between the atoms. Thus, if an atom has an appreciable moment that is quenched by exchange demagnetization with a neighbor, then increasing the distance between neighbors should restore the full moment. Since there is apparently no such effect observed in the highly hydrated sulfates, the low moment of rhodium in these compounds should not be attributed to interactions between neighboring Rh atoms. Rather, the low moment must be due to complexing.

The Rh^{+3} ion is probably of a d^6 configuration corresponding to 6.70 Bohr magnetons for the unperturbed ion or 4.90 for spin-only. In $RhCl_3$, the observed moment is essentially zero and suggests an inner orbital $d^2\ sp^3$ complex. It is probable that Rh is coördinated octahedrally to six chlorine atoms in some sort of infinite three-dimensional complex similar to $CrCl_3$. In atomic orbital language, electrons from the six chlorine atoms occupy two of the 4d, one 5s, and three 5p orbitals of the rhodium forcing the six electrons of Rh to pair up in the remaining three 4d orbitals. Alternatively, by the crystalline field method of Penney and Schlapp,[9] the cubic field of the surrounding chlorine octahedron could split the ^5D level so that the triply degenerate $d\epsilon$ level is lower and accommodates the six electrons as pairs. Finally, by the molecular orbital method, the low moment could be explained if the three $d\epsilon$ non-bonding orbitals were lower in energy than the two $d\gamma_2$ antibonding orbitals.

Conductometric and spectroscopic investigation of the aqueous solutions of the sulfates, to be reported in a following paper, suggest that in yellow $Rh_2(SO_4)_3 \cdot 14H_2O$, Rh is present as the complex $Rh(H_2O)_6^{+++}$ and in red $Rh_2(SO_4)_3 \cdot 6H_2O$ as a sulfato complex. In either case, the observed low moment can be accounted for as in $RhCl_3$, assuming sixfold coördination of oxygen atoms to the rhodium.

According to Klemm,[10] Rh^{+3} has a diamagnetic increment of -22×10^{-6}. This means that there is a "residual paramagnetism" of $+85 \times 10^{-6}$, $+66 \times 10^{-6}$ and $+95 \times 10^{-6}$ for the complexes in $RhCl_3$, $Rh_2(SO_4)_3 \cdot 6H_2O$ and $Rh_2(SO_4)_3 \cdot 14H_2O$, respectively. Such "residual paramagnetism" could be due to the existence of low-lying excited electronic energy levels such as apparently exist in Co(III) complexes.[4] Since rhodium, like cobalt, consists 100% of a single isotope, Rh^{103} with nuclear spin 1/2, it should be relatively easy to detect these low-lying states by investigating the nuclear resonance shift as a function of temperature.

ITHACA, NEW YORK

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[9] W. G. Penney and R. Schlapp, *Phys. Rev.*, **42**, 666 (1932).

[10] W. Klemm, *Z. anorg. allgem. Chem.*, **246**, 361 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Crystal Structure of an Ethylene–Palladium Chloride Complex

BY J. N. DEMPSEY AND N. C. BAENZIGER

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The crystal structure of ethylene–palladium chloride has been determined from single crystal Weissenberg data. The orthorhombic cell dimensions are $a = 15.41$ Å., $b = 9.29$ Å., $c = 7.23$ Å. The complex is a dimer, $(PdCl_2C_2H_4)_2$, with four dimers per unit cell. The coördination about the palladium atoms is planar square, the palladium atoms are joined by a bridge of two chlorine atoms, the ethylene groups are attached to the palladium atoms in the *trans* position. Electron density maps indicate that the axis of the ethylene molecule is perpendicular to the plane of the dimer and that the center of the ethylenic double bond lies in the plane of the dimer.

Introduction

Complexes of olefins with platinum and palladium chloride[1-7] and with other metals[8] have been studied previously by chemical and spectroscopic methods. A crystal structure determination has been reported for a related silver perchlorate–benzene complex[9] and a preliminary structure has been reported for Zeise's salt, $K(PtCl_3 \cdot C_2H_4) \cdot H_2O$.[10,11] In Zeise's salt the orientation of ethylene relative to the platinum atom appears to be similar to its orientation relative to platinum (or palladium) suggested by Chatt for the platinum chloride–ethylene dimer. The results of a study of the crystal structure of the palladium chloride–ethylene dimer which are reported below are in agreement with the structure proposed by Chatt.

