

Spectroscopic Studies of Charge Transfer Complexes

XIV. Ethyl Isothiocyanate and Allyl Isothiocyanate with Iodine

ELSE PLAhte, JUST GRUNDNES and PETER KLÆBOE

Universitetets Kjemiske Institutt, Blindern, Oslo 3, Norway

The charge transfer complexes between ethyl isothiocyanate and allyl isothiocyanate with iodine have been studied in the ultraviolet, visible, and infrared regions. Spectral data and the thermodynamic functions ΔG_{20}° , ΔH° and ΔS° for the 1:1 complexes have been determined. These data revealed that the isothiocyanates were much weaker Lewis bases than the sulphides. On the other hand methyl thiocyanate interacted so weakly with iodine that no quantitative data could be obtained.

During the last years the charge transfer complexes between iodine and various donors containing sulphur have been investigated. In these compounds the complex bond to iodine has been formed from a sulphur atom acting through a lone pair electron. Generally, these donors have formed very stable complexes with iodine. Thus, the aliphatic^{1,2} and cyclic^{3,4} sulphides are much stronger bases than the corresponding ethers.⁵ In the thioanisoles⁶ the electronegative phenyl group makes these compounds somewhat less basic. Moreover, Lang⁷ found that thiourea and thioacetamide were among the strongest donors known towards iodine and that the sulphur atom in both cases acted as the donor site. McCullough and Zimmermann⁸ reported that 1,4-dithiane and 1,4-thiodioxane formed 1:1 complexes with iodine, the sulphur atom being the donor site. In the heterocyclic compounds thiophene⁹ and thianthrene¹⁰ considerably lower basicity towards iodine was reported compared to the aliphatic sulphides. On the other hand it should be noted that unlike the compounds listed hitherto, the sulphoxides^{11,12} coordinate to iodine, to the interhalogens and to iodine cyanide not from the sulphur but from the oxygen atom.

On the basis of this information we felt it would be of interest to study some other sulphur compounds and particularly those having the group $>C=S$. However, the lower homologues of the thioketones are not stable but rearrange readily. We therefore decided to investigate some isothiocyanates (the mustard oils), which contain the group $R-N=C=S$, and their com-

plexes with iodine. While these molecules are of great pharmaceutical interest, comparatively little work has been done from a physical chemistry viewpoint. This is in sharp contrast to the thiocyanate ion which coordinates readily to transition metals¹³⁻¹⁵ and to iodine,¹⁶ and these complexes have been extensively studied.

Both the isothiocyanates and the thiocyanates $R-S-C\equiv N$ contain sulphur and nitrogen atoms having lone pair electrons which might be engaged in complex formation. In the present work we wanted to determine the formation constants (K), the standard heat of formation (ΔH°), and spectral parameters for the isothiocyanate-iodine complexes. Moreover, we would like to establish the site of the donor-acceptor bond and eventual variations in basicity with changing substituents R . We selected the two compounds ethyl isothiocyanate (ENCS) and allyl isothiocyanate (ANCS) which are commercially available and have low volatility. Moreover, we extended our studies to include methyl thiocyanate (MSCN) in order to establish eventual differences in basicity between the thiocyanates and the isothiocyanates.

EXPERIMENTAL

ENCS, ANCS, and MSCN were commercial products from Fluka AG. They were distilled twice in a Vigreux column under reduced pressure and only a small middle fraction was collected. It was found that ANCS decomposed fairly rapidly even in darkness at -20°C , and therefore this compound had to be redistilled before each spectrophotometric investigation. Iodine, reagent grade from Merck, and the solvents: heptane, carbon tetrachloride, chloroform, and dichloromethane, *Uvasole* from Merck, were used without further purification.

The ultraviolet and the visible spectra were recorded with a Beckman DK-1 spectrometer equipped with a thermostated cell holder. Matched pairs of ground glass stoppered silica cells of path length 1 cm were used. The infrared spectra were recorded with a Perkin-Elmer model 21 having sodium chloride optics.

