gilt. Das wird um so mehr der Fall sein, wenn $E_0$ den Wert $E_{0e}$ und $E$ den Wert $E_e$ gleich gut approximieren. Bei $Li^-$ und $O^-$ sind die Funktionen, die $E$ liefern, schlechtere Approximationen als diejenigen, die $E_0$ liefern. Bei $C^-$ werden sie fast gleich gut bzw. schlecht sein. Bei $F^-$ kann man sagen, daß wegen der Edelgaskonfiguration der Elektronen $E_e$ besser durch $E$ approximiert wird als $E_{0e}$ durch $E_0$. Der Wert 4,37 ist daher etwas zu groß.

Herrn Professor Dr. B. Kockel danke ich für die Anregung zu dieser Arbeit und für die stete Förderung.

# The Infra-Red Absorption Spectra of the Addition Complexes of Quinoline with Copper Salts

By C. S. Williams and K. F. Fouché

Department of Chemistry, University of Potchefstroom, Potchefstroom, South Africa

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The infra-red spectra of a number of halide, acetate and thiocyanate quinoline and quinolinium complexes of copper have been recorded for the first time. The significance of the frequency shifts of the quinoline bands in the complexes and the influence of the electronegativity of the halide ion on the frequency shifts in the monoquinoline cuprous halide complexes are discussed. Evidence is presented that the $Cu(NCS)_2 \cdot 2\,Q$ complex is probably binuclear.

The infra-red spectrum of pure quinoline (quinoline hereafter denoted by Q) has been frequently studied and tentative assignments were given for most of the observed bands [1–3]. In contrast to the extensively studied pyridine complexes, the infra-red spectra of the quinoline complexes with metal salts have received no attention at all.

A number of quinoline and quinolinium complexes with copper (I) and copper (II) halides, thiocyanate, acetate and nitrate have been synthesized. The infra-red spectra of the complexes were recorded in the range 4000 to 637 $cm^{-1}$. Small systematic changes in the positions of the main quinoline bands of the complexes were detected and correlated with the corresponding bands of pure quinoline liquid and with the electronegativity of the halide ion in the complex. Unfortunately the range of the spectrometer was unsufficient to detect the Me-Q stretching vibration which occurs below 600 $cm^{-1}$. The infra-red spectra of the thiocyanate quinoline complexes of Cu (II) and Cu (I) show that they are probably binuclear and mononuclear respectively.

## Results and discussion

### *Quinoline*

The infra-red spectrum of quinoline (liq.) is shown in Fig. 1 and the frequencies of vibrations are given in Table 1. The values of K. K. Deb [2] are also included for comparison in Table 1. Except for some small numerical differences in the frequencies and the appearance of a number of small bands on the wings of the main bands, the spectra are identical. The appearance of the small bands is attributed to the superior resolving power of the instrument used in this study.

### *Quinoline in the complexes*

The frequencies of the absorption bands of quinoline in the complexes $CuCl_2 \cdot 2\,Q$; $CuBr_2 \cdot 2\,Q$; $Cu(NCS)_2 \cdot 2\,Q$; $CuCl \cdot Q$; $CuBr \cdot Q$; $CuI \cdot Q$; $CuI \cdot 3\,Q$; $Cu(C_2H_3O_2)_2 \cdot Q$; $Cu(NCS) \cdot 2\,Q$ and $Cu(NO_3)_2 \cdot 2\,Q$ are also given in Table 1. The infra-red spectrum of $Cu(NCS)_2 \cdot 2\,Q$ is given in Fig. 1 as a representative illustration of the spectra of these complexes.

[1] L. J. Bellamy, The Infra-Red Spectra of Complex Molecules, Methuen, London 1959, p. 263.

[2] K. K. Deb, Indian J. Phys. **35**, 535 [1961].

[3] I. Ichishima, J. Chem. Soc. (Japan) **71**, 443 [1950].

