46. N.S.Kardash and V.A.Krongauz, Teor. Eksper. Khim., 1, 796 (1965).
47. K.Überreiter and W.Bruns, Makromol. Chem., 68, 24 (1963).
48. C.Parker and C.Hatchard, Proc. Roy. Soc., A269, 574 (1962).
49. K.Kopecky, G.Hammond, and P.Leermakers, J.Amer. Chem. Soc., 83, 2397 (1961).
50. K.Kopecky, G.Hammond, and P.Leermakers, J.Amer. Chem. Soc., 84, 1015 (1962).
51. G.Hammond, P.Leermakers, and N.Turro, J.Amer. Chem. Soc., 83, 2395 (1961).
52. G.Hammond and P.Leermakers, J.Amer. Chem. Soc., 84, 207 (1962).
53. J.Berman, J.Stanley, W.Sherman, and S.Cohen, J.Amer. Chem. Soc., 85, 4010 (1963).
54. S.Cohen and W.Sherman, J.Amer. Chem. Soc., 85, 1642 (1963).
55. F.Weigert and F.Pruckner, Z.phys. Chem., Bodenstein festband, 775 (1931).
56. G.Hammond, N.Turro, and A.Fischer, J.Amer. Chem. Soc., 83, 4674 (1961).
57. W.Dauben and R.Cargill, Tetrahedron, 15, 197 (1961).
58. G.Schenck and R.Steinmetz, Chem. Ber., 96, 520 (1963).
59. W.Dauben and R.Cargill, J.Org. Chem., 27, 1910 (1962).
60. G.Schenck and R.Steinmetz, Bull. Soc. chim. belges, 71, 781 (1962).
61. G.Wyman, Chem. Rev., 55, 625 (1955).
62. G.Lewis, T.Magel, and D.Lipkin, J.Amer. Chem. Soc., 62, 2973 (1940).
63. R.Dyck and D.McClure, J.Chem. Phys., 36, 2326 (1962).
64. D.Evans, J.Chem. Soc., 1735 (1960).
65. T.Förster, Z.Elektrochem., 56, 716 (1952).
66. R.Mulliken, Phys. Rev., 41, 751 (1932).
67. R.Mulliken and C.Roothaan, Chem. Rev., 41, 219 (1947).
68. H.Stegemeyer, J.Phys. Chem., 66, 2555 (1962).
69. S.Malkin and E.Fischer, J.Phys. Chem., 65, 1153 (1964).
70. D.Schulte-Frohlinde, H.Blume, and H.Güsten, J.Phys. Chem., 66, 2486 (1962).
71. G.Hammond and J.Saltiel, J.Amer. Chem. Soc., 84, 4983 (1963).
72. S.Malkin, Bull. Res. Council Israel, 11A, 208 (1962).
73. G.Hammond, N.Turre, and P.Leermakers, J.Phys. Chem., 66, 1144 (1962).
74. J.Saltiel and G.Hammond, J.Amer. Chem. Soc., 85, 2515 (1963).
75. G.Hammond and J.Saltiel, J.Amer. Chem. Soc., 85, 2516 (1963).
76. G.Hammond, J.Saltiel, A.Lamola, N.Turro, J.Bradshaw, D.Cowan, R.Counsel, V.Vogt, and C.Dalton, J.Amer. Chem. Soc., 86, 3197 (1964).
77. V.A.Krongauz, Dokl. Akad. Nauk SSSR, 155, 658 (1964).
78. V.A.Krongauz, Teor. Eksper. Khim., 1, 47 (1965).
79. Kh.S.Bagdasar'yan, Zhur. Fiz. Khim., 21, 25 (1947).
80. G.Schenck and R.Steinmetz, Tetrahedron Letters, No. 21, 1 (1960).
81. G.Schenck and R.Steinmetz, Naturwiss., 47, 514 (1960).
82. G.Schenck and R.Wolgast, Naturwiss., 48, 737 (1961).
83. G.Hammond and R.Liu, J.Amer. Chem. Soc., 85, 477 (1963).
84. V.Andersen and R.Norrish, Proc. Roy. Soc., 251, 1 (1959).
85. R.Norrish and J.Simons, Proc. Roy. Soc., 251, 4 (1959).
86. L.Basile, J.Chem. Phys., 36, 2204 (1962).
87. K.Überreiter and G.Sorge, Z.Elektrochem., 57, 795 (1953).
88. A.Watanabe, Bull. Chem. Soc. Japan, 32, 557 (1959).
89. T.Takemura, Bull. Chem. Soc. Japan, 32, 1073 (1962).
90. F.Takemura, Bull. Chem. Soc. Japan, 35, 1078 (1962).
91. A.Schönberg and A.Mustafa, Chem. Rev., 40, 181 (1947).
92. G.Ciamician and P.Silber, Ber., 33, 2911 (1900).
93. J.Pitts, R.Letsinger, R.Taylor, J.Patterson, G.Recktenwald, and R.Martin, J.Amer. Chem. Soc., 81, 1068 (1959).
94. M.Kasha, in "Comparative Effects of Radiation" (Edited by M.Burton, J.S.Kirby-Smith, and J.L.Magee), Wiley, New York, 1960, p.72.
95. G.Hammond and W.Moore, J.Amer. Chem. Soc., 81, 6334 (1959).
96. W.Moore and M.Ketchum, J.Amer. Chem. Soc., 84, 1368 (1962).
97. G.Hammond and P.Leermakers, J.Phys. Chem., 66, 1148 (1962).
98. H.Bäckström and K.Sandros, Acta Chem. Scand., 14, 48 (1960).
99. G.Porter and F.Wilkinson, Trans. Faraday Soc., 57, 1686 (1961).
100. A.Beckett and G.Porter, Trans. Faraday Soc., 59, 2038 (1963).
101. G.Porter, Proc. Chem. Soc., 291 (1959).
102. G.Ciamician and P.Silber, Ber., 34, 1530 (1901).
103. A.Berthoud and D.Porret, Helv. Chim. Acta, 17, 694 (1934).
104. B.Atkinson and M.Di, Trans. Faraday Soc., 54, 1331 (1958).
105. N.Bridge and G.Porter, Proc. Roy. Soc., A244, 276 (1958).
106. A.V.Karyakin, Uspekhi Khim., 30, 1050 (1961) [Russ. Chem. Rev., 460 (1961)].
107. G.Porter and M.Windsor, Proc. Roy. Soc., A245, 238 (1958).
108. R.Liu, N.Turro, and G.Hammond, J.Amer. Chem. Soc., 87, 3406 (1965).

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OPTICALLY ACTIVE CHELATE COMPOUNDS

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I. INTRODUCTION

The exceptional sensitivity of optical rotation to various types of reaction (structural changes, intermolecular interaction, etc.) and the unique nature of the properties of optically active compounds is leading to the broad extension of

studies of this phenomenon in the most varied branches of chemistry, particularly in the chemistry of chelate† compounds. It is known, for example, that many complex processes which take place in living organisms with the participation of metals include the formation of optically active compounds.

Optically active chelate compounds, which can be studied by spectropolarimetry, have in recent years been the object of a large number of studies. For a long time the spectropolarimetric method did not find extensive application because of the lack of available reliable instruments. About 1955 this difficulty was overcome by the production of the Rudolph spectropolarimeter [2]. Analogous instruments have been produced comparatively recently in the USSR. [3,4]

The foundations of the spectropolarimetric method in Russia were laid by Chugaev in the early nineteen-hundreds, in the period of the completion of the theory of the structure of organic compounds. Chugaev set himself the task of establishing the relationship between the optical activity of a substance and its chemical structure [5]. At that time it was customary to relate optical activity to an asymmetric carbon atom.

