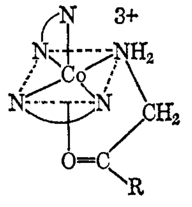
1c) and reacts rapidly with amines and alcohols to form the $[Co(en)_2(GlyNHR)]^{3+}$ and $[Co(en)_2(GlyOR)]^{3+}$ ions, respectively. For example, $[Co(en)_2(GlyOCH_3)](ClO_4)_3$ in acetone was treated with NH_3 (20 sec, 20°). The amide, precipitated with anhydrous ether and recrystallized from water (pH 4, $LiNO_3$) as $[Co(en)_2(GlyNH_2)](NO_3)_2ClO_4$ (*Anal.* Calcd: C, 15.12; H, 4.65; N, 23.51. Found: C, 15.11; H, 4.99; N, 23.61), was identical with that isolated from aqueous reaction 2, pmr spectrum given in Figure 1d.

$$[Co(en)_2Br(GlyNH_2)](ClO_4)_2 + Hg^{2+} \xrightarrow{\text{pH 1}} [Co(en)_2(GlyNH_2)]^{3+} + HgBr^+ + 2ClO_4^- \quad (2)$$



IV

The X-ray crystallographic study of $[Co(trien)(GlyGlyOC_2H_5)](ClO_4)_3 \cdot H_2O$,[3] its rapid formation from $[Co(trien)(GlyOC_2H_5)](ClO_4)_3$, and the rapid amination of $[Co(en)_2(GlyOCH_3)](ClO_4)_3$ suggest that all three classes of compounds (R = OR, NHR, $NHCHR'CO_2C_2H_5$) are analogous and have structural unit IV. Intermediates of this nature have been proposed,[4-6] and infrared evidence for the carbonyl coordinated chelated ester intermediate $[Co(en)_2(GlyOR)]^{3+}$ was recently obtained[5] in reaction 3. The properties of the isolated

$$[Co(en)_2X(GlyOR)]^{2+} + Hg^{2+} + H_2O \longrightarrow [Co(en)_2(Gly)]^{2+} + HOR + H^+ + HgX^+ \quad (3)$$

$$X = Cl, Br; \quad R = CH_3, C_2H_5, i\text{-}C_3H_7$$

chelated ester complexes support this claim as does isolation of the amide intermediate $[Co(en)_2(GlyNH_2)](NO_3)_2ClO_4$ from reaction 2.

We propose that one of the steps in the mechanism for peptide formation catalyzed by the CoN_4^{3+} unit is II → III. It is apparent that the cobalt(III) atom protects the NH_2 group of the chelated ester and also markedly activates the carbonyl carbon toward nucleophilic attack. Hydrolysis of a monodentate ester is much slower[5] than for the chelated ester and no Br^- is bound when the complex chelated ester is hydrolyzed in 7 *N* HBr. These results also suggest that chelation is essential for this activation of the ester moiety and that the chelate ring remains intact during the formation of the peptide bond.

The extension of this reaction to the incorporation of N-terminal amino acids other than glycine, and detailed kinetic studies of the hydrolysis reactions

$$\left.\begin{matrix}[Co(en)_2(GlyOR)]^{3+}\\ [Co(en)_2(GlyNR_1R_2)]^{3+}\\ [Co(en)_2(dipeptide\text{-}OR)]^{3+}\end{matrix}\right\} \xrightarrow{H_2O} [Co(en)_2Gly]^{2+} + \left\{\begin{matrix}ROH\\ NR_1R_2\\ \text{amino acid-OR}\end{matrix}\right.$$

and the esterification and amination reactions

$$[Co(en)_2(GlyOR)]^{3+} + R_1OH \rightarrow [Co(en)_2(GlyOR_1)]^{3+} + ROH$$
$$[Co(en)_2(GlyOR)]^{3+} + NHR_1 \rightarrow [Co(en)_2(GlyNHR_1)]^{3+} + ROH$$

are at present in progress. Also the recovery of the peptide, its optical purity, and the degree of stereospecificity incorporated in the syntheses are being examined.

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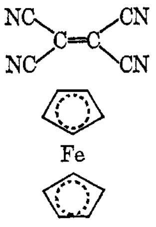
Structure of the Ferrocene–Tetracyanoethylene Complex

Sir:

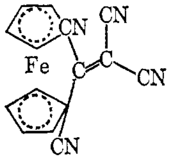
Recently[1] evidence was presented for the formulation of the complex formed by ferrocene with tetracyanoethylene (TCNE) as a charge-transfer complex rather than a salt.[2,3] With regard to the detailed structure of this substance, it was noted that, aside from the more classical formulation (**1**) involving electron donation from cyclopentadienyl ring orbitals, an alternative structure (**2**) was admissible on theoretical grounds but that the evidence was insufficient to decide in its favor.[4]

Collins and Pettit[5] have very recently confirmed the charge-transfer nature of the complex on the basis of Mössbauer experiments and have suggested **1** for its structure.

