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Bis(1,3,5-triketonato)dicopper(II) Chelates. Ferromagnetic and Antiferromagnetic Exchange between Copper(II) Ions[1]

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A new series of copper(II) chelates was prepared from substituted 1,3,5-triketone ligands. The generalized formula for this series is bis(1,3,5-triketonato)dicopper(II). The magnetic properties of these compounds were studied as a function of temperature from 77 to 423°K and as a function of field strength from about 3000 to 9000 G. The field dependence of the magnetic moments showed that ferromagnetic exchange is important throughout the series. In addition, certain of these chelates have the highest magnetic moments yet recorded for any copper(II) compound, another indication of ferromagnetic exchange. Antiferromagnetic exchange is also evident in all the members of the series since all the chelates have magnetic moments lower than the spin-only value at low temperatures. Since existing expressions for calculating magnetic moments do not adequately describe this complicated exchange behavior, the relationship $\mu_{\text{eff}} = 2.83\sqrt{\chi_{A}'T}$ BM was used at each given field strength. At 3100 G and 298°K, the range of magnetic moments for the series varied from 2.76 to 1.15 BM per copper(II) ion.

Introduction

Magnetic exchange between two or more transition metal ions contained in one molecular unit has been the topic of several recent papers. Most of these studies have dealt with copper(II) compounds,[2-6] which generally exhibit antiferromagnetic exchange and reduced magnetic moments. The first example of ferromagnetic exchange in an isolated metal cluster, $Ni_3(acac)_6$,[7] adds a great deal of interest to the possibility of using coordination compounds to study magnetic exchange mechanisms.

The 1,3,5-triketones are potentially dinegative, tridentate ligands. The well-developed π system of the dianion, however, imparts to the ligand a preference for a planar configuration. The planar configuration would preclude tridentate coordination to one metal ion. For this reason, it was believed that a series of copper(II) chelates could be prepared in which two copper(II) ions share bridging oxygens in a planar arrangement (Figure 1). Two brief mentions of copper(II) complexes of a few simple 1,3,5-triketonates exist in the early literature.[8,9] However, the physical properties of these complexes have not been studied to date. It is the purpose of this paper to investigate the magnetic properties of a series of substituted bis(1,3,5-triketonato)dicopper(II) chelates.

Experimental Section

Ligands.—The preparation of 2,4,6-heptanetrione from 2,6-dimethyl-γ-pyrone (K & K Laboratories, Inc.) is described in the literature.[10] All other triketones were prepared by the condensation of either 1-benzoylacetone (Aldrich Chemical Co.) or reagent grade acetone with the appropriate methyl ester using NaH as the condensing agent in refluxing monoglyme as described by Miles, Harris, and Hauser.[11]

Copper(II) Chelates.—The chelates were prepared using a 1:1 molar ratio of ligand to metal. The green powders are relatively insoluble in all common organic solvents except coordinating ones such as pyridine and dimethyl sulfoxide. Purification was accomplished by washing with water, methanol, and acetone. The washed products were dried overnight at 110°.

Bis(2,4,6-heptanetrionato)dicopper(II).—A solution of 1.2 g of $Cu(NO_3)_2 \cdot 3H_2O$ in 50 ml of absolute CH_3OH was added to 0.7 g of 2,4,6-heptanetrione dissolved in 150 ml of ammoniacal CH_3OH. The precipitate was washed and dried. The chelate starts decomposing at about 250° but does not melt up to 325°. *Anal.* Calcd: C, 41.28; H, 3.96; Cu, 31.2. Found: C, 41.46; H, 4.13; Cu, 29.3.

Bis(1-phenyl-1,3,5-hexanetrionato)dicopper(II).—A solution of 0.69 g of $Cu(CH_3COO)_2 \cdot H_2O$ in 60 ml of distilled water was added to 0.7 g of 1-phenyl-1,3,5-hexanetrione dissolved in 150 ml of ammoniacal CH_3OH. The precipitate was washed and dried. The chelate starts decomposing at about 305° but does not melt up to 325°. *Anal.* Calcd: C, 54.24; H, 3.79; Cu, 23.9. Found: C, 54.15; H, 3.87; Cu, 23.4.

