583. *Transition-metal Complexes with Aliphatic Schiff Bases. Part III.[1] Compounds Formed by Reaction of Some 1,2-Diamine Complexes of Copper(II) with Some Ketones.*

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The reaction of the bisdiaminecopper(II) complexes of ethylenediamine, propylenediamine, and 1,1-dimethylethylenediamine with acetone are described. With ethylene- and propylene-diamine, compounds formed by reaction with two and with four mol. of acetone were obtained, while with 1,1-dimethylethylenediamine only the former could be prepared. No reaction occurred with 1,2-dimethylethylenediamine. The bisethylenediaminecopper(II) ion reacted similarly with two and with four mol. of ethyl methyl ketone. Evidence supporting a cyclic, tetradentate secondary amine–Schiff base structure for the compounds containing four ketone residues, and a tetradentate primary and secondary amine–Schiff base structure for the compounds with two ketone residues, and for their nickel(II) analogues, is presented. The visible and ultraviolet absorption spectra, and the magnetic susceptibilities of the compounds, are reported.

IN Parts I and II of this series [1] the reaction of the nickel(II) complexes of various 1,2-diamines with acetone were described. The products were assigned N-isopropylidene-bisdiamine structures, compounds with two, three, and four isopropylidene groups being formed. These structures were supported by the infrared spectra, which indicated the presence of C:N bonds, and the absence of NH_2 groups in the tetra-N-isopropylidene compounds, and also by the ultraviolet spectra which suggested a conjugated π-bonding system. Acetone was readily recovered on acid hydrolysis of the compound with three acetone residues, and with more difficulty on acid hydrolysis of the compound with two acetone residues.

It has since been observed [3] that mesityl oxide is recovered when the compound with two acetone residues is decomposed by dilute acid or by a solution of disodium dihydrogen ethylenediaminetetra-acetete, and when the more resistant compound with four acetone residues is treated with cyanide solution; the mesityl oxide was recovered from the solution by steam-distillation. When the reaction solution was then rendered alkaline and steam-distillation continued, ethylenediamine was recovered. In the case of the compound with three acetone residues, which is slowly converted into the compound with two acetone residues in boiling water, steam-distillation of an aqueous solution resulted in recovery of acetone. It is unlikely that mesityl oxide would be formed from acetone under these conditions, and it is therefore probable that the acetone is present in the compounds as C_6 units. The tetradentate secondary amine–azomethine structures (I), (II), and (III) (which are isomeric with the N-isopropylidene Schiff base structures) more readily explain the observed properties of the compounds, particularly the resistance to hydrolysis, which is unusual for Schiff bases. Hydrolysis of the azomethine group would give a β-amino-ketone, which would decompose to form the amine and mesityl oxide.[4] The lower stability of compound (II) than of compound (I), and its loss of acetone in aqueous solution is explained by the easier hydrolysis of the free N-isopropylideneamino-group.

The infrared spectra of these compounds contain a band at about 3130 cm.$^{-1}$, not explicable in terms of the N-isopropylidene structures, but close to the values observed for secondary amine complexes [*e.g.*, dichlorobispiperidineplatinum(II) at 3174 cm.$^{-1}$ [5]

[1] Part II, Blight and Curtis, *J.*, 1962, 1204.
[2] Part I, Curtis, *J.*, 1960, 4409.
[3] Curtis and House, *Chem. and Ind.*, 1961, **42**, 1708.
[4] Cromwell, *Chem. Rev.*, 1946, **38**, 124.
[5] Chatt, Duncanson, and Venanzi, *J.*, 1956, 2712.

bis(diethylenetriamine)nickel(II) at 3162 and 3242 cm.$^{-1}$, and (triethylenetetramine)-copper(II) at 3195 and 3225 cm.$^{-1}$, and bistriethylenetetramine-μ-triethylenetetraminedi-nickel(II) at 3162 and 3242 cm^{-1}].

The cyclic structure for the nickel ethylenediamine and propylenediamine compounds with four acetone residues is supported by absorption of 4 equiv. on hydrogenation with a platinum catalyst at atmospheric pressure, with formation of compounds (to be described later) which show no infrared C:N absorption (the NH band remains at 3100 cm.$^{-1}$) and without the 280 mμ peak in the ultraviolet spectra of the unreduced compounds.

