

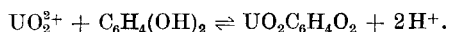
Stability and Polymerization of Uranyl-Catechol Chelates

By S. K. VERMA and R. P. AGARWAL

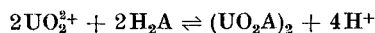
With 4 Figures

Summary

Interaction of uranyl ions with catechol has been investigated by the potentiometric and spectrophotometric techniques. Potentiometric titrations of uranyl nitrate with caustic potash in presence of catechol exhibited a sharp inflexion at $2^{2/3}$ moles of alkali per mole of the metal ion. At the initial stages of the titration, the reaction was shown to proceed as:



The equilibrium constant of the reaction was found to be $2.88 \cdot 10^{-7}$ giving a value of $3.87 \cdot 10^{14}$ for the formation constant of the chelate. Equilibrium constant of the reaction:



has been found to be $1.00 \cdot 10^{-10}$. The binuclear chelate species have been found to polymerize further through hydrolytic reactions.

Introduction

Catechol, o-dihydroxy benzene, gives a five membered ring on chelation. It, thus, forms stable chelates with a number of metallic ions like copper¹⁾, chromium²⁾, aluminium³⁾, zirconium⁴⁾ and thorium⁵⁾. Although catechol derivatives of uranium(VI) have been reported earlier⁶⁾ 7) but no systematic physico-chemical study of the system appears to have been carried out. ROSENHEIM and coworkers⁶⁾ in 1931 isolated a number of uranyl derivatives of catechol. Recently SHNAIDERMAN and GALINKER⁷⁾ have

¹⁾ G. A. L'HEUREUX and A. E. MARTELL, *J. Inorg. Nucl. Chem.* **28**, 481 (1966).

²⁾ R. WEINLAND and E. WALTER, *Z. anorg. allg. Chem.* **126**, 141 (1923).

³⁾ W. D. TREADWELL, G. SZABADOS and E. HAIMANN, *Helv. chim. Acta* **15**, 1049 (1932).

⁴⁾ R. N. KAPOOR and R. C. MEHROTRA, *Z. anorg. allg. Chem.* **293**, 92 (1957).

⁵⁾ R. P. AGARWAL and R. C. MEHROTRA, *J. Inorg. Nucl. Chem.* **24**, 821 (1962).

⁶⁾ A. ROSENHEIM, B. RAIMANN and G. SCHENDEL, *Z. anorg. allg. Chem.* **196**, 160 (1931).

⁷⁾ S. YA. SHNAIDERMAN and E. V. GALINKER, *Zh. Neorgan. Khim.* **7**, 279 (1962).

reported the formation of 1:1 derivative upto a pH of 5, above which the 1:2 compound was shown to be formed. More recently, however, PANDE, KAPOOR and MISRA⁸⁾ have reported the formation of 1:2 complex below pH 5 in a 1:2 mixture of uranyl and catechol system. In view of the strong tendency of the uranyl ion⁹⁾ and its chelate¹⁰⁾ to undergo polymerization in aqueous solutions, it was considered worth-while to carry out a systematic physico-chemical study of the above system. Attempts were also made to determine the stability and polymerization constants of the chelate.

Experimental

Reagents: A stock solution of uranyl nitrate was prepared from an Analar (B.D.H.) sample. The solution was standardized gravimetrically by precipitation of the oxinate and subsequent ignition to U_3O_8 . Catechol was a Merck (G. R.) product. Potassium nitrate (B.D.H.) A.R. was used for keeping ionic strength constant. All the solutions were made in conductivity water.

Apparatus and Procedure: pH measurements were made at room temperature ($30 \pm 1^\circ C$) with a Cambridge pH-meter, standardized against a 0.05 M solution of potassium hydrogen phthalate.

Potentiometric titrations of the reaction mixtures containing 1:1, 2:1 and 3:1 molar ratios of ligand to metal ions were carried out with 0.1 M KOH in a nitrogen atmosphere. Above pH 4.5, equilibrium was reached slowly and the stabilization of hydrogen ion concentrations sometimes took several hours. In such cases the procedure was modified by using a series of bottles containing equal aliquots of the metal chelate under identical conditions (as in the titration) to which varying amounts of the alkali were added. The reaction mixtures were allowed to equilibrate for 24 hours in a dark place at room temperature. The pH of each sample was then measured. All the observations were repeated twice to ensure reproducibility of the results.