RESULTS

Ultraviolet region. The isothiocyanates exhibit an absorption maximum of medium intensity ($\log \epsilon \sim 3$) in the region 244–248 $m\mu$ assigned¹⁷ as an $N \rightarrow V$ transition, but the alkyl thiocyanates¹⁸ have only a weak absorption band in this region. Around 290 $m\mu$ the three compounds ENCS, ANCS, and MSCN have low intensity absorption tails. The mixed solutions of iodine and ENCS in heptane display an ultraviolet absorption band around 290 $m\mu$ which is apparent from Fig. 1. This is undoubtedly the ENCS-iodine charge transfer (CT) band superposed on the free ENCS absorption tail and the free iodine absorption. By subtracting the latter two we obtained the slightly unsymmetrical absorption band with maximum at 288 $m\mu$. For the ANCS-iodine system the CT band was situated at 287 $m\mu$ in heptane. If the isothiocyanate and iodine were dissolved in more polar solvents, the absorption peak was somewhat displayed towards longer wave lengths as apparent from Table 1. Dissolved in acetonitrile, large amounts of triiodide ions were formed, suggesting irreversible reactions. Mixed solutions of MSCN and iodine showed a very weak, broad band around 280 $m\mu$ which probably can be

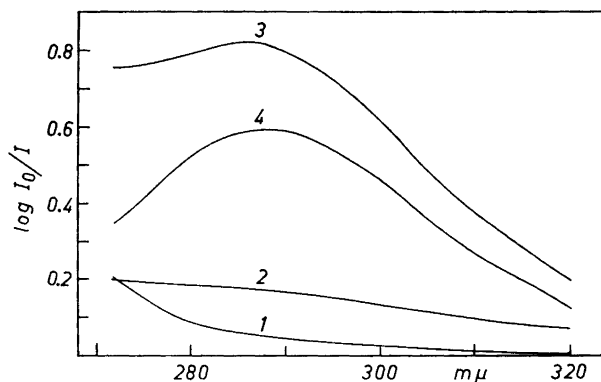


Fig 1. Ultraviolet absorption spectra of ethyl isothiocyanate and iodine in heptane at 20°C for 1 cm cell. The concentrations (M) are: (1) ENCS 0.005; (2) I₂ 0.003; (3) ENCS 0.005 and I₂ 0.003; (4) calculated complex absorption curve.

assigned to a *CT*-absorption. For very high MSCN concentrations, peaks at 290 and 360 m μ indicated the presence of triiodide ions.

The method of continuous variation¹⁹ was employed to determine the stoichiometry of the molecular complexes. As apparent from Fig. 2, distinct maxima for the complex absorption were observed for equal concentrations of isothiocyanate and iodine, indicating 1:1 complexes for both systems. The symmetrical shape of the curves seemed to exclude any significant amount of higher complexes for this concentration range.

Attempts were made to determine the formation constants of the isothiocyanate-iodine complexes at 20°C from the ultraviolet absorbance data.

Table 1. The absorption maxima, the half intensity widths and the maximum extinction coefficients of the ENCS-I₂ and ANCS-I₂ charge transfer bands in various solvents at 20°C.

Solvent	Dielectric constant	ENCS-I ₂			ANCS-I ₂		
		λ^a m μ	$\Delta \bar{\nu}_{1/2}$ 10 ³ × cm ⁻¹	ϵ^b M ⁻¹ cm ⁻¹	λ^a m μ	$\Delta \bar{\nu}_{1/2}$ 10 ³ × cm ⁻¹	ϵ^b M ⁻¹ cm ⁻¹
Heptane	1.9	288	2.2	32 000	287	2.2	
Carbon tetra- chloride	2.2	292	2.3	28 000	291	2.4	22 000
Chloroform	5.5	295	2.4		293	2.4	
Dichloro- methane	9.1	296	2.5	29 000	295	2.5	

^a The positions of the *CT*-bands refer to isothiocyanate concentrations of approx. 0.005 M and iodine concentrations of approx. 0.003 M.

