

The Structures of Four Complexes of 2,2,6,6-Tetramethyl-3,5-heptanedione Containing One, Four, Four and Nine Cu(II) Ions*

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The structures of bis-(2,2,6,6-tetramethyl-3,5-heptanedionato) Cu(II) **1**, di- μ_3 -methoxy-di- μ -methoxy-tetrakis[(2,2,6,6-tetramethyl-3,5-heptanedionato)Cu(II)] **2**, μ_4 -oxa-bispyrazolatotetrakis[(2,2,6,6-tetramethyl-3,6-heptanedionato)Cu(II)] **3**, and hexa- μ_3 -hydroxy- μ_6 -(hydrogendioxo-O,O')-nonakis[(2,2,6,6-tetramethyl-3,5-heptanedionato) Cu(II)] **4** were determined by X-ray diffraction techniques. Compound **1** is a planar molecule with weak packing interactions and high thermal motion due to the interactions between the bulky *t*-butyl groups. The observed density is only 1.14 Mg m^{-3} . Compound **2** is a step tetramer conceptually derived from square-planar dimers in which the axial site of one Cu(II) ion in each dimer is occupied by a bridging oxygen from an adjacent dimer. Compound **3** has four Cu(II) ions tetrahedrally coordinated to a central oxygen atom. Compound **4** has six Cu(II) ions occupying the corners of a trigonal prism and three lying above the rectangular faces. Six hydroxyl ions each coordinate three Cu(II) ions, one from each end of the prism and one from the face. In the center is an (O—H...O) $^{-3}$ unit which trigonally binds the Cu(II) ions on each end of the prism. The bulky *t*-butyl groups in the four complexes effectively isolate the central Cu(II) ions from any intermolecular interactions.

INTRODUCTION

Polynuclear transition metal complexes are intermediate between magnetically dilute and the magnetically concentrated systems. Magnetically dilute monomeric systems exhibit magnetic behavior that is independent of neighboring molecules. Magnetically concentrated systems such as CuO are characterized by strong magnetic exchange over a large number of paramagnetic centers. Ideally, isolated polynuclear transition metal complexes are limited to interactions involving the small number of paramagnetic centers within the same molecule. Magnetically dilute systems provide little information about metal-metal interactions, but do serve as important reference points for comparison purposes. Magnetically concentrated systems are extremely difficult to analyze in a rigorous theoretical manner and must be treated by approximate or statistical methods. In principal, isolated polynuclear transition metal complexes can be analyzed rigorously. Although the magnetic susceptibilities of many transition metal complexes have been investigated, weak intermole-

* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

cular exchange interactions are often invoked to rationalize experimental discrepancies.¹ Frequently, the large separation between centers makes this conceptually unsatisfactory. To minimize any possibility of intercluster exchange, we have synthesized a series of complexes containing bulky *t*-butyl groups. The ligand 2,2,6,6-tetramethyl-3,5-heptanedione or dipivaloylmethane (DPM) is suitable for this purpose. We would like to describe the structures of these complexes. The complete magnetic susceptibility analysis will be reported later.²

DISCUSSION

$\text{Cu}(\text{DPM})_2$ (1) is a centrosymmetric monomer with a squareplanar arrangement of coordinating oxygen atoms about the copper(II) ion, see Figure 1.

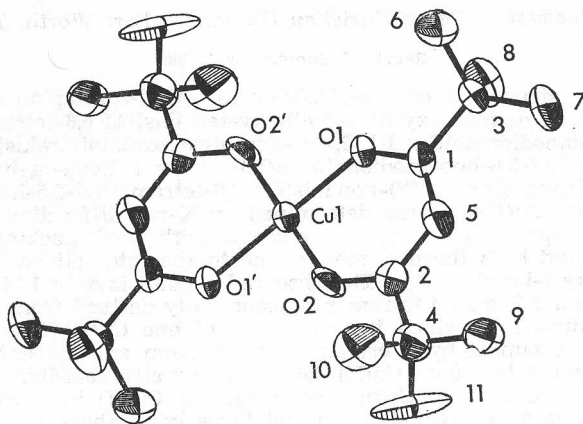


Figure 1. ORTEP drawing of bis-2,2,6,6-(tetramethyl-3,5-heptanedionato)Cu(II) 1

The structure is analogous to that of $\text{Ni}(\text{DPM})_2$ ³ which also refined to a large final R factor. The crystals of $\text{Cu}(\text{DPM})_2$ decompose rapidly upon exposure to X-rays, and three crystals were required to collect a complete data set. Because of the inefficient packing due to the bulky *t*-butyl groups ($d_o = 1.14 \text{ Mg m}^{-3}$) the thermal motion is large. The six-membered chelate rings and the attached methyl groups form a planar system with a maximum deviation from planarity of 0.04 Å by O(2). The Cu—O distances are 1.876(9) and 1.903(6) Å while $\text{O}(1) - \text{Cu} - \text{O}(2) = 93.2(3)^\circ$ and $\text{O}(1) - \text{Cu} - \text{O}(1') = 86.8(3)^\circ$. The C—O and C—C distances within the chelate ring average 1.293(3) and 1.404(5) Å while the external C—C bond lengths average 1.525(6) Å. The *t*-butyl groups sterically block the axial coordination sites and eliminate intermolecular magnetic exchange interactions.

