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The Structure and Properties of Complexes Formed between Aromatic N-Oxides and Copper(II) Compounds

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A variety of complexes may be formed between aromatic N-oxides and copper(II) compounds. The complexes have been classified as (a) low magnetic moment 1:1 complexes, (b) low and normal magnetic moment 2:1 dimeric complexes, (c) *trans* and distorted *cis* 2:1 monomeric complexes with normal magnetic moments, (d) polymeric complexes, (e) adducts of the above complexes, and (f) miscellaneous complexes. The structures of these complexes are discussed and the infrared spectra and magnetic properties are rationalized in terms of molecular structure and intermolecular interactions.

Introduction

There have been many reports on the physical properties of complexes formed between aromatic N-oxides and copper(II) halide compounds since their inital preparation a few years ago.[1-18] We initially were interested in these complexes because of interactions between the metal ions, which resulted in reduced magnetic moments. An understanding of the isolated magnetic interactions and the chemical properties of these systems should permit us to synthesize complexes with specific magnetic properties. After a preliminary study had been completed,[13] it was evident that the chemistry of copper(II) ions when mixed with aromatic N-oxides was quite complex. This report is an attempt to enumerate and rationalize the complexities of these systems.

The aromatic N-oxide–copper(II) complexes may be divided into general categories which reflect their chemical composition and physical properties. Most complexes which have been isolated and characterized are (a) low magnetic moment 1:1 complexes, (b) low and normal magnetic moment 2:1 dimeric complexes, (c) *trans* and distorted *cis* 2:1 monomeric complexes with normal magnetic moments, (d) polymeric complexes, (e) adducts of most of the above complexes with small polar molecules, like DMSO, DMF, CH_3OH, and H_2O, or (f) miscellaneous complexes. The crystal structures of a number of complexes have been determined, and we will use these data to discuss their geometry and physical properties. There have been more than 100 aromatic N-oxide–copper(II) complexes prepared, and we have included most of them in Table I. Assignments to structural categories in some cases are based upon limited data and are subject to revision when additional results become available; however, the generalizations proposed in this paper should be of value in formulating future experiments.

Experimental Section

Materials.—All aromatic N-oxides, not previously reported in the literature, were prepared from the corresponding amines by peroxide oxidation in acetic acid. The amines were purchased from Aldrich Chemical Co. and Reilly Tar and Chemical Co. or were synthesized by standard procedures. The aromatic N-oxides were recrystallized from ethanol and characterized by their melting points, elemental analyses, and spectra. The preparation and characterization of copper(II) complexes have been described adequately in many of the early papers included in the references. Enquiries concerning specific complexes or their physical properties may be referred to the author.

Spectra.—Infrared spectra were obtained with Perkin-Elmer Model 235 and Beckman Model IR-10 spectrophotometers using Nujol mulls or reflectance techniques. All infrared spectra were calibrated with peaks from a polystyrene film. The spectra on the IR-10 were scale expanded.

Molecular Weights.—Molecular weights were determined with a Mechrolab osmometer, Model 301A, using distilled nitroethane as a solvent.

Magnetic Susceptibility.—Magnetic susceptibilities were measured by the Faraday method using a Cahn automatic electrobalance, Model RH. Electrobalance output and thermocouple voltage were measured with a Hewlett-Packard digital voltmeter, Model 3440A, with a Model 3443A range plug-in unit. A digital recorder, Hewlett-Packard Model 562A, printed the ouput of the voltmeter upon receiving a 10-V pulse from an automatic control system. The automatic control system performed all switching for the magnet control system and reading. A thermocouple of silver with 0.37 atom % gold and gold with 2.10 atom % cobalt was used to measure the temperature. The thermocouple measuring junction was placed directly below the sample container and the reference junction was immersed in an ice bath. The temperature dependence of ammonium manganese sulfate hexahydrate was used to calibrate the thermocouple at low temperatures, and mercuric tetrathiocyanatocobaltate(II) was used at higher temperatures. A helium dewar was used for all low-temperature measurements. A special heating unit was constructed for measurement above room temperature. After the usual diamagnetic corrections had

