800. *Quinoxaline Complexes of Copper*(II)

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Quinoxaline forms complexes of the type $QCuX_2$ (Q = quinoxaline, X = Cl, Br, NO_3, $CH_3{\cdot}CO{\cdot}O$) and $QCuSO_4$. The halide complexes appear to be polymeric, involving both halogen and quinoxaline bridges. The structure of the acetate complex is similar to that of cupric acetate monohydrate except that quinoxaline replaces the water molecules.

A NUMBER of Papers have been published[1] describing a series of novel complexes of transition-metals with pyrazine and methylpyrazines. Many of the complexes are polymeric, containing both halogen and pyrazine bridges, and because of the interesting structures found it was decided to extend the work to study the effect of increase in size of the ligand on these polymeric structures, and to investigate this type of complex with metal salts other than the halides. Quinoxaline (Q) and substituted quinoxalines form[2] complexes with many compounds of Ni, Mn, Co, and Cr, analogous to those formed by pyrazine, and the stoicheiometry and properties of the product are affected by the number and nature of the substituents on the quinoxaline ligand. In this Paper the complexes formed between quinoxaline and copper(II) compounds are discussed.

EXPERIMENTAL

The magnetic determinations were carried out by the Gouy method, with a tube calibrated with mercury(II) tetrathiocyanatocobaltate(II). The reflectance spectra were determined on a Beckman DK2A spectrophotometer fitted with a standard reflectance attachment. The infrared spectra were determined with a Unicam S.P. 100 spectrophotometer as mulls in Nujol or Halocarbon Oil. Thin sheets of Polythene were used to protect the windows.

Carbon and hydrogen were determined in this department by Mr. P. Borda. Copper, nitrate, sulphate, and halide were determined gravimetrically[3] as ethylenediaminecopper mercuri-iodide, Nitron nitrate, barium sulphate, and silver halide, respectively.

Dichloroquinoxalinecopper(II).—Copper(II) chloride trihydrate (1·0 g.) was mixed with quinoxaline (1·5 g.) and heated for 2 hr. at 80°. The *complex*, obtained as a green powder, was washed with alcohol to remove excess quinoxaline, filtered, and dried in a vacuum desiccator (0·99 g., 64%) (Found: C, 36·1; H, 2·8; Cl, 27·0; Cu, 23·9. $C_8H_6Cl_2CuN_2$ requires C, 36·3; H, 2·3; Cl, 26·8; Cu, 24·0%).

Dibromoquinoxalinecopper(II).—Copper(II) bromide (3·43 g.) dissolved in water (8 ml.) was added to quinoxaline (2·0 g.) dissolved in hot water (5 ml.). The *complex*, a dark brown powder, was filtered off, washed with cold water, alcohol, and ether, and dried in a vacuum desiccator (3·3 g., 61%) (Found: C, 27·5; H, 2·1; Br, 44·4; Cu, 17·6. $C_8H_6Br_2CuN_2$ requires C, 27·2; H, 1·7; Br, 45·2; Cu, 18·0%).

Diacetatoquinoxalinecopper(II).—To quinoxaline (1·0 g.) in ethanol (10 ml.) was added cupric acetate monohydrate (1·0 g.) in warm ethanol (100 ml.). The *complex*, obtained as a microcrystalline leaf-green powder, was filtered off, washed with alcohol and ether, and dried in a vacuum desiccator (1·63 g., 73%) (Found: C, 45·9; H, 4·2; Cu, 20·4. $C_{12}H_{12}CuN_2O_4$ requires C, 46·2; H, 3·9; Cu, 20·4%).

Dinitratoquinoxalinecopper(II). Procedure was as above. The *complex* (70%) was obtained as a deep blue powder (Found: C, 30·1; H, 2·1; Cu, 19·8; NO_3, 38·6. $C_8H_6CuN_4O_6$ requires C, 30·2; H, 1·90; Cu, 20·0; NO_3, 39·0%).

Sulphatoquinoxalinecopper(II) *Tetrahydrate*.—Cupric sulphate pentahydrate (1·9 g.) was dissolved in the minimum amount of water (8 ml.), and quinoxaline (1·0 g.) in water (7 ml.) was added. After ½ hr. at 0°, the *complex* was obtained as pale blue crystals, filtered off, washed with alcohol and ether, and dried in a vacuum desiccator (0·6 g., 22%) (Found: C, 26·7; H, 3·9; Cu, 17·6; SO_4, 26·4. $C_8H_{14}CuN_2O_8S$ requires C, 26·6; H, 3·9; Cu, 17·6; SO_4, 26·6%).

