On Some Dark-colored Chlorocuprates(I, II) and Related Compounds. III. X-Ray Study and Reflectance Measurements

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In the majority of mixed valence compounds that exhibit abnormal light absorption, the metal atoms in different valence states are bound by atomic bridges or metal-metal bonds(1). The abnormal light absorption in these compounds is explained as due to an electron transfer through these bonds or bridges(2). In certain mixed valence halometallates as e. g. Rb_2SbCl_6, however, such bonds or bridges are hardly conceivable from crystallographic data, though they also are highly colored. The mechanism of interaction absorption in these compounds may not be essentially different, but is probably more complicated. Examples of such compounds are few: as far as the author is aware they are represented by one of the two general formulae, M_2SbX_6(3) and $[M^{III}A_6]\,[PbCl_6]$(4,5). The X-ray study which will be described below has proved that compounds, $[M^{III}A_6]\,[CuCl_5]_x\,[CuCl_4]_{1-x}$,(6) constitute another such series. Diffuse reflectance of powdered chlorocuprates was also measured in order to examine the existence and the qualitative feature of the light absorption in these compounds, especially in connection with the problem of interaction color.

Experimental

Samples.—The samples of chlorocuprates used for measurements of reflection were prepared according to the method described in the previous paper. The crystal used in the X-ray analysis was obtained by digesting the precipitate in the mother liquor at 30~40°C.

Hexamminechromium(III) chloride monohydrate which was used in the reflectance measurement and in the preparation of chlorocuprates was prepared by a procedure analogous to that for the preparation of $[Cr(NH_3)_6]_2(SO_4)_3\cdot 2H_2SO_4\cdot 3H_2O$, reported previously(7). At the stage of precipitating the complex, 300 ml. of 12 N hydrochloric acid was used instead of 200 ml. of 12 N sufuric acid, and the yield of the chloride was 23~24 g. (48~50%). The undesirable effect of the impurities in zinc, pointed out in the previous paper could be minimized by amalgamation of metal surfaces by warming granular or mossy zinc in ca. 5% solution of mercury(II) chloride in 1 N hydrochloric acid.

Potassium copper(II) chlorides were prepared by Meyerhoffer's method(8)

Reflectance Measurements.—The diffuse reflectance, R_d, of chlorocuprates, i. e. the ratio of the

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1) J. C. Bailar, Jr. et. al., "The Chemistry of the Coordination Compounds", Reinhold Publishing Corp., New York (1956), p. 19.

2) R. Tsuchida and S. Yamada, *Nature*, **174**, 1064 (1954).

3) K. A. Jensen, *Z. anorg. Chem.*, **232**, 193 (1937); ibid., **233**, 295 (1937); ibid., **252**, 317 (1944).

4) M. Mori, This Bulletin, **24**, 285 (1951).

5) M. Atoji and T. Watanabe, *J. Chem. Phys.*, **20**, 1045 (1952).

6) M. Mori, This Bulletin, **33**, 985 (1960); the chlorocuprates (I, II) in Ref. 6 is expressible in the above formula when the ratio, Cu(II)/Cu(total), is greater than 0.5. The water of crystallization is tentatively omitted in the expression since the percentage is very low (~1%) and hardly distinguishable from that of the adherent humidity.

7) M. Mori, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 253 (1953).

8) W. Meyerhoffer, *Z. physik. Chem.*, **3**, 339 (1889)., ibid., **5**, 98 (1890).

quantity of light reflected by a powdered sample to the quantity of light reflected by magnesium oxide powder was measured with a Shimazu spectrophotometer, Type QR-50, with its integration sphere attachment, in the wave number range of $(1.4\sim3.0)\times10^4\ \mathrm{cm}^{-1}$.

Crystal Analysis.—Oscillation photographs of a small crystal of $[Cr(NH_3)_6][CuCl_5]_x[CuCl_4]_{1-x}$ were taken using Cu-$K\alpha$ radiation. The relative intensities of reflections were visually estimated and corrected for Lorenz and polarization factors by means of Cochran's chart⁹⁾. The observed structure factors obtained in this way were compared with the calculated factors by the trial and error method. The lattice constant was determined with an X-ray diffractometer using Cu-$K\alpha_1$ radiation ($\lambda=1.5405$ Å).

