

interpreted to indicate that there is formed a binuclear structure containing one atom each of Co(II) and Co(III) linked by the polyamine condensation product of ethylenediamine. One nitrogen atom is coordinated with HCl.

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and infrared work included in this paper and to Mr. R. Strakna for the mass spectrometric data.¹⁶

(16) Material supplementary to this article has been deposited as Document number 5343 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. This material includes figures showing the reflectance spectra of the solid halides before and after irradiation, the absorption spectra of the chloride in aqueous solution and in 12 N HCl solution and the decomposition rate curves. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints, or \$1.25 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress, STORRS, CONN.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY AND HARVARD UNIVERSITY]

The Structure and Bonding of Cyclopentadienylthallium and Bis-cyclopentadienylmagnesium

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The infrared spectra of gaseous C_5H_5Tl and $(C_5H_5)_2Mg$ in the C-H stretching region are reported. They are in accord with C_{5v} molecular symmetry for C_5H_5Tl and a sandwich configuration for $(C_5H_5)_2Mg$. That the bonding in C_5H_5Tl is essentially ionic is suggested by chemical evidence, the magnitude of the overlap integrals involved in a molecular orbital treatment of the bonding and the ionization potentials. The concept of ionic bonding in sandwich molecules is discussed with special reference to $(C_5H_5)_2Mg$.

I. Cyclopentadienylthallium(I)

The compound C_5H_5Tl reported by E. O. Fischer¹ has properties so unusual that an inquiry into the structure of the molecule seemed of considerable interest. Its existence is in itself striking since no thalloy alkyls are known except as postulated reaction intermediates.² It is in fact quite stable, as evidenced by the facts that it is prepared in an aqueous medium, that it can be sublimed *in vacuo* and that it darkens only slowly on standing in air or light. Although Fischer reported it to be insoluble in common organic solvents, we have found it to react with several. It is practically insoluble in tetrahydrofuran, but does not seem to react with it. Since the methyl derivative is quite reactive the stability of solid C_5H_5Tl may be in part due to a very stable lattice packing as has been suggested by Fischer. These facts suggested that the compound was unlikely to be an alkylthallous compound containing a Tl-C σ -bond; instead a half-sandwich configuration seemed possible. Furthermore it appeared that a clear decision could be made between these possibilities by a study of the infrared spectrum. Since the substance is insoluble in or reactive toward suitable solvents, the spectra were taken on the gaseous substance in a hot cell. In order to obtain a strong spectrum in the C-H stretching region, which in itself provides necessary and sufficient information, a cell having glass windows was used as described below. The spectrum is shown in Fig. 1.

A molecule of the alkyl type would have symmetry C_{5v} , and a fairly complex spectrum in the C-H region would be expected. There would be five

infrared active C-H stretching modes due to both H-C(saturated) and H-C(olefinic) bonds. The half-sandwich configuration on the other hand would have the relatively high symmetry C_{5v} and there would be three C-H stretching modes of symmetry types A_1 , E_1 and E_2 of which only the first two could be infrared active. We might anticipate that they would be in the same general range as the C-H stretches for other sandwich molecules such as $(C_5H_5)_2Fe$ (3109 cm^{-1}), $(C_5H_5)_2Ni$ (3107 cm^{-1}), $(C_5H_5)_2Mn$ (3101 cm^{-1}), $(C_5H_5)_2Mg$ (3095)³ and for benzene (3099 cm^{-1}). It is also unlikely that the two vibrations would be coincident. Actually as Fig. 1 shows only one sharp band at 3101 cm^{-1} is observed in the range 2700–3300 cm^{-1} . This is not, however, inconsistent with the C_{5v} structure for the following reason.