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TABLE I

Compound[a]	μ, BM	2J, K	ν_{N-O},° K	ν_{Cu-Cl},° K
1:1 Complexes				
$[(pyO)CuCl_2]_2$	0.59–1.06,[b–d] 0.63	616,[e] 720,[f] 716	1203[g]	330, 311[h]
$[(2\text{-}CH_3pyO)CuCl_2]_2$	...	...	...	...
$[(3\text{-}CH_3pyO)CuCl_2]_2$	0.55,[d] 0.97[i]	680–810[i]	1253	316;[h] 323
$[(4\text{-}CH_3pyO)CuCl_2]_2$	0.52,[d,j] 0.49	986,[k] 829	1203;[j] 1204	327, 312[h]
$[(2,4\text{-}(CH_3)_2pyO)CuCl_2]_2$	0.22[d]	...	...	...
$[(2,6\text{-}(CH_3)_2pyO)CuCl_2]_2$	0.68,[i] 0.22[l]	930–1090[i]	...	326[h]
$[(2,4,6\text{-}(CH_3)_3pyO)CuCl_2]_2$	0.63[i]	960–1080[i]	...	327[h]
$[(4\text{-}Cl(pyO))CuCl_2]_2$	0.58,[j] 0.28	1090,[k] 1064	1208;[j] 1205	317;[h] 314
$[(4\text{-}Br(pyO))CuCl_2]_2$	0.30	1050	...	...
$[(4\text{-}OHpyO)CuCl_2]_2$	0[j]	2150[k]	1210[j]	...
$[(4\text{-}CNpyO)CuCl_2]_2$	0.36	966	...	...
$[(4\text{-}NO_2pyO)CuCl_2]_2$	1.01,[m] 1.20,[l] 0.95	529	1207	305;[h] 310
$[(4\text{-}CH_3OpyO)CuCl_2]_2$	0.33	994	1200	324;[h] 324
$[(4\text{-}C_2H_5OpyO)CuCl_2]_2$	0.30	1027	1200	320
$[(4\text{-}t\text{-}C_4H_9pyO)CuCl_2]_2$	0.56	776	1213	316, 310
$[(4\text{-}C_6H_5pyO)CuCl_2]_2$	0.32	966	1212	316
$[(4\text{-}Bz(pyO))CuCl_2]_2$	0.48	838	1209	338, 309
$[(4\text{-}CH_2OHpyO)CuCl_2]_2$	0.38	941	1208	316, 303
$[(4\text{-}COOCH_3pyO)CuCl_2]_2$	0.41	923	1199	329
$[(4\text{-}COOC_2H_5pyO)CuCl_2]_2$	0.50[l]	...	...	...
$[(3\text{-}Cl(pyO))CuCl_2]_2$	0.46[l]	...	...	...
$[(3\text{-}OHpyO)CuCl_2]_2$	0.38[l]	...	...	...
$[(3\text{-}CH_3OpyO)CuCl_2]_2$	0.55[l]	...	...	...
$[(3\text{-}COOHpyO)CuCl_2]_2$	0.53[l]	...	...	...
$[(3\text{-}COOCH_3pyO)CuCl_2]_2$	0.56[l]	...	...	...
$[(3\text{-}COOC_2H_5pyO)CuCl_2]_2$	0.48[l]	...	...	...
$[(quinO)CuCl_2]_2$	0,[f] 0.36[c]	...	...	344, 332[m]
$[(4\text{-}CH_3quinO)CuCl_2]_2$	0.56[m]	...	...	334, 325[m]
$[(6\text{-}CH_3quinO)CuCl_2]_2$	0.41[m]	...	...	340, 328[m]
$[(pyO)CuBr_2]_2$	0.24–0.65[b–d]	...	1200[j]	...
$[(2\text{-}CH_3pyO)CuBr_2]_2$	...	...	...	...
$[(3\text{-}CH_3pyO)CuBr_2]_2$	0.80[i]	890–1080[i]	1234	...
$[(4\text{-}CH_3pyO)CuBr_2]_2$	0.26[j]	...	1203;[j] 1208	...
$[(2,6\text{-}(CH_3)_2pyO)CuBr_2]_2$	0.65,[i] 0.40[l]	940–1100[i]	1198	...
$[(2,4,6\text{-}(CH_3)_3pyO)CuBr_2]_2$	0.60[i]	960–1120[i]	...	...
$[(4\text{-}Cl(pyO))CuBr_2]_2$	0.23,[j] 0.48[l]	...	1201	...
$[(4\text{-}CNpyO)CuBr_2]_2$	0.79	...	...	...
$[(4\text{-}NO_2pyO)CuBr_2]_2$	1.77,[i] 0.45[l]	143[k]	1238, 1225[j]	...
$[(4\text{-}CH_3OpyO)CuBr_2]_2$	...	...	1205	...
$[(4\text{-}C_2H_5OpyO)CuBr_2]_2$	...	...	...	...
$[(4\text{-}t\text{-}C_4H_9pyO)CuBr_2]_2$	...	...	1217	...
$[(4\text{-}C_6H_5pyO)CuBr_2]_2$	...	...	...	...
$[(4\text{-}COOC_2H_5pyO)CuBr_2]_2$	0.28[l]	...	...	...
$[(3\text{-}Cl(pyO))CuBr_2]_2$	0.25[l]	...	...	...
$[(3\text{-}Br(pyO))CuBr_2]_2$	0.45[l]	...	...	...
$[(3\text{-}OHpyO)CuBr_2]_2$	0.38[l]	...	...	...
$[(3\text{-}COOHpyO)CuBr_2]_2$	0.39[l]	...	...	...
$[(quinO)CuBr_2]_2$	0,[f] 0.40[c]	...	...	...
$[(4\text{-}CH_3quinO)CuBr_2]_2$	0.40[m]	...	...	...
$[(4\text{-}Cl(quinO)CuBr_2]_2$	0.39[m]	...	...	...
$[(6\text{-}CH_3quinO)CuBr_2]_2$	0.60[m]	...	...	...
$[(4\text{-}Cl\text{-}6\text{-}CH_3quinO)CuBr_2]_2$	0.38[m]	...	...	...
$[(3\text{-}NO_2\text{-}6\text{-}CH_3quinO)CuBr_2]_2$	1.72[m]	...	...	...
Adducts of 1:1 Complexes				
$[(pyO)CuCl_2(DMF)]_2$	0.53[d]	...	1203[j]	...
$[(pyO)CuCl_2(DMSO)]_2$	0.57[d]	...	1203[j]	...
$[(2\text{-}CH_3pyO)CuCl_2(CH_3OH)]_2$	...	...	...	...
$[(2\text{-}CH_3pyO)CuCl_2(DMSO)]_2$	...	...	...	...
$[(3\text{-}CH_3pyO)CuCl_2(DMSO)]_2$	...	...	...	...
$[(4\text{-}CH_3pyO)CuCl_2(DMSO)]_2$	...	...	...	...
$[(4\text{-}OHpyO)CuCl_2(H_2O)_2]_2$	0.31	1153	1217	316, 332
$[(2,6\text{-}(CH_3)_2pyO)CuCl_2(DMSO)]_2$	...	...	...	...
$[(pyO)CuBr_2(DMF)]_2$	0.46[d]	...	1202[j]	...
$[(pyO)CuBr_2(DMSO)]_2$	1.12[d]	...	...	...
$[(4\text{-}CH_3pyO)CuBr_2(DMSO)]_2$	0.97[j]	...	1211[j]	...

