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Synthesis and Magnetic Behavior of Three Novel Di-μ-halobis[halo(1,2-benzoquinonedioxime)copper(II)] Complexes. Ferromagnetic Exchange Coupling

Michel MÉGNAMISI-BÉLOMBÉ
Department of Physics, Stanford University, Stanford, California 94305, U.S.A.

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Synopsis. Variable-temperature magnetic susceptibilities measured from 4.2 to 300 K on the new dimeric clusters indicate ferromagnetic exchange coupling with $J=+4.63$ cm^{-1} and $J=+0.14$ cm^{-1} for di-μ-bromobis-[bromo-(4-chloro-1,2-benzoquinonedioxime)copper(II)] and di-μ-chlorobis[chloro-1,2-benzoquinonedioxime) copper(II)], respectively, and antiferromagnetic exchange coupling with $J=-0.11$ cm^{-1} for di-μ-bromobis[bromo(1,2-benzoquinonedioxime)copper(II)].

The investigation of exchange effects in paramagnetic cluster compounds has recently developed into a topic of focal and increasing interest to inorganic chemists, as well in theoretical[1] as in experimental[2,3] respect. Lately we reported[4] antiferromagnetic exchange coupling in di-μ-bromobis[bromo(dimethylglyoxime)copper(II), $[CuBr_2(dmgH)]_2$. This dimeric cluster, the first adduct of $CuBr_2$ with a 1,2-dionedioxime ligand, is isostructural[4] with the di-μ-chloro analogue.[5] We now have employed 1,2-benzoquinonedioxime(bqdH) ligands[6] to prepare the three new dimers listed above. We show in the following that, as a specific result of scientific innovation, it is possible to bring about desirable changes in magnetic properties of cluster compounds (in particular ferromagnetic orderings) by controlled chemical modifications of appropriate ligand systems.

Experimental

The brown solids were obtained in good yield by reacting equimolar solutions of the analytical grade reactants according to the equation $RR'bqdH+CuX_2 \xrightarrow[20°C]{(acetone)} CuX_2(RR'bqdH)$ (dimeric structure sketched in the Fig. 1). After washing with cold acetone and drying at ≈ 50 °C, the materials analyze as in the Table 1. The compounds are remarkably air stable, though the bromo derivatives show signs of decomposition after several weeks of exposure to air and light.

Near infrared spectra (KBr pellets) were recorded with a Perkin-Elmer 621 Grating Spectrophotometer, and X-band electron spin resonance spectra with a Varian Assoc. E-12 instrument at room temperature. Variable-temperature susceptibility data were collected at 36 different points from 4.2 to 300 K with a Superconducting Technology, Inc. SQUID-type susceptometer operating at ≈ 2 kG.[4]

Results and Discussion

The spectroscopic data are taken as conclusive evidence to infer the dimeric structure sketched in the Fig. 1. This is done by comparing the spectra with those recorded on the analogous, well-characterized

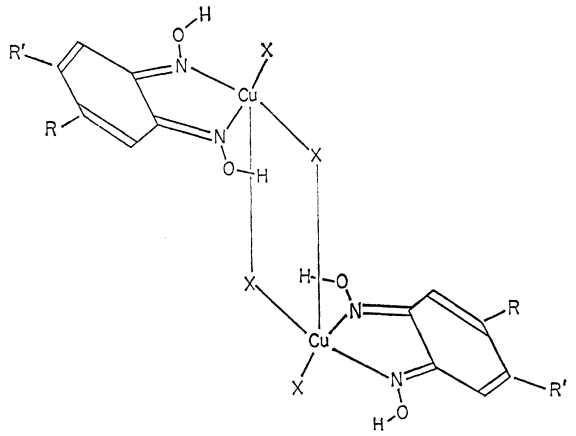

Fig. 1. Infrerred schematic structure of the $[CuX_2(RR'bqdH)]_2$ dimers (bqdH=1,2-benzoquinonedioxime):
a) R=Cl, R'=H, X=Br$^-$: $[CuBr_2(ClbqdH)]_2$,
b) R=R'=H, X=Cl$^-$: $[CuCl_2(bqdH)]_2$,
c) R=R'=H, X=Br$^-$: $[CuBr_2(bqdH)]_2$.

