that the values of ΔH and ΔS reported for the iron(III) chloride reactions[31] depend upon the very questionable assumption that the absorbancy indices are independent of temperature.[32] When the values of ΔH and ΔS for the iron(III) reactions are accurately known, the comparison with the values for the chromium(III) reactions will be particularly significant since in the latter system there is no change in coördination number with complexing.

Acknowledgment.—The authors wish to acknowledge both the financial assistance already cited[2] and helpful discussions regarding this subject with Professor H. Taube.

MADISON, WISCONSIN

[31] E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

[32] Some species for which this assumption has been demonstrated to be invalid were studied in ref. 24h. It has been shown recently that the absorbancy of hydrated metal ions in the solid state increases with an increase in temperature and that this temperature dependence has a theoretical basis (O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957)).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Isomeric Dichlorotetraaquochromium(III) Ions; their Separation, Spectra and Relative Stabilities[1]

BY EDWARD L. KING, SISTER M. JOHN MARK WOODS, O.P., AND HENRY S. GATES

RECEIVED FEBRUARY 14, 1958

The previously unresolved geometrical isomers of dichlorotetraaquochromium(III) ion have been separated by ion-exchange methods. The more easily eluted isomer is demonstrated on the basis of its spectrum and elution characteristics to be the same isomer as that present in the green solid $(Cr(OH_2)_4Cl_2)Cl\cdot 2H_2O$. This more easily eluted isomer is assigned the *trans* configuration in view of the precedent for an ion with such a configuration being less strongly held in the resin phase than the corresponding *cis* isomer. The spectra of the two isomers are reported. In conformity with the ligand-field theory, the unsymmetrical *cis* isomer has a greater absorbancy than the *trans* isomer. The *trans* isomer is slightly less stable than the *cis* isomer.

Octahedral dichlorotetraaquochromium(III) ion can exist in *cis* and *trans* isomeric forms. The solid green chromium(III) chloride which crystallizes from previously heated solutions of chromium(III) in concentrated hydrochloric acid has long been known to contain dichlorochromium(III) ion as its only chromium(III) species[2]; which isomer this is has not been definitely established.[3] The ion-exchange method, by which the *cis* and *trans* isomers of a number of octahedral complex ions have been separated,[4,5] has been used successfully in the present study.

Experimental Methods

Reagents.—Reagent grade chemicals were used and all solutions were prepared using doubly distilled water. The Dowex-50W resin was treated as described elsewhere.[5]

Equipment Used.—Both a Beckman model DU spectrophotometer and a Cary model 14 recording spectrophotometer were used. An eight foot long ion-exchange column with a jacket for the circulation of water at 3–6° was used. The low temperature was necessary to minimize the aquation and/or isomerization of the chromium(III) species.

Analytical Methods.—The quantitative determination of total chromium was carried out by the spectrophotometric measurement of the concentration of chromate ion[6] formed from chromium(III) species by the action of peroxide in alkaline solution. The analysis of eluent portions for total chloride ion was carried out by the conventional titration with silver nitrate using chromate ion as an indicator; the chromium(III) chloride species were first decomposed by base.

Experimental Results

Preliminary Studies.—Although the initial ion-exchange experiments failed to yield evidence for two different ions with the elution characteristics of a +1 ion, the species or mixture of species with this charge so isolated from an equilibrated solution was found to have a spectrum different from that exhibited by the species of charge +1 found in a solution prepared by dissolving $(Cr(OH_2)_4Cl_2)Cl\cdot 2H_2O$. This suggested that the cold concentrated hydrochloric acid solution from which $(Cr(OH_2)_4Cl_2)Cl\cdot 2H_2O$ precipitates would be enriched in the isomer[7] of $CrCl_2^+$ not present in the solid compound, it being assumed that isomerization occurs slowly at 0°. This was found to be the case. These preliminary experiments demonstrated the ratio of the molar absorbancy indices at 450 and 635 mμ for the two ions believed to have a charge of +1 to be different, 0.9 for the dichlorochromium(III) ion in the solid and 1.4 for the species (or mixture of species) of charge +1 in this mother liquor.

