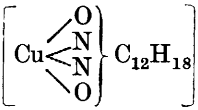
CXXVII.—*Researches on Residual Affinity and Co-ordination. Part XXVI. A Quadridentate Group in Combination with Bivalent Metals.*

By GILBERT T. MORGAN and J. D. MAIN SMITH.

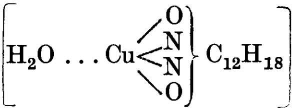
IN the preceding communication of this series we showed that ethylenediaminobisacetylacetone, first prepared by Combes, furnishes a bivalent quadridentate radical which is capable of behaving as a fourfold associating group in co-ordination compounds of the metals. This fact was demonstrated by a study of the co-ordination compounds of bivalent and tervalent cobalt and the investigation has now been extended to the corresponding derivatives of bivalent copper, nickel, and palladium.

Cupric ethylenediaminobisacetylacetone, prepared originally by Combes (*Compt. rend.*, 1889, **108**, 1252), is a well-defined, highly crystalline, dark violet derivative behaving as a non-ionised complex containing one bivalent copper atom in combination with one molecular proportion of the bivalent quadridentate radical. Its constitution may be expressed by formula (I), in which the quadridentate radical is grouped round the metallic atom either tetrahedrally or at four points in one plane. It is, however, not possible

(I.)



$$\left[\mathrm{Cu}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{N}\\ \mathrm{N}\\ \mathrm{O}\end{matrix}\right\}\mathrm{C_{12}H_{18}}\right]$$



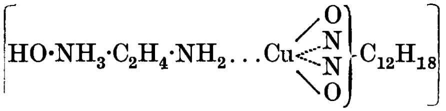
(II.)

$$\left[\mathrm{H_2O}\ldots\mathrm{Cu}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{N}\\ \mathrm{N}\\ \mathrm{O}\end{matrix}\right\}\mathrm{C_{12}H_{18}}\right]$$

to decide between these possibilities, because in either case the co-ordination complex is unsaturated and readily takes up another associating unit as when the anhydrous violet copper compound absorbs water to pass into its dark green monohydrate (II).

Other addenda can be added in a similar manner to the unsaturated complex, for when Combes's violet compound is dissolved in ethylenediamine hydrate, combination occurs with one molecular proportion of the solvent, giving rise to an analogue (III) of the foregoing aquo-derivative (II).

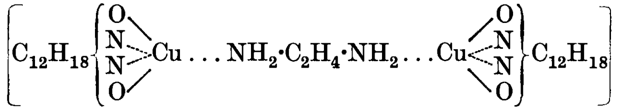
(III.)



$$\left[HO\cdot NH_3\cdot C_2H_4\cdot NH_2\ldots Cu\begin{matrix}O\\N\\N\\O\end{matrix}C_{12}H_{18}\right]$$

This ethylenediaminehydrato-compound, when exposed in a desiccator over solid caustic soda or calcium chloride, loses all its water and half of its ethylenediamine, giving rise to the anhydrous ethylenediamine derivative (IV), in which two molecular proportions of Combes's compound are associated with one molecule of ethylenediamine.

(IV.)



$$\left[C_{12}H_{18}\begin{matrix}O\\N\\N\\O\end{matrix}Cu\ldots NH_2\cdot C_2H_4\cdot NH_2\ldots Cu\begin{matrix}O\\N\\N\\O\end{matrix}C_{12}H_{18}\right]$$

It is evident from the existence of these three compounds (II, III, and IV) that one characteristic co-ordination number of copper is 5. This conclusion is borne out by the preparation of a stable light green mono-quinoline derivative of copper acetylacetone, $[Cu(C_5H_7O_2)_2,C_9H_7N]$ (V). Similar compounds are obtainable from ammonia and pyridine, but the derivatives of these more volatile bases are unstable, losing their addenda rapidly at the ordinary temperature.

Co-ordination Numbers of Bivalent Copper.

The literature of copper compounds exhibiting residual affinity is very extensive and furnishes many diverse examples of addenda in these copper derivatives varying in number from 1 to 6, with indications of even higher values. Among the lower values, 2 and 3 stand out prominently and are represented by compounds sufficiently stable and well-defined to warrant the belief that there are copper complexes corresponding with co-ordination numbers 2 and 3. There are also numerous and varied examples among copper compounds of the higher even co-ordination numbers 4 and 6.

