several identical papers were published by the IUPAC–IUB Commission on Biochemical Nomenclature. As an example, see *Biochemistry*, **9**, 3471 (1970).

[40] L. Sacconi, P. L. Orioli, P. Paoletti, and M. Ciampolini, *Proc. Chem. Soc., London*, 255 (1962).

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The Crystal Structure of Hydridopentaamminerhodium(III) Perchlorate

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The crystal structure of hydridopentaamminerhodium(III) perchlorate, [RhH(NH$_3$)$_5$][ClO$_4$]$_2$, has been determined by X-ray diffractometric methods. The structure has been refined in the orthorhombic space group $D_2{}^4$-$P2_12_12_1$ with a = 10.2866 (12), b = 8.0689 (10), c = 15.0146 (21) Å, ρ_{obsd} = 2.07 (2) g/cm^3, ρ_{calcd} = 2.07 g/cm^3, and Z = 4, to a final conventional R factor of 0.040 for 1298 reflections above background. The compound consists of discrete octahedral hydridopentaamminerhodium(III) and tetrahedral perchlorate ions. The cations are stacked in zigzag chains of essentially linear Rh–H···N–Rh elements, whose Rh atoms are 6.103 (1) Å apart. The ammine group which is directed toward the next cation in the chain is the closest to the Rh atom, with an Rh–N distance of 2.048 (11) Å. The other three ammine groups cis to the H ligand have an average Rh–N distance of 2.079 (7) Å. The NH$_3$ which is trans to the H ligand is 2.244 (13) Å from the Rh, so that the H ligand is exerting a pronounced trans effect of 0.165 (15) Å. The Rh–H distance is 1.82 (17) Å.

Introduction

Although scores of structures of transition metal hydride complexes have been determined by diffraction methods, only four of these were carried out by neutron diffraction techniques where high accuracy in the placement of the hydride ligand is possible.[1] Neutron diffraction studies of transition metal hydrides are rare, not necessarily because of the limited availability of suitable facilities but more likely because of the unsuitability of most transition metal hydrides for such work. Many such complexes contain a large number of atoms since multiatom ligands, such as P(C$_6$H$_5$)$_3$, are used to stabilize them.

The present compound, hydridopentaamminerhodium(III) perchlorate, [RhH(NH$_3$)$_5$][ClO$_4$]$_2$, is an air-stable solid with a relatively small number of atoms. This present X-ray study was initiated in part to assess the crystallographic suitability of the complex for neutron diffraction investigation. This was done at a time when there was still considerable discussion about the

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[1] B. A. Frenz and J. A. Ibers in "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, p 33.

metal–hydrogen bond length.[2,3] Crystallographic difficulties (see below) have delayed the present study and in the interim the question of the metal–hydrogen bond length has been virtually settled.[4] Nevertheless, the results obtained are of interest because they may be compared directly with those[5] on the analogous complex $[Rh(C_2H_5)(NH_3)_5]Br_2$ and because they bear directly on the question of the trans-labilizing effect of the hydride ligand in octahedral complexes. Wilkinson and his coworkers[6–8] initially prepared this compound and on the basis of kinetic and nmr evidence demonstrated the lability of one of the ammines (presumably that one trans to the hydride) upon aquation. We find from this study that there is indeed a large structural trans effect.