Results and Discussion

The Crystal Structure of $[Cr(NH_3)_6]$ $[CuCl_5]_x$ $[CuCl_4]_{1-x}$.—From the oscillation data the crystal was found to have an O_h symmetry, and only those reflections were observed which fulfilled the following conditions:

1) $h+k=2n,\ k+l=2n,\ l+h=2n$;

2) $h+k=4n$ for $(h\,k\,0)$ reflections;

3) $h\neq k,\ k\neq l,\ l\neq h$ for odd indices.

The space group is therefore determined to be O_h^8–Fd3c. The unit cube edge is $a=22.19$ $+0.02$ Å, and the unit cell contains 32 of the above formula units. The observed density was 1.89 g./cc. and the calculated density is 1.84 g./cc. for $x=0.5$ and 1.92 g./cc. for $x=1$. There has been an ambiguity as to the x value, i. e. the ratio, Cu(II)/Cu(total) for the sample used in X-ray work*.

General features of the intensity distribution were found to be similar to those observed for the chlorocuprate(II) of the same complex cation studied by Mori, Saito and Watanabe¹⁰⁾. In the latter compound, 160 chlorine atoms in the unit cell are classified into two groups, those in 64 (e) equivalent positions and those in 96 (g) equivalent positions. In the case of chlorocuprate(I, II) the number of chlorine atoms should be smaller than 160 by $32(1-x)$. An attempt was made to obtain the value of x by the method of least square, on the assumption that in chlorocuprate(I, II), either (e) or (g) equivalent positions are incompletely occupied. However, either assumption gave an x value slightly greater than unity (~1.03). It is ridiculous to assume an x value greater than unity, but it is probable that x has been close to unity, for the sample crystal was prepared by a long digestion of the precipitate in the mother liquor, during which the quantity of univalent copper has probably decreased by air oxidation. The observed structure factors were, therefore, compared with those calculated on a tentative assumption of $x=1$ and the same atomic coordinates as those obtained for the chlorocuprate(II) (Table I). This comparison gave a fairly low R (reliability factor) value, namely 0.152 for $(h\,k\,0)$ reflections (unobserved reflections included as $F_0=0$), and 0.212 for $(h\,k\,l)$ reflections up to $l=8$ (unobserved reflections excluded). Thus the present research could not find out the difference between the crystal structure of chlorocuprate (I, II) and that of chlorocuprate(II), although the sample crystal of chlorocuprate(I, II) appeared almost black in contrast to the yellow chlorocuprate(II) crystal. Because of the presence of heavy atoms, further refinement including the determination of the structure of chlorocuprate(I) ion probably necessitates more accurate intensity data for a sample with a higher Cu(I) content as well as a simultaneous study of chromium and cobalt compounds.

TABLE I. ATOMIC COORDINATES IN CHLOROCUPRATE(I, II)

32 Cu: (b), 1/4, 1/4, 1/4, etc.
32 Cr: (c), 0, 0, 0, etc.
(64) Cl: (e), u, u, u ($u=0.190$), etc.
(96) Cl: (g), 1/4, v, $-v$ ($v=0.075$), etc.
192 N: (h), x, y, z ($x=0.070$, $y=0.050$, $z=-0.030$), etc.
B (overall temperature factor): 2.5.

The information obtained is, therefore, that in hexamminechromium(III) chlorocuprate(I, II), too, the Cr and Cu atoms are arranged in the NaCl type and that the ionic species of Cu(II) is the trigonal-bipyramidal $[CuCl_5]^{3-}$ ion, the same ion as is found in the chlorocuprate(II). The chart prepared with a self-recording X-ray diffractometer for a powder sample of chlorocuprate(I, II) for which x was nearly equal to 0.5 also showed relative intensities similar to those for the chlorocuprate(II). The essential feature of the crystal structure of chlorocuprate(I, II), therefore, seems to be unaltered even when x approaches 0.5**. In particular, the Cu–Cu distance should remain about the same ($\sqrt{2}a/4=7.79$ Å), since any change in the Cu coordinate must result in a remarkable change in the structure factors. It

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9) W. Cochran, *J. Sci. Instr.*, **25**, 253 (1948).