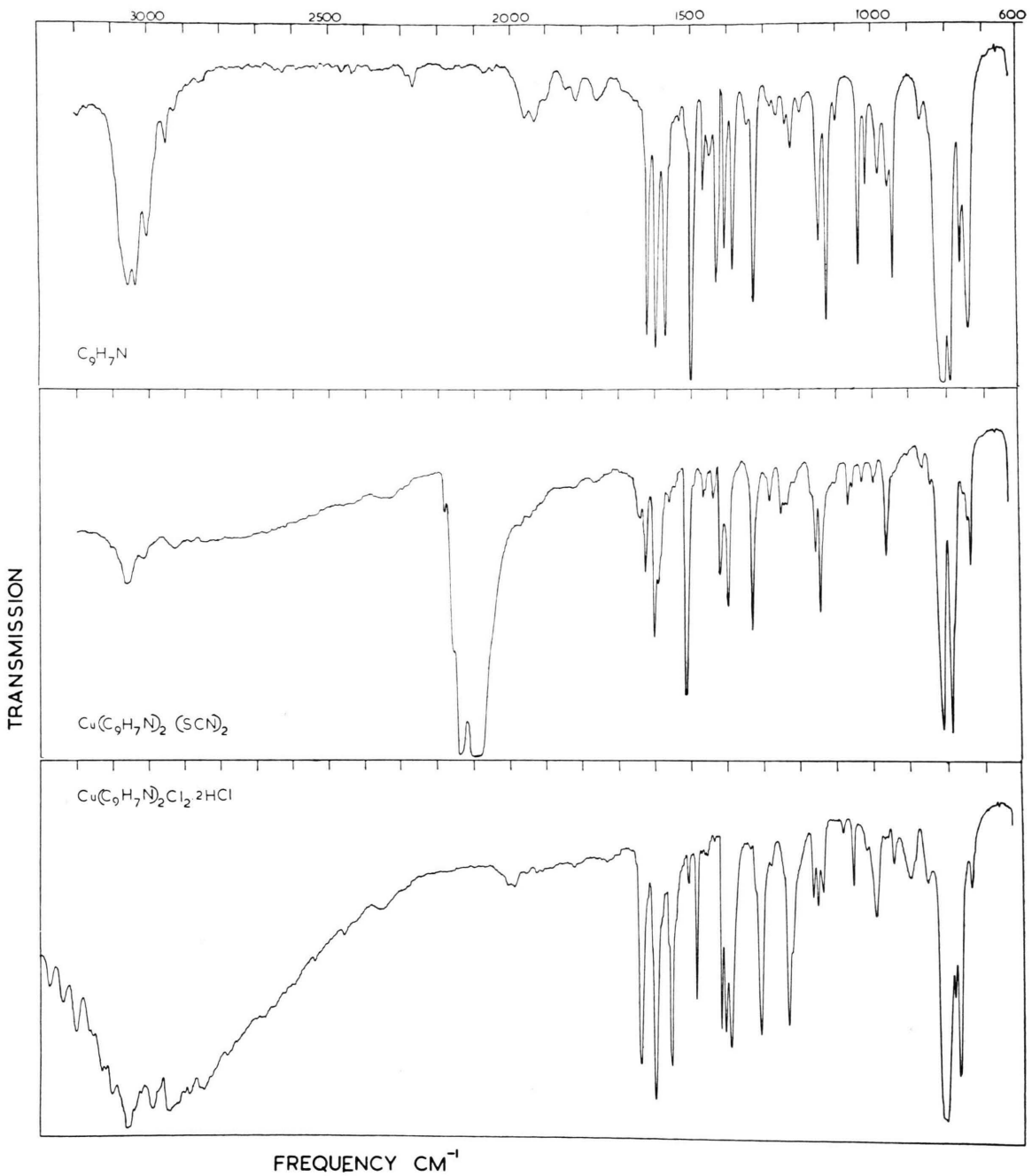



Fig. 1. The infra-red spectra of quinoline, $Cu(NCS)_2 \cdot 2\,Q$ and $CuCl_2 \cdot 2\,Q \cdot 2\,HCl$.

(a). The spectra of the various complexes resemble each other and that of quinoline very closely. Apart from some minor relative intensity changes, the only difference between the spectrum of pure quinoline and that of quinoline in the complexes is some small systematic frequency shifts. The positive frequency shifts of the characteristic quinoline bands at 1565, 1035, 1014, and 940 $cm^{-1}$, which are often accompanied by a reduction in relative intensity in the complexes, are given in Table 2.

