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A NEW COPPER(II) ALTERNATING-CHAIN STRUCTURE WITH CARBOXYLATO AND CARBOXYLIC ACID BRIDGES; THE STRUCTURE AND SPECTROSCOPIC PROPERTIES OF *CATENA*-POLY[{BIS{μ-[PENTANE-1,5-BIS(CARBOXYLIC ACID)-MONOATO-O^{α},O^{ω}]}-BIS(BENZIMIDAZOLE)COPPER}-μ-(PENTANE-1,5-BIS(CARBOXYLATO)-O^{α},O^{ω})]

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Abstract—Copper(II) bis(carboxylato) benzimidazole complexes of the type $Cu(Hbim)_2(A)$ and $Cu(Hbim)_2(A)_{1/2}(HA)$ (where Hbim stands for benzimidazole and A and HA for dianion and monoanion of a dicarboxylic acid) have been synthesized and characterized by elemental analyses, and electronic and IR spectroscopic measurements. The X-ray crystal structure of $\{[Cu_2(Hbim)_4(Pim)(HPim)_2]\cdot 8H_2O\}_n$ (where Pim and HPim stand for the di- and monodeprotonated forms, respectively, of pimelic acid) has been determined from three-dimensional X-ray diffraction data. Single dianionic and double monoanionic bridges link the metal centres in polymeric chains, where each carboxylate or carboxylic group acts as a monodentate moiety. The Cu^{II} ions are five-coordinated with a square-pyramidal CuN_2O_2O chromophore. Short O···O hydrogen bonds (2.6–2.8 Å) are found between carboxylate and carboxylic groups or water molecules.

Benzimidazole and its derivatives have interesting and useful biological properties. For example, 2-fluoromethylbenzimidazole derivatives are patented as herbicides[1] and 2-α-hydroxy-benzylbenzimidazole shows antivirus activity.[2] 2-Methylbenzimidazole is useful as a herbicide as well.[3] Benzimidazoles are also used extensively in industrial processes as corrosion inhibitors for metal and alloy surfaces, particularly of copper[4a] and ion exchangers.[4b]

The coordination chemistry of azoles acting as ligands in copper(II) compounds is widely studied in the context of modelling biological systems.[5] The structure of a benzimidazole copper(II) complex with acetate ions was shown to be dinuclear,[6] of the paddle-wheel type.

α,ω-Dicarboxylic acids and their anions can act as chains between copper ions coordinated further by benzimidazoles. So far, two structures of polymeric copper(II) compounds containing dicarboxylic acid anions have been published.[7,8] It appears interesting to study the behaviour of the copper(II) moiety upon lengthening the chain of

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the dicarboxylic acids between the copper ions. The spectroscopic properties of the carboxylic group in these compounds may be correlated to the structural parameters of the complexes.

A number of benzimidazole copper(II) dicarboxylic acid compounds have been synthesized with the general formula Cu(Hbim)$_2$(A) (where Hbim = benzimidazole and A = dianion of a dicarboxylic acid). The pimelic acid derivative, however, showed an unusual IR spectrum and therefore it was decided to investigate the structure by X-ray analysis.

The results of this structural analysis are presented in this paper, together with the magnetic, electronic and IR spectral properties.

EXPERIMENTAL

All starting materials were commercially available and used without further purification. The dicarboxylic acids used were: 1,3-ethanedicarboxylic acid (succinic acid, abbreviated as H$_2$Suc); 1,3-propanedicarboxylic acid (glutaric acid, abbreviated as H$_2$Glu); 1,4-butanedicarboxylic acid (adipic acid, abbreviated as H$_2$Adi); 1,5-pentanedicarboxylic acid (pimelic acid, abbreviated as H$_2$Pim).