The A_1 mode is a synchronized stretching of all 5 C-H coordinates which would absorb in the infrared only in proportion to the change in dipole moment produced in the z -direction (the C_5 axis and the z -axis are co-linear). In the free planar symmetrical C_5H_5 ring the symmetry would be D_{5h} and the corresponding totally symmetric C-H stretching mode (A_2) would be inactive in the infrared since no change in the z -component of dipole moment could be produced by such a motion. When bound to the Tl atom this mode becomes—in principle—infrared active because of the lower symmetry. If the bound ring remains perfectly planar the mode will still be inactive unless there is appreciable coupling of the C-H stretching with a change of some other coordinate so that the true normal vibration does result in a change of dipole moment in the z -direction. Such coupling is probably slight however because of the great disparity

(1) E. O. Fischer, *Angew. Chem.*, **69**, 207 (1957).

(2) Cf. G. E. Coates, "Organometallic Compounds," Methuen and Co. Ltd., London, 1956, pp. 95–102.

(3) Unpublished data of L. T. Reynolds, G. Wilkinson, and F. A. Cotton on the *gas phase* spectra of these molecules.

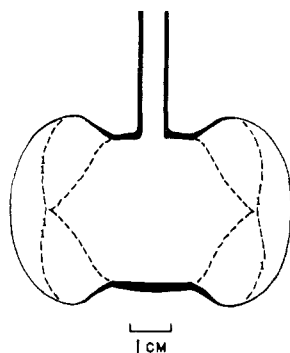


Fig. 1.—Glass infrared cell. Intermediate steps in construction are shown by broken lines.

between the frequencies of C-H stretching motions and other vibrations of the molecule. Actually of course the ring probably does not remain perfectly planar; the hydrogens are probably to some extent swept back. This would obviously also enhance the intensity of the A_1 mode. The E_1 vibration will of course have considerable intensity even in an isolated planar ring. It is possible to make a rough calculation of the relative intensities of the A_1 and E_1 modes by a method previously described.⁴ Such a calculation shows that the ratio $I(A_1)/(E_1)$ varies as $1/2 \tan^2 \alpha$ where α is the angle which the H-C bonds make with the C_5 plane. At an angle of 18° the intensity ratio is only 0.05, and becomes 0.1 only at $\alpha = 27^\circ$. It is not likely that the angle is so great that the A_1 band is not actually observed due to its negligible intensity.

Fischer¹ has postulated that the bonding in this molecule is covalent and such as to give a structure of C_{5v} symmetry. He proposes a scheme in which the two unused electrons of Tl remain in the 6s orbital, while the three 6p orbitals are used for bonding. One of them which can be regarded as containing the third thallium electron overlaps with a carbon $p\pi$ orbital containing an unpaired electron while the other two Tl 6p orbitals accept electron pairs from the double bonds of the C_5H_5 ring. Such a conception of the bonding has no rigorous theoretical foundation since it violates the symmetry requirements of a C_{5v} structure.⁵

An estimate of the effectiveness of covalent bonding in the molecule has been made using overlap integrals and following previous molecular orbital treatments of sandwich compounds.⁷ In symmetry C_{5v} the π levels of the cyclopentadienyl

(4) F. A. Cotton, A. D. Liehr and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 175 (1955).

(5) The same of course can be said of the "octahedral durchdringungs Komplexe" theory of bonding in the bis-cyclopentadienyl compounds. The recent treatment by Linnett⁶ in terms of Lennard-Jones theory of equivalent orbitals suffers the same defect, since a set of equivalent orbitals as defined by Lennard-Jones must belong to some irreducible representation of the point group of the molecule or a subgroup thereof. The trigonal sets of orbitals constructed by Linnett are not in fact equivalent orbitals in the Lennard-Jones sense since they fail in this requirement. Of course they must since it is quite impossible to have colinear 3- and 5-fold rotation axis in the molecule. We see little point to Linnett's approximation, since there is no particular difficulty in an MO treatment which is rigorous with regard to symmetry.

(6) J. W. Linnett, *Trans. Faraday Soc.*, **52**, 904 (1956).