Optical activity is not a property of an individual atom, but is a property of the asymmetric molecule as a whole. As a result of the unsymmetric arrangement of the ligands around the central metal atom, it was possible to separate optical isomers of chelate compounds of nickel $[Ni(bipy)_3]X_2 . yH_2O$, where bipy represents bipyridyl [6]; cobalt(III) with Schiff bases, 1,8-diamino-3,6-dithiaoctane, etc. [7-11]; ruthenium, $[Ru(bipy)_3]Cl_2 . 6H_2O$; [12] osmium, $[OsCl_2(bipy)_2]Cl_2 . 3H_2O$; [13] iron(III) with 8-(2-pyridylmethyleneamino)quinoline [14]; zinc with 8-quinoline-5-sulphonic acid [15]; chromium [16]; platinum [17,18]; and many others.

A large number of optically active chelate compounds, exhibiting rotatory power due to an optically active ligand, the asymmetry of the molecule as a whole, or the combined influence of both these factors, have now been prepared and studied. Since review papers on optically active chelate compounds cover chiefly material up to 1958, [19-22] our aim was to systematise the literature on the chemistry of optically active chelate compounds chiefly for the period 1959–1964 and also to outline the main tasks and problems which are being solved by the spectropolarimetric method.

II. PREPARATION OF CHELATE COMPOUNDS IN OPTICALLY ACTIVE FORMS

The preparation of chelates in optically active forms is the primary problem in the chemistry of chelate compounds. As noted above, chelate compounds may exhibit optical activity as a result of the presence in the molecule of a ligand which has been prepared beforehand in optically active form. In a number of instances, however, the ligand may not contain an asymmetric centre, and the molecule as a whole becomes asymmetric after the formation of the chelate. It thus becomes necessary to separate the optical isomers of the previously-prepared chelate compound. This problem is extremely complex and its solution is directly related to the specific nature and properties of the chelate compounds.

† We use the term "chelate" to describe metallocyclic compounds, in which the metal–ligand bonds may be different in character. A more detailed discussion of nomenclature has been published [1].

Two main methods are used for the resolution of chelate compounds. The first method is based on the chemical reaction of optically-resolving agents with the chelate molecules, which should either be ionic or contain some functional group. In this the resolution involves the formation of diastereoisomers, which are then separated by fractional crystallisation, extraction, or chromatography. The most widely used optically active resolving agents are tartaric acid [23,24], (+)-nitrocamphor [16], antimony oxide (+)-tartrate [13,14,25], arsenic oxide (+)-tartrate [26], etc.

The resolution of some ionic chelate compounds — for example, tris-1,10-phenanthrolineruthenium(II) perchlorate — was achieved owing to the difference in the solubility of their antipodes in the presence of optically active additions (*d*-bromocamphorsulphonate) [27,28]. Recently optically active chelate compounds have been successfully used for resolving ionic chelates [29-32].

The second method of resolution, applied chiefly to "neutral" compounds, that is, compounds which are not ionic and contain no functional groups, is based on the selective adsorption of the chelates on quartz, starch, lactose, and other adsorbents. The resolution of (±)-Cr(HFA), where HFA is the fluoro-derivative of acetylacetone, has been carried out successfully by gas chromatography on quartz [33].

Chelate compounds of copper and nickel with β-keto--imines have been resolved by chromatography on D-lactose [34]. The same adsorbent gave satisfactory results in the resolution of oxobis-[4,4′-(propylenedi-imino)di-(2--pentanone)vanadium(IV). [35] Alumina treated with (+)-tartaric acid can be used as well as quartz for the resolution of Cr^{3+} and Co^{3+} acetylacetonates [36]. An interesting paper by Ferroni and Cini [37] describes the use of crystals of sodium *d*- and *l*-chlorate for the resolution of bis(benzoylacetonato)beryllium(II).

Recently, selective adsorption has also been used for the resolution of ionic chelates. Thus Dwyer and coworkers [38,39], in a study of compounds of the type $[Co(\pm)pn_2en]Cl_3$, $[Co(\pm)pnen_2]Cl_3$, $[Co(\pm)pn]Cl_3$, etc., where en represents ethylenediamine and pn propylenediamine, resolved the products on a cellulose column.

Other methods and reagents which are proving effective for the resolution of chelates are equally interesting. Harada and Fox [40] resolved the copper complex of aspartic acid by the introduction of a seed crystal of the optically active chelate. Interesting data have also been published [41] on the resolution of chelates by diffusion in liquids with asymmetric molecules.

Attempts to find new reagents and methods for the resolution of chelate compounds, particularly the search for new adsorbents, naturally deserve constant attention.

III. THE USE OF SPECTROPOLARIMETRY AND POLARIMETRY FOR THE STUDY OF CHELATE COMPOUNDS

1. Study of Redox Reactions, Racemisation, and Substitution in Chelates

Measurements of the rate of change of the optical rotation were used by Dwyer and Gyarfas [42] in a study of the dynamic equilibrium between the oxidised and reduced forms of the ions $Os(bipy)_3^{2+}$ and $Os(bipy)_3^{3+}$. This work was continued and refined by Eichler and Wahl [43], who studied

the rate of electron exchange in $Fe(phen)_3^{2+}-Fe(phen)_3^{3+}$, where phen = phenanthroline, and $Os(bipy)_3^{2+}-Os(bipy)_3^{3+}$ systems from the change in optical rotation and by using isotopic tracers.

Dwyer and Sargeson[44] described the measurement of the rate of electron transfer from the change in the dispersion of the rotation of the $Coen_3^{2+}-Coen_3^{3+}$ system. A detailed study of rates of electron transfer was made by Im and Busch[45,46], who divided the systems studied into two categories. The first consists of systems in which the absolute configuration is not preserved on electron transfer. As an example, the dependence of the racemisation of ethylenediaminetetra-acetatocobaltate(III) on temperature, pH, and concentration was studied. The hexadentate complex d-$[Co^{III}EDTA]^-$, where EDTA represents ethylenediaminetetra-acetate, undergoes racemisation at 100°, 90°, 85°, and 74° and the racemisation is catalysed by $[Co^{II}EDTA]^{2-}$ ions. We thus have two processes

$$d\text{-}[Co^{III}EDTA]^- \rightleftharpoons l\text{-}[Co^{III}EDTA]^-,$$

$$d\text{-}[Co^{III}EDTA]^- + [Co^{II}EDTA]^{2-} \rightleftharpoons [Co^{II}EDTA]^{2-} + l\text{-}[Co^{III}EDTA]^-.$$

The second category consists of systems in which the absolute configuration is preserved on racemisation, for example, 1,2-propylenediaminetetra-acetatocobaltate(III).

Racemisation of the ionic complex $[Coen_3]^{3+}$ in the presence of active carbon takes place as a result of a redox reaction[47]. By making use of electron exchange and the difference in the solubilities of the diastereoisomers of the tris(ethylenediamine)cobalt(III) ion, Busch[48] increased considerably the yield in the resolution of this ion.

The spectropolarimetric method has also been used successfully to measure the rate of exchange of the free ligand 1,2-propylenediaminetetra-acetic acid (PDTA) with its complex[49]:

$$[M(+)PDTA]^{4-} + l\text{-PDTA} \rightleftarrows [M\,l\text{-PDTA}]^{4-} + d\text{-PDTA},$$

where M = Cu, Ni, Co, etc. It is obvious that the rotation falls to zero when half of the ligand has reacted.

