

A Dichlorine to Oxide Ion Charge-Transfer Complex. Oxidation of Hexasilver to Silver Chloride by Dichlorine. Crystal Structure of $H_{2.25}Ag_{12}Cl_{2.25}Si_{12}Al_{12}O_{48} \cdot 6Cl_2$, a Chlorine Sorption Complex of Partially Dehydrated Fully Ag^+ -Exchanged Zeolite A

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Abstract: The crystal structure of a chlorine sorption complex of partially dehydrated fully Ag^+ -exchanged zeolite A has been determined by single-crystal x-ray diffraction methods in the cubic space group $Pm\bar{3}m$ at 23 (1) °C: $a = 12.244$ (1) Å. The structure was refined to the final error indexes, $R_1 = R_2$ (weighted) = 0.082, using the 279 independent reflections for which $I_0 > 3\sigma(I_0)$. Crystallographic analysis shows that most of the Ag^+ ions in the structure occupy threefold-axis equipoints near the centers of 6-rings: 5.25 Ag^+ ions lie at sites of near trigonal planar coordination, and 2.25 nearly tetrahedral Ag^+ ions are recessed 0.64 Å into the large zeolite cavity where each coordinates to a threefold-axis chloride ion. A total of 2.25 $AgCl$ molecules have formed per unit cell by the oxidation of that many silver atoms (as hexasilver molecules) by dichlorine. Each chloride ion is coordinated to three Ag^+ ions, one of which approaches a chlorine atom of a dichlorine molecule. The number of Ag^+ ions which were newly oxidized, 2.25, lie opposite 4-oxygen rings in the large cavity to coordinate to Cl^- ions, and are no longer associated with 8-oxygen rings, sites which were occupied in the structure of vacuum-dehydrated fully Ag^+ -exchanged zeolite A. A total of six chlorine molecules were sorbed without reaction per unit cell; of these, 2.25 are associated with $AgCl$ molecules (vide supra). Each Cl_2 molecule approaches a framework oxide ion axially, with $O-Cl = 2.87$ (7) Å and $O-Cl-Cl = 166$ (2)°, indicating a charge-transfer interaction. The dichlorine bond length, 2.49 (7) Å, is very much elongated. A short 2.36 (7) Å approach between 75% of the pairs of chlorine molecules requires the presence of a H^+ ion between them. It must have been the complete dissociation of 1.125 residual water molecules which provided these protons, as well as the oxide ions which, by their oxidation to O_2 , initially reduced some Ag^+ ions to Ag_6 .

Introduction

Vacuum-dehydrated fully Ag^+ -exchanged zeolite A^{1,2} contains silver atoms, probably as hexasilver molecules centered within some of its sodalite cavities.³ The number of silver clusters in seven separate crystallographic determinations^{1,2} has been found to depend upon the dehydration/decomposition time and temperature. Ammonia at 25 °C displaces Ag_6 molecules from the zeolite structure and, in turn, trimerizes and is complexed by Ag^+ to form the saturated hydronitrogen complexes $Ag_2(N_3H_5)_3^{2+}$ and $Ag(N_3H_3)^+$.⁴

In the crystal structure of an iodine sorption complex of Ca_4Na_4A ^{5,6} and that of a bromine sorption complex of dehydrated fully Ag^+ -exchanged zeolite A,⁷ the halogen molecules interact with oxide ions of the zeolite framework. In these structures, the Br_2 and I_2 molecules act as Lewis acids with respect to framework oxide ion lone pairs. Linear X-X-O sequences, with the X_2 bond lengthened by complexation,^{8,9} were found in these charge-transfer complexes ($O-I-I = 178^\circ$ and $O-Br-Br = 174$ (4)°). On the other hand, in the structure of a bromine sorption complex of $Na_{12}A$,¹⁰ about six bromine molecules per unit cell were found to interact neither with the anionic framework nor with the 8 of the 12 Na^+ ions per unit cell which were located.