| Q(K. K. Deb[2]) | Q(Present authors) | CuI · Q | CuBr · Q | CuCl · Q | $Cu(NCS) \cdot 2Q$ | $Cu(NCS)_2 \cdot 2Q$ | CuI · 3Q | $CuCl_2 \cdot 2Q$ | $CuBr_2 \cdot 2Q$ | $Cu(NO_3)_2 \cdot 2Q$ | $Cu(C_2H_3O_2)_2 \cdot Q$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| — | 3090 sh | 3090 sh | 3091 sh | 3091 sh | 3098 vw | 3095 vw | 3085 sh | 3097 w | 3096 w | 3098 w | 3094 sh |
| — | 3080 sh | 3080 w | 3077 w | 3079 w | 3080 w | 3080 w | 3079 sh | 3078 sh | 3079 sh | 3085 sh | 3083 w |
| — | 3070 sh | — | — | — | — | 3070 w | 3071 sh | — | — | — | — |
| — | 3058 sh | 3062 sh | 3058 sh | 3060 sh | 3062 sh | 3058 sh | 3060 sh | 3062 sh | 3061 sh | 3062 sh | 3059 w |
| — | 3047 s | 3053 m | 3047 m | 3046 m | 3051 w | 3045 w | 3052 m | 3046 m | 3043 m | 3047 m | 3048 sh |
| 3025 s | 3028 s | 3040 m | 3039 sh | 3033 sh | 3041 sh | — | 3029 m | 3038 m | 3035 m | 3039 m | 3037 sh |
| — | — | — | — | — | 3019 w | — | — | 3011 w | 3010 w | 3014 w | — |
| 3000 s | 3002 sh | 3006 w | 3005 w | 3002 w | 3002 w | 3008 vw | — | 3002 w | 3000 w | 3003 w | 3005 w |
| 2980 s | 2996 m | 2999 w | 2999 w | 2998 sh | 2996 sh | — | 2995 m | 2998 sh | 2996 sh | — | 2998 sh |
| — | 2972 sh | — | — | 2974 vw | 2975 vw | — | 2973 sh | — | — | — | 2976 vw |
| — | 2941 w | 2952 vw | 2950 vw | 2950 vw | 2950 vw | — | 2941 vw | 2956 vw | 2955 vw | 2938 w | — |
| 2900 vw | 2920 vw | — | — | 2920 vw | — | 2912 vw | 2920 vw | — | — | — | 2927 w |
| — | — | — | — | — | — | — | — | 2865 vw | 2865 vw | — | — |
| 2840 vw | 2852 vw | — | — | 2846 vw | 2848 w | — | — | 2847 vw | 2851 vw | — | — |
| — | — | — | — | — | — | — | — | — | — | + 2427 w | + 2470 vw |
| — | — | — | — | — | — | — | — | — | — | + 2393 sh | — |
| 2340 vw | — | — | — | — | — | — | — | — | — | — | — |
| 2310 w | — | — | — | — | — | — | — | — | — | — | — |
| 2270 vw | 2264 vw | 2276 vw | 2278 vw | 2275 vw | — | — | — | 2285 vw | 2285 vw | — | — |
| 2230 vw | — | — | — | — | + 2100 s | +2130 s | — | — | — | — | — |
| — | — | — | — | — | + 2051 w | +2080 vs | — | — | — | — | — |
| — | — | — | — | — | — | — | — | 1985 w | 1982 w | 1988 w | + 1970 vw |
| 1950 w | 1958 w | 1960 vw | 1963 vw | 1950 w | 1970 w | 1965 w | 1958 w | 1956 sh | 1956 vw | 1958 sh | 1950 vw |
| 1918 w | 1930 w | 1932 vw | 1936 w | 1930 w | 1940 w | — | 1929 vw | 1946 w | 1945 w | 1945 vw | 1921 vw |
| 1900 w | 1901 vw | — | — | 1905 w | — | — | — | 1906 vw | 1906 vw | 1905 vw | — |
| 1860 vw | — | — | — | — | — | — | — | — | — | — | — |
| 1835 vw | 1818 vw | 1810 vw | 1813 vw | 1825 vw | 1820 w | 1815 vw | 1815 vw | 1817 w | 1815 w | 1817 vw | 1822 vw |
| 1718 vw | 1760 vw | 1748 vw | 1752 vw | 1748 vw | 1768 w | 1756 vw | 1765 vw | 1760 vw | 1768 vw | 1767 w | 1765 w |
| — | — | — | — | — | — | — | — | 1739 vw | 1739 vw | — | + 1703 vw |
| — | — | — | — | — | — | — | — | — | — | — | + 1686 sh |
| — | — | — | — | — | — | — | — | — | — | — | + 1675 sh |
| — | — | — | — | — | — | — | — | 1693 vw | 1690 vw | — | + 1669 sh |
| — | — | — | — | — | — | — | — | — | — | — | + 1663 sh |
| — | — | — | — | — | — | +1646 sh | — | — | 1646 sh | 1647 sh | — |
| — | — | — | — | — | — | +1637 w | — | 1640 sh | — | — | + 1648 sh |
| — | — | — | — | — | — | +1631 w | — | — | 1635 sh | — | + 1638 sh |
| — | 1628 sh | 1628 sh | — | 1627 sh | 1628 sh | 1631 w | — | 1628 sh | 1628 sh | 1632 w | 1628 sh |
| — | 1620 sh | 1622 sh | 1622 sh | — | 1622 sh | — | 1620 sh | 1622 sh | 1622 sh | 1623 sh | — |
| 1610 m | 1616 sh | 1619 m | 1618 w | 1619 m | 1620 m | 1618 w | 1616 m | 1620 m | 1619 m | 1620 m | + 1618 vs |
| — | — | 1617 sh | 1614 sh | 1616 sh | 1611 sh | — | — | — | — | — | — |
| — | — | — | — | — | 1609 sh | — | — | — | — | — | — |
| — | — | — | — | — | 1608 sh | — | — | — | — | — | — |
| 1588 m | 1593 s | 1592 m | 1590 m | 1591 s | 1592 s | 1591 m | 1590 s | 1592 m | 1592 m | 1593 m | 1595 m |
| — | 1575 sh | 1576 w | 1574 sh | 1575 sh | — | 1576 sh | 1567 m | 1583 s | 1581 s | 1583 m | 1580 m |
| 1565 m | 1565 s | 1580 w | 1581 w | 1582 sh | 1578 m | 1581 m | 1575 w | 1577 sh | 1577 sh | 1575 sh | 1575 sh |
| — | — | 1567 sh | 1570 sh | 1568 sh | 1569 sh | 1568 sh | — | 1568 sh | 1569 sh | — | 1570 sh |
| — | 1556 sh | 1561 sh | — | 1560 sh | 1556 sh | 1551 sh | 1554 w | 1554 sh | 1553 sh | 1555 sh | 1556 sh |
| — | 1546 w | — | — | — | — | 1543 sh | — | 1550 w | 1548 w | 1550 w | 1552 sh |
| 1540 w | 1530 w | 1536 vw | 1534 vw | 1531 vw | 1530 vw | 1530 sh | — | 1532 sh | 1531 sh | 1539 sh | 1537 sh |
| — | 1504 sh | 1503 sh | 1503 sh | 1505 sh | 1508 sh | 1507 sh | — | 1506 sh | 1506 sh | 1506 sh | 1507 sh |
| 1495 s | 1497 s | 1500 s | 1499 s | 1500 s | 1501 s | 1501 s | 1497 s | 1503 s | 1501 s | 1504 s | 1502 s |
| — | 1488 sh | 1488 sh | 1485 sh | 1488 sh | 1488 sh | 1488 sh | 1488 sh | 1487 sh | 1488 sh | 1490 sh | 1486 sh |
| — | — | — | — | — | — | — | — | 1485 sh | 1483 s | 1483 s | — |
| 1465 vw | 1463 w | 1456 w | 1453 w | 1453 w | 1467 vw | 1458 vw | 1463 vw | 1461 m | 1459 m | 1461 m | 1460 sh |
| 1450 vw | 1448 w | 1452 sh | — | — | 1452 w | 1454 sh | 1442 w | 1452 sh | 1452 sh | 1455 sh | 1445 sh |
| 1427 m | 1425 s | 1428 w | 1428 w | 1429 w | 1428 m | 1430 vw | 1428 m | 1436 m | 1434 m | 1431 m | + 1418 vs |
| — | 1402 m | 1403 m | 1404 m | 1408 s | 1406 m | 1410 w | 1402 s | 1406 m | 1405 m | 1420 to 1360 + | 1403 sh |