^b The maximum extinction coefficients are obtained using the formation constants calculated from the *BS* absorption data (Tables 2 and 3).

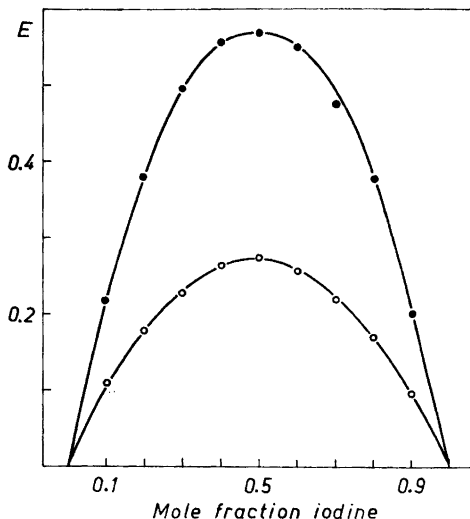


Fig. 2. Method of continuous variation of the ENCS-I₂ system in heptane (O) and the ANCS-I₂ system in carbon tetrachloride (●) at 20°C. The absorbance of the solution minus the calculated component absorbance was plotted *versus* the mole fraction of iodine at 290 mμ. The total concentration of ENCS plus I₂ was 5.58×10^{-3} M and of ANCS plus I₂ 1.04×10^{-2} M.

Series of ENCS-iodine solutions in heptane with a constant iodine concentration and varying ENCS concentrations were recorded. Since the complex was quite weak, high ENCS concentrations were necessary, resulting in a strong donor absorption around 290 mμ. Therefore, only the absorption data at the long wave length tail below 300 mμ²⁰ could be used for the quantitative calculations. The formation constants (*K*) varied between the values 1.6 and 1.1 l/mole at 20°C when the absorbance data in the region 300 to 315 mμ were employed. The iodine concentration was kept at 2.7×10^{-4} M, the ENCS concentration was varied between 0.07 and 0.2 M, and the Scott representation²¹ was employed. For the ANCS-iodine system, the corresponding calculations were based upon absorbance data in carbon tetrachloride solutions in the same spectral region, and even larger discrepancies between the *K*'s were observed. Thus, no reliable formation constants could be obtained from the ultraviolet absorbance data.

The concentration of 1:1 complex in a mixed isothiocyanate-iodine solution was further calculated, using the more reliable formation constants obtained in the visible region (Tables 2 and 3). The extinction coefficients (ϵ) of the *CT* band at the peak was then estimated from the ultraviolet absorbance data obtained with approximately equimolar donor and iodine solutions. The ϵ values are listed in Table 1 and even if large error limits must be allowed, the *CT*-bands of both the ENCS-iodine and the ANCS-iodine systems are undoubtedly quite strong. From the formula:²² $f_{CT} = 4.32 (\pi/2) \epsilon_{\max} \Delta \bar{\nu}_{1/2} \times 10^{-9}$ the oscillator strengths for the *CT*-band in the ENCS- and ANCS-iodine systems were equal to 0.5 and 0.35, respectively, when observed in heptane and carbon tetrachloride.

Visible region. When ENCS or ANCS were added to a solution of iodine in an inert solvent, the visible iodine absorption peak was blue shifted, characteristic of complex formation. In heptane solutions with the same iodine and

varying ENCS concentrations, the curves passed through an isosbestic point at $508\text{ m}\mu$ and the blue shifted (*BS*) peak was situated at approximately $460\text{ m}\mu$. Different series of ENCS-iodine solutions were recorded in the visible region at 20°C , using heptane, carbon tetrachloride and dichloromethane as solvents. Since the complex was weak, quite high concentrations of ENCS were employed.²³ The absorbance values at four different wave lengths near the *BS*-peak were treated by the Scott representation²¹ and the experimental points fitted with straight lines. The calculated formation constants (K) and extinction coefficients (ϵ) obtained in the various solvents at 20°C are listed in Table 2. Because the complexes are weak, the relative uncertainties

