It is difficult to formulate a structure for $(3\text{-}NO_2\text{-}6\text{-}CH_3quinO)_3Cu_4Cl_8$. 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 $(pyO)_4Cu(ClO_4)_2$ 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 $(pyO)_6Cu(ClO_4)_2$ also has been reported but few physical data are available. The complex $(pyO)_2Cu(ClO_4)_2$ 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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Experimental Section

Synthesis.—Two procedures were used to prepare the complexes.

Method A.—An ethanol solution of the ligand was added to a heated ethanol solution containing anhydrous $CuCl_2$ in slight excess of a 1:1 molar ratio. A green or yellow-green precipitate formed and was collected after standing for several minutes. The solid was added to enough boiling ethanol to achieve dissolution, and the complex was recrystallized by slow evaporation of the warm solvent. After the solution was reduced to less than one-fourth of its original volume, it was allowed to cool. The crystals were collected and dried under vacuum.

Method B.—Approximately 2 g of ligand was dissolved in enough ethanol to keep it in solution at room temperature. An amount of $CuCl_2$ slightly over the stoichiometric quantity was dissolved in 50 ml of ethanol. The ligand solution was added slowly to the $CuCl_2$ solution with stirring but no heating. A precipitate formed immediately, but the solution was allowed to stand for an additional few minutes. The precipitate was collected by vacuum filtration, washed with cold ethanol, and the filter funnel was placed immediately into a vacuum desiccator for drying.

Di-μ-(pyridine N-oxide)-bis[dichlorocopper(II)], $[(C_5H_5NO)CuCl_2]_2$.—This complex, synthesized by method A, was reported by Quagliano, *et al.*[11] The pyridine N-oxide was obtained from Reilly Tar and Chemical Co. *Anal.* Calcd for $Cu(C_5H_5NO)Cl_2$: C, 26.16; H, 2.20; N, 6.10. Found: C, 26.27; H, 2.18; N, 6.01.

Di-μ-(4-methylpyridine N-oxide)-bis[dichlorocopper(II)], $[(CH_3C_5H_4NO)CuCl_2]_2$.—The 4-methylpyridine N-oxide (Aldrich Chemical Co., Inc.) was recrystallized from toluene. The complex formed by method A appeared as fine green needles which were sensitive to atmospheric water. The complex melted with decomposition at 220°. *Anal.* Calcd for $Cu(C_6H_7NO)Cl_2$: Cu, 26.09; C, 29.58; H, 2.90; N, 5.76. Found: Cu, 26.10; C, 29.49; H, 2.96; N, 5.62.

Di-μ-(4-chloropyridine N-oxide)-bis[dichlorocopper(II)], $[(ClC_5H_4NO)CuCl_2]_2$.—The ligand was synthesized from 4-nitropyridine N-oxide by the method of Ochiai.[12] The complex was obtained by method A. The small dark green crystals of the complex melted with decomposition at 207–209°. *Anal.* Calcd for $Cu(C_5H_4ClNO)Cl_2$: Cu, 24.07; C, 22.75; H, 1.53; N, 5.30. Found: Cu, 23.97; C, 22.75; H, 1.44; N, 5.23.

Di-μ-(4-bromopyridine N-oxide)-bis[dichlorocopper(II)], $[(BrC_5H_4NO)CuCl_2]_2$.—The ligand was synthesized by refluxing 10 g of 4-nitropyridine N-oxide for 2 days in a mixture of acetic anhydride and acetic acid, 100 ml of each, and 50 ml of 48% HBr. The reaction mixture was concentrated and made slightly basic with $NaCO_3$. The 4-bromopyridine N-oxide was extracted with chloroform and recrystallized from benzene, mp 143–144°. The complex, formed by method A, appeared as small light green flakes which melted about 235° with decomposition. *Anal.* Calcd for $Cu(C_5H_4BrNO)Cl_2$: Cu, 20.66; C, 19.47; H, 1.31; N, 4.54. Found: Cu, 20.54; C, 19.62; H, 1.36; N, 4.30.

Di-μ-(4-*t*-butylpyridine N-oxide)-bis[dichlorocopper(II)], $[((CH_3)_3CC_5H_4NO)CuCl_2]_2$.—The ligand was obtained by oxidation of 4-*t*-butylpyridine (Reilly Tar and Chemical Co.) using the general method of Ochiai.[12] Yellow-green needles of the complex, obtained by method A, melted with decomposition at 257–260°. *Anal.* Calcd for $Cu(C_9H_{13}NO)Cl_2$: Cu, 22.24; C, 37.84; H, 4.59; N, 4.90. Found: Cu, 21.80; C, 37.92; H, 4.68; N, 4.89.

