

Magnetic Studies of Copper(II) Halogen-substituted Propionates and Their Dioxan Adducts

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The magnetic properties of a series of copper(II) halogen-substituted propionates are reported. The compounds all display antiferromagnetic behaviour typical of binuclear complexes with copper(II) acetate-type structures.

The singlet-triplet splitting energies ($|2J|$) are in the range 286–346 cm^{-1} , and the Néel temperatures in the range 257–311°K.

The compounds listed in Table 1 display antiferromagnetic behaviour. The results lead to the conclusion that there exist in crystals of these compounds paired copper atoms, held together by bridging carboxylate groups as in the crystals of copper(II) acetate monohydrate.^{1,2} The temperature dependence of the magnetic susceptibility of all the compounds is approximated by the Bleaney – Bowers' expression³

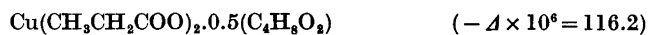
$$\chi_M' = \frac{g^2 N \beta^2}{3kT} \frac{1}{1 + \frac{1}{3} \exp(2|J|/kT)} + N\alpha \quad (1)$$

where χ_M' is the molar susceptibility, g the Landé factor, N Avogadro's number, β the Bohr magneton, k Boltzmann's constant, T temperature in °K, $2J$ the exchange coupling constant, and $N\alpha$ the temperature-independent paramagnetic contribution. The values of g , $|2J|$, $N\alpha$ and T_N , calculated from expression (1) by an iteration program drawn up by M. Väisänen, Ph.M., for the Elliott 803 B, are listed in Table 2, which also contains for comparison g_{av} values derived from EPR spectra of the compounds.^{4,5}

From the values of $|2J|$, we see that the exchange interaction is a little stronger in a compound with a terminal ligand (dioxan) than in the anhydrous compound or in the hydrate. Also, it seems, that the singlet-triplet splitting energy increases with the pK_a of the respective acid. On the other hand, the

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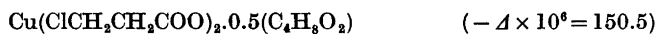
Table 1. Magnetic data.



$T^\circ\text{K}$	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		$\mu_{\text{eff.}}$ B.M.
		Obs.	Calc.	
93	0.14	150	140	0.34
123	0.72	300	307	0.54
153	1.46	480	477	0.77
183	1.97	610	608	0.95
213	2.32	698	694	1.09
243	2.45	740	743	1.20
273	2.53	760	765	1.29
293	2.54	766	770	1.34



$T^\circ\text{K}$	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		$\mu_{\text{eff.}}$ B.M.
		Obs.	Calc.	
93	0.56	308	306	0.479
123	1.087	464	466	0.676
153	1.575	609	622	0.864
183	2.01	738	738	1.04
213	2.297	822	811	1.185
243	2.418	858	850	1.29
273	2.44	865	866	1.376
293	2.433	864	868	1.424
303	2.427	861	866	1.446



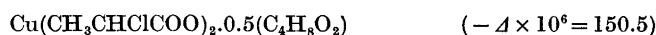
$T^\circ\text{K}$	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		$\mu_{\text{eff.}}$ B.M.
		Obs.	Calc.	
93	0.025	160	155	0.345
123	0.464	300	300	0.544
153	0.91	445	470	0.738
183	1.39	600	600	0.94
213	1.75	716	700	1.105
243	1.89	760	750	1.217
273	1.91	767	770	1.295
293	1.93	772	780	1.35



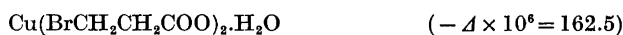
$T^\circ\text{K}$	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		$\mu_{\text{eff.}}$ B.M.
		Obs.	Calc.	
93	0.589	292	290	0.467
123	1.30	491	500	0.696
153	1.93	666	680	0.904
183	2.42	800	801	1.085
213	2.65	867	869	1.216
243	2.83	917	918	1.336
273	2.82	914	916	1.414
293	2.71	885	902	1.44

^a Recrystallised from methanol.

Table 1. Continued.



$T^\circ\text{K}$	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		$\mu_{\text{eff.}}$ B.M.
		Obs.	Calc.	
93	0.196	213	210	0.399
123	0.77	400	400	0.63
153	1.26	557	580	0.83
183	1.76	719	714	1.027
213	2.028	805	802	1.17
243	2.17	850	850	1.287
273	2.22	868	868	1.38
293	2.20	866	867	1.426



$T^\circ\text{K}$	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		$\mu_{\text{eff.}}$ B.M.
		Obs.	Calc.	
93	0.10	201	197	0.388
123	0.52	364	367	0.60
153	0.92	518	545	0.80
183	1.33	675	686	0.995
213	1.568	767	781	1.144
243	1.74	832	836	1.27
273	1.78	856	863	1.37
293	1.79	860	870	1.42



$T^\circ\text{K}$	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		$\mu_{\text{eff.}}$ B.M.
		Obs.	Calc.	
93	0.076	203	200	0.39
123	0.518	385	390	0.616
153	0.91	545	570	0.82
183	1.29	702	700	1.015
213	1.53	800	790	1.17
243	1.62	838	830	1.277
273	1.65	848	850	1.36
293	1.63	840	850	1.40



$T^\circ\text{K}$	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		$\mu_{\text{eff.}}$ B.M.
		Obs.	Calc.	
93	0.316	296	284	0.47
123	0.697	450	456	0.666
153	1.10	612	620	0.866
183	1.42	740	740	1.04
213	1.655	833	815	1.19
243	1.727	861	855	1.295
273	1.749	870	870	1.38
293	1.73	865	870	1.42

Table 1. Continued.