Preparations.—Bisethylenediaminecopper(II) perchlorate reacts slowly with acetone on prolonged refluxing, or at 110° in a sealed tube, or on ultraviolet irradiation. Bases, such as pyridine or ethylenediamine, speed the reaction (and also the formation of tarry acetone polymers); traces of water retard it. The initial product is the perchlorate (IV), but longer reaction leads to the macrocyclic perchlorate (V) as the major product. If the reaction is continued still further, metallic copper is deposited, and brown, tarry polymers are produced.
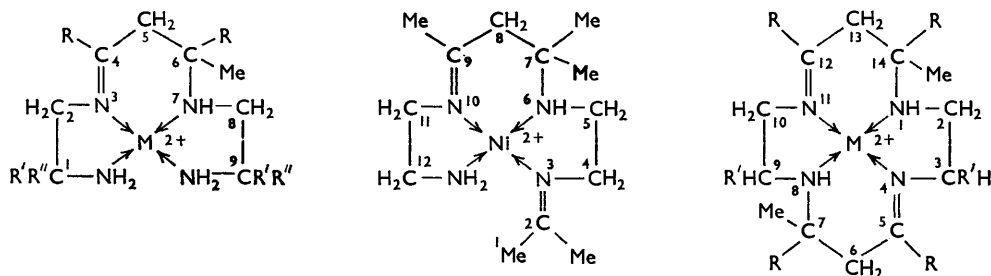
(I) M = Ni, R = Me, R′ = R″ = H
(IV) M = Cu, R = Me, R′ = R″ = H
(VI) M = Cu, R = R′ = Me, R″ = H
(VIII) M = Cu, R = R′ = R″ = Me
(IX) M = Cu, R = Et, R′ = R″ = H

(II)

(III) M = Ni, R = Me, R′ = H
(V) M = Cu, R = Me, R′ = H
(VII) M = Cu, R = R′ = Me
(X) M = Cu, R = Et, R′ = H

For alternative structure see the text.
(The numbering in the left-hand formula applies only when R′ = R″ = H.)

Under the same conditions, but more slowly, bispropylenediaminecopper(II) perchlorate reacts with acetone to form first the perchlorate (VI), and very much more slowly the macrocyclic perchlorate (VII).

Bis-(1,1-dimethylethylenediamine)copper(II) perchlorate reacts readily with acetone, to form the perchlorate (VIII). As with the nickel analogue, no compound with four acetone residues could be prepared. If further reaction occurred more slowly than with propylenediamine, it is unlikely that the product would be detected among the extensive polymerization and decomposition products.

Only unchanged starting material could be isolated when bis-(1,2-dimethylethylene-diamine)copper(II) perchlorate in acetone solution was heated or exposed to ultraviolet radiation, again as with the nickel analogue. If reaction could occur, at least the mono-azomethine compound should have been isolable, suggesting that the presence of a methyl group α to both the amino-groups prevents reaction.

Bisethylenediaminecopper(II) perchlorate reacts slowly with ethyl methyl ketone in a sealed tube at 110°, forming first a condensation product (IX), isolated as the tetra-chlorozincate (the perchlorate could not be obtained crystalline). On prolonged heating, the macrocyclic perchlorate (X) is formed. Ultraviolet radiation does not induce this reaction, but merely polymerizes the ketone.

A variety of configurations are possible for many of these compounds. With the cyclic compounds, the two azomethine groups could be *cis* or *trans*. As the diazomethine compounds are formed by reaction of the monoazomethine compounds with further ketone,

it is likely that the *trans*-directing influence of the first azomethine group will kinetically determine the configuration of the second azomethine-secondary amine ring. For convenience the *trans*-configuration is assumed in the formulæ. Geometric isomerism is also possible for the compounds formed from *C*-substituted ethylenediamines. The absence of reaction with 1,2-dimethylethylenediamine, and the ready reaction of propylene-diamine and 1,1-dimethylethylenediamine to form the monoazomethine compounds, suggest that reaction occurs at the amino-group adjacent to the methylene group. Further reaction is very slow with propylenediamine, supporting this view. On these grounds it is likely that the compounds have the structures shown.