Chlorine gas at 220 Torr and 25 °C was sorbed onto a single crystal of vacuum-dehydrated europium(II)-exchanged zeolite A, $Eu_{5.5}NaA$.⁶ The resulting crystal structure showed that the coordination numbers of four Eu(II) ions¹¹ per unit cell had increased from three to five by the addition of two one-coordinate chloride ions each at very short distances, 2.52 and 2.06 Å. It was concluded that dichlorine had oxidized Eu(II) to Eu(IV).¹¹ When Cl_2 gas was sorbed onto a single crystal of vacuum-dehydrated Co_4Na_4A ,⁶ the chlorine molecules coordinated to the transition metal ion in a bent manner. The chlorine molecule is equatorially basic with respect to the hard

acid Co(II), and the dichlorine bond is lengthened by a large amount, approximately 0.5 Å, upon complexation.¹²

This work was initiated to determine the positions of the sorbed chlorine molecules within the zeolite, and to observe the stability or the reactivity of the uncharged silver cluster (probably the hexasilver molecule) in the sodalite unit³ of vacuum-dehydrated Ag^+ -exchanged zeolite A. In addition, because the activation of a silver catalyst on α -alumina for the partial oxidation of ethylene is done by exposing the catalyst to chlorine compounds, the situation of potential chloride ions in this structure was of interest.¹³

Experimental Section

Crystals of zeolite 4A were prepared by Charnell's method,¹⁴ modified by the inclusion of seed crystals from a previous preparation. A single crystal 0.08 mm on an edge was selected and lodged in a fine capillary. $AgNO_3$ (0.05 M) was allowed to flow past the crystal at about 1.0 cm/s for 3 days; since the exchange of Ag^+ for Na^+ has been shown to be facile and complete after much milder treatment,¹⁵ complete exchange was assured in this case. The clear, colorless, hydrated Ag^+ -exchanged crystal was dehydrated for 4 days at 400 °C and 5×10^{-6} Torr. The crystal initially became black, but this color lightened to brick red and ultimately to clear yellow during the dehydration treatment. At this point, the crystal was treated with ca. 600 Torr of Cl_2 gas (99.96%, Matheson Co.) and immediately became black. After 2 h, the crystal, still in its chlorine atmosphere, was sealed in its capillary by torch.

X-Ray Data Collection. The cubic space group $Pm\bar{3}m$ (no systematic absences) was used throughout this work for reasons discussed previously.^{3a,16,17} A Syntex four-circle computer-controlled diffractometer with molybdenum radiation ($K\alpha_1$, $\lambda = 0.709$ 30 Å; $K\alpha_2$, $\lambda = 0.713$ 59 Å), a graphite monochromator, and a pulse-height analyzer was used throughout for preliminary experiments and for the collection of diffraction intensities. The unit cell constant, as determined by a least-squares refinement of 15 intense reflections for which $20^\circ < 2\theta < 24^\circ$, is 12.244 (1) Å at 23 °C. Reflections from two in-

Table I. Positional, Thermal,^a and Occupancy Parameters for the Chlorine Sorption Complex of Dehydrated Fully Ag⁺-Exchanged Zeolite A

	Position	x	y	z	β_{11}^b or B_{180}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy factor	
											Varied	Fixed ^c
(Si,Al)	24(k)	0	1824 (5)	3697 (4)	30 (4)	25 (4)	15 (4)	0	0	-4 (6)	1 ^d	1 ^d
O(1)	12(h)	0	2130 (17)	1/2	181 (30)	40 (18)	18 (15)	0	0	0	1	1
O(2)	12(i)	0	2962 (10)	2962 (10)	28 (14)	32 (9)	32 (9)	0	0	28 (26)	1	1
O(3)	24(m)	1121 (8)	1121 (8)	3374 (12)	49 (8)	49 (8)	96 (16)	65 (21)	0 (17)	0 (17)	1	1
Ag(1)	8(g)	1954 (11)	1954 (11)	1954 (11)	181 (16)	181 (16)	181 (16)	304 (32)	304 (32)	304 (32)	0.73 (5)	0.656
Ag(2)	8(g)	2177 (21)	2177 (21)	2177 (21)	66 (7)	66 (7)	66 (7)	71 (17)	71 (17)	71 (17)	0.28 (4)	0.281
Ag(3)	12(j)	2385 (8)	2385 (8)	1/2	100 (11)	100 (11)	50 (11)	-136 (30)	0	0	0.20 (1)	0.188
Cl(1)	8(g)	3258 (23)	3258 (23)	3258 (23)	112 (23)	112 (23)	112 (23)	-18 (49)	-18 (49)	-18 (49)	0.28 (4)	0.281
Cl(2)	24(l)	695 (44)	4329 (33)	1/2	546 (150)	168 (51)	445 (96)	105 (96)	0	0	0.26 (4)	1/4
Cl(3)	24(l)	1758 (39)	3940 (46)	1/2	18.0 (24) ^e						0.26 (2)	1/4
Ag(4)	24(l)	3044 (63)	3753 (85)	1/2	45.3 (64) ^e						0.12 (2)	0.094