The results obtained in this investigation with regard to the formation of complexes with co-ordination number 5 warrant a reconsideration of the constitutions often accepted for such substances as the following: $CuCl_2,4NH_3,H_2O$; $CuBr_2,5NH_3$; $CuSO_4,5H_2O$; $CuSO_4,4NH_3,H_2O$; $CuSO_4,5NH_3$ and $CuSO_4,5NH_2{\cdot}OH$.

In formulating these copper salts as co-ordination compounds, at least two alternative views present themselves. The associating units may be grouped exclusively round the metallic atom, giving rise to complex cations of the general type $[Cu5X]^{\cdot\cdot}$ or contrariwise one or more molecules of the various addenda may be wholly or partly associated with the anions, which thus become hydrated or ammoniated. If the latter condition could be demonstrated in any of these instances, then the co-ordination number for copper would, in such cases, become less than 5.

There are, however, other less equivocal examples of five associating units round copper in which the metallic atom is no longer in a cation but in an anion such as in pentachlorocupric acid, $H_3[CuCl_5]$ (G. Naumann, *Monatsh.*, 1894, **15**, 489) and in the double nitrites $K_3[Cu(NO_2)_5]$ and $Rb_3[Cu(NO_2)_5]$ (Kurtenacker, *Z. anorg. Chem.*, 1913, **82**, 204) and $Tl_3[Cu(NO_2)_5]$ (Cuttica and Paciello, *Gazzetta*, 1922, **52**, i, 141).

Further evidence on this type of copper co-ordination is now under investigation, particularly in regard to complexes derived from cupric iodide. These results, which indicate a descent from 6 to 5 in the number of associating units round bivalent copper, will shortly be submitted.

Electronic Structure of the Bivalent Copper Atom.

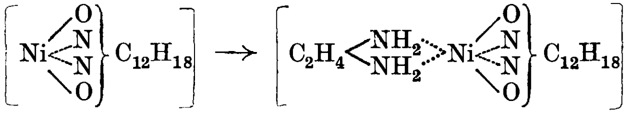
The foregoing evidence, which points to 5 as a characteristic co-ordination number for bivalent copper, has been shown by one of us (J. D. M. S.) to be a consequence of the electronic distribution in atoms first propounded two years ago (Main Smith, *J. Soc. Chem. Ind.*, 1924, **43**, 323). According to this general scheme, which was then applied to all elements, the probable structure of the bivalent cupric ion was shown to be 2, 224, 22445, 000, using ciphers to indicate the vacant sub-groups to be filled by electrons derived from associating units.

Then if, in combination with a quadridentate group, each associating atom of the group contributes two electrons to the three empty electronic sub-groups of the cupric ion, the electronic structure of the co-ordinated atom will be 2, 224, 22445, 224. This arrangement differs from the electronic structure 2, 224, 22446, 224 for the atom of krypton, the inert gas next higher than copper in atomic number, only in a shortage of one electron in the 9th sub-group, and this unsaturated arrangement may be accepted as the electronic structure for the co-ordinated cupric atom with co-ordination number 4. If this incomplete 9th sub-group could be completed by the addition of a single electron (Main Smith, *J. Soc. Chem. Ind.*, 1925, **44**, 944) from the fifth associating unit of a copper co-ordination compound, then the cupric atom of co-ordination number 5 would possess the electronic structure 2, 224, 22446, 224, identical with that of the inert gas krypton.

Co-ordination Numbers of Bivalent Nickel and Palladium.

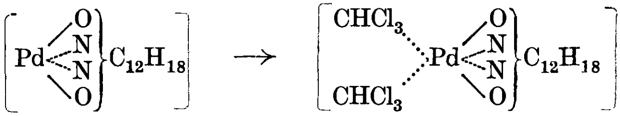
The bivalent quadridentate group from ethylenediaminobisacetylacetone also furnishes well-defined, stable derivatives of bivalent nickel and palladium.

Nickel ethylenediaminobisacetylacetone (VI), which melts and even boils without decomposition providing that air is excluded, resembles Combes's copper derivative and is an unsaturated substance forming additive compounds with two molecular proportions of ammonia or with one of ethylenediamine. The latter combination is the more stable of the two, its constitution being indicated by formula (VII).

