The formation of the dimer IV in CCl_4 may be regarded as an extreme result of the dipole–dipole attraction of ion-pairs. The ability of the cation to bridge the two anions leads to the observed spectral changes and probably explains the stability of the dimer. The absence of such dimers in the triethylamine–acetic acid system[6] is then expected since there could be no similar cation bridge. Specific solvent hydrogen bonding in $CHCl_3$ as indicated by II would tend to prevent dimerization and explains the absence of the dimer in $CHCl_3$. This effect is also demonstrated by the larger dimerization constant of acetic acid in CCl_4 than in $CHCl_3$.[12]

The specificity of the hydrogen bonding of chloroform to the ion-pairs and between the elements of the ion-pairs in the triethylamine–acetic acid and diethylamine–acetic acid systems suggests that similar structures are also to be expected for solvation of ions in dissociating solvents. Structural arrangements of water molecules have been proposed for cation solvation in water.[13,14] A model involving linear hydrogen bonding for anion solvation has been discussed by Verwey.[15] The structures for the diethylamine–acetic acid complexes reported here suggest that two hydrogens from the same water molecule may hydrogen bond to the same anion. This non-linear model is not intended to replace that of Verwey but would be favored in cases where additional good hydrogen acceptors are not readily available.

It is of interest, also, to consider the relative base strength of tri- and diethylamine toward acetic acid in CCl_4 and $CHCl_3$. On the basis of the inductive effect, triethylamine is expected to be a stronger base than diethylamine.[16] The relative basicity of these compounds may, however, be altered by differences in solvation. Assuming that there is no solvent interaction due to CCl_4, the larger equilibrium constant for the direct salt formation, reaction 1, and hence increased basicity of diethylamine when compared with triethylamine in CCl_4 must be attributed to differences in the ability of the acetate ion to interact with or "to solvate" the cation. This "solvation" by the acetate ion might be expected to be greater for diethylammonium ion than for triethylammonium ion since the former ion forms two hydrogen bonds with the acetate ion. Some steric effect due to increased shielding of the lone pair of electrons on the nitrogen atom of triethylamine[16] is also possible. In $CHCl_3$ there are, in addition to the differences in ion–ion interactions, solvent effects due to the relative hydrogen bonding energies of $CHCl_3$ to the amines and to the ion-pairs. The equivalence of the equilibrium constants for the reaction of diethylamine and triethylamine with acetic acid observed in $CHCl_3$ probably stems from the fact that although the diethylammonium ion is better "solvated" by the acetate ion, diethylamine forms a better hydrogen bond to $CHCl_3$ than does triethylamine.[17] The equivalence of the equilibrium constants for direct salt formation between diethylamine and acetic acid in CCl_4 and $CHCl_3$ indicates furthermore that the reactants and the products are equally well stabilized by hydrogen bonding to $CHCl_3$.

These results emphasize the important role of the solvent and of the ion-pair structures in determining relative basicities. The necessity of an accurate knowledge of the detailed structure of the products before equilibrium constants may be compared is also pointed out. These structures may also be of more general theoretical value in the interpretation of solvent-ion structures such as occur in aqueous solution.

(13) E. Wicke, M. Eigen and Th. Ackerman, *Z. physik. Chem. Neue Folge*, **1**, 340 (1954).

(14) E. Wicke and M. Eigen, *Z. Elektrochem.*, **57**, 319 (1953).

(15) E. J. W. Verwey, *Rec. trav. chim. Pays-Bas*, **61**, 127 (1942).

(16) H. C. Brown, *Science*, **103**, 385 (1946).

(17) This is reflected in the anomalously low heat of solvation of triethylamine in $CHCl_3$: M. Tamres, S. Searles, E. M. Leighly and D. W. Mohrman, THIS JOURNAL, **76**, 3983 (1954).

