

# Spin-Spin Coupling in Binuclear Complexes. IV.<sup>1</sup> Substituted Heterocyclic N-Oxide Complexes of Copper(II) Halides. III.<sup>2</sup> Magnetic and Spectral Properties of Complexes with Substituted Quinoline N-Oxides

Robin Whyman, Derek B. Copley, and William E. Hatfield

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received January 20, 1967

**Abstract:** The magnetic and spectral properties of 1:1 and 1:2 copper(II) halide complexes with substituted quinoline N-oxides have been investigated. The condensed complexes may be divided into three types based on these properties and dependent upon the donor characteristics of the ligands, as measured by their  $pK_a$  values. Members of the first class, containing ligands of relatively high  $pK_a$ 's, display the subnormal magnetic moments typical of the pyridine N-oxide-copper(II) halide systems. Complexes derived from ligands of low  $pK_a$  values constitute the second class, and the third is formed by species of empirical formula  $(CuCl_2)_mL_n$ , where  $1 < m/n < 2$ , containing ligands of intermediate  $pK_a$ 's. Both of these types exhibit normal magnetic moments. The differences in magnetic behavior are correlated with a change in structure from oxygen-bridged to halogen-bridged entities, a conclusion which is supported by far-infrared spectral evidence for the chlorides. The 1:2 complexes all display normal magnetic moments which are temperature independent.

Recently there has been considerable interest in the copper(II) halide complexes of substituted pyridine N-oxides.<sup>2,3</sup> From the observed antiferromagnetic behavior of the 1:1 complex of pyridine N-oxide with copper(II) chloride, the presence of a di- or polymeric species was inferred. This was later substantiated by an X-ray crystallographic examination,<sup>4</sup> where it was shown that the dimeric molecule consists of two distorted tetrahedra sharing an edge with the oxygen atoms of the pyridine N-oxide ligands acting as bridging units. The temperature dependence of the magnetic susceptibility of this and other 1:1 complexes with substituted pyridine N-oxides has been interpreted in terms of a spin-spin coupling occurring *via* a superexchange mechanism through the orbitals of the bridging oxygen atoms. The observed copper-copper internuclear distance of 3.23 Å for the pyridine N-oxide complex is consistent with the super-exchange mechanism. These studies have now been extended to include the magnetic and spectral properties of copper(II) halide complexes with substituted quinoline N-oxides, some of which show extremely interesting and unusual magnetic behavior, not observed with the pyridine N-oxide complexes. A previous communication indicated the preliminary results of our investigations,<sup>5</sup> and these are now reported in full.

## Experimental Section

**Preparation of the Substituted Quinoline N-Oxides.** Quinoline N-oxide, the 4-substituted quinoline N-oxides, and 6-methylquinoline N-oxide were prepared by the method of Ochiai.<sup>6</sup> Other literature methods were employed for the preparation of 4-chloro-

6-methylquinoline N-oxide,<sup>7</sup> 4-nitro-6-methylquinoline N-oxide,<sup>7</sup> and 3-nitro-6-methylquinoline N-oxide.<sup>8</sup> The melting points of all the ligands were consistent with reported values.

**Preparation of the Complexes. Method A.** In general, the complexes were prepared by mixing a solution of  $CuCl_2 \cdot 2H_2O$  or  $CuBr_2$  in warm ethanol, 2-propanol, or 1-butanol with a stoichiometric amount of the ligand in the same solvent. The products either crystallized immediately or after standing for a short time and were filtered, washed well with the solvent, and dried in the air.

**Method B.** In some cases the use of stoichiometric quantities for the preparation of 1:1 complexes resulted in the isolation of 1:2 species. The condensed complex was then prepared using a tenfold excess of the copper(II) halide in hot 1-butanol as solvent.

**Analytical Data.** Microanalyses for carbon, hydrogen, and nitrogen were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Copper analyses were determined by EDTA titration using Snazox as indicator.<sup>9</sup> The analytical data are presented in Table I together with the method of preparation of the complexes.

**$pK_a$  Determinations.** The  $pK_a$  values of the ligands were determined spectrophotometrically<sup>10</sup> using the ultraviolet absorption spectra of the free and protonated bases in solutions of known pH. Since the pH values involved were too low to be accurately measured with a pH meter, values of the acidity functions  $H_0$  were employed.<sup>11</sup> The spectra of the two species were compared and significant differences in peak maxima noted. In general, for the neutral, and presumably unprotonated solution of the ligand, one peak was found to increase markedly in intensity from that present in the strongly acidic, protonated solution. The wavelength of this peak was noted. A series of solutions, of pH approximately equal to the estimated  $pK_a$  of the ligand, and differing from each other by 0.2 pH unit, was prepared. The optical densities of these solutions were measured at the wavelength of the above peak, and by comparison with the spectra of protonated and unprotonated species the extent of protonation could be determined. Thus, for each solution a value of the  $pK_a$  of the ligand was obtained and the mean of these results gave the accurate  $pK_a$  value.

**Magnetic Susceptibility Determinations.** Magnetic susceptibilities were determined as a function of temperature by the Faraday method, using equipment and procedures which have been described