The problem of racemisation is related to the problem of electron exchange and ligand exchange in chelate compounds. Redox reactions are one factor responsible for the racemisation of chelate compounds. This phenomenon has been examined in detail by Lewis and Wilkins[22] and in a number of recent papers. It has been established that the racemisation of certain compounds, for example, *cis*--chloroaquobis(ethylenediamine)cobalt(III)[50,51] and *cis*--bis(oxalato)diaquochromate(III),[52] takes place as a result of the isomerisation of the optically active *cis*-compound into the symmetrical *trans*-compound. In other examples the racemisation is brought about by dissociation of the chelate. For example, the tris(acetylacetonato)silicon cation undergoes racemisation as a result of degradation by hydrolysis[53]. Dissociation is responsible for the racemisation of a large number of nickel chelates with phenanthroline and bipyridyl[26,44-56]. Brown and Ingold[57] used polarimetry to study the kinetics of the replacement of chloride ions in the *cis*-dichlorobis(ethylenediamine)cobalt(III) ion.

An important problem concerns the behaviour of chelate compounds in various chemical reactions, particularly substitution. In a number of instances spectropolarimetry makes it possible to establish whether the reaction involves the chelates themselves or free ligands liberated as a result of dissociation of the chelate. Study of the bromination and diazo-coupling of optically active catechol–arsenic(IV) chelates[58] showed no significant change in optical activity and configuration, from which it was concluded that the reaction involves the chelates themselves.

Preservation of the optical activity is also observed in electrophilic substitution (chlorination, bromination, nitration, etc.) in optically active tris(acetylacetonato)-compounds of Cr^{III}, Co^{III}, and Rh^{III}.[59] Thus the chelate compound reacts as a single aromatic system, since otherwise, racemic products would have been obtained after the reactions.

2. Quantitative Polarimetric Determination of Metals and Ligands in Chelates

The use of polarimetry for the quantitative determination of optically active natural products is well known. This method can also be used, however, for the quantitative determination of optically inactive compounds. In 1957, Freegarde[60] determined the metal ions Ag^+ and Fe^{3+} by means of the optically active reagent (+)-tartaric acid. Freegarde measured the rotation of a (+)-tartaric acid solution before and after the addition of a weighed specimen of the substance, which formed a precipitate with the optically active reagent.

Complex formation by molybdic acid with maleic and tartaric acids, mannitol, sorbitol, and other compounds has been used for the polarimetric determination of the latter in the presence of various other optically active compounds[61].

Haas and Faber[62] used (+)-tartaric acid for the quantitative determination of molybdenum by a polarimetric method. The ability of the Cu^{2+} ion to form a complex with L-(+)-histidine has been used for the spectropolarimetric determination of the metal ion and the optically active ligand[63].

3. Study of Chelate Formation and the Nature of the Bonding in Chelates

The study of optical activity assists in the deeper penetration into the essential features of the processes taking place on chelate formation and in the investigation of very slight molecular changes which cannot be observed by other methods.

By studying the optical rotatory power of L-propylenediamine in the presence of different quantities of metal ions (Zn^{2+}, Cd^{2+}, Hg^{2+}, or Ag^+) it is possible to gain information on chelate formation from the change in rotation. The optical activity of L-propylenediamine remains unchanged in the presence of Ba^{2+} and Mg^{2+} ions, apparently due to the absence of chelate formation[64].

Larsson[65] used polarimetry to study various outer--sphere complexes of (+)-tris(ethylenediamine)cobalt(III). It is a familiar fact that change in the composition of the second coordination sphere of complexes of transition metals (sulphate, chloride, etc. ions) does not produce marked changes in the absorption spectra, whereas the optical rotation of the ionic complexes depends to a marked extent on the nature of the counter-ion. Larsson measured the optical rotation of (+)-$[Coen_3]^{3+}$ in aqueous solutions with gradual increase in the concentration of sulphate,

thiosulphate, fluoride, chloride, and perchlorate ions, and observed a rotation minimum in the first two instances, indicating the formation of outer-sphere complexes.

A change in the dispersion of the rotation was also observed when optically inactive ions were added to (-)-*cis*--oxalatobis(ethylenediamine)cobalt(III) and (-)-tris(ethylenediamine)chromium(III) ions[66]. A polarimetric study of the conditions of the reaction of orthotellurate with (+)-tartrate established that a compound with 1:1 composition is obtained[67]. Polarimetric study of the Th^{4+}–tartaric acid system led to the conclusion that a stable chelate compound with the 1:1 composition is formed[68]. In analogous fashion, Chinese authors[69] established the existence of a cobalt tartrate with 1:1 composition by observing the change in the rotatory power, absorption coefficient, and refraction of the system.

The study of optical activity helps to solve the problem of the nature of the bonding in chelate compounds[70]. For example, the lack of success in attempts to resolve tris-(oxalato)manganates and tris(oxalato)ferrates[71] may be attributed to ionic bonding between the metal and the coordinated groups in these chelate compounds. In compounds which can be obtained in optically active form, these bonds are covalent.

4. Study of the Phenomenon of Stereospecificity in the Chemistry of Chelates

The phenomenon of stereospecificity has been observed in the study of optically active chelate compounds. This problem has been examined in a number of monographs[20-22] and reviews[72-76].

The problem of stereospecificity is related to the chemistry of mixed chelate compounds, in which different ligands are coordinated around the central metal atom. Mixed chelate formation is fairly common among ionic chelates and there is no need to deal specially with this question[77-80]. It may be noted that mixed tris-bidentate chelate compounds can be prepared by three methods: by adding ligands to the bis- or mono-chelate, by replacing ligands in tris-chelates, or by direct preparation. These compounds have been the subject of many studies[26,81].

The preparation of mixed chelates presents no obstacles so long as optically inactive ligands are dealt with. The preparation of chelates containing optically active ligands introduces the effect of stereospecificity, as a result of which some possible isomers (*Dlld*, *Ldll*, etc.) of these compounds are obtained in very small yield or not at all. Thus in the reaction of racemic propylenediamine (pn) with platinum(IV) chloride, Smirnoff[82] was able to obtain only two compounds *D*-$[Pt(L\text{-}pn)_3]^{4+}$ and *L*-$[Pt(D\text{-}pn)_3]^{4+}$.

Bailar and his coworkers[83] found that mixed isomers are probably formed, but undergo disproportionation with the formation of the products which were isolated by Smirnoff. The similar formation of a limited number of isomers of tris-(*trans*-1,2-diaminocyclopentane)cobalt(III) by Jaeger and Blumendal[84], who consider that two or more of the ligands in the chelate compound usually have the same configuration, that the chelate exists in a single configuration, and its sign of rotation may be the same as or opposite to that of the ligand.

Subsequent studies refuted this opinion to some extent. Lifschitz[85], for example, prepared tris-(D-alanine)-cobalt(III), from which two α-forms *Dddd* and *Lddd* and one β-form were isolated. The fact that the two α-forms have equal stabilities suggests that the stereospecific effect is not very strong in amino-acid chelates. Bailar and coworkers[86,87] found that the carbonatobis-(L-propylenediamine)cobalt(III) ion exists in both *D*- and *L*-forms, and that the configuration of its salt depends on the method of crystallisation. Another paper[88] reports the existence of both the (+)-tartratobis-(L-propylenediamine)cobalt(III) and (-)-tartratobis-(L-propylenediamine)cobalt(III) ions, but the stabilities of these isomers are different.

