spectively, while the hydroxy oxygen atom was found 0.695 Å out of the Cu_3 plane).

The two independent $[BF_4]^-$ anions are situtated in the hydrophobic cavities above and below the Cu_3 triangle (figures 1 and 2), with a mean B-F distance of 1.34 (1) Å and F-B-F angle of 109 (1)°. One of the $[BF_4]^-$ fluorine atoms, F(21), is positioned over the face of the Cu_3 triangle opposite the hydroxy oxygen atom, with Cu(1)···F(21), Cu(2)···F(21), and Cu(3)···F(21) distances of 3.008 (8), 2.674 (6), and 2.983 (7) Å, respectively. These distances are all significantly longer than reported Cu-F distances involving "semicoordinated" (2.56 Å)[28,29] or "weakly coordinated" (2.31 Å)[30] $[BF_4]^-$ anions. We thus conclude that the $[BF_4]^-$ interactions observed are predominately electrostatic in nature and that the structure of $[Cu_3(dpm)_3(OH)]^{2+}[BF_4]^-_2$ is best described as consisting of associated molecular ions in the solid state.

Discussion

Prior to this study, the only other trinuclear copper(I) dpm complexes structurally characterized were the two related compounds $[Cu_3(dpm)_3Cl_2]^+[Cl]^-$[6a] and $Cu_3(dpm)_2I_3$.[6b] As in the title compound of this work, the dpm molecules in these other two complexes were also found in bridging positions along the edges of Cu_3 triangles. $[Cu_3(dpm)_3Cl_2]^+[Cl]^-$ and $Cu_3(dpm)_2I_3$ are further similar in that triply bridging halide ligands are found situated over each face of the Cu_3 triangles to give a central trigonal-bipyramidal Cu_3X_2 core in each of these molecules. In contrast, only one of the two faces of the metallic triangle in $[Cu_3(dpm)_3(OH)]^{2+}[BF_4]^-_2$ is found to be capped, in this case by a μ_3-hydroxy ligand (presumably resulting from the deprotonation of a water of hydration in the $Cu(BF_4)_2 \cdot xH_2O$ starting material). Thus, while the two former compounds contain four-coordinate, closed-shell 18-electron metal centers, the $[Cu_3(dpm)_3(OH)]^{2+}$ dication differs in having three-coordinate, coordinatively unsaturated 16-electron copper atoms. The face of the Cu_3 triangle opposite the hydroxy group in $[Cu_3(dpm)_3(OH)]^{2+}$ may hence be viewed as a sort of a metal surface with three sites of unsaturation (one per copper atom) available for the absorption of small molecules, e.g., carbon monoxide.

In addition to the coordinative unsaturation of the title compound, the placement of the dpm phenyl groups about the metal atoms in $[Cu_3(dpm)_3(OH)]^{2+}$ is worthy of some discussion. As shown in Figures 2 and 3, the three copper atoms are encircled by a cylindrical array of phenyl rings and hence may be said to reside in a "picket-fence-like" environment. In effect, what we have here resembles a small triangular metal surface situated in a hydrophobic cavity. How this cavity or pocket may alter the binding and reactivity of substrate species on the Cu_3 surface is not known at this time. One can speculate about the possible catalytic potential of metal complexes of this type, in addition to their use as suitable precursor molecules from which group 1b cluster carbonyls and hydrides might be obtained.

Acknowledgment. We thank the National Science Foundation (Grants CHE-79-26479 and CHE-81-01122) for support of this research.

Registry No. $[Cu_3(dpm)_3(OH)]^{2+}[BF_4]^-_2$, 87761-85-1.

Supplementary Material Available: Listings of temperature factors (Table A) for this structure determination and observed and calculated structure factors (Table B) (29 pages). Ordering information is given on any current masthead page.

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(28) Brown, D. S.; Lee, J. D.; Melsom, B. G. A.; Hathaway, B. J.; Procter, I. M.; Tomlinson, A. A. G. *J. Chem. Soc., Chem. Commun.* **1967**, 369-371.

(29) Brown, D. S.; Lee, J. D.; Melson, B. G. A. *Acta Crystallogr., Sect. B* **1968**, *B24*, 730-734.

(30) Gaughan, A. P., Jr.; Dori, Z.; Ibers, J. A. *Inorg. Chem.* **1974**, *13*, 1657-1667.

