CCXVIII.—*Stereoisomerism of Disulphoxides and Related Substances. Part VI. Co-ordination Compounds of Some Disulphides and Diamines.*

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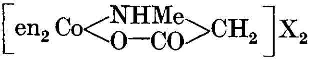
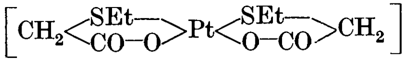
FROM the standpoint of modern views of the nature of co-ordination bonds it is reasonable to suppose that nitrogen and sulphur atoms, when co-ordinated to a metal atom, have their valency linkages disposed stereochemically as in the ammonium and sulphonium salts. The attached groups will be arranged, in fact, at four or three corners, respectively, of a tetrahedron circumscribing the atom in question.

A new factor is thus introduced into the possible configurations of many complexes. Such a possibility has already been suggested in at least two instances to account for observed isomerism: Meisenheimer (*Annalen*, 1924, **438**, 268) found forms of the optically active sarcosinediethylenediaminecobalt salts (I) in which dissymmetry both about the cobalt atom and about the sarcosine nitrogen atom appears to be involved; and Reihlen (*Z. anorg. Chem.*, 1926, **151**, 71; *Annalen*, 1926, **447**, 211) used the same conception in discussing the copper complexes from polymethylenebisiminoacetic acids and platinous ethylthiolacetate (II), of which two forms were obtained by Ramberg (*Ber.*, 1910, **43**, 580). There is, however, some doubt as to the identity in molecular weight of the latter substances.



$\left[\mathrm{en_2Co}{<}\begin{matrix}\mathrm{NHMe}\\ \mathrm{O{-}CO}\end{matrix}{>}\mathrm{CH_2}\right]\mathrm{X_2}$

(I.)



$\left[\mathrm{CH_2}{<}\begin{matrix}\mathrm{SEt{-}}\\ \mathrm{CO{-}O}\end{matrix}{>}\mathrm{Pt}{<}\begin{matrix}\mathrm{SEt{-}}\\ \mathrm{O{-}CO}\end{matrix}{>}\mathrm{CH_2}\right]$

(II.)

It appeared to be desirable to examine compounds of a simpler type where some evidence of the stereoisomerism in question might be found, and we now record a closer examination, from this point of view, of some chelate complexes of the general formulæ (III) and (IV) in which the presence of the two sulphur or nitrogen atoms should cause the formation of a pair of (optically inactive) diastereoisomerides. These would have the radicals R in the *cis*- and *trans*-positions, respectively, relative to the heterocyclic ring present in the molecule and would thus be analogous to the isomeric dioxides of dithian.

(III.)

$\left[\mathrm{C_2H_4}{<}\begin{matrix}\mathrm{SR}\\ \mathrm{SR}\end{matrix}{>}\mathrm{MX_2}\right]$

$\left[\mathrm{C_2H_4}{<}\begin{matrix}\mathrm{NRR'}\\ \mathrm{NRR'}\end{matrix}{>}\mathrm{MX_2}\right]$

(IV.)

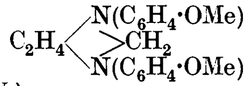
In the cases chosen, there is no complication such as spiran dissymmetry as in those referred to above. The question of the supposed alternative space arrangements round the 4-co-ordinated platinum or palladium atoms we ignored on two grounds. First, because this could not interfere here, as the chelate type chosen necessarily has the *cis*-configuration in this respect; and secondly, because we were sceptical as to the reality of the *cis-trans* isomerism in question, which involved the assumption that platinum and palladium are unique among the elements in having four groups attached to them arranged in a single plane rather than tetrahedrally. Recent experiments of Angell, Drew, and Wardlaw (this vol., p. 349) justify this view.

Two of the most stable of the complexes of the type under discussion described by Morgan and Ledbury (J., 1922, **121**, 2882) were re-examined, namely, those from dimethylthiolethane with palladous chloride and with mercuric iodide,  $\left[\mathrm{C_2H_4}{<}\begin{matrix}\mathrm{SMe}\\ \mathrm{SMe}\end{matrix}{>}\mathrm{R}\right]$, R being $PdCl_2$ or HgI_2, and the corresponding *compounds* from diethylthiolethane were prepared and examined at the same time. Among the co-ordination *compounds* from the aromatic disulphides diphenyl-, di-*p*-tolyl-, and dibenzyl-thiolethane, the palladous chloride complexes were the stablest: the first of these disulphides does not unite with mercuric iodide. A careful search in all cases failed to reveal any second isomeride. A crystallographic description is given of *di-*p*-tolylthiolethanepalladous chloride* and of two other substances obtained in crystallising it, but these proved to be *compounds* with one molecular proportion of acetone and chloroform respectively. *Dibenzylthiolethanemercuric iodide* was also examined crystallographically.