The Ion-exchange Separation of the Isomers.—The relative instability of $CrCl_2^+$ in solution ($Q_2 = (CrCl_2^+)/(CrCl^{++})(Cl^-) = 0.12$ at I (the ionic strength) $\cong 4$ at 95°)[8] imposed certain limitations upon the ion-exchange procedure. The presence, in an equilibrated solution, of a relatively high concentration of the ions of charge +3 and +2, Cr^{+3} and $CrCl^{++}$, was the complicating factor. In being taken into the resin phase, these ions

---

[1] Supported in part by grants from the Research Committee of the Graduate School, University of Wisconsin, and the U. S. Atomic Energy Commission (Contract AT(11-1)-64, Project No. 3).

[2] A. Werner and A. Gubser, *Ber.*, **34**, 1579 (1901).

[3] The recent assignment of the *cis* configuration to this isomer (ref. 13) on the basis of certain spectral characteristics suffers the disadvantage that but one of the isomers was studied.

[4] (a) E. L. King and R. R. Walters, THIS JOURNAL, **74**, 4471 (1952); (b) M. Mori, M. Shibata and J. Azami, *J. Chem. Soc. Japan*, **76**, 1003 (1955); (c) M. Mori, M. Shibata and M. Nanasawa, *Bull. Chem. Soc., Japan*, **29**, 947 (1956).

[5] J. T. Hougen, K. Schug and E. L. King, THIS JOURNAL, **79**, 519 (1957).

[6] G. W. Haupt, *J. Research Natl. Bur. Standards*, **48**, 414 (1952).

[7] Water molecules in the first coördination shell of chromium(III) species in solution will not, in general, be shown. It is assumed that chromium(III) has coördination number 6 in all species under consideration.

[8] H. S. Gates and E. L. King, THIS JOURNAL, **80**, 5011 (1958).

liberate hydrogen ion which makes the equilibrium in the reaction $CrCl_2^+$ (aq.) + H^+ (resin) = $CrCl_2^+$ (resin) + H^+ (aq.) unfavorable. A solution containing a relatively large fraction of the chromium(III) as $CrCl_2^+$ was prepared by heating chromium(III) chloride hexahydrate at 170–190° in a sealed tube for one hour; at this temperature, the material is a liquid. A portion of this hot syrup was quenched by delivering it into 10^{-3} *M* perchloric acid at 0°. The chromium(III) chloride species of charge +1 were completely taken up from this medium by the ion-exchange resin. Some chromium(III) species passed through the column with a transit time approximately equal to that of the solvent; presumably this was the neutral species $Cr(OH_2)_3Cl_3$. The column was washed with 0.001 *M* perchloric acid before the elution was started. (The rate at which the cationic chromium(III) species are eluted by 0.001 *M* perchloric acid is very low, immeasurably low as far as the present study is concerned.)

Many successful elution experiments were carried out at 3–6° using 0.10 *M* perchloric acid as the eluting agent; early successive chromium-containing eluent portions exhibited a relatively constant value of A_{450}/A_{635},[9] equal to ~0.9, and the late successive chromium-containing eluent portions exhibited relatively constant value of A_{450}/A_{635}, equal to $\cong 1.45$. In no experiment, however, was essentially all of the species with $a_{450}/a_{635} \cong 0.9$ separated from essentially all of the species with $a_{450}/a_{635} \cong 1.45$.

Nineteen eluent portions from five experiments were analyzed for total chromium and total chloride. In the case of the late eluent portions so studied, a value of (chloride)/(chromium) = 2.04 ± 0.01 was observed; this chromium(III) species has, therefore, the composition $CrCl_2^+$. In the case of the early eluent portions, the values of this ratio were significantly higher; nine of the eleven samples determined had values in the range 2.14 to 2.31. This might suggest that species containing more than two chloride ions per chromium(III) ion were present. The neutral species $Cr(OH_2)_3Cl_3$ went straight through the column, however, or was certainly washed out of the column with the 0.001 *M* perchloric acid. While the sample preparation conditions (the molten hydrated salt at 170–190° for one hour) might favor the formation of a dimeric chloride-bridged species, *e.g.*, $Cl_2CrClCrCl_2^+$, which might give this observation, another explanation seems reasonable. The aquation reaction $CrCl_2^+ \rightarrow CrCl^{++} + Cl^-$ occurs slowly during the course of elution; of the products of this reaction only the chloride ion moves from the point at which it is produced, and it moves with approximately the velocity of the solvent. While the early portions of the eluent are coming off the column considerable $CrCl_2^+$ is on the column, but while the late portions of eluent are coming off of the column there is little $CrCl_2^+$ on the column. Thus only the early eluent portions are contaminated with the free chloride liberated in the aquation reaction. Measurements of the absorbancy over the range λ 200 to 750 mμ disclose no significant differences in the absorbancy index values exhibited by the two types of solutions, early eluent and dissolved solid $(Cr(OH_2)_4Cl_2)Cl\cdot 2H_2O$. Thus absorbancy data aid in establishing the composition of the more easily eluted species, which was fixed with less certainty by the chloride and chromium analyses. Additional evidence is afforded by the observation that the elution pattern (relative chromium(III) concentration *vs.* volume of eluent) exhibited by the chromium(III) species derived from the solid is essentially the same as the early part of the elution pattern exhibited by the quenched equilibrated molten salt.[10]

