as well as the spin–orbit coupling effects are important in determining transition energies and intensities.

Registry No. K_2PtBr_4, 13826-94-3.

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 Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1366.

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Structure of *trans*-Chloro(methylimido)tetrakis(methylamine) rhenium(V) Perchlorate

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The crystal structure of the *trans*-chloro(methylimido)tetrakis(methylamine)rhenium(V) ion, $[Re(CH_3NH_2)_4(CH_3N)Cl]^{2+}$, has been determined as its perchlorate salt, using scintillation counter techniques in a three-dimensional X-ray diffraction study. The compound crystallizes in the orthorhombic space group *Pnam* with unit cell dimensions $a = 16.908$ (4) Å, $b = 8.641$ (2) Å, and $c = 12.759$ (5) Å. The density of 2.045 (1) g/cm^3 calculated on the basis of four formula units per unit cell is in agreement with the flotation density of 2.01 (2) g/cm^3. The structure was resolved by Patterson and Fourier methods and refined by full-matrix least-squares treatment to a conventional R factor of 4.1% using 1066 independent reflections. The perchlorate ion is disordered. The rhenium is octahedrally coordinated with a chlorine and five nitrogens. The Re–Cl distance is 2.403 (5) Å. The methylimido group is trans to the Cl with the Re–N(imido) distance 1.694 (11) Å and the N(imido)–C distance 1.46 (2) Å. The Cl–Re–N(imido)–C grouping is linear; Cl–Re–N = 179.4 (6)° and Re–N–C = 180 (2)°. The remaining four amine nitrogens are arranged in a plane around the rhenium with the metal above the plane toward the imido nitrogen. The average Re–N(amine) distance is 2.18 (2) Å. The average N(imido)–Re–N(amine) angle is 95.4 (7)°. The rates of Cl^- hydrolysis and isotopic exchange in dilute HCl solution are compared.

Introduction

Considerable interest has been developing in the nature of rhenium–ligand multiple bonds which are often found in complex compounds. Usually the metal is in a high oxidation state and is bonded through nitrogen[1] or oxygen[2,3] atoms. While there is no question as to which atoms are involved in these short bonds, as observed in crystal structure studies, there remains considerable doubt as to "normal distances" for single, double, and triple bonds.

This paper reports the structure of *trans*-chloro(methylimido)tetrakis(methylamine)rhenium(V) perchlorate. Previous work on this compound[3] gave its preparation and identified its basic molecular structure by nmr means. It was found that the rhenium(V) is coordinated to an imino nitrogen and four amine nitrogens of methylamine and that the coordinated chloride ion is trans to the methylimine. The compound thus gives the unique opportunity to compare the geometrical parameters of CH_3–NH_2 with those of CH_3–N while both are bonded to the same rhenium(V) ion. Also of interest is the kinetics of the substitution process involving the coordinated Cl^- trans to the multiple-bonded imine. This structure allows a comparison of the substitution and isotopic exchange parameters with bond distances in this and similar complexes.

Experimental Section

Crystal Preparation. $[Re(CH_3NH_2)_4(CH_3N)Cl](ClO_4)_2$ was prepared as previously described[3] and recrystallized from an acetone–water solution by the slow evaporation of solvent. The deep blue crystals were in the form of elongated octahedra.

X-Ray Data Collection. Precession photographs indicated an orthorhombic cell. The systematic extinctions observed on these photographs were h odd for $h0l$ and $k + l$ odd for $0kl$. Thus the compound is either in the centrosymmetric space group *Pnam*, in which mirror symmetry is present, or the noncentrosymmetric space group $Pna2_1$. Standard optical goniometric methods established the eight faces of the crystal to be 101, $10\bar{1}$, $\bar{1}01$, $\bar{1}0\bar{1}$, 210, $2\bar{1}0$, $\bar{2}10$, and $\bar{2}\bar{1}0$. Decomposition in the X-ray beam was observed and thus the data collection time was kept minimal. The crystal used for the intensity measurements had the dimensions 0.08 mm × 0.06 mm × 0.11 mm, small enough so that absorption corrections could be made with a reasonable degree of accuracy. The crystal was aligned on a Picker programed four-circle diffractometer with the c-axis coincident with the ϕ axis of the diffractometer. Twenty-five intense reflections found on the preliminary photographs were accurately centered using Mo Kα radiation (λ 0.7107 Å). From the setting angles found for these 25 reflections, the cell constants determined by a least-squares[4] refinement were $a = 16.908$ (4) Å, $b = 8.641$ (2) Å, and $c = 12.759$ (5) Å. The calculated density based on four formula units per unit cell was 2.045 (1) g/cm^3 which agrees with the experimental value of 2.01 (2) g/cm^3 determined by flotation. The above refinement was used to calculate the setting angles for all reflections. The intensities were measured with a scintillation detector linear to greater than 8000 counts/sec. The intensities of 2272 reflections were measured out to a 2θ angle of 45°, using Mo Kα radiation filtered through a 1-mil niobium foil in front of a 3 mm × 3 mm receiving aperture. The takeoff angle was 2.0°. A scan rate of 1.0°/min was used for the variable 2θ scan. This scan was taken from 0.19° below the 2θ setting for Kα_1 (λ 0.70926 Å) to 0.31° above the 2θ setting for Kα_2 (λ 0.71354 Å). Stationary-background counts of 20 sec were taken at both ends of the scan. One-mil brass foils were used for attenuation to prevent exceeding 8000 counts/sec. The precalibrated foils gave attenuation factors of about 3. Three reflections chosen as standards were measured every 50 reflections