Contribution from the Department of Chemistry,
Louisiana State University, Baton Rouge, Louisiana 70803

Crystal and Molecular Structures of Bis(cyclodecane-1,3-dionato)copper(II) and Bis(cyclotridecane-1,3-dionato)copper(II)

CHARLES L. MODENBACH,* FRANK R. FRONCZEK, EUGENE W. BERG, and THOMAS C. TAYLOR[†]

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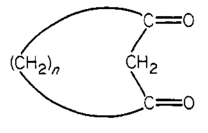
The crystal and molecular structures of bis(cyclodecane-1,3-dionato)copper(II), $Cu(CDD)_2$, and bis(cyclotridecane-1,3-dionato)copper(II), $Cu(CTDD)_2$, were determined by single-crystal X-ray diffraction analysis. The unit cell of $Cu(CDD)_2$ is monoclinic (space group $P2_1/n$) with dimensions a = 4.9657 (7) Å, b = 14.977 (2) Å, c = 12.670 (2) Å, β = 95.84 (1)°, and Z = 2. The unit cell of $Cu(CTDD)_2$ is also monoclinic (space group $P2_1/c$) with dimensions a = 4.900 (3) Å, b = 28.206 (7) Å, c = 9.060 (3) Å, β = 102.21 (3)°, and Z = 2. In both compounds the copper atom has square-planar coordination with the four oxygen atoms. However, there is a greater degree of distortion in the chelate ring of $Cu(CDD)_2$ as compared to that of $Cu(CTDD)_2$.

Introduction

In a survey of the chelation behavior of a series of macrocyclic 1,3-diketones of the type



where n = 4, 6, 7, 8, and 10, it was observed that the selectivity of the chelation increased with decreasing ring size.[1] The thirteen-carbon β-diketone formed chelates readily with many metal ions as expected whereas the ten-carbon diketone formed chelates only with Fe(III) and Cu(II). The seven- and nine-carbon diketones were not observed to form chelates with Be(II), Mg(II), Al(III), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), and Cd(II). This selectivity is in contrast to the nonselective chelation behavior of β-diketones in general. It was also observed that the degree of enolization in this series decreased with decreasing ring size down to n = 4-6 where there was a very limited tendency to enolize.[1-4]

[†] E. I. du Pont, Laplace, LA.

(1) Taylor, T. C. Ph.D. Dissertation, Louisiana State University, 1981.

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Table I. Crystal Data and Data Collection Summary

	$Cu(CDD)_2$	$Cu(CTDD)_2$
formula	$Cu(C_{10}H_{15}O_2)_2$	$Cu(C_{13}H_{21}O_2)_2$
fw	398.0	482.2
cryst system	monoclinic	monoclinic
space group	$P2_1/n^a$	$P2_1/c$
a, Å	4.9657 (7)	4.900 (3)
b, Å	14.977 (2)	28.206 (7)
c, Å	12.670 (2)	9.060 (3)
β, deg	95.84 (1)	102.21 (3)
cell vol, $Å^3$	937.4 (4)	1224 (2)
Z	2	2
d_{calcd}, g cm^{-3}	1.410	1.308
radiation	Cu Kα (λ = 1.54184 Å)	Mo Kα (λ = 0.71073 Å)
μ, cm^{-1}	18.47	9.58
min transmission	0.9447	0.8206
cryst size, mm	0.08 × 0.08 × 0.48	0.16 × 0.20 × 0.44
θ limits, deg	$2 \leqslant \theta \leqslant 75$	$1 \leqslant \theta \leqslant 20$
scan rates, deg min^{-1}	0.53-10.0	0.45-5.0
max scan time, s	120	180
unique data	1805 ($\pm h,k,l$)	1141 ($h,k,\pm l$)
obsd data	1582	799
parameters varied	142	142
R	0.040	0.041
R_w	0.049	0.051

^{a} Space group $P2_1/n$ is a nonstandard setting of $P2_1/c$.

