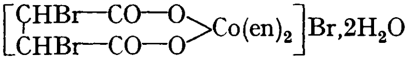
288. *Co-ordination Compounds of 2 : 2'-Diphenol.*

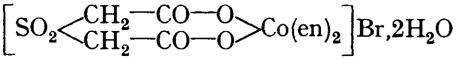
By O. L. Brady and E. D. Hughes.

Chelate rings containing more than six atoms are rare and are generally of Sidgwick's type A (" The Electronic Theory of Valency," p. 239), in which the rings are formed of normal, as distinct from co-ordinated, covalencies, generally by the replacement by a metal of two hydrogen atoms in a dibasic acid, such as, *e.g.*, the *cis*-succinatobisethylenediaminocobaltic salts (I) (Duff, J., 1921, **119**, 385) and the *cis*-sulphonyldiacetobisethylenediaminocobaltic salts (II) (Price and Brazier, J., 1915, **107**, 1367) containing seven- and eight-membered rings respectively.



$$\left[\begin{matrix}\mathrm{CHBr{-}CO{-}O}\\ \mathrm{CHBr{-}CO{-}O}\end{matrix}\!>\!\mathrm{Co(en)_2}\right]\mathrm{Br,2H_2O}$$

(I.)



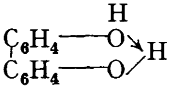
$$\left[\mathrm{SO_2}\!<\!\begin{matrix}\mathrm{CH_2{-}CO{-}O}\\ \mathrm{CH_2{-}CO{-}O}\end{matrix}\!>\!\mathrm{Co(en)_2}\right]\mathrm{Br,2H_2O}$$

(II.)

It has been suggested that the non-existence of rings of more than six atoms containing a true co-ordinate linkage is due to the strain involved in their formation. Although, in rings consisting solely of carbon atoms, ring formation becomes increasingly difficult as the number of members increases from seven to ten, yet once formed the compounds are remarkably stable owing to their departure from a plane configuration (Ruzicka, Stoll, and Schinz, *Helv. Chim. Acta*, 1926, **2**, 249; Ruzicka, Brugger, Pfeiffer, Schinz, and Stoll, *ibid.*, p. 499). It was thought, therefore, that if a compound could be chosen of such a nature that chelation would, of necessity, involve the formation of a non-planar ring, it might be possible to obtain seven-membered chelate rings containing co-ordinate linkages; this desideratum seemed to be supplied by 2 : 2'-diphenol.

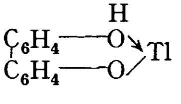
The stereochemical study of diphenyl compounds by Turner and others has indicated that two groups in the 2 : 2'-positions cannot pass one another; therefore, in 2 : 2'-diphenol, if the two hydroxyl groups are to take part in ring formation, they and the four carbon atoms of the diphenyl nuclei cannot become co-planar, and any ring formed on the two oxygen atoms will of necessity be non-planar.

Now the properties of 2 : 2'-diphenol suggest that it is itself co-ordinated (III). Its melting point (98°) is below that of its dimethyl ether (155°), whereas the reverse is the case in 3 : 3'-diphenol (123° and 36°) and 4 : 4'-diphenol (274° and 172°). 2 : 2'-Diphenol is remarkably soluble in all organic solvents, even light petroleum dissolving nearly 1% (Diels and Bibergeil, *Ber.*, 1902, **35**, 304). It is also more volatile (b. p. 194°/22 mm.)



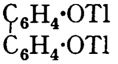
$$\begin{matrix} C_6H_4—\overset{H}{O}\searrow \\ C_6H_4—O\nearrow \end{matrix}H$$

(III.)



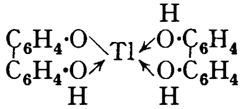
$$\begin{matrix} C_6H_4—\overset{H}{O}\searrow \\ C_6H_4—O\nearrow \end{matrix}Tl$$

(IV.)



$$\begin{matrix} C_6H_4\cdot OTl \\ C_6H_4\cdot OTl \end{matrix}$$

(V.)



$$\begin{matrix} C_6H_4\cdot O\searrow & & \swarrow \overset{H}{O}\cdot C_6H_4 \\ & Tl & \\ C_6H_4\cdot \underset{H}{O}\nearrow & & \nwarrow \underset{H}{O}\cdot C_6H_4 \end{matrix}$$

(VI.)

than the 2 : 4'- (b. p. 206—210°/11 mm.) and the 3 : 3'- (b. p. 247°/18 mm.) isomeride (cf. Sidgwick and Callow, J., 1924, **125**, 527).