Bis(1,5-diphenyl-1,3,5-pentanetrionato)dicopper(II).—A solution of 0.91 g of $Cu(NO_3)_2 \cdot 3H_2O$ in 50 ml of absolute CH_3OH was added to a solution containing 1.0 g of the ligand, 150 ml of acetone, and 5 ml of concentrated NH_4OH. The product was washed and dried. Melting with decomposition occurs at 323° for this chelate. *Anal.* Calcd: C, 62.28; H, 3.69; Cu, 19.4. Found: C, 62.20; H, 3.80; Cu, 18.9.

Bis(1-*p*-methoxyphenyl-5-phenyl-1,3,5-pentanetrionato)dicopper(II).—A solution of 1.42 g of $Cu(NO_3)_2 \cdot 3H_2O$ in 50 ml of absolute CH_3OH was added to a solution containing 1.51 g of the ligand, 200 ml of acetone, and 2 ml of concentrated NH_4OH. The precipitate was washed and dried. Melting with decomposition occurs from 292 to 302° for this compound. *Anal.* Calcd: C, 60.41; H, 3.94; Cu, 17.8. Found: C, 60.94; H, 4.25; Cu, 16.3.

Bis(1-*p*-chlorophenyl-5-phenyl-1,3,5-pentanetrionato)dicopper(II).—A solution of 0.90 g of $Cu(NO_3)_2 \cdot 3H_2O$ in 50 ml of absolute CH_3OH was added to a solution of 1.13 g of the ligand in 175 ml of acetone. The resulting solution was heated to boiling and concentrated NH_4OH was added until precipitation was complete. The product was washed and dried. The compound melts with

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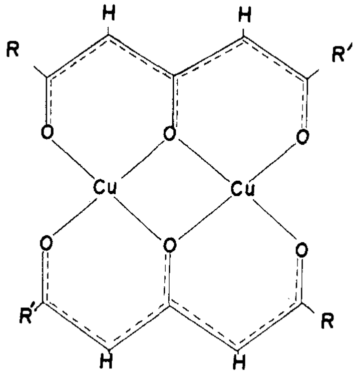
decomposition from 318 to 325°. *Anal.* Calcd: C, 56.36; H, 3.06; Cu, 17.5. Found: C, 56.75; H, 3.20; Cu, 17.0.

Bis(1-*p*-bromophenyl-5-phenyl-1,3,5-pentanetrionato)dicopper(II).—Solutions of 1.09 g of $Cu(NO_3)_2 \cdot 3H_2O$ in 45 ml of absolute CH_3OH and 1.53 g of the ligand in 175 ml of acetone containing 4 ml of concentrated NH_4OH were brought to boiling and mixed. The precipitate was collected, washed, and dried. The chelate melts with decomposition from 312 to 320°. *Anal.* Calcd: C, 50.20; H, 2.73; Cu, 15.6. Found: C, 50.66; H, 2.90; Cu, 14.9.

Bis(1-*m*-bromophenyl-5-phenyl-1,3,5-pentanetrionato)dicopper(II).—The preparation used was the same as for bis(1,5-diphenyl-1,3,5-pentanetrionato)dicopper(II). Melting with decomposition occurs from 297 to 302° for this chelate. *Anal.* Calcd: C, 50.20; H, 2.83; Cu, 15.6. Found: C, 50.30; H, 3.03; Cu, 15.4.

Bis(1,5-di-*p*-methoxyphenyl-1,3,5-pentanetrionato)dicopper(II).—The preparation used was the same as for bis(1-*p*-chlorophenyl-5-phenyl-1,3,5-pentanetrionato)dicopper(II). Melting with decomposition occurs from 303 to 310° for this compound. *Anal.* Calcd: C, 58.83; H, 4.16; Cu, 16.4. Found: C, 58.58; H, 4.22; Cu, 15.5.



No.	R	R′
1	C_6H_5	p-BrC_6H_4
2	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$
3	C_6H_5	CH_3
4	p-ClC_6H_4	p-ClC_6H_4
5	C_6H_5	p-ClC_6H_4
6	C_6H_5	p-$CH_3OC_6H_4$
7	C_6H_5	m-BrC_6H_4
8	CH_3	CH_3
9	C_6H_5	C_6H_5

Figure 1.

Bis(1,5-di-*p*-chlorophenyl-1,3,5-pentanetrionato)dicopper(II).—A solution containing 0.62 g of $Cu(NO_3)_2 \cdot 3H_2O$ in 50 ml of absolute CH_3OH was added to a solution of 0.85 g of the ligand in 275 ml of ammoniacal acetone. The precipitate was collected, washed, and dried. The chelate shows neither decomposition nor melting up to 325°. *Anal.* Calcd: C, 51.47; H, 2.54; Cu, 16.0. Found: C, 51.76; H, 2.83; Cu, 15.4.