(7) (a) W. Moffitt, *THIS JOURNAL*, **76**, 3386 (1954); (b) J. D. Dunitz and L. E. Orgel, *J. Chem. Phys.*, **23**, 954 (1955).

radical are occupied in the following way: $a_1^2 e_1^2 e_2^0$. The 6s and 6p levels of thallium can be classified as $a_1(6s)$, $a_1(6p_z)$ and $e_1(6p_x, 6p_y)$. The degree of mixing of the 6s and 6p_z orbitals cannot be estimated with any precision; we have assumed the following for convenience, and placed two electrons

$$a_1' = 1/\sqrt{2}(p_z + s)$$

$$a_1'' = 1/\sqrt{2}(p_z - s)$$

in a_1'' , the orbital directed away from the ring. The other orbital a_1' is empty, and is by symmetry permitted to overlap with the filled a_1 orbital of C_5H_5 and can accept electrons from it. The e_1 orbitals of C_5H_5 contain one unpaired electron and may overlap with the e_1 orbitals of Tl containing an unpaired electron. In order to calculate the net overlaps for the a_1 - a_1 and e_1 - e_1 bonds in terms of standard overlap integrals certain transformations of coordinates must be made. Similar transformations have been described by Dunitz and Orgel^{7b} in their treatment of ferrocene. They omitted any detailed discussion of the pe_{1u} - Cpe_{1u} type bonds in that case due to the difficulty of making a meaningful assignment of μ values to the iron 4p orbitals. Following the same nomenclature and conventions, we can write for the a_1 - a_1 and e_1 - e_1 overlaps in C_5H_5Tl

$$\begin{aligned} S(Tl a_1', C p a_1) &= \frac{1}{\sqrt{2}} \{ S(Tl p_z, C p a_1) + S(Tl s, C p a_1) \} \\ &= \frac{\sqrt{5}}{2} \{ S^{2p\sigma, 6p\sigma} \cos^2 \omega - S^{2p\pi, 6p\pi} \sin^2 \omega + \\ &\quad S^{2p\sigma, 6s} \cos \omega \} \quad (1) \end{aligned}$$

$$S(Tl e_1, C p e_1) = \frac{\sqrt{5}}{2} \{ S^{2p\sigma, 6p\sigma} + S^{2p\pi, 6p\pi} \sin \omega \cos \omega \} \quad (2)$$

where the angle ω is that between a Tl-C bond axis and the principal axis of the molecule. In order to carry through the numerical evaluation of the overlaps the following approximations had to be made.

(a) The Tl-C distance was estimated to be ~ 2.3 Å. Therefore calculations were made using 2.2, 2.3 and 2.4 Å. The results which depend on this through its effect on the angle ω and on the value of the parameter p in the formulas for the basic overlap integrals⁸ are not very sensitive to variations through this range.

(b) Basic overlap integrals involving AO's of principal quantum number 6 could not be used since the required Slater AO's have the effective principal quantum number 4.2. The non-integral value makes evaluation in closed form impossible. n^* was approximated as 4.0 so that the master formulas for overlap with orbitals of the 5th shell as given by Mulliken, *et al.*,⁸ could be used. This corresponds to making the calculation for the corresponding indium compound (of whose existence nothing is known). The radius of indium is very similar to that of Tl and the shielding parameters are precisely the same in both cases. Therefore, for purposes of an order of magnitude calculation none of these approximations are seriously objectionable.

The basic overlap integrals are presented in

(8) Mulliken, Rieke, Orloff and Orloff, *ibid.*, **17**, 1248 (1949).

Table I, where the range of p values corresponds to the range of Tl-C distances cited above.

TABLE I

OVERLAP INTEGRALS (SLATER AO'S), $t = 0.25$

	$p = 10$	$p = 11$	$p = 12$
$S^2p\sigma, 5p\sigma$	-0.10640	-0.09262	-0.05500
$S^2p\sigma, 5s$	+ .07018	+ .05614	+ .03480
$S^2p\pi, 5p\pi$	+ .02843	+ .01748	+ .01050