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(1) J. Chatt, J. R. Dilworth, and G. J. Leigh, *J. Chem. Soc. A*, 2239 (1970), and references therein.

(2) R. Shandles, E. O. Schlemper, and R. K. Murmann, *Inorg. Chem.*, 10, 2785 (1971), and references therein.

(3) R. Shandles and R. K. Murmann, *J. Inorg. Nucl. Chem.*, 27, 1869 (1965).

(4) All calculations were performed on the IBM 360/65 computer of the University of Missouri Computer Research Center using the following programs: W. Hamilton and J. A. Ibers, NUPIK, Picker input program; W. Hamilton, HORSE, general absorption program; R. Doedens and J. A. Ibers, NUCLS, least-squares program and a modification of W. R. Busing and H. A. Levy's ORFLS program; A. Zalkin, FORDAP, Fourier program; C. Johnson, ORTEP, thermal ellipsoid plot program; J. A. Ibers, FINDH, tetrahedral atom placement program.

in order to monitor and correct for the crystal decomposition which was known to occur.

Twenty sets of Friedel's pairs were carefully measured and compared. No significant differences in intensities were found. This along with negative results of a pyroelectric effect test[5] indicated that the centrosymmetric space group, *Pnam*, was correct.

Data Reduction. The 2272 reflections collected were corrected for background. A plot of the background-corrected intensities of the standard reflections *vs.* the observation number (assumed to be proportional to the cumulative X-ray exposure of the crystal) showed a linear decrease in the intensities through the first 1528 observations. These 1528 intensities were corrected using the expression

$$I_{\text{cor}} = I_{\text{obsd}}(1 + n(2.84 \times 10^{-5}))$$

where n is the observation number. After the 1528th observed reflection the intensity of the standards decreased more rapidly so the remainder of the data was not used in the refinement. The maximum correction for decomposition was less than 5%.

Corrections for Lorentz-polarization effects were made and the counting statistics calculated using the formulas previously described.[6] All intensities were corrected for absorption (μ = 73.6 cm^{-1}) using the dimensions of the crystal determined by microscopic techniques and the indices of the faces. The transmission correction factors ranged from 0.38 to 0.53. Equivalent and duplicate reflections were averaged giving 1367 independent reflection intensities. Of these 1367 independent data points, 1066, which were used to determine the structure, had intensities greater than 3σ, where $\sigma = [\sigma^2_{\text{counting}} + (0.04F_{\text{o}}^2)^2]^{1/2}$.

