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Super Exchange in Copper(II) Dimers. II. Synthesis, Characterization and Magnetic Properties of Binuclear Adducts of Copper(II) Halides with 1,2-Benzoquinone Dioximes. Ligand-induced Ferromagnetic Exchange Coupling

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Various 1,2-benzoquinone dioximes (bqdH) have been combined with $CuCl_2$ or $CuBr_2$ to afford the following new dimeric adducts: di-μ-chlorobis[chloro(1,2-benzoquinone dioxime)copper(II)], $[CuCl_2(bqdH)]_2$; di-μ-chlorobis[chloro(4-chloro-1,2-benzoquinone dioxime)copper(II)], $[CuCl_2(ClbqdH)]_2$; di-μ-chlorobis[chloro(4-methyl-1,2-benzoquinone dioxime)copper(II)], $[CuCl_2(MebqdH)]_2$; di-μ-chlorobis[chloro(4,5-dimethyl-1,2-benzoquinone dioxime)copper(II)], $[CuCl_2(Me_2bqdH)]_2$; di-μ-bromobis[bromo(1,2-benzoquinone dioxime)copper(II)], $[CuBr_2(bqdH)]_2$; di-μ-bromobis[bromo(4-chloro-1,2-benzoquinone dioxime)copper(II)], $[CuBr_2(ClbqdH)]_2$; di-μ-bromobis[bromo(4,5-dimethyl-1,2-benzoquinone dioxime)copper(II)], $[CuBr_2(Me_2bqdH)]_2$. These brown solids were characterized by variable-temperature magnetic susceptibility measured within 4.2—300 K, as well as by room temperature near infrared and electron spin resonance spectra from which the dimeric structure of the compounds was inferred. The intradimer magnetic exchange interaction was found to occur by a super exchange mechanism mediated by the valence p wave functions of the bridging halide ions. It was observed that the electrophilic character of the benzoquinonoid ligands affects the magnetic exchange *via* backbonding and through mesomeric π electron delocalization. It was found, most interestingly, that the tendency to ferromagnetic exchange interaction within a dimer is the stronger, the more electrophilic the bqdH ligands can be made.

We present here part II of our investigations of magnetic super exchange in di-μ-halobridged copper(II) dimers. In part I[1] we showed that this category of magnetic clusters provides the simplest solids that appear to be best suited for reliable studies of magnetic exchange effects within the frame of the molecular field approximation or Heisenberg-Dirac-Van Vleck (HDVV) model.[2] To test the existing theoretical models,[2,3] new materials with possibly flexible properties are needed.[4] We therefore focus our efforts primarily on the development of novel synthetic routes aimed at establishing a means for bringing about desirable changes in the magnetic properties of solids by a systematic chemical modification of the constituent molecules. Thus, part I of this research series dealt with the isomorphous dimers,[5,6] $[CuX_2(dmgH)]_2$, where $X=Cl^-$ or Br^-, and dmgH=dimethylglyoxime (or 2,3-butanedione dioxime). The results obtained there had revealed that the substantial difference noted in the super exchange effects of the two dimers ought to be linked to the nature of the halogen atom involved in the bridges, a result which is, in fact, quite consistent with a general trend.[7]

In the present work as well as in a recent note,[8] we have employed a series of 1,2-benzoquinone dioxime (bqdH) ligands (Fig. 1) instead of dimethylglyoxime (dmgH). The purpose is to check that the reported nephelauxetic effect[9] induced at the central metal site by the electrophilic benzoquinonoid ligands is likely to affect the intradimer exchange coupling. This ligand-induced nephelauxetic effect was first observed while searching for new Krogmann type one-dimensional conductors,[9—11] of interest in the study of high temperature superconductivity according to the hypothetical excitonic model of Little.[12] It was shown that the effect arises because the electrophilicity of the partially oxidized aromatic ligands couples more or less to the d-shell electron density of the central metal ions by means of backbonding[13] and mesomeric delocalization

