

MAGNETIC AND STRUCTURAL STUDY OF UNSOLVATED [Cu(acac)₂], (acac= acetylacetonate)Y. MORENO^{*a,c}, R. ARRUE^{a,f}, R. SAAVEDRA^{b,d}, J-Y PIVAN^e, O. PEÑAF, T. ROISNELL

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ABSTRACT

This work is the first of a series of studies on systems with a common basic structure, Cu-b-diketonate, whose ability to bind to other ligands is regulated by the presence of electron-withdrawing groups affecting the electronic density on the copper ion. In this paper the [Cu(acac)₂] system is studied. Its structure reveals discrete units linked through H bridges (*c.a.* 2.7Å). The crystallographic system and space group, are monoclinic and P21/n respectively; the cell parameters are a= 10.34Å, b= 4.71Å, c= 11.38Å, beta= 91.78°. The magnetic behaviour corresponds to a simple paramagnetism with $\mu = 1.8$ [BM]; however, a weak antiferromagnetic interaction is observed at lower temperatures.

Keywords: magnetism, copper, crystal structure

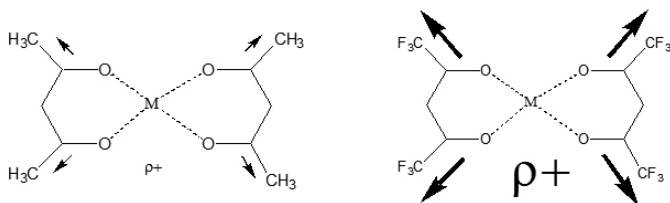
INTRODUCTION

The search of materials with specific magnetic properties has evidenced the need to produce and structurally explore as many ligand environments as possible, in order to find superexchange pathways adequate for the required needs. This need has boosted the development of new, imaginative synthetic techniques, far away of the traditional synthetic routes.¹⁻⁴

One of the strategies used to obtain magnetic molecular compounds with heterospins has been the assembly of different paramagnetic building blocks by reaction between organic ligands and metal complexes with desired features.⁵ Joining both moieties remains, however, a difficult task.

This problem will become harder if the ligand is not a good Lewis base, since it would be difficult to attach to a metal center. To solve this problem, the Lewis acid should be improved, by increasing the positive charge on the metal center.

Studies on metal(II)/b-diketonate systems like copper-hexafluoroacetylacetonate, [Cu(hfac)₂] have shown their ability to coordinate weak Lewis bases, resulting in compounds with different dimensionalities.⁶⁻⁸ The electron withdrawing group in the diketonate system increases the positive charge on the metal center. The scheme 1 presents the idea of increasing the positive charge on the metal center thanks to a CF₃ group. Therefore, copper(II) b-diketonate systems are starting materials in the preparation of polynuclear systems with magnetic properties.



Scheme 1

In order to compare the effect on the metal center of the electron-withdrawing group, it is necessary to synthesize families of compounds, including those with a CH₃ terminal group, until those with CF₃. Moreover, with the aim to easily understand the magnetic interactions in these compounds, simple monoelectronic spin carrier moieties should be used, such as copper (II) ion, i.e. d⁹ system with $S = \frac{1}{2}$.^{4,9-11}

In this work the magnetic properties of the unsolvated copper (II) acetylacetonate complex, [Cu(acac)₂] are discussed. While its structure is well known,¹² there are no reports on the magnetic behaviour, necessary to establish a systematic study of the β -diketonate family. Thus, this is the first of several works in which we synthesize this kind of systems, varying the type of ligand (to investigate the influence of the structural parameters on the magnetic behavior) or the paramagnetic ion (in order to study the different spin combinations).

EXPERIMENTAL

Reagents and solvents were used without further purification (Aldrich and Merck respectively).

The infrared spectra were recorded between 4000 and 500 cm⁻¹ using a FTIR spectrometer (NEXUS 470, NICOLET, USA) equipped with a photoacoustic detector (model PA-301, Gasera, Finland). A nitrogen purge was used to provide CO₂ and H₂O free dry air into the interferometer, while helium was used to purge the PA cell. Ten interferograms were averaged per spectrum at a resolution of 4 cm⁻¹. A carbon black reference was used to collect the corresponding background spectra for spectra-intensity normalization.