TABLE I (*Continued*)

Compound[a]	μ, BM	$2J$, K	ν_{N-O}, K	ν_{Cu-Cl}, K
2:1 Low and Normal Moment Dimers				
$[(pyO)_2CuCl_2]_2$	0.46,[f] 0.63[d]	. . .	1223, 1206[g]	310, 280[h]
$[(pyO)_2CuBr_2]_2$	1.4[f]	242[f]	1211, 1202[j]	. . .
$[(pyO)_2Cu(NO_3)_2]_2$	1.89[b]	. . .	1211, 1202	. . .
$[(quinO)_2Cu(NO_3)_2]_2$	1.88,[f] 1.91[c]	. . .	. . .	. . .
$[(4\text{-}CH_3pyO)_2CuCl_2]_2$	. . .	. . .	. . .	. . .
$[(4\text{-}CH_3pyO)_2CuBr_2]_2$	1.33[j]	. . .	. . .	. . .
trans 2:1 Monomers				
$(2\text{-}CH_3pyO)_2CuCl_2$	1.95	. . .	. . .	328[h]
$(3\text{-}CH_3pyO)_2CuCl_2$	. . .	. . .	. . .	322[h]
$(4\text{-}CH_3pyO)_2CuCl_2$[n]	. . .	. . .	. . .	339, 316, 296[h]
$(2,6\text{-}(CH_3)_2pyO)_2CuCl_2$	1.90[i]	. . .	. . .	. . .
$(2,4,6\text{-}(CH_3)_3pyO)_2CuCl_2$	1.91[i]	. . .	. . .	. . .
$(4\text{-}Cl(pyO))_2CuCl_2$	1.75[j]	. . .	. . .	341[h]
$(4\text{-}NO_2pyO)_2CuCl_2$	. . .	. . .	. . .	345[h]
$(4\text{-}CH_3OpyO)_2CuCl_2$	. . .	. . .	. . .	. . .
$(quinO)_2CuCl_2$	1.88[f]	. . .	. . .	. . .
$(4\text{-}Cl(quinO)_2CuCl_2$	1.88[m]	. . .	. . .	. . .
$(4\text{-}NO_2quinO)_2CuCl_2$	1.86,[m] 1.93[d]	. . .	. . .	327[h]
$(4\text{-}Cl\text{-}6\text{-}CH_3quinO)_2CuCl_2$	1.97[m]	. . .	. . .	. . .
$(4\text{-}NO_2\text{-}6\text{-}CH_3quinO)_2CuCl_2$	1.87[m]	. . .	. . .	. . .
$(3\text{-}NO_2\text{-}6\text{-}CH_3quinO)_2CuCl_2$	1.81[m]	. . .	. . .	. . .
Distorted *cis* 2:1 Monomers				
$(3\text{-}CH_3pyO)_2CuCl_2$	. . .	. . .	. . .	. . .
$(2,6\text{-}(CH_3)_2pyO)_2CuCl_2$	1.91[m]	. . .	. . .	319, 297[h]
$(2,4,6\text{-}(CH_3)_3pyO)_2CuCl_2$	. . .	. . .	. . .	318, 330[h]
2:1 Monomers				
$(3\text{-}CH_3pyO)_2CuBr_2$	. . .	. . .	. . .	. . .
$(2,6\text{-}(CH_3)_2pyO)_2CuBr_2$	2.04[i]	. . .	. . .	. . .
$(2,4,6\text{-}(CH_3)_3pyO)_2CuBr_2$	1.89			
$(4\text{-}CH_3OpyO)_2CuBr_2$	. . .	. . .	. . .	. . .
$(quinO)_2CuBr_2$	1.96[f]	. . .	. . .	. . .
$(4\text{-}Cl(quinO)_2CuBr_2$	1.83[m]	. . .	. . .	. . .
$(4\text{-}NO_2(quinO)_2CuBr_2$	1.83[m]	. . .	. . .	. . .
$(4\text{-}Cl\text{-}6\text{-}CH_3quinO)_2CuBr_2$	1.82[m]	. . .	. . .	. . .
$[(4\text{-}NO_2\text{-}6\text{-}CH_3quinO)_2CuBr_2]_2$	1.85[m]	. . .	. . .	. . .
$[(3\text{-}NO_2\text{-}6\text{-}CH_3quinO)_2CuBr_2]_2$	1.98[m]	. . .	. . .	. . .
Adducts of 2:1 Monomers				
$(pyO)_2CuCl_2(NCS)_2$	1.96[f]	. . .	. . .	. . .
$(4\text{-}NO_2pyO)_2CuCl_2(H_2O)_2$	1.96[f]	. . .	. . .	. . .
Polymeric Complexes				
$[Cu_3Cl_6(2\text{-}CH_3pyO)_2(H_2O)_{2n}$	1.22	. . .	. . .	315, 302, 291[h]
$Cu_3Cl_6(4\text{-}Cl(quinO))_2$	2.07[m]	. . .	. . .	308, 290[m]
$Cu_3Cl_6(4\text{-}Cl\text{-}6\text{-}CH_3quinO)_2$	1.69[m]	. . .	. . .	307, 280[m]
$Cu_4Cl_8(3\text{-}NO_2\text{-}6\text{-}CH_3quinO)_3$	1.91[m]	. . .	. . .	306, 290[m]
Miscellaneous Complexes				
$[(pyO)_4Cu(ClO_4)_2]_2$	1.62,[b] 1.80,[f] 2.09[c]	. . .	1215, 1205[g]	. . .
$(quinO)_4Cu(ClO_4)_2$	. . .	. . .	. . .	. . .
$(pyO)_6Cu(ClO_4)_2$	. . .	. . .	. . .	. . .