Table 1. Continued next page.

| Q(K. K. Deb[2]) | Q(Present authors) | CuI · Q | CuBr · Q | CuCl · Q | Cu(NCS) · 2Q | $Cu(NCS)_2$ · 2Q | CuI · 3Q | $CuCl_2$ · 2Q | $CuBr_2$ · 2Q | $Cu(NO_3)_2$ · 2Q | $Cu(C_2H_3O_2)_2$ · Q |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1390 m | 1381 m | 1383 m | 1386 m | 1389 m | 1384 m | 1390 m | 1381 m | 1391 s | 1390 s | — | 1383 m |
| 1365 m | 1347 w | — | — | — | 1347 vw | — | 1342 vw | 1337 sh | 1334 sh | — | + 1358 m |
| 1310 s | 1322 s | 1318 s | 1319 s | 1324 s | 1321 m | — | 1321 s | 1326 m | 1325 m | 1325 s | 1330 m |
| — | — | — | — | — | — | — | — | — | — | + 1297 s | — |
| — | 1290 vw | — | — | — | — | 1278 w | 1287 vw | 1278 vw | 1277 vw | 1291 sh | 1288 w |
| — | 1261 vw | 1268 vw | 1268 vw | 1273 vw | 1264 vw | — | 1266 vw | — | — | — | + 1270 vw |
| 1230 vw | 1238 w | 1244 w | 1244 vw | 1245 w | 1240 w | 1245 w | 1239 w | 1246 w | 1246 w | 1248 w | 1250 w |
| 1210 vw | 1221 w | 1225 w | 1225 vw | 1222 w | — | 1235 w | 1220 vw | 1217 m | 1216 m | 1217 m | 1228 vw |
| 1185 vw | 1196 vw | 1202 w | 1204 w | 1202 vw | 1203 w | 1210 w | 1206 w | 1197 w | 1196 w | 1200 sh | — |
| — | 1150 sh | 1156 w | 1155 w | 1156 sh | 1153 w | 1150 w | 1155 w | 1150 sh | 1150 sh | 1163 w | 1163 w |
| 1135 w | 1144 m | 1144 w | 1143 w | 1146 w | 1148 w | — | 1147 w | 1146 m | 1147 m | 1149 w | 1148 w |
| — | — | — | — | — | — | 1136 m | — | 1138 m | 1138 m | 1139 m | 1134 w |
| 1110 s | 1121 s | 1127 m | 1127 w | 1130 w | 1128 m | 1118 sh | 1124 m | 1123 sh | 1125 sh | — | 1121 vw |
| 1090 vw | 1098 w | 1094 vw | 1092 vw | 1094 vw | 1100 vw | 1095 vw | 1097 vw | 1096 vw | 1095 vw | 1095 vw | 1105 vw |
| 1030 m | 1035 m | 1051 w | 1050 w | 1052 m | 1048 m | 1060 w | 1048 m | 1061 w | 1061 w | 1061 w | + 1052 m |
| — | — | — | — | — | — | 1048 vw | 1034 m | 1034 vw | 1032 vw | 1050 sh | 1031 w |
| 1010 w | 1014 m | 1021 w | 1021 w | 1020 w | 1021 w | 1021 vw | 1019 w | 1024 w | 1023 m | 1023 m | 1020 sh |
| — | — | — | — | — | — | — | 1011 vw | — | — | — | — |
| — | — | — | — | — | — | — | 1000 w | 1001 w | 1001 w | 1002 w | 998 w |
| — | 995 sh | — | — | 992 sh | 995 sh | — | 998 sh | 998 sh | 998 sh | 999 sh | — |
| — | — | — | — | — | 990 vw | 990 vw | — | — | — | 980 sh | 982 sh |
| 975 vw | 981 w | 986 w | 988 vw | 980 w | 981 vw | — | — | — | — | — | — |
| 950 vw | 952 w | — | — | — | — | — | 940 w | 962 m | 962 m | 962 m | 951 m |
| 932 m | 940 s | 955 w | 954 w | 954 w | 950 m | 956 w | — | — | — | — | — |
| — | — | — | — | — | + 932 sh | — | — | — | — | — | — |
| — | — | — | — | — | + 928 w | — | — | — | — | — | — |
| — | — | — | — | — | + 898 w | — | — | — | — | — | — |
| — | — | — | — | — | 892 sh | — | 869 vw | 863 m | 863 m | 864 m | — |
| — | 865 w | 864 vw | 861 vw | 860 vw | 867 w | 860 vw | 818 s | — | — | + 837 m | — |
| — | — | — | — | — | — | — | 813 s | 811 s | 811 s | 812 s | 815 s |
| — | 814 sh | 812 sh | 812 sh | 810 sh | 817 sh | 812 sh | 803 s | 800 sh | 800 sh | — | 800 sh |
| 800 vs | 802 s | 806 s | 806 s | 802 s | 806 s | 803 s | 784 sh | 785 sh | 785 sh | 785 sh | 789 sh |
| 755 m | 757 m | 779 s | 779 s | 777 s | 766 m | — | 757 w | 767 sh | 767 sh | 745 m | 765 w |
| — | — | — | — | — | + 751 m | — | 743 s | — | — | — | — |
| 730 m | 736 s | 732 s | 736 m | 737 m | 732 sh | 738 w | 730 s | 745 m | 744 s | 738 sh | 744 w |
| — | — | 727 sh | 726 sh | 727 m | 730 sh | 730 w | — | 738 sh | 738 sh | 715 vw | 736 sh |
| — | — | — | — | — | — | — | — | — | — | — | + 679 s |