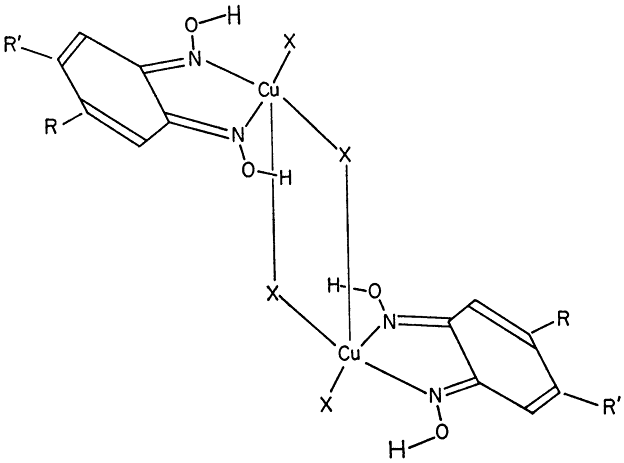

Fig. 1. Sketch of inferred molecular structure of the $[CuX_2(RR'bpdH)]_2$ dimers, with the planes of the individual molecules nearly perpendicular to the plane of the drawing. The *molecular planes* and the *intermolecular Cu–X bond direction* are taken roughly as the perpendicular (⊥) and parallel (//) orientations, respectively.[8]

$X=Cl^-$:

a)	$R=R'=H$	$[CuCl_2(bpdH)]_2$
b)	$R=Cl, R'=H$	$[CuCl_2(ClbpH)]_2$
c)	$R=Me(=CH_3), R'=H$	$[CuCl_2(MebpdH)]_2$
d)	$R=R'=Me$	$[CuCl_2(Me_2bpdH)]_2$

$X=Br^-$:

e)	$R=R'=H$	$[CuBr_2(bpdH)]_2$
f)	$R=Cl, R'=H$	$[CuBr_2(ClbpdH)]_2$
g)	$R=R'=Me$	$[CuBr_2(Me_2bpdH)]_2$

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of π electrons.[9] The effect is reminiscent of the through-bond phenomenon developed by Hoffmann.[14] Thus, the coupling between metal d-shell and ligand π-system provides a mechanism for d-shell "electron clouds" to be delocalized on to the spheres of the electrophilic benzoquinonoid rings. The degree of delocalization may be enhanced or reduced by appropriate substitution of these rings with electron withdrawing or electron releasing groups.

The objective of the present contribution, therefore, is three-fold: first to describe the synthesis of new di-μ-halobridged copper(II) dimers, second to examine the role of the bridging halide ion, third and most importantly, to check the impact of the ligand-induced nephelauxetic effect upon the super exchange coupling.

Experimental

Preparation of Materials. *The Reactants*: The commercially available anhydrous $CuBr_2$ crystals (Baker Analyzed Reagents, 99.4%) were used without further purification. $CuCl_2 \cdot 2H_2O$ crystals (90%+) from the same source were recrystallized from 99.5% acetone, finely ground and dehydrated at 105 °C over three consecutive nights to yield a dark-brown powder. The 1,2-benzoquinone dioxime ligands used were of analytical grade.[9]

Synthesis of the Compounds: The complexes listed in Table 1 were prepared according to the method reported earlier.[8] A general trend, however, was observed in the reaction yield which was found to be highest for the derivatives with less electrophilic bqdH ligands. The compounds decompose when heated above 200 °C.

Spectroscopic Experiments and Magnetic Susceptibility Measurements. The molar magnetic susceptibility data were collected at 36 closely spaced temperature points in the range 4.2—300 K, and near infrared and X-band electron spin resonance spectra were recorded at room temperature with the techniques described earlier.[1,15] A non-linear least-squares fitting procedure with a double-precision computer program[1,16] was employed to fit the susceptibility data to the conventional singlet-triplet Heisenberg equation.

Results

The Compounds. All the complexes listed in Table 1 crystallize as shiny, dark-brown tiny prisms or flakes. The ease of complex formation is apparently determined by the electrophilic character of the benzoquinonoid rings involved, since the reaction yield decreases noticeably with increasing electrophilic character of these rings (87% for the derivatives with methyl-substituted, and about 54% for those with chloro-substituted bqdH ligands). The stability of the complexes decreases in the same sense, particularly in the case of bromine-containing derivatives whose decomposition is obvious after a few weeks of exposure to air and light. The black body that results from this decomposition very probably consists of molecules with the Cu ions chelated by the quasi-coplanar 1,2-benzoquinone dioximate ligands, much like in $Cu(bqd)_2$[17] or in $Cu(dmg)_2$.[18] Note that the dimeric clusters reported here are very stable in vacuum or in a nitrogen atmosphere at room temperature. In solution, however, the likelihood of their decomposition increases considerably, especially at temperatures appreciably above ambient. For this reason, it is recommended that the syntheses be carried out at room temperature or lower.