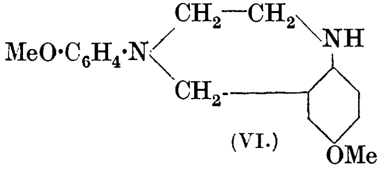
Co-ordination *compounds* of palladous chloride with ethylenediphenyldiamine, ethylenedi-*p*-anisyldiamine, and ethylenediphenyldimethyldiamine were prepared, but they could not be recrystallised unchanged and gave no evidence of being mixtures.

The negative results thus obtained may be attributed to an instability of the co-ordination bond with consequent ready conversion of one of the possible isomerides into the other, so that the less soluble of the forms is isolated. For this reason, as varied a selection of solvents as possible was used in crystallisation in the hope that the varying solubilities might lead to the isolation of different isomerides, but this was not in fact achieved.

An observation of some interest was made incidentally in connexion with the base ethylenedi-*p*-anisyldiamine, which was prepared from ethylene dibromide and *p*-anisidine. This base of m. p. 105° was converted by boiling in commercial methyl alcohol into a base, B, of m. p. 132°, the composition of which indicated that a single methylene group had been introduced into the molecule. The base B yielded derivatives of the parent base with acids or acyl halides, formaldehyde being eliminated in the process, and may be regarded as di-*p*-anisyltetrahydroglyoxaline (V). Diphenyltetrahydroglyoxaline, m. p. 124°, and the diethoxydiphenyl base, m. p. 214°, were prepared by Bischoff (*Ber.*, 1898, **31**, 3248) by the action of formaldehyde on the corresponding ethylenediamines. When, however, formaldehyde was added to an alcoholic solution of ethylenedi-*p*-anisyldiamine a third base, C, m. p. 226°, was at once produced which appears to be isomeric with base B. As this substance is not reconverted into the parent base by hydrochloric acid, we prefer tentatively to assign to it the structure (VI) in which nuclear condensation is assumed to have occurred. This makes it possible that the structure of the diethoxy-base may require revision.



(V.)



(VI.)

EXPERIMENTAL.

Co-ordinated Derivatives of Dimethyl- and Diethyl-thiolethane.—Dimethylthiolethanepalladous chloride, prepared as described by

Morgan and Ledbury (*loc. cit.*), formed small yellow octahedra, m. p. 234°. It was sparingly soluble in organic solvents, but was readily crystallised from warm water. In the preparation and in the purification of this and the compounds which follow, a search was made for the presence of any second substance.

Dimethylthiolethanemercuric iodide, prepared from its components in acetone, crystallised from that solvent in silvery-white diamond-shaped plates, m. p. 134—136° (Found: Hg, 34·5. Calc.: Hg, 34·7%).

Diethylthiolethanepalladous chloride, $[C_2H_4(SEt)_2,PdCl_2]$, was obtained by adding a solution of potassium palladochloride (1·63 g.) to the disulphide (0·75 g.) in alcohol. It formed minute orange-yellow crystals, m. p. 174°, and was crystallised from ethyl alcohol (Found: Pd, 32·6. $C_6H_{14}Cl_2Pd$ requires Pd, 32·6%).

Diethylthiolethanemercuric iodide, $[C_2H_4(SEt)_2,HgI_2]$, was formed from the components in acetone. It crystallised from acetone or alcohol in silvery plates, m. p. 103° (Found: Hg, 33·3. $C_6H_{14}I_2Hg$ requires Hg, 33·2%).

*Co-ordinated Derivatives of Diphenyl- and Di-*p*-tolyl-thiolethane.*—*Diphenylthiolethanepalladous chloride*, $[C_2H_4(SPh)_2,PdCl_2]$, from equivalent quantities of the sulphide in alcohol and potassium palladochloride in water, separated as a yellow microcrystalline precipitate, sparingly soluble in cold ethyl alcohol; m. p. 280° (Found: Pd, 25·3. $C_{14}H_{14}Cl_2S_2Pd$ requires Pd, 25·0%).

Diphenylthiolethane does not form a compound with mercuric iodide in acetone solution. Tschugaeff (*Ber.*, 1908, **41**, 2222) found a similar failure of this substance to unite with cupric chloride and nickel thiocyanate.