Experimental Section

White needles of hydridopentaamminerhodium(III) perchlorate, $[RhH(NH_3)_5][ClO_4]_2$, were kindly supplied by Professor G. Wilkinson. The crystals were assigned diffraction symmetry *mmm* on the basis of a preliminary optical and X-ray examination. Precession and Weissenberg photographs using Mo Kα radiation of the *hk*0, 2*h*,*k*,*h*, *hkh*, *h*,*k*,2*h*, and 0*kl* nets suggested either of the space groups D_{2h}^{16}-*Pnma* or C_{2v}^{9}-$Pn2_1a$ as consistent with the following systematic absences: *hkl*, none; *hk*0, $h = 2n + 1$; 0*kl*, $k + l = 2n + 1$; *h*0*l*, none. Attempts to refine the structure in each of these space groups left some unsatisfactory features. It was later found, however, by taking long-exposure precession photographs using Cu Kα radiation of the *hk*0 and 0*kl* nets that a few very weak spots were indeed present for $h = 2n + 1$ and for $k + l = 2n + 1$, respectively. Thus both glide planes are eliminated. The only systematic absences remaining are for *h*00, $h = 2n + 1$; for 0*k*0, $k = 2n + 1$; and for 00*l*, $l = 2n + 1$. The true space group is therefore D_2^4-$P2_12_12_1$, and this is corroborated by subsequent refinement. The lattice parameters, obtained as previously described[9] by carefully centering 23 high-angle reflections with Mo Kα_1 radiation (λ 0.70930 Å) at 23°, are $a = 10.2866$ (12), $b = 8.0689$ (10), and $c = 15.0146$ (21) Å. An observed density of 2.07 (2) g/cm^3, as measured by flotation in a mixture of carbon tetrachloride and diiodomethane, agrees with a calculated density of 2.07 g/cm^3 for 4 formula units per cell.

A crystal in the form of a second-order prism with faces {010} and {101} and of dimensions 0.062 × 0.010 × 0.010 cm elongated along the *b* axis was mounted on a Picker automatic four-circle diffractometer. The *b* axis was offset from the polar (φ) instrumental axis by some 5° in order to reduce the effects of multiple diffraction.[10] Preliminary narrow-beam and wide-counter ω scans of some representative peaks exhibited widths at half-height of some 0.05°, and so the data were collected in the θ–2θ scan mode in the manner previously described.[9] Mo Kα radiation, filtered through 3 mils of Zr foil, was employed. A receiving aperture 4 mm × 4 mm was placed 35 cm from the crystal, and the pulse height analyzer was set to admit 90% of the reflected intensity.

A total of 1189 observations over a unique octant were made out to a 2θ value of 50°, using a takeoff angle α of 1.4°, where 80% of the maximum peak height as a function of α was observed for a representative peak, a scan rate of 1°/min, and a scan range of 1.8°, symmetrically disposed with respect to each calculated peak center. After these data had been partially refined, a structure factor calculation was made for terms to a 2θ value of 80°, and 383 additional significant data were then collected. Background counts were taken for 10 sec at each end of the scan range. The intensities of three standard reflections were checked every 200 readings. Two of these showed a steady decrease, one of some 0.25% and the other of 0.5% per 100 reflections, and the crystal gradually changed color from white to gray in the course of the experiment.

The observed intensities were reduced to values of F_o^2 by applying the usual Lorentz and polarization corrections. A value of 0.04 for *p* was used in the expression for $\sigma(F_o^2)$ as previoulsy formulated.[9] Of the 1572 reflections observed, 1298 had $F_o^2 > 3\sigma(F_o^2)$, and these, which were used in subsequent calculations, we describe as being above background. An absorption correction[11] was made; the transmission factors varied from 0.81 to 0.86 ($\mu = 18.4$ cm^{-1}).

Solution and Refinement of the Structure

The function minimized in least-squares refinements was $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors, respectively, and where the weight *w* is equal to $1/\sigma^2(F_o)$ or $4F_o^2/\sigma^2(F_o^2)$. The residual indices R_1 and R_2 are defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. Scattering factors[12] used for the nonhydrogen atoms were taken from the usual tabulations, while those for hydrogen were from Stewart, *et al.*[13] Dispersion terms for the heavy atoms were taken from Cromer's[14] calculations and were applied to the calculated structure factors.[15]

Refinement was first effected in the space group *Pnma*, since this was judged to be likely from an inspection of a three-dimensional Patterson map. The rhodium atom was located from this map and the chlorine atoms were found in the next difference synthesis. These three atoms were all found to lie in position (4c) on the mirror plane at $y = {}^1/_4$.