In general the new materials are poorly soluble in the cold, even in water or in acetone and similar organic solvents. When a powdered sample of $[CuCl_2(bqdH)]_2$, for instance, is stirred for a while in H_2O at room temperature, it is rather transformed into the equally sparingly soluble $Cu(bqd)_2$ complex, presumably according to the reaction

$$[CuCl_2(bpdH)]_2 \xrightarrow{(2H_2O)} Cu(bpd)_2 + CuCl_2 \cdot 2H_2O + 2HCl,$$

as the resulting greenish-brown solution is strongly acidic. In hot acetone, the solubility is substantially higher, but the likelihood of chemical decomposition at that temperature is increased as well. The chemical decomposition taking place in the solution is recognizable by the formation of tear-causing bromoacetone in the case of the bromine-based derivatives. This suggests a redox reaction similar to the one noted previously on the related $[CuX_2(dmgH)]_2$ dimers.[1] The occurrence of this reaction is also indicated by the change in color of the solution which turns from dark-brown to light yellow-green after a few days. The true nature of this

Table 1. Microanalytical data of the $CuX_2(RR'bqdH)$ compounds

Compound	Element, %[a]					
	C	H	N	Br	Cl	Cu
$CuCl_2(bqdH)$	26.35 (26.44)	2.19 (2.22)	10.16 (10.28)		25.82 (26.01)	23.11 (23.31)
$CuCl_2(ClbqdH)$	23.52 (23.47)	1.55 (1.64)	8.84 (9.12)		34.64 (34.64)	20.30 (20.70)
$CuCl_2(MebqdH)$	29.47 (29.34)	2.81 (2.81)	9.44 (9.77)		24.56 (24.74)	21.98 (22.17)
$CuCl_2(Me_2bqdH)$	31.29 (31.96)	3.36 (3.35)	9.16 (9.32)		23.45 (23.59)	20.65 (21.14)
$CuBr_2(bqdH)$	20.09 (19.96)	1.64 (1.67)	7.68 (7.75)	43.63 (44.21)		17.50 (17.58)
$CuBr_2(ClbqdH)$	18.20 (18.20)	1.33 (1.27)	6.95 (7.08)	40.12 (40.37)	8.90 (8.95)	15.70 (16.50)
$CuBr_2(Me_2bqdH)$	25.92 (24.68)	2.63 (2.60)	6.97 (7.19)	39.73 (41.03)		15.80 (16.31)

a) Calculated values are given in parentheses.

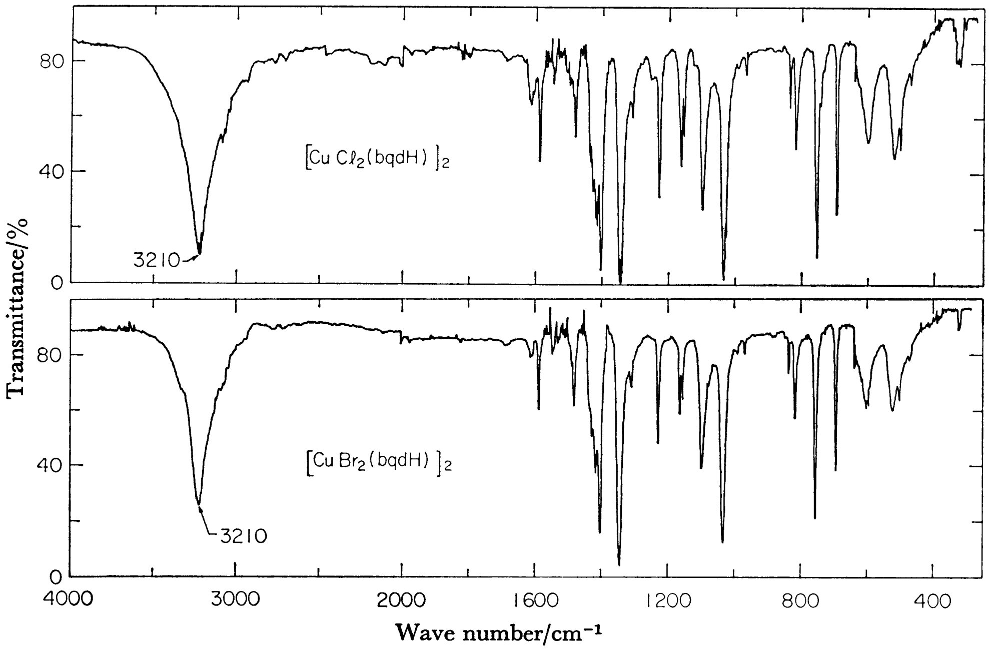

Fig. 2. Virtually identical near infrared spectra of $[CuCl_2(bpdH)]_2$ and $[CuBr_2(bpdH)]_2$ reflecting the matching structures of the compounds.