Spectrophotometric measurements were made with a Bausch and Lomb Spectronic 20 Spectrophotometer. The system was studied by the method of continuous variations¹¹⁾. As described above, the reaction mixtures were equilibrated for 24 hours before carrying out absorption studies.

In all the potentiometric and spectrophotometric studies, the ionic strength was maintained relatively constant by using a medium containing 0.1 M KNO_3 and low concentrations of ligand and the metal ions.

Analysis: The precipitated compounds were analysed for uranium by direct ignition of the compounds to U_3O_8 the catechol content was determined by the alkaline permanganate method⁵⁾.

Results and Discussion

Curves 1, 2 and 3 (Fig. 1) for the potentiometric titrations of the reaction mixtures of 1:1, 2:1 and 3:1 molar ratios of catechol to uranyl nitrate

⁸⁾ C. S. PANDE, S. N. KAPOOR and S. K. MISRA, *J. prakt. Chem.* **22**, 229 (1963).

⁹⁾ L. G. SILLEN and S. HIETANEN, *Acta chem. Scand.* **8**, 299, 1607 (1954).

¹⁰⁾ I. FELDMAN, J. R. HVILL and W. F. NEUMAN, *J. Amer. chem. Soc.* **76**, 4726 (1954).

¹¹⁾ W. C. VOSBURGH and G. R. COOPER, *J. Amer. chem. Soc.* **63**, 437 (1941).

respectively with caustic potash showed a sharp inflexion at $m = 2^2/3$, where m represents moles of base added per mole of the metal ion. The similar nature of these curves in the acid medium with a common inflexion point indicated formation of the 1:1 derivate only in acid medium, supporting the observation of the earlier workers⁷). PANDE, KAPOOR and MISRA⁸) have, however, reported the formation of a 1:2 complex in lower

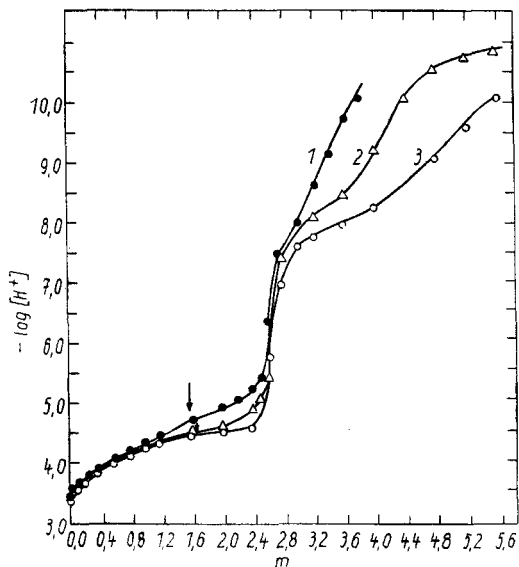


Fig. 1. Curves 1, 2 and 3 represent potentiometric titrations of uranyl nitrate ($5 \times 10^{-3} M$) with KON (0.1M) in presence of 1, 2 and 3 moles respectively of catechol. Volume of initial reaction mixture = 50 ml., m = moles of base added per mole of the metal ion. Arrows in the curves indicate the appearance of precipitate.

buffer region obtained in a potentiometric titration curve of the system containing two moles of catechol and one mole of uranyl acetate.

The stoichiometry of 1:1 of the chelate formed in acid medium was confirmed by spectrophotometry using the method of continuous varia-

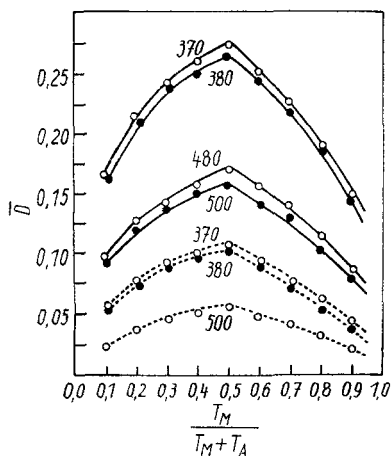
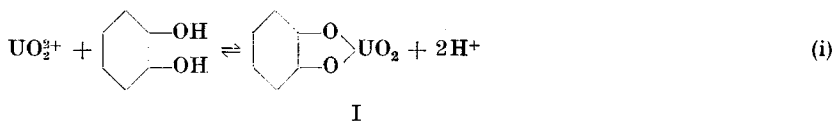