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Table I. Analytical Data

| Ligand                             | Halide            | Method of prepn | Ligand: salt ratio | C, %  |       | H, %  |       | N, %  |       | Cu, % |       |
|------------------------------------|-------------------|-----------------|--------------------|-------|-------|-------|-------|-------|-------|-------|-------|
|                                    |                   |                 |                    | Found | Calcd | Found | Calcd | Found | Calcd | Found | Calcd |
| 4-Methylquinoline N-oxide          | CuCl <sub>2</sub> | A               | 1:1                | 41.03 | 40.85 | 2.89  | 3.07  | 4.77  | 4.77  | 21.40 | 21.65 |
|                                    | CuBr <sub>2</sub> | A               | 1:1                | 31.60 | 31.37 | 2.48  | 2.35  | 3.49  | 3.66  | 16.42 | 16.62 |
| 6-Methylquinoline N-oxide          | CuCl <sub>2</sub> | B               | 1:1                | 40.86 | 40.85 | 3.12  | 3.07  | 4.58  | 4.77  | 21.79 | 21.65 |
|                                    | CuBr <sub>2</sub> | B               | 1:1                | 31.20 | 31.37 | 2.40  | 2.35  | 3.89  | 3.66  | 16.50 | 16.62 |
| Quinoline N-oxide                  | CuCl <sub>2</sub> | B               | 1:1                | 38.94 | 38.67 | 2.57  | 2.52  | 5.20  | 5.01  | 22.73 | 22.72 |
|                                    | CuBr <sub>2</sub> | A               | 1:1                | 29.10 | 29.33 | 1.87  | 1.92  | 3.90  | 3.80  | 16.82 | 17.24 |
| 4-Chloro-6-methylquinoline N-oxide | CuCl <sub>2</sub> | B               | 2:3                | 30.32 | 30.38 | 2.38  | 2.04  | 3.53  | 3.54  | 23.84 | 24.11 |
|                                    | CuCl <sub>2</sub> | A               | 2:1                | 45.42 | 46.04 | 2.44  | 3.10  | 5.25  | 5.36  | 12.16 | 12.18 |
|                                    | CuBr <sub>2</sub> | B               | 1:1                | 28.80 | 28.80 | 1.87  | 1.93  | 3.30  | 3.36  | 15.00 | 15.24 |
| 4-Chloroquinoline N-oxide          | CuBr <sub>2</sub> | A               | 2:1                | 40.15 | 39.34 | 2.72  | 2.64  | 4.59  | 4.59  | 10.16 | 10.41 |
|                                    | CuCl <sub>2</sub> | B               | 2:3                | 28.24 | 28.32 | 1.53  | 1.57  | 3.20  | 3.67  | 25.45 | 25.00 |
|                                    | CuCl <sub>2</sub> | A               | 2:1                | 43.52 | 43.78 | 2.46  | 2.43  | 5.68  | 5.44  | 12.88 | 12.87 |
| 3-Nitro-6-methylquinoline N-oxide  | CuBr <sub>2</sub> | A               | 1:1                | 26.89 | 26.80 | 1.52  | 1.49  | 3.53  | 3.47  | 15.73 | 15.77 |
|                                    | CuBr <sub>2</sub> | A               | 2:1                | 37.32 | 37.09 | 2.29  | 2.06  | 4.60  | 4.81  | 10.56 | 10.91 |
|                                    | CuCl <sub>2</sub> | B               | 3:4                | 31.11 | 31.32 | 2.17  | 2.10  | ...   | 7.31  | 22.30 | 22.10 |
| 4-Nitro-6-methylquinoline N-oxide  | CuCl <sub>2</sub> | A               | 2:1                | 44.47 | 44.26 | 3.19  | 2.97  | 10.31 | 10.32 | 11.56 | 11.71 |
|                                    | CuBr <sub>2</sub> | B               | 1:1                | 28.25 | 28.09 | 2.03  | 1.89  | 6.31  | 6.55  | 14.52 | 14.86 |
|                                    | CuBr <sub>2</sub> | A               | 2:1                | 37.73 | 38.03 | 2.81  | 2.55  | 8.55  | 8.87  | 10.20 | 10.06 |
| 4-Nitroquinoline N-oxide           | CuCl <sub>2</sub> | B               | 1:1                | 35.87 | 35.47 | 2.35  | 2.38  | 7.68  | 8.27  | 18.81 | 18.76 |
|                                    | CuCl <sub>2</sub> | A               | 2:1                | 44.04 | 44.26 | 2.97  | 2.97  | 10.18 | 10.32 | 11.78 | 11.71 |
|                                    | CuBr <sub>2</sub> | A               | 2:1                | 38.61 | 38.03 | 2.94  | 2.55  | 8.41  | 8.87  | 9.95  | 10.06 |
| 4-Nitropyridine N-oxide            | CuCl <sub>2</sub> | B               | 1:1                | 33.40 | 33.30 | 1.78  | 1.86  | 8.43  | 8.63  | 19.50 | 19.57 |
|                                    | CuCl <sub>2</sub> | A               | 2:1                | 42.07 | 41.99 | 2.50  | 2.35  | 10.74 | 10.88 | 12.20 | 12.34 |
|                                    | CuBr <sub>2</sub> | A               | 2:1                | 36.52 | 35.81 | 2.16  | 2.00  | 9.17  | 9.28  | 10.46 | 10.53 |
|                                    | CuCl <sub>2</sub> | B               | 1:1                | 21.99 | 21.85 | 1.66  | 1.46  | 10.05 | 10.20 | 23.09 | 23.14 |

previously.<sup>1</sup> Mercury tetrathiocyanatocobaltate(II) was used as magnetic susceptibility standard,<sup>12</sup> and diamagnetic corrections were estimated from Pascal's constants.<sup>13</sup>

**Spectral Measurements.** For the  $pK_a$  measurements ultraviolet absorption spectra were recorded with a Beckman DU spectrophotometer. Diffuse reflectance spectra of solid samples were measured using the standard reflectance attachment and employing a block of magnesium carbonate as standard. Infrared spectra in the range 1300–250  $\text{cm}^{-1}$  were recorded with a Perkin-Elmer 521 double-beam spectrometer.

## Results

**The Complexes.** As the data in Table I show, not all possible complexes were obtained. Thus 2:1 complexes of the ligands 6-methyl-, 4-methyl-, and quinoline N-oxide with both  $\text{CuCl}_2$  and  $\text{CuBr}_2$  did not form, and 4-nitro-6-methyl- and 4-nitroquinoline N-oxide yielded 1:1 adducts only with  $\text{CuCl}_2$ . The use of both methods A and B for the preparation of 1:1 copper(II) chloride complexes with several ligands did not yield the expected products but species of a polymeric nature, as indicated by elemental analyses. Thus both 4-chloro-6-methyl- and 4-chloroquinoline N-oxide afforded compounds of empirical formula  $(\text{CuCl}_2)_3\text{L}_2$  and 3-nitro-6-methylquinoline N-oxide yielded a species which analyzed as  $(\text{CuCl}_2)_4\text{L}_3$ .