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORIES OF THE UNIVERSITY OF CHICAGO]

Anions as Bridging and Non-bridging Ligands in Reactions of Co(III) Compounds with Cr^{++}

BY HENRY TAUBE

RECEIVED MARCH 25, 1955

Transfer of X to Cr takes place in the reaction of $(NH_3)_5Co(III)X$ with Cr^{++} when X is thiocyanate, azide, phosphate, pyrophosphate, acetate, butyrate, crotonate, oxalate, succinate or maleate. The rates of reaction are approximately the same with X = acetate, butyrate, crotonate or succinate, but are at least 100 times greater with oxalate or maleate as the bridging groups. The participation of some anions as non-bridging ligands has been demonstrated. Pyrosphosphate adds efficiently to Cr on reaction of $Co(NH_3)_5H_2O^{+++}$ with Cr^{++}, and $SO_4^{=}$ does so less efficiently. When $Co(NH_3)_5Cl^{++}$ is the oxidizing agent, and pyrophosphate is present, both Cl and pyrophosphate add to Cr. The reaction of Cr^{++} with Co en_2 *o*-$phen^{+++}$ is more rapid than that of Cr^{++} with Co en_3^{+++}.

The study of reactions of Cr^{++} with substitution-inert cationic oxidizing agents[1–3] has led to some definite conclusions about the geometry of the activated complexes involved. Each system studied thus far has furnished evidence for a "bridged activated complex"—one in which the central atoms in oxidant and reductant share a common group during the electron transfer process. The particular systems for which this feature of the transition state, as well as others, can be readily demonstrated provide models also for systems in which a similar direct demonstration of geometry is difficult

(1) H. Taube, H. Myers and R. L. Rich, THIS JOURNAL, **75**, 4118 (1953).

(2) H. Taube and H. Myers, *ibid.*, **76**, 2103 (1954).

(3) H. Taube and E. L. King, *ibid.*, **76**, 4053 (1954).

if not impossible. It has therefore seemed worthwhile to make an extension of the earlier observations. Although the experiments described in the present paper are mainly qualitative in nature, they provide the basis for new conclusions, and have exposed some effects worthy of more detailed, quantitative study.

Experimental

The Co(III) compounds were prepared by standard methods, referred to in Abegg,[4] or for those not previously described, using modifications of standard procedures for related compounds. The reaction medium for the substitution of H_2O in $Co(NH_3)_5H_2O^{+++}$ by various organic groups contained *ca.* 10 g. of the organic acid in 30 ml. of solution, with $^1/_2$ mole $NaHCO_3$ added for each mole of acid. The mixture was heated at 70° for 2–3 hours to complete the substitution. The anion at high concentration serves to suppress the concentration of binuclear ions relative to the mononuclear ones, an important consideration when maleate or succinate is the substituting group. The succinato (and to a lesser degree the maleato) compound crystallizes only with difficulty. Enough perchloric acid was added almost to convert succinate to the acid. The solution was then allowed to evaporate to small volume at room temperature, the solid acid was removed, and cold 6 *M* $HClO_4$ was added to the pre-cooled solution. The precipitate which formed was collected, and washed with 2 *M* $HClO_4$, with ethyl alcohol, and dried. The compound *cis*-$Coen_2Cl_3$ used in the preparation of $Coen_2$ *o*-phen $ClSO_4$ was supplied through the courtesy of Dr. E. L. King, University of Wisconsin, and the compound $Coen_3Cl_3$ through courtesy of Dr. Tom Cameron, University of Cincinnati.

In many of the experiments, the color of the solution resulting from the reaction of Cr^{++} and the Co(III) complex showed that at least some of the Cr(III) appeared in a form different from $Cr(H_2O)_6^{+++}$. An estimate of the fraction yielding a substitution product of $Cr(H_2O)_6^{+++}$ was made, using an ion exchange method of separation.[5] The substitution products encountered in the systems studied have a lower positive charge than $Cr(H_2O)_6^{+++}$, and can be separated from it using 1 *M* $HClO_4$ as eluent. Recovery of Cr(III) in the first eluent fraction was in no case complete, 75% or less being recovered for dipositive Cr(III), and 90% or less for Cr(III) of lower positive charge. A blank experiment with $CrCl^{++}$ under the same conditions showed only 70% being recovered. It is felt therefore that recovery of 70% or so of a dipositive ion, and 90% for one of lower positive charge corresponds to substantially complete conversion of Cr^{++} to substitution products of $Cr(H_2O)_6^{+++}$. However, a defect from these values does not necessarily mean incomplete conversion. While an ion such as $CrSO_4^+$ appears in the eluent almost as soon as the dead volume has passed, the maximum $CrCl^{++}$ concentration appears at *ca.* 25 ml. more eluent, with $CrOAc^{++}$ at 45 and $CrOBu^{++}$ at 80. Tailing is only partly responsible for the low values of recovery. Some Cr(III) undoubtedly is held back by inner sphere replacement on the Cr(III) by resin groups. This loss will be more severe, other things equal, for ions such as $CrOBu^{++}$ which have a long residence time in the resin, but will vary in extent also depending on the substitution lability of the particular ion.