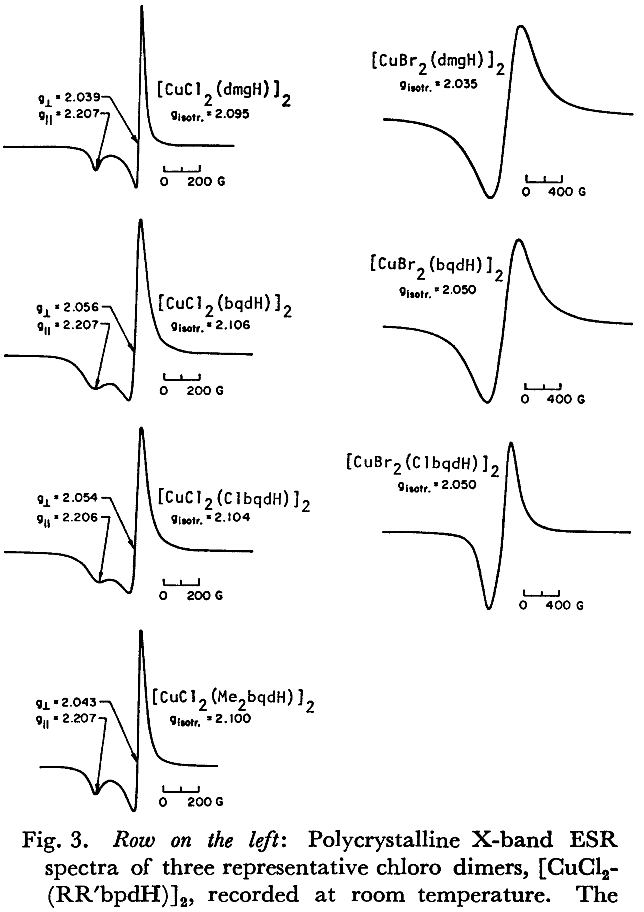

Fig. 3. *Row on the left*: Polycrystalline X-band ESR spectra of three representative chloro dimers, $[CuCl_2(RR'bpdH)]_2$, recorded at room temperature. The striking resemblance with the spectrum of the well-characterized dimer,⁽6⁾ $[CuCl_2(dmgH)]_2$ (top of the row), reflects the dimeric structural similarity.
Row on the right: ESR spectra of two representative bromo dimers, $[CuBr_2(RR'bpdH)]$ demonstating their structural analogy to the well-characterized $[CuBr_2(dmgH)]_2$ dimer[1,5] (top of the row).

chemical process has not been established as yet.

Spectroscopic Results. Figure 2 shows the near infrared spectra[19] of $[CuCl_2(bqdH)]_2$ and $[CuBr_2(bqdH)]_2$, which exhibit a striking resemblance reminiscent of that observed previously on the $[CuX_2(dmgH)]_2$ dimers.[1] Nevertheless, the doublet splitting of the O–H stretching absorption band characteristic of the latter is not observed in the former pair of dimers.

In Fig. 3 are displayed the ESR spectra of both the $[CuX_2(dmgH)]_2$ and the $[CuX_2(RR'bqdH)]_2$ dimeric clusters. The absorption lines of four chloro compounds are presented in the row on the left, and the lines of three bromo derivatives in the row on the right side of the figure. In either case, the line shapes are characterized by their remarkable similarity. For the chloro compounds, the anisotropy of the g tensor is well-resolved into the parallel ($g_{//}$) and the perpendicular ($g_{\perp}$) components. Note, in particular, that $g_{//}$ remains equal to 2.207 as the ligand is varied from compound to compound, whereas $g_{\perp}$ does change markedly. The line shapes of the bromo derivatives, on the other hand, exhibit no obvious evidence for such a resolution of the g tensor which appears rather isotropic with the lines being considerably broader. In both categories of the $[CuX_2(RR'bqdH)]_2$ dimers, however, a significant narrowing of the lines is observed. This is obviously the result of substituent effects induced at the benzoquinonoid rings. Hence, the linewidth for the perpendicular absorption varies, *e.g.*, from $\Delta H_{\perp}=70$ G in $[CuCl_2(bqdH)]_2$ to $\Delta H_{\perp}=50$ G in $[CuCl_2(Me_2bqdH)]_2$. Likewise the width decreases from $\Delta H_{\text{isotr}}=330$ G in $[CuBr_2(bqdH]_2$ to $\Delta H_{\text{isotr}}=230$ G in $[CuBr_2(ClbqdH)]_2$.