**Magnetic Data.** Magnetic susceptibilities were determined at 300, 196, and 77°K only, since these measurements sufficed to distinguish between different types of magnetic behavior. A considerable body of data already exists for the full temperature variation (350–77°K) of the magnetic susceptibility of substituted pyridine N-oxide-copper(II) halide complexes,<sup>2,3</sup> and it was considered unnecessary to repeat these detailed measurements for the quinoline N-oxide derivatives. The magnetic data, together with the observed  $pK_a$

values of the ligands, are presented in Table II. The molar magnetic susceptibilities were calculated on the basis of a molecular weight per copper(II) ion in all cases, and magnetic moments were obtained from the expression  $\mu_{\text{eff}} = 2.84(\chi_{\text{m}}^{\text{cor}}T)^{1/2}$ . It is immediately apparent that the complexes fall into two principal classes. The first class includes the condensed complexes, the majority of which display the low magnetic moments indicative of the binuclear oxygen-bridged unit which has been established for the pyridine N-oxide-copper(II) chloride complex.<sup>4</sup> The second class contains the complexes with a ligand:salt ratio of 2, which all exhibit normal magnetic moments, *i.e.*, a moment greater than or equal to 1.73 BM per copper(II) ion, and which are virtually independent of temperature. The condensed complexes may be further subdivided into those displaying low magnetic moments, the 1:1 species with normal magnetic moments, and thirdly, the compounds of polymeric nature which also show magnetically normal behavior. With the exception of the 3-nitro-6-methylquinoline N-oxide derivative, all the condensed copper(II) bromide complexes exhibit low magnetic moments. It may be significant that no polymeric species are formed when the salt is copper bromide.

**$pK_a$  Data.** The  $pK_a$  values of the ligands lie in the anticipated order, both by comparison with their pyridine N-oxide analogs and on the basis of simple electronic effects. The previously reported value of  $-0.8$  for the  $pK_a$  of 4-nitroquinoline N-oxide<sup>3c</sup> does not agree with our experimental results. However, the value of  $-1.39$  observed here is more consistent with the  $pK_a$  of  $-1.7 \pm 0.15$  reported for 4-nitropyridine N-oxide.<sup>14</sup>

**Far-Infrared Spectra.** Table III records the maxima observed in the spectra of the ligands and their copper(II) chloride complexes in the region 400–250  $\text{cm}^{-1}$ .

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Table II. Magnetic and  $pK_a$  Data

| Ligand                             | $pK_a$ | $\mu_{eff}$ , BM per Cu(II) ion |      |                     |             |      |      |
|------------------------------------|--------|---------------------------------|------|---------------------|-------------|------|------|
|                                    |        | Condensed complex               |      |                     | 2:1 complex |      |      |
|                                    |        | 300°                            | 196° | 77°                 | 300°        | 196° | 77°  |
| Copper(II) Chloride Complexes      |        |                                 |      |                     |             |      |      |
| 4-Methylquinoline N-oxide          | 1.44   | 0.56                            | 0.43 | 0.38                |             |      |      |
| 6-Methylquinoline N-oxide          | 1.01   | 0.41                            | 0.30 | 0.24                |             |      |      |
| Quinoline N-oxide                  | 0.86   | 0.37                            | 0.30 | 0.23                |             |      |      |
| 4-Chloro-6-methylquinoline N-oxide | 0.61   | 1.69                            | 1.66 | 1.55 <sup>a,b</sup> | 1.97        | 1.93 | 1.85 |
| 4-Chloroquinoline N-oxide          | 0.47   | 2.07                            | 2.04 | 1.89 <sup>a,b</sup> | 1.88        | 1.85 | 1.83 |
| 3-Nitro-6-methylquinoline N-oxide  | -0.69  | 1.91                            | 1.91 | 1.90 <sup>a,c</sup> | 1.81        | 1.87 | 1.82 |
| 4-Nitro-6-methylquinoline N-oxide  | -1.20  | 1.92                            | 2.01 | 1.96                | 1.87        | 1.89 | 1.92 |
| 4-Nitroquinoline N-oxide           | -1.39  | 2.13                            | 2.12 | 2.14                | 1.86        | 1.89 | 1.85 |
| Copper(II) Bromide Complexes       |        |                                 |      |                     |             |      |      |
| 4-Methylquinoline N-oxide          | 1.44   | 0.40                            | 0.43 | 0.34                |             |      |      |
| 6-Methylquinoline N-oxide          | 1.01   | 0.60                            | 0.31 | 0.24                |             |      |      |
| Quinoline N-oxide                  | 0.86   | 0.36                            | 0.32 | 0.21                |             |      |      |
| 4-Chloro-6-methylquinoline N-oxide | 0.61   | 0.38                            | 0.28 | 0.28                | 1.82        | 1.87 | 1.87 |
| 4-Chloroquinoline N-oxide          | 0.47   | 0.39                            | 0.34 | 0.30                | 1.83        | 1.90 | 1.82 |
| 3-Nitro-6-methylquinoline N-oxide  | -0.69  | 1.72                            | 1.75 | 1.75                | 1.98        | 1.90 | 1.95 |
| 4-Nitro-6-methylquinoline N-oxide  | -1.20  |                                 |      |                     | 1.85        | 1.88 | 1.84 |
| 4-Nitroquinoline N-oxide           | -1.39  |                                 |      |                     | 1.83        | 1.88 | 1.81 |

<sup>a</sup> 1:1 complexes not formed here. <sup>b</sup> Empirical formula  $(CuCl_3)_3L_2$ . <sup>c</sup> Empirical formula  $(CuCl_2)_4L_3$ .