^a Positional and anisotropic parameters are given $\times 10^4$. Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameter. The anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^b Root mean square displacements can be calculated from β_{ij} values using the formula $\mu_i = 0.225a(\beta_{ii})^{1/2}$, where $a = 12.244$ (1) Å. ^c All crystallographic parameters and esd's, with the exception of those in the previous column, were calculated using these internally consistent fixed occupancy numbers. ^d Occupancy for (Si) = 1/2; occupancy for (Al) = 1/2. ^e Isotropic thermal parameter in units of Å².

Table II. Selected Interatomic Distances (Å) and Angles (deg)^a

(Si,Al)-O(1)	1.638 (7)
(Si,Al)-O(2)	1.659 (14)
(Si,Al)-O(3)	1.667 (10)
Ag(1)-O(3)	2.26 (2)
Ag(2)-O(3)	2.34 (3)
Ag(3)-O(1)	2.94 (1)
Ag(4)-Cl(1)	2.23 (4)
Ag(4)-Cl(3)	2.55 (10)
Ag(2)-Cl(1)	2.29 (4)
Ag(3)-Cl(1)	2.61 (3)
Cl(2)-Cl(3)	2.49 (7)
Cl(2)-O(1)	2.82 (7)
Cl(2)-Cl(2)	2.36 (7)
O(1)-(Si,Al)-O(2)	109.6 (9)
O(1)-(Si,Al)-O(3)	110.4 (8)
O(2)-(Si,Al)-O(3)	107.7 (7)
O(3)-(Si,Al)-O(3)	110.9 (9)
(Si,Al)-O(1)-(Si,Al)	153.5 (8)
(Si,Al)-O(2)-(Si,Al)	155.7 (9)
(Si,Al)-O(3)-(Si,Al)	142.4 (9)
O(3)-Ag(1)-O(3)	119.4 (9)
O(3)-Ag(2)-O(3)	112.7 (12)
O(1)-Ag(3)-O(1)	77.8 (2)
O(3)-Ag(2)-Cl(1)	106 (1)
Ag(2)-Cl(1)-Ag(3)	90 (1)
Ag(2)-Cl(1)-Ag(4)	136 (3)
Ag(3)-Cl(1)-Ag(4)	127 (1)
Cl(1)-Ag(4)-Cl(3)	136 (3)
Ag(4)-Cl(3)-Cl(2)	84 (2)
O(1)-Cl(2)-Cl(3)	166 (2)

^a Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding value.

tensity-equivalent regions of reciprocal space (hkl , $h \leq k \leq l$; and hkl , $h \leq l \leq k$) were examined using the θ - 2θ scan technique. For each region of reciprocal space, the intensities of all lattice points for which $2\theta < 70^\circ$ were recorded.

The raw data from each region were corrected for Lorentz and polarization effects, including that due to incident beam monochromatization; the reduced intensities were merged; and the resultant estimated standard deviations were assigned to each averaged reflection by the computer program COMPARE.¹⁸ The standard deviation of each unmerged reflection is

$$\sigma(I_{hkl}) = [((CT + B_1 + B_2)\omega^2) + (pI_{hkl})^2]^{1/2}$$

The value of p was taken as 0.02,¹⁹ a value found to be appropriate for the instrumentation used. Other details of the data reduction have been discussed previously.²⁰ An absorption correction was judged to be negligible and was not applied.^{7,21} Of the 877 pairs of reflections examined, only the 279 whose net counts exceeded three times their corresponding esd's were used in structure solution and refinement.