Extensive studies of the phenomenon of stereospecificity have been made by Dwyer and coworkers. Ionic chelates of Co^{III} with D- and L-propylenediamine (*Dlll* and *Lddd*) have been prepared and the equilibria between the isomers *Dddd* $\rightleftharpoons$ *Lddd* and *Dlll* $\rightleftharpoons$ *Llll* have been studied[89]. Analogous isomers of Pt^{IV} were prepared[90]. An attempt to prepare chelates with mixed ligands by the reaction of dichlorobis(ethylenediamine)cobalt(III) chloride with L-propylenediamine was unsuccessful and gave a mixture of the chlorides $[Coen_3]Cl_3$ and $[Co(L\text{-}pn)_3]Cl_3$.[91] The reaction of tetrachloro(L-propylenediamine)platinum(IV) and tetrachloro(ethylenediamine)platinum(IV) with ethylenediamine and D-propylenediamine, however, led to the preparation and resolution of the mixed chelates $[Pten_2(L\text{-}pn)]Cl_4$, $[Pt(L\text{-}pn)_2en]Cl_4$, and $[Pt(D\text{-}pn)_2(L\text{-}pn)]Cl_4$. It was pointed out that unsuccessful attempts to isolate mixed chelates are apparently due not to differences in the stabilities of the chelates but to the establishment of an equilibrium between all possible isomers in the course of the reaction. This led to the isolation of the thermodynamically more stable isomers $[Pt(L\text{-}pn)_3]Cl_4$ and $[Pt(D\text{-}pn)_3]Cl_4$, which predominate in the mixture, whereas the small quantities of the mixed isomers could not be detected. It was suggested that the equilibrium is established either as a result of the formation of intermediate 7- or 8-covalent chelates, or as a result of the catalytic influence of small quantities of Co^{II} and Pt^{II} chelates. Recently, Dwyer and coworkers[93] described the preparation of a mixture of isomers, from which the following were separated by chromatography on a cellulose column: *L*-$[Co(-)pn_3]Cl_3$, *L*-$[Co(-)pn_2en]Cl_3$, *L*-$[Co(-)pnen_2]Cl_3$, *D*-$[Co(-)pn_3]Cl_3$, *D*-$[Co(-)pn_2en][ClO_4)_3$, and *D*-$[Co(-)pnen_2](ClO_4)_3$. It is considered that the degree of stereospecificity of the chelates is a property chiefly of the ligands and may vary from almost zero, for sodium bis(oxalato)-L-propylenediaminecobaltate(III)[94] to the almost complete stereospecificity of the chelates with propylenediaminetetra-acetic acid[95].

Partial stereospecificity was observed in a study of cobalt(III) chelates with 4-methyl-1,8-bis(salicylideneamino)-3,6-dithiaoctane[25]. It was established that the dextrorotatory isomer of the ligand gives chiefly the laevorotatory form of the chelate (85%), whereas the laevorotatory isomer gives the dextrorotatory form of the chelate. In a continuation of their study of stereospecificity, Dwyer and coworkers[38] recently described the isolation of various mixed chelates of Co^{III} with propylenediamine and gave the equilibrium constants for the systems

$$D\text{-}[Co(+)pn_3]^{3+} \cdot L(Co(-)pn_3]^{3+}/D[Co(+)pn_2(-)pn]^{3+} \times L[Co(-)pn_2(+)pn]^{3+}=1.0$$
$$D\text{-}[Co(+)pn_2(-)pn]^{3+}/L[Co(+)pn_2(-)pn]^{3+}=2.4$$
$$D\text{-}[Co(+)pn(-)pn_2]^{3+} \cdot L=[Co(-)pn(+)pn_2]^{3+}/D[Co(-)pn_3]^{3+} \cdot L=[Co(+)pn_3]^{3+}=6.1.$$

The stability of the isomers and their relative concentration in the mixture were explained on the basis of the possible conformations of the propylenediamine ring.

As well as being of purely theoretical importance, the phenomenon of stereospecificity has found practical appli-

cation. Bailar and coworkers[83] suggested that if the reaction between an optically active chelate and an excess of a racemic coordinating substance is selective, that is, if the chelate can accept only one optically active isomer from the racemate, resolution of the racemic ligand should be observed. The first experiments did not give satisfactory results, however. Later[88], partial resolution of racemic tartaric acid was achieved by heating the cobalt chelate $[Co(L\text{-pn})_2(rac\text{-tart})]Cl$ in aqueous solution with an excess of L-propylenediamine. The latter replaces the (-)-tartrate ion in the chelate, whereas the (+)-tartrate ion is much more firmly held in the coordination sphere, proving that the configurations of (+)-tartaric acid and L-propylenediamine are identical. Partial resolution of racemic mixtures of organic acids (tartaric, α-chloropropionic, and lactic) was achieved using the carbonatobis(L-propylenediamine)cobalt(III) ion[96]. In all instances the dextrorotatory form of the acid enters the coordination sphere more readily than the laevorotatory form, and this leads to resolution. This reaction can also be used to determine the configuration of optically active acids. An attempt to resolve racemic tartaric acid by the reaction of its silver salt with *trans*-dichlorobis[(-)-stilbenediamine]-cobalt(III) nitrate was unsuccessful[97], however.

Sarma and Bailar[98] described the partial resolution of diamines, amino-acids, and dibasic acids by coordination with an optically active chelate. Stereospecificity has also been used successfully to prepare optically active chelate compounds[29,99,100]. For example, when (±)-$[Co(EDTA)]^-$ is treated with L-propylenediamine, the amine reacts with (-)-$[Co(EDTA)]^-$, leading to partial resolution of the chelate. Stereospecific reactions were recently used to prepare optically active forms of propylenediamine[101] and propylenediaminetetra-acetic acid[102].

The phenomenon of stereospecificity in non-ionic optically active chelate compounds of the bis-[*o*-(α-phenylethyliminomethyl)phenolato]copper type was studied by Terent'ev and coworkers[103]. In a study of the possibility of preparing chelates with irregularly paired ligands, in which the metal atom would be combined with two different molecules of a Schiff base ligand, it was established that for the systems studied the compounds with regularly paired ligands are favoured energetically.

A mixture of (-)-*o*-(α-phenylethyliminomethyl)phenol and (+)-*o*-(α-phenylethyliminomethyl)phenol in the presence of an excess of one of the forms was taken for the original ligands, and the chelate formation was carried out with copper and nickel; it was concluded that the products are always the compounds in which the metal is coordinated to ligands with one configuration, to give chelates with regularly paired ligands (*ll* or *dd*). An interesting feature is that these compounds can be formed by crystallisation of the double crystal-racemates *ll*×*dd*. This intramolecular racemisation leads to separation of a racemic fraction of the ligand in the form of the chelate, and the remaining uncombined fraction of the ligand is enriched in one of the optically active forms (*l* or *d*) taken in excess. This makes it possible to carry out the further purification of incompletely resolved amines and to obtain them in optically pure form.

5. The Configuration of Chelate Compounds

The study of optical rotatory power assists in the solution of the problem of the three-dimensional structure of a number of chelate compounds. In some instances the production of optical activity can be explained if it is assumed, following Werner[104], that the chelate compounds of elements with a coordination number of 6 have an octahedral structure whereas compounds with coordination number 4 have a tetrahedral or square-planar structure. Thus to explain the optical activity of *meso*-stilbenediamineisobutylenediamineplatinum chloride, Mills and Quibell[105] suggested that the bonds have a planar arrangement, since only then is the molecule asymmetric. With tetrahedral arrangement of the bonds, a plane of symmetry appears, so that the optical activity disappears.