Fig. 2. Continuous variations measurements of uranyl catechol system at pH 4.5 and 3.6 at various wave lengths, Curves marked with dotted lines represent the measurements at pH = 3.6 and those marked with solid lines represent the measurements at pH = 4.5.

tions¹¹). These studies were carried out with reaction mixtures of pH 3.6 and 4.5 (Fig. 2). In both cases, at each wave length studied, maximum absorption was observed for solutions containing approximately equivalent amounts of catechol and uranyl ions. An increase in the optical densities of reaction mixtures of pH 4.5 as compared to those of the solutions of pH 3.6 indicated that the extent of chelation increases with a rise in the pH of the system.

The above conclusion of the formation of 1:1 chelate in acid medium was further confirmed by the isolation of precipitates obtained by the addition of $2\frac{2}{3}$ moles of alkali per mole of uranyl ion into reaction mixtures containing 1, 2 und 3 molar ratios of catechol to uranyl nitrate. Analysis of the precipitated compound, in all the three cases, corresponded to the ratio of catechol to uranyl ion of approximately 1:1 indicating the formation of 1:1 complex only in the lower buffer region of the curves (Fig. 1). In the acid medium, chelation thus occurs as:



On the basis of the above reaction alone, the potentiometric titration curves (Fig. 1) would have exhibited an inflexion point at $m = 2.0$. The occurrence of inflexion at $m = 2\frac{2}{3}$ indicated that (I) is not the final product of the reaction. An extra consumption of $\frac{2}{3}$ mole of alkali per mole of the metal ion together with the establishment of the stoichiometry of 1:1 of the chelate indicated polymerization of the compound which involves the use of hydroxyl ions. Such an observation has been reported earlier in literature in some uranyl¹⁰⁾¹²⁾ and thorium¹³⁾ chelate systems.

Equilibrium Constant of the Reaction: In view of the above interesting results, it was considered worth-while to carry out a quantitative study of the equilibria involved in the interaction of uranyl nitrate with catechol. In order to detect polymerization in the system, potentiometric titrations of 1:1 mixtures of uranyl nitrate and catechol with KOH were carried out in a four-fold concentration range of the metal chelate.

If H_2A represents catechol having two weakly acidic hydrogen atoms, formation of the chelate UO_2A , supposedly in a diaquo form, may be represented by the reaction:



¹²⁾ I. FELDMAN, C. A. NORTH and H. B. HUNTER, *J. physic. Chem.* **64**, 1224 (1960).

¹³⁾ R. F. BOGUCKI and A. E. MARTELL, *J. Amer. chem. Soc.* **60**, 4170 (1958).

The equilibrium constant, K , for the reaction may be expressed as:

$$K = \frac{[\text{UO}_2\text{A}][\text{H}^+]^2}{[\text{UO}_2^{2+}][\text{H}_2\text{A}]} \quad (1)$$

Water molecules of hydration and charges on the chelate species have been eliminated in writing their formulae throughout mathematical treatment of the data.

In order to account for the amount of the hydrolyzed species of uranyl ions present in solution, the constants $K_1 = 10^{-6.10}$, $K_2 = 10^{-5.84}$ and $K_4 = 10^{-17.60}$, where

$$K_{n+1} = \frac{[\text{UO}_2([\text{OH}]_2\text{UO}_2)_n][\text{H}]^{2n}}{[\text{UO}_2]^{n+1}} \quad (2)$$

reported by GUSTAFSON et al.¹⁴) in a 0.1 M KNO_3 medium, a condition used in the present investigation, were employed. From the values of these constants and an arbitrary assignment of $K_3 = 0$, made by AHRLAND¹⁵), it may be shown that concentration of the species corresponding to the 'n' values of 0, 2 and 3 are negligible below pH 4 as compared to the amount of other species present in the reaction mixture.