Table III. Far-Infrared Spectra in the Region 400–250  $cm^{-1}$  <sup>a</sup>

|   |           |           |           |           |           |           |
|---|-----------|-----------|-----------|-----------|-----------|-----------|
| Pyridine N-oxide                                  |           |           |           |           |           |           |
| CuCl <sub>2</sub> -L                              | 397 m     |           |           | 330 w, sh | 311 vs    |           |
| CuCl <sub>2</sub> -L <sub>2</sub>                 | 385 m     |           |           |           | 310 s     | 286 s     |
| 4-Methylquinoline N-oxide                         |           | 363 s     |           |           |           |           |
| CuCl <sub>2</sub> -L                              |           | 357 m     | 334 vs    | 325 s, sh |           |           |
| 6-Methylquinoline N-oxide                         |           | 359 m     |           |           |           |           |
| CuCl <sub>2</sub> -L                              |           | 362 m     | 340 m, sh | 328 s     |           |           |
| Quinoline N-oxide                                 | 390 vw    | 372 w     |           | 327 w, sh | 313 m     | 296 w, sh |
| CuCl <sub>2</sub> -L                              | 393 w, sh |           | 344 s     | 332 s     |           |           |
| 4-Chloro-6-methylquinoline N-oxide                | 392 m     | 355 w     | 336 m     |           | 302 w, sh | 298 m     |
| (CuCl <sub>2</sub> ) <sub>3</sub> -L <sub>2</sub> |           |           | 345 w     |           | 307 m, sh | 280 s     |
| CuCl <sub>2</sub> -L <sub>2</sub>                 | 396 w     |           | 336 w, sh | 320 m     |           | 290 s     |
| 4-Chloroquinoline N-oxide                         |           | 350 w     | 335 m     | 326 w, sh |           |           |
| (CuCl <sub>2</sub> ) <sub>3</sub> -L <sub>2</sub> | 388 m     | 347 m     |           | 317 w, sh | 308 s     | 290 s     |
| CuCl <sub>2</sub> -L <sub>2</sub>                 | 392 w     |           | 335 m     |           | 310 s     | 300 s, sh |
| 3-Nitro-6-methylquinoline N-oxide                 |           | 355 m     |           | 329 w     |           | 285 w     |
| (CuCl <sub>2</sub> ) <sub>4</sub> -L <sub>3</sub> |           |           | 335 w     |           | 306 m, sh | 290 s, sh |
| CuCl <sub>2</sub> -L <sub>2</sub>                 | 390 m     | 352 w, sh | 342 s     |           |           |           |
| 4-Nitro-6-methylquinoline N-oxide                 | 380 m     |           |           | 315 w     | 300 w     | 280 m     |
| CuCl <sub>2</sub> -L                              |           |           | 342 w     |           | 308 s, sh | 280 vs    |
| CuCl <sub>2</sub> -L <sub>2</sub>                 | 395 m     | 380 w, sh | 334 w, sh | 316 vs    |           |           |
| 4-Nitroquinoline N-oxide                          |           |           | 350 w     | 326 m     | 305 m, sh |           |
| CuCl <sub>2</sub> -L                              |           |           | 342 w     |           | 307 vs    | 290 s     |
| CuCl <sub>2</sub> -L <sub>2</sub>                 | 397 m     | 385 w     | 335 w, sh | 318 s     |           |           |

<sup>a</sup> Maxima which are italicized are assigned as copper-chlorine stretching frequencies. w = weak, m = medium, and s = strong intensity; v = very and sh = shoulder.

The spectra of the 1:1 and 2:1 adducts of pyridine N-oxide with copper(II) chloride are also included. Previous far-infrared spectral studies on complexes containing metal-halogen bonds indicate that metal-chlorine stretching frequencies occur in the range 250–350  $cm^{-1}$  and metal-bromine frequencies from below 200 to 250  $cm^{-1}$ .<sup>15</sup> Thus for the complexes discussed here the observation of infrared-active metal-chlorine stretching frequencies may be anticipated, whereas it is likely that the corresponding metal-bromine vibrations will lie outside the range of the instrument, the lower limit of which occurs at *ca.* 245  $cm^{-1}$ . Several of the ligands show no absorptions in the range 250–350  $cm^{-1}$ , and consequently the metal-chlorine vibrations may be assigned without difficulty. Although

(15) R. J. H. Clark, *Spectrochim. Acta*, **21**, 955 (1965).

maxima were observed with some ligands in this region of the spectrum, the bands present in the complexes were considerably more intense and may be assigned as infrared-active metal-chlorine stretching frequencies with a reasonable degree of certainty. Those peaks which are italicized in Table III are assigned as metal-chlorine stretching vibrations. For the copper(II) bromide complexes, as anticipated, the situation is considerably less clear. The region 290–350  $cm^{-1}$  is frequently free of absorptions, further substantiating the assignment of the metal-chlorine stretching frequencies. Below 290  $cm^{-1}$  spectra of all the bromides display an area of increasing absorption and several show maxima at *ca.* 250  $cm^{-1}$ . However, the bands were very broad and indistinct at this wavelength and are not recorded here.