If one assumes the values of the absorbancy indices observed for the dissolved solid to be characteristic of one isomer and the values observed for the late eluent portions to be characteristic of the other isomer, one can calculate the composition of each eluent portion from the measured absorbancy values at the two wave lengths. The results of such a calculation are presented in the lower part of Fig. 1[11]; the upper part of Fig. 1 shows a typical elution curve.

The Spectra of the Isomeric Species.—The absorbancy indices of the two isomeric species have been determined over the spectral range 200 to 750 mμ; most of these data are presented graphically in Fig. 2.[12] The absorbancy indices of the dichlorochromium(III) ion present in solid $(Cr(OH_2)_4Cl_2)Cl$ have been published recently by Elving and Zemel.[13] The absorbancy index of this species in the region of 450 mμ in concentrated electrolyte solution (6 and 8.7 *M* perchloric acid) is significantly different from that of either isomeric species studied in the present work in dilute perchloric acid. This puzzling discrepancy has been demonstrated to be a medium effect, as is shown in Table I. That the effect is not due primarily to the acidity is demonstrated by measurements on solutions of the composition 1 *M* perchloric acid–5 *M* sodium perchlorate which gave a value of a_{450} for species II of $23._4$. A much more spectacular medium effect upon the spectrum of a cationic inorganic species is that exerted by perchlorate ion in the concentration range up to 1–2 molar upon the absorbancy index of cerium(III) at 296.5 mμ.[14] While this effect has been interpreted as indicating that a cerium(III) perchlorate species is present,[14b,c] the argument is not convincing. An abnormally low value of the "apparent distance of closest approach" (3.7 Å.) is required in order to rationalize the ionic strength dependence of the value of the apparent equilibrium quotient for the formation of

---

(9) The absorbancy of the solution at the wave length λ is A_λ. The relationship of the various quantities used in describing the light absorption is $\log I_0/I = A = abc$, where *a*, *b* and *c* are the molar absorbancy index, the cell length in cm. and the molar concentration, respectively.

(10) These experiments were performed by Mr. Norton Zarem.

(11) The extent to which isomerization of the less easily eluted dichloro complex, during the ion-exchange experiment, leads to late eluent portions which contain some of the more easily eluted isomer is difficult to assess accurately. Rough experiments suggest the rate of this reaction in solution to be low enough to have a negligible effect on the isomer purity.

(12) A tabulation of the values of the absorbancy indices of these species will be sent upon request.

(13) P. J. Elving and B. Zemel, This Journal, **79**, 1281 (1957).

(14) (a) T. W. Newton and G. M. Arcand, *ibid.*, **75**, 2449 (1953), (b) L. J. Heidt and J. Berestecki, *ibid.*, **77**, 2049 (1955); (c) L. H. Sutcliff and J. R. Weber, *Trans. Faraday Soc.*, **52**, 1225 (1956).

