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Structural features of homo- and heteroleptic complexes of copper(II) with 2,2,6,6-tetramethyl-3,5-heptanedione and 3-chloro-2,4-pentanedione

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Abstract

The crystal structure of bis(2,2,6,6-tetramethyl-3,5-heptanedionato) copper, Cu(thd)$_2$, has been determined at 130, 250 and 293 K (monoclinic, space group $P2_1/c$, $a=10.200(3)$, $b=10.957(3)$, $c=11.491(4)$ Å, $\beta=112.05(2)°$ at 130 K). At 130 K the structure shows no disorder. One of the t-Bu groups is involved in an unusually short intermolecular contact. At higher temperatures this same group is disordered. The number of configurations increases with the temperature. The room temperature crystal structures of bis(3-chloro-2,4-pentanedionato)copper, Cu(Clacac)$_2$ (monoclinic, space group $P2_1/n$, $a=4.815(2)$, $b=17.107(3)$, $c=8.013(2)$ Å, $\beta=106.92(2)°$), and (2,2,6,6-tetramethyl-3,5-heptanedionato)(3-chloro-2,4-pentanedionato) copper, Cu(thd)(Clacac) (orthorhombic, space group $Pnma$, $a=19.213(4)$, $b=6.453(4)$, $c=15.725(4)$ Å) are also described. Two kinds of molecular stacking are observed depending on whether the complex is homo- or heteroleptic.

Introduction

Tetramethylheptanedione (Hthd) has become the most commonly used β-diketone to make volatile molecular precursors for the MOCVD deposition of thin films of the high-T_c superconducting ceramics $YBa_2Cu_3O_{7-x}$. The copper and yttrium derivatives, Cu(thd)$_2$ and Y(thd)$_3$, sublime quantitatively at around 150 °C under a few torr. The barium derivative easily forms oligomers [1, 2] and is therefore less volatile hence not as easy to carry as the copper and yttrium precursors. Several works based on structural investigations have been developed to design monomeric barium tetramethylheptanedionates, either fluorinated [3] or not fluorinated [4].

Another approach to both the transportation of barium and diminution of the number of precursors to be monitored in the reactor, could be found in using heteropolymetallic precursors. In the quest of such compounds we became interested in derivatives of 3-chloro-acetylacetone, HClacac, as possible starting materials for synthesis. The basic idea was to prepare heteroleptic derivatives of general formula M(Clacac)$_{m-n}$(thd)$_n$ and to use them to synthesize heterometallic compounds. This strategy has not given noticeable results yet. As side results we present here a structural study of the copper complexes Cu(thd)$_2$, Cu(Clacac)$_2$ and Cu(thd)(Clacac)$_2$.

Cotton and Wise published the crystal and molecular structure of Ni(thd)$_2$ in 1966 [5] mentioning its isomorphism with the Cu(II) analog. They found some temperature factors and intermolecular distances having no physical significance, which they attributed to lack of accuracy. This prompted us to investigate the structure of the Cu(II) analog. We did it at three temperatures (130, 250 and 293 K) in order to detect any structural change accompanying the increase of temperature of such an easily sublimable compound.

Experimental

Synthesis and characterization

2,2,6,6-Tetramethyl-3,5-heptanedione (Hthd) and 3-chloro-2,4-pentanedione (HClacac) were obtained from Aldrich and used as received.

Cu(thd)$_2$ was prepared according to the procedure described in ref. 6. Single crystals were grown from an n-heptane solution.

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TABLE 1. Experimental crystal data for $Cu(thd)_2$ at 130, 250 and 293 K, and $Cu(Clacac)_2$ and Cu(Clacac)(thd) at 293 K

	$Cu(thd)_2$			$Cu(Clacac)_2$	Cu(Clacac)(thd)
Formula	$C_{22}H_{38}CuO_4$			$CuC_{10}H_{12}ClO_4$	$CuC_{16}H_{25}ClO_4$
Molecular weight	430.09			330.66	380.37
Crystal system	monoclinic			monoclinic	orthorhombic
Space group	$P2_1/c$			$P2_1/n$	$Pnma$
Temperature (K)	130	250	293	293	293
a (Å)	10.200(2)	10.307(2)	10.355(6)	4.815(2)	19.213(4)
b (Å)	10.957(3)	11.004(2)	11.019(3)	17.107(3)	6.453(4)
c (Å)	11.491(4)	11.688(3)	11.772(6)	8.013(2)	15.725(4)
β (°)	112.05(2)	112.93(2)	113.00(2)	106.92(2)	
V (Å^3)	1190	1221	1236	631	1950
ρ_{calc} (g/cm^3)	1.20	1.17	1.16	1.74	1.29
Z	2			2	4
μ(Mo Kα) (cm^{-1})	8.89	8.67	8.56	20.56	12.09
Take-off angle (°)	3.5	2	2	3.5	4.5
Scan mode	θ–$2/3\theta$	θ–2θ	θ–$2/3\theta$	θ–2θ	θ–$1/3\theta$
Maximum Bragg angle (°)	29	20	30	35	26
Reflections collected	3343	1164	3793	2110	2230
Reflections used	2603 ($I>3\sigma(I)$)	998 ($I>1.5\sigma(I)$)	2218 ($I>3\sigma(I)$)	1687 ($I>3\sigma(I)$)	1077 ($I>1.5\sigma(I)$)
Weighting scheme					
$w=a/[\sigma^2(F)+b\times10^{-4}F^2]$	$a=1.215$, $b=20$	$a=1.496$, $b=25$	$a=0.529$, $b=12.5$	$a=0.764$, $b=10$	$a=1.685$, $b=11$
Variables	201	141	179	88	161
$R=\Sigma(\|F_o-F_c\|/\Sigma F_o$	0.027	0.029	0.044	0.047	0.057
$R_w=(\Sigma w(F_o-F_c)^2/\Sigma wF_o^2)^{1/2}$	0.046	0.047	0.070	0.066	0.072
$s=[\Sigma w(F_o-F_c)^2/(n_o-n_v)]^{1/2}$	1.03	1.14	1.16	1.32	1.99

$Cu(Clacac)_2$ was prepared according to the procedure described in ref. 7. Single crystals (green needles) were grown from a chloroform solution.