[a] pyO = pyridine N-oxide; quinO = quinoline N-oxide. [b] Reference 1. [c] Reference 3. [d] Reference 6. [e] Reference 10. [f] Reference 16. [g] Reference 5. [h] Reference 15. [i] Reference 11. [j] Reference 9. [k] Reference 8. [l] Reference 21. [m] Reference 17. [n] Mixture of *trans* and distorted *cis* forms. [o] Commas separate more than one infrared band; semicolons separate more than one measurement of the same band.

been made, the experimental data for the dimeric complexes were least-squares fitted to the expression

$$\chi_m^{\text{cor}} = \frac{Ng^2\beta^2}{3kT}\left[1 + \frac{1}{3}\exp(2J/kT)\right]^{-1} + N\alpha + \frac{C}{T}$$

The term C accounts for any paramagnetic impurity which might be present. The impurity was assumed to obey the Curie law and have an effective moment of 1.90 BM. The percentage of paramagnetic impurity was small in all cases. Expressions for the magnetic susceptibility of more than two intereacting transition metal ions may be derived from the Heisenberg–Dirac–Van Vleck spin-coupling Hamiltonian.[19]

Discussion

Low Magnetic Moment 1:1 Complexes.—The crystal structure of the 1:1 complex formed between pyridine N-oxide and copper(II) chloride, $[(C_5H_5NO)CuCl_2]_2$, was the first to be reported.[10,14] The molecular structure as shown in these papers probably represents the complex in solution, and it has been used extensively to

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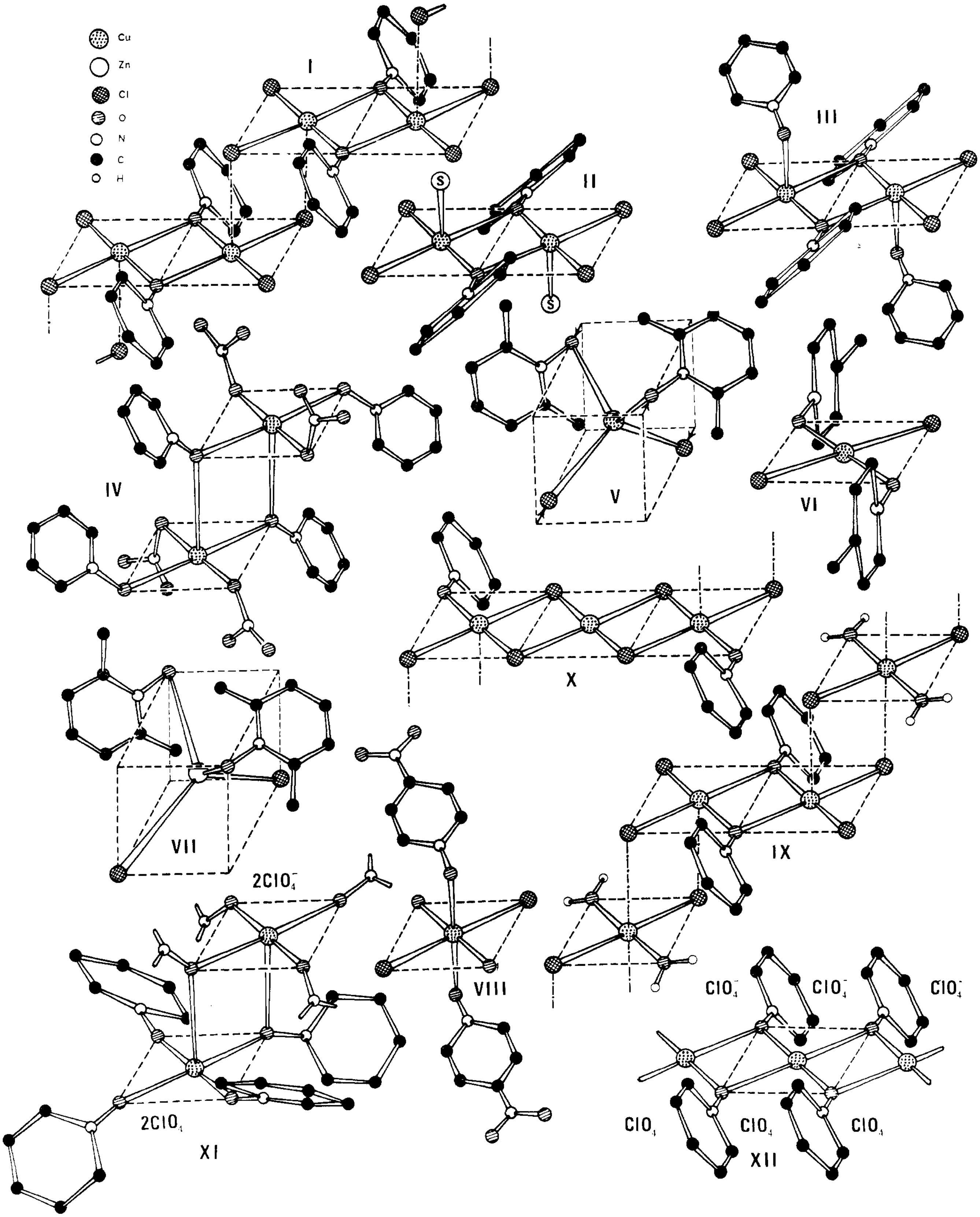