Magnetic Susceptibility Measurements.—The magnetic susceptibility was measured by the Gouy method, using $Hg[Co(SCN)_4]$ as the calibrant. The susceptibilities as a function of temperature were determined at four points in the range 77–423°K. The four temperatures were achieved with liquid nitrogen, Dry Ice–methanol, room temperature, and a heating tape. Temperatures were measured with a copper–constantan thermocouple connected to a Leeds and Northrup temperature potentiometer. The thermocouple junction was positioned at the midpoint of the Gouy tube. A Varian Associates Model V-4004 4-in. electromagnet was used to provide field strengths ranging from 3100 to 8800 G. Corrections for the diamagnetism of the ligands were made using Pascal's constants. An experimental determination of the ligand diamagnetism yielded a susceptibility identical with that calculated by Pascal's constants, within experimental error (-144×10^{-6} cgsu for 1,5-diphenyl-1,3,5-pentanetrione).

Spectra.—Electronic spectra were recorded for approximately 1.5×10^{-3} *M* pyridine solutions using a Cary 14 spectrophotometer. Mass spectra were recorded using an Atlas CH-4 mass spectrometer.

Analyses.—Carbon, hydrogen, and copper analyses were carried out by Midwest Microlab, Inc., Indianapolis, Ind.

Results

The series studied and the generalized formulas of these copper(II) dimers are shown in Figure 1. Each copper(II) ion is bonded to two terminal oxygen atoms and shares two bridging oxygen atoms with the other copper(II) ion. This molecular formula is supported by the analytical data and by the mass spectra of several members of the series.

The mass spectrum of bis(1,5-diphenyl-1,3,5-pentanetrionato)dicopper(II) shows a molecular ion at *m/e* 654 and additional peaks at *m/e* 656 (M + 2) and *m/e* 658 (M + 4) (calcd mol wt 654). The mass spectrum of bis(1-phenyl-1,3,5-hexanetrionato)dicopper(II) shows a strong molecular ion at *m/e* 530 and additional peaks at *m/e* 532 (M + 2) and *m/e* 534 (M + 4) (calcd mol wt 530). The correct intensity ratio (5:4.5:1) for this set of molecular ion peaks was observed. An abundance of lower mass peaks exists in all spectra.

Magnetic moments were calculated from the formula $\mu_{\mathrm{eff}} = 2.83\sqrt{\chi_{A'}T}$ BM, where $\chi_{A'}$ is the magnetic susceptibility corrected for diamagnetism. No attempt was made to correct $\chi_{A'}$ for temperature-independent paramagnetism.

The magnetic properties of these binuclear complexes are extremely sensitive to the functional groups attached to the phenyl ring(s) on the terminal carbon atoms. Several of these compounds show marked ferromagnetic exchange at room temperature and also at 150°. Table I shows the room-temperature magnetic moments for all the chelates studied at the lowest (3100 G) and highest (8800 G) fields employed. Ferromagnetism is indicated by the abnormally high moments of complexes 1 and 2 of Table I at low fields strengths. Normal magnetic moments for Cu(II) compounds never exceed 2.2 BM and are usually between 1.8 and 2.0 BM. All chelates

TABLE I

EFFECTIVE MAGNETIC MOMENT PER Cu(II) ION AT 3100 AND 8800 G (AT 298°K)

Compd no.	R, R′	μ_{eff}, BM 3100 G	8800 G
1	C_6H_5, *p*-BrC_6H_4	2.76	1.89
2	*p*-$CH_3OC_6H_4$, *p*-$CH_3OC_6H_4$	2.70	1.83
3	C_6H_5, CH_3	1.98	1.39
4	*p*-ClC_6H_4, *p*-ClC_6H_4	1.66	0.99
5	C_6H_5, *p*-ClC_6H_4	1.59	0.83
6	C_6H_5, *p*-$CH_3OC_6H_4$	1.47	1.17
7	C_6H_5, *m*-BrC_6H_4	1.44	0.89
8	CH_3, CH_3	1.15	0.80
9	C_6H_5, C_6H_5	1.15	0.68