Determination and Refinement of the Structure. The atomic scattering factors for neutral rhenium and chlorine were those by Cromer and Waber.[7] The anomalous scattering effects, both real and imaginary, were taken from Cromer.[8] The N, C, and O neutral atom scattering factor tables were those of Ibers.[9] The anomalous scattering effects for rhenium and chlorine were included in F_{c}[10] in the refinement. From a three-dimensional Patterson synthesis the rhenium atom was located, its z coordinate being $^1/_4$. A least-squares refinement of the rhenium position followed by a three-dimensional Fourier synthesis permitted the positions of Cl1 and N1 to be found, their z coordinates also being $^1/_4$. These atoms are on the mirror plane in *Pnam*. All other nonhydrogen atoms were discernible on the electron density map but gave some indication of two peaks for the nitrogen atoms. On the basis of the position of these peaks, the rhenium complex ion cannot be ordered in space group *Pnam*. Thus refinement was attempted in both *Pnam* and $Pna2_1$, but C1, C2, and C3 would not converge unless their z coordinates were fixed equal to $^1/_4$, the mirror plane in the centrosymmetric structure. For this reason, refinement was continued in *Pnam* with half-occupancy for the nitrogens across the mirror plane. Using all Re, Cl, N, and C atoms, the positional parameters, the isotropic temperature factors, and the isotropic extinction parameter[11] were refined. Several least-squares cycles, minimizing the function $\Sigma w(|F_{\text{o}}|^2 - |kF_{\text{c}}|^2)^2$, converged with $R_1 = \Sigma(||F_{\text{o}}|^2 - |kF_{\text{c}}|^2|)/\Sigma|F_{\text{o}}|^2 = 0.195$ and $R_2 = [\Sigma w \cdot (|F_{\text{o}}|^2 - |kF_{\text{c}}|^2)^2/\Sigma wF_{\text{o}}^4]^{1/2} = 0.303$. In these functions the weight, w, is $1/\sigma^2$ where $\sigma = [\sigma^2_{\text{counting}} + (0.04F_{\text{o}}^2)^2]^{1/2}$. The subsequent Fourier synthesis still left doubt as to the placement of the perchlorate oxygens. Five peaks were evident around Cl2 in a nearby trigonal-bipyramidal arrangement. This was interpreted as representing two tetrahedra having oxygens at each corner with the base of one tetrahedron nearly coincident with the base of the other to give an approximate trigonal plane. The oxygens in this triangle were elongated in the direction perpendicular to the plane. Refinement of these eight half-oxygens as individual atoms was unsuccessful. The oxygens were then placed in two groups such that all oxygen-group center distances were 1.43 Å, and within each group, the O-center-O angles were 109.47°. Both group centers were centered at the same position, that of Cl2. The groups could then rotate around Cl2 but always maintained their idealized tetrahedral structure. Refinement of these groups with constant-temperature factors for the group atoms, anisotropic temperature parameters for Re and Cl atoms, and the N and C thermal parameters isotropic converged to $R_1 = 0.136$ and $R_2 = 0.167$. With all nongroup atoms having anisotropic thermal parameters the full-matrix least-squares refinement yielded $R_1 = 0.085$ and $R_2 = 0.124$. The isotropic temperature factors of the oxygens ranged from 10 to 25. Since the group refinement program did not allow anisotropic thermal parameters for group atoms, the eight oxygens were removed from the groups but each oxygen constrained so that its x, y, and z coordinates relative to Cl2 remained constant. Several cycles with all atoms having anisotropic thermal parameters converged with $R_1 = 0.070$ and $R_2 = 0.102$. The inclusion of anisotropic thermal parameters was significant at the 95% confidence level according to Hamilton's R factor ratio test.[12] The conventional agreement factor

$$R = \Sigma(||F_{\text{o}}| - |kF_{\text{c}}||)/\Sigma|F_{\text{o}}|$$

was 0.041. The standard deviation of an observation of unit weight was 1.70. The isotropic extinction coefficient was (8.4 (5)) × 10^{-6}. A final difference Fourier synthesis was carried out as a check on the correctness of the structure. The largest residual peaks were found near the carbon atoms and showed an electron density of 0.7 e/Å^3 possibly due to the methyl hydrogens which would be disordered. No hydrogens were included in any refinement. The largest peaks near the rhenium atom were 0.6 e/Å^3. The observed and calculated structure factors (×10) appear only in the microfilm edition of this journal.[13] The final atom positional and thermal parameters are presented in Table I.

Kinetic Measurements. The kinetics of hydrolysis at 25° according to the equation

$$[\text{Re}(\text{CH}_3\text{NH}_2)_4(\text{CH}_3\text{N})\text{Cl}]^{2+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [\text{Re}(\text{CH}_3\text{NH}_2)_4(\text{CH}_3\text{N})\text{OH}]^{2+} + \text{Cl}^- + \text{H}_{\text{aq}}^+$$

were evaluated from spectral measurements following the decrease in $[\text{Re}(\text{CH}_3\text{NH}_2)_4(\text{CH}_3\text{N})\text{Cl}]^{2+}$ and the increase in $[\text{Re}(\text{CH}_3\text{NH}_2)\text{-}(\text{CH}_3\text{N})(\text{OH})]^{2+}$ as a function of time. Air was excluded since some oxidation of Re(V) occurred. LiCl or toluenesulfonic acid was used to modify the H_{aq}^+ and Cl^- concentrations. The rates of hydrolysis were sensibly identical for the two separate measurements. After equilibrium was reached, rate studies of isotopic exchange were initiated by adding a trace of $^{36}\text{Cl}^-$. At timed intervals $[\text{Re}(\text{CH}_3\text{NH}_2)_4(\text{CH}_3\text{N})\text{Cl}](\text{ClO}_4)_2$ was precipitated, purified, and counted. From the concentrations of the chloro and hydroxo complex determined spectrally, values for K_{eq} were obtained.