We now present the results of a single-crystal X-ray diffraction study which show definitively that the complex in the crystalline state is best represented by structure **1**, and that no apparent interaction between the metal atom and TCNE exists in this state.



1



2

The structure determination was complicated by decomposition of the substance on exposure to air and on irradiation with X-rays. In addition, crystals of the complex tended to deform easily and as a consequence led to poorly shaped spots on the diffraction photographs.[6]

Weissenberg and precession photographs revealed a triclinic cell with dimensions a = 7.77, b = 7.87, c =

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[1] M. Rosenblum, R. W. Fish, and C. Bennett, *J. Am. Chem. Soc.*, **86**, 5166 (1964).

[2] O. W. Webster, W. Mahler, and R. E. Benson, *ibid.*, **84**, 3678 (1962).

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[6] To minimize some of these difficulties, the crystals used in the analysis were immediately placed in thin-wall capillaries filled with Fluorolube (Hooker Chemical Corporation, Niagara Falls, N. Y.). The intensity data were obtained from equiinclination Weissenberg photographs of two different crystals using Cu $K\alpha$ radiation and a Ni foil placed between the crystal and the film to cut down fluorescent radiation.

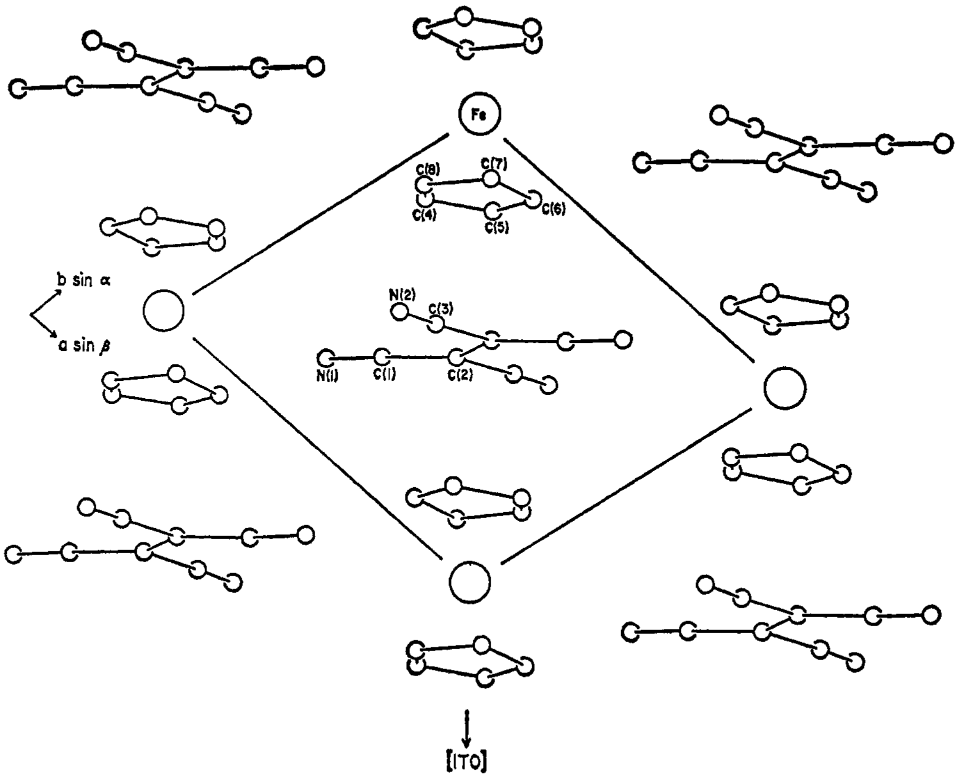

Figure 1.

6.78 A; $\alpha = 113.6, \beta = 96.7, \gamma = 77.0°$; one formula weight per unit cell.

Examination of the Patterson map[7] led us to postulate a centrosymmetric structure with the iron atom at the origin and the center of the TCNE molecule at $^1/_2\ ^1/_2\ 0$. This structure was refined by full-matrix least-squares calculations[8] to a value of

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.14$$

for 291 observed reflections. The final positional and isotropic thermal parameters are listed in Table I. The estimated standard deviation is 0.08 A for C–C and C–N bonds. Within experimental error, ferrocene and TCNE have the same bond lengths in the complex as in the pure substances.[9]

