1223. Transition-metal Quinoxaline Complexes. Part II.[1] Copper(I) Derivatives

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During a study [2] of the complexes formed between copper(II) compounds and substituted quinoxalines it was found that the stoicheiometry of the product depended on the nature of the substituents in the ligand. The compounds formed between copper(I) compounds and the same ligands are described in this Paper.

Quinoxaline (Q), 2-methylquinoxaline (Mq), and 2,3-dimethylquinoxaline (Dmq) all form complexes of the type Cu_2X_2L with copper(I) halides. These are of similar stoicheiometry to those reported [3] for copper(I) complexes with substituted pyrazines. It was suggested [3] that the pyrazine complexes were binuclear, with each pyrazine molecule co-ordinated to two copper atoms through the two nitrogen atoms, each copper atom being bonded to a halide atom and a nitrogen atom of the organic ligand. If these quinoxaline compounds have a similar structure to that suggested, then molecular models show that

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[1] The Paper by A. E. Underhill, *J.*, 1965, 4336, is considered to be Part I.

[2] D. E. Billing and A. E. Underhill, unpublished work.

[3] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J.*, 1963, 3156.

no appreciable steric hindrance will be involved. The infrared band due to the $C\equiv N$ vibration (see Table 1) in the cyanide consists of a single peak with three maxima at 2107, 2118, and 2127 cm.$^{-1}$. This lies in the region reported for the cyano-copper(I)–pyrazine complexes and is at an appreciably lower frequency than those reported for bridging cyanides.[4] This supports the postulated structure in indicating no anion-bridging in the cyano-compound and, by inference, in the halides.

TABLE 1

Principal infrared absorption bands (375—2200 cm.$^{-1}$)

All quinoxaline complexes: 414 ± 4s; 428 ± 2m; 763 ± 6vs; 867 ± 4s; 1055 ± 7vs; 1138 ± 8s; 1361 ± 2s; 1387 ± 3m; 1500 ± 1vs. Also as follows:

Cu_2Cl_2Q	1378m	1532s	1610m				
Cu_2Br_2Q	778m	962s	1207vs	1373s	1423m	1583w	
Cu_2I_2Q	962vs	968vs	1205vs	1373s	1420s	1581m	
$Cu_2(CN)_2Q$	790w	967m	1214m	1420m	2107vs *	2118vs *	2127vs *

All 2-methylquinoxaline complexes: 424 ± 1vs; 765 ± 5vs; 907 ± 2m; 960 ± 2m; 986 ± 2m; 1129 ± 1m; 1205 ± 3m; 1366 ± 4m; 1381 ± 1m; 1476 ± 1s; 1493 ± 1s; 1544 ± 4m. Also as follows:

Cu_2Br_2Mq	518m	628ms				
Cu_2I_2Mq	1035m	1295m	1305ms	1406ms	1432ms	1499s, sh

All 2,3-dimethylquinoxaline complexes: 443 ± 1s; 767 ± 6vs; 838 ± 3m; 960 ± 2m; 1003 ± 6s; 1141 ± 2s; 1179 ± 2s; 1203 ± 3s; 1334 ± 2m; 1402 ± 6s; 1490 ± vs. Also as follows:

Cu_2Cl_2Dmq	1552s					
Cu_2Br_2Dmq	628m	732m	1220m	1312m	1408vs	1432m
Cu_2I_2Dmq	630s	722ms	1215s	1352s	1382vs	1408vs

* CN stretching frequency.

Cu_2Br_2Q, Cu_2I_2Q, and the complexes containing substituted quinoxalines were prepared by direct synthesis from the copper(I) halide and the ligand in either water or 50% aqueous ethanol both containing the sodium, potassium, or calcium halide. Attempts to prepare Cu_2Cl_2Q by this method gave a mixture of yellow, orange, and brown products, but this complex was obtained by reduction of an aqueous solution of the copper(II) complex with hypophosphorous acid. Only indefinite products were obtained with 2,3-diphenylquinoxaline. Molecular models show that this is not due to a steric effect and therefore may be due to the weaker basicity of this ligand. The insolubility of the complexes in all solvents except mineral acids prevented a study of their properties in solution.