Optical isomerism could arise from the co-ordinated secondary amino-groups, which are asymmetric centres, and from the asymmetric carbon atoms present in the compounds formed with propylenediamine.

In the compounds formed from ethyl methyl ketone a further source of isomerism arises, depending on whether condensation occurs at the methyl or the methylene group. Trisethylenediaminenickel perchlorate reacts with many methyl ketones, but not with diethyl ketone, suggesting that it is the methyl group which is reactive, giving the structure shown. In this case, a further asymmetric centre is introduced.

The only example of isomerism observed with this series of compounds occurs with the diazomethine compound formed by reaction of trispropylenediaminenickel perchlorate with four mol. of acetone, where non-interconvertable orange and yellow isomers were isolated.[1] The same phenomenon was looked for with the copper analogue (VII) but not observed. The ion (VII) was difficult to prepare and isolate, and was obtained only in very low yield, and another modification which was more soluble, or present in smaller amount, may not have been detected.

Description.—The cyclic compounds with two azomethine groups (four ketone residues), like their nickel analogues, are very resistant to hydrolysis, being unaffected by most concentrated acids. Hydrochloric and hydrobromic acid are exceptional, the concentrated acids, and solutions of the concentrated acids in organic solvents, causing rapid hydrolysis. The compounds with one azomethine group (two ketone residues), are hydrolyzed slowly by dilute mineral acids, very slowly by acetic acid. They are also slowly decomposed by reagents which precipitate cupric ions, such as sulphide or salicyl-aldoxime solutions. All the compounds are decomposed by cyanide ions, and by oxidising agents such as acid permanganate or boiling peroxydisulphate solutions. As with the nickel analogues, mesityl oxide and the original diamine were recovered by steam-distillation of solutions of the compounds decomposed by acid or cyanide solutions (they were identified as 2,4-dinitrophenylhydrazone and dihydrochloride, respectively, by X-ray powder diffraction.)

The similar mode of preparation, and the same decomposition products, together

TABLE 1.

Absorption spectra in aqueous solution.

Compd.	Visible			Ultraviolet		
	$\lambda_{max.}$	ε	$\lambda_{\frac{1}{2}}$	$\lambda_{max.}$	ε	$\lambda_{\frac{1}{2}}$
IV	525	88	466—601	244	5200	217—276
VI	524	95	471—591	243	6300	218—275
VIII	524	92	468—594	244	6600	219—277
IX	528	91	473—594	244	6200	? —277
V	505	126	458—564	260	5400	235—289
VII	509	110	459—570	262	5930	230—294
X	508	131	458—567	263	7000	234—294

with very similar infrared spectra, indicate that the copper(II) and the nickel(II) compounds described earlier are completely analogous.

Visible and Ultraviolet Absorption Spectra (Table 1).—In the visible region the spectra contain one broad asymmetric band, as is characteristic of copper(II) complexes. This

band shifts increasingly to shorter wavelength in the sequence bisdiamine (ethylene-diamine and 1,1-dimethylethylenediamine, 550 mμ; propylenediamine 543 mμ), bis-diamine with two ketone residues, bisdiamine with four ketone residues. The position of the band varies with different solvents, the maximum shifts observed relative to water being -15 mμ for acetone, and $+8$ mμ for dimethylformamide.

The ultraviolet spectra are similar to those of the nickel analogues, with the bands shifted about 20 mμ to shorter wavelengths. (Hence the maxima for the bands observed at 205—220 mμ for the nickel compounds could not be determined.) The bands at 244 or 262 mμ are from their intensity, " allowed transitions," and probably involve the π-levels of the azomethine groups, delocalized by interaction with the copper $d_{xz/yz}$ orbitals (the corresponding band of the nickel compounds disappears on hydrogenation).

TABLE 2.

Magnetic susceptibilities.