Structure Determination. Full-matrix least-squares refinement was initiated using the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), and O(3)] and of the Ag⁺ position at (0.188, 0.188, 0.188) in an ethylene sorption complex of dehydrated fully Ag⁺-exchanged zeolite A.²¹ Anisotropic refinement of this structure model converged to an R_1 index, $\Sigma|F_o - |F_c||/\Sigma F_o$, of 0.30 and a weighted R_2 index, $(\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2)^{1/2}$, of 0.35. The number of Ag⁺ ions on the threefold axes refined to 9.6 Ag⁺ ions. This number was reset to 8.0, the maximum occupancy at this position.

A difference Fourier synthesis revealed two large peaks (11.6 and 4.1 e Å⁻³ in height, esd = 0.6 e Å⁻³) at (0.234, 0.234, 0.5) and (0.406, 0.406, 0.5). Only the first peak was stable in least squares; it refined to 2.5 Ag⁺ ions. The thermal ellipsoids of the threefold-axis Ag⁺ ions became very elongated in subsequent refinements, indicating the presence of two nonequivalent Ag⁺ ions at this position. These were refined at $x = 0.19$ and $x = 0.22$ on the threefold axes (see Table I). Anisotropic refinement including these Ag⁺ ions converted to $R_1 = 0.21$ and $R_2 = 0.27$. A subsequent difference synthesis showed three peaks (2.1-4.5 e Å⁻³ in height, esd = 0.4 e Å⁻³) at (0.12, 0.40, 0.5), (0.313, 0.313, 0.313), and (0.125, 0.5, 0.5). The first two peaks were stable in least-squares refinement. The first refined well as six chlorine atoms and the second as two. Anisotropic refinement, with the occupancy numbers of the Ag⁺ ions and chlorine atoms varying, led to the error indexes $R_1 = 0.17$ and $R_2 = 0.18$. A subsequent difference Fourier function revealed the Ag⁺ ions at Ag(4) and chlorine atoms at Cl(3) (see Table I). Simultaneous positional, occupancy, and anisotropic thermal parameter refinement for all atoms except Cl(3) and Ag(4), which were refined isotropically, converged to the error indexes $R_1 = 0.079$ and $R_2 = 0.078$.

The occupancy numbers at Cl(2) and Cl(3) each refined to 6.2 chlorine atoms, and were reset and fixed at 6.0, the maximum number of atoms at this position for packing reasons. The number of chlorine atoms at Cl(3) was constrained to be equal to the number at Cl(2) because the distances involved indicate that these positions represent dichlorine molecules. Interatomic distances (see Table II) and the occupancy numbers at Ag(2), Ag(3), Ag(4), and Cl(1) (see the "varied occupancy number" column of Table I) indicate that these ions are associated with each other (see Figure 1). By varying the occupancies of these species and Ag(1) so that the sum of Ag⁺ ions remains 12, a rather sharp minimum, as indicated by the R indexes (based on F), was found. These occupancy numbers, of Ag⁺ ions, Cl⁻ ions, and Cl atoms, are shown in the column labeled "fixed" in Table I. At convergence, $R_1 = R_2 = 0.082$. The goodness-of-fit is $(\Sigma w(F_o - |F_c|)^2/(m - s))^{1/2} = 4.7$, where m (279) is the number of observations and s (46) is the number of variables in least-squares refinement.

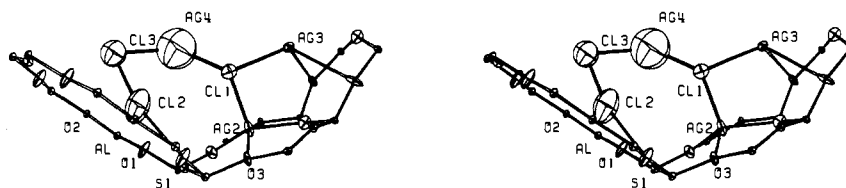


Figure 1. A stereoview of one corner of the large cavity showing the $Cl_2-AgCl-(Ag^+)_2$ complex. About 2.25 of the 6 chlorine molecules per unit cell are involved in such an arrangement. The dichlorine molecule forms a charge transfer complex with the framework oxide ion, O(1). Ellipsoids of 20% probability are used.