$\text{Cu}_4(\text{OCH}_3)_4(\text{DPM})_4$ (2) is a step tetramer, Figure 2. The Cu_4O_4 core (Figure 3) can be described in terms of two interacting methoxy bridged dimers of $\text{Cu}_2(\text{OCH}_3)_2(\text{DPM})_2$. In each dimer Cu(1) is square planar with a maximum deviation from the plane of 0.05 Å. The Cu(2) ion exhibits a distorted square-based pyramidal geometry. The Cu(2) ion lies 0.16 Å out of the basal plane and toward the apical oxygen. The planes formed by Cu(1)O(1)O(2)O(3)O(4) and Cu(2)O(1)O(2)O(5)O(6) make an interplanar angle of 19.7° . The 6-membered chelate ring involving Cu(1) is folded by 4.8° along the O(3) — O(4) line while

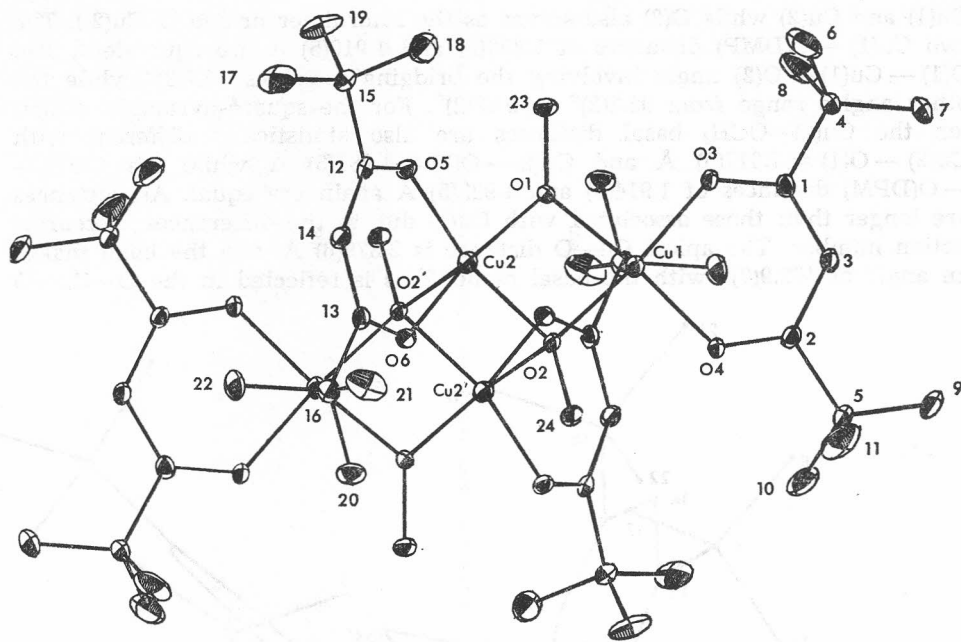


Figure 2. ORTEP drawing of di- μ_3 -methoxy-di- μ -methoxy-tetrakis[(2,2,6,6-tetramethyl-3,5-heptanedionato)Cu(II)] 2.

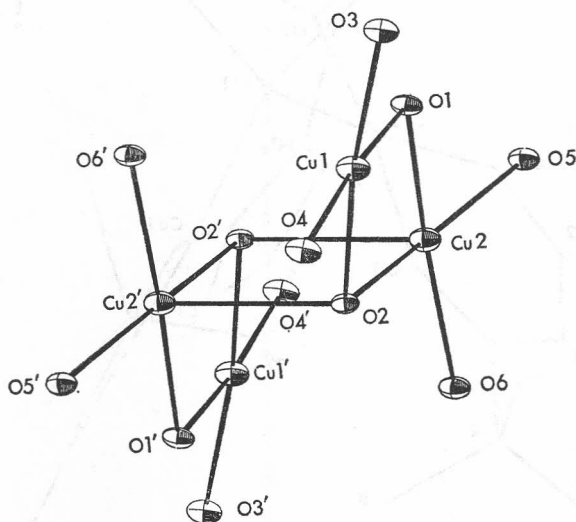


Figure 3. Central core of the step dimer 2.