Static Magnetic Results. The variable-temperature diamagnetic molar susceptibility of $Pt(bqd)_2$[9,10] (Table 2), along with Pascal's constants for H, Cl^-, and Br^-

atoms were used to correct for the diamagnetism of the ligands.

The corrected molar susceptibility data, χ_m, and the corresponding effective moments, μ_{eff}/Cu(II), of three representative dimers are listed in Tables 3, 4, and 5. The magnetic behavior of all three compounds is very similar over the temperature range examined. No maximum susceptibility is observed above 4.2 K, suggesting small J values in these materials. The trend in μ_{eff} data, on the contrary, is noticeably different. Whereas the effective moment per Cu(II) ion in $[CuCl_2(bqdH)]_2$ and in $[CuBr_2(bqdH)]_2$ remains virtually unchanged and close to the spin 1/2 value throughout the temperature range, the μ_{eff}/Cu(II) of $[CuBr_2(ClbqdH)]_2$ drops rather sharply in the lowest temperature region. A similar, though less dramatic, dropoff was observed in $[CuCl_2(ClbqdH)]_2$ as well. In all three cases, plots of inverse molar susceptibilities, $1/\chi_m$, *versus* temperature yielded nearly straight lines. From the slopes of these lines, the Curie constants of 0.804 for $[CuBr_2(ClbqdH)]_2$, 0.761 for $[CuBr_2(bqdH)]_2$,

TABLE 2. VARIABLE-TEMPERATURE DIAMAGNETIC MOLAR SUSCEPTIBILITY OF $Pt(bqd)_2$

Temp K	$10^{-3}\chi_m$ cgs emu mol^{-1}	Temp K	$10^{-3}\chi_m$ cgs emu mol^{-1}
4.2	0.057	34.1	−0.031
4.8	0.033	36.2	−0.035
5.7	0.021	38.3	−0.035
6.9	0.004	40.4	−0.044
8.0	−0.009	45.4	−0.044
9.4	−0.017	50.4	−0.061
10.6	−0.024	55.3	−0.044
12.5	−0.034	60.3	−0.026
15.0	−0.041	65.3	−0.013
16.2	−0.041	70.1	−0.017
17.6	−0.041	80.2	−0.020
19.7	−0.046	100.2	−0.039
21.8	−0.041	120.2	−0.035
23.8	−0.041	150.3	−0.044
25.7	−0.044	179.9	−0.044
27.6	−0.037	220.4	−0.050
29.8	−0.026	259.8	−0.052
31.9	−0.024	298.9	−0.068

TABLE 3. VARIABLE-TEMPERATURE MOLAR MAGNETIC SUSCEPTIBILITY (CORRECTED) χ_m, AND EFFECTIVE MOMENT, μ_{eff}/Cu(II), FOR $[CuBr_2(ClbqdH)]_2$