If T_M represents total concentration of all the metal species and T_A that of the various ligand species and if T_{OH} be the concentration of the alkali added to the solution during titration, we have

$$T_M = [\text{UO}_2^{2+}] + 2[\text{UO}_2(\text{OH})_2\text{UO}_2] + [\text{UO}_2\text{A}], \quad (3)$$

$$T_{\text{OH}} + [\text{H}^+] = 2[\text{UO}_2(\text{OH})_2\text{UO}_2] + 2[\text{UO}_2\text{A}], \quad (4)$$

$$T_A = [\text{H}_2\text{A}] + [\text{UO}_2\text{A}]. \quad (5)$$

In the pH range studied, concentrations of HA^- , A^{2-} and OH^- were negligible as compared to the concentrations of the other species present in the reaction mixture.

Combination of equations 3–5 and substitution of the value of K_2 , reported by GUSTAFSON¹⁴), gives

$$[\text{UO}_2^{2+}] = \frac{-1 \pm \sqrt{1 + 4ac}}{2a}, \quad (6)$$

where

$$a = \frac{1.445 \times 10^{-6}}{[\text{H}^+]^2} \quad \text{and} \quad c = T_M - \frac{1}{2}(T_{\text{OH}} + [\text{H}^+]).$$

After computation of the concentration of free uranyl ions, concentrations of the other species present in solution could be calculated from equations 3–5. The mean values of $-\log K$, thus calculated at various points of the

¹⁴) R. L. GUSTAFSON, C. RICHARD and A. E. MARTELL, J. Amer. chem. Soc. **82**, 1526 (1960).

¹⁵) S. AHRLAND, S. HIETANEN and L. G. SILLEN, Acta chem. Scand. **8**, 1907 (1954).

titration curves (Fig. 1 and 3) in range $m = 0$ to $m = 0.8$, are listed in table 1. In this connection it may be pointed out that the relatively constant values of $-\log K$ could be obtained upto 'm' values of about 0.8 only above which a gradual fall in the values of $-\log K$ was observed. This indicated occurrence of some side reaction above $m = 0.8$.

Table 1

T_A/T_M	T_M	$-\log K$
1	$5 \cdot 10^{-3} \text{ M}$	6.40 ± 0.05
1	$2.5 \cdot 10^{-3} \text{ M}$	6.54 ± 0.03
1	$1.25 \cdot 10^{-3} \text{ M}$	6.64 ± 0.03
2	$5 \cdot 10^{-3} \text{ M}$	6.58 ± 0.02

Average value of $-\log K = 6.54$

Stability of Chelate: From the value of the equilibrium constant of the reaction (i), given in table 1, the value of formation constant, k , of the chelate may be determined from the expression:

$$k = \frac{K}{K_{a1} \cdot K_{a2}} \quad (7)$$

where K_{a1} ($6.31 \cdot 10^{-10}$)^{ref.1} and K_{a2} ($1.18 \cdot 10^{-12}$)^{ref.1} represent dissociation constants of catechol. Substitution of the values of K , K_{a1} and K_{a2} in equation 7 gave a value of $3.87 \cdot 10^{14}$ for the stability constant of the chelate.

Polymerization of the Chelate. Titration curves 1–3 (Fig. 3), for 1:1 mixtures of uranyl nitrate and catechol with KOH, show that an increase in the metal ion concentration in the solution results in a shift of

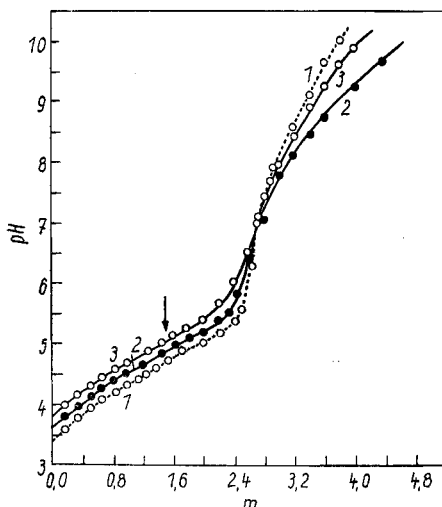
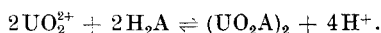


Fig. 3. Potentiometric titrations of 1:1 reaction mixtures of uranyl nitrate and catechol: curve 1, $5 \times 10^{-3} \text{ M}$; curve 2, $2.5 \times 10^{-3} \text{ M}$; curve 3, $1.25 \times 10^{-3} \text{ M}$. $m =$ moles of base added per mole of the metal ion.

the lower buffer regions to lower pH. The increased requirement of base at a particular pH with an increase in the concentration of the metal salt is an indication of polymerization of the chelate. A gradual increase in the value of $-\log K$ with a decrease in concentration of the metal salt also shows condensation of the normal diaquo 1:1 chelate to form chelate species of higher molecular weight supporting the above conclusion.