Results and Discussion

Nature of the Structure. The structure consists of discrete perchlorate ions and pseudooctahedral $[\text{Re}(\text{CH}_3\text{NH}_2)_4\text{-}(\text{CH}_3\text{N})\text{Cl}]^{2+}$ ions (Figure 1). There are two sets of equally occupied positions for the perchlorate oxygens and the methylamine nitrogens (Figure 2). The positive ion has a linear Cl-Re-N-C arrangement in which the short Re-N bond length of 1.69 (1) Å is indicative of a multiple bond in keeping with the ionization of two hydrogens from this methylimine nitrogen. Four methylamine nitrogens (average Re-N = 2.18 (1) Å) complete the octahedral coordination of the rhenium in an almost perfect square with the rhenium 0.2 Å above the plane toward the imido nitrogen.

When the amine nitrogens occupy one of the two sets of orientations shown in Figure 2, the perchlorate oxygens on one side of the mirror plane are apparently O1-O4 while those on the other side of the mirror are O5-O8. This assumption gives the most reasonable N(amine)---O(perchlorate) hydrogen bond distances and N---O-Cl angles (Table

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(5) C. W. Bunn, "Chemical Crystallography," Oxford University Press, London, 1961, p 321.

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

(7) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

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

(9) J. A. Ibers in "International Tables X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(10) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964).

(11) W. H. Zachariasen, *Acta Crystallogr.*, 16, 1139 (1963).

(12) W. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964, p 158.

(13) See paragraph at end of paper regarding supplementary material.

Table I. Final Atomic Parameters[a] for $[Re(CH_3NH_2)_4(CH_3N)Cl](ClO_4)_2$

	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	0.11606 (4)	0.19897 (7)	1/4	0.00371 (3)	0.01437 (1)	0.00647 (5)	−0.00022 (5)	0	0
Cl1	0.0062 (3)	0.0225 (6)	1/4	0.0052 (2)	0.0204 (8)	0.0102 (4)	−0.0025 (3)	0	0
Cl2	0.3548 (2)	0.1715 (3)	0.9940 (3)	0.0047 (1)	0.0176 (5)	0.0099 (3)	0.0004 (2)	0.0001 (2)	−0.0002 (3)
N1	0.1929 (7)	0.3248 (14)	1/4	0.0029 (5)	0.0148 (21)	0.0085 (11)	−0.0025 (9)	0	0
N2	0.184 (1)	0.005 (2)	0.190 (1)	0.006 (1)	0.021 (4)	0.010 (2)	0.004 (2)	−0.001 (1)	−0.004 (2)
N3	0.031 (1)	0.364 (2)	0.317 (2)	0.005 (1)	0.019 (3)	0.009 (2)	0.001 (2)	0.000 (1)	0.003 (2)
N4	0.073 (1)	0.253 (2)	0.094 (2)	0.006 (1)	0.017 (3)	0.008 (2)	−0.002 (2)	0.000 (1)	0.001 (2)
N5	0.139 (1)	0.114 (2)	0.407 (2)	0.005 (1)	0.019 (3)	0.008 (2)	−0.002 (2)	−0.001 (1)	−0.000 (2)
C1	0.259 (1)	0.433 (2)	1/4	0.006 (1)	0.021 (3)	0.011 (1)	−0.002 (2)	0	0
C2	0.258 (1)	0.955 (3)	1/4	0.006 (1)	0.025 (4)	0.015 (2)	0.005 (2)	0	0
C3	0.004 (2)	0.492 (3)	1/4	0.011 (1)	0.019 (4)	0.012 (2)	0.004 (2)	0	0
C4	0.089 (1)	0.163 (2)	0.500 (1)	0.008 (1)	0.025 (3)	0.009 (1)	0.001 (1)	0.001 (1)	0.003 (2)
O1	0.3493[a]	0.2793	0.0787	0.034 (6)	0.028 (6)	0.035 (8)	0.004 (6)	0.016 (5)	−0.013 (6)
O2	0.4278	0.0886	0.0012	0.020 (3)	0.037 (7)	0.042 (7)	0.008 (4)	−0.019 (4)	−0.010 (7)
O3	0.3519	0.2537	0.8976	0.038 (7)	0.065 (14)	0.014 (4)	0.009 (9)	0.003 (4)	0.009 (6)
O4	0.2903	0.0650	0.9994	0.012 (2)	0.034 (8)	0.044 (7)	−0.006 (3)	−0.001 (3)	0.002 (6)
O5	0.3965	0.2266	0.9039	0.013 (2)	0.035 (6)	0.022 (4)	0.009 (3)	−0.011 (2)	0.14 (4)
O6	0.2761	0.2319	0.9934	0.004 (1)	0.054 (7)	0.018 (3)	0.004 (2)	0.002 (1)	0.006 (4)
O7	0.3947	0.2215	0.0869	0.012 (2)	0.061 (10)	0.029 (5)	0.008 (4)	−0.007 (2)	−0.033 (6)
O8	0.3520	0.0062	0.9918	0.047 (8)	0.015 (4)	0.022 (4)	0.005 (5)	0.010 (4)	−0.002 (4)