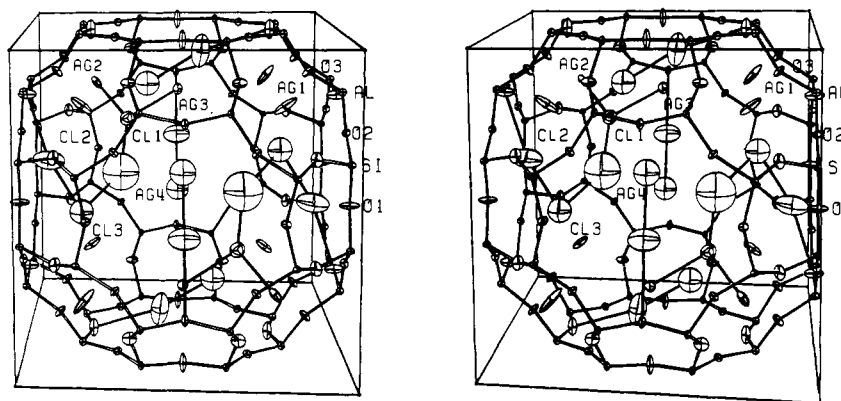


Figure 2. The unit cell of a chlorine sorption complex of dehydrated fully Ag^+ -exchanged zeolite A is shown in stereoview. The dichlorine molecules and $Cl_2-AgCl-(Ag^+)_2$ complexes are shown with dark bonds. About 75% of the unit cells have this arrangement. The remaining 25% contain three dichlorine molecules and three $Cl_2-AgCl-(Ag^+)_2$ complexes within the large cavity. Ellipsoids of 20% probability are used.

The O(1)-Cl(2)-Cl(3) angle is $166(2)^\circ$, indicating that the Cl_2 molecule has formed a nearly linear charge-transfer complex with a framework oxide ion. Actually, two nonequivalent chlorine atoms, which could not be resolved crystallographically, must be present at the Cl(3) position because, of the six atoms at Cl(3), only 2.25 coordinate to Ag^+ ions. The remaining 3.75 atoms must occupy positions which are at least somewhat different. Of course, the Cl(2) positions must also be affected. The conclusion that H^+ ions must be present in nonstoichiometric numbers (vide infra) adds further to the disorder of the dichlorine molecules.

The final difference function was featureless except for an insignificant peak at the origin (peak height = $4.2 e \text{ \AA}^{-3}$, esd = $0.12 e \text{ \AA}^{-3}$ at a general position, and therefore esd = $(0.12) (48) = 5.8 e \text{ \AA}^{-3}$ at this special position²²).

The quantity minimized in the least-squares treatment was $\sum w(F_o - |F_c|)^2$, where the weights (w) are the reciprocal squares of $\sigma(F_o)$, the standard deviation of each observation. Atomic scattering factors²³ for Ag^+ , Cl^0 , O^- , and $(Si, Al)^{1.75+}$ were used. The function describing $(Si, Al)^{1.75+}$ is the mean of the Si^0 , Si^{4+} , Al^0 , and Al^{3+} functions. All scattering factors were modified to account for the real component ($\Delta f'$) of the anomalous dispersion correction.²⁴ Bond lengths and selected angles are given in Table II.

Discussion

In this work, Ag^+ ions are found at two threefold-axis positions. Upon the sorption of dichlorine, 2.25 Ag^+ ions at Ag(2) have moved 0.64 \AA from the (111) plane at O(3) into the large cage. The length of the Ag(2)-O(3) bond has increased from 2.25 \AA in dehydrated $Ag_{12}A^{1-2}$ to 2.34 \AA in this structure as the coordination of Ag^+ has changed from trigonal to near tetrahedral, an increase of one in coordination number. The positions of the remaining 5.25 threefold-axis ions at Ag(1) have been affected little by the sorption of chlorine. The distances between Ag(1) and its nearest oxide ions at O(3), $2.26(3) \text{ \AA}$, remain short. These ions are nearly in the (111) plane at O(3), as can be seen in Table III.

