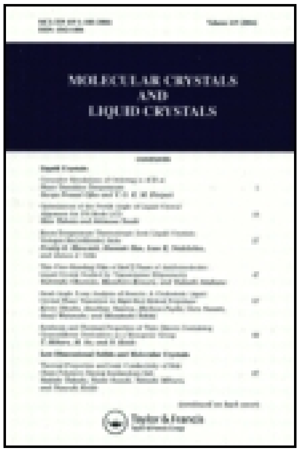

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Theoretical Study and Comparison with Experiments for Atacamite, $Cu_2Cl(Oh)_3$

Kenji Ueda [a] , Satoshi Takamizawa [a] , Wasuke Mori [b] , Shigehiro Kubo [a] & Kizashi Yamaguchi [a]

[a] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560, Japan

[b] Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa, 259-12, Japan

Version of record first published: 04 Oct 2006

To cite this article: Kenji Ueda, Satoshi Takamizawa, Wasuke Mori, Shigehiro Kubo & Kizashi Yamaguchi (1997): Theoretical Study and Comparison with Experiments for Atacamite, $Cu_2Cl(Oh)_3$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 33-40

To link to this article: http://dx.doi.org/10.1080/10587259708044546

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 33–40
Reprints available directly from the publisher
Photocopying permitted by license only

THEORETICAL STUDY AND COMPARISON WITH EXPERIMENTS FOR ATACAMITE, $Cu_2Cl(OH)_3$

KENJI UEDA[1], SATOSHI TAKAMIZAWA[1], WASUKE MORI[2],
SHIGEHIRO KUBO[1] AND KIZASHI YAMAGUCHI[1]

1) Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560, Japan

2) Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa 259-12, Japan

Abstract The dependency of the magnetic susceptibility on temperature has elucidated that the mineral atacamite $Cu_2Cl(OH)_3$ has the antiferromagnetic property. In order to explain this behavior and the spin arrangement derived from experimental studies, the ab initio UHF MO and UNO CASCI calculations were carried out for the tetranuclear cluster of copper(II), $Cu_4Cl(OH)_3$, which is the constitution in the atacamite crystal structure. The results of the CASCI calculations appreciate the relative stabilities among various spin arrangements for the tetranuclear cluster, being consistent with the experiments.

INTRODUCTION

The d-π conjugated systems have received continuous interest in relation to their unique electronic, magnetic and optical properties, together with potential applications to advanced technologies.[1-7] Among them, the copper complexes have been extensively investigated because of several reasons: the high T_c superconductivity, spin flustration, spin glass,[1] *etc.* Previously, the mineral atacamite, $Cu_2Cl(OH)_3$, was examined with magnetic susceptibility for the temperature.[1] 'According to the results,[1] it was found that the mineral atacamite exhibits the antiferromagnetic property. The crystal structure of the mineral atacamite had been already given from X-ray analysis by Wells, *et al.*[2] Considering this crystal structure,[2] the spin arrangement on Cu(II) cations of the atacamite can be determined so as to explain the antiferromagnetic behavior of the atacamite. In this paper, we wish to perform a theoretical study for reasonable explanation of the magnetism observed for the atacamite. For the purpose, the simplified model of the unit of the crystal structure are treated since it is difficult to consider and calculate continuous spin network in the crystal structure. Thus, ab initio unrestricted Hartree-Fock

(UHF) MO calculations are first carried out for various spin arrangements, *i.e.*, ferromagnetic, antiferromagnetic, and ferrimagnetic spin structures, which are possible for the simplified model, $Cu_4Cl(OH)_3$. The complete active space (CAS) configuration interaction (CI) calculations by use of the UHF natural orbitals (UNO)[8-11] are successively carried out for the singlet, triplet and quintet states of this cluster. The most stable spin arrangement calculated by the UNO CASCI will be compared and discussed with the spin arrangement expected from experimental studies. Implication of the calculated results will be discussed in relation to the magnetic behaviors of copper compounds.