Temp K	$10^{-3}\chi_m$ cgs emu mol^{-1}		μ_{eff}/Cu(II) B.M.	
	Exper.	Theor.	Exper.	Theor.
4.2	100.144	100.556	1.296	1.299
4.8	94.308	94.090	1.345	1.343
5.7	85.195	85.599	1.393	1.396
6.9	77.292	76.153	1.459	1.449
8.0	69.150	69.001	1.486	1.485
9.4	61.597	61.512	1.521	1.519
10.6	56.510	56.210	1.546	1.542
12.5	48.738	49.394	1.559	1.570
15.0	42.203	42.537	1.590	1.596
16.2	39.751	39.865	1.603	1.605
17.6	36.681	37.136	1.605	1.615
19.7	33.411	33.668	1.620	1.627
21.8	30.547	30.786	1.630	1.636
23.8	28.296	28.462	1.639	1.644
25.7	26.459	26.555	1.647	1.650
27.6	24.616	24.886	1.646	1.655
29.8	22.990	23.197	1.653	1.660
31.9	21.770	21.785	1.664	1.664
34.1	20.747	20.479	1.679	1.668
36.2	19.928	19.370	1.695	1.671
38.3	18.792	18.375	1.693	1.674
40.4	17.743	17.477	1.690	1.677
45.4	15.779	15.655	1.689	1.682
50.4	14.358	14.178	1.697	1.686
55.3	13.009	12.979	1.692	1.690
60.3	12.157	11.948	1.707	1.693
65.3	11.348	11.069	1.716	1.695
70.1	10.432	10.339	1.705	1.697
80.2	8.993	9.081	1.692	1.700
100.2	7.237	7.321	1.695	1.705
120.2	6.029	6.135	1.693	1.708
150.3	4.969	4.936	1.717	1.712
179.9	4.126	4.144	1.710	1.714
220.4	3.506	3.401	1.742	1.716
259.8	3.104	2.899	1.778	1.717
298.9	2.748	2.530	1.792	1.718

TABLE 4. VARIABLE-TEMPERATURE MOLAR MAGNETIC SUSCEPTIBILITY (CORRECTED) χ_m, AND EFFECTIVE MOMENT, μ_{eff}/Cu(II) FOR $[CuBr_2(bqdH)]_2$

Temp K	$10^{-3}\chi_m$ cgs emu mol^{-1}		μ_{eff}/Cu(II) B.M.	
	Exper.	Theor.	Exper.	Theor.
4.2	176.114	176.044	1.719	1.719
4.8	154.271	153.349	1.720	1.715
5.7	127.168	128.505	1.702	1.711
6.9	105.738	105.682	1.707	1.707
8.0	89.986	90.889	1.696	1.704
9.4	77.463	77.148	1.705	1.702
10.6	68.587	68.299	1.704	1.700
12.5	57.888	57.804	1.700	1.699
15.0	47.997	48.086	1.695	1.697
16.2	44.567	44.496	1.698	1.696
17.6	41.752	40.932	1.713	1.696
19.7	36.090	36.543	1.684	1.695
21.8	33.070	33.005	1.696	1.694
23.8	30.449	30.219	1.700	1.694
25.7	28.235	27.977	1.701	1.693
27.6	26.219	26.045	1.699	1.693
29.8	24.212	24.117	1.696	1.693
31.9	22.401	22.526	1.688	1.692
34.1	21.395	21.071	1.705	1.692
36.2	20.182	19.847	1.706	1.692
38.3	19.166	18.758	1.710	1.692
40.4	17.137	17.782	1.661	1.692
45.4	15.939	15.824	1.697	1.691
50.4	14.135	14.256	1.684	1.691
55.3	12.930	12.995	1.687	1.691
60.3	11.929	11.920	1.691	1.691
65.3	11.133	11.010	1.700	1.690
70.1	10.335	10.258	1.697	1.690
80.2	8.920	8.972	1.685	1.690
100.2	6.908	7.190	1.656	1.690
120.2	5.903	6.002	1.675	1.690
150.3	4.760	4.811	1.680	1.689
179.9	4.012	4.029	1.686	1.689
220.4	3.560	3.299	1.756	1.689
259.8	3.007	2.808	1.749	1.689
298.9	2.535	2.448	1.720	1.689

Table 5. Variable-temperature molar magnetic susceptibility (corrected) χ_m, and effective moment, μ_{eff}/Cu(II) for $[CuCl_2(bqdH)]_2$