Vacuum-dehydrated fully Ag^+ -exchanged zeolite A contains silver atoms, probably as hexasilver molecules, within some of its sodalite units.¹⁻² It appears that the present crystal contained 2.25 silver atoms per unit cell before Cl_2 gas was added. That is, ca. 38% of the sodalite units contained hex-

Table III. Deviation (\AA) of Atoms from the (111) Plane at O(3)^a

O(2)	0.21	Ag(2)	0.64
Ag(1)	0.17	Cl(1)	2.93

^a A negative deviation would indicate that the atom lies on the same side of the plane as the origin.

asilver clusters and the remaining 62% did not. This stoichiometry is approximately that expected, considering the dehydration treatment to which the crystal had been subjected.^{1,2} Dichlorine then oxidized hexasilver



to give, for the purposes of this discussion, $AgCl$ molecules at Ag(4) and Cl(1) in the large cavity. (An alternate Ag^+ position could have been used to define an $AgCl$ molecule.) These chloride ions are 2.93 \AA from the (111) plane at O(3) (Table III). The $AgCl$ molecule bridges between the ions at Ag(2) and Ag(3) and the chlorine atom at Cl(3) as can be seen in Figures 1 and 2. The gas-phase $AgCl$ bond length, 2.250 \AA ,²⁵ learned from the rotational fine structure of band spectra in the visible and the ultraviolet regions, agrees very well with the distances between the Ag^+ ions at Ag(2) and Ag(4), and the Cl^- ions at Cl(1); $Ag(2)-Cl(1) = 2.29(4) \text{ \AA}$ and $Ag(4)-Cl(1) = 2.23(4) \text{ \AA}$. These distances are all less than the value in $AgCl$ crystals, 2.78 \AA . The anisotropic thermal ellipsoids at Ag(1) and Cl(1) are relatively small, indicating that these ions are firmly bound at their positions (see Figures 1 and 2). The isotropic thermal ellipsoid at Ag(4) is large, indicating that those ions, which are only two coordinate, are less firmly positioned.

Chlorine atoms are found to one-quarter fill two 24-fold positions. These positions are interpreted to give 24 molecular sites which are occupied statistically by six Cl_2 molecules whose bond lengths are $2.49(7) \text{ \AA}$. Six molecules is the maximum number which can be accommodated at these sites; otherwise, unreasonably short Cl-Cl distances, corresponding to overlapping molecules, would result.

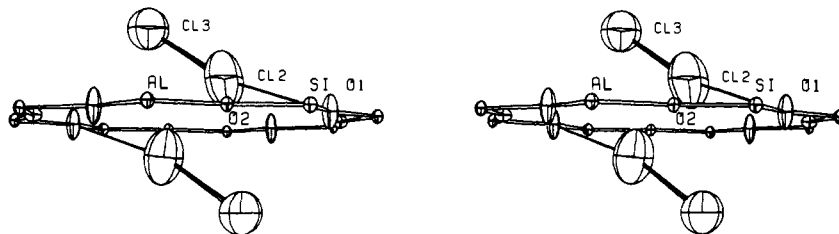
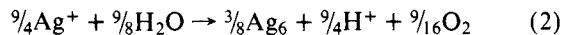


Figure 3. Each 8-oxygen ring in the structure participates in a charge transfer interaction with two dichlorine molecules approximately as shown. Of the 6 dichlorine molecules per unit cell, 2.25 coordinate to Ag^+ ions at Ag(4). Of these 6 molecules, 4.5 are bridged by 2.25 H^+ ions located between, perhaps precisely between, the two Cl(2) atoms. The structure shown, with ellipsoids of 20% probability, is an average over the several similar but different situations which must exist.

The closest approach of a chlorine atom to the zeolite framework is that of Cl(2) to O(1), and the O(1)-Cl(2)-Cl(3) angle, $166(2)^\circ$, is close to linear (see Figure 3). Also, the Cl(2)-O(1) distance, $2.82(7) \text{ \AA}$, is less than the sum of the appropriate nonbonded van der Waals radii, 3.20 \AA .²⁶ Such a pattern of angles and distances has been observed before in a complex between dichlorine and 1,4-dioxane⁸ (O-Cl-Cl = 178° , O-Cl = 2.67 \AA , and Cl-Cl = 2.02 \AA). This can be understood in terms of electron pair donation (charge transfer) from the electronegative O(1) ion to the axially electropositive chlorine molecule with its vacant $3p \sigma^*$ antibonding molecular orbital. The long dichlorine bond, $2.49(7) \text{ \AA}$ as compared to 1.99 \AA ²⁷ in free Cl_2 , is, of course, a consequence of the resulting reduced bond order, to which other factors contribute. Compared to the 1,4-dioxane- Cl_2 complex, a much greater elongation of the dichlorine bond is observed, in part because the oxygen donor is an anion. Such elongated dichlorine bonds were also found in the crystal structure of a chlorine sorption complex of $\text{Co}_4\text{Na}_4\text{-A}^{12}$ (Cl-Cl = 2.5 \AA).