the ring containing Cu(2) is folded by 15.6° along the O(5)—O(6) line. Steric interactions account for these differences. For the square-planar copper ion the Cu(1)—OCH₃ distances are statistically nonequivalent with Cu(1)—O(1) = $1.880(5)$ Å and Cu(1)—O(2) = $1.935(5)$ Å O(1) serves as a bridge between

Cu(1) and Cu(2) while O(2) also serves as the interdimer bridge to Cu(2'). The two Cu(1)—O(DMP) distances of 1.899(5) and 1.910(5) Å are equivalent. The O(1)—Cu(1)—O(2) angle involving the bridging atoms is $79.7(2)^\circ$ while the other angles range from $92.2(2)^\circ$ to $94.3(2)^\circ$. For the square-pyramidal Cu(II) ion the Cu(2)—OCH₃ basal distances are also statistically different with Cu(2)—O(1) = 1.917(5) Å and Cu(2)—O(2) = 1.982(5) Å while the Cu(2)—O(DPM) distances of 1.914(5) and 1.923(5) Å again are equal. All distances are longer than those associated with Cu(1) due to the differences in coordination number. The apical Cu—O distance is 2.379(6) Å, and the bond makes an angle of $102.9(7)^\circ$ with the basal plane. This is reflected in the O—Cu—O

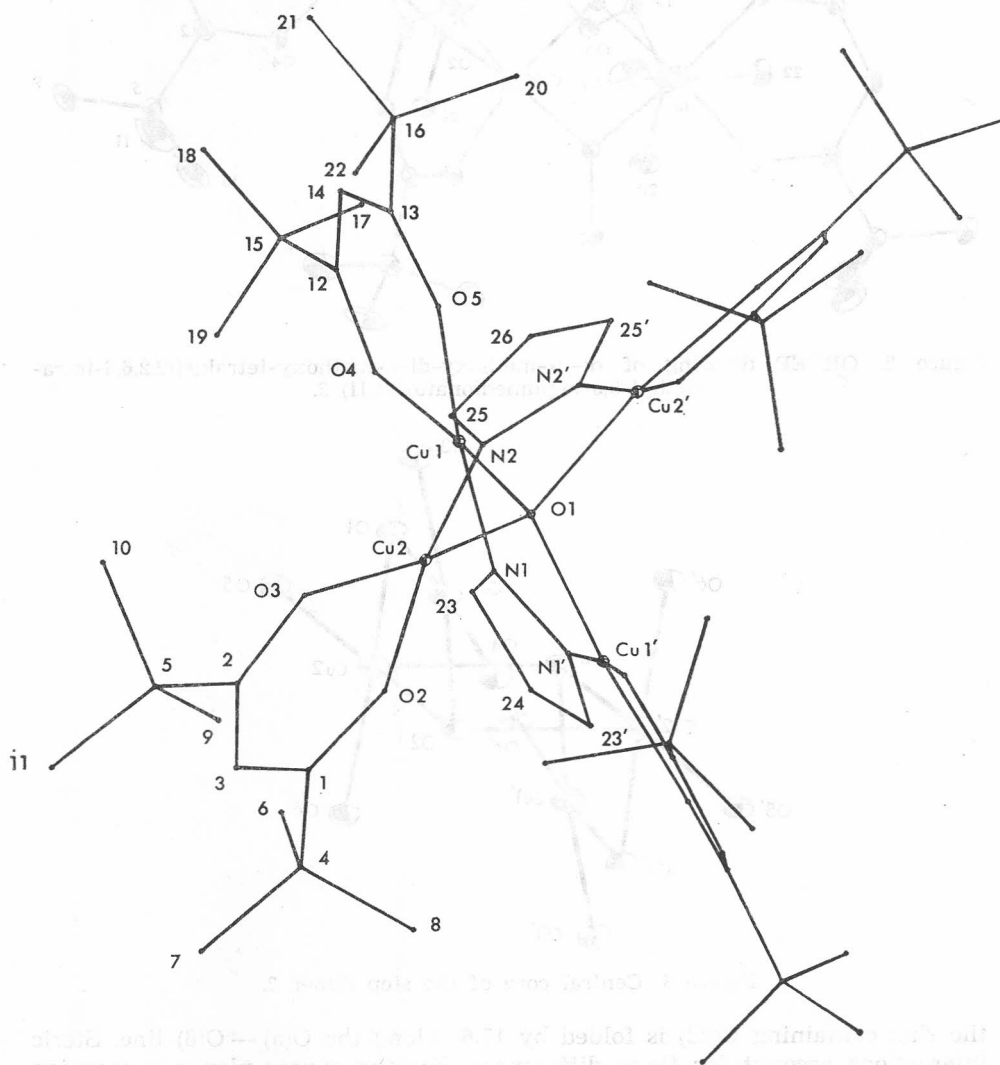


Figure 4. Drawing of compound 3, μ_4 -oxa-bispyrazolatotetrakis[(2,2,6,6-tetramethyl-3,6-heptanedionato)Cu(II)].