* Attention was not at first paid to this problem, for it was some time later that the author found the composition of the chlorocuprate(I, II) to be changeable.

10) M. Mori, Y. Saito and T. Watanabe, This Bulletin, **34**, 295 (1961).

** For x below this value the ratio Cu/Cr is not 1:1 any more (Ref. 6).

is, therefore, difficult to assume anything like an atomic bridge between copper atoms in hexamminechromium(III) chlorocuprate(I, II) of a low Cu(I) content.

Reflectance of Powdered Chlorocuprates.—In presenting the data of reflectance measurements it seems convenient to use Kubelka and Munk's expression[11], $f(R_d)=(1-R_d)^2/2R_d$, for there is a certain parallelism between this quantity and the extinction coefficient of the crystal—they should be proportional to one another when the effect of the specular reflection at crystal surfaces is small compared with the diffuse reflection. Kortüm and Schöttler[12] stated that this condition is nearly fulfilled for potassium permanganate and its mixed crystals when the powder is very fine. Kondo and others[13] examined this problem in detail by comparing the reflection data with the absorption curve of a single crystal and found that even when the powder is sufficiently fine some effect of specular reflection makes the curve of $(1-R_d)^2/2R_d$ somewhat different from the true extinction curve of potassium permanganate, and that some caution must be exercised when reflectance is measured for substances of varying refractive indices.

In the present research, use was made of this powder method, because: (1) the process of measurement is very simple and the experiment is at any rate possible even when the compound does not crystallize in thin plates; (2) the light reflected from crystal surfaces of most chlorocuprates studied appeared white to the naked eye, so that at least in the visible region the effect of the specular reflection was thought to be smaller than in the case of potassium permanganate, in which case the light reflected from crystal surfaces seems green; and (3) the main purpose was to examine the existence and the qualitative feature of usually very broad interaction absorption in the visible region. In Figs. 1—4 is plotted the quantity, $\log[(1-R_d)^2/2R_d]$ for various chlorocuprates against wave number.

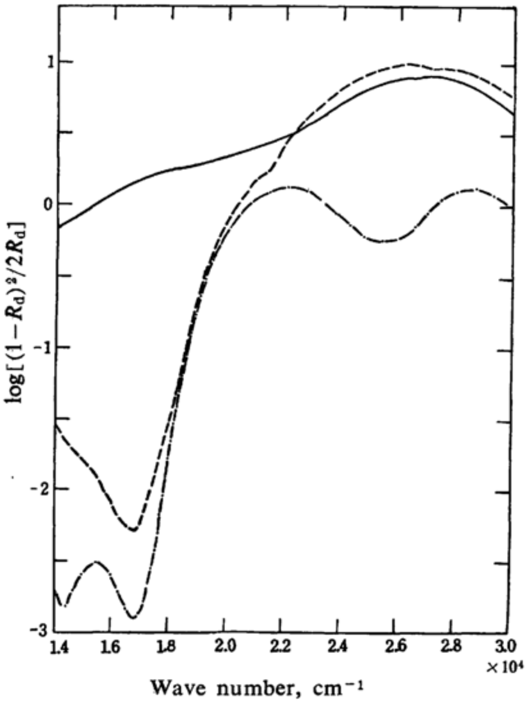

Fig. 1. Curves of $\log[(1-R_d)^2/2R_d]$ for hexamminechromium(III) chlorocuprates.

—— Curve A₁, $[Cr(NH_3)_6][CuCl_5]_x[CuCl_4]_{1-x}$ ($x \sim 0.5$)
---- Curve B₁, $[Cr(NH_3)_6][CuCl_5]$
-·-· Curve C₁, $[Cr(NH_3)_6]Cl_3 \cdot H_2O$