With thallium, diphenol formed a monothallium *compound*, m. p. 227—229°, for which we suggest the co-ordinated structure (IV); it was very sparingly soluble in cold but more so in hot water. The solution in cold water contained some thallous ions, since it gave a precipitate of thallous iodide with potassium iodide; the solution in boiling water gave with sodium or potassium hydroxide a precipitate of the less soluble *dithallium diphenol* (V), but was not affected by ammonia, although diphenol is readily soluble in this reagent. The solubility of (IV) in organic solvents could not be determined, for boiling with, *e.g.*, chloroform or benzene caused formation of diphenol together with (V); it was, however, readily soluble in chloroform containing excess of diphenol, in fused diphenol, and in fused mixtures of diphenol with naphthalene or camphor. It seems probable that in these circumstances further co-ordination occurred, giving compounds such as (VI).

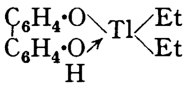
It should be possible to decide whether one or more extra diphenol molecules had been taken up, by observations on the change in boiling point of a solution of diphenol in chloroform or of freezing point of a mixture of diphenol and naphthalene or camphor on addition of monothallium diphenol, but unfortunately, experimental difficulties prevented any conclusive results being obtained by these methods.

With diethylthallium hydroxide, diphenol gave a *diethylthallium diphenol* (VII), m. p. 191°, sparingly soluble in water, readily in absolute alcohol, slightly in chloroform and benzene, but somewhat more so in xylene. It was readily soluble in chloroform containing excess of diphenol and in molten diphenol, suggesting further co-ordination. Its molecular weight in camphor was high, indicating association (compare Wiltshire and Menzies, J., 1932, 2734). The cold aqueous solution contained diethylthallium ions and gave a characteristic white precipitate with potassium iodide. Menzies, Sidgwick, Cutcliffe, and Fox (J., 1928, 1288) have found that other chelate compounds of diethylthallium are dissociated in water to give diethylthallium ions.

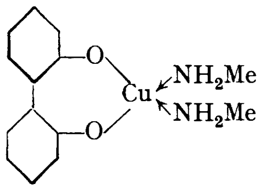
All attempts to isolate compounds containing more than one diphenol molecule to one thallium atom have been unsuccessful. The evidence for the chelate linkage in the thallium compounds actually prepared is not strong, but their general properties, particularly those of the diethylthallium compounds, and their solubility in solvents containing diphenol suggest that it exists but is easily broken. With copper, however, more conclusive evidence was obtained.

Diphenol with copper and methylamine gave a crystalline *compound* containing one molecule of diphenol and two of methylamine to each atom of copper (VIII). This compound was sparingly soluble in water but could be recrystallised from hot water containing a little methylamine; it was practically insoluble in organic solvents, but dissolved in chloroform containing diphenol and in molten diphenol, indicating that further co-ordination with diphenol occurred. With amines of higher molecular weight, *e.g.*, propylamine

(VII.)



$$\begin{matrix} C_6H_4\cdot O\searrow \\ C_6H_4\cdot \underset{H}{O}\nearrow \end{matrix}Tl\begin{matrix}\nearrow Et \\ \searrow Et\end{matrix}$$

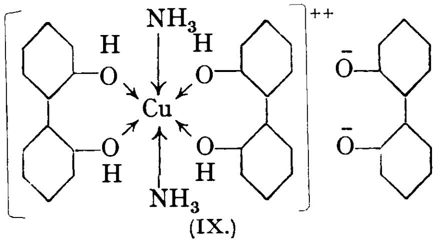


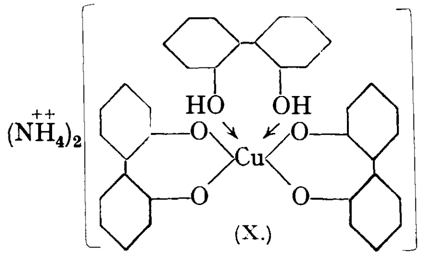
(VIII.)

and piperidine, *compounds* containing one molecule of base to one of copper diphenol were obtained.

Diphenol with copper and ammonia gave a crystalline *compound* containing three molecules of diphenol and two of ammonia to each atom of copper. The ammonia was firmly held and was not lost on keeping in a vacuum over concentrated sulphuric acid. The copper is present in the cupric state. The compound was insoluble in water but dissolved readily in chloroform to an olive-green solution which, however, decomposed, slowly at room temperature and more rapidly on boiling. This decomposition is facilitated by the presence of acetone, and a solution in acetone decomposes even more rapidly. The precipitate formed was of variable composition, but from the ratios of copper to carbon, nitrogen, and oxygen in various preparations it appeared to be a mixture of $(C_6H_4)_2O_2Cu$, $(C_6H_4)_2O_2Cu(NH_3)_2$, and $(C_6H_4)_2O_2Cu(H_2O)_2$.