Temp K	$10^{-3}\chi_m$ cgs emu mol^{-1}		μ_{eff}/Cu(II) B.M.	
	Exper.	Theor.	Exper.	Theor.
4.2	162.086	162.475	1.649	1.651
4.8	143.859	142.929	1.661	1.656
5.7	120.282	121.084	1.655	1.660
6.9	101.503	100.591	1.673	1.665
8.0	86.410	87.084	1.662	1.668
9.4	74.630	74.376	1.674	1.671
10.6	65.801	66.109	1.669	1.673
12.5	55.869	56.219	1.670	1.675
15.0	46.486	46.975	1.668	1.677
16.2	43.733	43.539	1.682	1.678
17.6	39.868	40.117	1.673	1.679
19.7	35.825	35.888	1.678	1.680
21.8	32.516	32.466	1.682	1.680
23.8	30.128	29.764	1.691	1.681
25.7	27.739	27.584	1.686	1.681
27.6	25.902	25.702	1.688	1.682
29.8	24.072	23.821	1.691	1.682
31.9	22.608	22.266	1.696	1.683
34.1	20.949	20.841	1.687	1.683
36.2	20.031	19.642	1.700	1.683
38.3	18.919	18.574	1.699	1.683
40.4	17.999	17.616	1.702	1.684
45.4	15.423	15.690	1.670	1.684
50.4	13.780	14.146	1.662	1.684
55.3	12.681	12.902	1.670	1.685
60.3	11.582	11.840	1.666	1.685
65.3	10.855	10.941	1.679	1.685
70.1	10.129	10.198	1.680	1.685
80.2	8.933	8.924	1.686	1.686
100.2	7.175	7.158	1.688	1.686
120.2	6.000	5.979	1.689	1.686
150.3	4.717	4.795	1.673	1.687
179.9	3.980	4.017	1.679	1.687
220.4	3.296	3.290	1.688	1.687
259.8	2.958	2.801	1.735	1.687
298.9	2.589	2.442	1.738	1.687

Table 6. Room temperature paramagnetic mass susceptibility, χ_g, as a function of the applied field, H for the $[CuCl_2(bqdH)]_2$ dimer

H/kG	$10^{-6}\chi_g$/emu g^{-1}
2.10	4.36
3.13	4.20
4.11	4.16
5.12	4.19
6.12	4.17
7.13	4.36
8.10	4.24

and 0.754 for $[CuCl_2(bqdH)]_2$ were calculated.

Table 6 shows the field-dependence of the mass susceptibility, χ_g, for $[CuCl_2(bqdH)]_2$ at room temperature.[19] It is clearly seen that the magnetic susceptibility is independent of the applied field, H.

Discussion

By analogy to the previously well-characterized $[CuX_2(dmgH)]_2$ dimers,[1,5,6] the spectroscopic results of this study reflect conclusive evidences for a closely related dimeric structure of the present $[CuX_2(RR'bqdH)]_2$ clusters sketched in Fig. 1.[8]

The observations of a constant parallel g value in the ESR spectra of all chloro-bridged dimers (Fig. 3, row on the left) may be taken as good grounds to believe that the axial Cu–X bonds (which coincide roughly with the molecular parallel orientation) do not vary in character, no matter how radically the organic ligands lying in the horizontal direction (perpendicular orientation of the molecule) may be chemically modified. In other words, the structural element defined by the CuXCuX quadrangle in Fig. 1 remains virtually the same for all the dimers. From the well-known structure of $[CuCl_2(dmgH)]_2$ dimer,[6] therefore, it is reasonable to conclude that the present chlorobridged clusters have fairly the same structure, the specific difference residing merely in the replacement of the dmgH by the RR'bqdH ligands.

Likewise the ESR spectra of the bromobridged dimers (Fig. 3, row on the right) suggest that the structure of these derivatives is analogous to that of $[CuBr_2(dmgH)]_2$ (top of the row) which, in turn, has been shown to be isomorphous with the $[CuCl_2(dmgH)]_2$ dimer.[1,5,6]

Just as was found in that pair of dimers, it is demonstrated here that the new pair, $[CuCl_2(bqdH)]_2$ and $[CuBr_2(bqdH)]_2$, exhibit quasi-identical infrared spectra (Fig. 2). Yet, the doublet splitting of the O–H stretching absorption band characteristic of the former pair is not observed in the latter pair of dimers, thus suggesting that in the latter case, the hydroxyimino hydroxyl groups of the bqdH ligands find themselves in crystallographically equivalent positions. On the basis of these matching spectroscopic results, the dimeric structure of the new clusters is most reasonably assumed to be as sketched in Fig. 1, with the bridging angle CuXCu approximately 85°—88°.