Compound	Temp. (K)	$10^6\chi_g$	$10^6\chi_M$	Diam. corr.	$10^6\chi_M'$	μ_{eff} (B.M.)
IV	289	2·66	1230	218	1448	1·84
V	287	2·07	1123	271	1394	1·80
VI	288	2·44	1197	242	1439	1·83
VIII	289	2·33	1210	266	1476	1·86
IX	289	2·44	1218	268	1486	1·86
X	293	1·98	1188	295	1483	1·87

Magnetic Susceptibilities (Table 2).—These were measured for the solid state by the Gouy method, with trisethylenediaminenickel(II) thiosulphate as calibrant.[6] The values all indicate the presence of one unpaired electron.

EXPERIMENTAL

1,1- and 1,2-Dimethylethylenediamine were prepared as described in Part II.[1].

4,6,6-*Trimethyl*-3,7-*diazanon*-3-*ene*-1,9-*diaminecopper*(II) *Perchlorate* (IV).—A solution of bisethylenediaminecopper perchlorate in dry acetone, containing a few drops of pyridine as catalyst, and anhydrous calcium sulphate to remove the water produced during the reaction, was heated in a sealed tube at 110° for 6 hr., then filtered and evaporated. The residue was dissolved in hot methanol, boiled with charcoal, and filtered. Isopropyl alcohol was added to the hot solution, which was allowed to cool slowly, with frequent scratching, or preferably nucleation with some solid product produced by the slow evaporation of a small portion of the solution, to counteract the tendency to deposit as an oil. The blue-violet *product* ($\sim$80%) recrystallized from methanol–ethanol [Found: Cu, 14·0; C, 26·0; H, 5·2; N, 11·9. $C_{10}H_{24}CuN_4(ClO_4)_2$ requires Cu, 13·8; C, 26·0; H, 5·2; N, 12·1%].

This compound, and the other " two-ketone " compounds, crystallize less readily as per-chlorates than as tetrachlorozincates, formed on addition of a concentrated solution of zinc chloride to the solution in methanol, followed by acetone, the precipitated product being re-crystallized from water–methanol.

5,7,7,12,14,14-*Hexamethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*dienecopper*(II) *Perchlorate* (V).—The preparation was as in the previous case but with heating for $\sim$36 hr. Alternatively, a solution of bisethylenediaminecopper perchlorate in acetone was irradiated in a silica flask with ultraviolet light for several days under reflux (with the heat supplied from the mercury-vapour lamp) with the condensate passing through an extraction thimble containing anhydrous calcium sulphate. In both cases the filtered solution was evaporated and the residue dissolved in hot water, boiled with charcoal, and filtered while hot; orange crystals of the *product* ($\sim$80%) separated on cooling. It was recrystallized from water–ethanol (orange form) or on extraction into boiling dioxan (red form) [Found, for orange form: Cu, 11·7; C, 35·8; H, 5·9; N, 10·2. For red form: Cu, 11·6; C, 35·4; H, 5·7; N, 10·6. $C_{16}H_{32}CuN_4(ClO_4)_2$ requires Cu, 11·7; C, 35·4; H, 5·9; N, 10·3%].

5,7,7-*Trimethyl*-4,8-*diazaundec*-4-*ene*-2,10-*diaminecopper*(II) *Perchlorate* (VI).—A solution of bispropylenediaminecopper perchlorate in acetone was treated as for the preparation of compound

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[6] Curtis, *J.*, 1961, 604.

(IV), with heating for ~9 hr. Crystallization from methanol yielded mauve crystals of the anhydrous *salt* (~80%) [Found: Cu, 13·0; C, 29·4; H, 6·0; N, 11·0. $C_{12}H_{28}CuN_4(ClO_4)_2$ requires Cu, 12·8; C, 29·4; H, 5·7; N, 11·4%]. Crystallization from water yielded deep blue crystals of a *dihydrate* (Found: loss at 110°, 6·9. $2H_2O$ requires 6·9%).