Subsequent least-squares and difference Fourier calculations revealed the ammine nitrogen atoms and the perchlorate oxygen atoms, with one of the N atoms disordered with the hydride ligand. The final residual indices in this space group were $R_1 = 0.115$ and $R_2 = 0.152$.

Similar refinement was attempted in the space group $Pn2_1a$, and similar molecular geometry was found without hydride–ammine disorder. This time the residuals were $R_1 = 0.094$ and $R_2 = 0.132$.

The final models in these space groups were judged as unsatisfacory on the following bases: (a) all residuals are high; (b) in the two cases respective spreads of 0.13 and 0.12 Å were found for the cis Rh–N distances within the cation; (c) in neither space group could all of the light atoms be refined anisotropically without some temperature factors becoming nonpositive definite; (d) most significantly, a scrutiny of the values of the final agreement factors R_1 revealed a trend from $k = 0$ to $k = 12$ of 0.077 to 0.246 in *Pnma* and from 0.068 to 0.195 in $Pn2_1a$; clearly something was amiss in the values of *y* for the Rh atom.

At this stage long-exposure precession photographs taken with Cu Kα radiation demonstrated the true space group to be $P2_12_12_1$. The Rh atom position was found by interpreting a three-dimensional, sharpened, origin-removed Patterson map. After two cycles of least-squares refinement the values of R_1 and R_2 were 0.302 and 0.377, respectively. Both Cl atoms were located in a difference Fourier map, and after two further cycles with individual isotropic thermal parameters the residuals were reduced to $R_1 = 0.174$ and $R_2 = 0.254$. The ensuing difference Fourier map showed all five N atoms at peak heights of 5.2–8.5 e/Å^3 and all eight O atoms at peak heights of 2.1–5.0 e/Å^3. Insertion of all these atoms, each with isotropic thermal parameters, into a further cycle yielded residuals of $R_1 = 0.077$ and $R_2 = 0.103$. Two further cycles in which all atoms were allowed to undergo anisotropic thermal motion reduced R_1 to 0.043 and R_2 to 0.050. All hydrogen atoms were than located in the next difference Fourier map. Those in the ammine groups were idealized (N–H = 1.01 Å, HNH = 111°) and included with fixed contributions ($B_H = 6.0$ Å^2) in the next round of calculations while all parameters of the hydride ligand were refined. The final residuals

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(2) J. A. Ibers, *Annu. Rev. Phys. Chem.*, **16**, 375 (1965).

(3) See, for example, T. C. Farrar, F. E. Brinckman, T. D. Coyle, A. Davison, and J. W. Faller, *Inorg. Chem.*, **6**, 161 (1967), and references therein.

(4) S. J. La Placa, W. C. Hamilton, J. A. Ibers, and A. Davison, *ibid.*, **8**, 1928 (1969).

(5) A. C. Skapski and P. G. H. Troughton, *Chem. Commun.*, 666 (1969).

(6) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 3594 (1963).

(7) J. A. Osborn, R. D. Gillard, and G. Wilkinson, *ibid.*, 3168 (1964).

(8) K. Thomas, J. A. Powell, and G. Wilkinson, *ibid.*, *A*, 1801 (1968).

(9) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(10) W. H. Zachariasen, *Acta Crystallogr.*, **18**, 705 (1965).

(11) In addition to local programs for the CDC 6400 computer, local versions of the following programs were used in this work: Hamilton's GONO absorption program, Busing and Levy's ORFFE error function program, Johnson' ORTEP thermal ellipsoid plotting program, Zalkin's FORDAP Fourier program, and Busing and Levy's ORFLS least-squares program.

(12) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, 2nd ed, Kynoch Press, Birmingham, England, 1968.

(13) R. F. Stewart, E. R. Davidson, and W. J. Simpson, *J. Chem. Phys.*, **42**, 3174 (1965).