The experiments on rate of reaction were performed using an excess of the oxidizing agent. After the selected time interval, the reaction was quenched by adding excess Fe^{+++} and the Fe^{++} produced by the residual Cr^{++} was determined by amperometric titration.

Results and Discussion

A summary of the results in transfer is presented in Table I.

TABLE I

TRANSFER OF GROUPS FROM OXIDIZING AGENT TO REDUCING AGENT IN THE REACTION OF $(NH_3)_5Co(III)$ WITH Cr^{++}

(Initial concentrations: Co(III), 0.015 *M;* Cr^{++}, 0.01 *M;* (H^+), 0.1 *M;* ClO_4^- the only free anion present initially; room temp. *ca.* 23°.)

X	Color of eluent	% Cr through column	*k*, l. mole^{-1} min.$^{-1}$
N_3^-	Bluish green	50	V. rapid[a]
CNS^-	Violet	80	Measurable
NO_3^-	. . .	<2	V. rapid[a]
OAc^-	Violet	80	10
n-Butyrate	Violet	55	5
Crotonate	Violet	40	13
Oxalate	Violet	90	>2000
Succinate	Violet pink	75	8
Maleate	Dark blue	80	>1500
Pyrophosphate	Green	90	V. rapid[a]

[a] $> \sim 10^3$. Visual observation only. Reaction apparently complete on mixing.

The results in Table I show that, in the reaction of Cr^{++} with Co(III) complexes, for every group except NO_3^- attached to Co(III), a large fraction of the Cr(III) is recovered having X in association with it. Transfer is substantially complete in the case of CNS^-, OAc^-, $C_2O_4^=$, pyrophosphate, maleate and succinate and, as noted earlier, may be complete in the other cases. The reaction of $Co(NH_3)_5CNS^{++}$ with Cr^{++} was studied also by adding Ag^+ to the mixture immediately after reaction. Only a faint cloudiness developed and the precipitate causing it was too fine to be caught on a filter mat. Comparisons with solutions containing known chloride showed that the free CNS^- corresponded to less than 5% of the amount equivalent to the Cr^{++} consumed. The failure to observe transfer with X = NO_3^- may result from a high substitution-lability for $CrNO_3^{++}$. This ion has never been described, a circumstance which argues for its instability, and to some extent for its lability. The high rate for the reaction of $Co(NH_3)_5NO_3^{++}$ with Cr^{++} indicates that the reaction does not limit itself to a path involving electron transfer through coördinated NH_3, which has been shown to be a very slow process.[2]

It was not possible to study the reaction of $Co(NH_3)_5PO_4$ with Cr^{++} ions. Strong acid, even at 0.01 *M*, causes very rapid release of $PO_4^=$ from the Co complex. The reaction with Cr^{++} was carried out in an $HOAc-OAc^-$ buffer mixture, of sufficient capacity to keep the *p*H below 5. Under these conditions, a bluish-gray precipitate forms, which contains substantially all the Cr(III). A similar precipitate forms when only a small amount of mineral acid is present initially. The precipitate dissolves very rapidly when acid is added, releasing Cr(III) as $Cr(H_2O)_6^{+++}$, and is presumably a $Cr(III)-PO_4^=$ compound.

The rate comparisons among the organic-substituted complexes suggest some interesting conclusions. Because the rates for X = acetate, butyrate, crotonate and succinate are nearly the same, it seems likely that attack by Cr^{++} takes place at a common group which, in view of the transfer observed, must be at the carboxyl adjacent to the metal ion. This rate is very much lower than it is for Cl^- and OH^- as bridging groups, or even for H_2O (for the latter group, *k* at 25° is approximately 80 l. mole^{-1} min.$^{-1}$), in part at least, because of the steric effect of the hydrocarbon radical. The

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[4] R. Abegg and F. Auerbach, "Handbuch der anorganischen Chemie," Band IV, Abt. 3, Teil 3, S. Hirzel, Leipzig, 1935.