The tetrahedral configuration of some beryllium chelates was confirmed by the successful resolution of their optically active isomers. Burgess and Lowry[106] observed the existence of optical isomers for benzoylcamphor complexes of beryllium, whose solutions exhibit mutarotation. This phenomenon was attributed to the gradual disappearance of the optical activity associated with the beryllium atom, which is the centre of the asymmetry.

Mills and Cotts[107] studied chelate compounds of beryllium, copper, and zinc with benzoylpyruvic acid; the optical isomers were separated using strychnine and brucine. They obtained an optically active solution almost free from alkaloid, but this rapidly underwent racemisation. Bis-(benzoylacetonato)beryllium, resolved by Busch and Bailar[108] by shaking a benzene solution of the chelate with optically active quartz powder, was found to be more stable.

The partial resolution of the tris(oxalato)germanate(IV) ion[109] proves the octahedral arrangement of the bonds in this ion and their covalent character. The successful resolution of bis(*o*-diethylphosphinophenyldiethylarsine)-copper(I) indicates that this compound has tetrahedral configuration[110]. The tris(biguanidine)-chelates of Co^{III} and Cr^{III}, like the tris(ethylenediamine)-chelates, have an octahedral configuration in which there are no elements of symmetry, and this was confirmed by separation of their optical isomers[23]. Ramaiah and coworkers[35] suggested that the five-coordinate chelate oxobis-[4,4′-(propylene-di-imino)di-(2-pentanone)]vanadium(IV) has a plane-pyramidal structure. In this instance the compound should exist in the form of optical isomers, and this was in fact proved. The partial resolution of the optical isomers of the β-keto-imine chelates of copper and nickel by a chromatographic method confirms that these compounds have tetrahedral configuration[34]. These and other examples[111,112] confirm that the existence of optical isomers provides a means of investigating the configuration of chelate compounds.

An important problem which has recently attracted the attention of research workers[113] is the determination of the absolute configuration of optically active chelates. A very important step in this direction was taken by Japanese scientists[114], who used X-ray diffraction methods to determine the absolute configuration of the *D*-(+)-$Coen_3^{3+}$ ion.

Later, Ballard and coworkers[115] proposed a new criterion for establishing absolute configuration, based on the sign of the optical rotatory power of the chelate in the long-wave range of the spectrum and on the sign of the rotatory power of the ligand[116]. Saito and coworkers gave data on the determination of the absolute configuration of the $[CoCl_2(L\text{-pn})_2]^+$ [117] and *L*-$[Co(L\text{-pn})_3]^{3+}$ [118] ions. The determination of the absolute configuration of some chelates is important since it makes possible the rapid determination of the configuration of many other analogous

compounds by comparison of their absorption spectra and rotatory dispersion curves. Japanese authors [119-122] have pointed out that if two optically active chelate compounds have similar bond character and hence similar stabilities, the sign of the Cotton effect should depend only on the absolute configuration. Compounds with the same absolute configuration should give Cotton effects with the same sign. This comparison of the rotatory dispersion curves of chelate compounds with known and unknown configurations has been used [24,36,76,123,124] to determine the configuration of chelates.

Optically active quartz and various other solids are being used successfully for the resolution of chelate compounds [37]. Bailar [125] has pointed out that if it were possible to show that a relationship exists between the configuration of quartz and the configuration of the isomer which is adsorbed by it, this would provide a simple method for determining the configuration of optically active substances.

The configuration of non-ionic optically active chelate compounds was discussed by Pfeiffer [126]. In a study of the rotatory dispersion curves for a number of chelates based on salicylaldehyde and various optically active amines and diamines and containing optically active formylcamphor, Pfeiffer reached the following conclusions.

1. The Cotton effect is shown by optically active chelate compounds of this type in the visible range of the spectrum only when a chromophoric metal atom is present.

2. As far as the manifestation of the Cotton effect is concerned, dicyclic and tricyclic compounds are in principle equivalent.

3. The position of the asymmetric carbon atom relative to the metal atom in the compounds studied plays no significant part in the manifestation of the Cotton effect.

Since the rotatory dispersion curve shows an anomalous shape when a metal is added to a Schiff base, it was concluded that in addition to the asymmetric carbon atom there should be another centre of asymmetry — the metal atom — and that it is the latter which produces the Cotton effect. From this Pfeiffer concluded that the chelates considered have tetrahedral configuration. Chelate compounds of the same type but containing no asymmetric carbon atom have planar configuration. Pfeiffer considered that the vicinal effect cannot be responsible for the Cotton effect. In an analysis of this work by Pfeiffer, Martell and Calvin [20] consider the rejection of the vicinal effect to be premature. The vicinal effect is apparently responsible for the anomalous shape of the rotatory dispersion curves. Evidence against tetrahedral configuration for these compounds is also provided by the fact that they could not be separated into optical isomers with respect to the central metal atom.

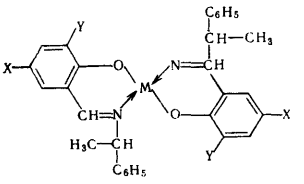
Thus Pfeiffer, on the basis of the normal rotatory dispersion curve for the nickel–formylcamphor complex, concluded that this chelate has square-planar configuration [126]. Later, however, French and Corbett [127] recorded the ultraviolet spectrum and rotatory dispersion curve and found that the rotatory dispersion curve shows a maximum at $\lambda = 3162$ Å, due to the absorption band of the nickel centre in the molecule. Measurement of the magnetic susceptibility of this compound in the solid state and in methanol solution shows that it is paramagnetic. On the basis of the data obtained, it was concluded that the nickel–formylcamphor complex has tetrahedral configuration. Subsequent study [128] of the absorption spectra, rotatory dispersion, and magnetic susceptibility of bis(formylcamphor)ethylenediaminenickel led to the conclusion that this compound has planar configuration in the solid state, but that in methanol solution, under the influence of the asymmetric centre present, equilibrium is established between the two configurations: planar and tetrahedral.

From these data it can be seen that the mere presence or absence of the Cotton effect does not provide proof for tetrahedral or planar configurations respectively in chelate compounds. In these compounds the central metal atom is a chromophore which reacts with the asymmetric centre in the molecule. The absorption band corresponding to the metal atom is optically active and a Cotton effect appears in this range of the spectrum.

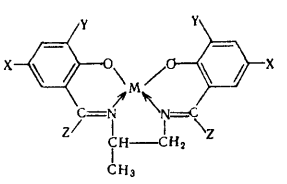
Lifschitz [129] in a study of the rotatory dispersion of chelate compounds, examined the question of the relationships which should exist between the chromophore and an optically active centre for production of the Cotton effect. He considers that in compounds containing optically active coordinated groups, a Cotton effect in the range of the absorption band of the central metal atom is observed only when the asymmetric atom is a member of a ring formed through the central atom by means of "inner-complex bonding (that is, where the metal atom is attached to the organic molecule by means of a principal valency and a subsidiary valency)". Lifschitz emphasises the difference in the behaviour of the copper and nickel chelates. Thus the compounds of $[Cu(L\text{-}pn)_2]^{2+}$ give an anomalous rotatory dispersion curve, whereas the compounds of $[Ni(L\text{-}pn)_2]^{2+}$ give a normal curve. Lifschitz considers that for the nickel chelate it is necessary to assume a symmetrical structure in which the rotation is due entirely to the optically active propylenediamine molecules present. The unique behaviour of copper is attributed to the possibility of partial asymmetric synthesis.

