Pergamon

0277–5387(94)00362–9

Polyhedron Vol. 14, No. 8, pp. 983–989, 1995

0277–5387/95 $9.50+0.00

PREPARATION AND CHARACTERIZATION OF COPPER(II) COORDINATION COMPOUNDS WITH LINEAR CHAIN FATTY ACIDS WITH 7–12 CARBON ATOMS AND PYRIDINE. CRYSTAL STRUCTURE OF $Cu(O_2CC_8H_{17})_2(py)_2(H_2O)$

M. PETRIČ*

Department of Wood Science and Technology, University of Ljubljana, Rožna dolina,
C. VIII/34, 61000 Ljubljana, Slovenia

and

I. LEBAN and P. ŠEGEDIN

Department of Chemistry and Chemical Technology, University of Ljubljana,
Aškerčeva 5, 61000 Ljubljana, POB 537, Slovenia

(*Received* 18 *July* 1994; *accepted* 31 *August* 1994)

Abstract—Mononuclear compounds of the composition $CuX_2(py)_2(H_2O)$ and binuclear of the composition $Cu_2X_4(py)_2$ (py = pyridine, X = heptanoate, octanoate, nonanoate, decanoate or dodecanoate) were prepared, analysed and characterized by vibrational spectroscopy and thermogravimetry. Generally, the complexes are unstable, the mononuclear being even less stable than binuclear, losing pyridine in air at room temperature. The X-ray crystal structure of the mononuclear adduct of copper(II) nonanoate with pyridine, $Cu(O_2CC_8H_{17})_2(py)_2(H_2O)$, was determined by X-ray diffraction. The copper(II) ion is in a square pyramidal environment with two pyridine nitrogen atoms and two oxygen atoms from unidentate nonanoato ligands forming the basal plane of the pyramid and a water molecule coordinated at the apex. The carboxylate oxygen O(2) is not coordinated to copper, but is bound to water from a neighbouring molecule by the O—H · · · O(2) hydrogen bond of 2.691(5) Å.

The preparation, structures and properties of many copper(II) carboxylates and their complexes, especially with nitrogen donor ligands, have already been extensively studied and the results published in several reviews.[1–6] However, investigations on copper(II) complexes with higher carboxylic acids apart from acetates, propionates and butyrates are not so frequent. Only a few crystal structures of copper(II) carboxylates with higher carboxylic acids have been reported.[7–10] Increased interest in copper(II) compounds exhibiting thermotropic columnar mesophases[11] have stimulated studies of copper(II) carboxylates with $n = 6$–22 (n being equal to the number of carbon atoms of the corresponding fatty acid). The main emphasis has been on the thermal behaviour of such compounds.[12–16]

With only one exception from 1965,[17] pyridine complexes of copper(II) carboxylates with 7, 8, 9, 10 and 12 carbon atoms have not been studied. This was the aim of the work presented in this article. The results of thermogravimetry, vibrational spectroscopy as well as the crystal and molecular structure of aquabis(nonanoato)bis(pyridine) copper(II) are reported herein.

---

* Author to whom correspondence should be addressed.

EXPERIMENTAL

Preparation of the complexes

$Cu_2(O_2CR)_4$. The starting compounds $Cu_2(O_2CR)_4$, where R is C_6H_{13}, C_7H_{15}, C_8H_{17}, C_9H_{19} and $C_{11}H_{23}$, were synthesized by the direct metathesis of the corresponding sodium soap in a slightly acidic aqueous solution with the required amount of copper(II) sulphate dissolved in water, as described by Mehrotra and Bohra.[1] The yields were from 95% to almost 100%. The copper soaps obtained were purified by recrystallization from boiling methanol with yields of 80–90%.