Figure 1.—Molecular structures of Cu(II) and Zn(II) complexes with aromatic N-oxides. The structures have been idealized to facilitate discussion.

rationalize the physical properties of the crystalline solid. Unfortunately, a number of significant inter- and intramolecular interactions were omitted.

The complex, structure I (see Figure 1) actually should be described as an infinite chain of oxygen-bridged dimers joined by weak chloride bridges.[20] The

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[20] R. J. Williams, R. S. Sager, and W. H. Watson, *Inorg. Chem.*, **8**, 694 (1969).

bridging Cu–Cl distance is 2.8 Å which is too long for a normal bond, but the interaction is of sufficient magnitude to affect the solubility, the infrared stretching vibrations, and probably the electronic properties. The distorted geometry around the copper ion can be rationalized in terms of the weak chloride bridge and a short intramolecular interaction between a chloride ion and an *ortho* hydrogen atom on the pyridine ring. A significant intermolecular interaction also occurs between the *para* ring hydrogen in one dimeric unit and the copper ion of an adjacent unit. The hydrogen shields the sixth coordination site and may provide a small electrostatic perturbation to the copper ion energy levels.

The physical properties of the other 1:1 complexes can be rationalized in terms of the structure of the pyridine N-oxide complex. Two bands in the infrared spectrum of the pyridine N-oxide complex have been assigned to Cu–Cl stretching vibrations,[15] Table I. The band at 311 cm^{-1} is associated with the bridged chloride ion and the band at 330 cm^{-1} with the nonbridged ion. The complex is too insoluble in nitroethane for an accurate molecular weight to be determined. The 1:1 complexes of 2,6-dimethylpyridine N-oxide and 2,4,6-trimethylpyridine N-oxide are soluble enough for molecular weight measurements, and the data indicate the complexes are dimeric in solution. These complexes are methyl substituted in the *ortho* positions, and the rings in the dimer would orient to the less sterically hindered position. Any gain in stability due to packing in an arrangement similar to the pyridine N-oxide structure would be negligible compared to the strong steric interactions between the *ortho* substituents and the chloride ion. The position of minimum steric interaction would place the methyl groups above and below the plane of the oxygen bridge which effectively shields the axial positions of the two copper(II) ions from interaction with other dimers. If there is no chloride bridge, the two chloride ions should be equivalent and the Cu–Cl stretching vibrations would be degenerate. Only one Cu–Cl stretching vibration has been reported for these two complexes. The band occurs at 326 cm^{-1} for the 2,6-dimethylpyridine N-oxide complex and 327 cm^{-1} for the 2,4,6-trimethylpyridine N-oxide complex, which is consistent with the frequency assigned to the unbridged chloride ion in the pyridine N-oxide complex. If the infrared band assignments for Cu–Cl stretching vibrations are correct, the following classifications can be made. The 4-methylpyridine N-oxide and 4-benzylpyridine N-oxide complexes show bands similar to the pyridine N-oxide complex and should have one bridged and one unbridged chloride ion. The 4-nitropyridine N-oxide (305 cm^{-1}), 3-picoline N-oxide (316 cm^{-1}), and 4-methylpyridine N-oxide (324 cm^{-1}), etc., each have one band assigned to the Cu–Cl stretching vibration and would indicate structures ranging from two strong chloride bridges to two very weak chloride interactions. The 1:1 complexes may exhibit no chloride ion bridging, one chloride ion bridged and one unbridged, or both chloride ions involved in bridging. In this context the term bridge implies a significant interaction of a chloride ion with two copper(II) ions and should not be taken to imply two bonds of about equal strength. The solubilities are consistent with these generalizations.

The Cu(II)–Cu(II) separation within the pyridine N-oxide dimer is 3.25 Å, and the magnetic exchange energy is larger than in many complexes with smaller separations. The interaction in these complexes is classified as superexchange. The magnetic electron probably occupies an orbital within the plane of the bridge. This orbital would have $d_{x^2-y^2}$ symmetry for a regular square-planar or square-based pyramidal geometry.