Cu(thd)(Clacac) was obtained incidentally in a tentative synthesis of a mixed barium–copper complex by reacting $Cu(Clacac)_2$ and $Ba(thd)_2$. $Ba(thd)_2$ (8×10^{-4} mol) in ethanol (50 ml) was added to a chloroform solution (50 ml) of $Cu(Clacac)_2$ (8×10^{-4} mol). The solution was stirred for 5 h at room temperature. A mixture of white powder and green particles progressively precipitated and was filtered off. On evaporation the dark green solution yielded three kinds of crystals. Purple blocks and green needles were identified as $Cu(thd)_2$ and $Cu(Clacac)_2$, respectively. The IR spectrum of the purple–grey, acicular crystals showed the massif of t-butyl peaks at 2977 (shoulder), 2954, 2919 and 2867 cm^{-1}, and a sharp medium peak at 1017 cm^{-1} characteristic of C–Cl. An elemental analysis (C, 51.0; H, 6.8; O, 16.6%) was consistent with the formula Cu(Clacac)(thd) (Calc. for $CuC_{11}H_{25}ClO_4$: C, 50.5; H, 6.6; O, 16.8%). The formula was confirmed by the X-ray structure analysis.

Crystal structure determinations

The crystal systems, accurate cell constants, space groups and intensity data were obtained from single crystals mounted on an Enraf-Nonius CAD4 diffractometer using graphite monochromatized Mo Kα radiation. A liquid nitrogen low temperature device was used for collecting intensity data of $Cu(thd)_2$ at 130 and 250 K.

Three different crystals of $Cu(thd)_2$ were used for the data collections at 130, 250 and 293 K. Data were first measured at 250 K using a crystal which proved to be rather small. A bigger crystal was mounted for collecting at 130 K. As the room temperature measurements were run several months later it was found to be more prudent to mount a fresh crystal.

The crystal data and conditions of intensity measurement and structure determination are gathered in Table 1. The data were corrected for Lorentz and polarization effects, not for absorption. The structure determinations were carried out by using the Patterson and Fourier map techniques, and refined by applying the full-matrix, least-squares techniques [8]. Throughout the refinement, the minimized function was $\Sigma|F_o|-|F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors and anomalous terms are those of Cromer and Waber [9].

Occupancies of the disordered t-Bu groups were estimated from electron density calculation, and introduced in a sequence of cycles where occupancies and isotropic thermal coefficients were refined alternatively. They were maintained constant during the rest of the structure refinement. The three carbons of a given orientation were attributed the same occupancy, and

TABLE 2. Final atomic fractional coordinates and equivalent displacement parameters for $Cu(C_{11}H_{19}O_2)_2$ at 130, 250 and 293 K. Occupancies less than 100% are indicated