(VI.)  (VII.)

$$\left[\mathrm{Ni}\left<\begin{matrix}\diagup\mathrm{O}\\ \mathrm{N}\\ \mathrm{N}\\ \diagdown\mathrm{O}\end{matrix}\right\}\mathrm{C_{12}H_{18}}\right] \longrightarrow \left[\mathrm{C_2H_4}\left<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right>\mathrm{Ni}\left<\begin{matrix}\diagup\mathrm{O}\\ \mathrm{N}\\ \mathrm{N}\\ \diagdown\mathrm{O}\end{matrix}\right\}\mathrm{C_{12}H_{18}}\right]$$

Palladous ethylenediaminobisacetylacetone (VIII) is a fairly stable, non-ionised complex insoluble in water but dissolving in the ordinary organic solvents. From these media it separates with addenda of crystallisation. The dichloroformo-derivative, for example (IX), contains two molecular proportions of solvent.

(VIII.)  (IX.)

$$\left[\mathrm{Pd}\left<\begin{matrix}\diagup\mathrm{O}\\ \mathrm{N}\\ \mathrm{N}\\ \diagdown\mathrm{O}\end{matrix}\right\}\mathrm{C_{12}H_{18}}\right] \longrightarrow \left[\begin{matrix}\mathrm{CHCl_3}\\ \\ \mathrm{CHCl_3}\end{matrix}\!\!>\mathrm{Pd}\left<\begin{matrix}\diagup\mathrm{O}\\ \mathrm{N}\\ \mathrm{N}\\ \diagdown\mathrm{O}\end{matrix}\right\}\mathrm{C_{12}H_{18}}\right]$$

The foregoing results indicate that nickel and palladium have a co-ordination number 4 in their combinations with the bivalent quadridentate group, but these compounds are unsaturated and take up addenda, suggesting that bivalent nickel and palladium have also the higher co-ordination number 6, displayed, however, in less stable derivatives.

Electronic Structures of the Bivalent Nickel and Palladium Atoms.

Nickel and bivalent palladium have yielded simple derivatives with ethylenediaminobisacetylacetone, in which the co-ordination number 4 is apparent as in Combes's simple cupric compound, and they further resemble the latter also in being co-ordinatively unsaturated, yielding addition compounds with various addenda, such as ammonia, ethylenediamine, and chloroform.

According to the general scheme of atomic structure above mentioned, the bivalent nickel atom has the probable electronic structure 2, 224, 22444, 000. If the quadridentate group, as with copper, adds four pairs of electrons to the three empty sub-groups, the electronic structure for the co-ordinated nickel atom will be 2, 224, 22444, 224. This differs from the electronic structure for the atom of the inert gas, krypton, only in a shortage of two electrons in the 9th sub-group, and this unsaturated arrangement may be accepted as the electronic structure for the co-ordinated nickel atom with co-ordination number 4.

The electronic structure of the bivalent palladium atom in the above scheme is 2, 224, 22446, 22444, 000, resembling that of the nickel atom with the interpolation of five sub-groups 22446. If the quadridentate group as before adds four pairs of electrons to the three empty sub-groups, the electronic structure for the palladous atom becomes 2, 224, 22446, 22444, 224. This differs from the structure of the inert gas, xenon, 2, 224, 22446, 22446, 224, only in a shortage of two electrons in the 14th sub-group, and this unsaturated arrangement may be accepted as the electronic structure for the co-ordinated palladous atom with co-ordination number 4.

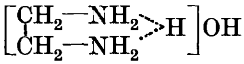
Both nickel and palladous atoms in combination with the quadridentate group, however, yield addition compounds with two molecules or equivalents of ammonia, chloroform, and anhydrous ethylenediamine, and thus differ from the cupric compounds, which yield addition compounds with only one molecule or equivalent of the addenda. As in the case of copper, the addenda for nickel and bivalent palladium atoms may be regarded as due to the intervention of only one electron per bond, for the addenda are even more feebly attached to the metallic atom than in the case of copper. This conclusion is supported by the very numerous cases of organic and inorganic stable nickel compounds having the co-ordination number 4, which yield much less stable addition compounds having the co-ordination number 6. Typical examples are found in nickel acetylacetone, $Ni\{(OCMe)_2CH\}_2$, and nickel tetrammines, $Ni(NH_3)_4X_2$, which yield much less stable addition compounds with two molecules or equivalents of water, ammonia or ethylenediamine. If, as suggested, the addenda are held by bonds of only one electron as in the case of copper, the addenda add only two electrons to the 9th sub-group of the nickel structure and two electrons to the 14th sub-group of the palladous structure, thus yielding atomic structures identical in electronic arrangement with those of the inert gases, krypton and xenon, respectively.