Hatfield and Paschal[8] measured the exchange energies for a series of 4-substituted pyridine N-oxides and reported a correlation with the substituent parameter σ_R. Kato, *et al.*,[21] investigated a more extensive series of complexes and reported no correlation of the magnetic moments with any σ value; however, they did report a correlation between an electronic absorption band in the region 700–1000 cm^{-1} and the room-temperature magnetic moments. This correlation would imply a proportionality between the first excited singlet state and the low-lying triplet state which arises owing to the scalar coupling interaction. This would imply that the factors which affect the electronic energy levels also affect the superexchange mechanism. Changes in the geometrical distribution of ligands around the copper ion change the crystal field and shift the energy levels. Changes in geometry may arise from the inter- and intramolecular interactions previously described. A change in the crystal field strength of a ligand also affects the energy levels. The crystal field strength of the aromatic N-oxide ligands may be modified by the addition of substituents to the pyridine ring. This may directly change the dipolar nature of the N–O bond, or it may exert its influence through a back-π-bonding mechanism. The singlet–triplet separation as determined by susceptibility measurements corresponds to energy in the infrared region of the spectrum. This transition is not observed in the infrared spectrum since it is forbidden, and the infrared sources are of too low intensity. For systems with more than two interacting copper ions or with spins other than $^1/_2$, some of the thermally accessible levels correspond to allowed electronic transitions. The study of these allowed transitions has not been exploited.

With the variety of factors which are present in the solid, it is evident that a correlation with a specific substituent effect might not be expected. Although molecular packing and inter- and intramolecular interactions must be considered, a correlation should exist for complexes with similar structures. We recently have determined the exchange energies for a series of 4-substituted complexes.[22] There is no correlation between all members of this series when σ_R is plotted against the

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[21] M. Kato, Y. Muto, and H. B. Jonassen, *Bull. Chem. Soc., Japan*, **40**, 1738 (1967).

[22] M. R. Kidd. Ph.D. Thesis, Texas Christian University, Fort Worth, Texas, 1968.

exchange energy, but the data appear to indicate two classes of complexes which correlate independently. Since the number of data points is small, such correlations may be misleading.

Low Moment Adducts of 1:1 Complexes.—Adducts are readily formed between 1:1 complexes and DMF, DMSO, H_2O, or CH_3OH, and a few complexes have been included in Table I. The magnetic moments of the adducts are similar to the parent 1:1 complexes which indicate the solvent molecule does not affect significantly the orbital containing the magnetic electron. This is consistent with the assumption that the magnetic electrons are localized within the plane of the bridge.

The substituents in the *ortho* positions of the pyridine ring should play a prominent role in determining the geometry of the adducts. Since the *ortho* substituents shield the axial sites of the copper ion, it would be difficult to form a six-coordinate complex. Substitution at one axial site would produce greater steric shielding at the other. This results in a *trans*-substituted dimer, structure II, with each copper ion being pentacoordinate.

Normal and Low Magnetic Moment 2:1 Dimeric Complexes.—Pyridine N-oxide forms a 2:1 dimeric complex. The structure of dichlorobis(pyridine N-oxide)copper(II) has been reported,[23] and the complex may be considered as a pyridine N-oxide adduct of the 1:1 complex. The copper(II) ions apparently are pentacoordinate with the extra pyridine N-oxide ligands lying *trans* to the plane of the joined bases, structure III. Two N–O stretching frequencies are observed, which is indicative of the two types of N-oxide coordination with the lower frequency being associated with the bridged ligand. Two Cu–Cl stretching vibrations also were observed. The dibromobis(pyridine N-oxide)copper(II) complex apparently has a structure similar to the chloride complex, but the reported magnetic moment is considerably larger. This is unusual since the bromide complexes in the 1:1 series exhibit smaller room-temperature magnetic moments than the corresponding chloride complexes. Again two N–O stretching bands are observed in the infrared spectrum. The 2:1 complex between 4-methylpyridine N-oxide and copper(II) bromide has a magnetic moment of 1.33 BM which is indicative of magnetic exchange. A recent crystal structure investigation of the corresponding chloride complex revealed a dimeric structure with very interesting properties. Two of the Cu–O bonds in the bridge are elongated, while the two other bridging Cu–O bonds and the two adduct Cu–O bonds are normal.[24] The implications of this structure will be discussed in a later section. The two chloride ions are not equivalent, and two Cu–Cl stretching frequencies should be observed. No magnetic data are available for this complex.

If copper(II) nitrate is used instead of copper(II) chloride, a 2:1 complex dinitratobis(pyridine N-oxide) copper(II) is obtained. The complex exhibits a normal magnetic moment. The crystal structure reveals the complex to be an oxygen-bridged dimer.[25] The geometry around each copper ion closely approximates a square-based pyramid, but the bridging N-oxide ligands occupy one basal site and one apical site, structure IV. The O–Cu–O angles are about 90° compared to 72° for the corresponding chloride complex. If the magnetic electrons are restricted to the basal plane of the pyramid, the two copper(II) magnetic wave functions do not overlap significantly at the shared oxygen atoms, and the exchange interaction is small. This is consistent with the normal magnetic moment observed for the complex.

The second pyridine N-oxide molecule occupies one of the basal sites such that the nitrate groups are *trans* to each other. The infrared spectrum indicates two N-O stretching frequencies, which is consistent with the two differently coordinated N-oxide ligands. The arrangement of the nitrate ions and unbridged N-oxide ligand effectively shields the sixth coordination site of the complex. The geometry can be rationalized in terms of steric interactions. The complex dinitratobis(quinoline N-oxide)copper(II) tentatively has been assigned the same structure as the pyridine N-oxide complex.