Atom	Temperature (K)	Occupancy (%)	*x/a*	*y/b*	*z/c*	U_{eq} (Å^2)[a]
Cu	130		0	0	0	0.0158(2)
	250					0.0312(9)
	293					0.0389(5)
O(1)	130		0.1804(1)	0.07051(9)	0.0369(1)	0.0216(9)
	250		0.1792(2)	0.0713(2)	0.0386(2)	0.039(3)
	293		0.1787(2)	0.0710(2)	0.0403(2)	0.049(2)
O(2)	130		−0.0687(1)	0.13997(9)	0.05739(8)	0.0183(8)
	250		−0.0684(2)	0.1379(2)	0.0573(2)	0.034(2)
	293		−0.0690(2)	0.1370(2)	0.0571(2)	0.044(2)
C(1)	130		0.3733(1)	0.2050(1)	0.0941(1)	0.021(1)
	250		0.3698(3)	0.2079(3)	0.0976(3)	0.040(4)
	293		0.3683(3)	0.2081(3)	0.1012(3)	0.050(3)
C(2)	130		0.2207(1)	0.1772(1)	0.0798(1)	0.017(1)
	250		0.2193(3)	0.1764(3)	0.0827(3)	0.031(3)
	293		0.2177(3)	0.1765(3)	0.0853(3)	0.042(3)
C(3)	130		0.1370(2)	0.2618(1)	0.1106(1)	0.018(1)
	250		0.1345(3)	0.2600(3)	0.1132(3)	0.035(4)
	293		0.1331(3)	0.2584(3)	0.1152(3)	0.044(3)
C(4)	130		−0.0026(1)	0.2394(1)	0.0989(1)	0.016(1)
	250		−0.0018(3)	0.2371(3)	0.1001(3)	0.030(4)
	293		−0.0028(3)	0.2348(2)	0.1010(2)	0.038(2)
C(5)	130		−0.0901(1)	0.3337(1)	0.1368(1)	0.018(1)
	250		−0.0907(3)	0.3297(3)	0.1365(3)	0.034(3)
	293		−0.0919(3)	0.3274(3)	0.1366(3)	0.044(3)
C(11)	130		0.4683(2)	0.1092(2)	0.1850(2)	0.038(2)
	250	80	0.4639(4)	0.1115(5)	0.1871(6)	0.064(6)
	293	43	0.4626(8)	0.1077(9)	0.196(1)	0.07(1)
C(21)	130		0.4236(2)	0.3316(2)	0.1474(2)	0.030(2)
	250	80	0.4220(5)	0.3306(4)	0.1600(5)	0.052(6)
	293	43	0.4182(7)	0.3322(6)	0.1639(7)	0.043(6)
C(31)	130		0.3818(2)	0.1911(2)	−0.0343(2)	0.038(2)
	250	80	0.3768(6)	0.1953(6)	−0.0271(5)	0.066(7)
	293	43	0.3775(9)	0.1980(8)	−0.0229(9)	0.055(9)
C′(11)	250	20	0.359(3)	0.321(2)	0.017(2)	0.097(7)*
	293	19	0.362(3)	0.320(2)	0.018(2)	0.078(6)*
C′(21)	250	20	0.429(2)	0.110(2)	0.038(2)	0.076(6)*
	293	19	0.427(2)	0.107(1)	0.042(2)	0.059(5)*
C′(31)	250	20	0.474(2)	0.233(2)	0.228(1)	0.093(8)*
	293	19	0.464(2)	0.241(3)	0.237(1)	0.092(8)*
C″(11)	293	19	0.390(3)	0.149(2)	−0.010(2)	0.062(7)*
C″(21)	293	19	0.466(5)	0.126(4)	0.211(3)	0.09(2)*
C″(31)	293	19	0.392(3)	0.3478(7)	0.113(3)	0.073(9)*
C‴(11)	293	19	0.353(3)	0.252(2)	−0.029(1)	0.058(6)*
C‴(21)	293	19	0.431(3)	0.308(2)	0.202(2)	0.058(8)*
C‴(31)	293	19	0.456(5)	0.092(3)	0.159(4)	0.11(2)*
C(15)	130		−0.0141(2)	0.4557(2)	0.1802(2)	0.025(1)
	250		−0.0163(2)	0.4520(3)	0.1796(3)	0.047(4)
	293		−0.0181(5)	0.4503(3)	0.1797(4)	0.075(4)
C(25)	130		−0.2268(2)	0.3551(2)	0.0228(2)	0.025(1)
	250		−0.2260(3)	0.3512(3)	0.0229(3)	0.047(4)
	293		−0.2267(4)	0.3485(4)	0.0236(4)	0.058(4)
C(35)	130		−0.1253(2)	0.2777(2)	0.2439(2)	0.025(1)
	250		−0.1241(4)	0.2736(3)	0.2412(3)	0.048(4)
	293		−0.1256(5)	0.2715(4)	0.2401(4)	0.093(4)

[a] Starred atoms were refined isotropically.

TABLE 3. Final atomic fractional coordinates and equivalent isotropic displacement parameters for $Cu(C_5H_6ClO_2)_2$

Atom	*x/a*	*y/b*	*z/c*	U_{eq} (Å^2)
Cu	0	0	0	0.0324(4)
Cl	−0.7086(2)	0.18736(5)	0.1189(1)	0.0450(7)
O(1)	−0.1051(5)	0.0274(1)	0.2041(2)	0.038(2)
O(2)	−0.2714(5)	0.0710(1)	−0.1408(2)	0.037(2)
C(1)	−0.3275(8)	0.0852(2)	0.3976(4)	0.054(3)
C(2)	−0.2927(6)	0.0764(2)	0.2178(4)	0.036(2)
C(3)	−0.4617(6)	0.1202(2)	0.0770(4)	0.033(2)
C(4)	−0.4451(6)	0.1163(2)	−0.0953(4)	0.035(2)
C(5)	−0.6382(9)	0.1656(2)	−0.2354(5)	0.053(3)

TABLE 4. Final atomic fractional coordinates and equivalent isotropic displacement parameters for $Cu(C_5H_6ClO_2)(C_{11}H_{19}O_2)$. Occupancies less than 100% are indicated

Atom	Occupancy (%)	*x/a*	*y/a*	*z/a*	U_{eq} (Å^2)
Cu		0.06204(6)	1/4	0.09456(7)	0.047(1)
Cl		−0.1013(2)	1/4	−0.1519(2)	0.066(3)
O(1)		0.1612(3)	1/4	0.1008(4)	0.056(8)
O(2)		0.0506(3)	1/4	0.2145(4)	0.054(8)
O(3)		0.0745(3)	1/4	−0.0252(4)	0.047(7)
O(4)		−0.0367(3)	1/4	0.0845(4)	0.047(7)
C(11)	70	0.292(1)	1/4	0.062(1)	0.10(4)
C(21)	70	0.304(1)	0.060(3)	0.198(2)	0.11(4)
C′(11)	30	0.321(2)	1/4	0.233(2)	0.1(1)
C′(21)	30	0.293(2)	0.054(9)	0.108(6)	0.1(2)
C(1)		0.2767(5)	1/4	0.1548(7)	0.07(1)
C(2)		0.1972(5)	1/4	0.1681(7)	0.05(1)
C(3)		0.1699(5)	1/4	0.2473(7)	0.06(1)
C(4)		0.0992(6)	1/4	0.2687(7)	0.05(1)
C(5)		0.0735(6)	1/4	0.3624(6)	0.06(1)
C(15)	60	0.125(2)	1/4	0.433(2)	0.11(7)
C(25)	60	0.028(1)	0.066(4)	0.375(1)	0.09(4)
C′(15)	40	−0.0038(9)	1/4	0.366(4)	0.1(1)
C′(25)	40	0.120(3)	0.10(1)	0.407(2)	0.1(1)
C(6)		0.0532(5)	1/4	−0.1720(6)	0.07(1)
C(7)		0.0286(5)	1/4	−0.0816(6)	0.04(1)
C(8)		−0.0427(5)	1/4	−0.0645(6)	0.05(1)
C(9)		−0.0723(5)	1/4	0.0157(6)	0.05(1)
C(10)		−0.1491(6)	1/4	0.0274(7)	0.07(1)