On substituting the values for $p = 11$ into equations 1 and 2 the final results obtained are

$$S(\text{Tl}e_1', \text{C}p_{e1}) = -0.03823$$

$$S(\text{Tl}e_1, \text{C}p_{e1}) = -0.02616$$

Thus the overlaps are negligible in magnitude and actually negative, suggesting that covalent bonding is of only slight importance. Certainly the exact values of the overlaps are not to be taken seriously in a case such as this, but the results are very extreme and for that reason probably qualitatively significant. $p\sigma$ - $p\sigma$ overlaps can become negative even in the range of bonding distances when the two orbitals are of widely differing size and diffuseness. The same tendency toward small and even negative values also exists with the $p\sigma$ - $d\sigma$ overlaps which are encountered in the sandwich bonds in the bis-cyclopentadienyl and bis-benzene derivatives of transition metals. This size difference effect probably accounts in part for the general decrease in the stability of such compounds in going down a group in the periodic table.

The ionization potentials of the e_1 electrons of Tl and C_5H_5 suggest the predominance of electrostatic forces. The first ionization potential of Tl is 6.1 volts while the ionization potential of an electron in the e_1 level of C_5H_5 can be estimated as ≥ 8 volts. In ferrocene on the contrary, Moffitt^{7a} estimates the valence state ionization potential of an electron in the e_{1g} orbital of iron to be about the same as that for an e_1 electron in C_5H_5 . With such a large difference as is found in the present case, the ionization of Tl to Tl^+ followed by attraction of Tl^+ and C_5H_5^- seems likely to be important. This would lead to C_{5v} symmetry and $\text{C}_5\text{H}_5\text{Tl}$ serves as a good example of the observation previously made⁹ that the existence of a sandwich configuration does not necessarily imply covalent (sandwich type) bonding.

A chemical test previously proposed⁹ for showing the ionicity of metal-ring bonds is based on the tendency of an ionic compound to ionize in moderately polar media, $\text{C}_5\text{H}_5\text{M} = \text{M}^+ + \text{C}_5\text{H}_5^-$, so that on adding Fe^{++} , ferrocene would form. It has been found that on shaking a suspension of $\text{C}_5\text{H}_5\text{Tl}$ in a tetrahydrofuran solution of FeCl_2 a metathesis to $(\text{C}_5\text{H}_5)_2\text{Fe}$ and TlCl takes place.

II. Bis-cyclopentadienylmagnesium(II)

It will be noted that only one C-H stretching frequency has been observed in the infrared for the molecules $(\text{C}_5\text{H}_5)_2\text{Fe}$ and $(\text{C}_5\text{H}_5)_2\text{Ni}$ although the selection rules permit the existence of two, of symmetry types A_{2u} and E_{1u} . These two molecules doubtless have sandwich geometry in the vapor

(9) G. Wilkinson, F. A. Cotton and J. M. Birmingham, *J. Inorg. Nucl. Chem.*, **2**, 95 (1956).

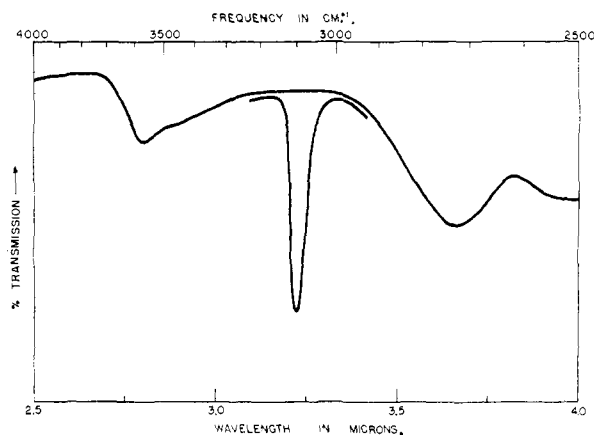


Fig. 2.—Infrared spectra; upper, glass cell blank; lower, $\text{C}_5\text{H}_5\text{Tl}$ at 210° .

phase. The observed band is again assigned as the E_{1u} mode and reasoning similar to that used above would suggest that the A_{2u} mode can be expected to be very weak. Lippincott and Nelson¹⁰ have reported frequencies for the A_{2u} bands obtained presumably from solution spectra. Even on very concentrated solutions of ferrocene in CS_2 we have observed only a dissymmetry of the E_{1u} band which indicates a second very weak band at about the position given by Lippincott and Nelson.