*Di-*p*-tolylthiolethanepalladous chloride*, $[C_2H_4(S{\cdot}C_6H_4Me)_2,PdCl_2]$, was isolated in the usual manner from aqueous alcohol as a crystalline yellow precipitate, m. p. 234° (decomp.) (Found: Pd, 20·8. $C_{16}H_{18}Cl_2S_2Pd$ requires Pd, 20·7%). The substance was too sparingly soluble in benzene or bromoform for cryoscopic measurements in these solvents. Large garnet-red crystals from acetone were examined goniometrically. The substance is monoclinic with axial ratios $a:b:c = 1{\cdot}695:1:0{\cdot}9804$ and axial angle $\beta = 96° 29'$. The following is a list of forms and mean angular values observed with four crystals:

	$a(100)$.	$b(010)$.	$l(210)$.	$o(111)$.	$p(\bar{1}11)$.
ϕ	0° 0′	90° 0′	39° 34′	*54° 38′	*115° 32′
ρ	90° 0′	90° 0′	90° 0′	*50° 15′	*47° 20′

The habit is tabular with *a* as a large hexagonal face (Fig. 1). The extinction on *a* is straight with the edge *ab*. In convergent polarised light the crystal is seen to be biaxial, an optic axis emerging almost perpendicular to *a*, the optic axial plane being parallel to *b*.

Sometimes, under conditions which could not be defined, crystals were deposited from acetone solutions by evaporation or cooling which consisted of a *compound* with acetone,

$$C_2H_4(S{\cdot}C_6H_4Me)_2,PdCl_2,Me_2CO$$

(Found: loss at 100°, 11·3; Pd, 21·1. $C_{19}H_{24}OCl_2S_2Pd$ requires loss at 100°, 11·4; Pd, 21·0%). The crystals became opaque on keeping. One crystal, examined crystallographically, proved to be anorthic, the angles observed being :

FIG. 1.

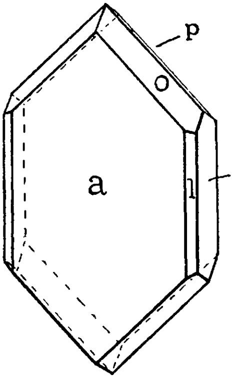
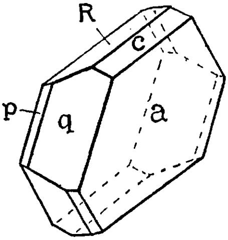


FIG. 2.



	a(100).	*m*(110).	*b*(010).	*r*(101).	*c*(001).
ϕ	0° 0′	53° 8′	99° 26′	42° 48′	147° 39′
ρ	90° 0′	90°	90°	20° 37′	25° 42′

from which the following angular elements are derived : *d* 46° 30′, *e* 75° 40′, *ab* 99° 26′, *f* 72° 33′, *g* 109° 45′. The habit is tabular with *a* large and the remaining faces as bevels equally developed.

By crystallisation from chloroform a *compound* with chloroform, $C_2H_4(S{\cdot}C_6H_4Me)_2,PdCl_2,CHCl_3$ was obtained in well-formed crystals which became opaque on keeping (Found : loss at 100°, 20·8; Pd, 18·6. $C_{17}H_{19}Cl_5S_2Pd$ requires loss at 100°, 20·9; Pd, 18·7%). The crystals are anorthic, the following forms and mean angular values having been found with two crystals :

	a(100).	*m*(110).	*b*(010).	*c*(001).
ϕ	0° 0′	51° 9′	97° 54′	37° 31′
ρ	90° 0′	90° 0′	90° 0′	21° 38′

These figures are insufficient for the calculation of the elements. The habit is tabular with *a* large and the remaining faces as bevels.

Di-p-*tolylthiolethanemercuric iodide*, $[C_2H_4(S{\cdot}C_6H_4Me)_2,HgI_2]$, was prepared from the components in acetone solution in crystals which had a pale yellow tinge, and on heating melted at 110° but partly resolidified, owing to decomposition, and finally melted at 215°, this being presumably the melting point of mercuric iodide as depressed by the disulphide. The substance was recrystallised from acetone or alcohol (Found : Hg, 27·8 ; I, 34·7. $C_{16}H_{18}I_2S_2Hg$ requires Hg, 27·6 ; I, 34·95%).

Co-ordinated Derivatives of Dibenzyldithiolethane.—The platinous and palladous chloride compounds were prepared by adding aqueous solutions of potassium platino- and pallado-chlorides to an alcoholic solution of the disulphide.