There are numerous ways in which the trisdiphenol copper diammine may be represented, but (IX) and (X) seem the most probable.


(IX.)


(X.)

Although trisdiphenol copper diammine is the only compound which could be isolated in a state of purity, we obtained evidence that compounds existed containing two molecules of diphenol to one atom of copper, together with ammonia or water, such as $[(C_6H_4)_2O_2H]_2,Cu(NH_3)_2,2H_2O$ and $[(C_6H_4)_2O_2H]_2,Cu(NH_3)_2,H_2O$.

EXPERIMENTAL.

Monothallium Diphenol.—Thallous acetate (10 g.) was dissolved in water (5 c.c.) and mixed with alcohol (25 c.c.) and ammonia (3 c.c.; *d* 0·880); diphenol (9 g.) in warm alcohol (25 c.c.) was then added, and a clear solution was obtained from which needle-shaped crystals began to separate almost at once. After 1 hour the solid was collected, washed with alcohol, and dried in a vacuum over sodium hydroxide; *monothallium diphenol* was obtained in colourless needles, m. p. 227° (Found : C, 36·9; H, 2·3; Tl, 52·0. $C_{12}H_9O_2Tl$ requires C, 37·0; H, 2·3; Tl, 52·4%), and recrystallised unchanged (Found : C, 37·1; H, 2·5%) from hot water, in which it was sparingly soluble. When it was boiled with chloroform, partial solution apparently took place followed by decomposition, for the solvent became cloudy, and on filtering and evaporating the solvent, diphenol was obtained. If monothallium diphenol (1 g.) was suspended in chloroform (20 c.c.), diphenol (4 g.) added, and the mixture warmed, complete solution occurred; these weights correspond approximately to 9 mol. of diphenol to 1 mol. of the thallium derivative; when alcohol (20 c.c.) containing diphenol (4 g.) was added to this solution, shining crystals slowly separated, which underwent no apparent change when washed with ether and consisted of monothallium diphenol (Found : C, 37·2; H, 2·4%).

Dithallium Diphenol.—When a solution of the above compound in boiling water was treated with aqueous sodium or potassium hydroxide, shining plates of dithallium diphenol separated. This compound was also prepared by dissolving diphenol (6 g.) in 2*N*-sodium hydroxide (50 c.c.) and adding a solution of thallous acetate (15 g.); a yellow precipitate was formed, which after a few moments became very thick and turned snow-white. After being collected and washed, a small quantity was crystallised from hot water, in which it was very sparingly soluble, *dithallium diphenol* being obtained in shining plates (Found : C, 24·7; H, 1·4. $C_{12}H_8O_2Tl_2$ requires C, 24·5; H, 1·4%).

Mono(diethylthallium) Diphenol.—Diphenol (0·62 g.) in benzene (5 c.c.) was added to a 0·335*N*-solution of diethylthallium hydroxide in benzene (10 c.c.), and a white crystalline precipitate formed after a few seconds. This was washed with benzene and dried in a vacuum. Part was crystallised from absolute alcohol, *mono(diethylthallium) diphenol* being obtained in shining plates, m. p. 191° (decomp.) (Found : C, 43·1; H, 4·2; *M*, in camphor, 569. $C_{16}H_{19}O_2Tl$

requires C, 43·0; H, 4·3%; *M*, 447). Another portion was crystallised from boiling benzene, in which it was sparingly soluble (Found : C, 42·8; H, 4·1%).

Di(methylamino)cupric Diphenol.—An 8% solution of copper acetate monohydrate (25 c.c.) was mixed with a 33% solution of methylamine (15 c.c.), and diphenol (3 g.) in alcohol (10 c.c.) added. The colour changed from blue to deep green, and crystals were slowly deposited. These were collected after some hours, washed with water containing methylamine, crystallised from hot water containing methylamine, and dried over sodium hydroxide in a desiccator containing the base. *Di(methylamino)cupric diphenol* was thus obtained in stout, dark olive-green needles (Found : C, 54·1; H, 5·9; N, 9·1; Cu, 20·1. $C_{14}H_{18}O_2N_2Cu$ requires C, 54·2; H, 5·8; N, 9·0; Cu, 20·5%); it is practically insoluble in organic solvents but dissolves in chloroform containing excess of diphenol.