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[1] (*a*) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *Nature*, 1961, **189**, 58; (*b*) *J.*, 1962, 1235; (*c*) *J.*, 1963, 3156; (*d*) *J.*, 1963, 5042.

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

[3] Vogel, " Textbook of Quantitative Inorganic Analysis," Longmans, London, 1961.

Sulphatoquinoxalinecopper(II).—This *complex* was obtained by heating the tetrahydrate at 110° for 2 hr. (Found: C, 31·8; H, 2·1; Cu, 22·4; SO_4, 33·6. $C_8H_6CuN_2O_4S$ requires C, 33·2; H, 2·1; Cu, 21·9; SO_4, 33·2%).

RESULTS AND DISCUSSION

Lever, Lewis, and Nyholm state [1a] that copper(II) complexes of pyrazine can be prepared but that investigation of them is difficult because of a tendency to undergo reduction to the copper(I) state. The copper(II) complexes of quinoxaline are quite stable and show no tendency to undergo reduction. Quinoxaline [4] is a slightly stronger base (pK_a ~0·8) than pyrazine (~0·6). Thus, quinoxaline will exhibit slightly stronger donor properties to the metal ion compared with pyrazine, and this increase will, it has been suggested, enhance the stability of the copper(II) state relative to the copper(I) provided that the π-acceptor strength of the two ligands is the same.[5] The copper(I) compounds corresponding to those described by Lever *at al.* have been prepared, and will be described in a later Paper.[2]

TABLE 1

	Room-temperature, magnetic moment (B.M.)	Diffuse-reflectance spectra (cm.$^{-1}$)	
		Charge-transfer and ligand bands	*d–d* Band
$QCuCl_2$	1·77	36,100, 31,500, 27,030	14,290
$QCuBr_2$	1·74	31,650, 21,050	13,990
$QCu(NO_3)_2$	1·81	31,850, 26,460	18,020
$QCu(CH_3\cdot CO\cdot O)_2$	1·41	37,740sh, 33,330, 25,640sh	14,290
$QCuSO_4,4H_2O$	1·99	40,820, 31,850	13,510
$QCuSO_4$	1·81	38,610, 31,350, 22,990	11,430

TABLE 2

Principal infrared absorption bands (400—1800 cm.$^{-1}$)

All complexes: 420 ± 9m—w; 630 ± 10m; 757 ± 5s; 870 ± 8s; 969 ± 11s; 1057 ± 7vs; 1143 ± 5m—s; 1212 ± 8s; 1355 ± 7s; 1471 ± 7s; 1499 ± 4vs.

Also as follows:

$QCuCl_2$	540w, 547w, 1013vw, 1279vw, 1375w
$QCuBr_2$	463w, 543vw, 1138m, 1408w, 1421w
$QCu(NO_3)_2$	537m, 547m, 667w, 744vs, 800vs,* 955w, 1008vs,* 1028vs,* 1260sh, 1285vs,* 1300vs,* 1308w
$QCu(CH_3\cdot CO\cdot O)_2$	538w, 617w, 682vs, 1037vs, 1361m, 1377m, 1418sh, 1434vs,* 1621vs *
$QCuSO_4,4H_2O$	493vs, 536w, 629m,br,* 737w,† 727w,† 715w,† 828m, 928m,† 980sh,* 1085vs,* 1098sh, 1600s, br †
$QCuSO_4$	530w, 547w, 596vs,* 626s,* 656,* 792w, 885m, 954m,* 994sh, 1000vs,* 1112m, 1160s,* 1221vs *

* Bands due to anion. † Bands due to water.

The magnetic moments of all the complexes (Table 1), apart from the acetate, lie in the region 1·70—2·20 B.M. normally associated with copper(II) compounds.[6] The value of 1·41 B.M. obtained for $QCu(CH_3\cdot CO\cdot O)_2$ at room temperature is much lower than those for the other complexes, and similar to that recorded for $[Cu(CH_3\cdot CO\cdot O)_2H_2O]_2$,[7] in which Cu–Cu interaction reduces the normal magnetic moment of the copper(II) ion. The diffuse-reflectance spectra of all the complexes (Table 1) contain a broad band with an ill-defined maximum in the region 11,000—18,100 cm.$^{-1}$. Above 17,000 cm.$^{-1}$ there is a sharp rise in the intensity of absorption with the onset of charge-transfer bands. The start of this band varies greatly with the ligand concerned, and is in the order (increasing energy) $Br^- < Cl^- < NO_3^- < SO_4^{2-} < 4H_2O,SO_4^{2-}$.