$Cu_2(O_2CR)_4(py)_2$. The green copper(II) carboxylate complexes with pyridine were prepared by the following procedure: 2 mmol of $Cu_2(O_2CR)_4$ were dissolved in methanol (20 cm^3) with excess of pyridine (1 cm^3). The solvent was rotary evaporated and needle-shaped green precipitates appeared. The yields were from 80% for copper(II) heptanoate and octanoate complexes to 95% for the dodecanoate complex. The complexes were recrystallized from boiling methanol with some pyridine added (two or three drops of pyridine per 20 cm^3 of methanol) and subsequent cooling to 7°C. The yields were 75–80%.

$Cu(O_2CR)_2(py)_2(H_2O)$. When 50 cm^3 of distilled water was added into copper(II) carboxylate solutions in methanol–pyridine, described above, blue crystals were formed. The crystals were filtered off and rapidly washed with a small amount of diethyl ether. The products were not recrystallized because they are unstable in air. The colour of the crystal powder turns from blue to green within a few minutes. However, when closed in small tubes and held in a desiccator, the compounds remain stable. The blue copper(II) heptanoate– and nonanoate–pyridine complexes seem to be more stable than the corresponding complexes of the carboxylate ligands with even numbers of carbon atoms. The reasons for the different stability of these complexes have not been determined and any regular rule controlling this behaviour has not been deduced.

The monocrystals of $Cu(O_2CC_8H_{17})_2(py)_2(H_2O)$ for the crystal structure determination were prepared as follows: 0.7 g of $Cu_2(O_2CC_8H_{17})_4$ was dissolved in pyridine (5 cm^3). The addition of water (300 cm^3) resulted in the precipitation of small blue crystals, which were filtered off. Blue plates grew from the filtrate after standing in air for 1 month at room temperature.

Elemental analysis results of the isolated copper(II) carboxylate complexes with pyridine are given in Table 1.

Physical measurements

IR spectra of the studied substances were obtained with a Perkin–Elmer FT-IR 1720X spectrophotometer using Nujol and poly(chlorotrifluoroethylene) oil suspension techniques. Some selected IR data are given in Table 2 and complete data with tentative assignments can be obtained on request.

Thermal decomposition of the compounds was studied with an OD 102 derivatograph (MOM Budapest). Ceramic crucibles were used. The sample weight was 100 mg and the heating rate was 2.5°C min^{-1}.

X-ray structure analysis

Data were collected on an Enraf–Nonius CAD-4 diffractometer. Owing to instability the crystal was sealed together with mother liquor in a capillary. Intensity variation of not greater than 2.5% in three standard reflections monitored during the data collection period indicated negligible crystal decay. The structure was solved by a routine Patterson method followed by subsequent electron-density map calculations. Full-matrix least-squares refinement with anisotropic thermal parameters on all non-hydrogen atoms gave R and R_w values of 0.069 and 0.087, respectively, with a value of $w = 1.85[\sigma^2(F_0)+0.0014(F_0)^2]^{-1}$. Hydrogen atom positions were generated. Neutral atom scattering factors were used.[22] The system of computer programmes NRCVAX,[23] adapted for a PC 486 computer, was used throughout the data reduction, determination, refinement and interpretation.

Details of the crystal parameters, data collection and structure refinement are given in Table 3.

Atomic fractional coordinates, hydrogen atom coordinates, anisotropic thermal parameters, and observed and calculated structure factor tables are deposited with the Editor as supplementary material, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

Binuclear complexes

As already reported,[9] the green tetrakis(μ-octanoato-*O,O′*)bis(pyridine)dicopper(II) consists of discrete binuclear units of the copper(II) acetate hydrate[24] structural type with pyridine rings instead of water molecules in the apical positions.