(14) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(15) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS IN $[RhH(NH_3)_5][ClO_4]_2$

Atom	x	y	z	$10^4\beta_{11}$[a] or B	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Rh	0.30655 (6)	0.23812 (9)	0.32538 (4)	49.2 (5)	89.5 (9)	27.3 (2)	0.5 (9)	5.6 (4)	−0.5 (7)
Cl(1)	0.31990 (19)	0.2532 (4)	−0.33152 (14)	71.6 (18)	132 (3)	48.5 (10)	12 (4)	8.1 (14)	2 (3)
Cl(2)	−0.00135 (26)	0.2616 (5)	−0.0341 (2)	129 (3)	132 (4)	44.5 (11)	−27 (4)	15.5 (16)	−3 (3)
N(1)	0.4230 (11)	0.4125 (13)	0.2666 (7)	107 (10)	128 (15)	42 (5)	−5 (11)	13 (6)	−4 (7)
N(2)	0.1837 (7)	0.2436 (16)	0.2161 (4)	97 (8)	152 (12)	40 (3)	6 (20)	−19 (5)	7 (9)
N(3)	0.1968 (21)	0.0496 (12)	0.3824 (8)	106 (14)	123 (16)	58 (7)	−5 (16)	15 (10)	27 (7)
N(4)	0.4371 (8)	0.2245 (19)	0.4315 (5)	88 (8)	225 (26)	47 (4)	39 (16)	−16 (5)	−16 (11)
N(5)	0.1923 (20)	0.4366 (12)	0.3950 (8)	69 (12)	160 (17)	57 (6)	13 (16)	19 (9)	−17 (8)
O(11)[b]	0.4029 (13)	0.1222 (17)	−0.3145 (18)	129 (16)	233 (27)	243 (19)	33 (15)	−13 (14)	102 (21)
O(12)	0.2289 (12)	0.2629 (36)	−0.2618 (8)	257 (16)	469 (37)	140 (9)	111 (31)	96 (11)	−3 (24)
O(13)	0.2493 (13)	0.2050 (56)	−0.4027 (8)	252 (19)	1668 (161)	89 (7)	−165 (55)	−47 (10)	−191 (36)
O(14)	0.3906 (17)	0.3920 (19)	−0.3432 (22)	230 (27)	208 (27)	354 (33)	−61 (20)	140 (23)	103 (24)
O(21)	0.4541 (27)	0.0882 (20)	0.0532 (15)	606 (52)	191 (26)	207 (20)	−87 (32)	−216 (27)	74 (19)
O(22)	0.4104 (16)	0.3664 (21)	0.0651 (8)	265 (21)	538 (50)	40 (5)	189 (27)	41 (10)	16 (13)
O(23)	0.1037 (12)	0.2328 (38)	−0.0852 (13)	189 (15)	495 (50)	305 (18)	81 (32)	138 (15)	−112 (35)
O(24)	0.5019 (14)	0.2737 (27)	−0.0543 (7)	471 (27)	637 (51)	108 (8)	390 (36)	167 (13)	207 (20)
H[c]	0.428 (15)	0.077 (23)	0.313 (12)	2.9 (51)					

[a] The expression for the anisotropic temperature factor is $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl]$. [b] Oxygen atoms O($mn$) are bonded to chlorine atom Cl(m). [c] This is the hydride ligand.

are $R_1 = 0.040$ and $R_2 = 0.043$, while the final error in an observation of unit weight is 1.86.

The only possibly significant shifts in the last cycle of least-squares refinement involve the y and z parameters of the H ligand and of the cis N(1) atom. The correspondng parameters of these two atoms are correlated, with correlation coefficients of about 0.5. There is an oscillation from one cycle to the next. Thus there are two equally good solutions to the structure, and these differ only in possibly significant differences in the H and N(1) positions from one cycle to the next. The effect is a small one, the Rh–N(1) distance changing from 2.072 (11) to 2.048 (11) Å. The refinement was terminated at the solution corresponding to the latter distance.

An examination of $|F_o|$ *vs.* $|F_c|$ as a function of Miller indices, scattering angle, and magnitude of $|F_o|$ reveals none of the disturbing trends that were apparent when refinement was carried out in *Pnma* or $Pn2_1a$. There is no indication that an extinction correction is necessary.