A review by Mat'e [130] gives several examples from the literature which have been attributed to partial asymmetric synthesis, and points out that in every instance where a complex capable of existing in two enantiomorphic forms is obtained, it is necessary to investigate carefully whether the Cotton effect arises from a bond between an active molecule and the central atom or is due to partial asymmetric synthesis.

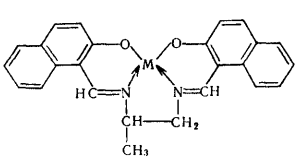
Recent papers by Terent'ev and coworkers [131-133] give the results of spectropolarimetric studies of chelates with structures A, B, C, D, and E, with optically active *o*-hydroxyaldimines and *o*-hydroxyketimines.



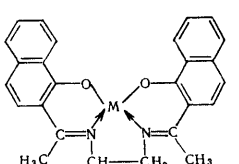
(A) X = H, Cl, Br, NO_2; Y = OCH_3, H; M = Cu, Ni, Co



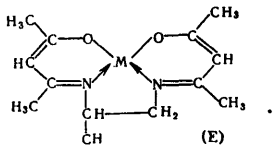
(B) X = H, Cl, Br, NO_2; Y = OCH_3, H; Z = CH_3, H; M = Cu, Ni, Co



(C)



(D)



(E)

On the basis of a comparison of the rotatory dispersion curves for these compounds, it was concluded that non-vicinal (distant) substituents (X, Y) in the chelates have little influence on the rotatory dispersion. The introduction of a vicinal substituent (Z = CH_3) in the metal-containing ring on going from the hydroxyaldimine derivatives to the hydroxyketimine derivatives, however, leads to a sharp increase in the absolute values of the molecular rotation without altering significantly the nature of the rotation, due to the difference in the degree of coplanarity of the chelate compounds.

Although spectrophotometry has been unable to record these fine changes in molecular structure, the conclusions reached on the basis of spectropolarimetric studies have been confirmed by data from the EPR spectra[134].

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It can be seen from the foregoing that the use of polarimetry and spectropolarimetry in the study of optically active chelate compounds opens up promising possibilities. The high sensitivity of these methods makes it possible in a number of instances to record fine changes in a molecule, difficult to detect by other methods.

The possibilities of the spectropolarimetric method in the chemistry of optically active chelate compounds are far from being exhausted, however. The increase observed every year in the number of studies in this field and the isolation of new chelates in optically active form enable us to hope that new properties and phenomena making it possible to reach a deeper understanding of the chemistry of optically active chelate compounds will be discovered and studied.

1. V.V.Rode, E.G.Rukhadze, and A.P.Terent'ev, Uspekhi Khim., 32, 1488 (1963) [Russ.Chem.Rev., 666 (1963)].
2. H.Rudolph, J.Opt.Soc.Amer., 45, 50 (1955).
3. V.M.Potapov and A.P.Terent'ev, Zhur.Obshch.Khim., 31, 1003 (1961).
4. G.A.Dvorkin, E.I.Golub, A.P.Gorbachev, L.G.Koreneva, and M.I.Mekshenkov, Dokl.Akad.Nauk SSSR, 151, 1211 (1963).
5. L.A.Chugaev, "Izbrannye Trudy" (Selected Works), Izd. Akad.Nauk SSSR, Moscow, 1955, Vol. 2, pp.355-532.
6. G.T.Morgan and F.H.Burstall, J.Chem.Soc., 2213 (1931).
7. F.P.Dwyer and F.Lions, J.Amer.Chem.Soc., 69, 2917 (1947); 72, 1545 (1950).
8. F.P.Dwyer, F.Lions, and D.P.Mellor, J.Amer.Chem. Soc., 72, 5037 (1950).
9. F.P.Dwyer, N.S.Gill, E.C.Gyarfas, and F.Lions, J.Amer. Chem.Soc., 74, 4188 (1952).
10. J.Collins, F.P.Dwyer, and F.Lions, J.Amer.Chem.Soc., 74, 3134 (1952).
11. F.P.Dwyer, N.S.Gill, E.C.Gyarfas, and F.Lions, J.Amer. Chem.Soc., 75, 2443 (1953).
12. F.H.Burstall, J.Chem.Soc., 173 (1936).
13. F.H.Burstall, F.P.Dwyer, and E.C.Gyarfas, J.Amer. Chem.Soc., 953 (1950).
14. F.P.Dwyer, N.S.Gill, E.C.Gyarfas, and F.Lions, J.Amer. Chem.Soc., 75, 3834 (1953).
15. C.J.Liu and J.C.Bailer, Jnr., J.Amer.Chem.Soc., 73, 5432 (1951).
16. O.Kling and F.Woldbye, Acta Chem.Scand., 15, 704 (1961).
17. I.I.Chernyaev and O.N.Andrianova, Zhur.Neorg.Khim., 6, 34 (1961) [Russ.J.Inorg.Chem., 16 (1961)].
18. I.I.Chernyaev, O.N.Andrianova, and N.Sh.Leites, Zhur. Neorg.Khim., 7, 749 (1962) [Russ.J.Inorg.Chem., 386 (1962)].
19. A.A.Grinberg, "Vvedenie v Khimiyu Kompleksnykh Soedinenii" (Introduction to the Chemistry of Complex Compounds), Goskhimizdat, Leningrad-Moscow, 1951, pp. 117-145.
20. A.E.Martell and M.Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1952, pp.238-336.
21. J.C.Bailar, Jnr., and D.H.Busch (Editors), "The Chemistry of the Coordination Compounds" (Translated into Russian), Inostr.Lit., Moscow, 1960, pp.256-292.
22. J.Lewis and R.G.Wilkins, "Modern Coordination Chemistry, Principles and Methods" (Translated into Russian), Inostr. Lit., Moscow, 1963, pp.173-210.
23. S.P.Ghosh and A.J.P.Sinha, J.Indian Chem.Soc., 40, 249 (1963).
24. T.E.McDermott and A.M.Sargeson, Austral.J.Chem., 16, 334 (1963).
25. F.P.Dwyer and T.E.McDermott, J.Amer.Chem.Soc., 85, 2916 (1963).
26. J.A.Broomhead and F.P.Dwyer, Austral.J.Chem., 15, 453 (1962); 16, 51 (1963).
27. F.P.Dwyer, E.C.Gyarfas, and M.F.O'Dwyer, Nature, 167, 1036 (1951).
28. F.P.Dwyer and E.C.Gyarfas, Nature, 168, 29 (1951).
29. F.P.Dwyer, E.C.Gyarfas, and D.P.Mellor, J.Phys.Chem., 59, 296 (1955).
30. F.P.Dwyer and A.M.Sargeson, J.Phys.Chem., 60, 1331 (1956).
31. F.P.Dwyer, I.K.Reid, and F.L.Garvan, J.Amer.Chem. Soc., 83, 1285 (1961).
32. F.P.Dwyer and F.L.Garvan, J.Amer.Chem.Soc., 81, 2955 (1959).
33. Chem.Eng.News, 40, 50 (1962).
34. T.M.Hseu, D.F.Martin, and T.Mocller, Inorg.Chem., 2, 587 (1963).
35. K.Ramaiah, F.E.Anderson, and D.F.Martin, Inorg.Chem., 3, 296 (1964).
36. T.S.Piper, J.Amer.Chem.Soc., 83, 3908 (1961).
37. E.Ferroni and R.Cini, J.Amer.Chem.Soc., 82, 2427 (1960).
38. F.P.Dwyer, A.M.Sargeson, and L.B.James, J.Amer. Chem.Soc., 86, 590 (1964).
39. F.P.Dwyer, T.E.McDermott, and A.M.Sargeson, J.Amer. Chem.Soc., 85, 2913 (1963).
40. K.Harada and S.W.Fox, Nature, 194, 768 (1962).
41. V.Carassiti, J.Inorg.Nuclear Chem., 8, 227 (1958).
42. F.P.Dwyer and E.C.Gyarfas, Nature, 166, 481 (1950).
43. E.Eichler and A.C.Wahl, J.Amer.Chem.Soc., 80, 4145 (1958).
44. F.P.Dwyer and A.M.Sargeson, J.Phys.Chem., 65, 1892 (1961).
45. Y.A.Im and D.H.Busch, Nature, 182, 1362 (1958).
46. Y.A.Im and D.H.Busch, J.Amer.Chem.Soc., 83, 3357, 3362 (1961).
47. F.P.Dwyer and A.M.Sargeson, Nature, 187, 1022 (1960).
48. D.H.Busch, J.Amer.Chem.Soc., 77, 2747 (1955).
49. B.Bosnich, F.P.Dwyer, and A.M.Sargeson, Nature, 186, 966 (1960).
50. R.G.Pearson, R.E.Meeker, and F.Basolo, J.Amer.Chem. Soc., 78, 2673 (1956).