Table IV. Diffuse Reflectance Spectra<sup>a</sup>

| Ligand                             | Maxima, m $\mu$                       |        |        |        |        |        |        |
|------------------------------------|---------------------------------------|--------|--------|--------|--------|--------|--------|
|                                    |                                       |        |        |        |        |        |        |
|                                    | Condensed CuCl <sub>2</sub> Complexes |        |        |        |        |        |        |
| 4-Methylquinoline N-oxide          | 390                                   | 420 sh | 500 sh | 610    | 730    | 875 sh |        |
| 6-Methylquinoline N-oxide          | 375                                   | 420    | 510 sh | 620 sh | 755    | 860 sh |        |
| Quinoline N-oxide                  | 380                                   | 430    | 510 sh | 610 sh | 720    | 850 sh |        |
| 4-Chloro-6-methylquinoline N-oxide | 385                                   |        | 530 sh |        | 835    | 900 sh |        |
| 4-Chloroquinoline N-oxide          | 385                                   | 450 sh | 520 sh | 570 sh | 840    | 900 sh |        |
| 3-Nitro-6-methylquinoline N-oxide  | 345                                   | 390 sh | 520 sh |        | 830    | 900 sh |        |
| 4-Nitro-6-methylquinoline N-oxide  |                                       | 410 sh | 550 sh |        | 840    |        |        |
| 4-Nitroquinoline N-oxide           | 350                                   |        | 530 sh |        | 840    | 930 sh |        |
|                                    | Condensed CuBr <sub>2</sub> Complexes |        |        |        |        |        |        |
| 4-Methylquinoline N-oxide          | 400                                   | 440 sh | 475 sh | 560 sh | 730    | 900 sh |        |
| 6-Methylquinoline N-oxide          |                                       | 420    | 480 sh | 510 sh | 735    |        |        |
| Quinoline N-oxide                  | 400                                   | 430 sh | 500 sh |        | 730    | 880 sh |        |
| 4-Chloro-6-methylquinoline N-oxide | 400                                   |        | 490 sh | 540 sh | 735    | 900 sh |        |
| 4-Chloroquinoline N-oxide          | 400                                   |        | 510    |        | 740    | 900 sh |        |
| 3-Nitro-6-methylquinoline N-oxide  | 365, 410 sh                           |        |        |        | 790    | 900 sh |        |
|                                    | 2:1 CuCl <sub>2</sub> Complexes       |        |        |        |        |        |        |
| 4-Chloro-6-methylquinoline N-oxide |                                       | 420 sh |        | 520 sh | 680 sh | 810    |        |
| 4-Chloroquinoline N-oxide          | 370                                   | 420 sh |        | 510 sh | 680 sh | 815    |        |
| 3-Nitro-6-methylquinoline N-oxide  | 380                                   |        |        | 520 sh | 760    | 820 sh |        |
| 4-Nitro-6-methylquinoline N-oxide  | 350                                   | 420 sh | 450 sh |        | 570 sh | 620    | 785    |
| 4-Nitroquinoline N-oxide           | 390 sh                                | 460 sh |        | 550    |        | 890    | 960 sh |

<sup>a</sup> sh = shoulder.

**Visible Spectra.** The diffuse reflectance spectra of the complexes are summarized in Table IV and representative spectra of the condensed complexes exhibited in Figures 1 and 2. Since the complexes were found to

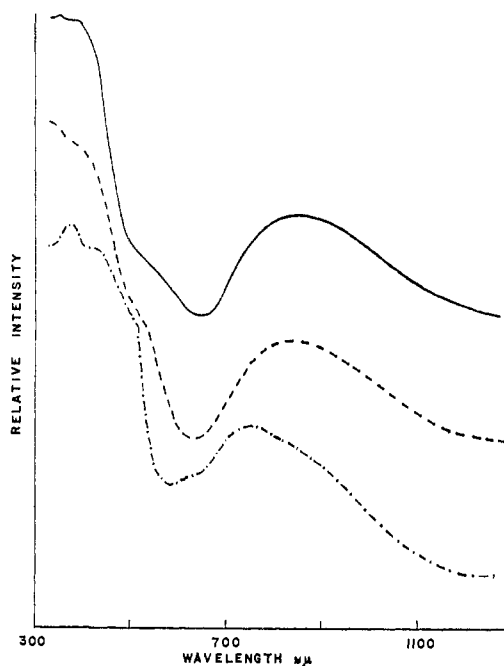


Figure 1. Diffuse reflectance spectra of three representative condensed copper(II) chloride complexes: - · - ·, CuCl<sub>2</sub>-4-methylquinoline N-oxide; - - - -, (CuCl<sub>2</sub>)<sub>2</sub>-(4-chloro-6-methylquinoline N-oxide)<sub>2</sub>; —, CuCl<sub>2</sub>-4-nitroquinoline N-oxide.

decompose in solution, no solution spectra are recorded. The copper(II) bromide complexes were all rather dark in color and several of the 2:1 compounds black. It was necessary to dilute the black compounds with magnesium carbonate in order to obtain a measurable spectrum, and even then only indistinct broad bands were observed. Consequently, the reflectance spectra of the 2:1 adducts of the ligands with copper(II)

bromide are not reported here. Figure 1 includes representative spectra of the three classes of condensed copper(II) chloride complexes. The main feature of interest is the shift in position of the band occurring at 700–900 m $\mu$  dependent upon the class of complex formed. For the compounds displaying low magnetic

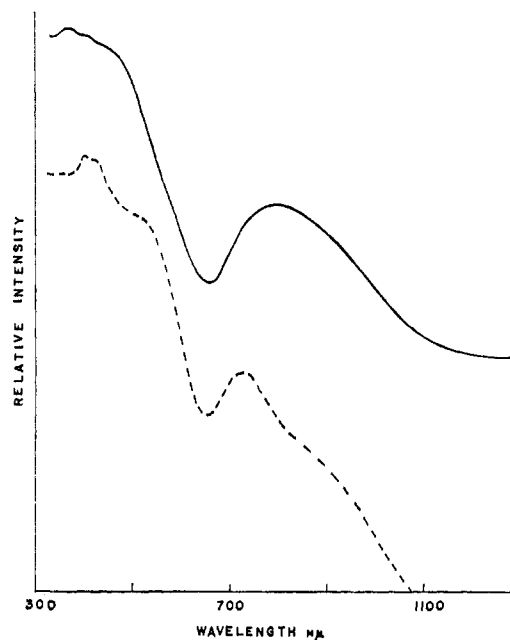


Figure 2. Diffuse reflectance spectra of two representative 1:1 copper(II) bromide complexes: - - - -, CuBr<sub>2</sub>-quinoline N-oxide; —, CuBr<sub>2</sub>-3-nitro-6-methylquinoline N-oxide.

moments, the maximum occurs at *ca.* 750 m $\mu$ , with a shoulder at *ca.* 875 m $\mu$ , and these are shifted to 850 and 900 m $\mu$ , respectively, in the magnetically normal complexes. In addition, a shoulder at *ca.* 570 m $\mu$  occurs in the spectra of the polymeric compounds but is absent for the other two classes. With the exception of 3-nitro-6-methylquinoline N-oxide, spectra of the 1:1 complexes of the ligands with copper(II) bromide are

extremely similar. Figure 2 shows a comparison of the spectrum of the copper(II) bromide complex of quinoline N-oxide with that of 3-nitro-6-methylquinoline N-oxide.