Table 2. Formation constants and extinction coefficients of the *BS*-band in the ENCS- I_2 system at 20°C in different solvents.^a

Solvent	440 $\text{m}\mu$		445 $\text{m}\mu$		450 $\text{m}\mu$		455 $\text{m}\mu$		460 $\text{m}\mu$	
	K M^{-1}	ϵ $\text{M}^{-1}\text{ cm}^{-1}$	K M^{-1}	ϵ $\text{M}^{-1}\text{ cm}^{-1}$	K M^{-1}	ϵ $\text{M}^{-1}\text{ cm}^{-1}$	K M^{-1}	ϵ $\text{M}^{-1}\text{ cm}^{-1}$	K M^{-1}	ϵ $\text{M}^{-1}\text{ cm}^{-1}$
Heptane ^b	1.00	1350	1.07	1380	1.14	1420	1.14	1500		
Carbon tetra- chloride ^c					1.06	1340	1.12	1380	1.18	1410
Dichloro- methane ^d	0.64	1590	0.64	1610	0.65	1620	0.64	1630		
Mean value	K (heptane) = $(1.1 \pm 0.1)\text{ M}^{-1}$ K (carbon tetrachloride) = $1.1 \pm 0.1)\text{ M}^{-1}$ K (dichloromethane) = $(0.65 \pm 0.15)\text{ M}^{-1}$									

^a Calculated by the Scott representation.

^b Calculated from absorption data of 8 mixed solutions; $[\text{I}_2] = 0.001\text{ M}$, $[\text{ENCS}]$ varied from 0.1 M to 0.8 M .

^c Calculated from absorption data of 7 mixed solutions; $[\text{I}_2] = 0.001\text{ M}$, $[\text{ENCS}]$ varied from 0.2 M to 0.9 M .

^d Calculated from absorption data of 7 mixed solutions; $[\text{I}_2] = 0.001\text{ M}$, $[\text{ENCS}]$ varied from 0.1 M to 1.0 M .

Table 3. Formation constants and extinction coefficients of the *BS*-band in the ANCS- I_2 system at 20°C in carbon tetrachloride.^a

455 $\text{m}\mu$		460 $\text{m}\mu$		465 $\text{m}\mu$		470 $\text{m}\mu$	
K M^{-1}	ϵ $\text{M}^{-1}\text{ cm}^{-1}$	K M^{-1}	ϵ $\text{M}^{-1}\text{ cm}^{-1}$	K M^{-1}	ϵ $\text{M}^{-1}\text{ cm}^{-1}$	K M^{-1}	ϵ $\text{M}^{-1}\text{ cm}^{-1}$
0.89	1200	0.94	1240	0.96	1280	1.01	1290
Mean value:		$K = (0.95 \pm 0.15)\text{ M}^{-1}$					

^a Calculated by the Scott representation on the absorption data of 8 mixed solutions; $[\text{I}_2] = 7 \times 10^{-4}\text{ M}$, $[\text{ANCS}]$ varied from 0.4 M to 1.2 M .

are fairly large. However, the formation constants obtained at the various wave lengths vary within the experimental uncertainties. As apparent from Table 3 the ANCS-iodine system was investigated quantitatively only in carbon tetrachloride solution, because of low solubility in heptane and the occurrence of irreversible reactions in dichloromethane.