[a] Standard deviations from the least-squares refinement are included in parentheses in this and subsequent tables. O1 through O8 are the "idealized" tetrahedral perchlorate oxygens whose x, y, and z coordinates were not refined. [b] The form of the anisotropic thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II. Interionic Distances[a] (Hydrogen Bonding)

Bond	Value, Å	Cl-O-N angle, deg	Bond	Value, Å	Cl-O---N angle, deg
N2---O4	3.07 (2)	126	N4---O2	3.06 (2)	120
N2---O5	3.02 (2)	111	N4---O8	2.75 (2)	142
N3---O2	3.13 (2)	120	N5---O3	3.11 (2)	117
N3---O7	2.72 (2)	134	N5---O6	2.85 (2)	129

[a] These are based on the most reasonable choice of perchlorate oxygen positions for a given arrangement of the amine nitrogens.

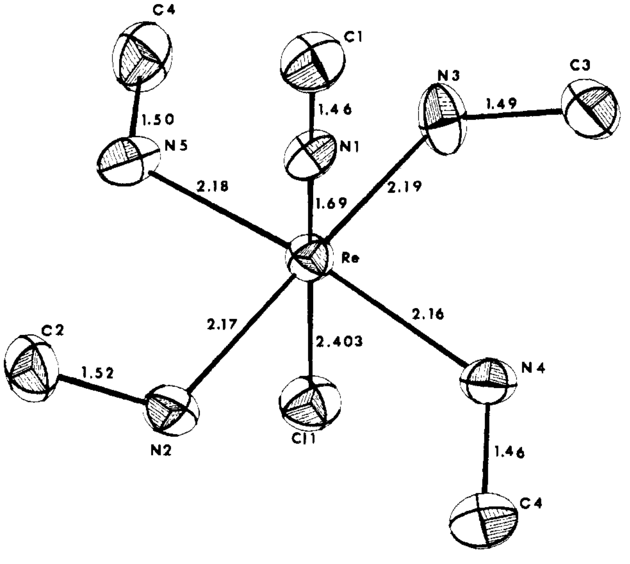

Figure 1. Bond distances in the $[Re(CH_3NH_2)_4(CH_3N)Cl]^+$ ion.

II) in which each amine nitrogen is involved in hydrogen bonds with two perchlorate oxygens.

The rms components of thermal motion (Table III) add credibility to the choice of the centrosymmetric space group. None of the atoms in the metal complex have highly anisotropic motion although the maximum vibration is frequently as much as 50% greater than the minimum. The atoms on the mirror plane except for C2 and C3 have their maximum vibration essentially in the mirror rather than perpendicular to it (Figure 2). For C2 and C3 the maximum is perpendicular to the mirror, but this could be a result of the disorder in the nitrogens. C2 and C3 might actually occupy slightly different positions when the nitrogens are reflected. C4 has the same possibility but the shape of the ellipsoid does not support a disordered carbon. Except for C2 and C3 there is no elongation perpendicular to the mirror to suggest the wrong choice of space groups. The thermal motion of the disordered oxygens, but not the chlorine, in the perchlorate group is high and very anisotropic. The rms components of the oxygens are 2-3 times those in the chlorine atom, but this is not without precedence.[14]

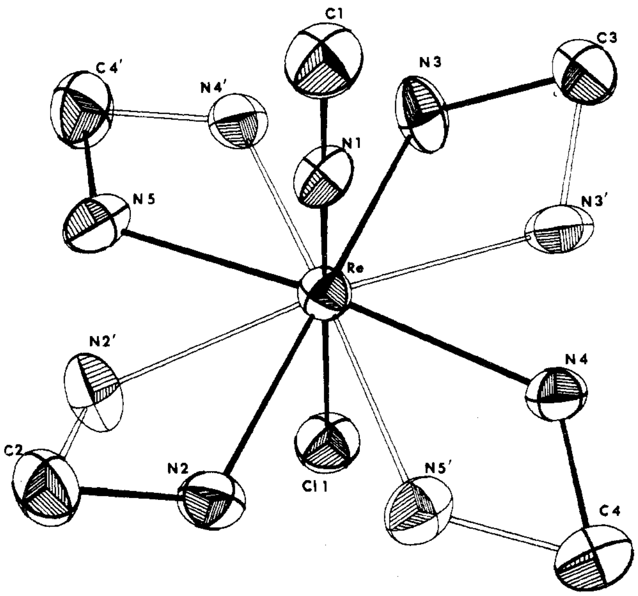

Figure 2. Open bonds illustrate the alternative positions for the amine nitrogens in the $[Re(CH_3NH_2)_4(CH_3N)Cl]^+$ ion.