angles involving the apical oxygen atom which range from 84.4(2) to 106.4(2)°. The O(1)—Cu(2)—O(2) angle is 77.7(2)° while the other basal angles range from 92.6(2) to 95.3(2)°. In the chelate rings the four C—O distances average 1.27(1) Å, the C—C distances average 1.398(4) Å and the exocyclic C—C bond lengths average 1.549(3) Å. Because of the bulky *t*-butyl groups the tetramers are magnetically isolated.

Cu₄(O)(Pz)₂(DPM)₄ is a tetramer with the Cu(II) ions arranged tetrahedrally about the μ₄-oxygen, O(1), Figure 4. There is a crystallographic 2-fold axis passing through C(24)O(1)C(26). The coordination about each Cu(II) ion is approximately square planar with two oxygen atoms from a DPM ligand, the μ₄-oxygen, and a nitrogen from the bridging pyrazolate ion forming the coordination sphere. Surprisingly, all Cu—X distances are equivalent with an average value of 1.930(6) Å. The X—Cu—X angles range from 87.7(2)° to 91.7(3)°. The chelate rings and the pyrazolate rings are almost planar with maximum deviations of 0.03 Å and 0.06 Å, respectively. Least-squares planes fitted to various atom combinations indicate the chelate rings are folded by 4° about the O(2) . . . O(3) and O(4) . . . O(5) lines. The chelate rings related by the 2-fold axis make interplanar angles of 19.6(6)° (Cu(1), Cu(1') pair) and 28.1(6)° (Cu(2), Cu(2') pair). The planes of the bridging pyrazole rings lie between the planes of the bridged chelate rings, N(1) plane and Cu(1) plane angle = 14.8(6)° and N(2) plane and Cu(2)-plane angle = 16.8(6)°. The pyrazole rings are almost perpendicular to each other, 82.9(6)° and to the chelate rings of opposing Cu(II) ions, 85.3(6)° to 92.5(6)°. If the tetrahedral geometry around the central μ₄-oxo atom was perfect all interplanar angles would be either 0 or 90°. This distortion is reflected in the Cu—O(1)—Cu angles which range from 99.3(1) to 116.1(1)°.

The average distance for the C—C, C—N and N—N bonds of the pyrazolate rings are 1.374(7), 1.335(1) and 1.359(1) Å, respectively. The average values for the C—C—C, C—C—N and N—N—C angles are 103.9(3) 110.5(0), and 107.5(2)°. In the chelate rings the average C—O and C—C distances are 1.282(9) Å and 1.376(13) Å while the exocyclic C—C distances average 1.558(7) Å.

The structure of Cu₉(OHO)(OH)₆(DPM)₉ is shown in Figure 5. The central core containing 9 Cu(II) ions and 8 oxygen atoms is shown in Figure 6. Copper atoms A, B, C, G, H, and I form a trigonal prism with copper ions D, E, and F lying above the rectangular faces, Figure 7. Atoms O(3) to O(8) are hydroxyl ions which bridge 3 Cu(II) ions. Each hydroxyl bridges Cu(II) ions from each end of the trigonal prism and a facial Cu(II) ion. The facial Cu(II) ions are square-planar with coordination of two oxygen atoms from a chelating DPM and two bridging hydroxyl ions. The chelate rings are planar with O . . . O folding angles of less than 2°. The chelate rings associated with Cu(E) and Cu(F) are almost coplanar while the Cu(E) ring is rotated by 16° from the other two. The Cu(II) ions of the trigonal prism exhibit a square-pyramidal geometry with two oxygen atoms furnished by the chelating DPM, two oxygen atoms furnished by the bridging hydroxyl ions and one oxygen furnished by a postulated OHO⁻ group. The chelate rings associated with these Cu(II) ions show folding angles from 3° to 8°, avg = 4°. The trigonal prism chelate rings are at a 45° angle to the equatorial (facial) chelate rings. The vacant axial sites of the 5-coordinate Cu(II) ions are sterically blocked by adjacent DPM ligands. The identification of O(1) and O(2) as an OHO⁻