CRYSTAL STRUCTURE

The structure of the mineral atacamite is shown in Figure 1, where each Cu(II) cation is numbered as 1, 2, 3 and 4. The atacamite crystal is composed of two kinds of Cu(II) cations, which have different atmosphere of the bridged anions; OH and Cl anions are considered as bridged anions. One kind of Cu(II) cations, which are described $Cu(II)_a$ in Figure 1, is bonded to four OH and two Cl anions as bridged anions, and the other, $Cu(II)_b$, is bonded to five OH anions and one Cl anion though the coordination number of both kinds is six. As shown in Figure 1, four Cu(II) cations and bridged anions constitute the distorted cubic unit of the atacamite crystal, and then the layer is made as the unit lies two-dimensionally. Distances between Cu(II) cations were determined from X-ray diffraction experiments, and they are summarized in Table I.

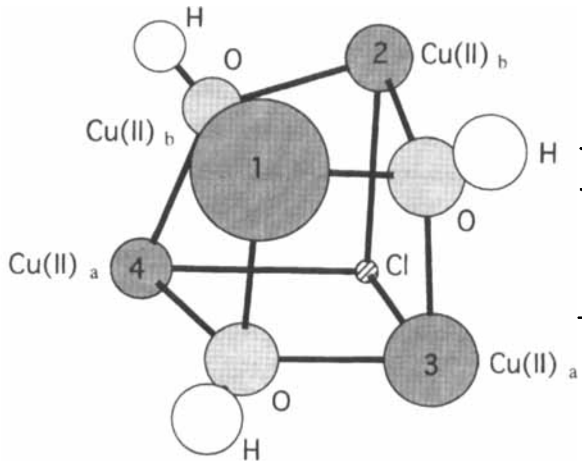

FIGURE 1 Crystal structure of the atacamite.

TABLE I Distances between each two Cu atoms.

Cu(II) cations	distance/Å
1 - 2	3.009
1 - 3 , 1 - 4	3.132
2 - 3 , 2 - 4	3.351
3 - 4	3.420

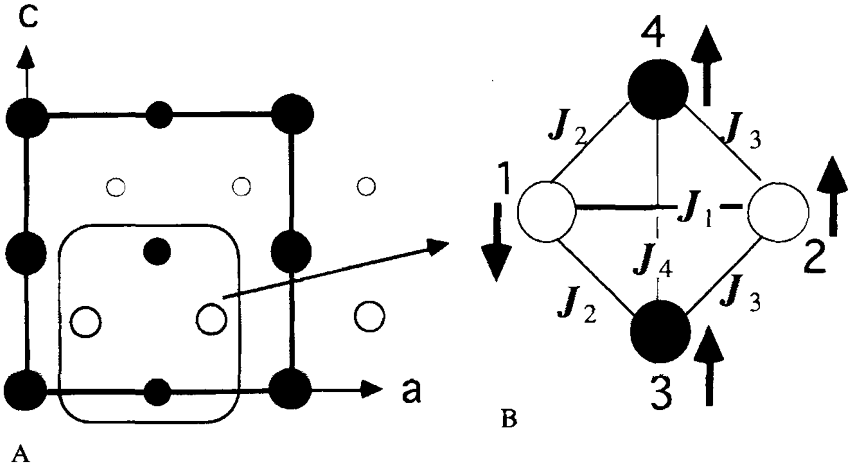

FIGURE 2 Only Cu(II) cations of the atacamite crystal are written. Here black circle is Cu(II)$_a$ and white one is Cu(II)$_b$. A; This figure is viewed along b axis. Relatively small black and white circles are Cu(II) cations on the layer which is under the layer of relatively large black and white circles. B; This figure is the tetranuclear cluster of Cu(II) cations. Each Cu(II) cation is numbered as 1, 2, 3 and 4, and the spin arrangement on Cu(II) cations is drawn. Each of J_1, J_2, J_3 and J_4 is the J_{ab} value between two Cu(II) cations.