### Discussion

**Magnetic Data.** Based on the similarity of the magnetic behavior of the complexes displaying low magnetic moments with that of the copper(II) halide-pyridine N-oxide series, the presence of a similar structure may be inferred, *i.e.*, a dimeric molecule composed of two copper atoms bridged by the oxygen atoms of the N-oxide system. Because of the extremely small forces measured for these complexes with low magnetic susceptibilities, the values of  $\mu_{\text{eff}}$  are only accurate to within 0.1 BM. Thus it is not possible to make any comments concerning the trend of these values. The previously reported 1:1 complexes of this type all exhibit low magnetic moments, with the exception of the copper(II) chloride 4-nitroquinoline N-oxide derivative, which is reinvestigated here. This complex has a room-temperature magnetic moment of 2.13 BM, which is temperature independent. The hitherto unreported 1:1 complex of copper(II) chloride with 4-nitropyridine N-oxide was prepared by mixing a hot 1-butanol solution of the ligand with a large excess of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  dissolved in hot 1-butanol. The product crystallizes as yellow-orange plates and has been characterized by elemental analysis. It shows a room-temperature magnetic moment of 1.01 BM which decreases to 0.33 BM at 77°K.

The normal magnetic moment of  $\text{Cu}(4\text{-nitroquinoline N-oxide})\text{Cl}_2$  has been interpreted in terms of the electronic effects incurred by the introduction of the nitro group to the 4 position of the quinoline ring.<sup>3c</sup> Muto and Jonassen postulate that an electron-attracting entity such as the nitro group will tend to reduce the electron density in the N-O bond (of the quinoline N-oxide system) and consequently the electron density in the  $\pi$  orbitals of the bridging oxygen atom. The interaction between the unpaired electrons in the  $\pi$  orbitals of the copper ions and oxygen  $\pi$  electrons is thus lessened, and the observed magnetic moment will be greater than that of the unsubstituted quinoline N-oxide complex. By this argument the energy difference between the singlet and triplet states is expected to be much greater for the copper(II) chloride complex of 4-nitroquinoline N-oxide than with the quinoline N-oxide derivative itself. The observed magnetic moments indicate that this is the case. However, if the electronic effects of the substituents are the only factors influencing the variation of singlet-triplet splitting energies, then these values for the condensed 4-nitroquinoline N-oxide and 4-nitropyridine N-oxide-copper(II) chloride complexes should be of comparable magnitude. The observed room-temperature magnetic moments of 2.13 and 1.01 BM, respectively, indicate that this is not so and that the "electronic" effect of 4-nitroquinoline N-oxide is considerably greater. Thus it becomes apparent that additional factors should be taken into consideration.

An alternative approach is to consider the increased steric requirements of the quinoline N-oxide system when compared with pyridine N-oxide. It is possible that the decreased donor strength of 4-nitroquinoline N-

oxide with respect to the unsubstituted quinoline N-oxide, *coupled* with the steric factors, cause a change in the structural properties of the molecule. It has been shown that binuclear species formed by bridging copper ions with chloride ions do not tend to be diamagnetic,<sup>16</sup> and thus a structure containing chloride bridges rather than oxygen bridges would account for the observed magnetic properties.

Thus for the condensed copper(II) chloride complexes, ligands with relatively low donor strengths, *i.e.*, very low  $\text{p}K_a$  values, would give rise to chloride-bridged species, whereas ligands with high donor strengths afford the usual oxygen-bridged species. For ligands of intermediate donor strengths a third class of compound is formed, members of which display a high magnetic moment and possess polymeric, halogen-bridged structures.

All the 1:1 copper(II) bromide complexes prepared in this study, with the exception of the 3-nitro-6-methylquinoline N-oxide derivative, exhibited low magnetic moments. The one exception possibly contains bromide bridges. No compounds of polymeric nature are formed with copper(II) bromide, and this may be due to the reduced tendency of the bromide ion, as compared with the chloride ion, to act as a bridging group.

The magnetic properties of the 4-nitropyridine N-oxide-copper(II) chloride complex may be explained solely in terms of the electronic effects of the substituent, and no change in structure from the oxygen-bridged parent compound of the series need be invoked.

Both copper(II) chloride and copper(II) bromide complexes with two molecules of the substituted quinoline N-oxide exhibit normal magnetic moments which are virtually independent of temperature.

**Far-Infrared Spectra.** The far-infrared spectral data provide support for the suggestion that there is a structural difference between the classes of condensed complexes. In this discussion it should be recognized that the terms "terminal" and "bridging" are used only in a relative sense. It is probable that a chloride ion bonded directly to one copper ion will interact to some extent with neighboring copper ions and in such a sense could then be termed as bridging. However, for our purposes a terminal chlorine atom is defined as one which is bonded to a copper ion when the binuclear oxygen-bridged species is known to be present, and a bridging chloride ion as one which is bridging two copper ions to form a dimeric or polymeric molecule. Two distinct types of bridging chlorine atoms may be envisaged: firstly, those which are symmetrically disposed between the two copper atoms giving equal bond lengths and, secondly, those which are unsymmetric giving rise to one short and one long copper-chlorine bond distance.