Di-μ-(4-methoxypyridine N-oxide)-bis[dichlorocopper(II)], $[(CH_3OC_5H_4NO)CuCl_2]_2$.—The 4-methoxypyridine N-oxide was obtained from Aldrich Chemical Co. Fine dark green crystals of the complex were obtained by method A. The complex melted with decomposition at 210–214°. *Anal.* Calcd for $Cu(C_6H_7NO_2)Cl_2$: Cu, 24.48; C, 27.76; H, 2.72; N, 5.39. Found: Cu, 24.33; C, 27.56; H, 2.65; N, 5.34.

Di-μ-(4-ethoxypyridine N-oxide)-bis[dichlorocopper(II)], $[(CH_3CH_2OC_5H_4NO)CuCl_2]_2$.—The ligand was obtained from Aldrich Chemical Co., and the complex, prepared by method A, was obtained as fine green crystals. The complex melted with decomposition at approximately 247°. *Anal.* Calcd for $Cu(C_7H_9NO_2)Cl_2$: Cu, 23.23; C, 30.73; H, 3.32; N, 5.12. Found: Cu, 23.02; C, 30.49; H, 3.24; N, 5.03.

Di-μ-(4-benzylpyridine N-oxide)-bis[dichlorocopper(II)], $[(C_6H_5CH_2C_5H_4NO)CuCl_2]_2$.—The ligand was obtained by oxidation of 4-benzylpyridine (Reilly Tar and Chemical Co.) using the general procedure of Ochiai.[12] The complex, obtained by method A, was in the form of thin green plates. Melting and decomposition occurred at 202–204°. *Anal.* Calcd for $Cu(C_{12}H_{11}NO)Cl_2$: Cu, 19.88; C, 45.09; H, 3.47; N, 4.38. Found: Cu, 19.86; C, 45.23; H, 3.47; N, 4.39.

Di-μ-(4-phenylpyridine N-oxide)-bis[dichlorocopper(II)], $[(C_6H_5C_5H_4NO)CuCl_2]_2$.—The ligand was prepared by Ochiai's general procedure[12] and recrystallized from toluene; the melting point was 150–151°. Dark green hexagonal prisms formed slowly after the addition of the $CuCl_2$ solution, method A. Melting and decomposition occurred at 245°. *Anal.* Calcd for $Cu(C_{11}H_9NO)Cl_2$: Cu, 21.42; C, 41.50; H, 3.06; N, 4.72. Found: Cu, 20.25; C, 41.67; H, 3.31; N, 4.39.

Di-μ-(4-pyridylcarbinol N-oxide)-bis[dichlorocopper(II)], $[(HOCH_2C_5H_4NO)CuCl_2]_2$.—The ligand was obtained from Aldrich Chemical Co. Method A was modified because the precipitate of the complex is very sparingly soluble. Instead of recrystallization, the fine yellow precipitate was digested for 1 hr in boiling ethanol, collected, and dried under vacuum. The yellow powdery material melted with decomposition at 226°. *Anal.* Calcd for $Cu(C_6H_7NO_2)Cl_2$: Cu, 24.48; C, 27.76; H, 2.72; N, 5.40. Found: Cu, 24.40; C, 27.69; H, 2.69; N, 5.21.

Di-μ-(4-carbomethoxypyridine N-oxide)-bis[dichlorocopper(II)], $[(COOCH_3C_5H_4NO)CuCl_2]_2$.—Ten grams of methyl isonicotinate (Reilly Tar and Chemical Co.) was oxidized in a mixture of 100 ml of acetic acid, 50 ml of acetic anhydride, and 25 ml of 30% H_2O_2. The reaction mixture was left at room temperature and 50 ml of H_2O_2 was added in small portions over a 2-day period. The product was isolated in the usual manner, mp 115–116°. Chemical analysis and spectra were in agreement with those expected for 4-carbomethoxypyridine N-oxide. Light green crystals of the complex were obtained by method A. The melting point with decomposition was approximately 232°. *Anal.* Calcd for $Cu(C_7H_7NO_3)Cl_2$: Cu, 22.09; C, 29.23; H, 2.45; N, 4.87. Found: Cu, 21.83; C, 29.20; H, 2.54; N, 4.72.

Di-μ-(4-nitropyridine N-oxide)-bis[dichlorocopper(II)], $[(NO_2C_5H_4NO)CuCl_2]_2$.—The 4-nitropyridine N-oxide was obtained from Aldrich Chemical Co. The complex, synthesized by method B, was obtained as gold-colored crystals, mp 253°. The synthesis of this complex by another method has been reported.[13] *Anal.* Calcd for $Cu(C_5H_4N_2O_3)Cl_2$: Cu, 23.14; C, 21.87; H, 1.47; N, 10.21. Found: Cu, 22.97; C, 21.66; H, 1.42; N, 9.66.