The gas phase spectra of $(\text{C}_5\text{H}_5)_2\text{Mn}$ and $(\text{C}_5\text{H}_5)_2\text{Mg}$ in the C-H stretching region are analogous to the spectra of $(\text{C}_5\text{H}_5)_2\text{Fe}$ and $(\text{C}_5\text{H}_5)_2\text{Ni}$ in showing only one absorption band. This can be taken as a strong indication that they retain sandwich structures in the free state, else a fairly rich spectrum would be seen. Thus the sandwich geometry already known to exist in the crystalline forms of these compounds is not attributable solely to crystal packing forces. It is remarkable also that the frequencies of the E_{1u} C-H stretching modes are so similar in the several compounds since the iron and nickel compounds have been regarded as essentially covalent while the magnesium and manganese compounds and now also the thallium compound have been considered essentially ionic for various reasons.⁹ It does not follow that a variation in metal-ring bond type must necessarily cause a great variation in the C-H stretching frequency. Nevertheless, it is well to consider whether the existence of ionic bonds in say $(\text{C}_5\text{H}_5)_2\text{Mg}$, as suggested by experimental evidence, is reasonable theoretically.

As pointed out before⁹ the most electrostatically favorable configuration of two C_5H_5 ions and an Mg^{+2} ion would be the sandwich arrangement, so that the existence of this configuration is not of itself evidence for sandwich bonding. Covalent bonding in $(\text{C}_5\text{H}_5)_2\text{Mg}$ could result from three principal types of overlap, from the molecular orbital viewpoint. First, if the valence electrons of Mg be promoted to the p_x and p_y orbitals, then a sandwich bond of the $(pe_{1u}-Cpe_{1u})$ type, analogous to the pe_1-Cpe_1 bonding discussed for $\text{C}_5\text{H}_5\text{Tl}$, could occur. Second, if the valence electrons of Mg be promoted to the d_{xz} and d_{yz} orbitals, then the usual type of

(10) E. R. Lippincott and R. D. Nelson, *THIS JOURNAL*, **77**, 4990 (1955).

sandwich bond (de_{1g} - Cpe_{1g}) found in the covalent transition metal sandwich compounds could be formed. Third, the formation of a dative bond between the filled a_{1g} orbitals of the C_5H_5 ring and the empty $3s$ orbital (a_{1g}) of the magnesium atom could occur in either of the previous cases.

There is no difficulty in calculating the overlaps for the (pe_{1u} - Cpe_{1u}) and (de_{1g} - Cpe_{1g}) bonds in $(C_5H_5)_2Mg$ using the equations given above for the former (after multiplication by $\sqrt{2}$), the equations of Dunitz and Orgel for the latter^{7b} and the tables of overlap integrals of Jaffé¹¹ and Mulliken.⁸ Assuming an Mg-C distance of 2.6 Å., the following overlaps are found

$$(pe_{1u}-Cpe_{1u}): 0.295$$

$$(de_{1g}-Cpe_{1g}): 0.293$$

Thus in this case it can be concluded that the two kinds of overlaps are about equally effective. The promotion energy required to put the Mg atom in the $3p^2$ valence state can be estimated fairly well since the spectroscopic state $3p^2(^3p)$ has been observed at 7.17 e.v.¹² above the ground state. The state $3d^2$ has not been observed, but one can guess that it would be at 12–13 e.v. It can easily be calculated from spectroscopic data that the energy required to ionize the Mg($3p^2$) configuration to Mg^{++} is 15.5 e.v. On the other hand the ionization potentials of the e_{1u} and e_{1g} orbitals of C_5H_5 can be estimated at ≥ 8 e.v. each, and the sum of the 1st and 2nd ionization potentials of Mg in the ground state is 22.7 e.v. Thus it would require less energy to transfer the two Mg valence electrons to the C_5H_5 groups than to promote the Mg atom to the $3p^2$ valence state. From another point of view, if the electrons were promoted to give the $3p^2$ valence state, they would then "fall" into the C_5H_5 orbitals. The same thing would be true *a fortiori* of the $3d^2$ valence state. The general conclusions are: (1) (de_{1g} - Cpe_{1g}) bonding is not favored over (pe_{1u} - Cpe_{1u}) bonding by overlap considerations and is quite disfavored by the promotion energies involved. (2) Neither type of covalent bonding seems as important as the tendency to ionic bonding although some (pe_{1u} - Cpe_{1u}) overlap will doubtless contribute to the over-all stability of a predominantly ionic bond.