51. A.M.Sargeson, Austral.J.Chem., 16, 352 (1963).
52. G.L.Welch and R.E.Hamm, Inorg.Chem., 2, 295 (1963).
53. S.K.Dhar, V.Doron, and S.Kirschner, J.Amer.Chem.Soc., 81, 6372 (1959).
54. G.K.Schweitzer and J.M.Lee, J.Phys.Chem., 56, 195 (1952).
55. R.G.Wilkins and M.J.G.Williams, J.Chem.Soc., 1763 (1957).
56. J.A.Broomhead, Austral.J.Chem., 16, 186 (1963).
57. D.D.Brown and C.K.Ingold, J.Chem.Soc., 2680 (1953).
58. T.N.Larkins and M.M.Jones, J.Inorg.Nuclear Chem., 25, 1487 (1963).
59. J.P.Coolman, R.P.Blair, R.L.Marschall, and L.Slade, Inorg.Chem., 2, 576 (1963).
60. M.Freegarde, Chem.and Ind., 984 (1957).
61. N.J.Kirsten and S.K.Nilson, Analyt.Chim.Acta, 27, 345 (1962).
62. W.Haas and H.Faber, Z.analyt.Chem., 193, 89 (1963).
63. S.Kirschner and D.C.Bhatnagar, Analyt.Chem., 35, 1069 (1963).
64. T.D.O'Brien and R.C.Toole, J.Amer.Chem.Soc., 76, 6009 (1954); 77, 1368 (1955).
65. R.Larsson, Acta Chem.Scand., 16, 2267 (1962).
66. M.J.Albinak, D.Bhatnagar, S.Kirschner, and A.Sonnessa, Canad.J.Chem., 39, 2360 (1961).
67. T.G.Lanese and B.Taselskis, Analyt.Chem., 35, 1878 (1963).
68. E.Darmois and Yen Ki-Heng, Compt.rend., 194, 703 (1932).
69. Yen Ki-Heng and Chon Tschg-Fa, Xibei daxue Xuebao, Ziran kexue, No. 3, 31, 1958 (1959); Ref.Zhur.Khim., 12 335 (1960).
70. Zh.P.Mat'e, Uspekhi Khim., 9, 849 (1940).
71. C.H.Johnson, Trans.Faraday Soc., 28, 845 (1932).
72. J.C.Bailar, Jnr., Uspekhi Khim., 6, 214 (1937) [Translated into Russian].
73. H.B.Jonassen, J.C.Bailar, Jnr., and E.H.Huffman, J.Amer.Chem.Soc., 70, 756 (1948).
74. N.E.Colley, Ch.F.Liu, and J.C.Bailar, Jnr., J.Amer.Chem.Soc., 81, 4189 (1959).
75. E.J.Corey and J.C.Bailar, Jnr., 81, 2620 (1959); translated in Uspekhi Khim., 29, 913 (1960).
76. D.H.Busch, J.Chem.Educ., 41, 77 (1964).
77. P.Pfeiffer, T.Gassmann, and H.Pietsch, Z.anorg.Chem., 58, 301 (1908).
78. F.McCullough, Jnr., and J.C.Bailar, Jnr., J.Amer.Chem.Soc., 78, 714 (1956).
79. R.Näsänen, P.Meriläinen, and S.Lukkari, Acta Chem.Scand., 16, 2384 (1962).
80. Y.J.Israeil, Canad.J.Chem., 41, 2710 (1963).
81. J.A.Broomhead, Austral.J.Chem., 15, 228 (1962).
82. A.P.Smirnoff, Helv.Chim.Acta, 3, 177 (1920).
83. J.C.Bailar, Jnr., C.A.Stiegman, J.C.Baltis, and E.H.Huffman, J.Amer.Chem.Soc., 61, 2402 (1959).
84. F.M.Jaeger and H.B.Blumendal, Z.anorg.Chem., 175, 161 (1928).
85. J.Lifschitz, Z.phys.Chem., 114, 493 (1925).
86. J.C.Bailar, Jnr., and J.P.Reynolds, J.Amer.Chem.Soc., 61, 3199 (1939).
87. Sr.M.Martinette and J.C.Bailar, Jnr., J.Amer.Chem.Soc., 74, 1054 (1952).
88. J.C.Bailar, Jnr., H.B.Jonassen, and A.D.Cott, J.Amer.Chem.Soc., 74, 3131 (1952).
89. F.P.Dwyer, F.L.Garvan, and A.Schulman, J.Amer.Chem.Soc., 81, 290 (1959).
90. F.P.Dwyer and F.L.Garvan, J.Amer.Chem.Soc., 81, 1043 (1959).
91. F.P.Dwyer and A.M.Sargeson, J.Amer.Chem.Soc., 81, 5269 (1959).
92. F.P.Dwyer and A.M.Sargeson, J.Amer.Chem.Soc., 81, 5272 (1959).
93. F.P.Dwyer, T.E.McDermott, and A.M.Sargeson, J.Amer.Chem.Soc., 85, 2913 (1963).
94. F.P.Dwyer, T.E.McDermott, and A.M.Sargeson, J.Amer.Chem.Soc., 85, 661 (1963).
95. F.P.Dwyer and F.L.Garvan, J.Amer.Chem.Soc., 83, 2610 (1961).
96. A.D.Gott and J.C.Bailar, Jnr., J.Amer.Chem.Soc., 74, 4820 (1952).
97. O.F.Williams and J.C.Bailar, Jnr., J.Amer.Chem.Soc., 81, 4464 (1959).
98. B.D.Sarma and J.C.Bailar, Jnr., J.Amer.Chem.Soc., 77, 5480 (1955); 78, 895 (1956).
99. S.Kirschner, Yung-Kang Wei, and J.C.Bailar, Jnr., J.Amer.Chem.Soc., 79, 5877 (1957).
100. F.P.Dwyer and T.E.McDermott, Inorg.Chem., 2, 871 (1963).
101. H.Irving and R D.Gillard, J.Chem.Soc., 5266 (1960).
102. H.Irving and R.D.Gillard, J.Chem.Soc., 2249 (1961).
103. A.P.Terent'ev, E.G.Rukhadze, and G.V.Panova, Dokl.Akad.Nauk SSSR, 155, 872 (1964).
104. A.Werner, Ber., 44, 2445, 3279 (1911).
105. W.H.Mills and T.H.Quibell, J.Chem.Soc., 839 (1935).
106. H.Burgess and T.M.Lowry, J.Chem.Soc., 2081 (1924).
107. W.H.Mills and R.A.Cotts, J.Chem.Soc., 3121 (1926).
108. D.H.Busch and J.C.Bailar, Jnr., J.Amer.Chem.Soc., 76, 5352 (1954).
109. T.Moeller and N.C.Nielsen, J.Amer.Chem.Soc., 75, 5106 (1953).
110. W.Cochran, F.A.Mart, and F.G.Mann, J.Chem.Soc., 2816 (1957).
111. G.B.Kauffman and L.T.Tanahashi, J.Chem.Educ., 39, 481 (1962).
112. J.Selbin and J.C.Bailar, Jnr., J.Amer.Chem.Soc., 82, 1524 (1960).
113. F.Woldbye, "Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, 7th–11th September, 1964", p.103.
114. Y.Saito, K.Nakatsu, M.Shiro, and H.Kuroja, Bull.Chem.Soc.Japan, 30, 795 (1957).
115. R.E.Ballard, A.J.McCaffery, and S.F.Mason, Proc.Chem.Soc., 331 (1962).
116. A.J.McCaffery and S.F.Mason, Proc.Chem.Soc., 211 (1963).
117. Y.Saito and H.Jwasani, Bull.Chem.Soc.Japan, 35, 1131 (1962).
118. Y.Saito, H.Jwasani, and H.Ota, Bull.Chem.Soc.Japan, 36, 1543 (1963).
119. Y.Shimura, Bull.Chem.Soc.Japan, 31, 315 (1958).
120. J.Hidaka, S.Yamada, and R.Tsuchida, Bull.Chem.Soc.Japan, 31, 921 (1958).
121. J.Hidaka, Y.Shimura, and R.Tsuchida, Bull.Chem.Soc.Japan, 33, 847 (1960).
122. J.Hidaka, Y.Shimura, and R.Tsuchida, Bull.Chem.Soc.Japan, 35, 567 (1962).
123. R.D.Archer and J.C.Bailar, Jnr., J.Amer.Chem.Soc., 83, 812 (1961).
124. D.H.Busch and D.W.Cooke, J.Inorg.Nuclear Chem., 23, 145 (1961).
125. J.C.Bailar, Jnr., J.Inorg.Nuclear Chem., 8, 165 (1958).
126. P.Pfeiffer, W.Christeleit, T.Hesse, H.Pfitzner, and H.Thielert, J.prakt.Chem., 150, (2), 261 (1937).
127. H.S.French and G,Corbett, J.Amer.Chem.Soc., 62, 3219 (1940).
128. H.S.French, M.Z.Magle, and E.Sheffild, J.Amer.Chem.Soc., 64, 1924 (1942).
129. J.Lifschitz, Z.phys.Chem., 105, 27 (1923).
130. Zh.P.Mat'ë, Uspekhi Khim., 9, 961 (1940).
131. A.P.Terent'ev, G.V.Panova, and E.G.Rukhadze, Zhur.