Di-μ-(4-cyanopyridine N-oxide)-bis[dichlorocopper(II)], $[(CNC_5H_4NO)CuCl_2]_2$.—The 4-cyanopyridine N-oxide was prepared from 4-cyanopyridine (Reilly Tar and Chemical Co.) by the method of Ochiai.[12] Fine yellow crystals of the complex were obtained by method B. Melting with decomposition occurred at 238°. This complex was decomposed readily by atmospheric water, especially while still wet with ethanol. The magnetic data reported by Muto, *et al.*,[8] indicate their complex is not identical with the one which we report. *Anal.* Calcd for $Cu(C_6H_4N_2O)Cl_2$: Cu, 24.96; C, 28.31; H, 1.58; N, 11.01. Found: Cu, 24.60; C, 28.01; H, 1.55; N, 10.93.

Magnetic Susceptibility.—Magnetic susceptibilities were measured by the Faraday method using a Cahn automatic electrobalance, Model RH. Electrobalance output and thermocouple

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voltage were measured with a Hewlett-Packard digital voltmeter, Model 3440A, with a Model 3442A range plug-in unit. A digital recorder, Hewlett-Packard Model 562A, printed the output of the voltmeter upon receiving a pulse from an automatic control system. The automatic control system performed all switching for the magnet control and read-out systems.[14] A manual mode of operation also was available. 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 the magnetic susceptibility of ammonium manganese sulfate hexahydrate[15] was used to calibrate the thermocouple at low temperatures and the susceptibility of mercuric tetrathiocyanatocobaltate(II)[16] was used at higher temperatures. A helium dewar was used for all temperatures below room temperature, and a special heating unit replaced the dewar above room temperature. Calibration of the magnetic field and standardization of the sample container were carefully checked. The molar susceptibility, χ_m, was corrected to give the susceptibility per mole of copper ion, χ_m^{cor}, by subtracting the atomic diamagnetic contributions.

A theoretical expression for the molar susceptibility of the copper ions may be derived from the Heisenberg–Dirac–Van Vleck spin-coupling Hamiltonian[17] by assuming a scalar coupling interaction $-2J_{ij}S_i \cdot S_j$. A modification of the expression yields

$$\chi_m{}^{cor} = \frac{Ng^2\beta^2}{3kT}[1 + {}^1/_3 \exp(2J/kT)]^{-1} + N\alpha + \frac{C_i}{T}$$

The term C_i represents an attempt to correct for any paramagnetic impurity which might contaminate the sample. The per cent impurity is estimated by assuming an effective magnetic moment of 1.9 BM. This is a logical correction since contamination probably is due to the corresponding 2:1 copper(II) complexes. The experimental data were least-squares fitted to the theoretical expression and the parameters g, $2J$, $N\alpha$, and C_i were printed out. For complexes with large values of $2J$, the least-squares fit was not sensitive to the magnitude of g. The value of g was fixed to 2.200 and the other parameters were refined. These parameters are reported in Table I. The experimental points and the theoretical curves were also plotted as part of the computer output. The value of $N\alpha$ probably reflects a compensation for small errors in the data rather than a true indication of excited-state admixture to the ground state. In some cases there were small differences between experimental points and the theoretical curves at the lowest temperatures. This is associated with the increased importance of the susceptibility of the paramagnetic impurity which must be subtracted from the total susceptibility. The corrected molar susceptibilities are given in Table II. The data are listed in the order of measurement and indicate several runs for some of the complexes. The least-squares curves and experimental data for three complexes are shown in Figures 1–3. The 4-nitropyridine N-oxide complex had the smallest estimated error in $2J$ while the 4-carbomethoxypyridine N-oxide complex had the largest estimated error in $2J$. The 4-cyanopyridine N-oxide complex contained the largest percentage of paramagnetic impurity. These complexes were chosen to indicate the agreement between the theoretical expression and the experimental data for the three most extreme cases.