Bond Distances and Angles. The intraionic bond distances in the rhenium complex are shown in Figure 1, and the bond angles are given in Table IV. The distances and angles are compared with those in related complexes[15,16] in Table V. Although there are no other Re-N(methylamine) distances to compare with the average Re-N(amine)

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(14) B. A. Coyle and J. A. Ibers, *Inorg. Chem.*, 11, 1105 (1972).
(15) D. Bright and J. A. Ibers, *Inorg. Chem.*, 8, 703 (1969).
(16) D. Bright and J. A. Ibers, *Inorg. Chem.*, 7, 1099 (1968).

Table III. Rms Components of Thermal Displacement along the Principal Axes (Å)

Atom	Axis 1	Axis 2	Axis 3
Re	0.223 (2)	0.228 (3)	0.246 (2)
Cl1	0.240 (6)	0.290 (5)	0.307 (6)
Cl2	0.254 (4)	0.266 (5)	0.286 (4)
N1	0.17 (2)	0.26 (2)	0.26 (2)
N2	0.23 (3)	0.26 (3)	0.35 (3)
N3	0.24 (3)	0.26 (3)	0.31 (3)
N4	0.24 (3)	0.25 (3)	0.31 (3)
N5	0.24 (3)	0.26 (3)	0.31 (3)
C1	0.25 (3)	0.30 (2)	0.30 (3)
C2	0.24 (3)	0.34 (3)	0.36 (3)
C3	0.26 (3)	0.31 (3)	0.38 (3)
C4	0.24 (2)	0.32 (2)	0.35 (2)
O1	0.24 (4)	0.49 (5)	0.77 (7)
O2	0.32 (4)	0.36 (4)	0.74 (6)
O3	0.32 (5)	0.50 (5)	0.75 (7)
O4	0.31 (4)	0.45 (4)	0.60 (5)
O5	0.25 (3)	0.29 (3)	0.59 (5)
O6	0.23 (3)	0.36 (3)	0.48 (3)
O7	0.22 (4)	0.38 (4)	0.68 (5)
O8	0.23 (3)	0.40 (4)	0.84 (6)

Table IV. Bond Angles in $[Re(CH_3NH_2)_4(CH_3N)Cl]^{2+}$

Angle	Value, deg	Angle	Value, deg
Cl1-Re-N1	179.4 (6)	N2-Re-N5	91.2 (8)
Cl1-Re-N2	85.5 (6)	N2-Re-N2	87.9 (8)
Cl1-Re-N3	84.8 (6)	N3-Re-N4	90.0 (8)
Cl1-Re-N4	83.1 (5)	N3-Re-N5	88.9 (8)
Cl1-Re-N5	85.1 (5)	N4-Re-N5	168.2 (7)
N1-Re-N2	95.1 (7)	Re-N1-C1	180 (2)
N1-Re-N3	94.7 (7)	Re-N2-C2	119 (1)
N1-Re-N4	96.7 (5)	Re-N3-C3	119 (1)
N1-Re-N5	95.1 (5)	Re-N4-C4	125 (1)
N2-Re-N3	169.9 (8)	Re-N5-C4	122 (1)

Table V. Selected Distances and Angles in Rhenium(V)-Imido Complexes

	A	B	C	D
Re≡N, Å	1.694 (11)	1.685 (11)	1.709 (4)	1.690 (5)
≡N–C, Å	1.46 (2)	1.40 (2)	1.373 (11)	1.379 (10)
Re–Cl (trans to imido) Å	2.403 (5)	2.411 (6)	2.432 (2)	2.410 (3)
Cl–Re≡N, deg	179.4 (6)	174.6 (4)	180	175.0 (2)
Re≡N–C, deg	179.8 (18)	173.4 (10)	175.8 (1)	171.8 (4)