In Figure 2 A, simplified crystal structure is shown, in which black and white circles show Cu(II)$_a$ and Cu(II)$_b$, respectively though bridged ions are omitted for simplicity. As described above, it was found with experimental studies that the magnetic property of the atacamite is antiferromagnetic. And also the effective exchange integrals (J_{ab}) between two Cu(II) cations have been experimentally presumed, which indicates that J_1 and J_2 are negative values, and, in contrast, that J_3 and J_4 are positive values. Judging from these results, a spin arrangement on the four Cu(II) cations is expected as shown in Figure 2 B, where the spin arrangement is drawn in terms of the classical spin vector model.

In order to explain the magnetic property of the atacamite, it is reasonable and appropriate to consider the spin arrangement of the tetranuclear cluster of Cu(II) cations, $Cu_4Cl(OH)_3$. In the next section, we consider possible spin structures for the cluster, and perform theoretical calculations for them.

THEORETICAL BACKGROUND

The spins in the mineral atacamite are localized on the Cu(II) ions.[1] Generally, exchange coupling between localized spins in molecular systems has been described by the total spin form of the spin Hamiltonian, *i.e.*, Heisenberg model,

$$H(HB)=-2\sum J_{ab}\mathbf{S}_a\cdot\mathbf{S}_b \qquad (1)$$

where J_{ab} is the effective exchange integral between the metal sites with total spin operators $\mathbf{S}_a$ and $\mathbf{S}_b$. Then the exchange split energy levels *E(HB)* between transition metal dimers are given by[3-7]

$$^{2S+1}E(HB) = -J_{ab}[s(s+1) - S_a(S_a+1) - S_b(S_b+1)] \qquad (2)$$

where S_a and S_b are the magnitudes of spins $\mathbf{S}_a$ and $\mathbf{S}_b$, and s is the magnitude of the total spin operator $\mathbf{s}$ of a whole system, which is given by

$$s = (S_a - S_b), (S_a - S_b) + 1, \ldots, (S_a + S_b). \qquad (3)$$

The Heisenberg model indeed explained the magnetic behavior of the atacamite.[1] The J_{ab} values between two Cu(II) cations are determined as shown in Figure 2 B. Thus, with the usage of the Kambe vector coupling method,[11] the energies of the spin states of the tetranuclear cluster of four Cu(II) cations are given by

$$\begin{aligned} E(HB) = &-J_1\{S_{12}(S_{12}+1) - S_1(S_1+1) - S_2(S_2+1)\} \\ &-J_2\{S_{13}(S_{13}+1) - S_1(S_1+1) - S_3(S_3+1) \\ &+S_{14}(S_{14}+1) - S_1(S_1+1) - S_4(S_4+1)\} \\ &-J_3\{S_{23}(S_{23}+1) - S_2(S_2+1) - S_3(S_3+1) \\ &+S_{24}(S_{24}+1) - S_2(S_2+1) - S_4(S_4+1)\} \\ &-J_4\{S_{34}(S_{34}+1) - S_3(S_3+1) - S_4(S_4+1)\} \end{aligned} \qquad (4)$$

where $S_{ij} = S_i + S_j$. (5)

The total energies for several spin states were calculated in an exact quantum manner using Equation (4), and they are expressed in terms of the J_{ab} values as summarized in Table II. The energy differences between the spin multiplets are also derived from energies calculated by the ab initio UNO CASCI method to determine these J_{ab} parameters (see Table IV).

The spin arrangement on four Cu(II) cations is also studied in terms of the classical spin vector model. Then the energy of the system is given by

$$E_{total} = -2J_1\mathbf{S}_1\cdot\mathbf{S}_2 - 2J_2\mathbf{S}_1\cdot\mathbf{S}_3 - 2J_2\mathbf{S}_1\cdot\mathbf{S}_4 - 2J_3\mathbf{S}_2\cdot\mathbf{S}_3 - 2J_3\mathbf{S}_2\cdot\mathbf{S}_4 - 2J_4\mathbf{S}_3\cdot\mathbf{S}_4 \qquad (6)$$

where $\mathbf{S}_i\cdot\mathbf{S}_j$ between Cu_i and Cu_j is determined as below.

a) $\mathbf{S}_i\cdot\mathbf{S}_j = 1/4$ for ferromagnetic interaction between Cu_i and Cu_j.

b) $\mathbf{S}_i\cdot\mathbf{S}_j = -1/4$ for antiferromagnetic interaction between Cu_i and Cu_j.