The IR spectrum of this complex (Table 2) is

Table 1. Analytical data for copper(II) carboxylate complexes with pyridine

No.	Compound	Analysis: Found (Calc.) (%)			
		Cu	C	H	N
1	$Cu_2(C_6H_{13}CO_2)_4(py)_2$	15.7 (15.9)	55.9 (56.9)	7.7 (7.8)	3.6 (3.5)
2	$Cu_2(C_7H_{15}CO_2)_4(py)_2$	15.0 (14.8)	58.6 (58.8)	8.2 (8.2)	3.3 (3.3)
3	$Cu_2(C_8H_{17}CO_2)_4(py)_2$	14.2 (13.9)	58.8 (60.4)	8.4 (8.6)	3.1 (3.1)
4	$Cu_2(C_9H_{19}CO_2)_4(py)_2$	13.4 (13.1)	61.6 (61.9)	9.0 (8.9)	3.0 (2.9)
5	$Cu_2(C_{11}H_{23}CO_2)_4(py)_2$	11.2 (11.7)	64.4 (64.4)	9.5 (9.5)	2.7 (2.6)
6	$Cu(C_6H_{13}CO_2)_2(py)_2(H_2O)$	13.1 (12.8)	54.9 (57.9)	7.5 (7.7)	5.0 (5.6)
7[a]	$Cu(C_7H_{15}CO_2)_2(py)_2(H_2O)$	12.0 (12.1)			
8	$Cu(C_8H_{17}CO_2)_2(py)_2(H_2O)$	11.4 (11.5)	58.6 (60.7)	8.2 (8.4)	4.9 (5.1)
9[a]	$Cu(C_9H_{19}CO_2)_2(py)_2(H_2O)$	10.7 (10.9)			

[a] Because of the large differences between measured and expected elemental analysis results, the missing results were omitted—see text for explanation.

Table 2. Selected IR absorption bands (cm^{-1}) of copper(II) carboxylates and their pyridine complexes

$Cu_2(O_2CR)_4$ n[a]					$Cu_2(O_2CR)_4(py)_2$ n[a]					$Cu(O_2CR)_2(py)_2(H_2O)$ n[a]	
7	8	9	10	12	7	8	9	10	12	9	Assignment[b]
										3205	ν(O—H) (water)
1588	1590	1588	1590	1586	1588	1590	1590	1590	1588	1590–1600	ν_{as}(CO)
1417	1413	1417	1413	1423	1417	1418	1417	1417	1421	1417	ν_s(CO)
171	177	171	177	163	171	172	173	173	167	183–173	Δ[c]
					1072	1073	1078	1072	1078	1073	
										1064	
										1046	py: δ(C—H) and totally symmetric in-plane breathing frequencies
					1036	1036	1038	1036	1037	1038	
										1020	
					1011	1011	1012	1011	1011	1013	

[a] n is the number of carbon atoms in the corresponding fatty acid.
[b] Assignment is based on the proposals in refs 14, 15 and 18–21.
[c] Δ means $\nu_{as}(CO) - \nu_s(CO)$.

characteristic for dicopper tetracarboxylates[14,15] with additional bands arising from pyridine ligand vibrations. The bands at 1590 and 1418 cm^{-1} can be assigned to asymmetric [ν_{as}(C—O)] and symmetric [ν_s(C—O)] carboxylate stretches.[14,15] As is well known,[18] the difference between ν_{as}(C—O) and ν_s(C—O) is correlated quite well with the nature of carboxylate coordination. The difference of 172 cm^{-1} found for the copper octanoate–pyridine binuclear complex is characteristic for symmetrically bound carboxylate groups,[1,18] and is almost the same as that determined by Strommen and co-authors[14] for dicopper tetracarboxylates with $n = 6$–22. Vibrational spectra of other green copper(II) carboxylate–pyridine complexes studied are practically identical with the spectrum of tetrakis(μ-octanoato-*O*,*O'*)bis(pyridine)dicopper(II) (Table 2). On the basis of vibrational spectra it can be proposed that these complexes have a binuclear structure of the same type.