Table I. Positional and Thermal Parameters

Atom	x	y	z	B (A^2)[a]
Fe	0.0	0.0	0.0	
N(1)	0.324	0.203	−0.316	5.2
N(2)	0.324	0.441	0.326	5.5
C(1)	0.398	0.313	−0.226	4.9
C(2)	0.496	0.477	−0.108	5.6
C(3)	0.399	0.485	0.232	4.4
C(4)	0.111	0.730	−0.182	5.0
C(5)	0.229	0.835	−0.170	8.3
C(6)	0.262	0.932	0.077	11.1
C(7)	0.160	0.894	0.191	7.5
C(8)	0.078	0.756	0.046	9.8

[a] The iron atom was refined anisotropically resulting in a temperature factor of exp $-(0.009h^2 + 0.020k^2 + 0.023l^2 + 0.000hk - 0.015hl + 0.030kl)$.

The crystal structure of the TCNE–ferrocene complex, depicted in Figure 1, is closely analogous to the structures found for charge-transfer complexes of benzenoid systems.[10] The donor and acceptor components are arranged in alternating sequence in stacks in which the C_2 axis passing through the midpoint of the C–C bond in TCNE is essentially coincident with the C_5 axis of the cyclopentadienyl ring. Each stack is surrounded by six others in quasi-hexagonal array. The distance between parallel TCNE and cyclopentadienyl ring planes is 3.14 ± 0.1 A, similar to the separations of donor and acceptor components found in complexes involving benzenoid compounds.[10,11] The distance between nearest neighbor atoms of donor and acceptor components in adjacent stacks is 3.8 A (C····N), precluding any strong interactions other than van der Waals forces between stacks.

The form of association of donor and acceptor components in solution is probably closely related to that found in the crystalline state. Thus, the association constants and derived thermodynamic properties for TCNE complexes of ferrocene and 1,1′-dimethylferrocene, which are summarized in Table II, reflect an increased stability for the latter complex. Such an effect, typical of methyl substituents in complexes of benzenoid systems[12] and reflecting a lower ionization potential of the donor, is more readily accommodated by structure **1**,

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(7) Fourier series were evaluated with a program by A. Zalkin.

(8) Least-squares calculations were carried out with the program of P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, modified to include corrections for anomalous dispersion, available from T. N. Margulis, Brandeis University, Waltham, Mass. 02154.

(9) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Cryst.*, **9**, 373 (1956); D. A. Bekoe and K. N. Trueblood, *Z. Krist.*, **113**, 1 (1960).

(10) J. C. A. Boeyens and F. H. Herbstein, *J. Phys. Chem.*, **69**, 2160 (1965).

(11) O. L. Carter, A. T. McPail, and G. A. Sim, *J. Chem. Soc., Sect. A*, 823 (1966), report an average separation of ring planes of 3.41 A in the complex formed by 1,3,5-trinitrobenzene with anisolechromium tricarbonyl.

(12) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958); G. Briegleb, "Electronen Donator-Acceptor Komplexe," Springer-Verlag, Berlin, 1961.

Table II. Association Constants and Thermodynamic Properties of Tetracyanothylene Complexes in Cyclohexane

Donor	Temp, °C	K_x	$\epsilon_{\max}{}^{c}$	
Ferrocene[a]	30	30.0	474	$\Delta H_f = -3800$ cal/mole
	40	25.5	474	$\Delta S_f = -5.5$ eu
	50	21.0	469	
	60	17.5	474	
	70	15.0	479	
1,1′-Dimethylferrocene[b]	30	52.0	462	$\Delta H_f = -4300$ cal/mole
	40	39.5	475	$\Delta S_f = -6.4$ eu
	50	31.9	472	
	60	26.5	464	
	70	21.5	472	

[a] Average of two separate determinations. [b] Average of three separate determinations. [c] $\lambda_{\max}$ for ferrocene–TCNE 1000 mμ, and for 1,1′-dimethylferrocene–TCNE 1025 mμ.

in which steric interactions between the substituted donor and the acceptor component are minimized, than by structure **2**.

Acknowledgment. This work was supported by Grant No. GP-4550 from the National Science Foundation and by Grant No. GM-05978 from the National Institutes of Health.

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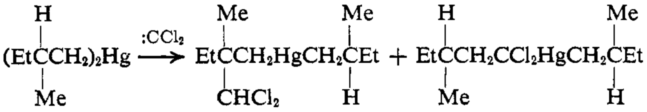
Insertion of Dichlorocarbene into a Carbon–Hydrogen Bond with Net Inversion of Configuration

Sir:

Recent reports have indicated an unusual and very specific preference for dichlorocarbene insertion into carbon–hydrogen bonds located β to either silicon,[1] tin,[1] or mercury.[2] The stereochemistry of this reaction is of particular interest with regard to the evaluation of possible mechanistic pathways.