vs=very strong; s=strong; w=weak; m=medium; vw=very weak; sh=shoulder.
+ vibrational frequencies due to anion group of complex.

Table 1. The absorption frequencies of quinoline, some copper salts and their complexes.

| Quinoline absorptions in $cm^{-1}$ | Shifts found in complexes | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | CuCl · Q | CuBr · Q | CuI · Q | CuI · 3Q | CuNCS · 2Q | $Cu(NSC)_2$ · 2Q | $CuCl_2$ · 2Q | $CuBr_2$ · 2Q | $Cu(C_2H_3O_2)$ · Q | $Cu(NO_3)_2$ · 2Q |
| 1565s | 17r | 16r | 15r | 2r | 13r | 16r | 18 | 16 | 15 | 18 |
| 1035m | 17 | 15 | 16 | 13 | 13 | 25r | 26r | 26r | — | 26r |
| 1014m | 6 | 7 | 7 | 5 | 7 | 7r | 10r | 9r | 6 | 9 |
| 940s | 14 | 14 | 15 | 0r | 10 | 16r | 22 | 22 | 11 | 22 |

r denotes reduced intensity, m=medium, s=strong.

Table 2. Characteristic positive frequency shifts in $cm^{-1}$ of some bands of quinoline on co-ordination.

The 1565 $cm^{-1}$ band is a member of a triad of strong and well defined absorption bands around 1600 $cm^{-1}$ (C – C and C – N stretching region in quinoline). The shift in the vibrational frequency of this band illustrates the perturbing effect of the co-ordinating metal ion (through the N of the quinoline) on these vibrations. There is a small amount of electronic transfer from the ring as required by the donor-acceptor nature of the bond. This causes the deviations in the C – N absorption frequencies.

(b). For the halide complexes there exists a definite trend in the extent of the shifts of some bands and the electronegativity of the halide [4, 5]. The stronger a charge transfer force acts (greater inductive effect) between an electron donor and acceptor, the more the C – N stretching and ring deformation vibrations for quinoline will be shifted to higher frequencies. The same effect is observed for the monoquinoline complexes of the cuprous halides as shown in Table 3. For the quinoline-rich cuprous halide complexes the inductive effect of the halogen on the quinoline vibrations will be greatly reduced as illustrated by the absorption frequencies of CuI·3 Q also given in Table 3.

| Quinoline absorptions | Corresponding absorptions of complexes in $cm^{-1}$ | | | |
|---|---|---|---|---|
| in $cm^{-1}$ | CuCl · Q | CuBr · Q | CuI · Q | CuI · 3Q |
| 1402 m | 1408 | 1404 | 1404 | 1402 |
| 1381 m | 1389 | 1386 | 1383 | 1381 |
| 1322 s | 1324 | 1319 | 1318 | 1321 |
| 1121 s | 1130 | 1127 | 1127 | 1124 |
| 736 s | 737 | 736 | 732 | 730 |

m=medium, s=strong.

Table 3. Effect of electronegativity of the halide on frequency shifts for the cuprous halide complexes.