TABLE II

MAGNETIC SUSCEPTIBILITY ($\times 10^6$ CGSU) AND MOMENTS (BM) PER Cu(II) ION AT 3100 G FROM 78 TO 423°K

Compd no.	R, R′	Parameter	T, °K			
			423	298	196	78
1	C_6H_5, *p*-BrC_6H_4	$\chi_{A'}$	3126	3217	2846	3038
		μ_{eff}	3.26	2.76	2.11	1.37
2	*p*-$CH_3OC_6H_4$, *p*-$CH_3OC_6H_4$	$\chi_{A'}$	2931	3062	2591	3176
		μ_{eff}	3.15	2.70	2.01	1.41
3	C_6H_5, CH_3	$\chi_{A'}$	2329	1653	2181	2328
		μ_{eff}	2.81	1.98	1.86	1.21
6	C_6H_5, *p*-$CH_3OC_6H_4$	$\chi_{A'}$	1177	908	995	1419
		μ_{eff}	2.00	1.47	1.25	0.95

TABLE III

FIRST LIGAND FIELD BAND OF THE COPPER(II) DIMERS IN PYRIDINE

Compd no.	R, R′	ν_{max}, cm^{-1}	ϵ
1	C_6H_5, *p*-BrC_6H_4	13,441	109
2	*p*-$CH_3OC_6H_4$, *p*-$CH_3OC_6H_4$	13,699	≥ 125
3	C_6H_5, CH_3	13,459	90
4	*p*-ClC_6H_4, *p*-ClC_6H_4	13,423	108
5	C_6H_5, *p*-ClC_6H_4	13,441	111
6	C_6H_5, *p*-$CH_3OC_6H_4$	13,569	114
7	C_6H_5, *m*-BrC_6H_4	13,405	108
8	CH_3, CH_3	13,369	≥ 75
9	C_6H_5, C_6H_5	13,587	169

studied showed a decrease in χ_A and μ_{eff} with increasing field strength, behavior characteristic of ferromagnetism. Even chelates with low moments showed the same field dependence, indicating that both ferromagnetism and antiferromagnetism are operating in these compounds.

The temperature dependence of these copper(II) dimers at 3100 G is shown in Table II. Only the compounds which gave large enough weight changes to ensure confidence in our measurements were run at temperatures other than room temperature. An almost linear relationship between μ_{eff} and temperature exists for these compounds in the temperature range studied. This is due to the fact that $\chi_{A'}$ changes only slightly over the temperature range 78–423°K. Compounds **3** and **6** show the unusual property that $\chi_{A'}$ increases significantly at temperatures both above and below room temperature. There are several interesting points to be noted from the temperature data. First, the magnetic moments per copper(II) ion determined for compounds **1** and **2** increase to 3.2 BM at 423°K and 3100 G. To our knowledge, these are the highest moments ever recorded for a copper(II) compound. We recognize, of course, the relative nature of these magnetic moments as calculated from the formula $\mu_{eff} = 2.83\sqrt{\chi_{A'}T}$. Second, compounds **3** and **6** exhibit large increases in the magnetic moment on going from 298 to 423°K at 3100 G.

At lower temperatures the moments of all chelates studied were significantly lowered. The most notable among these are **1**, **2**, and **3** which exhibit moments extremely high and low within the temperature range studied. From the temperature data it is obvious that ferromagnetism predominates at high temperatures and antiferromagnetism begins to predominate as the temperature is lowered. However, the observed ferromagnetic field dependence is still present at 78°K.

All starting materials (chemicals and Gouy tubes) were checked for ferromagnetic impurities by measuring their magnetic properties at various field strengths. No magnetic properties were detected that would influence the results reported above. In all cases the analytical data reflect slight ligand impurities in the chelates. Therefore, the reported susceptibility values are probably slightly lower than the true values.

The position and extinction coefficient of the lowest energy ligand field band that occurs in the electronic spectra is shown in Table III. The band is very broad, extending about 300 mμ in width. Higher energy ligand field bands are obscured by intense absorptions at energies above 20,000 cm^{-1}. No attempt was made to study in detail these electronic spectra as it appears that there is no correlation between the ligand field bands observed and the magnetic properties of the different chelates.