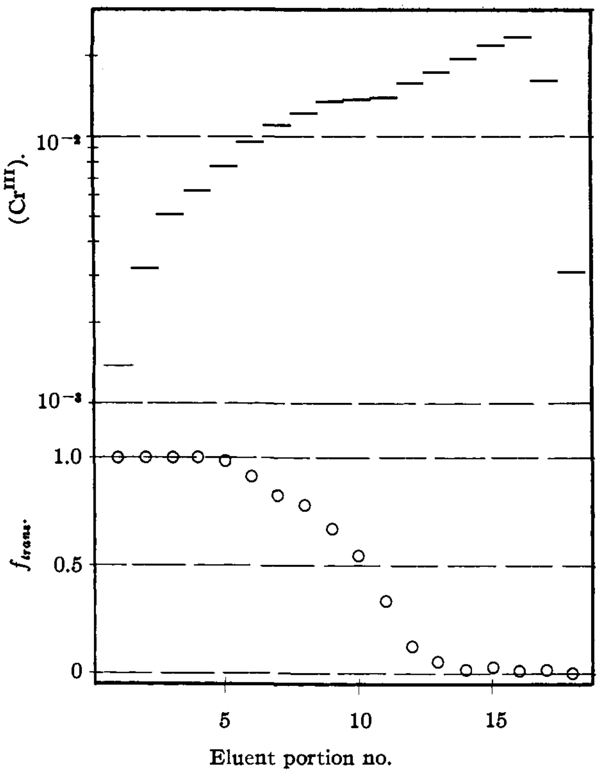

Fig. 1.—Upper, molarity of chromium(III) in eluent as function of volume 0.1 *M* perchloric acid. (Each eluent portion has volume of ~15 ml.) Lower, calculated fraction of the $CrCl_2^+$ which is the more easily eluted isomer (the *trans* isomer) in each eluent fraction.

$CeClO_4^{++}$,[14b] and an essentially unprecedented negative value of ΔS for the association of two ions of unlike charge sign follows from the treatment of the absorbancy data in terms of ion association to give a new species.[14b,c] While these arguments, in themselves, do not prove that $CeClO_4^{++}$ is nonexistent in cerium(III) perchlorate solutions, they do suggest that this interpretation is open to question. The problem of distinguishing ill-defined medium effects upon a spectrum of a species and specific interaction to form new species as the causes of variations in absorbancy with composition has been discussed by Newton and Baker.[15] That the cause of the spectral change in the cerium(III) perchlorate system is a non-specific medium effect seems very likely in view of the observation that the absorbancy of cerium(III) at 296.5 mμ is altered dramatically by changing the solvent to D_2O.[16] There seems to be no reason to ascribe the medium effect upon spectrum shown in Table I to the formation of a new species involving $CrCl_2^+$ and ClO_4^-.

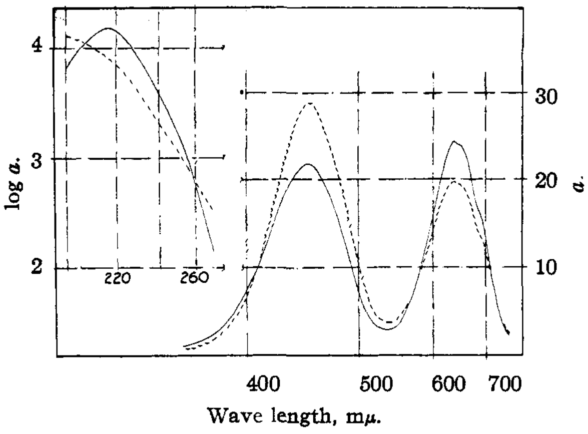

Fig. 2.—Absorbancy indices of isomeric $CrCl_2^+$ species: more easily eluted isomers (*trans*), ———, less easily eluted isomer (*cis*), --------.

Discussion

The Assignment of Configuration to the Isomers.—The fact that, for all systems of isomeric pairs of known configuration which have been studied, the *trans* isomer of an octahedral complex $CoA_4X_2^{+n}$ (or $Co(AA)_2X_2^{+n}$) is more easily eluted than the corresponding *cis* isomer[4] suggests the same assignment for the present system. The ion-exchange behavior thus indicates the $Cr(OH_2)_4Cl_4^+$ species with $a_{450}/a_{635} = 0.90$ to be the *trans* isomer and the $Cr(OH_2)_4Cl_2^+$ species with $a_{450}/a_{635} = 1.4_6$ to be the *cis* isomer. Do any of the other properties of these species lend support to this assignment of configuration? The isomer to which the *trans* configuration is assigned shows the maximum of an absorption band in the accessible region of the ultraviolet. The empirical generalization that *trans* isomers of octahedral complexes show such "third bands"[17] appears also to have some theoretical support.[18]

TABLE I

ABSORBANCY INDICES OF $Cr(OH_2)_4Cl_2^+$ SPECIES IN VARIOUS AQUEOUS PERCHLORIC ACID MEDIA

Species[a]	$(HClO_4)$	a_{450}	a_{640}
I	0.1–1.0	28.8	19.6
II	0.1–1.0	21.8	24.1
	4	23.4	24.1
	6	24.6	23.5
	8	26.8	22.9
III[13]	6.0	27.8	23.4
	8.7	30.4	22.5

[a] I, the less easily eluted $CrCl_2^+$ species; II, species present in solid $(Cr(OH_2)_4Cl_2)Cl \cdot 2H_2O$ (*or* the more easily eluted $CrCl_2^+$ species). (These measurements were made on freshly prepared solutions of the solid.) III, species present in solid $(Cr(OH_2)_4Cl_2)Cl$.