Propylaminocupric diphenol was immediately precipitated when diphenol in alcohol was added to copper acetate solution containing excess of propylamine; after being washed with water containing the amine and dried in a desiccator also containing the amine, it was obtained as an olive-green, microcrystalline powder, which could not be crystallised (Found : C, 58·9; H, 5·7; N, 4·6; Cu, 19·1. $C_{15}H_{17}O_2NCu$ requires C, 58·7; H, 5·5; N, 4·5; Cu, 20·7%).

Piperidinocupric Diphenol.—Diphenol (2 g.) in alcohol (10 c.c.) was mixed with piperidine (2 c.c.) and added to 25 c.c. of 8% hydrated copper acetate solution, whereupon an olive-brown precipitate separated, which was washed with water by decantation, collected, and dried over sodium hydroxide; *piperidinocupric diphenol* forms an olive-brown powder (Found : C, 61·3; H, 5·9; N, 4·2; Cu, 18·4. $C_{17}H_{19}O_2NCu$ requires C, 61·3; H, 5·7; N, 4·2; Cu, 19·1%).

Diamminocupric Trisdiphenol.—An 8% solution of hydrated copper acetate (25 c.c.), treated with ammonia until the precipitate first formed redissolved, was added slowly to diphenol (5 g.) in alcohol (15 c.c.). The solution was filtered, kept, and again filtered, this process being repeated until the deposited solid appeared crystalline and homogeneous. The final crystals were washed with water by decantation, collected, again washed, and dried in a vacuum over sodium hydroxide, being obtained in stout greenish-black prisms (Found in diff. prepns.: C, 66·2, 66·1; H, 5·4, 5·3; N, 4·5, 4·4; Cu, 9·7, 9·8. $C_{36}H_{34}O_6N_2Cu$ requires C, 66·2; H, 5·2; N, 4·3; Cu, 9·7%), soluble in chloroform to a deep olive-green solution, which decomposed on keeping or boiling. Decomposition was more rapid on addition of an equal volume of acetone, whereupon a solid separated as a brown powder (A) (Found : C, 49·7; H, 4·4; N, 3·8; Cu, 21·1%). When diamminocupric trisdiphenol was percolated with acetone, the solution rapidly deposited olive-brown needles (B) (Found : C, 52·5; H, 4·2; N, 3·3; Cu, 23·2%); another preparation gave an olive-brown crystalline powder (C) (Found : C, 54·2; H, 4·2; N, 1·8; Cu, 22·7%). The ratios Cu : C : N : O in these three preparations are (A) 1 : 12·5 : 0·82 : 4; (B) 1 : 12·0 : 0·65 : 2·9; (C) 1 : 12·6 : 0·4 : 3·0; indicating that the product is probably a mixture of compounds containing one molecule of diphenol to one atom of copper with either water, ammonia, or neither. For example, (B) agrees closely with $[(C_6H_4)_2O_2]Cu + [(C_6H_4)_2O_2]Cu(NH_3)_2 + [(C_6H_4)_2O_2]Cu,2H_2O$ (Calc.: C, 53·1; H, 4·1; N, 3·2; Cu, 23·5%). The solid diammine does not lose ammonia when kept for a week in a vacuum over concentrated sulphuric acid, the nitrogen content of a specimen so treated remaining at 4·4%.

There is evidence that copper forms compounds with two molecules of diphenol and varying amounts of ammonia and water, the latter replacing the third diphenol molecule in the diamminocupric complex; *e.g.*, excess of ammonia was added to 8% copper acetate solution (25 c.c.), the mixture added to diphenol (3 g.) in alcohol (10 c.c.), and more ammonia added to dissolve the precipitate and the solution kept; the first sludge was discarded, and the solid which subsequently separated was collected, washed with water, and dried over sodium hydroxide, a greenish-yellow powder being obtained of approximately the composition $[(C_6H_4)_2O_2H]_2Cu(NH_3)_2,2H_2O$ (Found : C, 58·0; H, 5·5; N, 5·2; Cu, 13·4. Calc.: C, 57·2; H, 5·5; N, 5·5; Cu, 12·6%); dried over concentrated sulphuric acid for several days, it turned chocolate-brown and had approximately the composition $[(C_6H_4)_2O_2H]_2Cu(NH_3)_2,H_2O$ (Found : C, 59·8; H, 5·4; N, 4·0; Cu, 14·0. Calc.: C, 59·9; H, 5·4; N, 5·7; Cu, 13·1%). Two other preparations gave products containing C, 59·5; H, 4·8; N, 3·8; Cu, 14·7; and C, 62·1; H, 4·8; N, 3·5; Cu, 14·6; *i.e.*, Cu : C = 1 : 21·4 and 1 : 22·5 respectively, indicating two molecules of diphenol to one atom of copper.

We thank Dr. Menzies for the gift of a solution of diethylthallium hydroxide.

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