[a] A = $[Re(CH_3NH_2)_4(CH_3N)Cl](ClO_4)_2$; B = $Re(CH_3N)[P(C_6H_5)_2C_2H_5]_2Cl_3$;[15] C = $Rc(NC_6H_4OCH_3)[P(C_2H_5)_2C_6H_5]_2Cl_3$;[16] D = $Re(NC_6H_4COCH_3)[P(C_2H_5)_2C_6H_5]_2Cl_3$.[16]

distance (2.18 (2) Å), the distance is comparable to that observed[17] for Os-N(ammonia) of 2.14 (1) Å in $OsCl_3(NH_3)[P(C_6H_5)_3]_2$ and is probably representative of a Re-N single bond. In contrast there are several measurements of Re-N "triple-bond" distances (Table V) including that (1.69 (1) Å) in $Re(CH_3N)[P(C_6H_5)_2C_2H_5]_2Cl_3$[15] which compares well with the Re-N(imine) distances of 1.69 (1) Å observed in this study. The remaining bond angles and distances are also comparable with those observed by others. The average Re-N-C angle of 121 (2)° is surprisingly large but is supported by that (122.1 (4) Å) observed[18] in $[Co(NH_2CH_3)_5Cl](NO_3)_2$. The range of N-C distances observed in that study was 1.479-1.516 Å in agreement with this work (average 1.49 (2) Å). This is also in reasonable agreement with the sum of the covalent radii[19] 1.47 Å. The N(imine)-Re-N(amine) angles (94.7-96.7°) reflect the displacement of the rhenium from the amine square plane toward the imido group. This results in average Cl---N distances of 3.09 (2) Å considered to be optimum nonbonded contact distances while the N(imine)---N(amine) distances average 2.88 (2) Å. The methyl groups alternate above and below the square plane in the pinwheel-like arrangement. The Re-Cl distances are in good agreement with those found for other complexes[13-15] with the chlorine trans to an imino nitrogen. In those complexes it was found that the cis Re-Cl distances were essentially identical with the trans. Unlike the situation in the phosphine complexes, there is little difficulty with steric interaction of the ligands because of the relatively small methylamine groups. For this reason the observed metal-ligand bond distances probably reflect more nearly the preference of the metal atom so that the Re-N(imine) distance (1.69 (1) Å) probably represents an "ideal" distance for this type of nitrogen bonded to rhenium(V). The linear Re-N-C arrangement suggests that the nitrogen orbitals are hybridized appropriately for a formal "triple bond." That this distance is longer than that observed[20] for the Re-N(nitrido) distance (1.60 (1) Å) in the five-coordinate complex $ReNCl_2(P(C_6H_5)_3)_2$ may be a reflection of the presence of a sixth ligand trans to a Re-N multiple bond. However in $OsNCl_5^{2-}$, the Os-N distance (1.61 (1) Å)[21] tends to discredit that argument so that the longer Re-N distance in the imine complexes is apparently a result of an organic substituent on the nitrogen. This lengthening is not surprising in light of the unfavorable formal charge which would be associated with such a "triple-bonded" nitrogen.

Hydrolysis and Isotopic Exchange Rates. The results of six runs with $[H^+] = 0.1\,M$ and $[Cl^-] = 0.12$-$0.87\,M$ at 25° were $K_{eq} = (3.7 \pm 0.1) \times 10^{-2}\,M^{-2}$, while for six runs at $[Cl^-] = 0.12\,M$ and $[H^+] = 0.10$-$0.89\,M$, $K_{eq} = (3.3 \pm 0.3) \times 10^{-2}\,M^{-2}$. The average is $(3.5 \pm 0.2) \times 10^{-2}\,M^{-2}$. For first-order hydrolysis constants averages of $(1.85 \pm 0.50) \times 10^{-2}$ and $(1.70 \pm 0.44) \times 10^{-2}$ min^{-1} were found following the concentration of reactant and product, respectively. The average is $(1.8 \pm 0.5) \times 10^{-2}$ min^{-1}. For the same solutions first-order isotopic exchange values were $k_{exch} = (0.97 \pm 0.11) \times 10^{-2}$ min^{-1}. From these values one calculates first-order rate constants of hydrolysis and exchange of $[Re(CH_3NH_2)_4(CH_3N)Cl]^{2+}$ of $(6 \pm 1) \times 10^{-4}$ min^{-1} and $(1 \pm 0.1) \times 10^{-2}$ min^{-1} respectively, K_{eq} of $(3.5 \pm 0.2) \times 10^{-2}\,M^{-2}$ and k_r of $(1.7 \pm 0.2) \times 10^{-2}\,M^{-2}$ min^{-1} in acidic media at 25°.

From these results two conclusions emerge. First the rate constant of isotopic exchange is twenty times larger than the rate constant of hydrolysis. This may result from the partially dissociated activated complex preferring a negative ion, Cl^-, to water because of its own positive charge. Second, while the Cl^- trans to the CH_3N^{2-} group is more labile than that in, for example, $ReCl_6^{2-}$, a large effect is not found. This may be rationalized on the basis of opposing effects: one due to increased metal ion and complex positive charge and the other to the trans effect of electron donation by the strongly bound CH_3N^{2-}.