dimethylglyoxime Cu(II) dimers.[4,5] The striking resemblance of the two sets of spectra is interpreted as an intimate reflection of the similar ligand field geometry surrounding the Cu sites in both dimer types. This is rationalized by considering the two analogues $[CuCl_2(bqdH)]_2$ and $[CuCl_2(dmgH)]_2$,[5] which exhibit the same ESR line shape with the identical parallel g factor of 2.207, but have, as to be expected, the different perpendicular g factors of 2.056 and 2.039, respectively.

The corrected molar susceptibility data, χ_m, were fitted with a standard non-linear least-squares computer program[4,7] to the singlet-triplet equation

$$\chi_m = \frac{Ng^2\beta^2}{3k(T-\theta)}\left[1+\frac{1}{3}\exp\left(-\frac{2J}{kT}\right)\right]^{-1} + N\alpha,$$

where the exchange parameter J is defined by the Heisenberg Hamiltonian $H_{ex}=-2JS_1\cdot S_2$. The van Vleck constant, $N\alpha$, was fixed at 60×10^{-6} emu/mol for all three dimers, and the best fits gave a) $J=+4.63$ cm^{-1}, $g=1.99$, $\theta=-5.53$ K for $[CuBr_2(ClbqdH)]_2$; b) $J=+0.14$ cm^{-1}, $g=1.95$, $\theta=-0.29$ K for $[CuCl_2(bdqH)]_2$; c) $J=-0.11$ cm^{-1}, $g=1.95$, $\theta=+0.22$ K for $[CuBr_2(bqdH)]_2$. The fitting g factors differ slightly from the correspeonding isotropic values of 2.050, 2.106, and 2.050 observed with ESR, but the deviations of less than ±0.2 lie within the range expected for the observed J values to be regarded as reliable and "meaningful measurements of the exchange interaction."[3] The experimental magnetic data agreed to within 3% or less with the corresponding theoretical values

Table 1. Microanalytical data

Element	$[CuBr_2(ClbqdH)]_2$		$[CuCl_2(bqdH)]_2$		$[CuBr_2(bqdH)]_2$	
	Found(%)	Calcd(%)	Found(%)	Calcd(%)	Found(%)	Calcd(%)
C	18.20	18.20	26.35	26.44	20.09	19.94
H	1.33	1.27	2.19	2.22	1.64	1.67
N	6.95	7.08	10.16	10.28	7.68	7.75
Cl	8.90	8.95	25.82	26.01		
Br	40.12	40.37			43.63	44.21
Cu	15.70	16.05	23.11	23.31	17.50	17.58

calculated using the above equation. The intradimer exchange coupling, measured by J, is presumably mediated by a *super exchange* mechanism involving the valence orbitals of the bridging halide ligands. Substitution of the bqdH rings (Fig. 1) with electron withdrawing Cl stoms is accompanied by a remarkable increase in J value which passes from -0.11 cm^{-1} in $[CuBr_2(bqdH)]_2$ to $+4.63$ cm^{-1} in $[CuBr_2(ClbqdH)]_2$ Obviously this result demonstrates that the reported ligand-induced nephelauxetic effect[8] may provide a mechanism for modulating electron spin orderings in paramagnetic cluster compounds.

Provided this trend could prove to be generally valid, the present effect might be anticipated to have a far-reaching significance with respect to the better understanding of solid state magnetic phenomena as well as in connection with sounder studies of bonding mechanisms in coordination chemistry for the years ahead. Synthetic details of these and other new Cu(II) dimeric clusters will appear in a subsequent, more comprehensive report.

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** The three-dimensional single crystal X-ray structure of $[CuBr_2(dmgH)]_2$ has now been fully solved (H. Endres, submitted to *Acta Crystallogr., Sect. B.* The results are in excellent agreement with our preliminary findings.