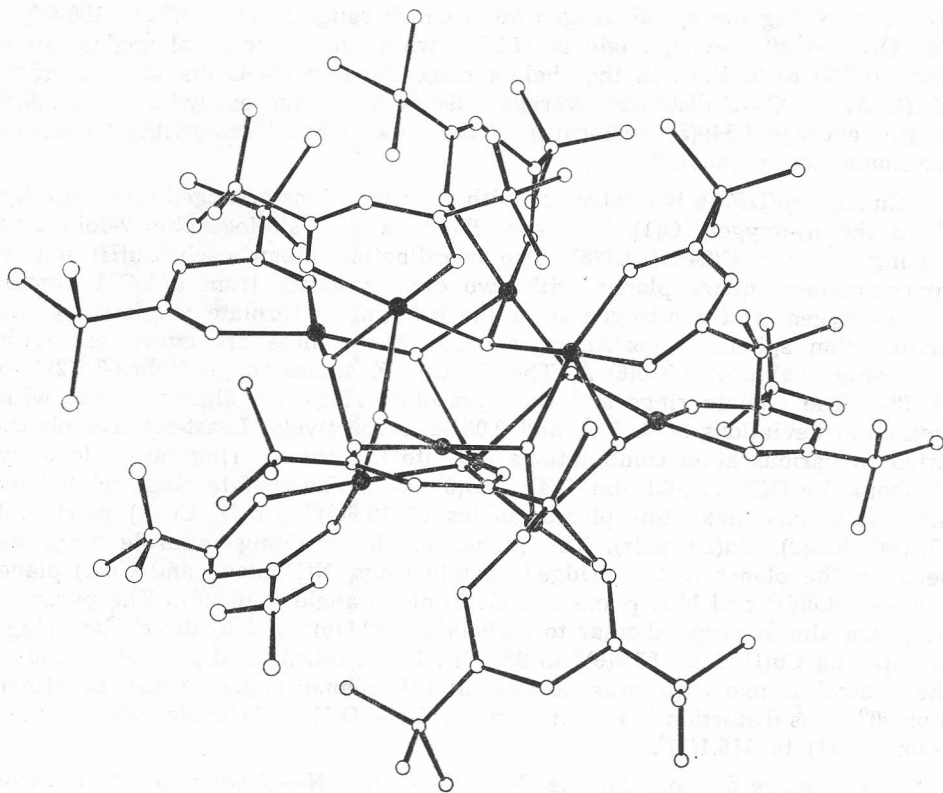


Figure 5. Drawing of compound 4, hexa- μ_3 -hydroxy- μ_6 -(hydrogendioxo-O,O')-nonakis[(2,2,6,6-tetramethyl-3,5-heptanedionato)Cu(II)]. One DPM ligand has been omitted from a Cu(II) at the rear of the drawing.

unit is based upon charge and structure considerations. The bridging hydroxyl groups and 9 coordinating DPM ligands require an additional -3 charge for electrical neutrality. O(1) and O(2) are separated by 2.40(2) Å and lie along a line which is perpendicular to the ends of the trigonal prisms. The two oxygen atoms lie out of the planes of the trigonal faces by 0.44 Å and toward the center of the prism. The separation is ideal for an O—H...O entity. Whether there is a statistical placement of the hydrogen atom or whether it dynamically transfers between the two oxygen atoms is unknown at the present time.

The eighteen *t*-butyl groups point away from the central core and provide an almost spherical distribution of methyl groups, see Figure 5. It is possible to take one chelating DPM oxygen atom of a 5-coordinate Cu(II) ion and shift it to the unoccupied axial site; however, steric interactions require that other DPM ligands on the same triangular face be shifted in concert. Therefore, two orientations of DPM ligands are possible for each of the two independent triangular faces. Each isomer again leads to an almost spherical distribution of CH₃ groups. While the core atoms, the DPM ligands attached to the facial Cu(II) ions and one of the DPM oxygen atoms associated with the 5-coordinate