2-Methylbenzimidazole was prepared according to a published method.[3] The benzimidazole copper(II) dicarboxylic acid compounds were synthesized according to a published procedure.[7]

All compounds crystallized from water as blue to violet-blue crystals. The products were characterized by elemental analysis. The analytical data are (calculated values in parentheses): for [Cu(Hbim)$_2$(Glu)(H$_2$O)] ($C_{19}H_{20}N_4O_5Cu$): C, 52.1 (51.0); H, 4.3 (4.5); N, 12.4 (12.5); Cu, 14.6 (14.2). For [Cu(Hbim)$_2$(Adi)(H$_2$O)] ($C_{20}H_{22}N_4O_5Cu$): C, 53.8 (52.0); H, 4.7 (4.8); N, 12.7 (12.1); Cu, 13.0 (13.8). For [Cu(Hbim)$_2$(Pim)$_{1/2}$(HPim)(H$_2$O)$_4$] ($C_{49}H_{72}N_8O_{20}Cu_2$): C, 47.6 (48.2); H, 5.9 (6.0); N, 9.2 (9.1); Cu, 9.7 (10.4). For [Cu(HMebim)$_2$(Suc)$_{1/2}$(HSuc)(H$_2$O)] ($C_{22}H_{25}N_4O_7Cu$): C, 51.1 (50.7); H, 4.7 (4.8); N, 9.9 (10.8); Cu, 12.2 (12.2).

Physical measurements

Carbon, hydrogen, nitrogen and copper analyses were performed by the Microanalytical Laboratory of University College, Dublin, Ireland and the Microanalytical Department of the University at Groningen, The Netherlands. UV–vis spectra were obtained on a Perkin–Elmer 330 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. X-band powder EPR spectra were obtained on a Jeol RE2X ESR spectrometer. Spectra were calibrated with DPPH ($g = 2.0036$) as a field marker. The IR spectra were recorded on a Bruker 113v FT-IR spectrophotometer as KBr pellets and Nujol mulls between KBr discs (resolution 2 cm^{-1}).

X-ray analysis of {[Cu$_2$(Hbim)$_4$(Pim)(HPim)$_2$]·8H$_2$O}$_n$

A blue single crystal of approximate dimensions 0.2 × 0.3 × 0.4 mm was used for the X-ray diffraction experiments carried out on a Siemens AED diffractometer on-line controlled by an IBM PC. The crystal data and the most relevant parameters adopted in the data collection and crystal structure refinement are summarized in Table 1.

The cell parameters were obtained by least-squares fit of 30 $(\theta, \chi, \phi)_{hkl}$ reflections found in a random search on the reciprocal lattice in the range $31.93 \leqslant \theta \leqslant 39.95°$. The intensities were determined by profile analysis according to the Lehman and Larsen method.[9] One standard reflection collected every 100 excluded any measurable decay of the specimen. At the end of the systematic data collection the intensities were corrected for Lorentz and polarization effects.

The structure was solved by Patterson and direct phasing methods using the SHELX86 program[10] and the atom search was completed by the standard Fourier synthesis of the SHELX76 program.[11] The atomic positions were refined by blocked full matrix least-squares methods (381+402 parameters). The hydrogen atom coordinates were calculated with the geometrical constraint C—H = 0.96 Å and refined "riding" on the corresponding carbon atoms, with the exception of the two carboxylic hydrogen atoms and all 16 hydrogen atoms of the water molecules, which were found in the Fourier ΔF map and included in the last stage of the refinement.

The final reliability R factor was 0.035 (unit weights). Atomic scattering factors and anomalous scattering coefficients were taken from the literature.[12] The geometrical calculations were obtained by PARST.[13] The calculations were carried out on a GOULD ENCORE 91 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma.

Fractional coordinates for the non-hydrogen atoms, lists of anisotropic thermal parameters, fractional coordinates of the hydrogen atoms, bond distances and angles and a list of observed and calculated structure factors are available from the authors on request. Coordinates have been

Table 1. Crystal data and experimental parameters for the crystallographic analysis of $\{[Cu_2(Hbim)_4(Pim)(HPim)_2]\cdot 8H_2O\}_n$