their distances to the pivot carbon were allowed to vary around reasonable values by using the DFIX option.

The non-H atoms were refined anisotropically except those of some disordered groups with low occupancies. The H atoms of non-disordered groups were localized. For $Cu(thd)_2$ at 130 K they were refined isotropically. For the other structure determinations, they were introduced in the refinements as fixed contributors. No significant feature appeared in the final difference-Fourier maps. The final reliability factors appear in Table 1. The atomic positional parameters and equivalent isotropic thermal coefficients are listed in Tables 2, 3 and 4 for $Cu(thd)_2$, $Cu(Clacac)_2$ and Cu(thd)(Clacac) respectively.

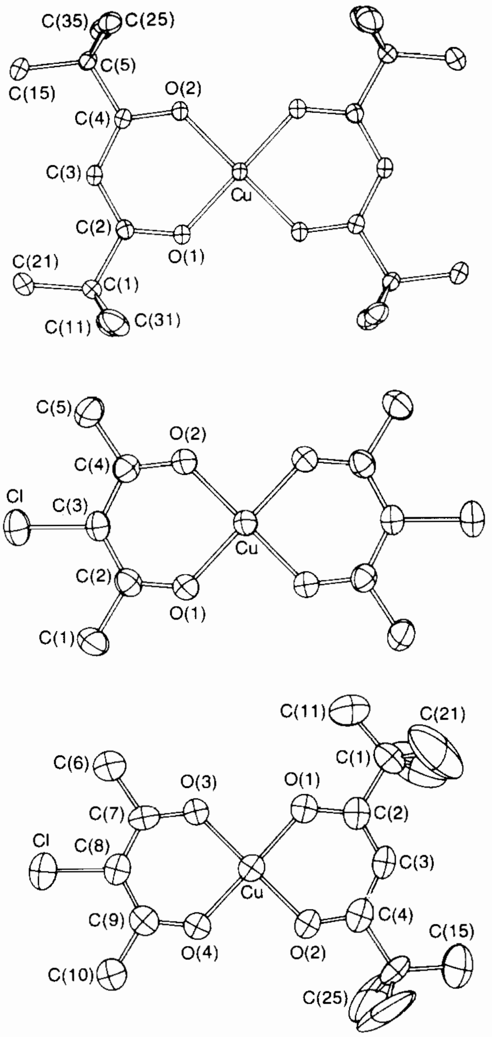

Fig. 1. ORTEP views of the complexes $Cu(thd)_2$ (at 130 K, top), $Cu(Clacac)_2$ (middle) and Cu(thd)(Clacac) (bottom). For the disordered t-Bu groups the most probable configurations are drawn. 50% probability ellipsoids are shown.

Description and discussion of the structures

$Cu(thd)_2$

The structure is that of $Ni(thd)_2$ previously described by Cotton and Wise [5] using space group $P2_1/a$ instead of $P2_1/c$ (permutation of vectors *a* and *c*). The molecule is centrosymmetrical and quite planar (Fig. 1). Main bond lengths and angles at 130, 250 and 293 K are gathered in Table 5.

A most interesting feature is the disorder affecting one, and only one, of the t-butyl groups according to the temperature. At 130 K the structure shows no disorder. Both the t-butyl groups (numbered t-bu(1)

TABLE 5. Synopsis of bond lengths (Å) and angles (°) for Cu(thd)$_2$ at 130, 250 and 293 K