$\text{Cu}(\text{CH}_3\text{CHBrCOO})_2$ ($-\Delta \times 10^6 = 149.5$)

$T^\circ\text{K}$	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		$\mu_{\text{eff.}}$ B.M.
		Obs.	Calc.	
93	0.32	268	267	0.447
123	0.93	494	497	0.70
153	1.43	676	691	0.91
183	1.82	819	818	1.096
213	2.01	890	886	1.23
243	2.08	915	915	1.335
273	2.09	917	918	1.416
293	2.03	898	911	1.45

$\text{Cu}(\text{CH}_3\text{CHBrCOO})_2 \cdot 0.5(\text{C}_4\text{H}_6\text{O}_4)$ ($-\Delta \times 10^6 = 171.5$)

$T^\circ\text{K}$	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		$\mu_{\text{eff.}}$ B.M.
		Obs.	Calc.	
93	0.09	208	210	0.395
123	0.65	445	430	0.65
153	1.06	625	630	0.95
183	1.40	750	760	1.05
213	1.63	848	845	1.20
243	1.69	882	882	1.31
273	1.73	895	895	1.40
293	1.72	880	888	1.44

$\text{Cu}(\text{BrCH}_2\text{CHBrCOO})_2$ ($-\Delta \times 10^6 = 205$)

$T^\circ\text{K}$	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		$\mu_{\text{eff.}}$ B.M.
		Obs.	Calc.	
93	0.18	300	286	0.47
123	0.63	530	537	0.72
153	1.01	738	742	0.95
183	1.26	870	871	1.13
213	1.405	942	939	1.268
243	1.465	970	965	1.37
273	1.445	964	964	1.45
293	1.39	937	955	1.48

$\text{Cu}(\text{BrCH}_2\text{CHBrCOO})_2 \cdot \text{C}_4\text{H}_6\text{O}_4$ ($-\Delta \times 10^6 = 248.9$)

$T^\circ\text{K}$	$\chi_g \times 10^6$	$\chi_M' \times 10^6$		$\mu_{\text{eff.}}$ B.M.
		Obs.	Calc.	
93	0.08	298	293	0.47
123	0.41	500	520	0.70
153	0.72	700	710	0.92
183	0.98	840	842	1.11
213	1.06	898	900	1.24
243	1.12	932	934	1.35
273	1.11	930	932	1.426
293	1.10	924	930	1.47

Table 2. Néel temperatures (T_n), singlet-triplet splitting energies ($|2J|$), Landé factors (g), g_{av} derived from EPR spectra for comparison, and $N\alpha$.

Compound	T_n °K	$ 2J $ cm ⁻¹	g	g_{av}	$N\alpha \times 10^6$
Cu(CH ₂ CH ₂ COO) ₂ ·0.5(C ₄ H ₈ O ₂)	300	333	2.17	2.221	30
Cu(ClCH ₂ CH ₂ COO) ₂ ·H ₂ O	289	322	2.22	2.209	60
Cu(ClCH ₂ CH ₂ COO) ₂ ·0.5(C ₄ H ₈ O ₂)	311	346	2.18	2.172	60
Cu(CH ₂ CHClCOO) ₂	271	302	2.13	2.2 (broad)	120
Cu(CH ₂ CHClCOO) ₂ ·0.5(C ₄ H ₈ O ₂)	293	326	2.20	2.197	86
Cu(BrCH ₂ CH ₂ COO) ₂ ·H ₂ O	306	340	2.22	2.204	90
Cu(BrCH ₂ CH ₂ COO) ₂ ·CH ₃ OH	285	318	2.18	2.204	80
Cu(BrCH ₂ CH ₂ COO) ₂ ·0.5(C ₄ H ₈ O ₂)	292	325	2.19	2.168	80
Cu(CH ₂ CHBrCOO) ₂	263	293	2.18	2.2 (broad)	65
Cu(CH ₂ CHBrCOO) ₂ ·0.5(C ₄ H ₈ O ₂)	274	304	2.22	2.194	36
Cu(BrCH ₂ CHBrCOO) ₂	257	286	2.22	2.175	60
Cu(BrCH ₂ CHBrCOO) ₂ ·C ₄ H ₈ O ₂	262	292	2.18	2.140	80

effective magnetic moment increases, as the pK_a value of the respective acid increases.

The values of g calculated by expression (1) are in good agreement with those derived from EPR spectra. The lowest value of the g tensor was observed in the case of anhydrous copper(II) α -chloropropionate; the probable reason is a weaker orbital contribution to the magnetism.

The values of the effective magnetic moment at room temperature for all compounds are in good agreement with those reported previously.^{6,7} The value, 1.34 B.M., for the dioxan adduct of copper(II) propionate is slightly higher than the value 1.31 B.M., reported previously.⁸ The reason for this is that the diamagnetic contribution used in calculating the latter value did not include any magnetic contribution of copper.

EXPERIMENTAL

The compounds listed in Table 1 were prepared as described earlier.^{6,7}

Magnetic measurements. The magnetic susceptibilities of the compounds were measured over the temperature range 90–300°K by the Gouy method, using an apparatus manufactured by Newport Instruments Ltd. Copper sulphate pentahydrate was used for calibrations.⁹ Molar magnetic susceptibilities were corrected for the diamagnetism of the constituent atoms by means of Pascal's constants.¹⁰

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