*Anion-ligand vibrations*

(a) Thiocyanate group

Infra-red spectra provide a method for distinguishing between differently bound thiocyanate groups in complexes [6–8]. A shift toward higher frequencies in the C – N and C – S stretching modes (which occur at ca. 2000 $cm^{-1}$ and 750 $cm^{-1}$ respectively in the "free" thiocyanate ion) indicates an increase in bond order of the respective links. The extent of the frequency shift will depend on the donor-acceptor nature of the bond and therefore on the number and nature of the surrounding atoms. The effect of the relative number of electrons contained in the d-orbitals of the central metal ion is illustrated by the complexes examined by FUJITA et al. [9] in which the electron-rich Co(III)-complexes exhibit higher C – N stretching frequencies than the corresponding Cr(III)-complexes. Co-ordination to Cu(II) containing nine d-electrons results in an even higher triple-bond character of the C – N bond, and it would be expected that a thiocyanate group co-ordinated to more than one copper ion will exhibit a still higher stretching frequency. Thus SCN bound as bridging groups and terminally or ionically bound groups can be readily distinguished since the former would exhibit higher stretching frequencies.

As indicated in Table 4, Cu(NCS)·2 Q contains only one type of thiocyanate group, whilst the Cu(II)-complex in which the C – N vibration is doubled, is composed of two differently bound groups. The possibility of the splitting of the C – N vibration being due to a doubly degenerate bending mode is ruled out, since it would involve a much smaller difference in the observed frequencies. The C – N stretching frequencies of the thiocyanate group in the two complexes are higher than that of the "free" thiocyanate ion, indicating a higher

| CuNCS | CuNCS · 2 Q | shift ($cm^{-1}$) | $Cu(NCS)_2$ | $Cu(NCS)_2 \cdot 2Q$ | shift ($cm^{-1}$) |
|---|---|---|---|---|---|
| 2170 s | 2100 s | ca. 70 | 2150 | 2130 s<br>2080 vs | ca. 20<br>ca. 70 |

s=strong, vs=very strong.

Table 4. Influence of complex formation on the C–N stretching vibrations of the thiocyanate group.

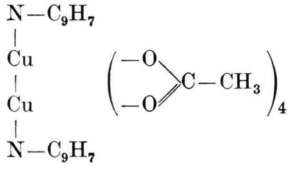
[4] F. WATARI and K. KINNMAKI, Chem. Abstr. **9**, 9594 a [1962].
[5] G. S. RAO, Z. Anorg. Allg. Chem. **304**, 176 [1960].
[6] J. CHATT and L. A. DUNCANSON, Nature **178**, 997 [1956].
[7] M. M. CHAMBERLAIN and J. C. BAILAR, J. Amer. Chem. Soc. **81**, 6412 [1950].
[8] C. J. H. SCHUTTE, Z. Naturforschg. **18 a**, 525 [1963].
[9] J. FUJITA, K. NAKAMATO, and M. KOBAYASHI, J. Amer. Chem. Soc. **78**, 3295 [1956].

triple-bond character and thus also a shorter bond length.

When compared with the results of CHATT and DUNCANSON [6], the vibrational frequencies at 2100 $cm^{-1}$ and 2080 $cm^{-1}$ in the Cu(I) and Cu(II) complexes respectively can be attributed to thiocyanate groups outside the co-ordination sphere, whilst the 2130 $cm^{-1}$ band in the Cu(II) complex can be correlated with a bridging NCS group linked to two Cu atoms, viz. $-Cu-S-C\equiv N\rightarrow Cu-$, implying the $Cu(NCS)_2 \cdot 2\,Q$ complex to be binuclear. The Cu(I) thiocyanate complex seems to be mononuclear with the NCS ion outside the co-ordination sphere.

(b) Acetate

The acetate ion functions as a unidentate ligand in compounds like nickel dihydrate, but as a bidentate bridge in cupric acetate monohydrate [10] in which the ion is linked to two copper atoms. The bond orders of the two types of C–O bonds become different in the complexes thus causing an even greater separation of the asymmetric and symmetric C–O stretching frequencies than exists in the free acetate ion at ca. 1578 and ca. 1425 $cm^{-1}$ respectively. ABLOV et al [11] have shown by means of electron-paramagnetic resonance that the green monoquinoline complex with cupric acetate displays a triplet state similar to that found in the monohydrate of cupric acetate so that the former complex is also a dimer with structure



In this investigation it has been found that few or no shifts occur in the positions of the asymmetric and symmetric C–O stretching bonds in passing from the salt to the complex so that the difference in absorption frequencies, ca. 200 $cm^{-1}$ (see Table 5), which is well above the difference for the symmetric and asymmetric stretching modes, ca. 150 $cm^{-1}$ for the free acetate ion, nearly remains constant. The acetate is thus probably similarly bound in the salt and the complex.

[10] K. NAKAMATO, J. FUJITA, S. TANAKA, and M. KOBAYASHI, J. Amer. Chem. Soc. **79**, 4904 [1957].

| Compounds | Assignments | | Difference in $cm^{-1}$ |
|---|---|---|---|
| | symmetric stretching band | asymmetric stretching band | |
| free acetate ion | 1425 | 1578 | 153 |
| $Cu(C_2H_3O_2)_2 \cdot H_2O$ | 1400 | 1605 | 205 |
| $Cu(C_2H_3O_2)_2 \cdot Q$ | 1418 | 1618 | 200 |

Table 5. The C–O stretching vibrational bands of the acetate group in $cm^{-1}$.