Thermogravimetric analyses show the complexes to decompose by loss of the organic ligand. The residue, in the case of the quinoxaline complexes, was identified as the copper(I) halide by its *X*-ray powder photograph. The decomposition temperatures for the complexes are given in Table 2. Many bisquinoline-metal(II) halides have been shown [5] to decompose in the same way to leave the anhydrous metal halide.

TABLE 2

Decomposition temperatures as recorded on the thermobalance

Cu_2Cl_2Q	Cu_2Br_2Q	Cu_2I_2Q	Cu_2Cl_2Mq	Cu_2Br_2Mq	Cu_2I_2Mq	Cu_2Cl_2Dmq	Cu_2Br_2Dmq	Cu_2I_2Dmq
220°	190°	200°	100°	100°	90°	240°	190°	200°

Experimental.—Infrared spectra, and copper and halide analyses were determined as described previously.[1] Thermal decompositions were carried out on a Stanton Thermobalance

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[4] D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nuclear Chem.*, 1961, **21**, 33.

[5] D. H. Brown, R. N. Nuttall, and D. W. A. Sharp, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1151.

working at a chart speed of 3 in./hr. and a temperature rise of approximately ⅔°/min. *X*-Ray powder photographs were taken on a Unicam 9-cm. diameter camera using Cu K_α radiation and a nickel filter. All compounds were dried at 20°/25 mm.

Dichloro(quinoxaline)dicopper(I). Quinoxaline (1·5 g., 1 mol.) and copper(II) chloride dihydrate (3·9 g., 2 mol.) were dissolved in water (150 ml.), 50% hypophosphorous acid (8 ml.) was added, and the mixture kept at 90° for 1 hr. The initial yellow precipitate rapidly turned to dark brown flakes of the *product* (2·4 g., 63%) which were filtered off and washed with water (Found: C, 29·6; H, 2·0; Cl, 22·1; Cu, 38·8. $C_8H_6Cl_2Cu_2N_2$ requires C, 29·3; H, 1·8; Cl, 21·6; Cu, 38·7%).

Dibromo(quinoxaline)dicopper(I). Copper(I) bromide (4·4 g., 2 mol.) was dissolved in an acidified cold saturated solution of potassium bromide (110 ml.), and the solution was added slowly to a stirred solution of quinoxaline (2·0 g., 1 mol.) in water (100 ml.). The initial yellow precipitate turned into the orange *product* (5·9 g., 92%) during the addition. The *product* was filtered off and washed with dilute potassium bromide solution and water (Found: C, 23·4; H, 1·6; Br, 39·0; Cu, 30·5. $C_8H_6Br_2Cu_2N_2$ requires C, 23·0; H, 1·5; Br, 38·3; Cu, 30·5%).

Di-iodo(quinoxaline)dicopper(I). This *complex* was similarly prepared (Found: C, 19·2; H, 1·5; Cu, 24·7; I, 49·5. $C_8H_6Cu_2I_2N_2$ requires C, 18·8; H, 1·2; Cu, 24·9; I, 49·7%).

Dichloro-(2-methylquinoxaline)dicopper(I). This *complex* was also obtained as above, but with the addition of the 2-methylquinoxaline to the solution of copper(I) chloride (Found: C, 31·7; H, 2·5; Cl, 20·8; Cu, 36·4. $C_9H_8Cl_2Cu_2N_2$ requires C, 31·6; H, 2·4; Cl, 20·7; Cu, 37·1%).

Dibromo-(2-methylquinoxaline)dicopper(I). This *complex* was similarly prepared, but without the presence of acid (Found: C, 25·6; H, 1·9; Br, 37·0; Cu, 29·0. $C_9H_8Br_2Cu_2N_2$ requires C, 25·1; H, 1·9; Br, 37·1; Cu, 29·5%), as was *di-iodo-(2-methylquinoxaline)dicopper*(I) (Found: C, 20·7; H, 1·7; Cu, 24·0; I, 48·0. $C_9H_8Cu_2I_2N_2$ requires C, 20·6; H, 1·5; Cu, 24·2; I, 48·3%).