Therefore, the energy expression of each spin arrangement is easily derived from the classical spin vector model as shown in Table II.

In order to determine the J_{ab} values in Equation (6), the ab initio UHF solution was constructed for each classical spin arrangement, and the energy differences among the spin arrangements were used (see Table VI).

TABLE II Energy expressions by the classical spin vector and Heisenberg models.

unit model	(2s+1)	Energy (Classical spin vector)	Energy (Heisenberg)
model 1	3	$J_1/2+J_2-J_3-J_4/2$	$3J_1/2+3J_2-J_3-J_4/2$
model 2	1	$J_1/2+J_4/2$	$3J_1/2+J_2+J_3+3J_4/2$
model 3	1	$J_1/2+J_4/2$	$3J_1/2+J_2+J_3+3J_4/2$
model 4	3	$J_1/2-J_2+J_3-J_4/2$	$3J_1/2-J_2+3J_3-J_4/2$
model 5	5	$-J_1/2-J_2-J_3-J_4/2$	$-J_1/2-J_2-J_3-J_4/2$
model 6	3	$-J_1/2+J_4/2$	$-J_1/2+J_2+J_3+3J_4/2$
model 7	3	$-J_1/2+J_4/2$	$-J_1/2+J_2+J_3+3J_4/2$
model 8	1	$-J_1/2+J_2+J_3-J_4/2$	$-J_1/2+3J_2+3J_3-J_4/2$

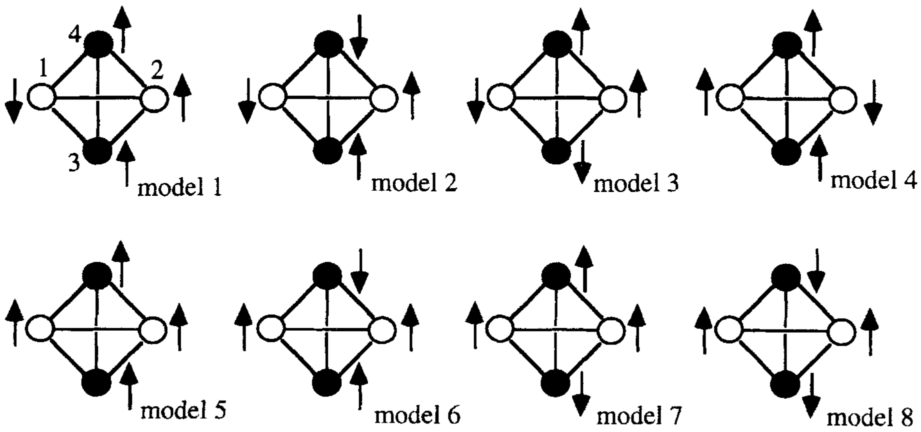

FIGURE 3 Simplified unit models of the atacamite and the spin arrangement presumed theoretically. The notation of Cu(II) cations is the same as it in Figure 2 B.

AB INITIO CALCULATIONS FOR THE MODELS

As shown in Figure 3, eight kinds of the spin arrangements of the simplified unit model, which is composed of two black circles as $Cu(II)_a$ cations and two white ones as $Cu(II)_b$ cations, are considered. Here, bridged anions are not drawn for simplicity. The spin arrangement expected from experiments is identical with the unit model 1. The ab initio UHF and CASCI calculations were carried out for the unit models in order to get the total energy of each unit model. The basis set used here for Cu atom is the Tatewaki-Hujinaga basis set 5333/53/5.[12] The UHF natural orbital analysis showed that the ten active orbitals ten electrons {10,10} is necessary for CAS. The calculations were carried out by using GAUSSIAN[13] and HONDO[14] program packages.