A structure factor calculation of F_c^2 for the 265 reflections for which $F_o^2 < 3\sigma(F_o^2)$ reveals none for which $|F_o^2 - F_c^2| > 2.6\sigma(F_o^2)$. A calculation for those reflections omitted from data collection, owing to the assumption of the wrong space group, namely, $hk0$ for h odd and $0kl$ for $k + l$ odd, reveals about 30 that should be above background. Had we collected these, the error in the space group determination would have been apparent. This is probably a strong argument for collecting all reflections in a diffractometer experiment, save those eliminated through lattice centering.

Since $P2_12_12_1$ is an acentric space group, albeit not a polar one, the effects of change of configuration (hkl into $\bar{h}\bar{k}\bar{l}$) were tested and found to be negligible compared with the errors associated with $|F_o|$.

In Table I are listed the final positional and thermal parameters, along with the standard deviations as obtained from the inverse matrix. In Table II the positions of the ammine hydrogen atoms, which were included in the final calculations, are given. Table III lists the final values of $10|F_o|$ and $10|F_c|$ (in electrons) for the 1298 reflections above background.[16]

TABLE II

POSITIONS OF THE AMMINE H ATOMS IN $[RhH(NH_3)_5][ClO_4]_2$

Atom	x	y	z
H(11)[a]	0.3690	0.5157	0.2509
H(12)	0.4923	0.4520	0.3103
H(13)	0.4648	0.3711	0.2124
H(21)	0.1194	0.1481	0.2173
H(22)	0.1296	0.3500	0.2152
H(23)	0.2327	0.2381	0.1583
H(31)	0.1315	0.0002	0.3384
H(32)	0.2502	−0.0427	0.4069
H(33)	0.1403	0.0940	0.4346
H(41)	0.4823	0.1168	0.4336
H(42)	0.5085	0.3155	0.4234
H(43)	0.3936	0.2487	0.4893
H(51)	0.1027	0.4413	0.3743
H(52)	0.1938	0.4157	0.4623
H(53)	0.2362	0.5488	0.3857

[a] Hydrogen atom H(mn) is attached to nitrogen atom N(m).

Description of the Structure

The unit cell, which can be seen in Figure 1, consists of well-separated octahedral hydridopentaamminerhodium(III) cations and tetrahedral perchlorate anions. The cations are stacked as zigzag chains (Figure 2) whose Rh atoms are 6.103 (1) Å apart and whose (2_1 screw) axes are parallel to y. Each unit cell intercepts two such chains. The hydride ligand of each cation is pointing almost directly into the trigonal hole created by the ammine group (1) of the adjacent cation in the chain. The N(1)–H nonbonded distance is 2.35 (17) Å, while the nonbonded H–H distances between the hydride ligand and the ammine hydrogen atoms average 2.20 Å.

Table IV presents some selected interatomic distances and angles, together with standard deviations as derived from the variance–covariance matrix. The geometry of the cation is displayed in Figure 3.

Although the Rh–N(1) distance is possibly significantly shorter than the other three cis hydride Rh–N distances, recall that the N(1) position is correlated with the hydride H position and that this Rh–N(1) distance on the penultimate least-squares cycle was 2.072 Å. Accordingly, in the enusing discussion we shall use the value of 2.079 (7) Å as the average cis Rh–N distance, where the average value is obtained from the Rh–N(2) through Rh–N(4) distances. This Rh–N distance may be compared with that of 2.072 (7) Å for Rh–N distances cis to ethyl in the analogous ethyl complex.[5] Since there is a hydride ligand trans to an ammine ligand in the present complex, one does not expect the Rh atom to lie in the plane of the four N atoms cis to the hydride. Indeed the equation of the weighted, least-squares plane through the rhodium and four cis nitrogen atoms has the equation $5.491x - 5.727y - 6.900z + 1.925 = 0$ in orthorhombic fractional coordinates and the N atoms lie 0.047 (10), 0.082 (15), 0.062