Attempts were made to calculate the standard enthalpies of formation (ΔH°) by determining the formation constants independently at various temperatures. However, since the relative uncertainties in the K 's are so large, a poor accuracy was obtained by this method. Therefore, it was found advantageous to calculate ΔH° from the absorbance data of a single mixed ENCS-iodine solution at different temperatures. In this procedure the difference between the extinction coefficients of the complex and of the free iodine ($\epsilon_c - \epsilon_f$) was assumed to be constant with temperature at the actual wave length. Two different ENCS-iodine solutions of various concentrations were measured in heptane at 10.5, 25.5, and 44.2°C. From the absorbance data at 450, 455, and 460 μ , ΔH° was calculated independently for each solution and each wave length after the equation given by Briegleb.²⁴ These data and those obtained for the ANCS-iodine system in carbon tetrachloride are listed in Table 4. The MSCN-iodine complex, however, was so weak that no reliable enthalpy of formation could be calculated.

Table 4. Thermodynamic functions ^a for the ENCS-I₂ and the ANCS-I₂ systems.

	ENCS ^b			ANCS ^c		
	450 μ	455 μ	460 μ	460 μ	465 μ	470 μ
— ΔH° kcal/mole	3.8	4.0	3.9	3.7	3.5	3.4
— ΔH° kcal/mole		3.9 ± 0.8			3.6 ± 0.8	
— ΔG°_{20} ^d kcal/mole		0.06 ± 0.05			−0.02 ± 0.03	
— ΔS° e.u.		13 ± 3			12 ± 3	

^a Calculated from the absorbance data of two mixed isothiocyanate-iodine solutions at: 10.5°C, 25.5°C, 44.2°C (ENCS-I₂) and 9.0°C, 28.3°C, 43.6°C (ANCS-I₂), assuming constant ($\epsilon_c - \epsilon_f$) (Ref. 24).

^b [I₂]: 8.0 × 10^{−4} M, [ENCS]: 0.20 and 0.40 M in heptane.

^c [I₂]: 1.2 × 10^{−3} M, (ANCS): 0.15 and 0.38 M in carbon tetrachloride.

^d Calculated from the mean formation constants listed in Tables 2 and 3.

Infrared region. The infrared spectra of several isothiocyanates have been reported^{17,25,26} and complete vibrational analysis has been published for isothiocyanic acid,²⁷ methyl thiocyanate,²⁸ methyl isothiocyanate,²⁸ and the thiocyanate ion.²⁹ It seems well established²⁸ that the isothiocyanates have an antisymmetrical —N=C=S stretching fundamental around 2100 cm^{−1} with neighbouring absorption peaks caused by combination bands in Fermi resonance with the fundamental. The symmetrical —N=C=S stretching mode, on the other hand, has been assigned to weak infrared and Raman bands situated at 995 and 1088 cm^{−1} for isothiocyanic acid²⁷ and methyl isothiocyanate,²⁸ respectively.

First a 0.02 M solution of ENCS in carbon tetrachloride and then a mixed solution of 0.02 M ENCS and 0.08 M iodine were recorded in the 2100 cm^{-1} region. It was found that the $-\text{N}=\text{C}=\text{S}$ antisymmetrical stretching band at 2092 cm^{-1} was reduced in intensity and a new shoulder appeared at approx. 2136 cm^{-1} . The latter can probably be assigned to the corresponding mode in the ENCS-iodine complex. A distinct enhancement of the 2187 cm^{-1} band might be explained by increased Fermi resonance from the 2136 cm^{-1} band in the complex. Dissolved in dichloromethane, ENCS has a different absorption pattern in this region,¹⁷ but still the antisymmetrical $-\text{N}=\text{C}=\text{S}$ stretching mode seemed to be displaced approx. 40 cm^{-1} towards higher frequencies. Negligible changes occurred in the remaining infrared region above 650 cm^{-1} . In the ANCS-iodine solutions in carbon tetrachloride the 2087 cm^{-1} was displaced to 2120 cm^{-1} and the 2172 cm^{-1} band enhanced. Thus, even if irreversible reactions made the latter perturbations less conclusive, the two isothiocyanates showed a parallel behaviour in this region on complex formation to iodine.