[5] E. L. King and E. B. Dismukes, THIS JOURNAL, **74**, 1674 (1952).

greater rate for oxalate and maleate indicates that a different point of attack can be made use of with these bifunctional ions as bridges, which therefore must be the carboxyl end away from the metal atom. Such a mechanism requires electron transfer through the bridging ion, possible for the conjugated system of bonds in oxalate and maleate, but not for the saturated carbon chain in succinate. The comparison of rates for crotonate and maleate shows that for efficient transfer by this means, a polar group is needed to interact strongly with the reducing agent. The reaction of Cr^{++} with the Co(III)–crotonate may proceed in part by attack at the carbon double bond, but this mode cannot be a very important one. Attack at this site would lead to $Cr(H_2O)_6^{+++}$ as product—the Cr(III)–C bonds would probably not resist attack by water—but the results show the recovery of the Cr(III)–crotonate complex is almost as complete as that with butyrate. Experiments comparing the rate of reaction of Cr^{++} with Co en_3^{+++} and with Co en_2 *o*-phen^{+++} showed reaction to be considerably more rapid in the latter case, although the rate is much lower than for oxalate and maleate, each of which has a polar group as part of the conjugated systems. The experiments were done with H_2SO_4 in place of $HClO_4$, because of the low solubility of the perchlorate salt containing Co en_2 *o*-phen^{+++}. The experiments set an upper limit of 5×10^{-2} l. mole^{-1} min.$^{-1}$ on the specific rate of Cr^{++} reducing Co en_3^{+++}, and show the specific rate with Co en_2 *o*-phen^{+++} to be about 1 l. mole^{-1} min.$^{-1}$. The reaction of Cr^{++} with Co en_2 *o*-phen^{+++} is autocatalytic, and the approximate value of specific rate quoted was arrived at by extrapolating the specific rates to zero time. Cr^{++} reacts rapidly with *o*-phenanthroline and the autocatalysis may be caused by products of this reaction.

In the previous papers of this series as well as in the foregoing, the role of anions as bridging groups has been stressed. An effect of such groups acting simply as ligands is to be expected—the rate of electron transfer must depend on the nature of all the groups in the activated complex—and is possibly realized in the activated complex of composition $Fe^{++}\cdot Fe^{+++}\cdot 3F^-$.[6] Experiments with Cr^{++} and Co(III) complexes provide a definite demonstration also of the ligand role of negative ions. It is observed that when $Co(NH_3)_5H_2O^{+++}$ reacts with Cr^{++} in the presence of pyrophosphate ion, this anion is efficiently added to Cr^{++}. When concentrations are the same as those in the experiments of Table I, except that 0.035 *M* $Na_4P_2O_7$ is added, Cr(III) appears almost completely as the pyrophosphate complex (85% was recovered in the first effluent fraction). Ligands differ very greatly in their efficiency in promoting electron transfer by this means. Thus with 0.09 *M* Na_2SO_4 replacing the pyrophosphate, only 30% of the Cr(III) is recovered as the sulfato complex. With maleate present at 0.02 *M*, less than 5% of the Cr(III) produced appeared as the maleato complex (the experiment shows that in the formation of Cr(III)–maleate complex from Co(III)–maleate and Cr^{++}, the mechanism is not by release and re-entry of maleate). The simple ligand participation of Cl^- in the reaction $Co(NH_3)_5H_2O^{+++} + Cr^{++}$ has already been shown to be slight.[2] It is important to note that even with pyrophosphate participating as a ligand, a bridging group is still involved in the activated complex. Thus, when the reaction of $Co(NH_3)_5Cl^{++} + Cr^{++}$ takes place in the presence of pyrophosphate, *both* Cl^- and pyrophosphate are added to the Cr. There is no free chloride in the solution immediately after reaction, as can be demonstrated by adding cold $AgNO_3$ solution to the cooled product solution. No AgCl is formed initially, but a precipitate does appear gradually. The absorption spectrum of the product using $Co(NH_3)_5Cl^{++}$ as oxidant is different from that obtained with $Co(NH_3)_5H_2O^{+++}$, although the former does change to that of the latter after a day or so, Cl^- but not pyrophosphate being released.