Reflectance Spectra.—Reflectance spectra were run on a Beckman DK-2A reflectometer over the range 700–2400 nm. MgO was used as the reference. The absorption band in the 700–1000-nm region is broad and it is difficult to locate a maximum accurately. In general, agreement with the values reported by Kato, *et al.*,[10] was very good; however, agreement on the ν_{max} assignment for the di-μ-(4-nitropyridine N-oxide)-bis[dichlorocopper(II)] and di-μ-(3-methylpyridine N-oxide)-bis[dibromocopper(II)] was poor. We find ν_{max} for these two complexes to be 1025 and 1250 kK compared to 910 and 1190 kK. These peaks are very broad and the change in sensitivity of their single-beam instrument over this range may account for the discrepancy. There are other interesting absorption bands in the region 1500–2100 nm; however, data will have to be collected on additional complexes before they can be interpreted. The ν_{max} values for the 4-bromo-, 4-phenyl-, and 4-*t*-butyl-substituted pyridine N-oxide complexes were not obtained because of insufficient sample size.

Table I

Parameters Obtained from a Least-Squares Fit to the Magnetic Susceptibility Equation with g Fixed at 2.200

Complex	$2J$, cm^{-1}	$10^6N\alpha$, cgsu	10^3C_i, cgsu deg	% impurity
$[(pyO)CuCl_2]_2$	716 ± 27	96	0.0	0.0
$[(4\text{-}picO)CuCl_2]_2$	829 ± 40	14	2.2	0.5
$[(4\text{-}t\text{-}C_4H_9pyO)CuCl_2]_2$	776 ± 38	37	0.53	0.1
$[(4\text{-}Bz(pyO))CuCl_2]_2$	838 ± 50	54	2.1	0.5
$[(4\text{-}CH_2OHpyO)CuCl_2]_2$	941 ± 43	26	4.6	1.0
$[(4\text{-}Cl(pyO))CuCl_2]_2$	1064 ± 48	40	2.2	0.5
$[(4\text{-}Br(pyO))CuCl_2]_2$	1050 ± 49	36	5.3	1.2
$[(4\text{-}CH_3OpyO)CuCl_2]_2$	994 ± 45	29	2.4	0.5
$[(4\text{-}C_2H_5OpyO)CuCl_2]$	1027 ± 47	37	2.0	0.5
$[(4\text{-}C_6H_5pyO)CuCl_2]_2{}^a$	1027 ± 48	48	0.63	0.1
$[(4\text{-}CNpyO)CuCl_2]_2$	966 ± 39	35	1.6	0.3
$[(4\text{-}COOCH_3pyO)CuCl_2]_2{}^a$	923 ± 50	23	4.3	1.0
$[(4\text{-}NO_2pyO)CuCl_2]_2$	529 ± 30	60	10.6	2.4

[a] Low-temperature data only.

Discussion

Figure 4 shows a plot of the exchange energy $2J$ *vs.* ν_{max} for the absorption band in the 700–1000-nm range. The diagram indicates a reasonable correlation between the two quantities. Figure 5 shows a plot of $2J$ *vs.* σ_R where σ_R is the portion of the substituent parameter assigned to the resonance contribution. There is no single correlation between σ_R and the exchange energy; however, the data possibly indicate two independent correlations, and two lines have been drawn through the points.

If inter- and intramolecular interactions were identical in the solid for all 4-substituted complexes, a correlation might be expected between some parameter related to the substituent effect and the magnitude of the exchange energy. The crystal structure[18,19] of the 1:1 complex of pyridine N-oxide and copper(II) chloride shows several significant intermolecular interactions. The structure basically is composed of oxygen-bridged dimers which are associated into long chains by weak chloride bridges. The copper ion is pentacoordinate, and the geometry may be described as a highly distorted square-based pyramid. There is a strong intermolecular steric interaction between the *ortho* pyridine hydrogens of one dimer and the chloride ions of an adjacent dimer in the same chain. This interaction depends upon the substituent in the 2 position; however, it should be similar for all 4-substituted complexes if

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TABLE II
MAGNETIC SUSCEPTIBILITY DATA FOR 1:1 COMPLEXES[a]