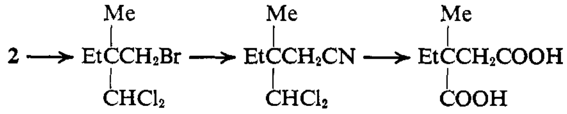
(+)-Bis((*S*)-2-methylbutyl)mercury (**1**), $[\alpha]^{27.5}\mathrm{D}$ $+8.01^{\circ}$ (neat)[3] was prepared from 98% optically pure (*S*)-(−)-2-methyl-1-butanol (Aldrich) *via* the intermediate chloride. The configuration of **1** has been well established by simple chemical transformations which allow a direct correlation with (−)-isoleucine,[6,7] the absolute configuration of which has been determined by X-ray diffraction studies.[8] Treatment of **1** with ethyl trichloroacetate and excess sodium methoxide in pentane resulted in the formation of the carbon–hydrogen insertion product **2** and the corresponding carbon–mercury bond insertion product[2] in a ratio of ~93:7.



$$(\mathrm{Et}\overset{\mathrm{H}}{\underset{\mathrm{Me}}{\mathrm{C}}}\mathrm{CH_2})_2\mathrm{Hg} \xrightarrow{:\mathrm{CCl_2}} \mathrm{Et}\overset{\mathrm{Me}}{\underset{\mathrm{CHCl_2}}{\mathrm{C}}}\mathrm{CH_2HgCH_2}\overset{\mathrm{Me}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{Et} + \mathrm{Et}\overset{\mathrm{H}}{\underset{\mathrm{Me}}{\mathrm{C}}}\mathrm{CH_2CCl_2HgCH_2}\overset{\mathrm{Me}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{Et}$$

1 (+) **2**

Purified **2** was then cleaved with bromine in carbon tetrachloride to give a mixture of (−)-1,1-dichloro-2-(bromomethyl)-2-methylbutane (**3**), $[\alpha]^{25}\mathrm{D}$ -1.13° ($CHCl_3$), and (+)-1-bromo-2-methylbutane. Trihalide **3** was converted to nitrile **4**, $[\alpha]^{25}\mathrm{D}$ -1.61° ($CHCl_3$), in low yield by treatment with sodium cyanide in dimethyl sulfoxide (50–90°), and the nitrile was hydrolyzed and oxidized with a basic aqueous silver oxide suspension to give (*S*)-(−)-α-methyl-α-ethylsuccinic acid (**5**), $[\alpha]^{25}\mathrm{D}$ -6.41° ($CHCl_3$).[9,10] The method of quasi-racemates has been used to establish the relative configuration of **5** with that of each of a series of α-monosubstituted and α-disubstituted succinic acids,[12,13] including α-methylsuccinic acid, the absolute configuration of which was recently established by X-ray diffraction techniques.[14]



$$\mathbf{2} \longrightarrow \mathrm{Et}\overset{\mathrm{Me}}{\underset{\mathrm{CHCl_2}}{\mathrm{C}}}\mathrm{CH_2Br} \longrightarrow \mathrm{Et}\overset{\mathrm{Me}}{\underset{\mathrm{CHCl_2}}{\mathrm{C}}}\mathrm{CH_2CN} \longrightarrow \mathrm{Et}\overset{\mathrm{Me}}{\underset{\mathrm{COOH}}{\mathrm{C}}}\mathrm{CH_2COOH}$$

3 (−) **4** (−) **5** (−)

The results clearly indicate that the insertion of dichlorocarbene into the β-carbon–hydrogen bond of **1** has occurred with *net inversion of configuration*, an unprecedented stereochemical result for a divalent carbon insertion process.[2] One can therefore rule out any mechanistic path which requires a direct attack of the divalent carbon atom on the carbon–hydrogen bonding electrons or a direct transfer of dichlorocarbene into the carbon–hydrogen bond *via* an ylide intermediate, as has been postulated for the analogous reaction in the tetraalkylsilane series.[1]

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(10) The rotation of the resolved acid has been reported as $[\alpha]^{22}\mathrm{D}$ -5.92° ($CHCl_3$).[11]

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Nuclear Magnetic Resonance of Phosphorus Compounds. III. Phosphorus-31 Overhauser Effects and Utilization of Simultaneous Observation of the Spectra of Two Types of Nuclei in Double-Resonance Experiments[1,2]

Sir:

In homonuclear magnetic double-resonance experiments it is possible by irradiation of one or more transitions to achieve departures from thermal spin distributions with concomitant redistribution of spectral line intensities.[3] Although observed signal-intensity

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(1) This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National Aeronautics and Space Administration.

(2) Previous paper in this series: S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Am. Chem. Soc.*, **88**, 2689 (1966).