When the X-rays scattered by carbon atoms make up only a small fraction of the total scattered rays, it is very difficult to fix their positions accurately, especially when their contribution to the scattered rays is about equal to the error in estimating the structure factors. In addition, the positions of the hydrogen atoms are still more difficult to determine, so that the orientation of the ethylene molecule is unknown. In order to determine the orientation of the ethylenic group the structure of a related olefinic complex, the styrene–palladium chloride dimer, has also been determined and is reported in a separate paper.[12]

Experimental

The complex $(PdCl_2C_2H_4)_2$ (I) was prepared by the method of Kharasch and Ashford.[2] The palladium chlo-

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[1] J. S. Anderson, *J. Chem. Soc.*, 970 (1934); 1042 (1936).

[2] M. S. Kharasch and T. A. Ashford, THIS JOURNAL, **58**, 1733 (1936).

[3] M. S. Kharasch, R. C. Seyler and F. R. Mayo, *ibid.*, **60**, 884 (1938).

[4] J. Chatt, *J. Chem. Soc.*, 3340 (1949).

[5] J. Chatt and R. G. Wilkins, *Nature*, **165**, 860 (1950).

[6] J. Chatt, *J. Chem. Soc.*, 2622 (1952).

[7] J. Chatt and L. A. Duncanson, *ibid.*, 2939 (1953).

[8] S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938).

[9] R. E. Rundle and J. H. Goring, *ibid.*, **72**, 5337 (1950).

[10] J. A. Wunderlich and D. P. Mellor, *Acta Cryst.*, **7**, 130 (1954).

[11] J. A. Wunderlich and D. P. Mellor, *ibid.*, **8**, 57 (1955).

[12] J. R. Holden and N. C. Baenziger, THIS JOURNAL, **77**, 4987 (1955).

ride was dissolved in warm benzonitrile forming the complex $PdCl_2$(benzonitrile)$_2$ (II). On cooling, crystals of II separated out. When ethylene was bubbled through a solution of the intermediate II dissolved in benzene or xylene, the final product I separated as a fine powder. In the finely powdered form I is unstable in moist air, but it is stable in a desiccator in which an ethylene atmosphere is maintained.

To obtain single crystals large enough for X-ray diffraction purposes, the complex I was dissolved in dry xylene, placed in a vacuum desiccator and the solution slowly evaporated in an atmosphere of dry ethylene. The needle-like crystals prepared in this manner were much more stable than the powder. Powder diagrams of the crushed needles showed that the needles were the same as the finely powdered starting material.

Weissenberg diagrams using the multiple film technique were made with the crystal rotating about the *c*- and *b*-axes. Cu Kα radiation was used. Intensities were determined visually by comparison with a standard set of spots made with the same crystal. The crystal was so small that absorption corrections were not necessary. The density of the crystals was measured by the pycnometer method using Skellysolve B as the displacement liquid.

Unit Cell Dimensions.—The orthorhombic unit cell dimensions of the complex I are a = 15.41 Å., b = 9.29 Å., c = 7.23 Å., vol. = 1038 Å.^{3}, D_m = 2.58 ± 0.07 g./cm.^{3}, Z = 4, D_x = 2.63 g./cm.^{3}, formula weight based on the dimer = 411.332. X-Ray reflections occur in all orders for (*hkl*) and (*hk*0) planes, but only if *h* is even for (*h*0*l*) and only if *k* is even for (0*kl*) planes. These absences are characteristic of space groups Pbam and Pba2. In addition, all reflections are weak unless $h + k + l = 2n$; hence, the cell is nearly body-centered.

Structure Determination.—Approximate values of the palladium x and y parameters were obtained from a Patterson projection on (001) and independently from trial and error calculations using the (*h*00) and (0*k*0) data. The palladium atoms determined sufficient signs so that the refinement of the structure could be carried out by electron density projections.