*The quinolinium complexes*

There exists a sharp difference between the spectra of the free quinoline molecule, the co-ordinated quinoline and of the quinolinium ion in the complexes. The presence of an extra hydrogen atom on the nitrogen increases the number of vibrational modes. An intense and widely spread band with several absorption maxima, due to the symmetrical N–H stretching vibrations occurs between 3200 and 2700 $cm^{-1}$ (see Fig. 1). In quinoline this is limited to a triplet of major bands at 3047, 3028, and 2996 $cm^{-1}$.

The spectra of $CuCl_2 \cdot 2\,Q \cdot 2\,HCl$ and $CuBr_2 \cdot 2\,Q \cdot 2\,HBr$ are identical implying that both structures can be written $(HQ^+)_2 \cdot CuX_4^{2-}$. The shifts in some principal absorptions of quinoline in these complexes in which the quinolinium ion exists, are given in Table 6.

| Absorptions for quinoline | Corresponding absorptions in quinolinium complexes | shifts in $cm^{-1}$ |
|---|---|---|
| 1616 s | 1633 | +17 |
| 1565 s | 1550 | −15 |
| 1497 s | 1480 | −17 |
| 1425 s | 1416 | − 9 |
| 1381 m | 1392 | +11 |
| 1322 s | 1310 | −12 |

s=strong, m=medium.

Table 6. Band shifts for quinoline absorptions in the quinolinium ion in $cm^{-1}$.

The strong bands at 1463, 785, and 736 $cm^{-1}$ for quinoline are absent or show greatly reduced intensity, while the intensity of the 1221 and 1238 $cm^{-1}$ bands are increased in the spectra of the quinolinium complexes.

[11] A. V. ABLOV, Y. V. YABLOKOV, and I. I. ZHERU, Dokl. Akad. Nauk, SSSR **141**, 1116 [1961].

| $CuCl_2 \cdot 2\,Q \cdot 2\,HCl$ | $CuBr_2 \cdot 2\,Q \cdot 2\,HBr$ | $CuCl_2 \cdot 2\,Q \cdot 2\,HCl$ | $CuBr_2 \cdot 2\,Q \cdot 2\,HBr$ | $CuCl_2 \cdot 2\,Q \cdot 2\,HCl$ | $CuBr_2 \cdot 2\,Q \cdot 2\,HBr$ |
|---|---|---|---|---|---|
| 3268 w | 3262 w | 2532 w | 2531 vw | 1152 w | 1149 w |
| 3233 w | 3228 w | 2452 vw | 2450 vw | 1139 w | 1136 w |
| 3193 m | 3191 m | 1990 vw | 1985 vw | 1081 vw | 1080 vw |
| 3159 m | 3157 m | 1634 s | 1632 s | 1053 w | 1050 w |
| 3149 m | 3148 m | 1620 sh | 1622 sh | 1019 vw | 1018 vw |
| 3122 s | 3122 m | 1615 sh | 1615 sh | 1000 w | 1000 sh |
| 3114 s | 3112 s | 1594 s | 1593 s | 990 w | 989 w |
| 3093 s | 3093 s | 1575 sh | 1573 sh | 944 w | 942 w |
| 3072 sh | 3068 sh | 1556 sh | 1557 sh | 899 w | 894 vw |
| 3062 sh | 3060 sh | 1551 s | 1550 s | 850 w | 848 w |
| 3050 s | 3048 sh | 1544 sh | 1545 sh | 814 sh | 814 sh |
| 3036 s | 3030 sh | 1540 sh | 1537 sh | 810 s | 810 s |
| 3015 s | 3015 sh | 1532 sh | 1531 sh | 803 s | 803 s |
| 2987 sh | 2987 sh | 1521 sh | 1520 sh | 782 m | 782 s |
| 2981 s | 2980 s | 1505 w | 1502 w | 767 s | 766 m |
| 2967 sh | 2967 sh | 1483 s | 1480 m | 752 sh | 750 sh |
| 2933 s | 2932 s | 1452 vw | 1450 vw | 738 w | 733 vw |
| 2920 s | 2917 s | 1418 s | 1416 s | | |
| 2895 s | 2895 sh | 1408 s | 1404 m | | |
| 2880 s | 2880 s | 1394 s | 1392 s | | |
| 2852 sh | 2853 s | 1378 sh | 1375 sh | | |
| 2840 s | 2842 s | 1325 sh | 1325 sh | | |
| 2824 s | 2822 sh | 1311 s | 1308 s | | |
| 2780 s | 2776 m | 1280 w | 1279 w | | |
| 2768 m | 2762 m | 1246 sh | 1246 sh | | |
| 2702 sh | 2700 sh | 1237 s | 1233 s | | |
| 2675 m | 2675 w | 1225 m | 1221 m | | |
| 2650 w | 2648 w | 1192 vw | 1195 sh | | |
| 2620 w | 2620 w | 1167 w | 1163 w | | |

vs=very strong; s=strong; m=medium; w=weak; vw=very weak; sh=shoulder.

Table 7. Absorption frequencies of the quinolinium complexes.

The frequencies of all the absorption bands of the two quinolinium complexes are given in Table 7.