The Complex $QCuCl_2$.—The chloro-complex is an amorphous powder, insoluble in ethanol, acetone, and other organic solvents. It dissolves slightly in water but the resulting solution has a conductivity and absorption spectrum very similar to that of copper(II)

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[4] A. Albert, R. Goldacre, and J. Phillips, *J.*, 1948, 2240.

[5] B. R. James and R. J. P. Williams, *J.*, 1961, 2007.

[6] B. N. Figgis and J. Lewis in " Modern Co-ordination Chemistry," ed. J. Lewis and R. G. Wilkins, Interscience, New York, 1960, p. 406.

[7] B. N. Figgis and R. L. Martin, *J.*, 1956, 3837.

chloride itself, which suggests that the complex has dissociated into ionised copper(II) chloride and quinoxaline. These properties prevent the study of the complex in solution. The reflectance spectrum is very similar, in the shape and position of the 14,290 cm.$^{-1}$ band, to that of $CuCl_2$(pyridine)$_2$.[8] The environment of the copper ion in the quinoxaline complex is therefore likely to be very similar to that of the copper ion in the pyridine complex. Quinoxaline having two nitrogen atoms capable of co-ordinating to the copper ions will be equivalent to the two pyridine molecules. The structure of $CuCl_2$(pyridine)$_2$ [9] consists of a flat endless chain of $CuCl_2$ with the pyridine molecules above and below each copper atom. The environment of each copper atom is a distorted octahedron of four chlorine atoms and two pyridine molecules. The four short planar bonds are two Cu–N bonds at 2·02 Å and two Cu–Cl bonds at 2·28 Å. Two longer Cu–Cl bonds at 3·05 Å complete the octahedron. In $QCuCl_2$ a similar structure would involve the use of quinoxaline molecules as bridging units between copper atoms in different $CuCl_2$ chains. This structure is very similar to that proposed for (methylpyrazine)$NiBr_2$[1a] except that the d^9 configuration of the copper ion will result in a distorted octahedral structure compared with the regular octahedral environment of the nickel.

The Complex $QCuBr_2$.—The bromo-complex is very similar to the chloro-complex in its solution and spectral properties. The reflectance spectrum of the bromide is very similar to that of the chloride, with the maximum at 13,990 instead of 14,290 cm.$^{-1}$. This is consistent with the weaker ligand field strength of bromide compared with chloride. The infrared bands due to quinoxaline are almost identical with those for the chloro-complex, and thus the structure of the bromide appears to be identical with that of the chloride; also, their *X*-ray powder photographs are almost identical.

The Complex $QCu(CH_3{\cdot}CO{\cdot}O)$.—The magnetic moment of the acetate is much lower (1·41 B.M.) than those of the other quinoxaline complexes, and lies in the region observed [10] for copper(II)–carboxylic acid compounds having dimeric structures similar to copper(II) acetate monohydrate. The room-temperature magnetic moment of the monohydrate is 1·43 B.M.[7] In the monohydrate the bridging acetate groups give rise to two C–O stretching frequencies,[11] at 1603 and 1418 cm.$^{-1}$. This compares with the two bands at 1621 and 1434 cm.$^{-1}$ observed for the quinoxaline complex. The low magnetic moment and the position of the C–O stretching bands suggest that the quinoxaline complex has the same dimeric structure as the monohydrate,[12] with quinoxaline replacing the water molecules. This is supported by the reflectance spectrum, which is very similar [8] to that of monopyridinecopper(II) acetate, which has a similar structure [13] to the hydrate, and the monohydrate itself.

The Complex $QCuSO_4,4H_2O$.—The infrared spectrum of the sulphate ion [11] (T_d symmetry) contains a very strong band in the region 1100—1140 cm.$^{-1}$ and a strong band at about 615 cm.$^{-1}$. The ν_1 vibration, although strictly forbidden, sometimes appears as a weak band at about 970 cm.$^{-1}$. The infrared spectrum of $QCuSO_4,H_2O$ contains a broad strong band at 1085, very similar to that in $CuSO_4,5H_2O$ at 1113 cm.$^{-1}$, and a medium band at 629 similar to one at 621 cm.$^{-1}$ in the pentahydrate. The forbidden ν_1 vibration which appears as a weak band at 982 cm.$^{-1}$ in the pentahydrate can just be seen as a shoulder at 980 on the 1057 cm.$^{-1}$ quinoxaline band. Thus, the sulphate group in the quinoxaline complex gives rise to an infrared spectrum very similar to that in the pentahydrate, that is, one possessing essentially T_d symmetry. In addition to bands due to quinoxaline and sulphate, the spectrum of $QCuSO_4,4H_2O$ contains a broad strong band due to water at 1600 cm.$^{-1}$. $CuSO_4,5H_2O$ [14] shows a vibrational mode, due to co-ordinated water, at

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[8] B. J. Hathaway, personal communication.