The electron density projections on (001) produced overlaps of several palladium and chlorine atoms. Further consideration of the structure indicated that similar overlaps would exist for (010) and (100) projections. Since all the atoms except the carbon atoms lay either in the plane z = 0 or z = $^1/_2$, sections of the three dimensional electron density were calculated at z = 0 and $^1/_2$. Figure 1 showing the section at z = 0 is typical of the appearance of the electron density sections.

The electron density maps indicated that the carbon atoms must be in the sets 8 (*i*). For values of the z parameter near zero and one-half, this set places the ethylene molecule perpendicular to the plane z = 0 or $^1/_2$ and with the carbon–carbon bond bisected by the plane. (This would not be required in space group Pba2.) Using an assumed value of 1.353 Å. for the carbon–carbon distance in ethylene, the z parameters were calculated to be 0.094 and 0.594. Sections of the three-dimensional electron density plot were calculated at these levels. Peaks which could be ascribed to the carbon atom positions were observed, but they were lower in height than corresponding peaks observed at the z = 0 and $^1/_2$ levels. Peaks due to palladium and chlorine atoms also persisted in the sections at z = 0.094 and 0.594, but, proportionately, they were lowered more than the peak for the carbon atom, the peak due to chlorine being less than that due to the carbon atom in this section. A comparison of the palladium and carbon peak heights is shown in Fig. 2. It is unfortunate that the carbon atoms could not be resolved, but appeared only as an elongated blob.

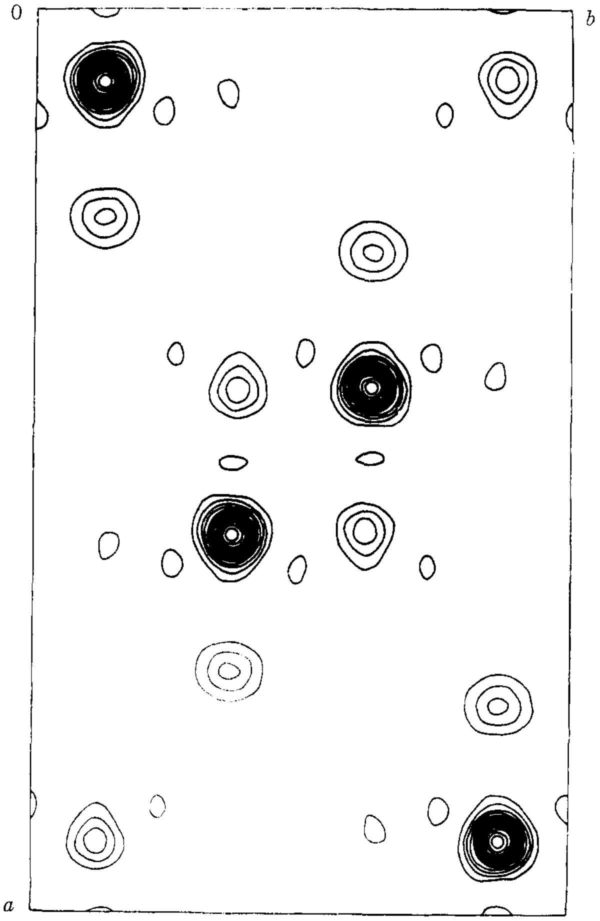

Fig. 1.—Section of the electron density of ethylene palladium chloride at z = 0.

Structure factors calculated from the coördinates as found from the sections of the three-dimensional

TABLE I

ATOMIC PARAMETERS FOR $(PdCl_2C_2H_4)_2$

	Final values		Errors in Å.	
	x	y	$a\sigma(x)$	$b\sigma(y)$
Pd_1	0.080	0.130	0.01	0.01
Pd_2	.418	.372	.01	.01
Cl_1	.424	.380	.03	.02
Cl_2	.076	.123	.03	.02
Cl_3	.230	.132	.03	.02
Cl_4	.408	.138	.03	.02
C_1	.079	.376	.1	.1
C_2	.266	.371	.1	.1