Normal Magnetic Moment 2:1 Monomers.—Two additional crystalline modifications may be isolated for some of the 2:1 complexes and they usually may be identified by their green and yellow-green colors. Molecular weight determinations on those complexes soluble enough for accurate measurement indicate the complexes are monomeric.[13] This could be misleading since polymeric forms would be insoluble and weakly coordinate dimers might dissociate in solution. It is significant to note that the yellow crystalline form is irreversibly converted into the green crystalline form upon heating.

The crystal structure[26] of the yellow form of dichlorobis(2,6-dimethylpyridine N-oxide)copper(II) shows the geometry around the copper(II) ion to be distorted and intermediate between *cis* square planar and tetrahedral, structure V. The green crystalline form of dichlorobis-(4-methylpyridine N-oxide)copper(II) has a *trans*-square-planar geometry,[27] structure VI. This complex was too insoluble in nitroethane for an accurate molecular weight determination and might have been polymeric. There are no intermolecular distances to the copper ions closer than 4 Å. The yellow form is denoted as distorted *cis* to aid in visualizing the differences between the two isomers.

Attempts to recrystallize the yellow distorted *cis* form from warm solvents gives predominantly the *trans* form, and if crystals of the yellow form are left in the solvent, they soon are replaced by the green form. These observations imply the *trans* form is thermodynamically more stable, and the equilibrium must be greatly in its favor.

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[23] J. C. Morrow, presented at the National Meeting of the American Crystallographic Association, Gatlinburg, Tenn., June 1965.

[24] D. R. Johnson and W. H. Watson, unpublished work.

[25] S. Scavnicar and B. Matkovic, *Chem. Commun.*, 297 (1967).

[26] R. S. Sager and W. H. Watson, *Inorg. Chem.*, **8**, 308 (1969).

[27] D. R. Johnson and W. H. Watson, unpublished work.

If this is true, the initial formation of the two complexes is kinetically controlled and not thermodynamically controlled. We have not been able to detect the presence of the distorted *cis* structure in solution. Its properties are either obscured by other species present or the concentration is too low. Since we recently found the structure of the yellow-green form of dichlorobis(4-methylpyridine N-oxide)copper(II) to be dimeric, we postulate the following mechanism. The 2:1 dimeric complex initially forms and either crystallizes or dissociates to the monomer. The monomer rapidly isomerizes to the thermodynamically more stable *trans* form. The crystalline dimeric complex may dissociate in the solid phase and be trapped as the distorted *cis* structure. When the crystal is warmed, the *cis* isomer is converted to the stable *trans* configuration with a minimum of crystal deformation. This mechanism is consistent with all experimental observations. Whether we have the distorted *cis* structure or the dimeric structure depends upon the temperature of the synthesis and the stability of the dimer. The *ortho*-substituted dimers are less stable because of steric interactions and dissociate at a lower temperature, but the bulky methyl groups make it difficult to isomerize in the solid. The *cis*-2,6-dimethylpyridine N-oxide complex does not convert to the *trans* form until it melts. If the above mechanism is correct, we should be able to devise methods for preparing larger quantities of the distorted *cis* structure.

The *trans* complex is described as square planar since the bond angles are about 90°; however, the Cu–Cl bonds are longer than the Cu–O bonds as expected. The tetrahedral geometry would be most stable from strictly electrostatic and steric considerations since the structure of dichlorobis(2,6-dimethylpyridine N-oxide)zinc(II) is tetrahedral,[28] structure VII. Back-π-bonding of the d orbitals of the copper ion with the antibonding orbitals of the aromatic N-oxide may stabilize the *trans* structure. There is some indication from infrared studies that back-π-bonding occurs. The *trans* complex exhibits one Cu–Cl stretching vibration while the *cis* complex has been assigned two; however, it would be difficult to distinguish between the 2:1 dimer and the distorted *cis* configuration by infrared data alone.

Adducts of 2:1 Monomeric Complexes.—Polar solvent molecules form adducts with the *trans* 2:1 complexes. When the *trans* complex is compressed into KBr pellets, the color changes from green to reddish brown, and the infrared spectrum does not match that recorded in Nujol or by reflectance techniques. No color change is observed for the distorted *cis* complex, and the infrared spectrum is identical with that obtained by the other techniques. This is assumed to be indicative of an interaction with the bromide ions at the axial sites and not a displacement of chloride ion.

The crystal structure of *trans*-dichlorodiaquobis(4-nitropyridine N-oxide)copper(II), structure VIII, has been determined.[29] The geometry around the copper ions is that of a highly distorted octahedron with the N-oxide ligands occupying axial sites. The large Cu–O distance of 2.69 Å for the N-oxide ligand was unexpected since its crystal field strength is relatively large. The displacement may be attributed partially to steric interactions, but it is predominantly due to an intricate hydrogen-bonding network. Each oxygen of the N-oxide ligand is tetrahedrally coordinated. The two additional interactions are with hydrogen atoms from water molecules on adjacent complexes. The interactions with the water molecules effectively reduce the crystal field strength of the N-oxide ligand.