Diffraction spectra were recorded in a Bruker SMART AXS CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Semi-empirical absorption correction based on equivalent symmetry reflections was applied. A total of 5718 reflections were collected, of which 1264 reflections were unique ($R_{int} = 5.3\%$). The structure was solved by direct methods and refined by the full-matrix least-squares method based on F². Structure solution, refinement, and generation of publication materials were performed with the use of the SHELXTL crystallographic software package. The final refinement includes anisotropic displacement parameters for the non-hydrogen atoms. The crystal data and structure refinement of [Cu(acac)₂] are summarized in Table 1.

Table 1. Selected structural data.

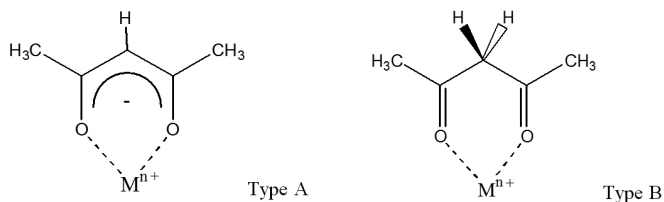
Empirical formula	C10 H14 Cu O4
a =	10.3416(11)
b =	4.7104(4)
c =	11.3828(11)
Alpha	90.000
Beta	91.780(5)
Gamma	90.000
Crystal size	0.14 x 0.05 x 0.02 mm
Reflections collected / unique	5718 / 1264 [R(int) = 0.0533]
Volume	554.22(9) Å ³
Z, Calculated density	2, 1.568 mg/m ³
Final R indices [I > 2 σ (I)]	R1 = 0.0424, wR2 = 0.0809

The magnetic susceptibility was recorded in Quantum Design MPMS XL5 susceptometer and measured at an applied field of 500 Oe (0.05 Tesla), between 2 K and 300 K. Powder samples were placed inside a gelatine capsule. The temperature independent magnetic contribution due to the sample holder was subtracted at all temperatures. The diamagnetic and other contributions due to the core electrons were estimated using Pascal constants and subtracted from the experimental values.

RESULTS AND DISCUSSION

Infrared study

In general the b-diketone coordination are of two types, depending on whether or not is the alpha carbon deprotonated¹³ (see scheme 2)



Scheme 2

Nakamoto and collaborators¹³ have studied similar systems and have found that, for systems in which the metal-ligand ratio is 1:2, a the planar arrangement commonly exists. The figure 1 shows the infra-red photoacoustic spectrum for [Cu(acac)₂].

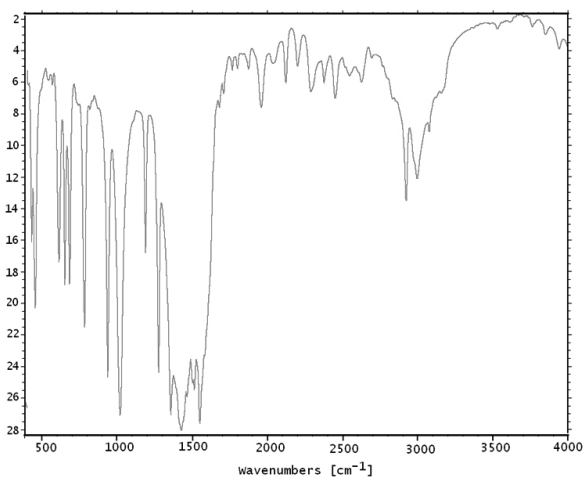


Figure 1: Infra-red photoacoustic spectrum for [Cu(acac)₂].

The 1577 and 1529 cm⁻¹ bands are assigned to $\nu(\text{C}=\text{C})$ coupled with $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{O})$ coupled with $\nu(\text{C}=\text{C})$ respectively. This kind of data leads to suppose that this is a type A coordination mode, which is confirmed by X-ray diffraction

Structure

Figure 2 shows an ellipsoid plot of [Cu(acac)₂]. The asymmetric unit is composed of acetylacetonate, acac, and a copper(II) cation.