Pd_1, Cl_1 and Cl_3 in 4 (*g*): $x,y,0;\ \bar{x},\bar{y},0;\ \frac{1}{2}+x,\frac{1}{2}-y,0;\ \frac{1}{2}-x,\frac{1}{2}+y,0$

Pd_2, Cl_2 and Cl_4 in 4 (*h*): $x,y,\frac{1}{2};\ \bar{x},\bar{y},\frac{1}{2};\ \frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2};\ \frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}$

C_1 in 8 (*i*): $x,y,z;\ \bar{x},\bar{y},z;\ \frac{1}{2}+x,\frac{1}{2}-y,\bar{z};\ \frac{1}{2}-x,\frac{1}{2}+y,\bar{z};\ \bar{x},\bar{y},\bar{z};\ x,y,\bar{z};\ \frac{1}{2}-x,\frac{1}{2}+y,z;\ \frac{1}{2}+x,\frac{1}{2}-y,z;$ with z assumed to be 0.094

C_2 in 8 (*i*): with z assumed to be 0.594

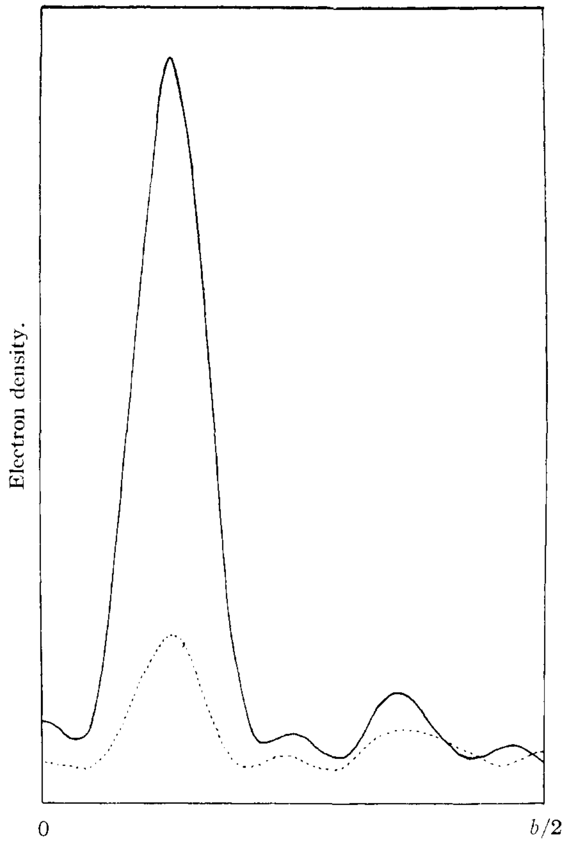

Fig. 2.—Comparison of the electron density at $z = 0$ (smooth line) and $z = 0.094$ (dotted line) for $x = 0.08$. Major peak is Pd, minor peak is due to carbon atoms of ethylene.

electron density plots were used to make "back-shift" corrections. In addition, one stage of least squares refinement was made. The final atom positions are an average of the least squares and back-shift corrected values. These parameter values are listed in Table I.

Since the structure is very nearly body-centered, only about one-half of the total possible number of reflections were observed. Structure factors calculated for absent reflections were small and with only a few exceptions, less than the minimum observable F value for that angle. The discrepancy factor, $R = \Sigma|F_{\text{obsd.}}| - |F_{\text{calcd.}}||/\Sigma|F_{\text{obsd.}}|$, based on observed data only but including $F_{\text{calcd.}}$ values of absent reflections when the calculated F was greater than the minimum observable F is 0.16. Including all the calculated F values, $R = 0.39$, the much higher number due to the large number of absent reflections which had small calculated F values. (Out of 940 possible forms in the region of reciprocal space investigated, 350 were observed as present and 590 as absent.)