The binuclear structures of $Cu_2(O_2CR)_4(py)_2$ were also confirmed by EPR spectroscopy.[25,26] The EPR spectra measured at room temperature and at 100 K exhibit four transitions, B_{z1}, B_{x2}, B_{y2} and B_{z2}. Thus, the spectra are typical of the triplet state of dimeric copper(II) compounds.

The pyridine adducts slowly decompose when left to stand in air. Within approximately 24 h the green colour turns to a pale blue similar to that of the starting complexes. Vibrational spectra and

Table 3. Crystallographic data for $Cu(O_2CC_8H_{17})_2(py)_2(H_2O)$ and processing parameters of X-ray structure determination

Molecular formula	$C_{28}H_{46}CuN_2O_5$
Molecular weight	554.2
Colour	blue
Crystal size (mm)	$0.42 \times 0.38 \times 0.05$
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	15.603(6)
b (Å)	5.612(1)
c (Å)	33.789(11)
β (°)	90.80(2)
V (Å^3)	2958.5
Z	4
$F(000)$	1188
D_{calc} (g cm^{-3})	1.244
Radiation	Mo-K_α $\lambda = 0.71067$ Å
μ(Mo-K_α)	9.78 cm^{-1}
Observed reflections, $I > 2.5\sigma(I)$	3402
Unique reflections	8668
Measured reflections	13206
Intensity variation	$\pm 2.5\%$
$R = \Sigma \|\|F_0\| - \|F_c\|\| / \Sigma \|F_0\|$	0.069
$R_w = w(\|\|F_0\| - \|F_c\|\|^2 / \Sigma \|F_0\|^2)^{1/2}$	0.087
GOF	1.14
ρ, min. and max. (e A^{-3})	−0.810, 0.990

elemental analysis results of the products of decomposition indicate the formation of the original dicopper(II) tetracarboxylates.

The decomposition of $Cu_2(O_2CR)_4(py)_2$ was also observed by TG analysis. TG curves for $Cu_2(O_2CC_7H_{15})_4$ and $Cu_2(O_2CC_7H_{15})_4(py)_2$ are presented in Fig. 1. Whereas under experimental conditions of measurement copper(II) octanoate is stable up to 210°C, for $Cu_2(O_2CC_7H_{15})_4(py)_2$ gradual weight loss, most likely due to loss of pyridine, was observed. The process of giving off pyridine cannot be clearly distinguished from other thermal decomposition processes because the mass loss corresponding to two pyridine molecules per one molecule of $Cu_2(O_2CC_7H_{15})_4(py)_2$ does not occur before 240°C. The observed residual mass for both compounds corresponds approximately to CuO as the final product of thermal decomposition. Similarly, CuO is a thermal decomposition product of some copper(II) formate, acetate and propionate complexes with dimethyl pyridines,[27] pyridine and picolines.[28] TG curves of the other studied binuclear copper(II) carboxylate–pyridine complexes do not significantly differ from that of $Cu_2(O_2CC_7H_{15})_4(py)_2$ (Fig. 1). In some cases the residual mass indicates some decomposition of the CuO to copper, as already reported by Seddon and Wood[29] for copper(II) dodecanoate. The residual mass data are given in Table 4.

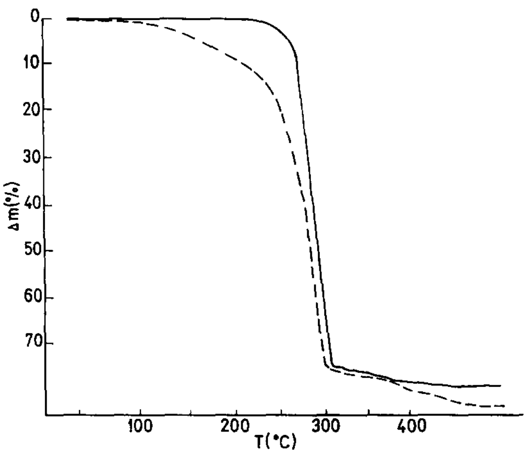

Fig. 1. TG curves for $Cu_2(O_2CC_7H_{15})_4$ (solid line) and $Cu_2(O_2CC_7H_{15})_4(py)_2$ (dashed line).