Formula	$C_{49}H_{56}Cu_2N_8O_{12}\cdot 8H_2O$
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell parameters at 295 K[a]	
a (Å)	9.198(3)
b (Å)	9.994(2)
c (Å)	32.651(4)
α (°)	98.03(2)
β (°)	94.88(2)
γ (°)	95.66(2)
V (Å^3)	2943(1)
Z	2
D_{calcd}(g cm^{-3})	1.377
F(000)	1280
Molecular weight	1220.241
Linear abs. coeff. (cm^{-1})	15.53
Diffractometer	Siemens AED
Scan type	θ–2θ
Scan speed (° min^{-1})	3–12
Scan width (°)	$(\theta-0.65),(\theta+0.65+\Delta\lambda\cdot\lambda^{-1}\cdot\mathrm{tg}\,\theta)$
Radiation	Cu-K_α (λ = 1.54178 Å)
2θ range (°)	6–140
Reflections measured	$\pm h, \pm k, +l$
Total data measured	11385
Criterion for observation	$I \geqslant 2\sigma(I)$
Observed data measured	8708
Unique observed data	8536
Agreement between equivalent observed reflections	0.01
No. of variables	783
Max. Δ/σ on last cycle	0.10
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.035
$R_w = \Sigma w^{1/2}\lvert\Delta F\rvert/\Sigma w^{1/2}\lvert F_o\rvert$	0.035
GOF = $[\Sigma w\lvert\Delta F\rvert^2/(NO-NV)]^{1/2}$	1.1

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 30 carefully centred reflections chosen from diverse regions of reciprocal space.

deposited at the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

IR spectroscopic results

In the IR spectrum of the compounds, the most characteristic bands are from the antisymmetric and symmetric vibrations of the carboxylate groups. The absorptions of the CO stretching vibrations of the present compounds are listed in Table 2, together with the ligand field absorptions and the g values of the EPR spectrum. It is shown in Table 2 that all antisymmetric CO frequencies are observed in the 1550–1600 cm^{-1} region and the symmetric CO frequencies in the 1420–1450 cm^{-1} region.

Compounds **1**–**4** exhibit general carboxylate frequencies in the neighbourhood of the frequencies of the dehydrogenated ions of the dicarboxylic acids.[14,15] The separation between these two absorptions varies between 130 and 150 cm^{-1}. This separation is lower than that reported in the literature for monodentate carboxylate groups.[16–22] In fact, they might indicate a chelating coordination mode. However, as the present structure indicates, the pimelic acid ions are only monodentate coordinating and bridge between the copper ions. Perhaps the strong hydrogen bonding may have the same effect as chelating on the IR spectra.

The IR spectrum of **4** shows an additional absorption that can be assigned to the non-ionized carboxylic group (R—COOH) present (for the free pimelic acid these absortions are at 1698 and 1433 cm^{-1}).

Table 2. Copper(II) bis(carboxylato) benzimidazole compounds

Compound[a]	IR		Ligand field absorption (10^3 cm^{-1})	EPR	
	ν_{as}(CO)	ν_s(CO)		$g_\perp$	$g_\parallel$
1 Cu(Hbim)$_2$(Suc)(H$_2$O)[b]	1577	1430	15.9	2.07	2.30
2 Cu(Hbim)$_2$(Glu)(H$_2$O)	1551	1442	15.7 13.0^{sh}	2.10 vbr	
3 Cu(Hbim)$_2$(Adi)(H$_2$O)	1608, 1592	1433	14.9	2.07	2.28
4 Cu(Hbim)$_2$(Pim)$_{1/2}$(HPim)(H$_2$O)$_4$[c]	1696 1601, 1566	1438	15.9	2.07	2.29
5 Cu(HMebim)$_2$(Suc)$_{1/2}$(HSuc)(H$_2$O)	1711 1539	1444	18.0 14.5	2.07	2.23

[a] Abbreviations: Hbim = benzimidazole; HMebim = 2-methyl-benzimidazole; H$_2$Suc = 1,3-ethanedicarboxylic acid (succinic acid); H$_2$Glu = 1,3-propanedicarboxylic acid (glutaric acid); H$_2$Adi = 1,4-butanedicarboxylic acid (adipic acid); H$_2$Pim = 1,5-pentanedicarboxylic acid (pimelic acid); sh = shoulder; vbr = very broad.