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[16] Table III will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1105. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

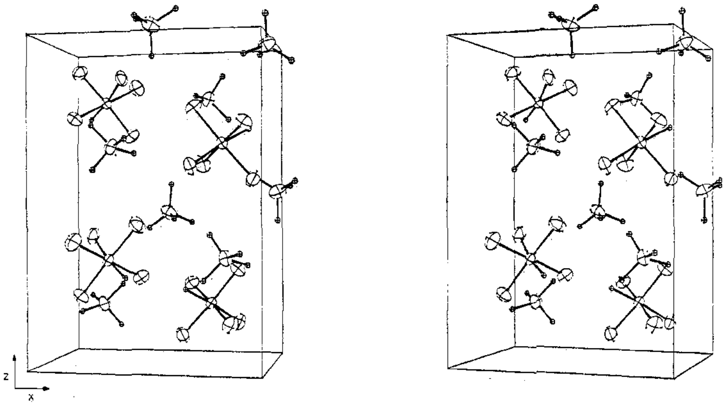

Figure 1.—A stereoscopic pair of views of the unit cell in [RhH(NH$_3$)$_5$][ClO$_4$]$_2$. For the sake of clarity the perchlorate oxygen atoms and the hydrogen atoms have been drawn artificially small. The other atoms are drawn at 50% electron probability.

TABLE IV
SELECTED BOND DISTANCES (Å) AND ANGLES (DEG) FOR [RhH(NH$_3$)$_5$][ClO$_4$]$_2$

The Cation			
Rh-N(1)	2.048 (11)	H-Rh-N(1)	93 (5)
Rh-N(2)	2.071 (6)	H-Rh-N(2)	111 (6)
Rh-N(3)	2.079 (14)	H-Rh-N(3)	84 (6)
Rh-N(4)	2.086 (8)	H-Rh-N(4)	66 (6)
Rh-N(5)	2.244 (13)	H-Rh-N(5)	157 (6)
Rh-H	1.82 (17)		
N(1)-Rh-N(2)	90.1 (4)	N(2)-Rh-N(4)	176.9 (4)
N(1)-Rh-N(3)	176.3 (6)	N(2)-Rh-N(5)	92.0 (5)
N(1)-Rh-N(4)	89.3 (5)	N(3)-Rh-N(4)	89.8 (6)
N(1)-Rh-N(5)	91.0 (5)	N(3)-Rh-N(5)	92.6 (3)
N(2)-Rh-N(3)	90.6 (6)	N(4)-Rh-N(5)	91.1 (6)
The Anions			
Cl(1)-O(11)	1.383 (13)	Cl(2)-O(21)	1.327 (19)
Cl(1)-O(12)	1.407 (9)	Cl(2)-O(22)	1.452 (14)
Cl(1)-O(13)	1.349 (14)	Cl(2)-O(23)	1.346 (11)
Cl(1)-O(14)	1.347 (13)	Cl(2)-O(24)	1.359 (10)
		Av Cl-O	1.37 (4)
O(11)-Cl(1)-O(12)	108.4 (14)	O(21)-Cl(2)-O(22)	111.4 (13)
O(11)-Cl(1)-O(13)	105.0 (20)	O(21)-Cl(2)-O(23)	108.1 (17)
O(11)-Cl(1)-O(14)	109.0 (8)	O(21)-Cl(2)-O(24)	114.3 (14)
O(12)-Cl(1)-O(13)	104.3 (9)	O(22)-Cl(2)-O(23)	101.3 (13)
O(12)-Cl(1)-O(14)	114.2 (16)	O(22)-Cl(2)-O(24)	100.3 (8)
O(13)-Cl(1)-O(14)	115.3 (20)	O(23)-Cl(2)-O(24)	120.1 (13)
		Av O-Cl-O	109.3 (6)

(12), and 0.046 (11) Å out of the plane toward the hydride ligand, while the Rh atom lies 0.0008 (7) Å on the other side of the plane.