The ligand field theory has been applied to the spectra of isomeric complex ion of this type.[19] The prediction that the total absorption under both

---

(15) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **61**, 934 (1957).

(16) Drs. T. W. Newton and F. B. Baker of the Los Alamos Scientific Laboratory have made the unpublished observation that the absorbancy of cerium(III) at the peak at 296.5 mμ (in H_2O) is lowered 19.4% by changing the solvent from H_2O to 94% D_2O. The solution composition was 2.2×10^{-3} *M* cerium(III) perchlorate, 8.4×10^{-3} *M* perchloric acid and 7.2×10^{-4} *M* sodium perchlorate. The absorbancy at the peaks at 221.7, 238.8 and 252.6 mμ (in H_2O) were all increased by ~1.5% in D_2O. The maxima in all four of the peaks were displaced ~0.5 mμ toward shorter wave length in D_2O.

(17) R. Tsuchida and S. Kashimoto, *Bull. Chem. Soc. Japan*, **11**, 785 (1936).

(18) K. Nakamoto, J. Fujita, M. Kobayashi and R. Tsuchida, *J. Chem. Phys.*, **27**, 439 (1957).

(19) C. J. Ballhausen and C. K. Jorgensen, *Kgl. Danske Videnskab. Selskab, Mat. fys., Medd.*, **29**, No. 14 (1955); L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

bands in the visible region of the spectrum is larger for the *cis* isomer[20] tends to confirm the assignment being suggested; the area under the *cis* curve is ~5% greater than the area under the *trans* curve.

The Equilibrium, *cis*-$Cr(OH_2)_4Cl_2^+$ = *trans*-$Cr(OH_2)_4Cl_2^+$.—Measurement of the absorbancies of all of the eluent portions at the two wave lengths, 450 and 635 mμ, allows the calculation of the total amount of each isomeric dichlorochromium(III) ion in the quenched equilibrated mixture. Such measurements in two experiments give (*trans*)/(*cis*) = $0.5_6 \pm 0.0_3$; this is the value of the equilibrium quotient for the isomerization reaction in the molten hydrated salt if the quenching procedure is effective. An estimate of the value of this quotient in solutions of I (the ionic strength) $\cong 4$, at temperatures in the range 30–95° can be obtained from the apparent absorbancy index value of the equilibrium mixture of the two isomers.[8] The value so determined is 0.5 ± 0.2. This value is within experimental error of the value observed in the dithiocyanatotetraaquochromium(III) system.[5] The *cis* and *trans* complexes in the dihydroxobis-(ethylenediamine)-cobalt(III) and the hydroxoaquobis-(ethylenediamine)-cobalt(III) systems are also of comparable stability, (*trans*)/(*cis*) = 0.7 and 1.2, respectively, at 25° in 1 *M* sodium nitrate.[21] Statistical considerations alone suggest a value of 0.25 for this ratio. The observed somewhat greater stability of the *trans* complex in these systems might be rationalized in terms of electrostatic considerations, although the diaquobis-(ethylenediamine)-cobalt(III) system, in which such electrostatic factors might be expected to be less pronounced, has an equilibrium value of (*trans*)/(*cis*) of 0.017.[21]

Taube and Myers[22] report that the oxidation of chromium(II) by iron(III) in 2 *M* hydrochloric acid results in chromium(III) chloride species which are not, exclusively, a mixture of $CrCl^{++}$ and the $CrCl_2^+$ species here identified as the *trans* isomer. The absorbancy data which they report suggests that *cis*-$CrCl_2^+$ is a component of the mixture of chromium(III) chloride species so produced.

MADISON, WISCONSIN

[20] F. Basolo, C. J. Ballhausen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

[21] J. Bjerrum and S. E. Rasmussen, *ibid.*, **6**, 1265 (1952).