Bearing in mind this structural similarity, it appears interesting next to examine the role of the halogen ligands in the super exchange effect. Considering, again, the pair of dimers, $[CuCl_2(bqdH)]_2$ and $[CuBr_2(bqdH)]_2$ (which differ only in their halogen ligands), it is seen that the variation of the exchange parameter, J, between the two compounds follows consistently the trend observed previously on the pair, $[CuCl_2(dmgH)]_2$ and $[CuBr_2(dmgH)]_2$.[1] For either dimer pair, the exchange coupling in the bromo derivative turns out to be antiferromagnetic ($J=-1.51$ cm^{-1} for the dmgH-based dimer, $J=-0.11$ cm^{-1} for the bqdH-based dimer), whilst in the chloro derivative it is found to be ferromagnetic ($J=+0.31$ cm^{-1} for the dmgH-based dimer, $J=+0.14$ cm^{-1} for the bqdH-based dimer). These observations indicate that, at least for the particular dimeric structure sketched in Fig. 1, bromo ligands are more likely to induce antiferromagnetic exchange coupling, while chloro ligands tend to drive a ferromagnetic coupling of the single electron spins at very low temperatures.

When, however, the ligand-induced nephelauxetic effect introduced above is modulated by appropriate substitutions of the benzoquinonoid rings, remarkable variations in the value of the exchange parameter result.[8] Considering the following dimers: $[CuCl_2(MebqdH)]_2$, $[CuCl_2(bqdH)]_2$, $[CuCl_2(ClbqdH)]_2$, where the electrophilic character of the benzoquinonoid rings is progressively enhanced in the same order, the corresponding J values of $-3.32\ cm^{-1}$, $+0.14\ cm^{-1}$ and $+0.38\ cm^{-1}$ are observed. For $[CuBr_2(bqdH)]_2$ and $[CuBr_2(ClbqdH)]_2$ likewise, the exchange coupling constant changes from $J=-0.11\ cm^{-1}$ to $J=+4.63\ cm^{-1}$, respectively. Clearly, electron releasing groups such as Me (methyl) at the bqdH moities are likely to induce antiferromagnetic exchange coupling, whereas electron withdrawing substituents such as Cl definitely drive the exchange process towards a ferromagnetic ordering of the intradimer single electron spins. In other words, the more electrophilic the bqdH ligands can be made, the more ferromagnetic the exchange coupling at lowest temperatures is expected to be. This finding constitutes the innovation of central interest in the present research.

The overall magnetic behavior of the binuclear Cu(II) clusters studied here is very much alike for the temperature region appreciably above 4.2 K. In particular the μ_{eff}/Cu(II) for $[CuCl_2(bqdH)]_2$ and $[CuBr_2(bqdH)]_2$ remains comparable to the spin 1/2 value over the temperature range considered. This indicates Curie-like behavior and agrees well with the small J values observed on these derivatives. The μ_{eff}/Cu(II) for $[CuBr_2(ClbqdH)]_2$, by contrast, departs markedly from this behavior at lowest temperatures, which is consistent with the larger J value found for this compound. Thus, it turns out that when the effect of the bridging halogen and the ligand-induced nephelauxetic effect are considered together with respect to their impact upon the exchange interaction within a dimer, the latter effect dominates overwhelmingly.

Although the dmgH-based copper(II) dimers on the one hand, and the bqdH-based dimers on the other hand, exhibit very similar magnetic and hence analogous structural features, the colors of the two compound classes differ radically. The blue-green crystals of the first class exhibit a color that is common to and characteristic of copper(II) derivatives of this type. The dark-brown color of the second class of compounds, by contrast, is rather unusual for such copper(II) derivatives.

The observed narrowing of the ESR lines upon substitution of the bqdH ring may be interpreted as a tangible manifestation of the ligand-induced nephelauxetic effect acting at the microscopic level. These observations indicate that there is a finite degree of involvement of the paramagnetic electrons in the phenomenon of ligand-induced nephelauxetic effect.

As a novel aspect of scientific interest, one may view the experimental evidence gained here on the basis of this nephelauxetic effect as a potential input to guide new developments in the field of magnetism. It is hoped that such developments might lead to the derivation of a model generally valid for predicting the occurrence of ferromagnetism in magnetic coordination compounds. Other effects such as the degree of coplanarity of the individual molecules, the magnitude of the bridging angle, the degree of the copper-halogen bondings, as well as the extent of the Cu–Cu contacts, considered together or separately, may play a non-negligible role in the intradimer exchange interactions. Detailed structural analyses, however, must be awaited in order to assess the importance of these factors. For more accurate and quantitative correlations of anisotropic spin-lattice relaxation processes, magnetic measurements on single crystals—possibly supplemented by neutron diffraction studies— are needed.

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