Errors in the palladium, chlorine and carbon atom positions estimated from the least squares treatment are given in Table I. Errors due to random errors in the observed F values as estimated by Cruickshank's method[13,14] averaged about one-third smaller than the errors estimated

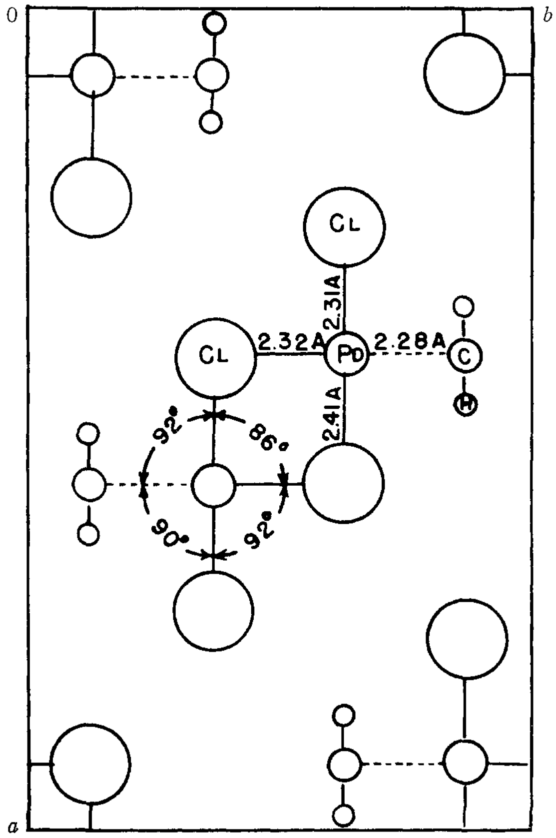

Fig. 3.—The ethylene–palladium chloride dimer at $z = 0$.

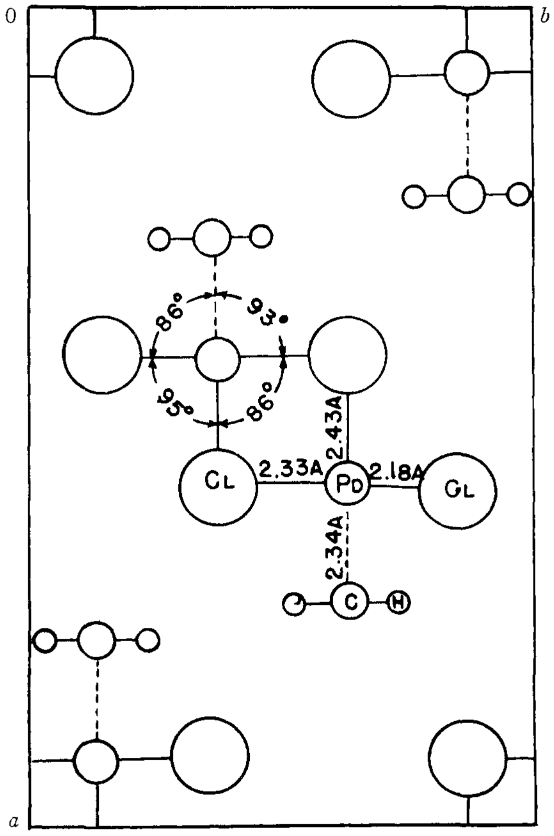

Fig. 4.—The ethylene–palladium chloride dimer at $z = 1/2$.

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[13] D. W. J. Cruickshank, *Acta Cryst.*, **2**, 65 (1949).

[14] D. W. J. Cruickshank and J. S. Rollett, *ibid.*, **6**, 705 (1953).

from the least squares treatment. A complete list of calculated and observed structure factor values based on the observed electron density map values has been deposited with the American Documentation Institute.[15]

Discussion of the Structure

The arrangement of the palladium and chlorine atoms is quite definitely established; the positions of the carbon atoms may be considered fairly uncertain. The palladium atoms are joined by two bridge chlorine atoms as shown in Figs. 3 and 4. The dimers stack above one another in the *c* direction so that the chlorine atoms are located in the octahedral positions about the palladium atoms above and below the plane of the dimer although too far away for appreciable covalent binding. The two crystallographically different dimers do not have exactly the same dimensions although the angles between the bonds are similar.