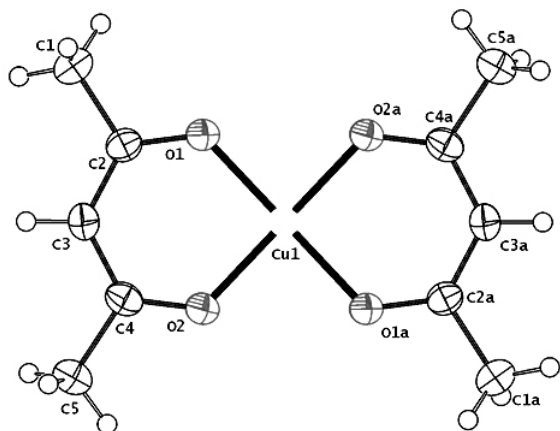


Figure 2: Ellipsoid plot (50% probability level) of [Cu(acac)₂].

The environment of the copper ion is planar square and there is no connection with other molecules. The vertices of this square are occupied by O atoms of the ligand carboxylic group. Figure 3 shows a packing view drawn along the [001] direction.

Table 2. Selected distances and angles.

Atoms	Distance [Å]	Atoms	Angle [°]
Cu1-O1	1.920	O1-Cu1-O2	93.23
Cu1-O2	1.922	C3-C2-O1	123.18
O1-C2	1.266	C3-C4-O2	124.67
O2-C4	1.276	Atoms	Torsion Angle [°]
C1-C2	2.041	O1-C2-C3-C4	-1.99
C2-C3	1.389	O2-C4-C3-C2	2.26
C3-C4	1.401	C1-C2-C3-C4	179.49
C4-C5	1.507	C2-C3-C4-C5	178.20

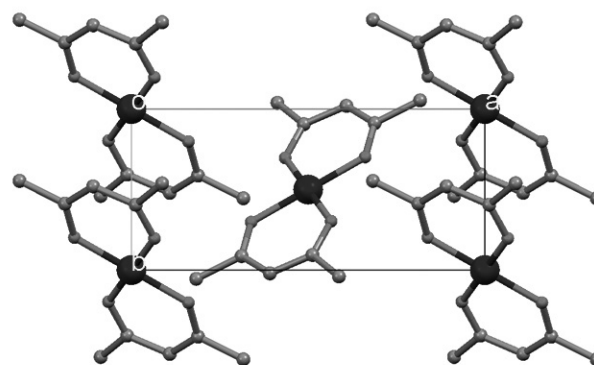


Figure 3: Packing view of [Cu(acac)₂] drawn along the [001] direction. H atoms have been omitted, for clarity.

The shortest copper-copper distance between neighboring isolated molecules is *c.a.* 4.71 Å. The structure is stabilized by hydrogen bonds (*c.a.* 2,716 Å); these H-bridges are established between one of the hydrogen atoms of the C5 carbon and one oxygen, O2, of the carboxylate group of the neighboring unit. This distance is in agreement with that observed in similar systems.¹⁴ See Figure 4.

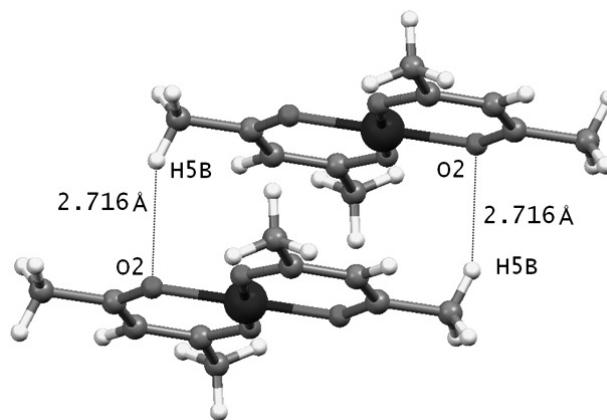


Figure 4: Hydrogen bonds between two [Cu(acac)₂] units.