The results of some of the experiments reported are of interest in relation to work on other electron transfer reactions. The reaction of Fe^{++} with Fe(*o*-phen)$_3^{+++}$ is known from general experience in oxidation titrations of Fe^{++} to be rapid, and has been shown[7] to have a specific rate exceeding 10^5 l. mole^{-1} sec.$^{-1}$. The reaction of Cr^{++} with the same oxidizing agent can reasonably be expected to be just as rapid. The reaction of Cr^{++} with Co en_2 *o*-phen^{+++}, however, proceeds at a specific rate of only *ca.* 10^{-2} l. mole^{-1} sec.$^{-1}$. An important difference between the two oxidizing agents is that Fe(III) but not Co(III) has a stable orbital for occupation by the electron absorbed, available without drastic reorganization of the association groups. In the case of the Co(III) complex, all the inner d as well as 4s and 4p orbitals are occupied. Thus no orbital of stability comparable to that in Fe is available. While Co(III) in the "outer orbital" electronic structure would have orbitals available for occupancy, the ligand fields at the normal distance of separation between ligands and central ion in Co(III) make this state accessible only with expenditure of energy. The reaction path apparently found by the Co(III) complexes having a polar exposed group in the co-ördination sphere is to lose the bridging ligand, thereby vacating an orbital for occupancy by the incoming electron. As noted before, this reaction mode requires a suitable interaction between bridge group and reducing agent, the reducing agent exchanging a ligand for an electron. Such a group is absent in the case of *o*-phenanthroline as the ligand.

Other examples of the influence on rates of electron transfer exerted by anions acting purely as ligands are found in the acceleration by $C_2O_4^=$ of the reaction of Mn^{++} and MnO_4^-,[8] and in the effect of oxalate complexing on the rate of electron transfer between $C_2O_4^=$ and Mn(III).[9,10] The influences described earlier, as well as those now mentioned can be understood qualitatively as ligand stabilization of one oxidation state over another, *e.g.*, the presence of $C_2O_4^=$ or $P_2O_7^=$ on Cr^{++} favors its change to Cr^{+++}. A general relation for a par-

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[6] J. Hudis and A. C. Wahl, THIS JOURNAL, **75**, 4153 (1953).

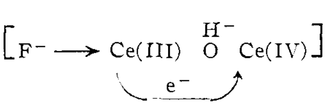
[7] P. George and D. H. Irvine, *J. Chem. Soc.*, 587 (1954).

[8] J. M. Malcolm and R. M. Noyes, THIS JOURNAL, **74**, 2796 (1952).

[9] F. R. Duke, *ibid.*, **69**, 2885 (1947).

[10] H. Taube, *ibid.*, **70**, 1216 (1948).

ticular cation between the equilibrium stabilization of an oxidation state by a ligand, and its pure ligand influence on rate can be expected, and is realized in the few data quoted for Cr^{++}. While the pure ligand effect seems obvious enough, its possibilities have not been exploited in conjectures about the geometry of activated complexes for electron transfer. In considering the catalytic effect of F^{-}[11] on the rate of electron transfer between Ce^{+++} and Ce(IV), taking account of the facts that Ce(IV) has a strong tendency to hydrolyze, and that F^{-} exerts an enormous stabilizing effect on Ce(IV) over Ce(III), the activated complex corresponding to the rate term (Ce^{+3})(Ce(IV)) (F^{-}) can reasonably be formulated as



$$\left[\mathrm{F}^- \longrightarrow \mathrm{Ce(III)}\ \overset{\mathrm{H}^-}{\mathrm{O}}\ \mathrm{Ce(IV)}\right]$$

e^-

i.e., electron transfer accompanying the movement of F^{-} into the coördination shell of Ce^{+++}. From this point of view, symmetry in the activated complex is not a necessary condition for electron exchange, even between two ions of the same element; in fact, the act producing electron transfer is approached by F^{-} in such a manner that the environments of the two Ce ions are made different, thus favoring the change Ce$^{+++} \rightarrow$ Ce(IV). In systems in which an efficient bridging group is not otherwise provided, the role of F^{-} as simple ligand might be less important than its role as bridging group.

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[11] H. C. Hornig and W. F. Libby, *J. Phys. Chem.*, **56**, 869 (1952).