The intensity data quite definitely place the ethylene groups in the *trans* position of the dimer. In an earlier stage of refinement an ethylene group and a chlorine atom were interchanged on one of the dimers. Changing them to their present positions caused a very noticeable improvement in the agreement of the calculated and observed structure factors, especially for the non-body-centered type reflections. The carbon atoms of ethylene could not be resolved nor could a choice be made between space groups Pbam and Pba2 since it depends only on the carbon atom positions. The most probable arrangement is to assume that the plane of the ethylene molecule is perpendicular to the line joining the palladium atom and the center of the double bond.

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[15] The list has been deposited as Document number 4604 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $2.50 for photoprints, or $1.75 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Crystal Structure of Styrene–Palladium Chloride

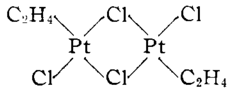
BY J. R. HOLDEN AND N. C. BAENZIGER

RECEIVED MAY 16, 1955

The crystal structure of styrene–palladium chloride has been determined. The unit cell is monoclinic with $a = 13.50$ Å., $b = 4.99$ Å., $c = 19.19$ Å., $\beta = 135.5°$. The space group is $P2_1/c$. The molecules are dimers joined by a double chlorine bridge. The atomic configuration indicates that the styrene–palladium bond consists of interaction between the pi orbital of the double bond and a dsp^2 orbital of palladium.

Introduction

Palladium dichloride and platinum dichloride form complexes with olefins containing one molecule of olefin per metal atom. Molecular weight determinations indicate that the compounds usually exist in solution in the form of dimers.[1-3] Anderson[4] and later Chatt[3] proposed the structure to account for the molecular formula, the dimeric nature



and the customary planar square (dsp^2 hybridization) configuration of palladium and platinum. Chatt[5] describes the olefin–metal bond as consisting of an interaction of the pi orbital of the double bond with the dsp^2 orbital of the metal atom. Overlap of these two orbitals requires that a dsp^2 orbital lie approximately in a plane perpendicular to the plane of the ethylene group of the olefin and be directed toward the axis of the double bond.

Although the platinum compounds are more stable than their palladium analogs, the latter are more suitable for X-ray diffraction studies of their structure because of the lower atomic number of palladium. The crystal structure of ethylene–palladium chloride has been studied by Baenziger and Dempsey.[6] Although the ethylene part of the structure was not resolved, the data indicated that the axis of the ethylene group is perpendicular to the plane of the complex, the carbon atoms of the ethylene being equal distances above and below the plane of the complex. A substituted ethylene complex presents the possibility of resolving the carbon atoms and determining the orientation of the double bond. Attempts to obtain crystals of large enough size for X-ray diffraction purposes were successful only for the styrene complex.

Experimental

Styrene–palladium chloride was prepared by the method of Kharasch and Ashford[1] employing bis-benzonitrile–palladium chloride as an intermediate. Single crystals of sufficient size and perfection for diffraction study were grown from a solution of the compound in styrene. The crystals are extremely slender, amber needles.

Single crystal X-ray data were obtained by the Weissenberg and Buerger precession methods. General (*hkl*) intensity data were obtained by the multiple film, equiinclination Weissenberg technique. (*hk*0) and (0*kl*) data were obtained from a Buerger precession camera using the same crystal and several timed exposures. Intensities were estimated by visual comparison of the photographic blackenings with those of a graduated intensity scale.

Structure Determination.—The unit cell of styrene–palladium chloride is monoclinic with the symmetry of space group $P2_1/c$. The dimensions are $a' = 13.50$ Å., $b' = 4.99$ Å., $c' = 19.19$ Å., $\beta' =$

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[1] M. S. Kharasch and T. A. Ashford, THIS JOURNAL, **58**, 1733 (1936).

[2] M. S. Kharasch and R. C. Seyler, *ibid.*, **60**, 884 (1938).

[3] J. Chatt, *J. Chem. Soc.*, 3340 (1949).

[4] J. S. Anderson, *ibid.*, 970 (1934).

[5] J. Chatt and L. A. Duncanson, *ibid.*, 2939 (1953).

[6] N. C. Baenziger and J. N. Dempsey, THIS JOURNAL, **77**, 4984 (1955).