	130 K	250 K	293 K
Around copper			
Cu–O(1)	1.8910(11)	1.8922(21)	1.8908(24)
Cu–O(2)	1.9037(11)	1.9020(22)	1.9012(22)
O(1)–Cu–O(2)	92.68(5)	92.66(9)	92.80(10)
Ligand thd			
Ordered parts			
C(2)–O(1)	1.2751(16)	1.267(4)	1.276(4)
C(4)–O(2)	1.275(2)	1.282(3)	1.273(3)
C(1)–C(11)[a]	1.5400(24)	1.540(5)	1.60(10)
C(1)–C(21)[a]	1.5248(23)	1.530(5)	1.544(8)
C(1)–C(31)[a]	1.517(3)	1.493(7)	1.504(12)
C(1)–C(2)	1.5332(21)	1.531(4)	1.537(5)
C(2)–C(3)	1.3930(22)	1.407(5)	1.396(5)
C(3)–C(4)	1.4005(22)	1.377(5)	1.375(5)
C(4)–C(5)	1.5319(21)	1.537(5)	1.539(5)
C(5)–C(15)	1.5313(21)	1.533(5)	1.540(5)
C(5)–C(25)	1.5308(18)	1.523(4)	1.524(4)
C(5)–C(35)	1.5338(26)	1.525(5)	1.523(6)
C(11)–C(1)–C(21)	108.46(12)	105.77(29)	106.3(5)
C(11)–C(1)–C(31)	109.84(17)	110.0(4)	111.8(6)
C(21)–C(1)–C(31)	110.38(16)	113.9(4)	113.2(5)
C(2)–C(1)–C(11)	107.00(14)	105.3(3)	104.0(4)
C(2)–C(1)–C(21)	113.52(14)	114.0(3)	113.1(4)
C(2)–C(1)–C(31)	107.56(12)	107.47(28)	108.1(4)
C(1)–C(2)–O(1)	113.00(13)	114.11(28)	113.51(29)
C(3)–C(2)–O(1)	124.68(13)	124.24(28)	124.48(29)
C(1)–C(2)–C(3)	122.32(12)	121.63(27)	121.99(27)
C(2)–C(3)–C(4)	123.82(12)	124.05(27)	124.07(26)
C(3)–C(4)–O(2)	124.15(13)	124.6(3)	124.90(29)
C(5)–C(4)–O(2)	113.59(13)	112.72(27)	112.77(27)
C(3)–C(4)–C(5)	122.26(11)	122.72(26)	122.33(25)
C(4)–C(5)–C(15)	113.85(13)	113.40(29)	113.6(3)
C(4)–C(5)–C(25)	107.51(12)	107.70(25)	107.82(27)
C(4)–C(5)–C(35)	107.14(12)	107.36(25)	107.38(26)
C(15)–C(5)–C(25)	109.36(11)	108.69(24)	108.74(27)
C(15)–C(5)–C(35)	109.30(13)	109.39(27)	109.3(3)
C(25)–C(5)–C(35)	109.59(13)	110.28(29)	110.0(3)
Cu–O(1)–C(2)	127.32(10)	127.52(22)	126.93(23)
Cu–O(2)–C(4)	127.30(10)	126.93(22)	126.78(22)

Disordered part	250 K	293 K		250 K	293 K
C(1)–C′(11)[b]	1.536(21)	1.553(23)	C′(11)–C(1)–C′(21)	103.7(14)	102.1(13)
C(1)–C′(21)[b]	1.533(25)	1.562(22)	C′(11)–C(1)–C′(31)	109.0(12)	108.1(14)
C(1)–C′(31)[b]	1.515(13)	1.564(14)	C′(21)–C(1)–C′(31)	109.8(11)	115.4(13)
C(1)–C″(11)[c]		1.557(28)	C(2)–C(1)–C′(11)	106.5(10)	108.3(10)
C(1)–C″(21)[c]		1.57(4)	C(2)–C(1)–C′(21)	110.6(8)	109.8(7)
C(1)–C″(31)[c]		1.555(9)	C(2)–C(1)–C′3(1)	116.5(8)	112.5(10)
C(1)–C‴(11)[c]		1.553(17)	C″(11)–C(1)–C″(21)		100.2(21)
C(1)–C‴(21)[c]		1.561(24)	C″(11)–C(1)–C″(31)		114.7(18)
C(1)–C‴(31)[c]		1.57(4)	C″(21)–C(1)–C″(31)		118.0(19)
			C(2)–C(1)–C″(11)		106.1(11)
			C(2)–C(1)–C″(21)		105.7(22)
			C(2)–C(1)–C″(31)		110.9(13)
			C‴(11)–C(1)–C‴(21)		112.3(14)
			C‴(11)–C(1)–C‴(31)		121.1(24)
			C‴(21)–C(1)–C‴(31)		103.7(17)
			C(2)–C(1)–C‴(11)		104.1(10)
			C(2)–C(1)–C‴(21)		110.9(14)
			C(2)–C(1)–C‴(31)		104.4(20)

(continued)

TABLE 5. (*continued*)

	130 K	250 K	293 K
Intermolecular van der Waals contacts			
C(11)–C(21)^{i}	3.5478(29)	3.535(7)	3.446(12)
C(11)–C(25)^{ii}	3.9786(26)	4.002(6)	3.971(10)
C(21)–C(31)^{iii}	3.847(4)	3.873(9)	3.886(14)
C(21)–C(25)^{iv}	4.0851(24)	>4.10	>4.10
C(15)–C(35)^{v}	3.7812(25)	3.799(5)	3.812(5)
C(35)–C(25)^{iii}	3.9940(29)	4.065(6)	4.088(7)
C′(11)–C(25)^{iv}		3.826(19)	3.880(20)
C′(21)–C(11)^{vi}		4.043(26)	>4.10
C′(21)–C(31)^{vi}		3.937(22)	3.973(20)
C′(31)–C′(11)^{iii}		4.03(3)	3.90(4)
C′(31)–C(25)^{ii}		3.738(14)	3.764(18)
C(21)–C″(11)^{iii}			3.964(28)
C(21)–C‴(11)^{iii}			4.036(21)
C′(21)–C‴(31)^{vi}			3.78(6)
C′(31)–C′(11)^{iii}			3.90(4)
C″(11)–C″(11)^{vi}			3.95(6)
C″(11)–C‴(31)^{vi}			3.87(6)
C″(21)–C(25)^{ii}			3.83(4)
C″(31)–C(25)^{iv}			3.821(15)
C‴(31)–C′(31)^{i}			4.03(4)