χ_m^c	T°K	χ_m^c	T°K	χ_m^c	T°K	χ_m^c	T°K	χ_m^c	T°K	χ_m^c	T°K	χ_m^c	T°K
(Pyridine N-oxide)$CuCl_2$													
268	301	244	281	206	249	129	188	85	91	309	330	367	387
269	302	240	277	201	247	124	182	85	84	309	329	365	385
269	303	236	273	199	243	115	176	86	78	323	343	364	384
267	301	233	270	194	239	110	163	267	297	323	342	269	298
264	298	229	266	189	232	108	160	275	304	339	358	268	297
259	295	225	263	180	228	105	155	285	310	338	357	363	383
257	291	218	259	171	221	104	152	286	311	351	370	376	395
251	285	211	253	156	212	100	143	294	318	365	386	378	404
247	283	207	251	135	194	86	105	295	319	365	386	386	415
(4-methylpyridine N-oxide)$CuCl_2$													
113	299	77	259	108	292	37	190	18	115	111	297	181	360
113	299	80	263	90	269	34	178	16	104	118	304	200	376
90	268	82	265	62	236	31	168	15	103	128	313	214	389
81	261	85	268	57	229	30	164	13	92	129	314	214	390
76	255	88	273	53	224	24	140	13	94	139	323	230	404
74	254	94	280	50	218	22	133	11	86	152	335	228	402
72	251	98	282	46	211	109	296	12	87	154	336	236	411
72	253	102	286	44	206	27	150	12	89	167	348	249	423
74	256	110	297	41	198	19	120	111	297	181	360	252	423
(4-t-butylpyridine N-oxide)$CuCl_2$													
168	301	147	281	87	217	43	141	165	299	206	332	268	385
167	301	143	276	78	206	40	123	165	299	207	334	268	385
166	301	137	269	72	199	40	122	166	300	222	346	282	400
166	301	128	258	63	187	39	108	176	308	224	347	299	417
162	297	121	250	58	179	39	98	177	308	237	359	300	417
159	294	112	242	59	160	39	80	184	314	242	362	312	431
155	289	102	232	48	157	39	79	186	316	256	375	312	431
151	286	100	231	45	151	40	79	195	323	256	375	314	433
(4-pyridylcarbinol N-oxide)$CuCl_2$													
85	298	74	280	44	206	28	118	83	300	122	347	175	400
85	299	69	269	38	178	26	109	83	299	123	347	177	402
85	300	66	262	37	174	25	102	89	307	125	359	186	410
85	300	64	256	33	155	27	92	89	308	124	359	185	410
83	296	60	247	31	142	27	87	98	319	146	372	197	420
81	293	57	241	31	136	22	79	99	320	147	373	197	419
80	290	54	232	29	127	24	80	110	333	158	383		
78	287	47	217	29	125	83	299	111	335	159	384		
(4-benzylpyridine N-oxide)$CuCl_2$													
150	298	114	256	85	212	56	126	150	298	181	331	239	381
147	295	112	253	81	205	55	118	151	298	182	331	252	396
143	290	110	250	78	199	54	101	154	304	200	342	252	395
140	287	108	246	71	184	54	90	156	304	200	342	260	406
138	284	105	241	67	178	55	89	157	304	214	356	259	405
135	280	103	238	67	175	55	90	166	312	214	356	258	405
132	276	100	234	64	165	53	79	166	312	226	367		
129	273	94	226	62	158	53	78	173	319	226	367		
117	258	88	218	57	132	149	298	175	320	240	382		
(4-chloropyridine N-oxide)$CuCl_2$													
71	298	58	262	44	174	44	197	39	101	88	325	108	352
73	298	55	253	69	292	43	183	39	90	89	325	128	379
68	287	51	240	68	288	41	170	39	91	95	336	140	393
66	283	50	233	62	273	40	149	37	79	104	348	139	391
64	278	43	168	52	244	40	138	37	89	114	362	148	403
64	275	43	163	49	235	40	135	71	298	125	376	156	414
62	271	43	160	47	228	40	130	75	304	72	298	155	413
60	265	43	143	46	216	40	121	81	314	76	305	166	425
59	263	43	140	45	205	40	120	82	316	76	307	166	425
(4-bromopyridine N-oxide)$CuCl_2$													
72	300	65	281	47	219	35	144	75	302	74	301	121	378
73	300	60	269	45	205	35	127	87	312	74	301	128	389
74	301	57	259	43	196	36	121	80	312	83	317	128	388
75	303	54	251	42	183	40	93	90	328	84	318	137	402
74	300	52	243	38	174	35	79	90	329	102	347		
71	294	50	236	36	161	37	80	96	338	105	351		
67	287	49	230	36	149	74	302	96	338	112	363		
(4-methoxypyridine N-oxide)$CuCl_2$													
83	310	71	291	47	229	32	133	27	80	84	314	134	378
83	310	69	287	44	217	31	129	27	79	89	321	134	378
82	310	73	280	39	194	31	123	76	301	91	323	146	392
81	310	61	267	38	187	30	119	77	302	102	338	151	397
77	303	57	257	37	176	29	93	77	302	116	356	169	416
75	298	49	236	36	167	30	95	81	309	116	356	168	415
(4-ethoxypyridine N-oxide)$CuCl_2$													
75	298	64	268	46	203	39	123	75	298	88	320	111	354
75	297	62	263	43	175	39	121	75	299	95	332	123	370
73	291	59	254	43	171	37	98	75	299	96	332	133	384
69	283	56	243	42	162	35	89	80	307	101	341	146	400
67	278	53	231	42	140	33	79	80	307	102	343	157	415
66	274	47	207	39	127	33	79	87	319	110	354	164	424
												164	423
(4-phenylpyridine N-oxide)$CuCl_2$													
91	298	81	280	71	258	59	213	50	170	48	139	48	96
90	299	78	274	68	251	57	204	49	163	48	125	51	93
88	294	75	266	66	242	55	194	49	156	47	119	49	80
85	288	73	261	61	228	51	181	48	144	47	109	49	78
(4-cyanopyridine N-oxide)$CuCl_2$													
90	299	73	268	55	222	34	140	28	78	104	318	144	366
90	299	72	266	53	217	31	123	89	299	105	319	143	366
88	296	69	262	47	205	32	121	89	299	112	330	156	381
84	289	65	253	45	199	34	109	89	299	112	330	155	380
81	283	63	250	43	192	43	92	93	305	119	340		
78	278	61	243	41	183	41	94	94	305	120	341		
76	274	60	239	39	161	44	85	98	311	132	354		
73	270	56	227	34	144	30	79	98	311	132	354		
(4-carbomethoxypyridine N-oxide)$CuCl_2$													
94	300	87	292	66	264	53	239	29	176	22	128	23	92
94	300	82	286	62	257	47	225	28	172	22	122	25	94
94	300	77	280	59	250	45	220	23	140	21	110	25	83
92	300	69	268	56	244	34	194	24	136	21	107	23	79
(4-nitropyridine N-oxide)$CuCl_2$													
442	298	389	265	289	217	154	160	76	88	473	321	527	396
443	298	394	268	284	215	146	156	61	79	481	328	526	394
442	298	382	260	239	197	143	155	63	80	482	329	529	402
436	293	371	255	231	193	117	142	442	298	493	340	532	410
425	286	364	251	217	188	83	121	442	298	503	352	532	410
416	279	358	247	203	182	81	119	450	304	503	352	535	418
409	275	343	238	184	173	79	118	452	305	513	366	535	424
400	270	325	230	174	169	74	110	460	310	522	382	535	423
392	266	320	228	165	165	75	104	461	311	521	382	534	430