[9] J. D. Dunitz, *Acta Cryst.*, 1957, **10**, 307.

[10] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.

[11] K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.

[12] J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, 1953, **6**, 227.

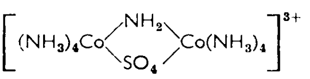
[13] G. A. Barclay and C. H. L. Kennard, *J.*, 1961, 5244.

[14] J. Fujita, K. Nakamoto, and M. Kobayashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3963.

875 cm.$^{-1}$, which is probably shifted to give the band of medium intensity at 928 cm.$^{-1}$ in the new complex.

The reflectance spectrum of the tetrahydrate is very similar to that reported[15] for $CuSO_4,5H_2O$ in which the band maximum occurs at 13,250 cm.$^{-1}$ compared with 13,510 cm.$^{-1}$ for the quinoxaline complex. In copper sulphate pentahydrate there are four oxygen atoms for the water molecules co-ordinated to the copper atom in a plane at about 2·0 Å, with the sulphate groups forming a bridge between copper atoms perpendicular to this plane. The fifth water molecule is held between water molecules attached to copper atoms and an oxygen of a sulphate group. In the quinoxaline complex the quinoxaline molecule may have replaced the fifth water molecule. Alternatively, the quinoxaline may be co-ordinated to the copper at right angles to the plane of the four water molecules. The sulphate group might then be present as a weakly co-ordinated unidentate ligand with a long metal–oxygen bond or as a purely ionic species. The infrared spectrum of the complex would agree with this. The environment of the copper would still consist of four water molecules as its nearest neighbours, as in the pentahydrate, and thus the spectra of the two compounds would be very similar.

The Complex $QCuSO_4$.—The anhydrous copper(II) sulphate–quinoxaline complex is prepared by heating the hydrated complex discussed above for 2 hr. at 110°. Analysis of the product obtained under a variety of heating conditions always showed a somewhat high copper and sulphate content and a low carbon content, indicating a copper : quinoxaline ratio of 1 : 0·9—0·95. The position of the reflectance spectra absorption band is shifted to 11,430 cm.$^{-1}$ from 13,510 cm.$^{-1}$ in the hydrate. This is consistent with SO_4^{2-} being a weaker ligand than water. The infrared spectrum of the sulphate group in the complex gives rise to absorption bands at 596, 626, 656, 954, 1000, 1160, and 1221 cm.$^{-1}$. A sulphate group which is co-ordinated through two oxygen atoms possesses C_{2v} symmetry and should therefore possess eight infrared-active vibrations. Nakamoto *et al.*[11] studied the complex (I) and found infrared absorption bands due to the bridging sulphate group at 462, 571, 610, 641, 995, 1050—1060, 1105, and 1170 cm.$^{-1}$. The infrared spectrum of $[Co(en)_2SO_4]Br$, which contains a chelate sulphate group, contains[16] bands due to the sulphate group at 515m, 632s, 647s, 993s, 1075vs, 1176vs, and 1211vs cm.$^{-1}$. The infrared spectrum of the sulphate group in $QCuSO_4$ clearly shows the sulphate group to be co-ordinated through two oxygen atoms, and the presence of a band at 1222 rather than at about 1170 cm.$^{-1}$ may indicate that the sulphate group is chelate rather than bridging. The quinoxaline will be present as a ligand bridging between adjacent copper atoms, thus giving a polymeric structure.



$$\left[(\mathrm{NH_3})_4\mathrm{Co}\begin{matrix}\mathrm{NH_2}\\ \\ \mathrm{SO_4}\end{matrix}\mathrm{Co}(\mathrm{NH_3})_4\right]^{3+}$$

(I)

The Complex $QCu(NO_3)_2$.—The infrared spectrum of $QCu(NO_3)_2$ contains, in addition to the bands due to quinoxaline, bands at 800vs, 1008vs, 1028vs, 1285vs, and 1300vs cm.$^{-1}$. Recently,[17] it was shown that both unidentate and bidentate nitrate groups give rise to bands in the regions 1531—1481, 1290—1253, 1034—970, and 800—781 cm.$^{-1}$. Thus, the complex $QCu(NO_3)_2$ clearly exhibits bands due to co-ordinated nitrate. The band at about 1500 cm.$^{-1}$ expected for co-ordinated nitrate will be masked by intense quinoxaline bands in this region. The quinoxaline will complete the distorted octahedral environment of the copper atom by bridging between adjacent copper atoms.

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[16] C. G. Barraclough and M. L. Tobe, *J.*, 1961, 1993.

[17] F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, 1963, **2**, 1162.