[b] Reference 7.

[c] Present X-ray investigation.

The same is observed for compound **5**, which has the same composition as **4** but with 2-methyl-benzimidazole instead of benzimidazole and with succinate ions instead of pimelate. Here the additional absorption is observed at 1711 cm^{-1} (for the free succinic acid the CO absorptions are at 1693 and 1420 cm^{-1}).

Ligand field spectroscopy

The ligand field *d–d* transition band of the copper–benzimidazole compounds is asymmetric. The main band is centred around 15.0–16.0 × 10^3 cm^{-1} and a shoulder is in some cases visible at around 13.0 × 10^3 cm^{-1}. These values are in agreement with the CuN$_2$O$_2$(O) chromophore with square pyramidal geometry.[17,18,21,23]

EPR

The EPR spectra (measured as powdered room temperature samples) of the benzimidazole compounds (Table 2) are situated at $g_\perp$ at about 2.07 and $g_\parallel$ at about 2.28. These spectra are in accordance with an axially elongated tetragonal–octahedral environment and an (N$_2$O$_2$O′) chromophore.[24,25] With the exception of compound **4**, the compounds do not show hyperfine splitting as a result of exchange narrowing.[22,23,25] Interestingly, compound **4** shows a barely resolved seven-line hyperfine pattern (A = 7.8 mT), most probably due to a small Cu—Cu interaction; no zero-field splitting could be detected.

Crystal and molecular structure of {[Cu$_2$(Hbim)$_4$(Pim)(HPim)$_2$]·8H$_2$O}$_n$ (**4**)

Figure 1 shows a perspective view of the symmetry-independent polymeric moiety of **4**, with the

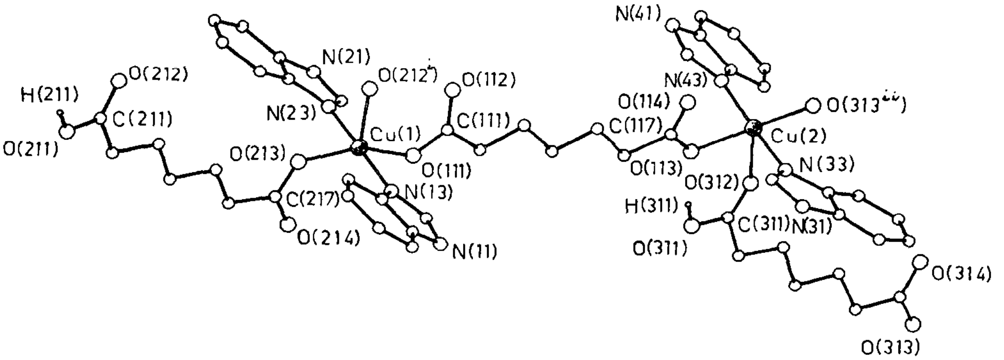

Fig. 1. Perspective view of the building block (unprimed atoms) of the polymeric chain in **4** with the atom numbering scheme.

Table 3. Relevant bond distances (Å) and angles (°) in $\{[Cu_2(Hbim)_4(Pim)(HPim)_2]\cdot 8H_2O\}_n$

Cu(1)—N(13)	2.005(2)	Cu(2)—N(33)	2.001(2)
Cu(1)—N(23)	1.995(3)	Cu(2)—N(43)	1.993(2)
Cu(1)—O(111)	1.962(3)	Cu(2)—O(113)	1.985(2)
Cu(1)—O(213)	1.950(2)	Cu(2)—O(312)	2.331(3)
Cu(1)—O(212^{i})	2.293(5)	Cu(2)—O(313^{ii})	1.940(2)
N(13)—C(12)	1.324(4)	N(33)—C(32)	1.325(4)
C(12)—N(11)	1.339(4)	C(32)—N(31)	1.340(4)
N(11)—C(15)	1.379(4)	N(31)—C(35)	1.379(4)
C(15)—C(14)	1.398(4)	C(35)—C(34)	1.397(4)
C(14)—N(13)	1.403(4)	C(34)—N(33)	1.403(4)
N(23)—C(22)	1.326(4)	N(43)—C(42)	1.321(4)
C(22)—N(21)	1.339(5)	C(42)—N(41)	1.341(4)
N(21)—C(25)	1.379(4)	N(41)—C(45)	1.380(4)
C(25)—C(24)	1.401(4)	C(45)—C(44)	1.396(4)
C(24)—N(23)	1.408(4)	C(44)—N(43)	1.402(4)
C(111)—O(111)	1.275(3)	C(311)—O(311)	1.322(3)
C(111)—O(112)	1.237(5)	C(311)—O(312)	1.206(4)
C(217)—O(213)	1.265(4)	C(317)—O(313)	1.254(4)
C(217)—O(214)	1.246(5)	C(317)—O(314)	1.242(5)
C(211)—O(212)	1.204(4)	C(117)—O(113)	1.295(4)
C(211)—O(211)	1.307(4)	C(117)—O(114)	1.238(5)