The distance between the chlorine atoms at Cl(2) and neighboring Cl(2) atoms generated from these by inversion at $(0, \frac{1}{2}, \frac{1}{2})$, which is in the middle of the 8-ring, is very short ($2.36(7) \text{ \AA}$; see Figure 3). This indicates that a H^+ ion exists at or near each 8-ring center where it bridges between two dichlorine molecules. These Cl_2 molecules carry a residual partial negative charge due to their charge-transfer interaction, especially equatorially⁵ where the $3p_x$ and $3p_y$ atomic orbitals would be filled. Water molecules, 1.125 per unit cell, must have decomposed to give these H^+ ions, as well as Ag_6 and O_2 , according to the following net reaction, which would have occurred during the dehydration procedure.



The water involved has been retained by the zeolite long enough to participate in this reaction instead of being lost as a result of the dehydration conditions. The evacuation of hydrated $\text{Ag}_{12}\text{-A}$ at 350°C and 10^{-5} Torr was found to be incomplete;²⁸ three water molecules, at least, were retained per unit cell. Studies of that system indicated that it is unlikely that as many as six molecules per unit cell would be retained at this or higher temperatures. Therefore the above reaction should not have been able to proceed until all Ag^+ ions are reduced. The extent to which it has proceeded is reasonable, and it is consistent with previous observations.^{1,2}

Only 2.25 H^+ ions per unit cell have formed by reaction 2, considering the number of Ag atoms which were produced during the dehydration process. Therefore only 4.5 of the 6 chlorine molecules could be bridged by H^+ ions—the remaining 1.5 molecules must occupy similar but somewhat different positions. Least-squares refinement could not resolve either of the two chlorine positions at Cl(2) and Cl(3). Still the large thermal ellipsoid of the atom at Cl(2) can be expected to include the effects of disorder. Similarly, H^+ ions were found in the crystal structure of a bromine sorption complex of dehydrated fully Ag^+ -exchanged zeolite A.⁷

The distance between the Ag^+ ion at Ag(4) and the chlorine atom at Cl(3), $2.55(10) \text{ \AA}$, may be considered short as compared to the sum of the ionic radius of Ag^+ and the van der Waals radius of chlorine,²⁶ $1.26 + 1.80 = 3.06 \text{ \AA}$. This indicates that 2.25 dichlorine molecules per unit cell are coordinated to the 2.25 Ag^+ ions at Ag(4).

The anisotropic thermal ellipsoids of the ions at Ag(3) are relatively small, indicating that they are firmly bound. However, the distance between the ions at Ag(3) and the nearest oxide ions at O(2), 2.91 \AA , is rather long; the sum of the ionic radii of Ag^+ and O^{2-} is 2.58 \AA .²⁹ It appears that the ions at Ag(3) have their strongest interaction with Cl(1) chloride ions (see Table II and Figure 1).

The Ag(3) position is occupied so that those Ag^+ ions can coordinate to the chloride ions of the newly formed AgCl molecules. Without those molecules, the 8-ring sites would have been more fully occupied, as indicated by the crystal structure of vacuum-dehydrated fully Ag^+ -exchanged zeolite A.^{1,2}

It is expected that the severe change in the color of the crystal, from yellow to black, upon the sorption of dichlorine, is due to charge-transfer bands involving the short Ag(2)-Cl(1) and Ag(4)-Cl(1) bonds. Alternatively, or in addition, the dichlorine to oxide ion charge-transfer bond may be involved.

Acknowledgments. This work was supported by the National Science Foundation (Grant CHE76-81586). We are also indebted to the University of Hawaii Computing Center.