[a] $\chi_m^{cor} \times 10^6$ cgsu and T°K are listed for the two overlapping temperature ranges.

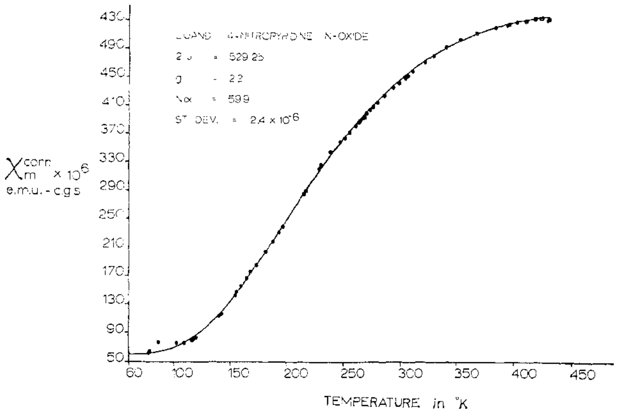

Figure 1.—Least-squares fit of temperature dependence of χ_m^{cor} to a modified Bleaney–Bowers equation for di-μ-(4-nitropyridine N-oxide)-bis[dichlorocopper(II)].

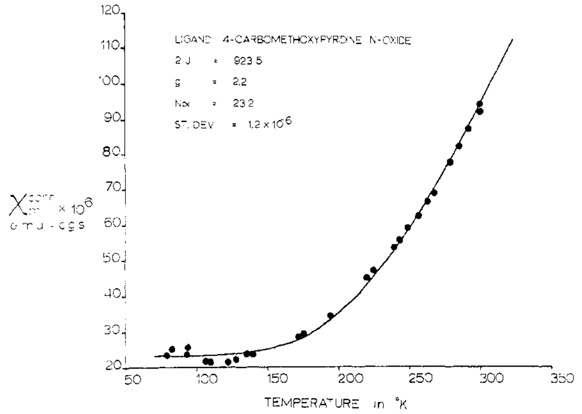

Figure 2.—Least-squares fit of temperature dependence of χ_m^{cor} to a modified Bleaney–Bowers equation for di-μ-(4-carbomethoxypyridine N-oxide)-bis[dichlorocopper(II)].