In view of the indication of polymerization in the system, it was considered worth-while to carry out a mathematical analysis of the potentiometric data. Considering the formation of binuclear chelate species which seems to be the first step in the polymerization of the chelate, the reaction may be represented as:



The equilibrium constant, K_D , for the reaction may be expressed as:

$$K_D = \frac{[(\text{UO}_2\text{A})_2][\text{H}^+]^4}{[\text{UO}_2^{2+}]^2[\text{H}_2\text{A}]^2} \quad (8)$$

Other pertinent equations are:

$$T_M = [\text{UO}_2^{3+}] + 2[\text{UO}_2(\text{OH})_2\text{UO}_2] + [\text{UO}_2\text{A}] + 2[(\text{UO}_2\text{A})_2] \quad (9)$$

$$T_{\text{OH}} + [\text{H}^+] = 2[\text{UO}_2(\text{OH})_2\text{UO}_2] + 2[\text{UO}_2\text{A}] + 4[(\text{UO}_2\text{A})_2] \quad (10)$$

$$T_A = [\text{H}_2\text{A}] + [\text{UO}_2\text{A}] + 2[(\text{UO}_2\text{A})_2] \quad (11)$$

Combination of equations 1, 8 and 9 and substitution of the value of K_D (from equation 2) gives

$$T_M - [\text{UO}_2^{3+}] - \frac{2.89 \times 10^{-6}}{[\text{H}^+]^2} [\text{UO}_2^{2+}]^2 \left/ \frac{[\text{UO}_2^{3+}][\text{H}_2\text{A}]}{[\text{H}^+]^2} \right. = 2K_D \frac{[\text{UO}_2^{3+}][\text{H}_2\text{A}]}{[\text{H}^+]^2} + K \quad (12)$$

After determining the concentrations of $[\text{UO}_2^{3+}]$ and $[\text{H}_2\text{A}]$ with the help of equations 9–11, a plot of the expression on the left side of equation 12 against the corresponding values of $[\text{UO}_2^{3+}][\text{H}_2\text{A}]/[\text{H}^+]^2$ should give a straight line of slope $2K_D$ and intercept on Y-axis equal to K , if the chelate exists in solution mainly as a dimer. Likewise it may be shown that a plot of the values on the left side of equation 12 against the corresponding values of $[\text{UO}_2^{3+}]^2[\text{H}_2\text{A}]^2/[\text{H}^+]^4$ should yield a straight line, if a trimer is the predominant species present in the solution. A plot of the potentiometric data in the range $m = 0$ to $m = 0.8$ obtained over a four-fold concentration range of the metal chelate, in accordance with equation 12, is shown in Fig. 4. The straight line (Fig. 4) gave a value of $-\log K_D = 10.00$ and $-\log K = 6.68$. This value of $-\log K$ is in close agreement with the value of $-\log K$ given in Table 1. Moreover a plot of the expression on the left side of equation 12 against the corresponding value of $[\text{UO}_2^{3+}]^2[\text{H}_2\text{A}]^2/[\text{H}^+]^4$ did not give a linear relationship indicating that the binuclear chelate (2:2 dimer) is the predominant species present in the solution under the experimental conditions.

Hydrolysis of the 2:2 Dimer: A gradual fall in the values of $-\log K$ calculated above $m = 0.8$ and the occurrence of the inflexion point in curves 1–3 (Fig. 3) at $m > 2$ indicated hydrolysis of the chelate

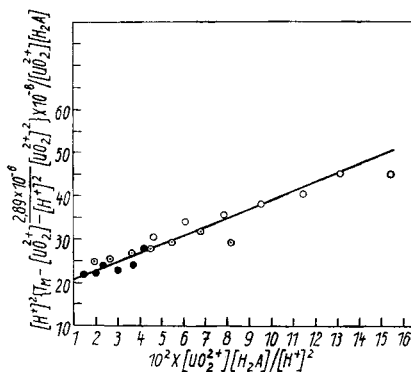
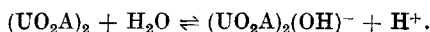