N(13)—Cu(1)—N(23)	177.2(1)	N(33)—Cu(2)—N(43)	174.5(1)
O(111)—Cu(1)—O(213)	156.6(1)	O(113)—Cu(2)—O(312)	85.8(1)
O(111)—Cu(1)—O(212^{i})	112.8(1)	O(113)—Cu(2)—O(313^{ii})	177.4(1)
O(213)—Cu(1)—O(212^{i})	90.5(1)	O(312)—Cu(2)—O(313^{ii})	91.6(1)
N(13)—Cu(1)—O(212^{i})	90.2(1)	N(33)—Cu(2)—O(313^{ii})	90.0(1)
N(23)—Cu(1)—O(212^{i})	92.3(1)	N(43)—Cu(2)—O(313^{ii})	89.6(1)
O(111)—C(111)—O(112)	125.0(3)	O(311)—C(311)—O(312)	123.1(3)
O(111)—C(111)—C(112)	113.9(3)	O(311)—C(311)—C(312)	113.5(3)
O(112)—C(111)—C(112)	121.1(3)	O(312)—C(311)—C(312)	123.4(3)
O(213)—C(217)—O(214)	124.4(3)	O(113)—C(117)—O(114)	122.3(3)
O(213)—C(217)—C(216)	116.4(3)	O(113)—C(117)—C(116)	115.7(3)
O(214)—C(217)—C(216)	119.3(3)	O(114)—C(117)—C(116)	122.0(3)
O(211)—C(211)—O(212)	123.7(3)	O(313)—C(317)—O(314)	124.6(3)
O(211)—C(211)—C(212)	112.7(3)	O(313)—C(317)—C(316)	117.1(3)
O(212)—C(211)—C(212)	123.6(3)	O(314)—C(317)—C(316)	118.3(3)

Relevant intermolecular hydrogen bonds

O(311)···O(113)	2.653(5)	O(311)—H(311)—O(113)	169(5)
H(311)···O(113)	1.86(5)		
O(211)···O(112^{i})	2.595(5)	O(211)—H(211)—O(112^{i})	170(4)
H(211)···O(112^{i})	1.75(4)		
N(11)···O(2w^{iii})	2.874(4)	N(11)—H(11N)—O(2w^{iii})	170(5)
H(11N)···O(2w^{iii})	1.92(1)		
N(21)···O(7w^{iv})	2.779(4)	N(21)—H(21N)—O(7w^{iv})	169(4)
H(21N)···O(7w^{iv})	1.83(1)		
N(31)···O(3w^{v})	2.795(4)	N(31)—H(31N)—O(3w^{v})	169(3)
H(31N)···O(3w^{v})	1.85(1)		
N(41)···O(4w^{vi})	2.779(4)	N(41)—H(41N)—O(4w^{vi})	173(4)
H(41N)···O(4w^{vi})	1.82(1)		
O(1w)···O(114^{vii})	2.744(4)	O(1w)—H(1w)—O(114^{vii})	173(4)
H(1w)···O(114^{vii})	1.76(5)		
O(5w)···O(314^{viii})	2.677(4)	O(5w)—H(10w)—O(315^{viii})	174(4)
H(10w)···O(314^{viii})	1.68(5)		
O(1w)···O(314^{viii})	2.731(4)	O(1w)—H(2w)—O(314^{viii})	167(5)
H(2w)···O(314^{viii})	1.91(4)		
O(8w)···O(214^{ix})	2.666(4)	O(8w)—H(15w)—O(214^{ix})	172(4)
H(15w)···O(214^{ix})	1.66(4)		
O(6w)···O(214^{ix})	2.816(4)	O(6w)—H(12w)—O(214^{ix})	166(5)
H(12w)···O(214^{ix})	1.96(4)		