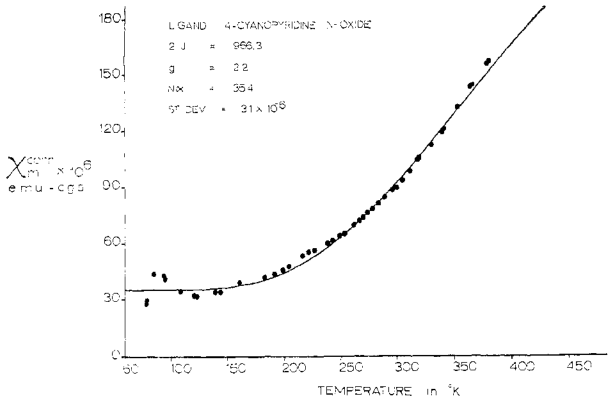

Figure 3.—Least-squares fit of temperature dependence of χ_m^{cor} to a modified Bleaney–Bowers equation for di-μ-(4-cyanopyridine N-oxide)-bis[dichlorocopper(II)].

packing permits the pyridine rings to achieve the same orientation. The Cu–Cl stretching frequencies imply the steric interactions may not be identical for all of the 4-substituted complexes. There also is a significant interaction between the hydrogen atom in the 4 position and the copper(II) ion of an adjacent chain. No chemical bonding is implied, but the electrostatic interaction may affect the electron distribution around the copper ion. This interaction must depend upon the substituent in the 4 position. Either of the two effects described above should affect the magnitude of the exchange energy, and it is not too surprising that no single correlation exists between a parameter related to the substituent effect and $2J$. We suggest there may be several correlations which depend upon the nature of the intermolecular interactions in the solid. For complexes with similar crystal structures and intermolecular interactions, the exchange energy should correlate with a substituent parameter. It is difficult *a priori* to rationalize why the hydrogen-, *t*-butyl-, and methoxy-substituted complexes show similar intermolecular interactions since they differ greatly in size and polarity. We propose to determine the crystal structures of several complexes in each series shown in Figure 4.

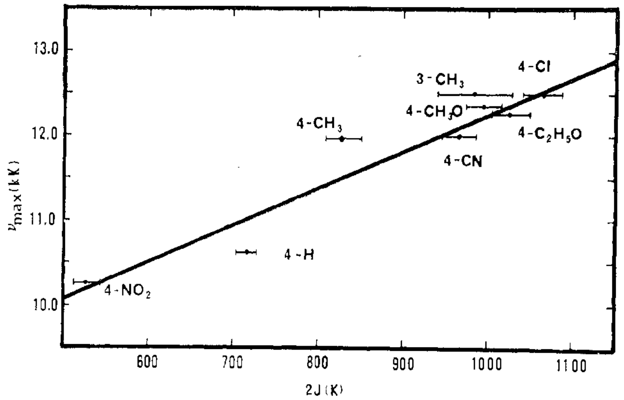

Figure 4.—A plot of the ligand field bands against the exchange energies for a series of 4-substituted pyridine N-oxide complexes, $[(RC_5H_4NO)CuCl_2]_2$. The values for the 3-CH₃ complex, $[(3\text{-}CH_3C_5H_4NO)CuBr_2]_2$, are taken from ref 10 and W. E. Hatfield and J. C. Morrison, *Inorg. Chem.*, **5**, 1390 (1966).

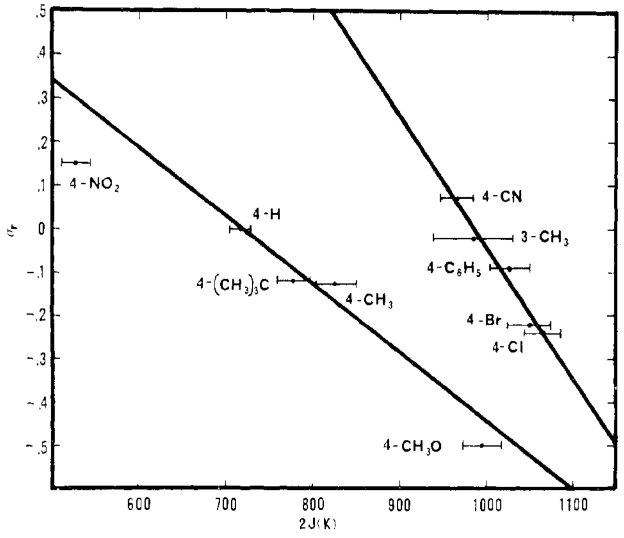

Figure 5.—A plot of the substituent parameters σ_R against the exchange energies for a series of 4-substituted pyridine N-oxide complexes, $[(RC_5H_4NO)CuCl_2]_2$. The 3-CH₃ complex, $[(3\text{-}CH_3C_5H_4NO)CuBr_2]_2$, has been included.