Dichloro-(2,3-dimethylquinoxaline)dicopper(I). This was similarly prepared in 50% aqueous ethanol. The impure red product was dissolved in boiling water (200 ml.) by adding concentrated hydrochloric acid. The resulting brown solution was neutralised with dilute ammonia and then slightly acidified with dilute hydrochloric acid while still hot. The pure, red *product* which precipitated as the solution cooled was filtered off and washed with water (Found: C, 33·9; H, 3·0; Cl, 20·0; Cu, 36·0. $C_{10}H_{10}Cl_2Cu_2N_2$ requires C, 33·7; H, 2·8; Cl, 19·9; Cu, 35·7%).

Dibromo-(2,3-dimethylquinoxaline)dicopper(I). This *complex* was also obtained as above, but with addition of the copper solution to the solution of 2,3-dimethylquinoxaline. No acid was used in the initial reaction, and dilute sulphuric acid was used in the purification (Found: C, 27·0; H, 2·2; Br, 36·2; Cu, 28·9. $C_{10}H_{10}Br_2Cu_2N_2$ requires C, 27·0; H, 2·3; Br, 35·9; Cu, 28·5%).

Di-iodo-(2,3-dimethylquinoxaline)dicopper(I). This *complex* was similarly prepared, but without reprecipitation (Found: C, 23·0; H, 2·1; Cu, 23·6; I, 46·8. $C_{10}H_{10}Cu_2I_2N_2$ requires C, 22·3; H, 1·9; Cu, 23·6; I, 47·1%).

Dicyano(quinoxaline)dicopper(I). Quinoxaline (0·9 g., 1 mol.), potassium cyanide (1·8 g., 4 mol.), and hydroxylamine hydrochloride (2·0 g.) were dissolved in water (20 ml.) and the mixture was added slowly to a solution of copper(II) chloride dihydrate (2·2 g., 2 mol.) in water (20 ml.). A yellow-brown complex was formed initially and converted into the orange *product* (1·5 g., 75%) on boiling the solution for ½ hr. This was filtered off and washed with ethanol, dilute sodium chloride solution, dilute potassium cyanide solution, and water (Found: C, 38·9; H, 2·3; Cu, 40·8; N, 18·1. $C_{10}H_6Cu_2N_4$ requires C, 38·8; H, 2·0; Cu, 41·1; N, 18·1%).

2,3-*Dimethylquinoxaline*. *o*-Phenylenediamine (43·2 g., 1 mol.), biacetyl (35·0 ml., 1 mol.), glacial acetic acid (100 ml.), and water (700 ml.) were refluxed together for 3 hr. Yellow-brown needles of the product were deposited when the mixture cooled to room temperature. These were filtered off and the filtrate added, with stirring, to water (3000 ml.). The filtrate was neutralised with sodium hydroxide and more product was obtained on leaving the mixture for 24 hr. The product was refluxed with decolourising charcoal in alcohol for 1 hr. The resulting solution was filtered, and the pure *product* (21 g., 33%) crystallised as yellow needles, m. p. 105·5—106°, from the filtrate (Found: C, 76·1; H, 6·5; N, 17·9. $C_{10}H_{10}N_2$ requires C, 75·9; H, 6·4; N, 17·7%).

2,3-*Diphenylquinoxaline*. *o*-Phenylenediamine (21·6 g., 1 mol.), benzil (42·0 g., 1 mol.), and glacial acetic acid (500 ml.) were refluxed together for 3 hr. The cold reaction mixture was added slowly, with stirring, to water (1500 ml.), whereupon the white *product* precipitated. This was purified as above to give needles, m. p. 124—125° (48 g., 85%) (Found: C, 85·2; H, 5·0; N, 10·0. $C_{20}H_{14}N_2$ requires C, 85·1; H, 5·0; N, 9·9%).

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