Magnetism

Figure 5 shows a $c_M T$ versus T plot for the [Cu(acac)₂] compound. At 300K, the $c_M T$ value is 0.41 cm³mol⁻¹K, close the expected value for three

uncorrelated $S = \frac{1}{2}$ spins ($m_{\text{eff}} = 1.8 \text{ BM}$) for one Cu(II). Upon cooling, $c_M T$ slowly decreases down to *c.a.* 10 degrees, then decreasing abruptly which indicates a weak antiferromagnetic interaction.

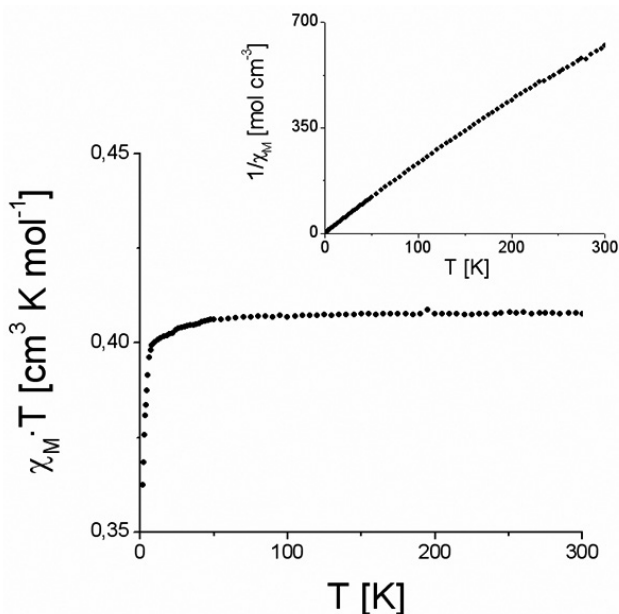


Figure 5: Temperature dependence of $c_M T$ for $[\text{Cu}(\text{acac})_2]$. The insert shows $1/c_M$ vs Temperature

The magnetic behaviour is in agreement with the molecular structure,¹⁵⁻¹⁷ because it are isolated units. The shortest distance between copper atoms belonging to different units is *c.a.* 4.71 Å.

By way of comparison with the $[\text{Cu}(\text{acac})_2]$, it has considered some compounds with different types of bridging ligands. One can conclude that the copper-copper distance is an important factor, however also other factors strongly influence on the magnetic behaviour. For example, the azido-bridged copper(II) dinuclear compounds, whose magnetic properties present a rather intriguing versatility. For the azide copper complex $[\text{Cu}(\text{N}_3)_2(\text{C}_{18}\text{H}_{38}\text{N}_2\text{S}_4)]$ (where the ligand is di- μ -azido-bis[[N,N,N',N'-tetramethylethylenediamineazido-copper(II)]) the copper-copper distance is 5.145 Å and in spite of this large separation, the metal ions are so strongly coupled in an antiferromagnetic fashion that the compound is diamagnetic.¹⁸

Other azido bridged compound, di- μ -azido-bis[[N,N,N',N'-tetramethylethylenediamineazido-copper(II)] has a copper-copper separation of 5.004 Å and its magnetic susceptibility follows the Curie law expected for two noncoupled copper(II) ions.¹⁹

In other systems as pyridine derivatives $[\text{Cu}_2(\text{t-bupy})_4(\text{N}_3)_2](\text{ClO}_4)_2$, where t-bupy stands for 4-terbutylpyridine, the copper-copper separation is 3.045 Å and the interaction between them is weakly ferromagnetic.²⁰

In the classic work of Bleaney and Bowers about copper acetate, the copper-copper distance is 2.64 Å and its magnetic moment is 1.4 BM, therefore antiferromagnetic.²¹

Therefore through the mentioned compounds and many others, we can conclude that the nature of the bridging groups and symmetry of the system are important factors for understand the magnetic behaviour of a molecular system.

CONCLUSIONS

A copper-b-diketonate $[\text{Cu}(\text{acac})_2]$ was synthesized. The infra-red analysis agrees with the X-ray crystal structure, showing discrete units interconnected by bridges H. The magnetic behaviour reveals single paramagnetism, however, at lower temperature, a weak antiferromagnetic interaction is revealed.

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