Anything which affects the electron distribution around the copper(II) ion affects the magnitude of the exchange energy and also the position of the electronic absorption bands. The band in the 700–1000-nm region of the spectrum apparently is characteristic of the dimeric structure of the molecule. The electron distribution may be affected by changing the crystal field strength of the ligand through substitution or changing the symmetry of the crystal field by steric interactions or by intermolecular interactions. While the direct relationship between the singlet–singlet transition in the 700–1000-nm range and the singlet–triplet separation corresponding to infrared frequencies has not been elucidated, it appears to be reasonable qualitatively.

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The Oxidation of Hydrazoic Acid by Bromate Ion in Perchlorate Solution

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Nitrogen and nitrous oxide are the only oxidation products produced when *excess* hydrazoic acid is oxidized by bromate ion in perchloric acid–lithium perchlorate solution. The reduction products of the bromate ion are hypobromous acid and bromine. The rate expression is $-d[BrO_3^-]/dt = k_0[BrO_3^-][HN_3][H^+]$. At 25.0° and 2.0 M ionic strength, the value of k_0 is $(6.22 \pm 0.06) \times 10^{-2}\ M^{-2}\ sec^{-1}$, and the associated activation parameters are $\Delta H^{\ddagger} = 13.5 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = -18.7 \pm 0.6$ eu. Oxygen-18 tracer studies reveal that most, but not all, of the oxygen in the nitrous oxide product is derived from the solvent.

Introduction

Ce(IV),[1] Co(III),[2] and Mn(III)[3] react with HN_3 to produce the stoichiometric quantity of N_2. While HNO_2 oxidizes HN_3 to produce the stoichiometric amounts of N_2 and N_2O,[4] most multiequivalent oxidizing agents, if they react at all, have been reported to produce in addition higher oxidation states of nitrogen.[5] A previous report[2] has demonstrated that the reaction of $HN^{15}–N^{14}–N^{15}$ with bromate produces $N^{15}–N^{14}$ and $N^{15}–N^{15}–O$. This communication reports a stoichiometric and kinetic study of this latter reaction. In addition, we have investigated the source of the oxygen in the N_2O product through oxygen-18 tracer studies.

Experimental Section

Reagents.—Reagent grade sodium bromate and allyl alcohol were used without further purification. The preparation and standardization of the perchloric acid and lithium perchlorate solutions have been described in a previous communication.[6] Purified sodium azide was recrystallized twice using previously reported procedures,[7] and solutions of this salt were standardized by the cerate procedure.[1] A mixture of bromine and hypobromous acid was prepared in the dark by vacuum distillation from a mixture of bromine water and mercuric oxide at 0°. These solutions were used the same day. Bromine water was prepared by the dissolution of reagent grade bromine. The water used was doubly distilled in an all-glass apparatus after distillation of deionized water from an alkaline permanganate still.

Oxygen-18-enriched sodium bromate was prepared by allowing a nearly saturated solution of the salt to equilibrate with enriched solvent in 2 M perchloric acid for 1 hr at 25°. The solution was then neutralized with solid sodium hydroxide, and the enriched sodium bromate was precipitated with a minimum amount of anhydrous, reagent grade methanol. Blank experiments demonstrated that no sodium perchlorate is precipitated in this procedure. The precipitate was washed with additional methanol, dissolved in the minimum amount of water, and reprecipitated as before. The salt was then carefully dried under vacuum and stored in a desiccator. The oxygen-18 enrichment of the sodium bromate was determined by conversion to carbon dioxide by the Anbar technique,[8] separation by gas chromatography, and mass spectrometric analysis of the $46/(44 + 45)$ mass ratio on a nuclide RMS-16 mass spectrometer. The oxygen-18-enriched water was purchased from Volk Radiochemical Co.

Procedures. Kinetic Studies.—Attempts to monitor the reaction by spectrophotometry proved to be impractical for reasons to be discussed later. Consequently, a titrimetric method for determining the bromate concentration during the reaction was used. Allyl alcohol in *ca.* 50% excess over the initial bromate concentration was present to scavenge the hypobromous acid product (*vide infra*). In a typical run, 400 ml of a solution containing the desired amounts of sodium bromate, lithium perchlorate, and perchloric acid was brought to temperature equilibrium in a constant-temperature bath. The desired amount of allyl alcohol was then added, and the reaction was initiated by addition of a sodium azide solution with vigorous stirring. All reactions were run in the absence of light. Suitable aliquots were withdrawn at appropriate times and added to an excess of acidified sodium iodide solution. The recorded time corresponded to half-delivery of the reaction solution; time

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