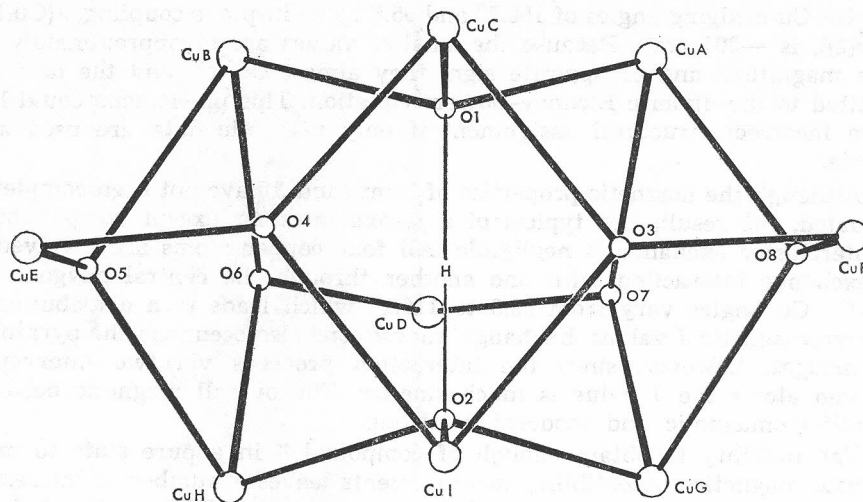


Figure 6. Core of compound 4 showing the 9 Cu(II) ions, 6 bridging OH ions and the proposed O—H...O³ system.

Cu(II) ions refined smoothly, the remainder of the DPM atoms did not. The thermal motion of these atoms is large and there is considerable electron density remaining in difference electron density maps. After considerable effort it was determined that both orientations of the DPM ligand are present, and in an approximate 3:2 ratio. This ratio may vary from crystal to crystal. Since both isomers provide an almost spherical environment of methyl groups, the packing interactions are essentially identical, and there is little discrimination during crystallization. Distances and angles associated with the disordered positions are less accurate than the others.

The 6 Cu—O(1) and Cu—O(2) distances average 1.93(1) Å with a range of 1.91 to 1.95 Å. The 12 distances from 5-coordinate Cu(II) ions to bridging hydroxyl ions average 2.20(5) Å while the 6 distances from the 4-coordinate Cu(II) ions average 1.89(1) Å. The Cu—O(H)—Cu angle involving 5-coordinate Cu(II) ions average 123(2)° while the average value of the angle involving 5-coordinate and a 4-coordinate Cu(II) ions is 96(1)°.

Magnetic Properties²

The molecules of compound 1 interact via van der Waals forces and there are no significant intermolecular exchange interactions. The room temperature magnetic moment is 1.90 B. M. (23.5 °C).

The magnetic data for compound 2 can be fitted to the Bleaney-Bowers dimer equation yielding a $2J$ value of -412 cm^{-1} ; however, fitting the data to a tetrameric model produces a slightly better fit.² Direct coupling between Cu(1)—Cu(1') is negligible and J for this interaction is assigned the value of 0.0; however, $J(\text{Cu}(1) - \text{Cu}(2'))$ and $J(\text{Cu}(2) - \text{Cu}(2'))$ were found to be -24 cm^{-1} and $+36\text{ cm}^{-1}$, respectively. These values are consistent with the

Cu—O—Cu bridging angles of 106.7° and 95.6° . The in-plane coupling, $J(\text{Cu}(1)\text{—Cu}(2))$, is -207 cm^{-1} . Because the smaller values are of approximately the same magnitude and of opposite sign, they almost cancel, and the data can be fitted to the dimeric Bleaney-Bowers equation. This phenomena could lead to an incorrect structural assignment if only magnetic data are used as a criteria.

Although the magnetic properties of compound 3 have not been completely evaluated, the results are typical of a μ_4 -oxa tetramer except the possibility of intercluster exchange is negligible. All four copper atoms are involved in an exchange interaction with one another through the central oxygen. The Cu—O—Cu angles vary from 99.3 to 116.1° which leads to a distribution of antiferromagnetic J values. Exchange interactions also occur via the pyrazolate ion bridges; however, since the interaction proceeds via two intervening nitrogen atoms the J value is much smaller. The overall magnetic behavior is antiferromagnetic and moderately strong.

The inability to obtain enough of compound 4 in a pure state to make accurate magnetic susceptibility measurements leaves a number of interesting coupling interactions uninvestigated. Low temperature EPR studies indicate the ground state of the cluster to be $S = 1/2$.

EXPERIMENTAL

All X-ray data were collected on a Syntex P2₁ diffractometer system by the $\theta : 2\theta$ scanning technique. Unit cell and crystal data are given in Table I. Room-temperature lattice parameters were refined by a least-squares procedure using 15 reflections whose angles were measured by a centering routine associated with the diffractometer. Space groups were determined by systematic absences and statistics. Periodically monitored reflections were used to check the stability of the crystals. Lorentz and polarization corrections were applied.