The (sa_{1g} - Cpa_{1g}) overlap also has been computed, and has the value 0.419. While the $3s$ orbital of the magnesium atom is probably a few volts above the Cpa_{1g} orbital, it will drop considerably on ionization of the Mg so that it is possible that this kind of dative bonding could appreciably offset the charge separation which otherwise tends to result. It would not seem possible to make very meaningful calculations of this effect at present. The best that can be said is that the compound does behave as though the net charge separation is appreciable leading to a tendency toward ionic dissociation and that such behavior is explicable in terms of the bonding scheme outlined.

In the bis-cyclopentadienyl compounds of transi-

tion metals, a covalent primary bond^{7a}—although other contributions appear to be significant^{7b}—is formed using the metal $3de_{1g}$ orbitals, since these are at about the same energy as the Cpe_{1g} orbitals. There is a tendency toward ionicity, however, in the compounds of metals preceding iron⁹ (*viz.*, Ti, V, Cr) which is probably a reflection of the fact that for these metals the d levels are of higher energy. It has been shown previously⁷ that $(C_5H_5)_2Mn$ behaves magnetically as though it contains Mn^{+2} ions in the 6S state, and because of this and a variety of chemical evidence the compound has been regarded as ionic. This need only mean that there is no covalent bonding involving de_{1g} electrons. Actually it is interesting to observe that the state $3d^5(^6S)4p^2$ lies 7.11 e.v. above the ground state and the sum of the 1st two ionization potentials is 23.07 e.v. These values are quite similar to those of the analogous processes in Mg, so that in the same way there is probably some covalent contribution due to pe_{1u} - Cpe_{1u} overlap, though it may be still less here owing to the smaller overlap of the C_5H_5 orbitals with the more diffuse $4p$ orbitals of Mn.

Experimental

Preparation and Properties of Thallium(I) Cyclopentadienide.—This compound was prepared in the manner outlined by Fischer.¹ Thallous sulfate (5.04 g.; 0.2 equiv.) was dissolved in 15 ml. of 4 *N* aqueous NaOH under nitrogen in a 40-ml. centrifuge tube, 3 ml. (0.037 equiv.) freshly distilled cyclopentadiene added, and the mixture shaken vigorously for 20 minutes. The white curdy precipitate was centrifuged, dried *in vacuo* over KOH and purified by repeated sublimation through a fiber glass plug at 80° (0.005 mm.), yield 3.37 g. (61% based on Tl) of pale yellow acicular crystals, blackening at $\sim 60^\circ$ in air and at $\sim 230^\circ$ in an evacuated capillary, and not melting below 270°. *Anal.* Calcd. for C_5H_5Tl : Tl, 75.82. Found: Tl, 75.3. The compound is fairly stable in air, showing only superficial darkening after many months. It may be remarked in passing, however, that thallium-(methylcyclopentadienide)³ is oxidized by air so vigorously as to char the paper on which it stands.