Mononuclear complexes

The blue complexes studied were unstable in air and all attempts to obtain vibrational spectra of the pure compounds of this type apart from aquabis(nonanoato)bis(pyridine)copper(II) were not successful. In the process of recording spectra the blue

Table 4. Mass of residuals (%) after TG analysis of $Cu_2(O_2CR)_4$ and $Cu_2(O_2CR)_4(py)_2$

	$Cu_2(O_2CR)_4$ *n*					$Cu_2(O_2CR)_4(py)_2$ *n*				
	7	8	9	10	12	7	8	9	10	12
Experimental	23.0	21.5	20.5	16.5	14.0	17.0	17.0	14.0	14.0	13.5
Calc. for CuO	24.7	22.7	21.0	19.6	17.2	19.8	18.5	17.4	16.4	14.7
Calc. for Cu	19.7	18.2	16.8	15.6	13.7	15.8	14.8	13.9	13.1	11.7

colour at least partially turned to green and we obtained spectra of mixtures of different species.

The instability of the mononuclear compounds and problems connected with their manipulation was also the reason for disagreement between the theoretical and experimental values of carbon, hydrogen and nitrogen analysis (Table 1). The best agreement between expected and experimental elemental analysis results was obtained for the most stable compound among mononuclear complexes, $Cu(O_2CC_8H_{17})_2(py)_2(H_2O)$. We succeeded in growing monocrystals of this complex, to perform X-ray structure analysis and to interpret its vibrational spectrum.

The crystal structure of blue aquabis(nonanoato)bis(pyridine)copper(II) consists of mononuclear units and is shown in Fig. 2. The selected bond lengths and angles are presented in Table 5. The coordinate geometry of the copper atom can be described as approximate square pyramidal. The two pyridine nitrogen atoms and two carboxylate oxygen atoms form a tetrahedrally distorted basal square plane. The deviations from the mean plane for the nitrogen and O(1) atoms are large, 0.119 Å. The copper atom is shifted out of the mean basal plane towards the apex of the pyramid by 0.098 Å. Presumably, steric reasons are responsible for the tetrahedral distortion of the basal plane. The water oxygen atom is in the apical position and lies together with copper on a two-fold rotation axis. The distances Cu—O(1) [1.944(4) Å], Cu—N [2.028(4) Å], as well as Cu—OH_2 [2.196(6) Å], are comparable with those found for bis(phenoxyacetato)aquabis(pyridine)copper(II),[31] bis(6 - methoxy - α - methylnaphthalene - 2 -acetato) aquabis(pyridine)copper(II)[32] and *trans*-aquabis (pyridine)dibenzoato copper(II).[33] The copper(II) ions in these complexes are also in a square pyramidal environment, carboxylate ligands are unidentate and the distortions of the basal planes are similar to the distortion described herein. In our complex, the carboxylate O(2) oxygen is not coordinated to copper but is bound to water from a neighbouring molecule by the O—H···O(2) hydrogen bond of 2.691(5) Å (Fig. 3).

The packing of the mononuclear units, presented in Fig. 4, is determined by the intermolecular hydrogen bond as well as by arrangement of long hydrocarbon chains. Layers of metal–oxygen cores are separated by a layer of parallel alkyl chains. The minimum distance between neighbouring chains is between C(13) and C(19) ($-x$, $-1-y$, $-z$) (4.023 Å).