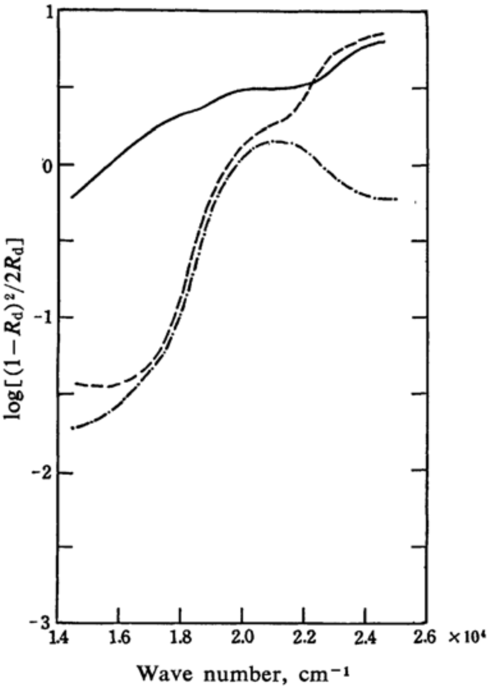

Fig. 2. Curves of $\log[1-R_d)^2/2R_d]$ for hexamminecobalt(III) chlorocuprates.

—— Curve A₂, $[Co(NH_3)_6][CuCl_5]_x[CuCl_4]_{1-x}$*
---- Curve B₂, $[Co(NH_3)_6][CuCl_5]$
-·-· Curve C₂, $[Co(NH_3)_6]Cl_3$

* The value of x was determined by iodometry to be in the neighborhood of 0.7 although this analytical method is not adequate for the cobalt compound (Ref. 6).

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[11] P. Kubelka and F. Munk, *Z. techn. Physik.*, **12**, 593 (1931).

[12] G. Kortüm and H. Schöttler, *Z. Elektrochem.*, **57**, 353 (1953).

[13] Y. Kondo and T. Uemura, Pvesented at the Symposium on Coordination Chemistry of the Chemical Society of Japan, November, 1957; T. Uemura, Y. Kondo and S. Fujieda, ibid., September, 1960.

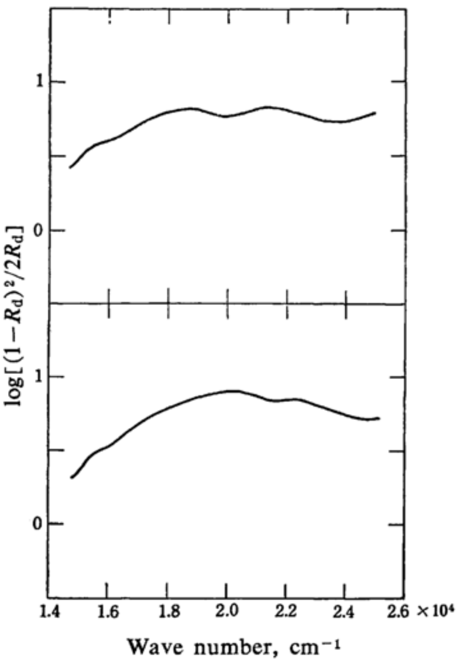

Fig. 3. Curves of $\log[(1-R_d)^2/2R_d]$ for chloroplumbates(II, IV).
Upper: Curve A_3, $[Co(NH_3)_6][PbCl_6]$
Lower: Curve B_3, $[Cr(NH_3)_6][PbCl_6]$

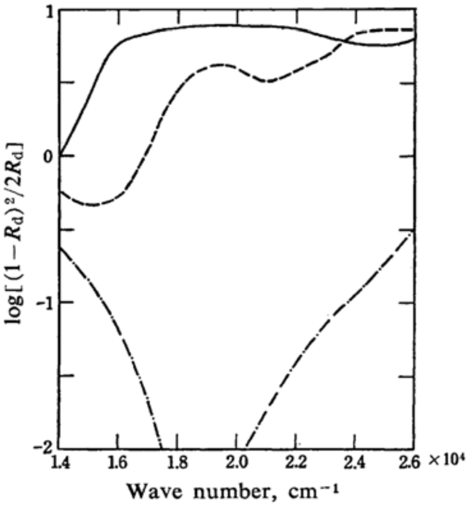

Fig. 4. Curves of $\log[(1-R_d)^2/2R_d]$ for some copper complexes.
—— Curve A_4, $[Cr(NH_3)_6][CuBr_5]$
-·-·- Curve B_4, $[CuCl_2(H_2O)_2]\cdot 2KCl$
---- Curve C_4, $KCuCl_3$