These considerations give powerful mutual support to the view that the characteristic co-ordination number is 5 for the cupric atom, and 6 for the nickel and palladous atoms, and to the above-mentioned scheme of distribution of electrons in atoms and in particular to the electronic structures assigned to the atoms of copper, nickel, and palladium.

Constitution of Ethylenediamine Hydrate.

It may be inferred from the knowledge that the co-ordination number of the cupric atom is 5 in addition compounds of cupric complexes with a quadridentate group, that the ethylenediamine hydrate addition compound herein described has the constitution $ecCuNH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_3{\cdot}OH$, the ethylenediamine hydrate molecule not being a chelate group and being attached to the cupric atom by only one nitrogen atom, and the molecule of water being in consequence necessarily combined with the other nitrogen atom. This view is supported by the fact that on dehydration a compound of chelate ethylenediamine and the cupric atom with the co-ordination number 6 is not obtained. The product contains per cupric atom only half a molecule of ethylenediamine, which is thus still not a chelate group but has the two nitrogen atoms combined with separate cupric atoms having the co-ordination number 5. This product is obtained only by the loss of water and ethylenediamine hydrate simultaneously from two molecules of the original compound, thus indicating that the water molecule of the original compound is not in combination with the cupric atom and is firmly attached to only one nitrogen atom.

Ethylenediamine hydrate is an exceedingly stable substance and is a base nearly as strong as the alkalis, indicating that it has the constitution of an ammonium hydroxide, $(C_2H_4N_2H_5)OH$. As ethylenediamine does not give rise to basic salts containing only one molecule of acid per molecule of base, it follows that the two basic ammino-groups are completely equivalent, and that separation of the water molecule can only be effected by acids on condition that both ammino-groups react simultaneously. The two ammino-groups consequently must equally share the single hydrogen atom ionised from the hydroxyl group of the hydrate, thus leading to the constitution $[C_2H_4(NH_2)_2H]OH$. The graphic formula for ethylenediamine hydrate should thus be written:



$$\left[\begin{array}{l}CH_2{-}NH_2\\ |\\ CH_2{-}NH_2\end{array}\!\!>H\right]OH$$

being a five-membered cyclic structure containing a hydrogen atom with co-ordination number 2.

This formulation is in complete harmony with the known properties of ethylenediamine hydrate and other polymethylenediamine hydrates, and with the foregoing considerations relating to the ethylenediamine addition compounds of the cupric atom.

EXPERIMENTAL.

$C_2H_4[N:C(CH_3)\cdot CH:C(CH_3)\cdot O-]_2$ = ec (dibasic acid radical of ethylenediaminobisacetylacetone).*

1. *Copper Series.*

Aquo-cupric Ethylenediaminobisacetylacetone, H_2O Cuec.—On adding a solution of ethylenediaminobisacetylacetone to an aqueous ammoniacal solution of any cupric salt, glistening, bright violet scales of Combes's anhydrous cupric ethylenediaminobisacetylacetone, Cu ec, are immediately and quantitatively precipitated, but when left in contact with the mother-liquor or on exposure of the damp salt to moist air, the violet scales are wholly transformed into transparent scales varying from sage to dark green in colour. This green salt is the monohydrate of Combes's salt and is the sole product formed when the purple solution of Combes's salt in acetone is poured into dilute aqueous ammonia solution. When the pale blue cupric salt of acetylacetone undergoes prolonged treatment with aqueous ethylenediamine, a simple ethylenediammino-addition compound is not formed, although the copper salt dissolves to an indigo-blue solution. From this solution the green hydrate of Combes's salt alone separates, the ethylenediamine undergoing organic condensation with two molecules of acetylacetone, the aminated dienolic diketone being formed in combination with the cupric atom by elimination of water (Found: N, 9·2; Cu, 21·0; loss at 100°, 6·0. $C_{12}H_{20}O_3N_2Cu$ requires N, 9·2; Cu, 21·0; H_2O, 5·9%).