TABLE I
Unit Cell and Crystal Data

Compound	1	2	3	4
Formula	$\text{Cu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$	$\text{Cu}_4(\text{OCH}_3)_4 \cdot (\text{C}_{11}\text{H}_{19}\text{O}_2)_4$	$\text{Cu}_4\text{O}(\text{C}_3\text{H}_3\text{N}_2)_2 \cdot (\text{C}_{11}\text{H}_{19}\text{O}_2)_4$	$\text{Cu}_9(\text{OH})(\text{OH})_6 \cdot (\text{C}_{11}\text{H}_{19}\text{O}_2)_9$
Space group	$P2_1/n$	$P2_1/a$	$A2/a$	$P2_1/c$
a Å	12.273(6)	10.110(2)	21.430(9)	15.108(8)
b	11.040(4)	30.162(9)	24.70(8)	29.487(17)
c	10.383(3)	9.657(2)	13.759(6)	30.528(12)
β ($^\circ$)	117.98(1)	103.20(2)	111.24(3)	113.56(3)
V (\AA^3)	1242.5(4)	2867(1)	5964(4)	1247(1)
Z	2	2	4	4
d_0 (Mgm^{-3})	1.14	1.29	—	—
d_c (Mgm^{-3})	1.149	1.27	1.267	1.25
μ (cm^{-1})	18.7	21.2	20.2	21.6
No. Ind. Refl.	2576	3824	4010	9646
No. Refl. $> 3\sigma(I)$	1930	3177	3293	6621
max. 2θ ($^\circ$)	61	115	115	119
Radiation	MoK α	CuK α	CuK α	CuK α
R	0.107	0.067	0.067	0.125

Cu(DPM)₂ (1) decomposed upon exposure to X-rays. Three crystals ground into spheres with diameters of 0.11, 0.13 and 0.15 mm were used to collect intensity data. Absorption corrections were applied. The Cu(II) ion and attached atoms were located in a sharpened Patterson map. For Cu₄(OCH₃)₄(DPM)₄ (2) a crystal of dimensions 0.3 × 0.3 × 0.5 was used for data collection. No absorption corrections were made. The direct methods program MULTAN⁴ was used to locate the Cu(II) ions. For Cu₄O(Pyz)₂(DPM)₄ (3) a crystal of 0.2 × 0.2 × 0.4 was used to collect all data. Absorption corrections were applied. MULTAN⁴ was used to locate the Cu(II) ions. For Cu₉(OHO)(OH)₆(DPM)₉ (4) a crystal of dimensions 0.1 × 0.1 × 0.2 mm was used to collect all data. Absorption corrections were applied. A sharpened Patterson map was used to locate the positions of the Cu(II) ions. Least-squares refinements and difference electron density maps were used to locate the remaining atoms in the structure. Hydrogen atom positions were not found. The Cu(II) ions and bridging atoms were refined isotropically. Because of the number of parameters and observed reflections block-diagonal least-squares refinement was used. Compound 4 was not refined optimally because the large number of parameters (134 atoms) and reflections (6621) required too much computer time.

Final difference maps were checked for residual electron density. XRAY76⁵ was used for all computations, and anomalous dispersion corrections were applied. Tables of atomic positional parameters, bond distances and valence angles have been deposited.*

Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)Copper(II) (1)

was prepared by the addition of 3.68 g (20 mmol) of 2,2,6,6-tetramethyl-3,5-heptanedione (DPM) to a 100 ml absolute ethanol solution of 2.00 g (10 mmol) of Cu(II)acetate monohydrate. The mixture was stirred for 1 h at 0 °C. The dark purple crystalline solid was filtered, washed with cold ethanol, and dried in vacuo over P₄O₁₀, mp 196 °C (recovered yield 80%). The compound is soluble in alcohols, aromatic and non-aromatic hydrocarbons, and ethyl ether, but it is insoluble in water. IR spectrum shows C—H stretching vibrations at 2935, 2885, and 2835 cm⁻¹; a strong C=O stretch of 1583 cm⁻¹ and five strong C—C stretching vibrations at 1555, 1535, 1490, 1395, and 1352 cm⁻¹; and a number of C—C bending vibrations.

Di-μ₃-methoxo-di-μ-methoxo-tetrakis[(2,2,6,6-tetramethyl-3,5-heptanedionato)Cu(II)] (2)

was prepared by dissolving 4.30 g (10 mmol) of 1 in 50 ml of dry methanol, cooling to 0 °C, adding dropwise 1.08 g (20 mmol) of sodium ethoxide in 50 ml methanol, and stirring for 4 h. The light-blue preprecipitate was filtered, washed with cold methanol, and dried in vacuo over P₄O₁₀, mp 232—224 °C (recovered yield 75%). The IR spectrum is similar to that of 1 except for a moderately strong peak at 1045 cm⁻¹ which is assigned to the C—O stretching vibration of the bridging OCH₃ group.⁶