Registry No. $[Re(CH_3NH_2)_4(CH_3N)Cl](ClO_4)_2$, 51014-18-7.

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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 Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1373.

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Platinum Bronzes. IV.[1] Preparation, Crystal Chemistry, and Physical Properties

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The syntheses of several ternary platinum oxides are reported. The Na and Cd bronzes $Na_xPt_3O_4$ and $Cd_xPt_3O_4$ as well as the bronze-like $CaPt_2O_4$ were prepared in powder form under atmospheric pressure. The existence of Pt_3O_4 is discussed. Syntheses for $Cd_xPt_3O_6$ and a poorly defined new simple oxide of platinum with stoichiometry Pt_5O_6 are given. The stability of these various oxides is discussed and their lattice parameters are given. The crystal chemistry of these oxides is systematized using stability fields for the platinum bronzes and for A_3BX_4 compounds. The close structural relationship between the bronzes and Ag_3PO_4 and Ag_3AsO_4 is discussed. Photoelectron spectroscopic, magnetic susceptibility, and electrical conductivity data for the bronzes and various other platinum oxides are reported. From these data it is concluded that most bronzes are metallic oxides and a qualitative one-electron energy-band scheme is given explaining this metallic character. The nonexistence of $CaPt_3O_4$ is discussed in terms of both this scheme and thermodynamics. The tendency of the bronzes to incorporate large quantities of foreign cations is explained in terms of the cage-like bronze structure.

Introduction

As stated in the previous papers in this series[1] one of the main reasons for the study of platinum oxides arises from the use of platinum as a supposedly inert material in high-temperature chemistry. Because most high-temperature reactions and processes are studied under normal-pressure conditions, those oxides that form under atmospheric pressure are of special importance. Interest in platinum oxides is by no means new. Ever since the early studies of Jorgensen and Wohler[2] these oxides have been a matter of controversy. Several oxides have been reported and forgotten because their existence could not be verified.[3] Even today the electrochemical literature abounds with electrode reactions involving "PtO," a compound whose existence is at least doubtful.[4] The catalytic activity of some oxides of this noble metal provides a further impetus for investigating their existence, formation, and stability.

This last point, the stability of the noble metal oxides, was stressed by Shannon and coworkers in their report on ABO_2 delafossite-type noble metal oxides.[5] Although new thermodynamic data for PdO, PtO_2, and "Pt_3O_4" (see below) tend to ascribe a higher stability to these oxides than was previously accepted ($\Delta G_f^\circ = -40, -75$, and -88 kcal/mol, respectively, for 2 PdO,[6a] PtO_2,[6b] and $^1/_2$ Pt_3O_4[6c]), their contention that ternary noble metal oxides (especially with a transition metal) are difficult to prepare remains valid. Yet most platinum-metal bronzes, which are ternary oxides of general formula $A_3B_xO_4$, where B is commonly a group I or II cation, $0 < x < 1$, and A is Pt or Pd, can be prepared at atmospheric pressure in powder form. We have thus concentrated our studies on the platinum bronzes. Earlier we reported the crystal structure of $Ni_{0.25}Pt_3O_4$, as derived from single-crystal X-ray diffraction data.[1a] A neutron- and X-ray powder diffraction study showed $Cd_{0.3}Pt_3O_4$ to have essentially the same structure, while that of $CaPt_2O_4$ turns out to be closely related.[1b] Also the catalytic activity of some platinum bronzes and other platinum oxides has been reported.[1c] Both the structural and catalytic data show that the bronzes are an unusual family of metal oxides. The present paper deals with the preparation of $Cd_xPt_3O_4$, $CaPt_2O_4$, $Na_xPt_3O_4$, and related platinum oxides. The crystal chemistry of the platinum and palladium bronzes and the silver "pseudobronzes" Ag_3PO_4 and Ag_3AsO_4 will be discussed. In the second part of this paper the results of X-ray photoelectron spectroscopic (XPS = XPES = ESCA), magnetic susceptibility, and electrical conductivity studies of the bronzes are presented and interpreted in terms of the bronze structure and a qualitative energy-band scheme.

Experimental Section

Reagents. The starting materials used were all reagent grade or better. The Pt-containing starting materials were prepared from either Pt sponge or K_2PtCl_4. $(NH_4)_2PtCl_6$ and $H_2PtCl_6 \cdot 6H_2O$ were prepared according to well-known literature methods.[7] For the preparation of Pt black we found the method of Tetenyi and Babernics[8] to give better results than that of Brauer.[9] Contrary to what has been reported by Scheer for $NaPt_3O_4$, we found that drying

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