Table II. Coordinates and Equivalent Isotropic Thermal Parameters for $Cu(CDD)_2$

atom	x	y	z	U_{eq},^{b} $Å^2$
Cu	0	0	0	0.0386
O1	0.2039 (4)	−0.0309 (1)	0.1329 (2)	0.048
O2	0.1722 (4)	0.1153 (1)	−0.0010 (1)	0.042
C1	0.4331 (6)	0.0033 (2)	0.1637 (2)	0.043
C2	0.5592 (5)	0.0700 (2)	0.1116 (2)	0.038
C3	0.4083 (5)	0.1305 (2)	0.0457 (2)	0.037
C4	0.5088 (6)	0.2244 (2)	0.0403 (2)	0.049
C5	0.4109 (7)	0.2815 (2)	0.1306 (3)	0.060
C6	0.4994 (7)	0.2507 (2)	0.2428 (2)	0.059
C7	0.3114 (7)	0.1819 (2)	0.2867 (2)	0.061
C8	0.438 (1)	0.1215 (3)	0.3728 (3)	0.084
C9^a	0.6384 (9)	0.0587 (4)	0.3515 (3)	0.062
C9′^{a}	0.469 (4)	0.015 (1)	0.354 (1)	0.059
C10	0.5610 (8)	−0.0265 (3)	0.2718 (3)	0.050

^{a} C9 has a multiplicity of 0.76; C9′ has a multiplicity of 0.24. ^{b} $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

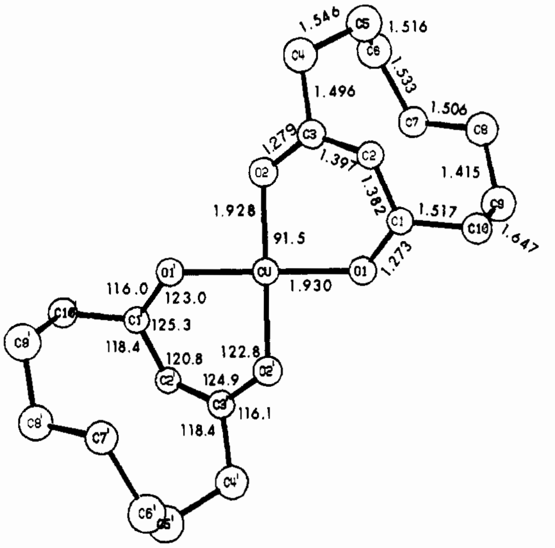

Figure 1. Bond distances and some important angles for $Cu(CDD)_2$. Esd's are 0.003 Å for Cu–O and 0.004–0.008 Å for other distances. C9 has a multiplicity of 0.76 (not shown: C9′, multiplicity 0.24; C8–C9′ = 1.63 (2) Å, C9′–C10 = 1.32 (2) Å). Symmetry-related atoms generated by $\bar{x}$, $\bar{y}$, $\bar{z}$ are flagged.

The crystal and molecular structures of two copper chelates of this series, bis(cyclodecane-1,3-dionato)copper(II), $Cu(CDD)_2$, and bis(cyclotridecane-1,3-dionato)copper(II), $Cu(CTDD)_2$, were determined by single-crystal X-ray diffraction analysis. This study was undertaken to determine any change in the chelate structure as the size of the hydrocarbon ring is changed.

Experimental Section

Cyclodecane-1,3-dione, $C_{10}H_{16}O_2$, and its copper chelate were first prepared by Schank and Eistert.[2] Cyclotridecane-1,3-dione, $C_{13}H_{22}O_2$, and its copper chelate were first prepared by Hunig and Hoch.[4] Both diketones were prepared by Taylor[1] according to a modification of a synthetic method developed by Ito and co-workers.[5] The copper chelates were prepared by addition of 1 mL of a 10% solution of the diketone in ethanol to a 5% aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ containing 5% sodium acetate. The chelates were filtered and recrystallized from chloroform, and satisfactory elemental analyses were obtained. Satisfactory crystals for X-ray analyses were obtained by slow evaporation of a benzene–chloroform solution of the chelate.

X-ray data obtained at 25 °C for both compounds from small blue needles on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. Scans were performed at variable rates by the ω–2θ method. Details of the individual experiments are given in Table I. One quadrant of data was collected in both cases. Data reduction included corrections for background, Lorentz, polarization, and absorption effects, which were based upon ψ scans of reflections near $\chi = 90°$. In addition, each reflection for $Cu(CDD)_2$ was collected at the ψ angle for which absorption effects were minimized. Correction was also made for $Cu(CDD)_2$ for crystal decay, which amounted to 6% of the original intensity.