Obshch. Khim., 34, 3013 (1964).
132. A. P. Terent'ev, G. V. Panova, and E. G. Rukhadze, Zhur. Obshch. Khim., 34, 3019 (1964).
133. A. P. Terent'ev, E. G. Rukhadze, G. V. Panova, and N. M. Viktorova, Zhur. Obshch. Khim., 34, 3025 (1964).
134. A. P. Terent'ev, G. V. Panova, D. N. Shigorin, and E. G. Rukhadze, Dokl. Akad. Nauk SSSR, 156, 1174 (1964).

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MASS SPECTRA AND MOLECULAR STRUCTURE OF HYDROCARBONS

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I. INTRODUCTION

Modern ideas on the molecular structure of organic compounds are to a large extent linked with the study of physical properties, such as absorption spectra in all regions from the ultraviolet to the microwave, dipole moments, atomic and electronic polarisation, etc. In the last two decades a new method for investigating organic compounds — molecular mass spectrometry — has been developed; this deals with the interaction of molecules and electrons. The overall relative probability of the formation of various ions that arise when a molecule is bombarded with slow (20–70 eV) electrons is characteristic of the stability of the molecule, and, what is very important for the organic chemist, of its structure, since the possible rupture of a given bond depends mainly on the distribution of electron density.

The formation of mass spectra is generally considered from the point of view of the Franck–Condon principle[1], according to which the first act in any inelastic collision between an electron and a molecule is electronic excitation of the latter, which occurs as an electronic transition while the distance between nuclei remains unchanged. In the inelastic collision of an ionising electron with a molecule, one of the valence electrons is removed and a molecular ion corresponding to the molecular weight and empirical formula of the compound is formed. Electrons acting on the molecule in the ion source of the mass spectrometer usually possess energy of several tens of electron volts; therefore, in the bombardment of polyatomic molecules, in addition to ionisation, decomposition of molecular ions occurs with rupture of C–C and C–H bonds and the formation of ionic fragments, which may also decompose in turn. This multiplicity of processes is responsible for the complexity of the mass spectra of polyatomic molecules with their multiplicity of lines.

The stability of organic molecules to electron impact is characterised by the probability of decomposition of molecular ions[2], W_Z, and is determined by the ratio of the number of molecular ions (I_{mol}) to the number of fragmentation ions (ΣI_{frag}): $W_Z = \Sigma I_{frag}/(I_{mol} + \Sigma I_{frag})$. The value of $W_M = (1 - W_Z)$ determines the stability of the molecule to electron impact.

This ratio, in turn, reflects the rate of decomposition of the molecular ion; since the time between the formation of ions and their detection is usually 10^{-5} s, the absence of particular molecular-ion peaks in the mass spectrum indicates that these ions have a short life. The rate of decomposition of the molecular ion is a function of the energy acquired by the ion during its formation; when the energy of the ionising electrons falls to a value close to the ionisation potential of the molecule, the proportion of molecular ions is increased in relation to that of fragmentation ions.

The ionisability of molecules and radicals formed in the rupture of chemical bonds is characterised by what is termed complete ionisation, which represents the quantity of ions formed by unit quantity of the compound[3]. It is determined by the sum of the intensities of all the peaks in the spectrum multiplied by the coefficient of sensitivity of the strongest peak; the latter is expressed in units of ion current referred to unit pressure.

In addition to the ions formed by simple rupture of bonds, the mass spectra of nearly all molecules containing more than two carbon atoms show the presence of ions that are produced as a result of rearrangement of atoms at the moment of dissociation. Rearrangements with migration of a hydrogen atom are observed very frequently[4]. The activation energy of rearrangements in ions is low and commensurable with the activation energy of rearrangements in neutral molecules; accordingly, rearrangements in the molecular ion proceed comparatively easily[3]. With hydrocarbons the difference in activation energies of various rearrangements is very small, and therefore competing reactions lead to the formation of diverse fragments.

Although the number of carbon and hydrogen atoms in the ion can be readily established, the question as to which of the hydrogen atoms has separated with a given fragment can only be decided by a study of the mass spectra of isotopically "labelled" compounds[6,7]. Information on the structure of ionised fragments can also be obtained by measuring the energy changes in the reactions that occur and by studying metastable transitions.