[22] H. Taube and H. Myers, THIS JOURNAL, **76**, 2103 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Infrared Absorption Spectra of Inorganic Coördination Complexes. XVI. Infrared Studies of Glycino-Metal Complexes[1,2]

BY A. J. SARACENO, I. NAKAGAWA, S. MIZUSHIMA,[3] COLUMBA CURRAN AND J. V. QUAGLIANO

RECEIVED APRIL 14, 1958

The assignment of infrared bands of glycino-metal complexes, based on the study of normal vibrations of glycine, mercuric amidohalides and 1,2-dichloroethane has been made. Significant differences in the spectra of geometrical isomers of Pt(II) and Co(III) have been observed. An interesting dehydration effect has been found to occur for the spectrum of bis-(glycino)-zinc(II) monohydrate.

Previous work on the infrared spectra of some glycino-metal complexes dealt primarily with the nature of the metal-to-ligand bond.[4,5] Recently, calculations of normal vibrations of molecules closely related to these complexes, and assignments of the spectra of glycine and deuterated glycine have also been reported.[6–9] In the present investigation the infrared spectra of several glycino-metal complexes are reported in the 2-15μ region together with a detailed assignment of the observed bands. Assignment of the observed bands for the coördination compounds has been made on the basis of the study of normal vibrations of glycine, mercuric amido halides and 1,2-dichloroethane. Studies on the nature of the metal-to-ligand bond and *cis*–*trans* isomerism are further discussed in relation to the spectra observed for the metal complexes.

Experimental

Preparation of Compounds.—*cis*- and *trans*-**Bis-(glycino)-platinum(II)**, $Pt(NH_2CH_2CO_2)_2$, were prepared as described by Pinkard and co-workers[10] and were twice recrystallized from water.

Anal. Calcd. for $Pt(NH_2CH_2COO)_2$: C, 13.99; H, 2.35; Pt, 56.86; N, 8.16. Found: *cis*: C, 14.22; H, 2.36; Pt, 57.04; N, 8.50. *trans*: C, 14.20; H, 2.25; Pt, 56.80; N, 7.93.

Bis-(glycino)-copper(II) monohydrate, $Cu(NH_2CH_2COO)_2 \cdot H_2O$, was prepared as reported by Abderhalden and Schnitzler.[11]

Anal. Calcd. for $Cu(NH_2CH_2COO)_2 \cdot H_2O$: C, 20.91; H, 4.39. Found: C, 21.06; H, 4.39.

Bis-(glycino)-nickel(II) dihydrate, $Ni(NH_2CH_2COO)_2 \cdot 2H_2O$, was prepared according to the directions of Stosick.[12]

Anal. Calcd. for $Ni(NH_2CH_2COO)_2 \cdot 2H_2O$: C, 19.78; H, 4.98; Ni, 24.17; N, 11.54. Found: C, 20.42; H, 5.01; Ni, 24.53; N, 11.48.

Bis-(glycino)-zinc(II) monohydrate, $Zn(NH_2CH_2COO)_2 \cdot H_2O$ was prepared according to the method of Dubsky and Rabas.[13]

---

[1] Paper XV in series, *Spectrochim. Acta*, in press.

[2] Supported in part under A.E.C. Contract At(11-1)-38, Radiation Project of the University of Notre Dame.

[3] Visiting Professor from Faculty of Science, Tokyo University.

[4] D. N. Sen, S. Mizushima, C. Curran and J. V. Quagliano, THIS JOURNAL, **77**, 211 (1955).

[5] D. M. Sweeny, C. Curran and J. V. Quagliano, *ibid.*, **77**, 5508 (1955).

[6] S. Mizushima, I. Nakagawa and D. M. Sweeny, *J. Chem. Phys.*, **25**, 1006 (1956).

[7] I. Nakagawa and S. Mizushima, *ibid.*, **21**, 2195 (1953).

[8] I. Nakagawa and S. Mizushima, *Bull. Chem. Soc. Japan*, **28**, 589 (1955).

[9] M. Tsuboi, T. Onishi, I. Nakagawa, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, in press.

[10] F. W. Pinkard, E. Sharratt, W. Wardlaw and E. G. Cox, *J. Chem. Soc.*, 1012 (1934).

[11] E. Abderhalden and E. Schnitzler, *Z. physik. Chem.*, **163**, 96 (1927).

[12] A. J. Stosick, THIS JOURNAL, **76**, 362, 365 (1954).

[13] J. V. Dubsky and A. Rabas, *Spisy vydávané přirodovědeckou Fakultou Masarykovy Univ.*, No. 123, 3 (1930); *C. A.*, **25**, 2655 (1931).