Asymmetric codes: (i) $2-x$, $-1-y$, $1-z$; (ii) $-2-x$, $-2-y$, $-z$; (iii) x, $-1+y$, z; (iv) $1+x$, $-2+y$, z; (v) $-1+x$, $-1+y$, z; (vi) x, $-2+y$, z; (vii) $1+x$, $2+y$, z; (viii) $-1-x$, $-y$, $-z$; (ix) $-1+x$, $1+y$, z.

atom numbering scheme. Table 3 reports the most relevant bond distances and angles.

The two crystallographically independent copper atoms are held together by the carboxylate oxygen atoms O(111) and O(113) from the dianion (Pim) of the pimelic acid (H_2Pim), with distances Cu(1)—O(111) = 1.962(3) Å and Cu(2)—O(113) = 1.985(2) Å. Each copper atom is further bonded to two *trans* nitrogen atoms from two benzimidazole ligands [Cu(1)—N(13) = 2.005(2), Cu(1)—N(23) = 1.995(3), Cu(2)—N(33) = 2.001(2) and Cu(2)—N(43) = 1.993(2) Å] and to two oxygen atoms from two centrosymmetrically related HPim monoanions [Cu(1)—O(213) = 1.950(2), Cu(1)—O(212^{i}) = 2.293(5), Cu(2)—O(312) = 2.331(3) and Cu(2)—O(313^{ii}) = 1.940(2) Å]. Around each copper atom, four of the five coordinated atoms form a nearly square planar arrangement, although a small distortion towards trigonal bipyramidal coordination in Cu(1) is present [O(111)—Cu(1)—O(213) = 156.6(1)°]; the fifth, weaker bonded atom [O(212^{i}) to Cu(1) and O(312) to Cu(2)] completes the distorted square-pyramidal coordination around the metal centres. The very long contacts Cu(1)···O(214) = 3.068(3) and Cu(2)—O(314^{ii}) = 3.190(3) Å (omitted in the figure), involving the uncoordinated carboxylate oxygen atoms of the HPim ligands, are not considered as bonding.

Single dianionic and double monoanionic bridges between the metal centres generate polymeric chains running along [$\bar{1}04$] (Fig. 2). The distance between the metal atoms Cu(1) and Cu(2), held together by a single dianionic bridge, is 13.424(1) Å, whereas the distances Cu(1)—Cu(1^{i}) and Cu(2)—Cu(2^{ii}), involving metal centres connected by double monoanionic bridges, are 12.736(1) and 11.489(1) Å, respectively. Both monoanionic and dianionic forms of H_2Pim show an extended conformation and each carboxylate or carboxylic group forms only one covalent bond with the nearest copper(II) ion. The OH fragments of the carboxylic groups are involved in intramolecular hydrogen bonds; in particular, the interaction between the OH donor moiety of the O(312)C(311)O(311)H(311) carboxylic group and the acceptor carboxylate oxygen O(113) gives rise to a pseudo-chelate six-membered ring around Cu(2).

Clusters of eight water molecules link the chains by quite strong hydrogen bonds. They act as acceptors with the neighbouring NH imidazole groups and as donors with uncoordinated carboxylate oxygen atoms from different chains.