Structure Solution and Refinement for $Cu(CDD)_2$. The structure was solved by calculation of a difference map phased on a Cu atom at the origin. Refinement was carried out by using the SHELX-76 system of programs[6] by weighted, full-matrix least squares based upon F. Non-hydrogen atoms were treated anisotropically, and hydrogen atoms were allowed to "ride" on carbon atoms to which they are bonded, with individually refined isotropic thermal parameters. The scattering factors used were those in ref 7 corrected for dispersion.[8] Only data for which $F > 3\sigma(F)$ were used in the refinement. A difference map computed in the early stages of refinement indicated that one of the methylene carbon atoms (C9) is disordered into two positions separated by 1.07 Å. Populations were estimated from electron densities to be 0.76 for C9 and 0.24 for C9′; these multiplicities were assigned, and both partial atoms were successfully anisotropically refined. The maximum feature in a final difference map was 0.47 e $Å^{-3}$.

Structure Solution and Refinement for $Cu(CTDD)_2$. The structure was solved in a fashion similar to that for $Cu(CDD)_2$, using the Enraf-Nonius SDP programs.[9] Hydrogen atoms were located in difference maps and were included in structure factor calculations with $B = 7$ $Å^2$ but were not refined. All other atoms were refined anisotropically, by weighted, full-matrix least squares, from data for which $F^2 > 3\sigma(F^2)$. The largest feature in a final difference map was 0.55 e $Å^{-3}$, near the Cu position. Agreement factors are listed in Table I for both compounds.

Results and Discussion

Both molecules have crystallographic C_i symmetry. The atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Tables II and III. Bond

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(2) Schank, K.; Eistert, B. *Chem. Ber.* **1966**, *99*, 1414.

(3) Kirrmann, A.; Wakselman, C. *Bull. Soc. Chim. Fr.* **1967**, *10*, 3766.

(4) Hunig, S.; Hoch, H. *Liebigs Ann. Chem.* **1968**, *716*, 68.

(5) Ito, Y.; Fujii, S.; Saegusa, T. *J. Org. Chem.* **1976**, *41*, 2973.

(6) Sheldrick, G. M. "SHELX-76 Program for Crystal Structure Determination", University of Cambridge, Cambridge, England, 1976.

(7) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101.

(8) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(9) Frenz, B. A.; Okaya, Y. "Enraf-Nonius Structure Determination Package"; Enraf-Nonius: Delft, Holland, 1980.

Table III. Coordinates and Equivalent Isotropic Thermal Parameters for Cu(CTDD)$_2$

atom	x	y	z	U_{eq}, Å^2	atom	x	y	z	U_{eq}, Å^2
Cu	0	0	0	0.0282	C6	−0.293 (1)	0.1730 (2)	−0.0534 (7)	0.047
O1	−0.1147 (8)	0.0142 (1)	0.1861 (4)	0.033	C7	−0.489 (2)	0.1945 (2)	0.0359 (7)	0.060
O2	−0.2300 (8)	0.0491 (1)	−0.1090 (4)	0.030	C8	−0.343 (2)	0.2216 (2)	0.1768 (8)	0.085
C1	−0.332 (1)	0.0380 (2)	0.1947 (6)	0.030	C9	−0.157 (2)	0.1944 (2)	0.2930 (9)	0.068
C2	−0.497 (1)	0.0623 (2)	0.0762 (6)	0.029	C10	−0.277 (2)	0.1519 (2)	0.3603 (7)	0.055
C3	−0.431 (1)	0.0684 (2)	−0.0635 (6)	0.024	C11	−0.065 (2)	0.1136 (2)	0.4105 (7)	0.054
C4	−0.603 (1)	0.1038 (2)	−0.1746 (6)	0.035	C12	−0.163 (2)	0.0672 (2)	0.4626 (6)	0.044
C5	−0.436 (1)	0.1469 (2)	−0.1981 (7)	0.046	C13	−0.393 (1)	0.0411 (2)	0.3513 (6)	0.036