Polymeric Complexes.—The structure of $[Cu_3Cl_6(2\text{-}CH_3pyO)_2(H_2O)_2]_n$, structure IX, can be described as an infinite chain of 1:1 oxygen-bridged dimers joined by chloride bridges to copper ions with distorted octahedral geometry.[18] The oxygen-bridged copper ions are pentacoordinate with a chloride ion from the square plane of the hexacoordinate component located at the apex of the square-based pyramid. The two apical chloride ions are *trans* with respect to the plane of the copper–oxygen bridge. The bond angles and bond lengths around the copper–oxygen bridge are identical with those in the 1:1 pyridine N-oxide complex. The hexacoordinated copper ion has two water molecules and two chloride ions forming the square plane, with two chloride ions from adjacent dimer units occupying the axial sites. The infinite chains are held together by a hydrogen-bonding network. Magnetic susceptibility measurements down to 77°K indicate a magnetic moment of slightly greater than one unpaired electron per three Cu(II) ions. This is consistent with strong antiferromagnetic exchange coupling between the oxygen-bridged copper(II) ions and negligible exchange through the chloride bridges. Over this limited temperature range, the magnetic susceptibility can be fitted by the equation

$$\chi_{\mathrm{Cu(II)}} = \frac{2N}{3}\chi(\text{Bleaney–Bowers}) + \frac{N}{3}\chi(\text{Curie–Weiss})$$

The infrared spectrum shows three Cu–Cl stretching frequencies which is consistent with the three types of chloride ions in the structure.

Several polymeric complexes have been formulated as $Cu_3Cl_6L_2$. The complexes exhibit normal magnetic moments and may be represented by structure X. In addition to the strong chloride bridges within the chain, the terminal chloride ions may be weakly bridged to adjacent units. The infrared spectrum shows two low-frequency bands which is consistent with a strong halogen bridge (290 cm^{-1}) and a weak halogen bridge (308 cm^{-1}). The latter corresponds to the stretching frequency of the bridged chloride ion in some of the 1:1 complexes while the former is analogous to the 291-cm^{-1} band in $[Cu_3Cl_6(2\text{-}CH_3pyO)_2(H_2O)_2]_n$. The N–O stretching vibration should be similar to those found in the 2:1 *trans* monomers.

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It is difficult to formulate a structure for (3-NO_2-6-CH_3quinO)$_3Cu_4Cl_8$. A detailed study of the infrared spectrum might allow a tentative structure to be assigned. The two frequencies assigned to Cu–Cl stretching are similar to those reported for the complexes with the formula $Cu_3Cl_6L_2$, and the basic halogen coordination must be the same. Why these complexes do not exhibit oxygen bridging is unknown.

Miscellaneous Complexes.—The infrared spectrum of (pyO)$_4$Cu(ClO_4)$_2$ indicates two N–O stretching frequencies; however, the structure[30] shows the four pyridine N-oxide molecules in a square-planar array. The axial sites are not occupied. The complex (pyO)$_6$Cu(ClO_4)$_2$ also has been reported but few physical data are available. The complex (pyO)$_2$Cu(ClO_4)$_2$ has not been reported, but it should exist as an infinite linear polymer, structure XII.

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Magnetic Susceptibility Study of Copper(II) Halide Complexes with 4-Substituted Pyridine N-Oxides

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The magnetic susceptibilities have been measured for 12 1:1 copper(II) halide complexes with 4-substituted pyridine N-oxides from 77°K to near the melting or decomposition temperatures. The magnetic susceptibility data were least-squares fitted to a modified Bleaney–Bowers equation. The correlations of the exchange energy, $2J$, with the reflectance spectra and the substituent parameter σ_R are discussed in terms of the molecular and crystal structures.

Introduction

The magnetic properties have been reported for a number of complexes formed between aromatic N-oxides and copper(II) halides.[1–10] Some of these complexes have abnormally low magnetic moments, and they usually are characterized as oxygen-bridged dimers or polymeric species. The magnetic susceptibility of the copper(II) ions in the complexes can be fitted to an equation which is derived from the assumption of a simple scalar interaction of the form $-2J_{ij}S_i \cdot S_j$. For a binuclear complex the exchange energy $2J$ is the separation between the singlet and triplet states generated by the scalar interaction. The interaction usually is antiferromagnetic and the ground state is the singlet.

In aromatic N-oxide complexes the exchange interaction occurs through the bridging oxygen atoms and is defined as superexchange. Since the intervening oxygen atoms aid in the expansion of the d orbital containing the magnetic electrons, it is logical to assume any change in electron density around the oxygen atoms or copper(II) ions should affect the magnitude of the exchange interaction. It is anticipated that substitution at the 4 position of the pyridine N-oxide molecule should affect the electron density at the oxygen atom and hence the singlet–triplet separation. A correlation was reported between the substituent parameter σ_R and the exchange energy $2J$, for a limited number of 1:1 4-substituted complexes,[4] [$CuCl_2L$]$_2$; however a subsequent report on a more extended series of complexes reported no correlation.[10] The latter paper did report a correlation between the room-temperature magnetic moments and ν_{max} of an electronic transition in the region of 700–1000 nm. This implies a relationship between an electronically allowed singlet–singlet transition in the visible–infrared region of the spectrum with an electronically forbidden singlet–triplet separation of approximately 1 kK which corresponds to the infrared region.

We have measured accurately the magnetic susceptibilities of a more extended series of 1:1 complexes between 4-substituted pyridine N-oxides and copper(II) chloride. We wish to discuss these results in terms of the crystal and molecular structures.

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