Occupancy: [a]100% at 130 K, 80% at 250 K, 43% at 293 K; [b]20% at 250 K, 19% at 293 K; [c]19% at 293 K. Code of equivalent positions: ^{i}: $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; ^{ii}: $1+x, \frac{1}{2}-y, \frac{1}{2}+z$; ^{iii}: $x, \frac{1}{2}-y, \frac{1}{2}+z$; ^{iv}: $-x, 1-y, -z$; ^{v}: $-x, \frac{1}{2}+y, \frac{1}{2}-z$; ^{vi}: $1-x, -y, -z$.

and t-bu(5) from their pivot C atom) have one carbon atom, namely C(21) and C(15), lying close to the plane of the ring on the side of the α-carbon atom. At higher temperatures, t-bu(1) (C(1)–(C(i1))$_3$, $i=1$–3)) is disordered (Fig. 2). The orientation observed at 130 K is still the most frequent one with probabilities of 80% at 250 K and 43% at 293 K. The reverse orientation (180° rotation about the three-fold axis of the t-butyl group, as shown in Fig. 2) is present at 250 K with a probability of 20% (atoms C′(i1)). It is still observed at 293 K with two new orientations (atoms C″(i1) and C‴(i1)) which result from the most frequent one by rotations of *c.* 30 and −30° about the three-fold axis (Fig. 2). The three of them have probabilities estimated at 19%.

It is worth pointing out that the disorder is related to intermolecular contacts. At 130 K one intermolecular methyl group–methyl group distance is 3.548(3) Å. This is definitely shorter than the usual van der Waals distance of 4 Å for a methyl–methyl contact [10]. It occurs between two t-bu(1) groups related by a two-fold screw axis. Such a low value may be indicative of hyperconjugation between the two groups. At 250 and 293 K this interaction is still possible virtually since the corresponding distances are 3.535(7) and 3.45(1) Å, respectively. However the disorders observed at these temperatures allow more conventional van der Waals contacts to occur, so that hyperconjugation is no longer likely to exist.

For the isomorphous structure of Ni(thd)$_2$ determined at room temperature from film data, Cotton and Wise did not mention disorder [5]. They noticed that the anisotropic temperature factors of one t-butyl group were too high and that an intermolecular contact between two methyl groups was unusually short at 3.65 Å. No significance was attached to this. In fact, the methyl group involved in the unusually short contact belonged to the abnormally agitated t-butyl group. In the light of the present study it may be inferred that these observations are consistent with disorder of the t-butyl group as in Cu(thd)$_2$.

Cu(Clacac)$_2$

Main bond lengths and angles are gathered in Table 6. The whole molecule is centrosymmetrical and quasi planar (Fig. 1). The non-H atoms do not deviate by more than 0.03 Å from their least-squares plane, and the dihedral angle between the OCuO and mean OCCCO planes is 179.2°. There are two molecules per unit cell. The molecules stack with a as a repeat parameter. The angle between the stacking direction and the normal to the mean molecular plane is 48.0°; therefore, the interplanar spacing is 3.22 Å. This inclined mode of stacking results from interactions between chelate cycles and chlorine atoms. Two neighbouring molecules within a stack widely overlap as shown in Fig. 3: each chelate cycle quite exactly covers another chelate cycle, and is above or below a chlorine atom. Normal methyl–methyl and methyl–chlorine intermo-

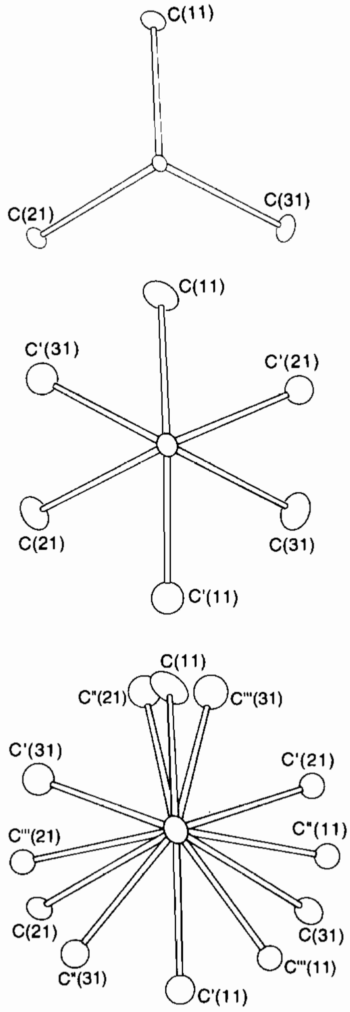

Fig. 2. The group t-bu(1) in $Cu(thd)_2$ at 130 (top), 250 (middle) and 293 (bottom) K.

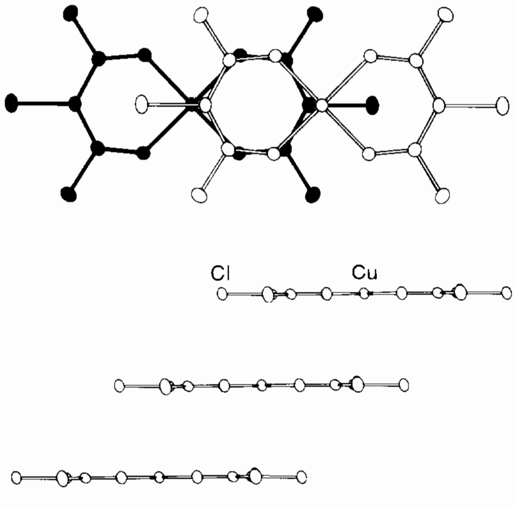

Fig. 3. The stacking of molecules in $Cu(Clacac)_2$: the overlapping of two molecules (top) and side view of three molecules (bottom).

lecular van der Waals contacts (Table 6) occur between molecules from neighbouring stacks. This kind of overlap is common to $M(3\text{-R-acac})_2$ derivatives when R is H or a non-bulky group such as CH_3. It has been thoroughly discussed in ref. 11.