The perchlorate anions have their expected tetrahedral geometry. In fact, the distortions from perfect tetrahedra are smaller here than is generally found.

The Structural Trans Effect

Selected data on the structural trans effect in d^6 octahedral complexes are given in Table V. Comparison of the data on the two hydrides indicates a much larger trans effect when NH$_3$, rather than CO, is opposite the hydride ligand. The hydride ligand and the ammine both form σ bonds, whereas the carbonyl is primarily involved in a π bond. These data, as well as a more extensive tabulation,[1] bear out the fact that a trans effect is large only when the trans ligands are competing for the same types of bonding orbitals.

The trans effect is essentially the same in the present complex and in the corresponding ethyl complex. This is in agreement both with various calculations[17,18] and

TABLE V
STRUCTURAL TRANS EFFECT OF THE X LIGAND IN SELECTED d^6 OCTAHEDRAL MXL$_5$ COMPLEXES (Å)

Compd	M–L (trans)	M–L(cis)	Trans–cis	Ref
[RhH(NH$_3$)$_5$][ClO$_4$]$_2$	2.244 (13)	2.079 (7)	0.165 (15)	Present work
α-MnH(CO)$_5$	1.821 (9)	1.840 (10)	−0.019 (14)	*a*
β-MnH(CO)$_5$	1.822 (12)	1.853 (13)	−0.031 (17)	*b*
[Rh(C$_2$H$_5$)(NH$_3$)$_5$]Br$_2$	2.256 (8)	2.072 (7)	0.184 (10)	*c*
[Co(NO)(NH$_3$)$_5$]Cl$_2$	2.220 (4)	1.981 (5)	0.239 (7)	*d*

[a] S. J. La Placa, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3,** 1491 (1964). [b] Reference 4. [c] Reference 5. [d] C. S. Pratt, B. A. Coyle, and J. A. Ibers, *J. Chem. Soc. A*, 2146(1971).

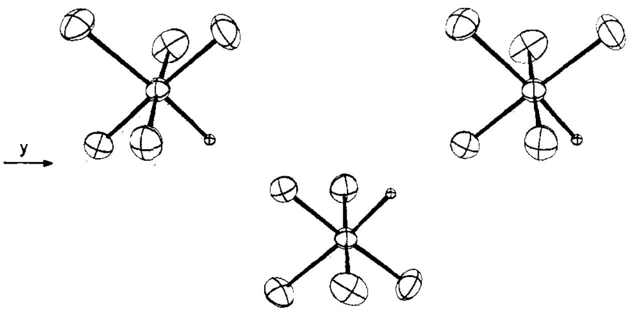

Figure 2.—The zigzag chain of cations along the 2$_1$ screw axis parallel to *y*.

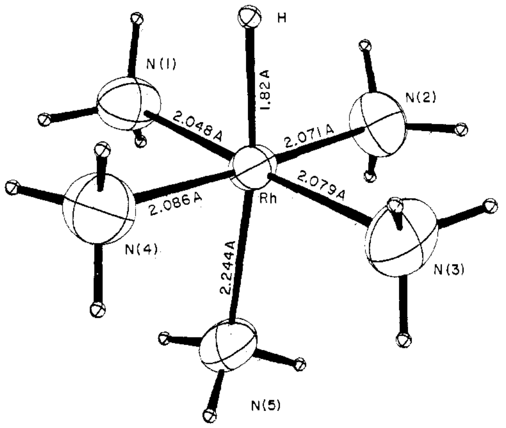

Figure 3.—The [RhH(NH$_3$)$_5$]$^{2+}$ cation. The 50% probability ellipsoids are shown, except for the hydrogen atoms.

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with the kinetic trans effect,[19] with which one hopes there is some correlation.