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE, NAGOYA UNIVERSITY]

Electron Diffraction Investigation of Tetramethylcyclodi- and Hexamethylcyclotrisilthiane

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RECEIVED OCTOBER 29, 1954

The molecular structures of tetramethylcyclodi- and hexamethylcyclotrisilthiane were studied by electron diffraction; the Si-S bond distances were found to be 2.18 ± 0.03 Å. for the former and 2.15 ± 0.03 Å. for the latter compound. Assuming ∠CSiC to be 110°, we estimated the bond angles as follows: ∠SiSS 105° and ∠SiSSi 75° for the disilthiane; ∠SSiS 115° and ∠SiSSi 110° for the trisilthiane.

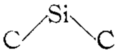
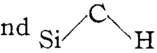
The vapors of tetramethylcyclodi- and of hexamethylcyclotrisilthiane $(\mathrm{Si(CH_3)_2S})_2$ and $(\mathrm{Si(CH_3)_2S})_3$ were studied by electron diffraction to determine the Si–S bond length and the SiSSi bond angle.

Experimental

Tetramethylcyclodisilthiane was prepared by the thermal rearrangement of hexamethylcyclotrisilthiane at 200° in a stream of hydrogen sulfide.[1] Hexamethylcyclotrisilthiane was synthesized[1] by the method of Champetier, *et al.*,[2] who had prepared the ethyl homolog.

The electron diffraction photographs of the vapors of these compounds were taken with a camera of the vertical type at a camera distance of 11 cm. and at an electron wave length of about 0.06 Å. as determined by calibration with gold foil. The samples of disilthiane and trisilthiane were kept at about 30 and 100°, respectively.

Results

The radial distribution functions and the theoretical intensity curves were calculated by the approximation of Spurr and Schomaker.[3] In the temperature factor, $e^{-b_{ij}q^2}$ for the theoretical intensity curves, b_{ij} was assumed to be zero for all bonded distances, 0.0002 for the atom pairs of  and , and 0.0004 for other unbonded long distances. The C–H distance was assumed to be 1.09 Å. and the HCH angle tetrahedral. The parameters which determine the structure are the ratio of the distances Si–C/Si–S, the bond angles ∠SiSSi, ∠SSiS, ∠CSiC, and the form of the ring.

Tetramethylcyclodisilthiane.—The visual (V) and radial distribution curves (R.D.) are shown in Fig. 1. The peaks at 1.87 and 2.18 Å. are due to bonded Si–C and Si–S; the peak at 3.29 Å. may be due to unbonded S . . . C along with Si . . . Si or S . . . S distances. As the total scattering power of S . . . C distances is about three times as large as that of Si . . . Si or S . . . S distances, the S . . . C distance should appear in the neighborhood of this 3.29 Å. peak. If S . . . C is 3.29 Å., ∠SSiS is 113° for ∠CSiC = 110° or 106° for ∠CSiC = 115°, hence ∠SiSSi should be less than 74° to close the four-membered ring of this compound. A comparison of visual and theoretical curves was made with models having the assumed value 110 or 115° for ∠CSiC; these are shown in Fig. 2. The ratio of the distances, Si–C/Si–S, obtained from the R.D. is 1.87/2.18 = 0.86, and bond angles ∠SiSSi and ∠SSiS, were examined with ∠CSiC equal to 110° (curves A to F in Fig. 1) or 115° (curves A′ to F′ in Fig. 1). The parameter values for each model are shown diagrammatically in Fig. 2, in which models situtated on the broken line, *i.e.*, A, A′, B, B′, C and C′, have planar rings. The observed maxima and minima are most satisfactorily reproduced by curves B and B′.

Hexamethylcyclotrisilthiane.—The visual (V) and radial distribution curves (R.D.) are shown in Fig. 3. In the R.D. the peaks representing bonded Si–C and Si–S appear at 1.90 and 2.14 Å., respectively. The peak ranging from 3.1 to 3.6 Å. is attributed to unbonded Si . . . Si, S . . . S and S . . . C

[1] T. Nomura, M. Yokoi and K. Yamasaki, *Proc. Japan Acad.*, **29**, 342 (1953). Y. Etienne obtained this compound by thiohydrolysis of dimethyldichlorosilane (*Compt. rend.*, **235**, 966 (1952)).

[2] G. Champetier, Y. Etienne and R. Kullmann, *Compt. rend.*, **234**, 1985 (1951).

[3] R. A. Spurr and V. Schomaker, THIS JOURNAL, **64**, 2693 (1942).