Fig. 4. Plot of the data of fig. 3, illustrating dimerization of monohydroxo- uranyl catechol chelate. $\circ = 5 \times 10^{-3} \text{ M}$; $\odot = 2.5 \times 10^{-3} \text{ M}$; $\bullet = 1.25 \times 10^{-3} \text{ M}$.

with the formation of hydroxo complexes in the system. If we represent the reaction as:



The equilibrium constant, K_h , for the reaction may be expressed as:

$$K_h = \frac{[(\text{UO}_2\text{A})_2(\text{OH})][\text{H}^+]}{[(\text{UO}_2\text{A})_2]} \quad (13)$$

Other pertinent equations are:

$$T_M = [\text{UO}_2^{2+}] + 2[\text{UO}_2(\text{OH})_2\text{UO}_2] + [\text{UO}_2\text{A}] + 2[(\text{UO}_2\text{A})_2] + 2[(\text{UO}_2\text{A})_2(\text{OH})] \quad (14)$$

$$T_{\text{OH}} + [\text{H}^+] = 2[\text{UO}_2(\text{OH})_2\text{UO}_2] + 2[\text{UO}_2\text{A}] + 4[(\text{UO}_2\text{A})_2] + 5[(\text{UO}_2\text{A})_2(\text{OH})], \quad (15)$$

$$T_A = [\text{H}_2\text{A}] + [\text{UO}_2\text{A}] + 2[(\text{UO}_2\text{A})_2] + 2[(\text{UO}_2\text{A})_2(\text{OH})]. \quad (16)$$

Combination of equations 1, 2, 8 and 14–16 gives,

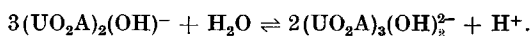
$$\frac{8K_2^2 \cdot K_D}{[\text{H}^+]^8} [\text{UO}_2^{2+}]^6 + \frac{8K_2 \cdot K_D}{[\text{H}^+]^6} [\text{UO}_2^{2+}]^5 + \frac{2K_D}{[\text{H}^+]^4} [\text{UO}_2^{2+}]^4 + \frac{2K_2 \cdot K}{[\text{H}^+]^4} [\text{UO}_2^{2+}]^3 + \left(\frac{6K_2}{[\text{H}^+]^2} + \frac{K}{[\text{H}^+]^2} \right) [\text{UO}_2^{2+}]^2 + 5[\text{UO}_2^{2+}] - 5T_M + 2T_{\text{OH}} + 2[\text{H}^+] = 0. \quad (17)$$

Knowing the values of K , K_2 and K_D , computation of the equilibrium concentrations of the free uranyl ions present in solution could be made by the use of equation 17. Concentration of the other species present in the reaction mixture could then be calculated from equations 14–16. The mean values of $-\log K_h$, thus calculated in the range $m = 0.96$ and $m = 1.6$ from the curves (Fig. 3) in a four-fold concentration range of the metal salt are presented in table 2.

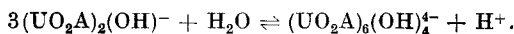
Table 2

T_A/T_M	T_M or T_A	$-\log K_h$
1	$5 \cdot 10^{-3}$ M	5.26 ± 0.03
1	$2.5 \cdot 10^{-3}$ M	5.49 ± 0.06
1	$1.25 \cdot 10^{-3}$ M	5.69 ± 0.04

In this case also, calculations above m values of 1.6 showed a gradual fall in the values of $-\log K_h$. This fact together with the occurrence of an inflexion point at $2^{2/3}$ moles of alkali per mole of the metal ion may be explained on the basis of the formation of trinuclear chelate species having two hydroxo groups. A probable reaction may be represented as:



The results may also be explained on the basis of the formation of an hexamer in accordance with the reaction:



Due to the appearance of solid phase in the reaction mixture above pH 5.0, the potentiometric data could not be analysed and, therefore, it has not been possible to distinguish between above alternative reactions.

The authors are thankful to Prof. W. U. MALIK, Head of the Chemistry Department, for providing laboratory facilities and to the C.S.I.R. authorities for providing a research fellowship to one of them (S.K.V.).

Roorkee (India), Chemical Laboratories, University of Roorkee.

Bei der Redaktion eingegangen am 3. August 1966.