The IR spectrum of aquabis(nonanoato)bis (pyridine)copper(II) showed a wide band at about 3200 cm^{-1}, which can be assigned as ν(O—H) (Table 2). This relatively low value can be explained taking into account the described hydrogen bond.[34]

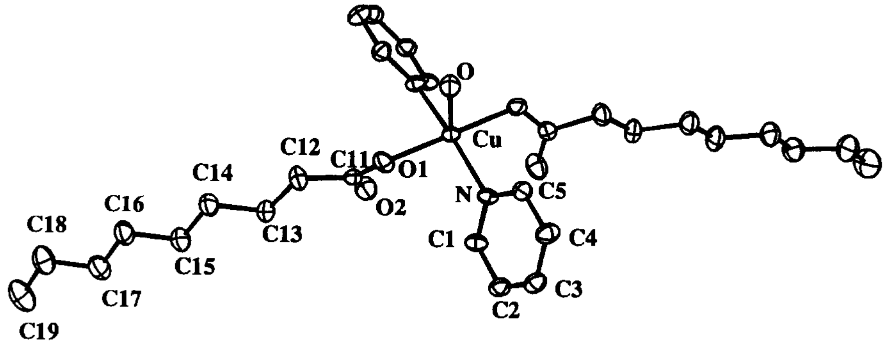

Fig. 2. ORTEP[30] view of the structure of $Cu(O_2CC_8H_{17})_2(py)_2(H_2O)$ showing the atom labelling scheme.

Table 5. Bond lengths (Å) and angles (°) with standard deviations in parentheses

Cu—O	2.196(6)	C(3)—C(4)	1.380(9)
Cu—O(1)	1.944(4)	C(4)—C(5)	1.392(8)
Cu—N	2.028(4)	C(12)—C(13)	1.540(9)
O(1)—C(11)	1.252(7)	C(13)—C(14)	1.528(9)
O(2)—C(11)	1.230(7)	C(14)—C(15)	1.541(10)
C(11)—C(12)	1.503(9)	C(15)—C(16)	1.513(10)
N—C(1)	1.340(7)	C(16)—C(17)	1.533(10)
N—C(5)	1.318(7)	C(17)—C(18)	1.509(12)
C(1)—C(2)	1.397(7)	C(18)—C(19)	1.562(12)
C(2)—C(3)	1.374(9)		
O(1)—Cu—O(1)^i	178.79(20)	N—C(1)—C(2)	121.6(5)
O(1)—Cu—N	88.84(16)	C(1)—C(2)—C(3)	118.6(6)
O(1)—Cu—N^i	91.29(16)	C(2)—C(3)—C(4)	119.4(5)
O(1)—Cu—O	89.40(14)	C(3)—C(4)—C(5)	118.7(6)
N—Cu—O	96.14(13)	N—C(5)—C(4)	122.1(5)
N—Cu—N^i	167.71(18)	C(11)—C(12)—C(13)	114.1(5)
Cu—O(1)—C(11)	122.1(4)	C(12)—C(13)—C(14)	113.1(6)
O(1)—C(11)—O(2)	124.9(6)	C(13)—C(14)—C(15)	109.9(6)
O(1)—C(11)—C(12)	115.4(5)	C(14)—C(15)—C(16)	112.7(6)
O(2)—C(11)—C(12)	119.7(5)	C(15)—C(16)—C(17)	111.2(6)
Cu—N—C(1)	120.1(4)	C(16)—C(17)—C(18)	112.4(7)
Cu—N—C(5)	120.3(4)	C(17)—C(18)—C(19)	110.4(7)
C(1)—N—C(5)	119.6(5)		

Symmetry code: ^{i} $-x, y, 1/2-z$.

The band assigned as ν_{as}(C—O) is split into two partially overlapping bands and shifted slightly towards higher frequencies, from 1588 cm^{-1} to approximately 1590–1600 cm^{-1}. Its value cannot be determined accurately because of the overlap with very strong pyridine bands in the region between 1600 and 1620 cm^{-1}. The ν_s(C—O) retains the value of 1417 cm^{-1} and the separation between ν_{as}(C—O) and ν_s(C—O) only increases slightly. For the unidentate carboxylate ligands an appreciably higher separation value would be expected.[1,18] It was shown,[18] however, that the occurrence of hydrogen bonding between the non-coordinated oxygen atom of a unidentate carboxylate ligand and other ligands or a solvent may give a "pseudo-bridging" arrangement. In that case, the unidentate carboxyl group retains the symmetrical structure. As already described, such unidentate symmetrical carboxylate groups are characteristic of aquabis(nonanoato)bis(pyridine)copper(II) and this fact is reflected in the observed low ν(C—O) frequency separation.