## Experimental

The spectra of the complexes were recorded as crystalline solids in KBr discs with a Perkin Elmer Model 221 spectrophotometer with sodium-chloride and grating-interchange optics, and the spectrum of quinoline as the pure liquid at room temperature. The spectra of the complexes were obtained in vaseline mulls as well, but no solid state anomalies, i. e. ion-exchange or pressure-shifting of the bands in the pellet spectra were found.

The complexes were prepared from Analytical Reagent-grade copper salts and chemically pure quinoline. The quinoline was twice distilled and the fraction boiling at 232 °C was collected.

### *Preparation methods*

(Unless otherwise stated, all preparation methods are according to Fouché [12].)

$CuCl_2 \cdot 2\,Q$: Cupric chloride dihydrate was thorougly mixed with an excess of quinoline and the resulting light-blue compound washed with $CCl_4$.

Calculated: % Cu = 16.07; % Q = 65.8; % Cl = 18.11.
Found : % Cu = 16.11; % Q = 66.4; % Cl = 18.31.

$CuBr_2 \cdot 2\,Q$: Quinoline was added to a methanolic cupric bromide solution; the mixture was shaken for 1 hour. The precipitate was light-brown in colour.

Calculated: % Cu = 13.14; % Q = 55.0; % Br = 33.10.
Found : % Cu = 13.06; % Q = 53.8; % Br = 33.09.

$Cu(NCS)_2 \cdot 2\,Q$: Molecular quantities of $CuCl_2 \cdot 2\,Q$ and KCNS were mixed, moistened with methanol and triturated for one hour. The resulting green compound was washed with water and dried at 65 °C.

Calculated: % Cu = 14.51; % NCS = 26.53.
Found : % Cu = 14.36; % NCS = 26.74.

$Cu(NO_3)_2 \cdot 2\,Q$ was prepared according to Pfeiffer and Pimmer [13]. The final product was a light-blue substance.

Calculated: % Cu = 14.26; % Q = 57.9; % N = 12.6.
Found : % Cu = 14.29; % Q = 58.0; % N = 12.7.

$Cu(C_2H_3O_2)_2 \cdot Q$: $Cu(C_2H_3O_2)_2 \cdot H_2O$ was dissolved in an excess of quinoline at 100 °C. A precipitate consisting of light-green crystals formed on cooling and was washed with $CCl_4$.

[12] K. F. Fouché, MSc.-dissertation, University of Potchefstroom, Potchefstroom, South Africa 1963.

[13] P. Pfeiffer and V. Pimmer, Z. Anorg. Chem. **48**, 107 [1906].

Calculated: % Cu = 20.45; % acetate = 38.0; % N = 4.5.
Found : % Cu = 20.57; % acetate = 37.1; % N = 4.5.

CuJ · 3 Q: CuJ was dissolved in boiling quinoline. After cooling, a precipitate consisting of orange crystals was formed. The crystals were filtered off, washed with a very dilute solution of quinoline in $CCl_4$ and dried in a desiccator over $H_2SO_4$ (c) for 18 hours.

CuJ · 3 Q when heated at 70 °C loses two molecules of quinoline and turns yellow, forming CuJ · Q.

Calculated for CuJ · 3 Q: % Cu = 10.92; % J = 21.95.
Found : % Cu = 11.00; % J = 21.96.

CuCl · Q, CuBr · Q, CuJ · Q and Cu(NCS) · 2 Q [14] were prepared by dissolving the corresponding salts in boiling quinoline. The needle-shaped crystals which formed on cooling were filtered off and washed with $CCl_4$. The colours ranged from dark-yellow for the chloride complex, yellow for the bromide to light-yellow for the iodide complex. The thiocyanate complex consisted of dark-yellow needles.

For CuCl · Q:
Calculated: % Cu = 27.85; % Cl = 15.53; % N = 6.1.
Found : % Cu = 27.89; % Cl = 15.41; % N = 6.2.

For CuBr · Q:
Calculated: % Cu = 23.32; % Br = 29.32; % N = 5.1.
Found : % Cu = 23.37; % Br = 29.25; % N = 5.2.

For CuI · Q:
Calculated: % Cu = 19.88; % I = 39.71.
Found : % Cu = 19.92; % I = 39.53.

For Cu(NCS) · 2 Q:
Calculated: % Cu = 16.73; % NCS = 15.29.
Found : % Cu = 16.62; % NCS = 15.07.

$CuCl_2 \cdot 2\,Q \cdot 2\,HCl$: $CuCl_2 \cdot 2\,H_2O$ was dissolved in an ethanolic hydrochloric acid solution. Light-yellow needles separated from the solution. The crystals were filtered off and dried in a desiccator over NaOH pellets.
Calculated:
% Cu = 13.63; % Cl = 30.49; % Q = 55.5; % N = 6.0.
Found:
% Cu = 13.42; % Cl = 30.35; % Q = 55.8; % N = 6.1.

$CuBr_2 \cdot 2\,Q \cdot 2\,HBr$ was synthesized according to PFEIFFER and PIMMER [13]. The precipitate was found to consist of black micaceous crystals.
Calculated: % Cu = 9.87; % Br = 49.68; % N = 4.4.
Found : % Cu = 9.84; % Br = 49.61; % N = 4.6.

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[14] J. H. WALTON and C. L. LIANG, J. Amer. Chem. Soc. **41**, 1027 [1919].