Aquo-cupric ethylenediaminobisacetylacetone, forming large, black tablets, dark green by transmitted light, is insoluble in water, dissolves in nearly all organic solvents to form purple solutions of the anhydrous salt, and becomes anhydrous at 100°, but is unaffected by dry or moist air at the ordinary temperature. It melts at the temperature of the anhydrous salt, 137°, to a purple liquid, and, out of contact with air, boils at a high temperature without decomposition. The vapour in contact with air deposits a copper mirror on heated glass surfaces.

Cupric Ethylenediaminobisacetylacetone Ethylenediamine Hydrate, $ecCuNH_2\cdot CH_2\cdot CH_2\cdot NH_3\cdot OH$.—A hot solution of Combes's anhydrous cupric ethylenediaminobisacetylacetone in ethylenediamine hydrate, on cooling, deposits large, grass-green plates of a new salt in which

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* For certain details of preliminary work on the metallic derivatives of this quadridentate group we are indebted to Dr. H. D. K. Drew.—G. T. M.

one molecule of the cupric salt is combined with one molecule of the ethylenediamine hydrate (Found: Cu, 17·6, 17·4. $C_{14}H_{28}O_3N_4Cu$ requires Cu, 17·5%).

Cupric ethylenediaminobisacetylacetone ethylenediamine hydrate crystallises from ethylenediamine hydrate in large, grass-green or ivy-green plates, which are slowly decomposed on exposure to air, emitting white fumes of ethylenediamine hydrate and yielding Combes's violet salt. It dissolves to a purple solution in hot benzene, but is reprecipitated unchanged on addition of a mixture of ethylenediamine hydrate and light petroleum, in which it is insoluble. It loses all its water and half of its ethylenediamine on exposure over solid sodium hydroxide, and is converted into a new salt, sage green in colour.

Ethylenediammino-dicupric Bisethylenediaminobisacetylacetone, $C_2H_4(NH_2Cu\,ec)_2$.—On exposure of the foregoing bright green addition compound of Combes's violet salt and ethylenediamine hydrate in a confined space over solid caustic soda or fused calcium chloride, fumes of ethylenediamine hydrate are continuously emitted and a green salt is produced in which two molecules of Combes's salt are combined with one molecule of anhydrous ethylenediamine (Found: N, 13·0; Cu, 19·7. $C_{26}H_{44}O_4N_6Cu_2$ requires N, 13·3; Cu, 20·2%).

Ethylenediammino-dicupric bisethylenediaminobisacetylacetone forms glistening, sage-green scales which are stable in a confined space but are slowly decomposed on exposure to air with the formation of Combes's violet salt; it is insoluble in water and in 2*N*-caustic soda solution, but is slowly decomposed to form Combes's violet salt, and is thus distinguished from the foregoing hydrated salt, which is not decomposed by 2*N*-caustic soda solution and is only very slowly decomposed by water.

Quinolino-cupric Acetylacetone (V).—Pale blue cupric acetylacetone was dissolved in boiling quinoline, forming a dark green solution, from which, on cooling, large, sage-green plates separated. These were removed and dried in air (Found: Cu, 15·9. $C_{19}H_{21}O_4NCu$ requires Cu, 16·3%). This quinoline addition compound is stable in dry air, but is slowly decomposed by moist air and by water, or by solution in organic solvents, quinoline being lost and the simple cupric salt regenerated.

Cupric acetylacetone forms similar sage-green addition compounds with ammonia and with pyridine on addition of an alcoholic solution of the salt to a concentrated aqueous solution of the base, but these more volatile bases are rapidly lost on removal from the precipitating medium and consequently these addition compounds cannot be dried for analysis.