Cu(thd)(Clacac)

Main bond lengths and angles are gathered in Table 7. The molecule lies on a mirror (Fig. 1). The t-butyl groups have two, unequally distributed, 180° staggered orientations. The orientation for which the in-plane C atom is *trans* to the α-C atom has a probability of 70% for the group t-bu(1) and 40% for the group t-bu(5). Conversely the reverse orientations have probabilities of 30% and 60%, respectively. Thus the most frequent orientations with respect to the α-C atom are not similar for the two groups.

The molecules stack at intervals of $b/2 = 3.226$ Å (quite the same value as for $Cu(Clacac)_2$), in planes strictly parallel to each other and perpendicular to the stacking direction (Fig. 4). Within a stack, the molecules are related by inversion. As for $Cu(Clacac)_2$, the geometry of stacking results from interactions between neighbouring chlorine atoms and chelate cycles. But the presence of two different ligands induces a zig-zag mode of stacking allowing van der Waals interactions between next neighbouring thd ligands through contacts between methyl groups related by mirror symmetry (Fig. 4, Table 7). Consequently, the Cu(Clacac) moieties

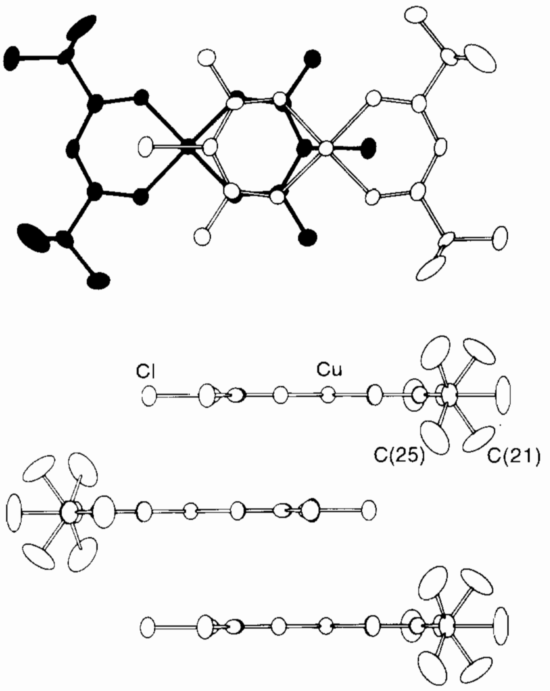

Fig. 4. The stacking of molecules in Cu(thd)(Clacac): the overlapping of two molecules (top) and side view of three molecules (bottom).

TABLE 6. Bond lengths (Å) and angles (°) in Cu(Clacac)$_2$

Around Cu					
Cu–O(1)	1.9057(22)	O(1)–Cu–O(2)	92.49(9)		
Cu–O(2)	1.8965(19)				
Cu...Cl$^{\text{i}}$	3.5172(8)				
Ligand Clacac					
C(2)–O(1)	1.260(4)	O(1)–C(2)–C(1)	115.64(25)	C(3)–C(4)–O(2)	122.69(23)
C(4)–O(2)	1.269(4)	C(1)–C(2)–C(3)	121.13(28)	C(3)–C(4)–C(5)	120.71(29)
C(3)–Cl	1.755(3)	O(1)–C(2)–C(3)	123.33(28)	O(2)–C(4)–C(5)	116.59(28)
C(1)–C(2)	1.505(4)	C(2)–C(3)–C(4)	125.45(28)	Cu–O(1)–C(2)	127.95(18)
C(2)–C(3)	1.400(4)	C(2)–C(3)–Cl	117.60(24)	Cu–O(2)–C(4)	128.18(18)
C(3)–C(4)	1.408(4)	C(4)–C(3)–Cl	116.93(20)		
C(4)–C(5)	1.492(4)				
van der Waals contacts					
C(1)–C(1)$^{\text{iv}}$	3.943(8)	Cl–C(5)$^{\text{ii}}$	3.656(4)		
C(1)–C(5)$^{\text{v}}$	3.917(6)	Cl–C(5)$^{\text{iii}}$	3.657(4)		
C(1)–C(5)$^{\text{vi}}$	3.984(5)				

Code of equivalent positions: $^{\text{i}}$: $1+x, y, z$; $^{\text{ii}}$: $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; $^{\text{iii}}$: $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; $^{\text{iv}}$: $-1-x, -y, 1-z$; $^{\text{v}}$: $x, y, 1+z$; $^{\text{vi}}$: $1+x, y, 1+z$.