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The Crystal and Molecular Structure of Tris(1,10-phenanthroline)nickel(II) Pentacarbonylmanganate(−I), $[Ni(1,10\text{-phen})_3][Mn(CO)_5]_2$

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The crystal structure of tris(1,10-phenanthroline)nickel(II) pentacarbonylmanganate(−I), $[Ni(phen)_3][Mn(CO)_5]_2$, has been determined from X-ray counter data collected at $-123 \pm 2°$. Discrete $Ni(phen)_3{}^{2+}$ cations and $Mn(CO)_5{}^-$ anions crystallize in space group $P\bar{1}$ with lattice constants $a = 13.618$ (5), $b = 14.325$ (5), $c = 12.399$ (8) Å, $\alpha = 102.16$ (4), $\beta = 113.22$ (4), $\gamma = 98.46$ (3)° at −121°. The observed density of 1.535 (10) g/cm^3 at 25° agrees well with that of 1.546 g/cm^3 calculated for two formula units in the cell found at −123°. The $Ni(phen)_3{}^{2+}$ cations show approximate threefold symmetry. The N–Ni–N bite averages 79.4 (5)°; the variations in N–C and C–C bond distances in the ring system are consistent with previous structures. The $Mn(CO)_5{}^-$ anions are trigonal bipyramidal with a small distortion most noticeable in the equatorial plane, where the C–Mn–C bond angles range from 117.5 (3) to 125.0 (4)°. The average of the axial Mn–C bonds is slightly, but not significantly, longer than the average of the equatorial bonds. The Mn–C bond lengths range from 1.77 (1) to 1.82 (1) Å; the difference in axial and equatorial bond averages is 0.02 (2) Å. This difference is considered together with other d^8 complexes having five identical ligands about the central metal atom.

Introduction

Although almost 200 structures[1] of monomeric five-coordinate transition metal complexes have been studied by X-ray diffraction, only a dozen of these are compounds with five identical unidentate ligands. Multidentate ligands often impose steric restrictions on the geometry of the complexes and it is difficult to separate these restrictions from electronic effects. For complexes with several different unidentate ligands, the various effects of the ligands cannot be readily distinguished unless a series of similar structures is studied, *e.g.*, $Mn(NO)(CO)_{4-x}[P(C_6H_5)_3]_x$, $x = 0\text{–}2$,[2–4] or the twelve structures of the form $IrXYZ[P(C_6H_5)_3]_2$.[1] A comparison of structures with five identical ligands is desirable because only a few factors need to be considered for interpreting distortions in bond angles and bond distances.

Most of the ML_5 structures are regular trigonal bipyramids, *viz.*, $CuCl_5{}^{3-}$,[5] $Fe(CO)_5$,[6] $Fe(N_3)_5{}^{2-}$,[7] $Ni[P(OCH)_3(CH_2)_3]_5{}^{2+}$,[8] $Co(C_6H_7NO)_5{}^{2-}$,[9] and $Co(CNCH_3)_5{}^+$.[10] The structures of $Nb[N(CH_3)_2]_5$,[11] $Nb(NC_5H_{10})_5$,[11] and $MnCl_5{}^{2-}$[12] are better described as tetragonal pyramidal. Both trigonal-bipyramidal and tetragonal-pyramidal forms of $Ni(CN)_5{}^{3-}$ have been reported.[13–15] The structure of $Ni(OAsMe_3)_5{}^{2+}$[16] is a tetragonal pyramid and those of $CdCl_5{}^{3-}$[17] and $Pt(SnCl_3)_5{}^{3-}$[18] are trigonal bipyramids, although structural details have not been published for these three complexes.

In most of the trigonal-bipyramidal complexes the axial M–L bond distances differ from the equatorial bond lengths. Such distortions were predicted[19] by Gillespie for low-spin d^7, d^8, and d^9 systems. Because the d_{z^2} orbital is empty or only half-filled, the shape of the d-shell electron cloud will be oblate ellipsoidal. Thus repulsions between nonbonding d electrons and valency-shell electrons will be greater in the equatorial plane and cause the equatorial bonds to be longer than the axial bonds. Acting in the opposite direction are ligand–ligand electrostatic repulsion forces which always favor axial lengthening.

For each of the d^8 and d^9 ML_5 structures studied thus

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