Since larger interactions are expected with a stronger acceptor like iodine monochloride, an attempt was made to study the ENCS-iodine monochloride system in the infrared region. However, irreversible reactions completely obscured the spectrum. In agreement with the results from the ultraviolet and visible regions the MSCN-iodine interaction was so weak that no effects were observed in the infrared region.

DISCUSSION

The two isothiocyanates ENCS and ANCS form fairly weak complexes with iodine as indicated by the formation constants and enthalpies of formation. The spectral data show beyond doubt that these complexes are of the charge transfer type. Thus, the ionization potential of ENCS is reported to be $9.10 \pm 0.15\text{ eV}$ ³⁰ and employing the well-known frequency *versus* ionization potential relation,³¹ the wave length $292\text{ m}\mu$ is obtained for the *CT* band in good agreement with the experiments. The nearly coinciding *CT* band maxima for the two systems indicate that the ionization potential of ANCS is also close to 9.10 eV .

The formation constants and thermodynamic functions listed in Tables 2–4 could not be determined with a high precision since the interaction was low. As recently discussed by Person²³ mixed solutions with high donor concentrations²³ should be measured in such cases. However, for ENCS concentrations higher than approximately 2 M, curved Scott plots were obtained, which might suggest higher complexes or large deviations from ideality. The ANCS system was still more unfavourable since irreversible reactions occurred for donor concentrations above 1.5 M. However, the data show that ENCS and ANCS are of approximately the same basicity and there is accordingly no significant conjugation in ANCS which affects the lone pair electrons. The fact that ENCS and ANCS have very similar ultraviolet absorption spectra¹⁷ support this conclusion.

Generally, the ultraviolet absorption data should be better fitted for quantitative calculations since the *CT* band has a much higher intensity. When strong donor absorption prevents calculations based on the *CT*-peak absorption, however, completely erroneous *K*-values are often obtained. As we have discussed for other iodine *CT*-complexes^{20,32} such conditions are likely to occur for polar donors which change the bulk dielectric constant considerably when present in large concentrations. ENCS and ANCS have dipole moments equal to 3.31 and 3.30 D, respectively,³³ which probably account for the spectral changes.

The data in Table 1 indicate that the position of the *CT*-peaks for both the ENCS and the ANCS systems are influenced by the dielectric constant of the solvent, the peak absorption being red-shifted in polar solvents. This is in agreement with the Mulliken theory since the excited state would be expected to be much more dative than the ground state for these weak complexes. The extinction coefficients of the *CT* bands are surprisingly high and comparable to those of strong complexes like the amine-iodine systems. However, the *CT*-bands are fairly narrow, but get broader in more polar solvents. Even if the extinction coefficients were obtained indirectly and are subject to large error limits, it seems significant that the ENCS-iodine complex has the more intense *CT* band. Moreover, the ENCS-iodine system also has the more intense *BS* band. Thus, even if the formation constants at 20°C and the standard enthalpies of formation for the two isothiocyanate-iodine complexes are the same within the error limits, the spectral data suggest that ENCS is a slightly stronger base than ANCS towards iodine.

A much stronger interaction was reported¹⁶ for the iodine-thiocyanate ion complex (in water). According to Jones²⁹ the resonance from $\text{N}\equiv\text{C}-\text{S}^-$ contributes approximately 71% to the thiocyanate ion structure and the higher electron density on the sulphur should make it a stronger donor site than in the isothiocyanates.

We had hoped that the infrared spectra would reveal if the nitrogen or the sulphur acted as the donor site to iodine. However, the spectral changes were so small that no firm conclusions can be drawn. It is not even clear how the complex formation from the nitrogen or the sulphur will perturb the $-\text{N}=\text{C}=\text{S}$ asymmetrical and symmetrical stretching bands. According to Pearson³⁴ soft acids like iodine prefer coordination to the soft sulphur atom in the thiocyanate ion. As an hypothesis we believe that the isothiocyanate-iodine bond is localized at the sulphur atom, but X-ray crystallographic methods seem necessary to determine the complex geometry.