TABLE 7. Bond lengths (Å) and angles (°) in Cu(thd)(Clacac)

Around Cu					
Cu–O(1)	1.907(7)	O(1)–Cu–O(2)	93.70(28)	O(2)–Cu–O(3)	179.42(28)
Cu–O(2)	1.898(6)	O(1)–Cu–O(3)	85.72(28)	O(2)–Cu–O(4)	88.10(27)
Cu–O(3)	1.898(6)	O(1)–Cu–O(4)	178.20(28)	O(3)–Cu–O(4)	92.48(27)
Cu–O(4)	1.903(6)				
Cu...Cl	3.434(4)				
Ligand thd					
C(2)–O(1)	1.265(12)	C(11)–C(1)–C(21)	112.1(11)	C(3)–C(4)–O(2)	123.7(9)
C(4)–O(2)	1.264(13)	C(21)–C(1)–C(21)$^{\text{i}}$	109.6(18)	C(3)–C(4)–C(5)	122.4(9)
C(1)–C(11)[a]	1.497(20)	C′(11)–C(1)–C′(21)	106.5(28)	C(5)–C(4)–O(2)	113.9(9)
C(1)–C(21)[a]	1.499(21)	C′(21)–C(1)–C′(21)$^{\text{i}}$	115(6)	C(4)–C(5)–C(15)	119.6(17)
C(1)–C′(11)[b]	1.49(4)	C(11)–C(1)–C(2)	109.4(12)	C(4)–C(5)–C(25)	108.0(8)
C(1)–C′(21)[b]	1.49(7)	C(21)–C(1)–C(2)	106.7(9)	C(4)–C(5)–C′(15)	110.7(26)
C(1)–C(2)	1.540(14)	C′(11)–C(1)–C(2)	117.1(18)	C(4)–C(5)–C′(25)	105.0(18)
C(2)–C(3)	1.352(15)	C′(21)–C(1)–C(2)	105.9(16)	C(15)–C(5)–C(25)	107.4(12)
C(3)–C(4)	1.399(15)	C(1)–C(2)–O(1)	115.4(9)	C(25)–C(5)–C(25)$^{\text{i}}$	105.5(21)
C(4)–C(5)	1.555(14)	C(1)–C(2)–C(3)	120.7(9)	C′(15)–C(5)–C′(25)	125.0(27)
C(5)–C(15)[c]	1.50(4)	C(3)–C(2)–O(1)	123.9(9)	C′(25)–C(5)–C′(25)$^{\text{i}}$	82(5)
C(5)–C(25)[c]	1.489(26)	C(2)–C(3)–C(4)	126.8(10)	Cu–O(1)–C(2)	126.2(6)
C(5)–C′(15)[d]	1.487(21)			Cu–O(2)–C(4)	125.8(7)
C(5)–C′(25)[d]	1.49(6)				
Ligand Clacac					
C(7)–O(3)	1.250(12)	O(3)–C(7)–C(6)	116.9(9)	O(4)–C(9)–C(8)	123.3(9)
C(9)–O(4)	1.281(12)	C(6)–C(7)–C(8)	119.5(9)	C(8)–C(9)–C(10)	121.5(9)
C(8)–Cl	1.776(10)	O(3)–C(7)–C(8)	123.7(9)	O(4)–C(9)–C(10)	115.2(9)
C(6)–C(7)	1.497(14)	C(7)–C(8)–C(9)	125.4(9)	Cu–O(3)–C(7)	128.0(6)
C(7)–C(8)	1.396(14)	C(7)–C(8)–Cl	118.2(7)	Cu–O(4)–C(9)	127.1(6)
C(8)–C(9)	1.384(14)	C(9)–C(8)–Cl	116.3(8)		
C(9)–C(10)	1.486(14)				
Intramolecular H bonds					
Cl–C(6)	2.984(10)	Cl–H(16)–C(6)	119.7(9)		
Cl–C(10)	2.966(11)	Cl–H(110)–C(10)	118.6(10)		
van der Waals contacts					
C(6)–C(21)$^{\text{ii, iii}}$	3.960(22)	C′(11)–C(35)$^{\text{viii}}$	3.70(5)	C(10)–C′(11)$^{\text{iv}}$	3.82(4)
C′(21)–C′(25)$^{\text{ii}}$	3.71(9)	C(10)–C′(21)$^{\text{v, vi}}$	4.00(6)	C(15)–C′(21)$^{\text{ix, x}}$	3.72(8)
C(11)–C′(25)$^{\text{ii, iii}}$	3.72(6)	C′(15)–C(21)$^{\text{xi, xii}}$	4.02(3)	C(21)–C(21)$^{\text{vii}}$	4.00(4)

Site occupancy: [a]70%; [b]30%; [c]60%; [d]40%. Code of equivalent positions: $^{\text{i}}$: $x, \frac{1}{2}-y, z$; $^{\text{ii}}$: $\frac{1}{2}-x, -y, -\frac{1}{2}+z$; $^{\text{iii}}$: $\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}+z$; $^{\text{iv}}$: $-\frac{1}{2}+x, y, \frac{1}{2}-z$; $^{\text{v}}$: $-x, -y, -z$; $^{\text{vi}}$: $-x, \frac{1}{2}+y, -z$; $^{\text{vii}}$: $x, -\frac{1}{2}-y, z$; $^{\text{viii}}$: $\frac{1}{2}+x, y, \frac{1}{2}-z$; $^{\text{ix}}$: $\frac{1}{2}-x, -y, \frac{1}{2}+z$; $^{\text{x}}$: $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; $^{\text{xi}}$: $-\frac{1}{2}-x, y, \frac{1}{2}-z$; $^{\text{xii}}$: $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

overlap almost exactly as in $Cu(Clacac)_2$, but they are piled up into columns which is not the case for $Cu(Clacac)_2$.

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