Although the literature contains numerous references to metal-chlorine vibrations of bridging chlorine atoms in copper(II) chloride complexes, the evidence for terminal copper-chlorine stretching frequencies is rather meager, presumably owing to the lack of suitable compounds. Thus the complex  $\text{Cu}(\text{pyridine})_2\text{Cl}_2$  is polymeric in the solid state and its structure composed of distorted octahedra connected by bridging chlorine atoms.<sup>17</sup> In each octahedron there are two long (3.05

(16) P. H. Vossos, L. D. Jennings, and R. E. Rundle, *J. Chem. Phys.*, **32**, 1590 (1960); R. D. Willett, C. Dwiggins, Jr., R. Kruh, and R. E. Rundle, *ibid.*, **38**, 2429 (1963).

(17) J. D. Dunitz, *Acta Cryst.*, **10**, 307 (1957).

A) and two short (2.28 Å) copper–chlorine bonds. In the far-infrared spectrum of this compound, absorptions attributed to copper–chlorine stretching vibrations occur at 228 and 287  $\text{cm}^{-1}$ , and these probably represent the vibrations of the long and short bonds, respectively.<sup>18,19</sup> Conversely, for steric reasons, the complex  $\text{Cu}(\text{quinoline})_2\text{Cl}_2$  cannot contain two bridging chlorine atoms of the above type since the presence of the quinoline ring results in a copper–chlorine “long” bond distance too great to give rise to a stretching frequency.<sup>18</sup> Thus the assignment of a copper–chlorine stretching mode at 330  $\text{cm}^{-1}$  should represent the vibration of the copper–chlorine “short” bond, which is also bridging in character. The addition of substituents adjacent to the nitrogen atom in pyridine complexes of this type has a pronounced effect on the metal–halogen stretching frequency,<sup>18,20</sup> on substituting the 2 and 5 positions with various groups, the maxima are found to occur in the range 323–309  $\text{cm}^{-1}$ , whereas, for substituents in the 3 and 4 positions, corresponding peaks occur at 294–278  $\text{cm}^{-1}$ . Recently a report of the far-infrared spectra of some substituted quinoxaline derivatives of copper(II) halides indicates that for these compounds terminal metal–chlorine bonds show absorptions at 368–337  $\text{cm}^{-1}$ , and bridging bonds occur at *ca.* 320  $\text{cm}^{-1}$ .<sup>21</sup>

Considering the available evidence, it becomes apparent that the values of metal–chlorine stretching frequencies are very dependent upon the ligand used, even when the structures of the complexes are thought to be the same. However, as a rough guide, the dividing line between bridging and terminal metal chlorine stretching frequencies may be considered to lie at *ca.* 330–340  $\text{cm}^{-1}$ .

The structure of the 1:1 complex of pyridine N-oxide is known to contain copper–chlorine bonds which do not interact with any neighboring copper atoms,<sup>4</sup> and thus these are terminal in character. The far-infrared spectrum of this complex shows maxima at 311 (vs) and 330  $\text{cm}^{-1}$  (w, sh) which may be attributed to copper–chlorine stretching frequencies. Thus for the quinoline N-oxide complexes, we may infer that the observation of metal–chlorine stretching vibrations at frequencies higher than, say, 320  $\text{cm}^{-1}$  indicates the presence of terminal metal–chlorine bonds and hence oxygen-bridged structures.

For clarity, maxima assigned as metal–chlorine stretching vibrations in the condensed copper(II) chloride–quinoline N-oxide complexes are summarized in Table V. In the compounds with low magnetic moments and presumably oxygen-bridged structures, maxima observed at *ca.* 330 and 340  $\text{cm}^{-1}$  are assigned as terminal metal–chlorine stretching frequencies. These bands are absent in the spectra of complexes with normal magnetic moments and here two peaks at *ca.* 280 and 300  $\text{cm}^{-1}$  are observed in all cases. This significant shift to lower wavelength, which correlates with the change in magnetic properties, is considered to reflect the difference between structures containing terminal and bridging metal–chlorine bonds. In support of this conclusion the magnitude of the shift, *ca.*

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(19) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

(20) C. W. Frank and L. B. Rogers, *ibid.*, **5**, 615 (1966).

(21) D. E. Billing, A. E. Underhill, D. M. Adams, and D. M. Morris, *J. Chem. Soc., Sect. A*, 902 (1966).

Table V. Summary of Metal–Halogen Stretching Vibrations for the Condensed Copper(II) Chloride Complexes<sup>a</sup>

| Ligand                             | $\text{cm}^{-1}$ |           |           |           |
|------------------------------------|------------------|-----------|-----------|-----------|
|                                    |                  |           |           |           |
| 4-Methylquinoline N-oxide          | 334 vs           | 325 s, sh |           |           |
| 6-Methylquinoline N-oxide          | 340 m, sh        | 328 s     |           |           |
| Quinoline N-oxide                  | 344 s            | 332 s     |           |           |
| 4-Chloro-6-methylquinoline N-oxide |                  |           | 307 m, sh | 280 s     |
| 4-Chloroquinoline N-oxide          |                  |           | 308 s     | 290 s     |
| 3-Nitro-6-methylquinoline N-oxide  |                  |           | 306 m, sh | 290 s, sh |
| 4-Nitro-6-methylquinoline N-oxide  |                  |           | 308 s, sh | 280 vs    |
| 4-Nitroquinoline N-oxide           |                  |           | 307 vs    | 290 s     |
| Pyridine N-oxide                   | 330 w, sh        | 311 vs    |           |           |

<sup>a</sup> w = weak, m = medium, s = strong intensity; v = very and sh = shoulder

35–45  $\text{cm}^{-1}$ , is of a similar order to that observed with the quinoxaline complexes mentioned above.<sup>21</sup>

X-Ray crystallographic evidence for the 2:1 complex of pyridine N-oxide with copper(II) chloride shows the presence of the same basic structure as in the corresponding 1:1 species.<sup>22</sup> In the far-infrared spectrum of the former complex, two metal–chlorine stretching frequencies are observed at 310 and 286  $\text{cm}^{-1}$ . Although the oxygen bridged unit is still present, the inclusion of an extra pyridine N-oxide ligand into the coordination sphere of each copper ion presumably has the effect of weakening the metal–chlorine bonds, thus causing a reduction in the metal–halogen stretching frequencies.