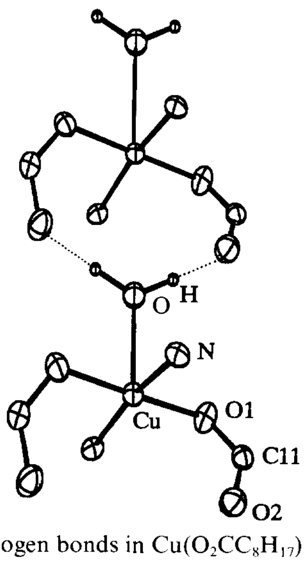

Fig. 3. Hydrogen bonds in $Cu(O_2CC_8H_{17})_2(py)_2(H_2O)$.

The most obvious difference between spectra of binuclear and mononuclear copper(II) nonanoate–pyridine complexes is in bands at about 1078, 1038 and 1013 cm^{-1}. These bands in the series of mononuclear complexes are split and probably arise from pyridine in-plane breathing vibrations.[19–21]

In spite of the lack of firm proof, on the basis of indications in IR spectra and elemental analysis results for the other four blue complexes of copper(II) heptanoate, octanoate, decanoate and

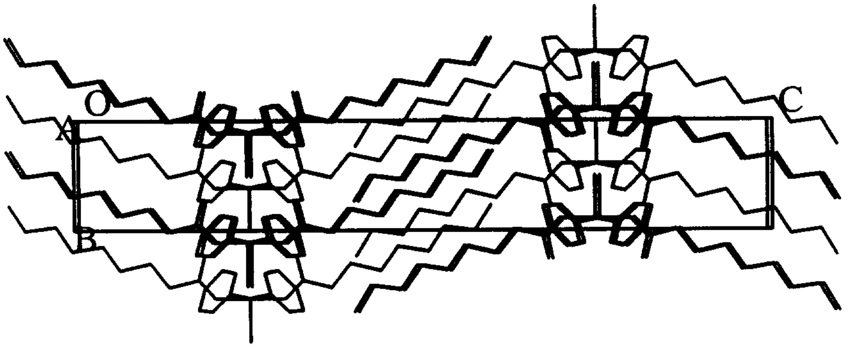

Fig. 4. Packing diagram for $Cu(O_2CC_8H_{17})_2(py)_2(H_2O)$.

dodecanoate with pyridine, we strongly believe that they are mononuclear with the stoichiometry $Cu(O_2CR)_2(py)_2(H_2O)$.

Acknowledgements——The authors would like to thank Prof. Dr Milan Melnik and his co-workers from Slovak Technical University, Department of Inorganic Chemistry, Bratislava, Slovakia, where thermogravimetry and chemical analysis were performed. The helpful comments of Prof. Dr Milan Melnik are gratefully acknowledged.