3,5,7,7,9,12,14,14-*Octamethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*dienecopper*(II) *Perchlorate* (VII).—Bispropylenediaminecopper perchlorate was heated in a sealed tube with acetone, and a few drops of propylenediamine and isopropylamine (or pyridine) plus a large excess of anhydrous calcium sulphate for several days at 110°, during which the mixture became brown and tarry. The reaction was stopped when deposition of copper commenced. The mixture was filtered and evaporated under reduced pressure, and the residue dissolved in water and boiled several times with charcoal. The charcoal was boiled with several successive portions of water, and the solutions combined and evaporated to small volume. Sodium perchlorate was added to the solutions, which were then set aside for several days, during which the product separated as red crystals, mainly from the charcoal extractant. The *product* recrystallized from hot water (yield, variable, <5%) [Found: Cu, 11·2; C, 37·9; H, 6·1; N, 9·3. $C_{18}H_{36}CuN_4(ClO_4)_2$ requires Cu, 11·15; C, 37·9; H, 6·4; N, 9·8%].

2,4,6,6,9-*Pentamethyl*-4,8-*diazaundec*-4-*ene*-2,10-*diaminecopper*(II) *Perchlorate* (VIII).—1,1-Dimethylethylenediaminecopper perchlorate was used as in the preparation of the salt (IV). Crystallization from methanol yielded pink crystals of the anhydrous *salt* (>80%) [Found: Cu, 12·3; C, 32·6; H, 6·1; N, 10·9. $C_{14}H_{32}CuN_4(ClO_4)_2$ requires Cu, 12·3; C, 32·4; H, 6·2; N, 10·8%]. Slow crystallization from water yielded deep blue crystals of a *dihydrate* (Found: loss on desiccation, 6·6. $2H_2O$ requires 6·5%).

4,6-*Diethyl*-6-*methyl*-3,7-*diazonon*-3-*ene*-1,9-*diaminecopper*(II) *Tetrachlorozincate* (IX).—Preparation was as for (IV) but with ethyl methyl ketone in place of acetone and heating for 24 hr. The solution was evaporated, the residue dissolved in methanol, and a concentrated aqueous solution of zinc chloride added, the *product* being precipitated. Recrystallization from hot methanol gave blue-violet crystals (>80%) (Found: Cu, 12·7; C, 28·6; H, 5·1; N, 11·2. $C_{12}H_{24}Cl_4CuN_4Zn$ requires Cu, 12·7; C, 28·9; H, 5·7; N, 11·3%).

5,7,12,14-*Tetraethyl*-7,14-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*dienecopper*(II) *Perchlorate* (X).—Preparation as for (IX), but with heating for about 5 days gave the *product* (~10%), sparingly soluble in hot water, and best recrystallized from hot water–methanol [Found: Cu, 10·5; C, 40·1; H, 6·6; N, 9·2. $C_{20}H_{40}CuN_4(ClO_4)_2$ requires Cu, 10·6; C, 40·1; H, 6·7; N, 9·4%].

Polymorphism and Hydrates.—The perchlorate (V) is dimorphic: orange plates and ruby-red crystals are interconvertible; they give different X-ray powder diffraction patterns, but have very similar infrared spectra. If a concentrated aqueous solution of this salt is boiled for a few minutes, and then allowed to crystallize on a glass slide, microscopic examination reveals the formation of blue crystals among the orange and red ones. This form is more soluble than the other two, and hence difficult to isolate, although large crystals were several times obtained from evaporating aqueous solutions when the other forms fortuitously failed to separate. On exposure to the air the blue crystals develop orange patches which slowly spread over the crystals, the product giving the same X-ray powder diffraction pattern as the red form. When heated, *e.g.*, to 100°, the blue crystals become orange, reversibly at first, but the change rapidly becomes irreversible as water is lost. By analogy with salts (VI) and (VIII) the blue compound is probably a dihydrate.

Compounds (VI) and (VIII) crystallize from methanol as pink anhydrous forms, and from water as the blue-violet dihydrates. The hydrate of salt (VIII) slowly loses water on exposure to the air, rapidly on desiccation. If the hydrate of salt (VI) is dehydrated under mild conditions, *e.g.*, in a vacuum or by gentle heating, the structure of the crystals is not disrupted (same X-ray powder diffraction pattern) and the water is rapidly regained on exposure to the air. The colour changes reversibly from blue-violet, for the hydrate, to pink, for the anhydrous materials, during these changes. The anhydrous material produced by strongly heating the hydrate, or by recrystallization from methanol, is not hygroscopic.

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