Dibenzyldithiolethaneplatinous chloride, $[C_2H_4(S{\cdot}CH_2Ph)_2,PtCl_2]$, was an almost colourless, microcrystalline powder. The precipitate first formed had a brownish colour which it gradually lost, probably owing to the presence of the bimolecular compound of structure $[Pt\{C_2H_4(S{\cdot}CH_2Ph)_2\}_2][PtCl_4]$ (compare Tschugaeff and Kobljamski, *Z. anorg. Chem.*, 1913, **83**, 14). The substance was not appreciably soluble in any solvent, and when heated it decomposed without melting (Found : Pt, 35·7. $C_{16}H_{18}Cl_2S_2Pt$ requires Pt, 36·1%).

Dibenzyldithiolethanepalladous chloride, $[C_2H_4(S{\cdot}CH_2Ph)_2,PdCl_2]$, formed an orange-yellow crystalline precipitate, m. p. 181° (decomp.) (Found : Pd, 23·9. $C_{16}H_{18}Cl_2S_2Pd$ requires Pd, 23·7%). The substance was readily soluble in bromoform and somewhat soluble in chloroform, toluene, acetone, and ethyl alcohol. The melting point and analyses showed, however, that the substance could not be recovered unchanged from these solvents either by cooling or by evaporation of the solution. Crystals from alcohol were once obtained containing combined solvent which was lost at 108—110°, but the observation could not be repeated.

Dibenzyldithiolethanemercuric iodide, $[C_2H_4(S{\cdot}CH_2Ph)_2,HgI_2]$, was formed from its components in warm acetone solution and separated from this solvent in large plates, m. p. 111—113° (decomp.) (Found : Hg, 27·2 ; I, 34·7. $C_{16}H_{18}I_2S_2Hg$ requires Hg, 27·6 ; I, 34·9%). The determination of iodine as silver iodide by the Carius method required special precautions owing to the solubility of the halide in mercuric nitrate solutions (compare Morse, *Z. physikal. Chem.*, 1902, **41**, 709). The error was negligible if the solution was considerably diluted and allowed to stand with an excess of cold silver nitrate solution.

A careful search in the mother-liquors of the preparation of this compound failed to reveal the presence of any second substance.

The crystals from acetone were examined goniometrically. They are monoclinic with axial ratios $a : b : c = 1{\cdot}1812 : 1 : 0{\cdot}8531$ and axial angle $\beta = 115° 8'$. The following is a list of forms observed and mean angular values from four crystals :

	$a(100)$.	$c(001)$.	$R(\bar{1}01)$.	$q(011)$.	$p(\bar{1}11)$.
ϕ	0° 0′	*64° 52′	107° 20′	65° 10′	*107° 12′
ρ	90° 0′	90°	90°	*52° 19′	*51° 26′

The habit is tabular with *a* large as in Fig. 2. The extinction on *a* is straight with the edge *ac*. In convergent polarised light the crystal is biaxial, an optic axis being visible through *a*, the axis and the acute bisectrix being equally inclined to the face. The optic axial plane is parallel with *b*.

Bisdibenzylthiolethanenickel thiocyanate,

$$[Ni\{C_2H_4(S{\cdot}CH_2Ph)_2\}_2(SCN)_2],$$

was precipitated as a sky-blue crystalline powder by shaking together a toluene solution of the disulphide (0·5 g.) and an aqueous solution containing nickel chloride (2·5 g.) and ammonium thiocyanate (1·2 g.). The compound became green after exposure to the atmosphere. It decomposed on heating to high temperatures without melting (Found : Ni, 8·2, 7·9. $C_{34}H_{36}N_2S_6Ni$ requires Ni, 8·1%). The substance could not be recrystallised from any solvent tested.

Preparation of Substituted Ethylenediamines from p-*Anisidine*.—*p*-Anisidine (4 mols.) was heated with ethylene dibromide (1 mol.) in a brine bath for 1½ hours. The mixture was made alkaline, and the excess of anisidine removed in steam. The residue in the flask solidified and was dried. Extraction with chloroform left behind some dimethoxydiphenylpiperazine, m. p. 232° (Found : N, 9·4. Calc. : N, 9·4%). The more soluble portions consisted of *ethylenedi*-p-*methoxyphenyldiamine*, $C_2H_4(NH{\cdot}C_6H_4{\cdot}OMe)_2$ (base A), which was obtained in colourless plates, m. p. 105°, by repeated crystallisation from ethyl alcohol or from carbon tetrachloride, chloroform, benzene, carbon disulphide, or acetone. Analyses of this base gave low figures for carbon until the combustion was carried out slowly with the substance mixed with fine copper oxide (Found : C, 70·6; H, 7·6; N, 10·5; OMe, 21·1; *M*, in camphor, 260. $C_{16}H_{20}O_2N_2$ requires C, 70·6; H, 7·4; N, 10·3; OMe, 22·7%; *M*, 272). The *dihydrochloride* formed silvery plates sparingly soluble in concentrated hydrochloric acid; m. p. 238° (Found: Cl, 20·3. $C_{16}H_{22}O_2N_2Cl_2$ requires Cl, 20·5%). The *di*-p-*toluenesulphonyl* derivative separated from benzene as a colourless microcrystalline powder, m. p. 188° (Found : N, 4·8. $C_{30}H_{32}O_6N_2S_2$ requires N, 4·8%). The *diacetyl* derivative formed minute needles from ethyl alcohol; m. p. 164° (Found : N, 7·9. $C_{20}H_{24}O_4N_2$ requires N, 7·9%).