Financial support from *Norges Almenvitenskapelige Forskningsråd* is gratefully acknowledged.

REFERENCES

1. Tsubomura, H. and Lang, R. P. *J. Am. Chem. Soc.* **83** (1961) 2085.
2. Good, H., Major, A., Nag-Chaudhuri, J. and McGlynn, S. P. *J. Am. Chem. Soc.* **83** (1961) 4329.
3. Tamres, M. and Searles, S. J. *Phys. Chem.* **66** (1962) 1066.
4. Brandon, M., Tamres, M. and Searles, S. J. *Am. Chem. Soc.* **82** (1960) 2129.
5. Tamres, M. and Brandon, M. *J. Am. Chem. Soc.* **82** (1960) 2134.

6. Veen, J. and Stevens, W. *Rec. Trav. Chim.* **82** (1963) 287.
7. Lang, R. P. *J. Am. Chem. Soc.* **84** (1962) 1185.
8. McCullough, J. D. and Zimmermann, I. C. *J. Phys. Chem.* **65** (1961) 888.
9. Lang, R. P. *J. Am. Chem. Soc.* **84** (1962) 4438.
10. Kuboyama, A. *J. Am. Chem. Soc.* **86** (1964) 164.
11. Drago, R. S., Wayland, B. and Carlson, R. L. *J. Am. Chem. Soc.* **85** (1963) 3125.
12. Grundnes, J. and Klæboe, P. *Trans. Faraday Soc.* **60** (1964) 1991, and earlier papers listed there.
13. Cotton, F. A., Goodgame, D. M. L., Goodgame, M. and Sacco, A. *J. Am. Chem. Soc.* **83** (1961) 4157.
14. Tramer, A. *J. Chim. Phys.* **59** (1962) 232, 637.
15. Larsson, R. and Miezis, A. *Acta Chem. Scand.* **19** (1965) 47.
16. Lewis, C. and Skoog, D. A. *J. Am. Chem. Soc.* **84** (1962) 1101.
17. Svátek, E., Zahradnik, R. and Kjær, A. *Acta Chem. Scand.* **13**. (1959) 442.
18. Pestemer, M. and Litschauer, B. *Monatsh.* **65** (1935) 233.
19. Job, P. *Ann. Chim.* (10) **9** (1928) 113.
20. Klæboe, P. *Acta Chem. Scand.* **18** (1964) 27, 999.
21. Scott, R. L. *Rec. Trav. Chim.* **75** (1956) 787.
22. Briegleb, G. *Elektronen-Donator-Acceptor-Komplexe*, Springer-Verlag, Berlin 1961, p. 61.
23. Person, W. B. *J. Am. Chem. Soc.* **87** (1965) 167.
24. Ref. 22, p. 226.
25. Caldow, G. L. and Thompson, H. W. *Spectrochim. Acta* **13** (1959) 212.
26. Lieber, E., Rao, C.N.R. and Ramachandran, J. *Spectrochim. Acta* **13** (1959) 296.
27. Reid, C. *J. Chem. Phys.* **18** (1950) 1512.
28. Miller, F. A. and White, W. B. *Z. Electrochem.* **64** (1960) 701.
29. Jones, L. H. *J. Chem. Phys.* **25** (1956) 1069.
30. Hobrock, B. G., Shenkel, R. C. and Kiser, R. W. *J. Phys. Chem.* **67** (1953) 1684.
31. McConnel, H., Ham, J. and Platt, J. *J. Chem. Phys.* **21** (1953) 66.
32. Augdahl, E. and Klæboe, P. *Acta Chem. Scand.* **19** (1965) 807.
33. Hunter, E. C. E. and Partington, J. R. *J. Chem. Soc.* **1932** 2826.
34. Pearson, R. G. *J. Am. Chem. Soc.* **85** (1963) 3533.

Received June 18, 1965.