Hexamminechromium(III) Chlorocuprate(I, II), Hexamminechromium(III) Chlorocuprate(II) and Hexamminechromium(III) Chloride Monohydrate (Curves A_1, B_1 and C_1 Respectively in Fig. 1).— Curve A_1 of the chlorocuprate(I, II) shows an existence of interaction absorption in the entire visible region, which is not observed in the case of the chlorocuprate(II) (curve B_1) or the chloride (curve C_1). At the same time both curves A_1 and B_1 show very great value of $\log[(1-R_d)^2/2R_d]$ (poor reflection) in the neighborhood of 2.7×10^4 cm^{-1}, suggesting the existence of strong absorption bands. It seems difficult to determine the exact positions of their peaks, owing to the insufficient accuracy of this method for low reflection values*, to the probable contribution of the specular reflection in this region and also to the effect of the complex cation; but there seems to be little doubt as to their high intensity. These absorption bands are probably charge transfer spectra[14,15] of $[CuCl_5]^{3-}$ ion; the chloride shows no such strong absorption in this region (curve C_1). That similar bands are observed for both chlorocuprate(II) and chlorocuprate(I, II) seems to be consistent with the result of X-ray analysis, which shows that in either compound the ionic species of Cu(II) included is the trigonal-bipyramidal $[CuCl_5]^{3-}$ ion.

The qualitative features of curves A_1 and

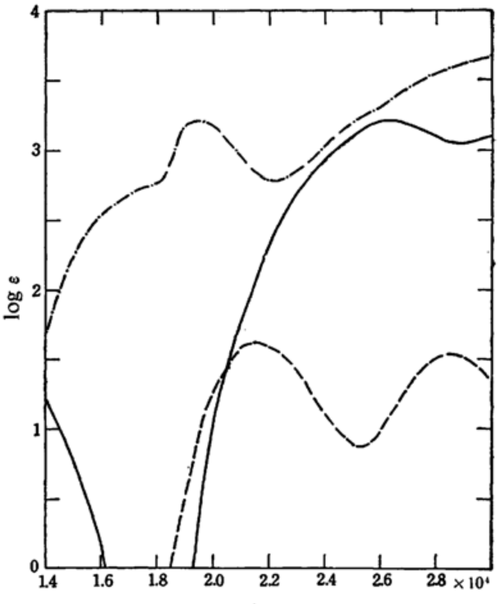

Fig. 5. Absorption spectra (in log ε*) of some aqueous solutions.
—— Curve A_5, 0.000124 M $CuSO_4$ in 10 N HCl
-·-·- Curve B_5, 0.000087 M $CuSO_4$ in 8.7 N HBr
---- Curve C_5, 0.0216 M $[Cr(NH_3)]Cl_3$
* ε is expressed on the basis of g. ion Cu or Cr.

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* Prof. Yukio Kondo of St. Paul's University kindly suggested that measurements with samples diluted with white substances are effective in these instances. The present author, therefore, wishes to apply this method to a more comprehensive study of halocuprates(II) as soon as possible.

14) E. Rabinowitch, *Rev. Modern Phys.*, **14**, 112 (1942).

15) L. E. Orgel, *Quart. Rev.*, **8**, 422 (1953).

B_1 are somewhat similar to those of the absorption curves of systems, copper(II)-copper(I) and copper(II) respectively, in concentrated calcium chloride solution, studied by Doehlemann and Fromherz(16), when the effect of the complex cation is taken into account (cf. also curves A_5 and C_5 in Fig. 5). The resemblance is probably not sufficient to prove that the ionic species is the same, but it may be worth noting that the compounds of this series are the only chlorocuprates in which an interaction color of copper(I) and copper(II) is observable, just as in the case of chloride solution.

Usefulness of reflectance measurements for samples with weak absorption bands may be exemplified by the comparison of the $\log f(R_d)$ curve of the powder sample (curve C_1, Fig. 1) with the $\log \varepsilon$ curve of an aqueous solution (curve C_5, Fig. 5) for the same stable complex compound, $[Cr(NH_3)_6]Cl_3 \cdot H_2O$. The peaks of the two absorption bands are found at almost the same positions although the heights of the peaks are found to be somewhat different. Moreover, a low peak is clearly perceptible at $1.55 \times 10^4\ cm^{-1}$ in curve C_1, which probably corresponds to the transition of the d_ε electron. It is not easy to find this peak even by absorption measurements when a sample solution is dilute.