Chemical reactions were carried out in evacuated sealed tubes, with carefully purified solvents distilled in a vacuum system. Thallous cyclopentadienide is virtually insoluble in all organic solvents. It slowly reacts with $CHCl_3$ and CCl_4 , forming $TlCl$, and with CS_2 , forming unidentified black and reddish materials. Shaken with a clear solution of crystalline anhydrous ferrous chloride in tetrahydrofuran, it is metathesized slowly to $TlCl$ and ferrocene (87% based on C_5H_5Tl recovered after 30 hours). Thallous cyclopentadienide reacts with maleic anhydride in tetrahydrofuran, yielding a deep red solution and a flocculent brown precipitate; the interpretation of this reaction is not unambiguous, however.⁹ The possibility of the a_1 electron pair possessing donor properties was tested. No significant amount of BF_3 or BCl_3 is absorbed by C_5H_5Tl in 48 hours at 30° or at -78° ; the crystals are merely darkened on the surface.

Infrared Hot Cell.—The hot gas cell with KBr windows described previously¹³ has not proven satisfactory in operation at the temperatures (150–250°) required to obtain sufficient vapor pressure of the compounds. A very simple and inexpensive cell blown entirely of glass¹⁴ is useful to about 4.7 μ and to at least 400°. Figure 1 shows this cell and details of its fabrication: thin points are pulled around a 2 cm. section of 41 mm. Pyrex tubing and a side tube is attached. The points are pulled off close to the body of the cell and then expanded radially to a diameter of 50 mm. Finally, using a large bushy flame, the ends are expanded to their final hemispherical shape and thickness of 0.12–0.20 mm. Despite their fragility, only one cell out of 14 has imploded in use.

(11) H. H. Jaffé, *J. Chem. Phys.*, **21**, 258 (1953); H. H. Jaffé and G. O. Doak, *ibid.*, **21**, 196 (1953).

(12) C. E. Moore, Atomic Energy Levels, NBS Circular 467, Vol. I, U. S. Government Printing Office, Washington, D. C.

(13) F. A. Cotton, A. D. Liehr and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 141 (1956).

(14) We are much indebted to Prof. W. A. Klemperer who called to our attention the transparency of glass in this range.

The sample is introduced through the sidearm and the cell is evacuated and sealed, leaving 2-3 cm. of sidearm. A blank spectrum, with the cell in its oven, is taken at room temperature: typically such a cell has a transmission vs. air greater than 80% to 3.5 μ , 50% to 4.5 μ , and dropping to zero beyond 4.8 μ (cf. Fig. 2). The oven is then heated to 10-20° higher than the desired temperature, whereupon the compound sublimes into the cool sidearm. The vapor pressure in the cell is then controlled by the temperature of a small Nichrome-wound glass tube placed over the sidearm.

Infrared Spectra.—Spectra were taken with a Perkin-Elmer Model 21 double-beam recording spectrophotometer with NaCl prism, programmed for maximum resolution (in-

creased source intensity, decreased slit width, expanded scale, and slow scanning). Each spectrum was calibrated against the 3.267 and 3.303 μ bands of Baird polystyrene calibration film. The values quoted are thus internally consistent and accurate to ± 5 cm.⁻¹. Repetition of these glass cell spectra using LiF optics, as well as the remainder of the infrared spectra of these compounds in an improved hot gas cell, will be reported later. The gas-phase infrared spectrum of C₆H₅Tl in the range 2.0-4.5 μ at 150-249° shows only a single absorption peak at 3101 \pm 5 cm.⁻¹ (Fig. 2). Slight decomposition, giving a thin black film on the cell, occurred on prolonged heating.

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Kinetics of the Silver(I)-Silver(II) Exchange Reaction

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In 5.87 *f* HClO₄ the isotopic exchange reaction between Ag^I and Ag^{II} obeys the rate law Rate = $k(\text{Ag}^{\text{II}})^2$. At 0° the value of k is 1020 \pm 40 *f*⁻¹ sec.⁻¹. The experimental activation energy is 12.5 \pm 1.2 kcal. It is proposed that the exchange occurs *via* the reaction 2Ag^{II} \rightleftharpoons Ag^I + Ag^{III}. The exchange rate increases rapidly with decreasing HClO₄ concentration. No evidence was found for exchange by direct electron transfer from Ag^I to Ag^{II}, and a limit for the specific rate of this path at 0° is set at <10 *f* sec.⁻¹. The rapid-mixing, flow, and quenching techniques used in the measurements of half-times in the range 0.1 to 1 sec. are described.