Discussion

Since it is apparent that both ferromagnetism and antiferromagnetism are present in varying degrees in all the compounds studied, it remains to construct a model to account for these phenomena. This is not easily done since the structural details are not known. As yet, we have been unable to prepare single crystals suitable for a structural determination. It is, however, reasonable to assume that the dimers are close to planar, since the chelate ring carbon atoms of the ligands must be nearly sp^2 hybridized. In addition, the highly developed resonance system that extends throughout the entire molecule should give planarity and rigidity to the molecule. A model which explains part of the experimental observations involves ferromagnetic exchange through the bridging oxygens. It was first proposed by Anderson[12,13] and is entitled electron transfer plus intraatomic direct exchange. The reasonableness of such an exchange mechanism depends upon three assumptions: (1) the two copper(II) ions and the six oxygens lie approximately in the same plane, (2) the Cu–O–Cu and O–Cu–O angles do not deviate greatly from 90°, and (3) the predominant bonding mechanism is one in which oxygen p orbitals interact with the metal orbitals. If these structural assumptions are correct, the exchange through the Cu–O–Cu bridge should be ferromagnetic. A plausible explanation for the antiferromagnetic exchange observed is that there is strong intermolecular exchange occurring as well as intramolecular exchange and that the two are opposite in sign.

It should be mentioned that the probable structure of the copper(II) triketonate complexes differs significantly from other copper(II) dimers which show only antiferromagnetism and reduced magnetic moments. Cupric acetate monohydrate[14] consists of two copper-

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(II) ions each in square-pyramidal geometry and oriented so that the basal planes of the pyramids are parallel to each other. The crystal structure of di-μ-(pyridine oxide)-bis(dichloro)copper(II)[15,16] and presumably its substituted analogs consists of each copper(II) ion in distorted tetrahedral geometry. The crystal structure of acetylacetone(mono-O-hydroxyanil)copper(II)[17] which also has many substituted derivatives places one copper ion in a distorted square-pyramidal coordination and the other copper ion in a distorted square-planar coordination. Furthermore, the copper ions deviate significantly from coplanarity. The point to be noted from this discussion is that a comparison of the magnetic properties of copper(II) triketonate chelates with other copper(II) dimers from the literature is not really justified. We believe that the probable planar structure of the copper(II) triketonate dimers is significantly different from other copper(II) dimer structures such that the intramolecular magnetic exchange possibilities are very different.

Explaining the large differences in magnetic moments within our series of chelates and trying to correlate these differences with the functional groups attached to the phenyl ring(s) on the terminal carbon atoms is impossible at this juncture. There appears to be no correlation between the inductive and resonance electronic effects of the functional groups attached to the phenyl ring(s) and the magnetic moments observed. The two molecules which differ only by replacement of a *para*-chloro group for a *para*-bromo group on two of the four phenyl rings show great variance in their magnetic properties (Table I) although there is little difference in their inductive and resonance effects as measured by the Hammett σ constants. Inspection of other results reported in Tables I and II shows the futility of trying to correlate the magnetic properties with the electronic effects of the substituent groups. Resonance effects in a planar system such as that proposed for these copper(II) triketonate chelates should influence only electron density in the out-of-plane orbitals. Since the unpaired spin density is primarily in the molecular plane, resonance should have little influence on the intramolecular magnetic exchange. However, it is conceivable that resonance differences may affect intermolecular magnetic exchange since intermolecular interactions could take place between the oxygen p_z orbitals or carbon p_z oribtals on one molecule and copper(II) ions above and below the molecular plane.

The tentative conclusion is reached that the large differences in magnetic properties among the compounds studied cannot be accounted for by the electronic effects of various functional groups. It seems a plausible explanation for these very interesting magnetic effects is intermolecular structural differences, possibly caused by size differentials among the substituted functional groups. The large difference in the magnetic properties of **5** when compared with **1** supports this argument.

It should be mentioned that we do not mean to place a great amount of significance on the absolute values of μ_{eff} as calculated from the relationship $\mu_{\text{eff}} = 2.83\sqrt{\chi_{A'}T}$ BM. This expression is useful in an absolute sense only when $\chi_{A'}$ is independent of the magnetic field strength. For example, to say that a particular compound has a magnetic moment of 2.7 BM at 3100 G is only relative since its moment will be higher at lower field strengths and lower at higher field strengths. Nonetheless, the formula for calculating μ_{eff} is very useful for showing the existence of ferromagnetism by showing the field dependence of μ_{eff}. This was our primary objective.

Since the chelates discussed herein show the very unusual property of exhibiting both strong antiferro- and ferromagnetic exchanges, they are potentially important models for the poorly understood area of magnetic exchange. Work presently in progress includes X-ray structural studies, electron spin resonance, and magnetic studies on more magnetically dilute samples.

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