Hexamminecobalt(III) Chlorocuprate(I, II), Hexamminecobalt(III) Chlorocuprate(II) and Hexamminecobalt(III) Chloride (Curves A_2, B_2 and C_2, Respectively in Fig. 2).—The general feature of the curves is quite similar to that of the corresponding chromium(III) compounds, except in the case of the difference of the position of the absorption peaks of hexammine complex cation.

Hexamminecobalt(III) and Hexamminechromium(III) Chloroplumbates(II, IV) (Curves A_3 and B_3 Respectively in Fig. 3).—Reflectance is very small in the entire visible region showing an existence of interaction absorption of Pb(II) and Pb(IV).

Hexamminechromium(III) Pentabromocuprate (II) (Curve A_4 in Fig. 4).—Reflectance is very small in the visible region, but it increases a little toward the lower wave number region. The relationship is somewhat similar to the absorption curve of $CuSO_4$ in 48% hydrobromic acid (curve B_5, Fig. 5)**. The flattening of the curve at the range of low reflectance is probably due to the effect of the specular reflection.

Dipotassium Copper(II) Tetrachloride Dihydrate and Potassium Copper(II) Trichloride (Curves B_4 and C_4 Respectively in Fig. 4).—Reflectance of these salts was measured for comparison with that of chlorocuprates described above. The former compound, which is known to have the structure, $[CuCl_2(H_2O)_2] \cdot 2KCl$(17,18), shows much weaker absorption in the neighborhood of $2.7 \times 10^4\ cm^{-1}$ than do the chlorocuprates described above, and the charge transfer band seems to lie at the region of higher wave number. This has been ascertained by measurements up to wave number $3.0 \times 10^4\ cm^{-1}$, though the curve is given only in the range, $(1.4 \sim 2.6) \times 10^4\ cm^{-1}$.

In the case of $KCuCl_3$ the curve obtained is very different from those of other chloro complexes of copper studied in the present research or the absorption curve of copper(II) in a solution of high chloride concentration. This difference suggests that in $KCuCl_3$, copper(II) exists in a state quite different from those in the usual chlorocomplexes;—a polynuclear structure with chlorine bridges might, for example, be assumed as in the case of $CsCuCl_3$(19).

Summary

The ionic species of Cu(II) in hexamminechromium(III) chlorocuprate(I, II) has been found to be a trigonal-bipyramidal $[CuCl_5]^{3-}$ ion. Reflectance measurements have shown the existence of diffuse interaction absorption in some chlorocuprates(I, II) and chloroplumbates (II, IV). A strong charge transfer band of $[CuCl_5]^{3-}$ was also found in the neighborhood of $2.7 \times 10^4\ cm^{-1}$ for hexamminechromium(III) chlorocuprate(I, II) and hexamminechromium (III) chlorocuprate(II).

The present author is pleased to express his sincere thanks to Dr. Masayoshi Nakahara of St. Paul's University who kindly advised him to undertake reflectance measurements of chlorocuprates. He is grateful to Professor Yoshihiko Saito of the University of Tokyo for his kind guidance in X-ray study. The research would never have been possible without many valuable suggestions and constant encouragement accorded by Professor Shin'ichi Kawaguchi of our Institute. The author could utilize the spectrophotometer through the kindness of the Faculty of the Science of Living of our University.

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16) E. Doehlemann and H. Fromherz, *Z. physik. Chem.*, **171A**, 353 (1934).

** The value of $\log \varepsilon$ in the absorption curve of $CuSO_4$ in 48% hydrobromic acid given in the previous paper (Fig. 1 in Ref. 6) has been too small by unity. The correct values are given in Fig. 5 in the present paper.

17) S. B. Hendricks and R. G. Dickinson, *J. Am. Chem. Soc.*, **49**, 2149 (1927).

18) L. Chrobak, *Z. Krist.*. **88**, 35 (1934).

19) A. F. Wells, *J. Chem. Soc.*, **1947**, 1662.