Anal. Cu₄C₄₈H₈₈O₁₂ calc'd.: Cu 22.87; C 51.88; H 7.98%
found: Cu 22.75; C 51.31; H 8.04%

μ₄-Oxo-bis(pyrazolato)-tetrakis[(2,2,6,6-tetramethyl-3,5-heptanedionato)Cu(II)] (3)

A 5.58 g (5 mmol) sample of 2 was added to a solution consisting of 1.36 g (20 mmol) of pyrazole dissolved in 75 ml of acetone. The mixture was maintained at 0 °C with stirring for 1 h. At the end of this time 25 ml of hexane was added and the mixture left standing at 0 °C for several hours. A blue precipitate was filtered, washed with hexane, and recrystallized from acetone/water (20 : 1), mp 212—213 °C. The IR contain peaks characteristic of DPM plus those of deprotonated pyrazole.

* Lists of atomic positional parameters, bond distances and valence angles have been deposited with the Editorial Board of *Croatica Chemica Acta*.

Hexa- μ_3 -hydroxo- μ_6 -(hydrogendioxo-O,O')-nonakis[(2,2,6,6-tetrametil-3,5-heptanedionato)Cu(II)] (4)

Several different solvents were used in an attempt to grow large single crystal of 2. In one case a sample of 2 was dissolved in *p*-xylene, and the sample was forgotten for several weeks. Examination of the evaporated material revealed large single crystals of 1 (99+%) and a number of light-blue crystals shaped like parallelepipeds. Other byproducts were Cu(OH)₂ and CuO which indicated water from the atmosphere had dissolved in the *p*-xylene and reacted with compound 2. The preparation of the blue compound could be reproduced but the yields could not be increased significantly nor could enough pure material be obtained for accurate measurement of physical properties. The structure of the compound was elucidated by X-ray diffraction and the compound was formulated as Cu₉(OHO)(OH)₆(DPM)₉. The impure sample gave an IR spectrum identical to 1 except for a peak at 3660 cm⁻¹ which was assigned to O—H vibrations.

REFERENCES

1. R. C. Dickenson, F. T. Helm, W. A. Baker, and W. H. Watson, *Inorg. Chem.* **16** (1977) 1530.
2. L. Theriot and P. Pruettiangbura, to be submitted.
3. F. A. Cotton and J. J. Wise, *Inorg. Chem.* **5** (1966) 1200.
4. G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.* **A27** (1971) 368.
5. J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck, and H. Flack, *The XRAY76 SYSTEM*, Technical Report TR-446, Computer Science Center, University of Maryland, College Park, MD, 1976.
6. *Infrared Spectroscopy*, R. T. Conley, Boston, Allyn and Bacon, 1972, 2nd ed.

SAŽETAK

Strukture četiri 2,2,6,6-tetrametil-3,5-heptandionova kompleksa s jednim, četiri, četiri i devet Cu(II) iona

W. H. Watson i W. W. Holley

Strukture spojeva bis-(2,2,6,6-tetrametil-3,5-heptandionato)Cu(II) 1, di- μ -metoksi-di- μ -metoksi-tetrakis[(2,2,6,6-tetrametil-3,5-heptanedionato)Cu(II)] 2, μ_4 -oksa-bispirazolato-tetrakis[2,2,6,6-tetrametil-3,6-heptandionato)Cu(II)] 3, i heksa- μ_3 -hidroksi- μ_6 -(hidrogendioksio-O,O')-nonakis[(2,2,6,6-tetrametil-3,5-heptandionato)Cu(II)] 4 određene su pomoću rendgenske strukturne analize. Spoj 1 je planarna molekula sa slabim interakcijama pakovanja i velikim terminalnim gibanjem zbog interakcija između prostranih *t*-butil grupa. Mjerena gustoća je samo 1.14 Mgm⁻³. Spoj 2 je tetramer dobiven iz sp (square-planar) dimera u kojima na osi jednog Cu(II) iona u svakom dimeru leži kisik iz susjednog dimera. Spoj 3 ima četiri Cu(II) iona tetraedrijski koordinirana prema centralnom atomu kisika. Spoj 4 ima šest Cu(II) iona koji se nalaze u uglovima trigonske prizme i tri koje leže iznad pravokutnih ploha. Od šest hidroksilnih iona svaki koordinira tri Cu(II) iona, jedan sa svakog kraja prizme i jedan sa plohe. U centru se nalazi (O—H...O)⁻³ grupa koja trigonalno veže Cu(II) ione sa svakog kraja prizme. Prostrane *t*-butil grupe u četiri kompleksa zapravo izoliraju centralne Cu(II) ione od bilo kakve intermolekularne interakcije.