Supplementary Material Available: Listings of the observed and calculated structure factors (Supplementary Table I) (2 pages). Ordering information is given on any current masthead page.

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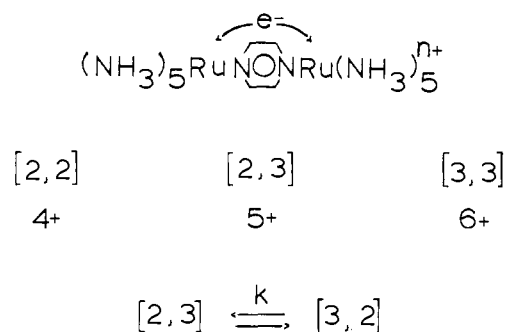
Experimental Evidence for Trapped Valences in the Mixed-Valence Complex μ -Pyrazine-bis(pentaammineruthenium) Tosylate. Electron Paramagnetic Resonance, Magnetic Susceptibility, and Nuclear Magnetic Resonance Results

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Abstract: The results of the variable-temperature magnetic susceptibility, EPR, and NMR experiments on salts of $[((\text{NH}_3)_5\text{Ru})_2\text{pyr}]^{n+}$ ($n = 4, 5, 6$) and on a salt of $[((\text{NH}_3)_5\text{Ru})_2\text{pyr}]^{3+}$ are presented. The unpaired electron in the mixed valence [2,3] oxidation state of the dimer is localized in a (d_{xz}, d_{yz}) orbital on the Ru(III) center. The electron from the Ru(II) center is transferred through the pyrazine bridge to the other metal site at a rate which is fast on the NMR time scale, but slow on the EPR time scale. The energy barrier to the thermal electron transfer is calculated to be between 3.4 and 6.7 kcal/mol.

Since Creutz and Taube¹ first reported the synthesis of $[((\text{NH}_3)_5\text{Ru})_2\text{pyr}]^{3+}$, this mixed valence dimer has fostered a great deal of interest and controversy in the literature. Most of the controversy centers on the thermal electron transfer process postulated to occur between the two metal centers in the complex. Accurate rate data for the thermal electron transfer in this simple model system could provide insight into



the current theories of electron transfer phenomena. Although many workers have attempted to obtain such rate data for the thermal electron transfer process, the experimental conditions appropriate for observing the phenomenon as a dynamic process have not been found. The unpaired electron either appears to be completely localized or completely delocalized on the time scale of all of the experiments carried out to date, as shown in Table I. The conclusions of several of these experimental studies are based on subtle effects, making it difficult to decide whether the data indicate that the electron is localized or delocalized. Thus, it is not surprising that there is disagreement in the literature concerning the rate of thermal electron transfer.

There is also disagreement about the nature and magnitude of the energy barrier to thermal electron transfer in this interesting complex. Robin and Day¹² have distinguished three classes of mixed-valence complexes based on the extent of overlap between the metal orbitals containing the unpaired electron and the orbitals of the bridging ligand. A similar classification scheme is depicted in Figure 1. If the orbital interactions between the two metal centers through the bridge are negligible (class I), the potential barrier to thermal electron transfer can be defined by two harmonic oscillator potential wells. This vibronic barrier is predicted by the Hush theory¹¹ to have an energy which is one-fourth the energy of the intervalence transfer band observed in the electronic spectrum of the complex at 1570 nm. If there are extensive metal-metal interactions (class III), the orbital containing the unpaired electron could be delocalized over the entire complex. Here, electronic effects totally remove the vibronic barrier to the electron transfer. The optical and electronic properties of the pyrazine bridged dimer have led Taube and others to classify it as a class II complex described by a localized site molecular orbital scheme in which the vibronic barrier to the electron transfer is lowered to some extent by electronic effects but is not eliminated. Hush argues in favor of a class III designation based on the IR results mentioned in Table I and in light of the fact that the so-called intervalence transfer band shows neither the solvent dependence nor the bandwidth predicted for intervalence transfer transitions by the Hush theory.

Clearly, there is confusion concerning both the molecular orbital description of the mixed valence pyrazine bridged dimer and the rate of thermal electron transfer between the two metal centers. In an attempt to further our understanding of both of these features of this interesting compound, we have carried out a series of EPR, NMR, and magnetic susceptibility ex-