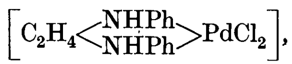
When base A was boiled with commercial methyl alcohol it was converted into *base B*, m. p. 134°. This effect was not obtained when specially purified methyl alcohol was used. The product was isolated as a crystalline powder much more soluble in benzene and less soluble in ethyl alcohol than base A (Found: C, 71·7; H, 7·3; N, 9·5, 9·6; OMe, 21·1; *M*, 264. $C_{17}H_{20}O_2N_2$ requires C, 71·9; H, 7·0; N, 9·8; OMe, 21·7%; *M*, 284). When the preparation of derivatives of this base was undertaken it yielded the hydrochloride, diacetyl, and di-*p*-toluenesulphonyl derivatives of base A. Base B, distilled with dilute hydrochloric acid, gave a distillate in which an aldehyde could be detected: a similar test with base A gave no indication of production of aldehyde.

The addition of aqueous formaldehyde to alcoholic solutions of base A yielded, nevertheless, not base B but a third *base*, C, which formed silvery plates, m. p. 226°, sparingly soluble in ethyl alcohol and less soluble in benzene than base B (Found: C, 71·8; H, 7·2; N, 9·85%; *M*, 254). The action of hydrochloric acid did not regenerate the pure base A, but a red substance was produced and the solution contained formaldehyde.

Co-ordination Compounds of Diarylethylenediamines.—The following complexes were examined: in no case was any evidence found of the presence of two substances.

Ethylenediphenyldiamineplatinous chloride, $\left[C_2H_4<\substack{NHPh\\NHPh}>PtCl_2\right]$, was deposited as a brown powder when the base and potassium platinochloride were allowed to stand together in aqueous-alcoholic solution. The substance was insoluble in water, ethyl or methyl alcohol and decomposed on heating without melting (Found: Pt, 40·3. $C_{14}H_{16}N_2Cl_2Pt$ requires Pt, 40·8%).

Ethylenediphenyldiamine palladous chloride,

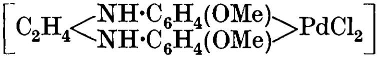


$$\left[C_2H_4<\substack{NHPh\\NHPh}>PdCl_2\right],$$

was obtained as a buff-yellow microcrystalline powder by the action of potassium palladochloride solution on the hydrochloride of the base in water, and was pure after being washed with dilute acetic acid and methyl alcohol (Found: Pd, 27·2. $C_{14}H_{16}N_2Cl_2Pd$ requires Pd, 27·3%). This and the following two complexes decomposed on heating without melting. They were practically insoluble in water, ethyl and amyl alcohols, acetic acid, acetone, chloroform, bromoform, *cyclo*hexanol, carbon disulphide, benzene, ligroin, and decalin. They dissolved in pyridine or aniline, but not unchanged. The above compound, for example, dissolved in pyridine, yielded a crystalline solid which was essentially dipyridinepalladous chloride (Found: Pd, 30·6. Calc.: Pd, 31·8%). The complexes also dissolved in *m*-cresol, but crystallisation from this liquid could not be effected.

Ethylenediphenyldimethyldiaminepalladous chloride,

$$\left[\mathrm{C_2H_4}{<}\genfrac{}{}{0pt}{}{\mathrm{NMePh}}{\mathrm{NMePh}}{>}\mathrm{PdCl_2}\right],$$

formed an insoluble buff powder (Found : Pd, 25·8. $C_{16}H_{20}N_2Cl_2Pd$ requires Pd, 25·6%); *ethylenedi*-p-*methoxyphenyldiaminepalladous chloride,*  $\left[\mathrm{C_2H_4}{<}\genfrac{}{}{0pt}{}{\mathrm{NH{\cdot}C_6H_4(OMe)}}{\mathrm{NH{\cdot}C_6H_4(OMe)}}{>}\mathrm{PdCl_2}\right]$, was a similar buff powder (Found : Pd, 23·6. $C_{16}H_{20}O_2N_2Cl_2Pd$ requires Pd, 23·7%).

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