Table III summarizes the total energies calculated by the ab initio UHF(5D and

6D) and UNO CASCI {10,10} methods. The spin multiplicity (2s+1) of the system is also summarized in Table III. The total energies for the models 2 and 3 are equivalent under the UHF approximation, and the situation is the same for the models 6 and 7. Here, the UHF (6D) calculations for the unit models 4 and 7 were carried out, but the resulting total energies were indeed the same as that of the unit model 1. Therefore, the CAS {10,10} for models 4 and 7 were not obtained under the 6D approximation: it is noteworthy that we performed the CASCI using the 6D basis set in the HONDO program package.[14]

CALCULATIONS OF THE EFFECTIVE EXCHANGE INTEGRALS

Judging from the total energies calculated by the UHF method, the unit model 5 with the quintet spin structure has the most stable spin arrangement. However, in this model the value J_1 must be positive because of the ferromagnetic spin arrangement between Cu(II) cations although the magnetic measurements have indicated the antiferromagnetic behavior. Thus, the results from the calculations by the UHF method are not appropriate to discuss the spin arrangement of the atacamite. On the other hand, the total energies calculated by the UNO CASCI method indicate that the unit model 1, which is expected

TABLE III Total energies of each unit model (a.u.).

unit model	multiplicity	UHF (5D)	UHF (6D)	CASCI {10,10}
model 1	3	-7237.52431686	-7237.53953965	-7237.54960020
model 2	1	-7237.52431178	-7237.53953800	-7237.54834491
model 3	1	-7237.52431180	-7237.53953687	-7237.54828598
model 4	3	-7237.52435488	——> model 1	
model 5	5	-7237.52455654	-7237.53977126	-7237.54872856
model 6	3	-7237.52445634	-7237.53967633	-7237.54529309
model 7	3	-7237.52445620	——> model 1	
model 8	1	-7237.52440432	-7237.53962547	-7237.54724778

TABLE IV Energy differences by CASCI and Heiseberg model (cm^{-1}).

unit model	Energy difference (CASCI)	Energy difference (Heisenberg)
model 1	0.0	0.0
model 2	+275.6	$-2J_2 + 2J_3 + 2J_4$
model 3	+288.6	$-2J_2 + 2J_3 + 2J_4$
model 5	+191.4	$-2J_1 - 4J_2$
model 6	+945.2	$-2J_1 - 2J_2 + 2J_3 + 2J_4$
model 8	+516.4	$-2J_1 + 4J_3$

from the experimental studies, has the most stable spin arrangement.

The energies calculated for each unit model by the CASCI method are resummarized as in Table IV in terms of the difference from the energy of the unit model 1. Each J_{ab} value was evaluated from energies in Table IV with the energy equations of Heisenberg. Similarly the energy differences from the quintet spin model 5 were calculated from the UHF total energies as shown in Table V, in combination with the energy expressions based on the classical spin vector models. Table VI summarizes the calculated J_{ab} values and also the values from experimental studies.[7]

From Tables IV-VI, the UNO CASCI calculations can reproduce the experimental result that J_1 and J_4 should be negative and positive, respectively. Judging from the signs of J_2 and J_3, the exchange integrals by the CASCI calculations predict that the model 4 should be the most stable, though we could not obtain the CASCI {10,10} result for the model 4. The model 4 is consistent with the antiferromagnetic behavior of the atacamite. It is however noteworthy that the J_2, J_3 and J_4 values were not determined respectively from experimental studies, but an absolute value was derived as the average value of them. The calculated $|J_3|$ integral is rather small, and therefore its sign should be sensitive to the structural deformation. Probably this is the origin for the spin glass behavior of synthetic atacamite investigated previously.[1]

On the other hand, the UHF (5D and 6D) calculations showed that all the J_1-J_4

TABLE V Energy difference by UHF and classical vector model (cm^{-1}).

unit model	(UHF: 5D)	(UHF: 6D)	Energy difference (Classical)
model 1	+52.67	+50.91	$J_1 + 2J_2$
model 2		+51.13	$J_1 + J_2 + J_3 + J_4$
model 4	+44.33		$J_1 + 2J_3$
model 5	0.0	0.0	0.0
model 6	+21.95	+20.85	$J_2 + J_3 + J_4$
model 8	+33.36	+32.04	$2J_2 + 2J_3$

TABLE VI Calculated J_{ab} in terms of classical vector and Heisenberg model, and experimental J_{ab} values (cm^{-1}).