REFERENCES

1. R. C. Mehrotra and R. Bohra, *Metal Carboxylates*. Academic Press, London (1983).
2. C. Oldham, *Prog. Inorg. Chem.* 1968, **10**, 223.
3. J. Catteric and P. Thornton, *Adv. Inorg. Chem. Radiochem.* 1977, **20**, 291.
4. M. Melnik, *Coord. Chem. Rev.* 1981, **36**, 1.
5. M. Melnik, *Coord. Chem. Rev.* 1982, **47**, 239.
6. M. Kato and Y. Muto, *Coord. Chem. Rev.* 1988, **92**, 45.
7. T. R. Lomer and K. Perera, *Acta Cryst.* 1974, **B30**, 2912.
8. T. R. Lomer and K. Perera, *Acta Cryst.* 1974, **B30**, 2913.
9. M. Petrič, I. Leban and P. Šegedin, *Polyhedron* 1993, **12**, 1973.
10. N.-E. Ghermani, C. Lecomte, C. Rapin, P. Steinmetz, J. Steinmetz and B. Malaman, *Acta Cryst.* 1994, **B50**, 157.
11. J. C. Marchon, P. Maldivi, A. M. Giroud, D. Guillon, M. Ibn-Elhaj and A. Skoulios, in *Nanostructures Based on Molecular Materials* (Edited by W. Göpel and Ch. Ziegler), pp. 285–291. VCH, Weinheim (1992).
12. H. D. Burrows and H. A. Ellis, *Thermochim. Acta* 1982, **52**, 121.
13. H. Abied, D. Guillon, A. Skoulios, P. Weber, A. M. Giroud-Godquin and J. C. Marchon, *Liq. Crystals* 1987, **2**, 269.
14. D. P. Strommen, A. M. Giroud-Godquin, P. Maldivi, J. C. Marchon and B. Marchon, *Liq. Crystals* 1987, **2**, 689.
15. K. N. Mehrotra and D. Pooranchand, *Tenside, Surfactants, Deterg.* 1988, **25**, 180.
16. M. Sola Akanni, E. K. Okoh, H. D. Burrows and H. A. Ellis, *Thermochim. Acta* 1992, **208**, 1.
17. V. V. Zelentsov, *Zh. Strukt. Khim.* 1965, **6**, 854.
18. G. B. Deacon and R. J. Philips, *Coord. Chem. Rev.* 1980, **33**, 227.
19. P. C. H. Mitchell, *J. Inorg. Nucl. Chem.* 1961, **21**, 382.
20. J. S. Strukl and J. L. Walter, *Spectrochim. Acta* 1971, **27A**, 223.
21. D. A. Thornton, *Coord. Chem. Rev.* 1990, **104**, 251.
22. *International Tables for X-ray Crystallography*, Vol. 4. Kynoch Press, Birmingham (1974).
23. E. J. Gabe, Y. Le Page, J. P. Charland, F. L. Lee and P. S. White, *J. Appl. Cryst.* 1989, **22**, 384.
24. J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.* 1953, **6**, 227.
25. M. Petrič, PhD thesis. University of Ljubljana, Slovenia (1994).
26. C. J. Williams, H. Morris, M. Valko, R. Klement, M. Melnik, M. Petrič, F. Pohleven and P. Šegedin, in preparation.
27. M. A. Bernard, A. Busnot, F. Busnot and J. F. Le Querler, *Thermochim. Acta* 1985, **86**, 33.
28. M. M. Borel, A. Busnot, F. Busnot and A. Leclaire, *Thermochim. Acta* 1979, **31**, 189.
29. A. B. Seddon and J. A. Wood, *Thermochim. Acta* 1986, **106**, 341.
30. C. K. Johnson, ORTEP—A Fortran Thermal Ellipsoid Plot Program. Technical Report ORNL-5138, Oak Ridge (1976).
31. C. K. Prout, M. J. Barrow and F. J. C. Rossotti, *J. Chem. Soc.* (*A*) 1971, 3326.
32. C. Dendrinou-Samara, P. D. Jannakoudakis, D. P. Kessissoglou, G. E. Manoussakis, D. Mentzafos and A. Terzis, *J. Chem. Soc., Dalton Trans.* 1992, 3259.
33. W. M. Willingham, J. R. J. Sorenson, F. Yarberry and W. Cordes, *J. Cryst. Spectra Res.* 1993, **23**, 505.
34. L. J. Bellamy and A. J. Owen, *Spectrochim. Acta* 1969, **25A**, 329.