The silver(I)-silver(II) exchange system was chosen for investigation because the charges of the hydrated cations are lower than those of any other pair of simple hydrated cations previously studied.² It was hoped that something of interest could be learned about the importance of coulombic repulsion for such electron-exchange systems.

Perchloric acid solutions were chosen for the reaction media to minimize complex formation. It was necessary to use rather concentrated (\sim 6 *f*) HClO₄ solutions to prevent the rapid reduction of silver(II) by water. Preliminary exchange runs had indicated that the rate of exchange was too large to be measured by conventional techniques, so a rapid-mixing and flow technique first used by Hartridge and Roughton³ was adapted.

Experimental

Silver Tracer.—The tracer used in these experiments was the 270-day⁴ Ag^{110m}, produced by an n,γ reaction on silver nitrate, and obtained from the Oak Ridge National Laboratory on allocation from the U. S. Atomic Energy Commission. The silver nitrate was dissolved in water, filtered, and before each run an aliquot of the solution was fumed with perchloric acid and diluted with perchloric acid of the desired concentration to form one of the reactant solutions. A four-point decay curve over a period of 600 days showed a half-life of 255 days.

The γ -rays⁵ emitted from silver solutions, contained in calibrated six-inch test-tubes, were counted on a scintillation counter having a stilbene crystal.

Chemicals.—Silver(II) solutions were produced by dissolving AgO in 6 *f* HClO₄. The AgO was prepared by anodic oxidation of silver nitrate solution.⁶ The preparation,

analyzed by heating to drive off oxygen and weighing the metallic silver residue, was found to contain 0.99 mole of silver per mole of oxygen atoms. The silver(II) oxide was stable for the duration of the investigation. Because of extensive reduction on solution, silver(II) oxide was also the source of silver(I) in most reaction solutions. For a few runs, silver(I) oxide was also added.

Mallinckrodt A.R. silver(I) oxide, nitric acid, ammonium thiocyanate, ferric ammonium sulfate, perchloric acid, sodium carbonate and Eimer and Amend sodium perchlorate monohydrate were used without further purification. G. F. Smith *o*-phenanthroline was dissolved in 6 *f* HNO₃ to make a 0.10 *M* solution, which was stored at -18°. Perchloric acid (70%) was diluted with doubly distilled water to the desired concentrations, which were determined by titration with standard sodium hydroxide solution. Reaction solutions containing sodium perchlorate were analyzed for perchlorate ion gravimetrically by weighing slightly soluble tetraphenylarsonium perchlorate.⁷

Silver Analysis.—Silver solutions were analyzed after being counted by titration with 0.01 *f* NH₄SCN solution, ferric ion being the indicator.⁸ The blank correction was 0.02 ml., and the error was estimated to be \pm 0.02 ml. Most exchange runs were at such silver(II) concentrations as to require 0.70 ml. or more of titrant. For a few runs, the amount of titrant required was as little as 0.20 ml., leading to a titration error of 10%. A more sensitive potentiometric titration⁹ was attempted, but it was not successful because of end-point drift in the acidic solutions.

The unit of specific activity used throughout these experiments was counts/min./ml. of thiocyanate solution.

Rapid Mixing and Flow Apparatus.—The rapid mixing and flow technique developed by Hartridge and Roughton³ was used. The apparatus in our experiments is diagrammed in Fig. 1. The two reactant solutions (in 35-ml. reservoirs R and R') were forced by compressed air (applied through stopcock S₁) up tubes T and T' into the mixing chamber M. The mixed reaction solution flowed through reaction tube A and tip B, from which it squirted into the quench solution 10 cm. below.

The first \sim 4 ml. of reaction solution was intercepted and discarded. It served to cool the walls of the reaction tube and contained any incompletely mixed reaction solution. About 6 ml. of reaction solution was collected in the quench

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