	J_{ab}(APUHF: 5D)	J_{ab}(APUHF: 6D)	J_{ab}(CASCI)	experimental J_{ab}
J_1	+31.83	+30.28	−331.6	-98.0
J_2	+10.43	+10.32	+117.9	
J_3	+6.26	+5.70	−36.7	
J_4	+5.26	+4.83	+295.7	
$(J_2+J_3+J_4)/3$	+7.32	+6.95	+125.6	$\mid 24.6 \mid$

values are positive (ferromagnetic). The UHF calculations by use of the minimum basis set overestimated the stability of the high-spin states for the cluster $Cu_4Cl(OH)_3$ because of overestimation of the spin polarization effect; Cu(II)($\uparrow$)-OH($\downarrow$)-Cu(II)($\uparrow$).[6]

In conclusion, the UNO CASCI {10,10} calculations provide the reasonable effective exchange integrals for the tetranuclear copper cluster, $Cu_4Cl(OH)_3$ in the mineral atacamite. They can explain the spin glass behavior of the synthetic atacamite.[1]

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support of the Ministry of Education, Science and Culture of Japan (Specially Promoted Research No.06101004). Ab initio calculations have been carried out on the IBM RS/6000 workstations by using the GAUSSIAN 94[13] and HONDO 95.3[14] program package.

REFERENCES

1. W. Mori and K. Yamaguchi, Mol. Cryst. Liq. Cryst., 274 (1995) 113.
2. A. F. Wells, Acta Cryst., 2 (1949) 175.
3. M. Fujiwara, T. Matsushita, K. Yamaguchi and T. Fueno, Synthetic Metals, 41-43 (1991) 3267.
4. M. Fujiwara, S. Takamizawa, W. Mori and K. Yamaguchi, Mol. Cryst. Liq. Cryst., 279 (199) 1.
5. M. Fujiwara, M. Nishino, S. Takamizawa, W. Mori and K. Yamaguchi, Mol. Cryst. Liq. Cryst., in press (1996).
6. M. Nishino, M. Tanaka, S. Takeda, K. Mashima, W. Mori, K. Tani, A. Nakamura and K. Yamaguchi, Mol. Cryst. Liq. Cryst., in press (1996).
7. M. Nishino, M. Tanaka, S. Takeda, K. Mashima, W. Mori, K. Tani, A. Nakamura and K. Yamaguchi, Mol. Cryst. Liq. Cryst., (the same issue for this paper) (1996).
8. K. Yamaguchi, M. Okumura, W. Mori, J. Maki, K. Takada, T. Noro and K. Tanaka, Chem. Phys. Lett., 210 (1994) 201.
9. S. Yamanaka, M. Okumura, H. Nagao and K. Yamaguchi, Chem. Phys. Lett., 233 (1995) 88.
10. M. Nishino, S. Kubo, Y. Yoshioka, A. Nakamura and K. Yamaguchi, Mol. Cryst. Liq. Cryst., (the same issue for this paper) (1996).
11. H. Tatewaki and S. Hujinaga, J. Chem. Phys., 72, (1980) 339.
12. K. Kambe, J. Phys., Soc., Jpn., 5 (1950) 48.
13. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Oritiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.
14. M. Dupuis, A. Marquez, and E. R. Davidson, "HONDO 95.3 from CHEM-Station", (1995) IBM Corporation, Neighborhood Road, Kingston, NY. 12401.