Since this compound displays a subnormal magnetic moment, whereas all the 2:1 quinoline N-oxide complexes show normal magnetic properties, it is not possible to effect comparisons. However, in view of the magnetic results and the relatively low metal–halogen stretching frequencies, it seems likely that the latter compounds possess polymeric halogen-bridged structures.

Spectra of the 2:1 derivatives with ligands containing nitro groups show only one band attributable to a metal–chlorine stretching vibration, and these occur at slightly higher frequencies than the mean value of 300  $\text{cm}^{-1}$  for complexes not containing nitro substituents. In particular, the 3-nitro-6-methylquinoline N-oxide complex shows a maximum at 342  $\text{cm}^{-1}$ . The explanation of this is not clear.

**Visible Spectra.** The spectra of the condensed copper(II) chloride complexes may be divided into two main band systems, the first occurring at 350–450  $\mu\text{m}$  and the second at 700–850  $\mu\text{m}$ , of which the relative intensity of the latter is considerably less. The first band system is probably associated with charge-transfer transitions, and the second may be attributed to transitions within the d shell. Most of the bands are obviously multiple in character, and an indistinct shoulder is observed in all cases at about 900  $\mu\text{m}$  on the side of the lower energy band. The shift in position of the maximum associated with the d–d transition, which correlates with the differences in magnetic proper-

(22) J. C. Morrow, private communication.

ties of the complexes, probably reflects the differing environments of the copper ion in the two cases.

Except for the appearance of an intense band at *ca.* 500  $m\mu$ , spectra of the 1:1 copper(II) bromide derivatives are essentially similar to those of the chlorides displaying low magnetic moments. Also, the shoulder at 900  $m\mu$  is more pronounced in the case of the bromides. The origin of the 500- $m\mu$  band is uncertain, although as seen in Figure 1 spectra of the chlorides do show shoulders of much weaker relative intensity in this region. As with the condensed chloride complexes with high magnetic moments, the spectrum of the 1:1 copper(II) bromide-3-nitro-6-methylquinoline N-oxide derivative is significantly different from those of the corresponding complexes displaying low magnetic moments. As indicated in Table IV, the d-d band is shifted from *ca.* 730  $m\mu$  down to 790  $m\mu$  in the bromide-bridged species. This again is probably an indication of the different environments of the copper ion in the oxygen-bridged and bromide-bridged species.

The spectra of the 2:1 complexes with copper(II) chlorides show similar features to those of the con-

densed complexes. The maxima due to transitions within the d shell are shifted to slightly higher energy in the 2:1 derivatives.

### Conclusion

The spectral and magnetic properties of the condensed copper(II) halide complexes of substituted quinoline N-oxides indicate that either oxygen-bridged or halogen-bridged derivatives may be formed. The experimental evidence indicates that there must be a critical relationship between such factors as the donor properties and steric requirements of the ligands and the lattice energies of the various compounds in favoring the formation of one species over another.

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## The Dissociative Interchange Mechanism for the Formation of Acidopentaamminecobalt(III) Ions<sup>1</sup>

Cooper H. Langford and Warren R. Muir

*Contribution from the Moore Laboratory of Chemistry, Amherst College, Amherst, Massachusetts 01002. Received January 21, 1967*

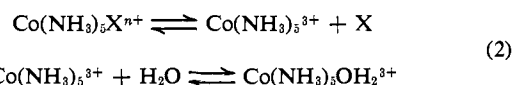
**Abstract:** The rates of formation of the complex ions,  $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$ , are discussed with special attention to the rate of reaction in the outer-sphere complex (or ion pair)  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+} \cdots \text{X}^{(3-n)-}$ . (New data are presented for entry of chloride and thiocyanate ions at 45° and unit ionic strength.) It is observed that the rates are similar for all anions studied so far and are a nearly constant fraction (0.2) of the water exchange rate for  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ . These results may be understood in terms of an activation process which is *dissociative*, leading to a *transition state* in which entering and leaving ligands are at most weakly bound *but* in which no intermediate of significant lifetime is formed. The similarity of rates of entry implies weak binding in the transition state. The anion entry rates appear to be related to the water exchange rate through a statistical factor connected with the probability that an anion is to be found in an outer coordination sphere site when a cobalt-water dissociation event occurs.

This paper is concerned with the kinetics and equilibrium of reaction 1, where X is a univalent anionic ligand or sulfate and *n* is 2 or 1, respectively. Two



mechanistic pathways for this process have often been discussed, and neither seems to give an entirely felicitous account of the details. In one case,<sup>2</sup> the process has been regarded as a simple nucleophilic attack of the entering group on the complex, leading to a concerted substitution which is bimolecular and adequately represented by eq 1. The alternative account<sup>3</sup> suggests

the participation of five-coordinate intermediate of the pathway represented by



The kinetics of eq 2 require the prediction that X and H<sub>2</sub>O compete for the intermediate. Strong evidence against eq 2 was presented by Pearson and Moore<sup>4</sup> who were able to show for the case of X = Br<sup>-</sup> or NO<sub>3</sub><sup>-</sup> that addition of SCN<sup>-</sup> to the solution did not lead to any detectable direct production of  $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ . The experiment is conclusive because sufficient kinetic and equilibrium data are available to predict<sup>3</sup> the rate of capture of the intermediate by SCN<sup>-</sup> if the reaction were going by mechanism 2.

The alternative account which focuses attention on the bimolecularity of the substitution is unsatisfactory in the

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