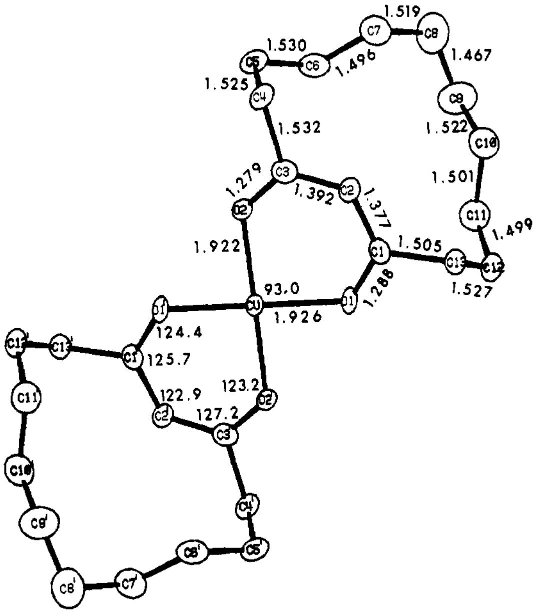

Figure 2. Bond distances and some important angles for Cu(CTDD)$_2$. Esd's are 0.003 Å for Cu–O and 0.006–0.009 Å for other distances. Symmetry-related atoms generated by $\bar{x}$, $\bar{y}$, $\bar{z}$ are flagged.

distances and some important angles are given in Figures 1 and 2.

In both compounds the copper atom has square-planar coordination with the four oxygen atoms. The Cu–O, C–O, and C–C bond lengths in the chelate ring are similar to those found in other copper β-diketonates.[10-12] Disorder was observed in the hydrocarbon ring structure of Cu(CDD)$_2$, with two partially occupied positions determined for C9. This disorder causes bond distances involving C9 in the refined model to deviate slightly from expected values (Figure 1).

To a first approximation the carbon and oxygen atoms of the chelate ring of Cu(CTDD)$_2$ are planar with a maximum deviation of 0.03 Å from the mean plane for C2. The copper atom is 0.38 Å from this plane, giving rise to a slightly folded chelate ring. This behavior is similar to that of bis(acetylacetonato)copper(II) and other copper β-diketonates.[10-12] In the chelate ring of Cu(CDD)$_2$ deviations from planarity are greater with a maximum deviation of 0.11 Å from the mean plane of carbon and oxygen atoms for C2. The copper atom is 0.64 Å from this mean plane. The O1–O2 "bite" distance for Cu(CDD)$_2$ (2.764 Å) is smaller than for Cu(CTDD)$_2$ (2.792 Å).

The enolization behavior of β-cycloalkanediones was explained by Schank and Eistert in terms of mobility and conformational effects.[2] β-Cycloalkanediones with up to six ring carbons are rigidly "trans fixed" with a high degree of enolization observed but no chelation possible. β-Cycloalkanediones with seven through nine carbon atoms have a higher ring mobility but are not large enough for coplanar cis enol chelation to occur. With ten carbon atoms cyclodecane-1,3-dione is just large enough for a cis enol chelate to form.

The fact that greater distortion is observed in the chelate ring of Cu(CDD)$_2$ as compared to the case of Cu(CTDD)$_2$ is consistent with the trends in degree of enolization and selectivity in chelation for this series. Since planarity in the chelate ring is required for delocalization of electrons to occur, one would expect deviation from planarity to result in lower stability and this could result in the higher selectivity in chelation observed for cyclodecane-1,3-dione. For cyclotridecane-1,3-dione the macrocyclic ring is large enough to allow chelation to occur with less distortion in the chelate ring and thus a large number of metal chelates can form.

The packing of molecules in the crystals is illustrated in the supplementary material. In both compounds the closest intermolecular contact involves the Cu atom and the central carbon atom of the chelate ring, C2. In Cu(CTDD)$_2$, this distance is 2.985 Å, and in Cu(CDD)$_2$, in which C2 is puckered out of the chelate plane, it is shortened to 2.919 Å. The closest contact between Cu atoms is, in both cases, translation along the *a* axis (Table I).

Registry No. Cu(CDD)$_2$, 15751-28-7; Cu(CTDD)$_2$, 21496-12-8.

Supplementary Material Available: Hydrogen atom coordinates (Tables S1 and S2), bond angles (Tables S3 and S4), anisotropic thermal parameters (Tables S5 and S6), structure factors (Tables S7 and S8), and side views of Cu(CDD)$_2$ and Cu(CTDD)$_2$ illustrating molecular stacking (Figures S1 and S2) (22 pages). Ordering information is given on any current masthead page.

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(10) Starikova, J. A.; Shugam, E. A. *Zh. Strukt. Khim.* **1969**, *10*, 290.
(11) Hon, P. K.; Pfluger, C. E.; Belford, R. L. *Inorg. Chem.* **1966**, *5*, 516.
(12) Knyazeva, A. N.; Shugam, E. A.; Shkol'nikova, L. M. *Zh. Strukt. Khim.* **1969**, *10*, 83.