2. *Nickel Series.*

Nickel Ethylenediaminobisacetylacetone, Ni ec.—Hexa-aquo-nickel chloride (2·4 g. = 1 mol.) was dissolved in water (20 c.c.) and mixed with ethylenediaminobisacetylacetone (2·2 g. = 1 mol.) in alcoholic solution (29 c.c.), forming a dark reddish-brown liquid, to which was added 5*N*-sodium hydroxide solution (4 c.c. = 2 mols.). An olive-green precipitate separated, which dissolved to a reddish-black solution on heating on the steam-bath, large, brilliant bronze-red, rhomboidal, transparent scales and plates rapidly separating, which were washed with water, recrystallised from alcohol and air-dried (Found : Ni, 20·8. $C_{12}H_{18}O_2N_2Ni$ requires Ni, 20·9%).

Nickel ethylenediaminobisacetylacetone, crystallising in bronze-red scales or plates or reddish-black tablets, is insoluble in water, readily soluble in most organic solvents to red solutions, and soluble in mineral acids only with decomposition, forming acetylacetone and nickel and ethylenediamine salts. It melts at 200° to a black liquid, and, out of contact with air, boils without decomposition at a temperature approaching a red heat, forming a heavy yellow vapour, which condenses in bright red needles. The vapour, in contact with air, deposits a glistening nickel mirror on a heated glass surface, similar to the cobalt mirror obtained by heating the corresponding cobaltous salt.

Ethylenediammino-nickel Ethylenediaminobisacetylacetone, $C_2H_4(NH_2)_2Ni$ ec.—The foregoing nickel salt was dissolved in the minimum quantity of boiling ethylenediamine hydrate, forming a brownish-red solution, from which, on rapid cooling, elongated, brownish-red needles separated. These were removed, washed with light petroleum and dried over solid caustic soda (Found : Ni, 17·2 $C_{14}H_{26}O_2N_4Ni$ requires Ni, 17·2%).

The acicular form of ethylenediammino-nickel ethylenediaminobisacetylacetone slowly loses ethylenediamine on exposure; it is insoluble in water and decomposed by this medium, forming the foregoing simple salt and a strongly alkaline solution of ethylenediamine.

Diammino-nickel Ethylenediaminobisacetylacetone, $(NH_3)_2Ni$ ec.—On pouring a saturated solution of the simple nickel salt in alcohol into 18*N*-ammonia solution, brilliant red prisms separated. On drying, these rapidly lost ammonia, even over sodium hydroxide and ammonium carbonate. Analysis was possible only of the partly deamminated salt, the highest percentage of ammonia found being 7·9. The diammine requires 10·8 and the monammine 5·7%, indicating that the product was almost certainly the diammino-nickel salt.

3. *Palladous Series.*

Palladous Ethylenediaminobisacetylacetone. Pd ec.—Palladous chloride (0·9 g. = 1 mol.) was dissolved in boiling 10*N*-hydrochloric acid, and the solution rather more than neutralised with sodium carbonate. Ethylenediaminobisacetylacetone (1·2 g. = 1 mol). and 5*N*-sodium hydroxide solution (2 c.c. = 2 mols.) were then added. On heating on the steam-bath, the yellow mixture assumed a brownish-black colour. After cooling, the liquid was filtered, and the solid residue extracted with acetone until the extracts were colourless. On concentrating the orange-coloured acetone extracts, yellow prisms separated, which were recrystallised from benzene and air-dried (Found : N, 8·3; Pd, 32·4. $C_{12}H_{18}O_2N_2Pd$ requires N, 8·5; Pd, 32·5%).

Palladous ethylenediaminobisacetylacetone forms canary-yellow needles, m. p. 228°. It is insoluble in water, sparingly soluble in light petroleum, and freely soluble in most other organic solvents, from which it separates in pale yellow prisms with solvent of crystallisation, readily lost on exposure, yielding the simple salt.

Dichloroformo-palladous Ethylenediaminobisacetylacetone, $(CHCl_3)_2$Pd ec.—From a saturated solution of palladous ethylenediaminobisacetylacetone in chloroform, large, elongated, hexagonal, pale yellow tablets separated, which were removed and dried by a very short exposure to air (Found : loss at 100°, 41·7. $C_{14}H_{20}O_2N_2Cl_6Pd$ requires $CHCl_3$, 42·1%). The addition compound, on exposure to air, only slowly loses chloroform (identified by odour), but is rapidly converted into the simple salt by heating for about an hour at 100°.

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