So far, to the best of our knowledge, no structural determination of pimelate complexes has been reported in the literature; in fact, only the structure of a benzimidazole copper(II) derivative with the dicarboxylate succinate ligand is known.[7] The polymeric structure of this compound, compared with that of **4**, maintains the extended conformation of the dianion and the *trans* configuration of the benzimidazole groups, but shows the donor atoms involved in a slightly distorted copper(II) octahedral environment, obtained by coordinating two water molecules. The introduction of water molecules in the metal coordination sphere, due to recrystallization and usual for copper (II), could have prevented the formation of double monoanionic bridges between the metals, as observed in our complex.

CONCLUSIONS

α,ω-Dicarboxylic acids can form polymeric chains of Cu^{2+} and carboxylate ions, e.g. with succinic acid.[7] However, with the rather long chain of pimelic acid, a unique structure is formed with carboxylato and carboxylic acid bridges. The structure was studied and verified by IR spectroscopy by the observation of the CO vibrations, indicating that the vibrations of the ionized carboxylic group are present as well as the vibrations of the non-ionized carboxylic group.

When using 2-methylbenzimidazole as a ligand to copper, the same spectral features are observed, from which it is concluded that in this case also ionized and non-ionized carboxylic groups are present.

Attempts to make good crystals of compounds

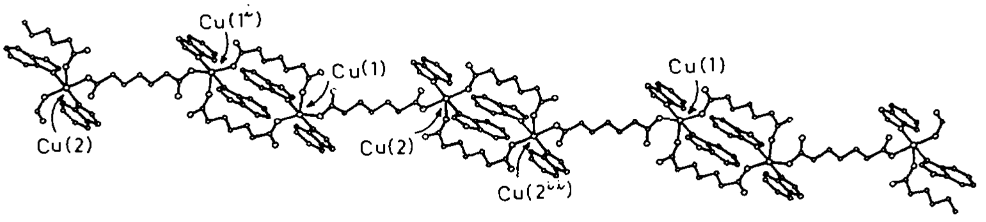

Fig. 2. Polymeric chain of **4** running along [$\bar{1}04$].

with α,ω-dicarboxylic acids with even larger carbon chains have so far failed.

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REFERENCES

1. D. E. Burton, A. H. Lambie, J. C. L. Ludgate, G. T. Newbold, A. Percival and D. T. Saggers, *Nature* 1965, **208**, 1166.
2. A. C. Hollinshead and P. K. Smith, *J. Pharmac. Exp. Ther.* 1958, **123**, 54.
3. U. S. Borax and Chemical Corp., British Patent 1, 015, 937 (1966).
4. (a) D. P. Drolet, D. M. Manuta and A. J. Lees, *Inorg. Chim. Acta* 1988, **146**, 173; (b) P. D. Verweij, T. Dugué, W. L. Driessen, J. Reedijk, B. Rowatt and D. C. Sherrington, *Reactive Polym.* 1991, **14**, 213.
5. E. Bouwman, W. L. Driessen and J. Reedijk, *Coord. Chem. Rev.* 1990, **104**, 143.
6. M. Bukowska-Strzyzewska, J. Skoweranda and A. Tosik, *Acta Cryst.* 1982, **B38**, 2904.
7. A. Tosik and M. Bukowska-Strzyzewska, *J. Cryst. Spectrosc. Res.* 1992, **22**, 225.
8. M. R. Udupa and B. Krebs, *Inorg. Chim. Acta* 1980, **42**, 251.
9. M. S. Lehman and F. K. Larsen, *Acta Cryst.* 1974, **A30**, 580.
10. G. M. Sheldrick, SHELX86: Program for Crystal Structure Solution. University of Gottingen (1986).
11. G. M. Sheldrick, SHELX76: Program for Crystal Structure Determination. University of Cambridge (1976).
12. D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, Vol. IV, Table 2.28. Kynoch Press, Birmingham, U.K. (1974).
13. M. Nardelli, *Comput. Chem.* 1983, **7**, 95.
14. H. Susi, *Spectrochim. Acta* 1959, **12**, 1063.
15. M. St. C. Flett, *Spectrochim. Acta* 1962, **18**, 1537.
16. G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.* 1980, **33**, 227.
17. L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, L. Menabue and G. C. Pellacani, *J. Am. Chem. Soc.* 1980, **102**, 2663.
18. L. P. Battaglia, A. Bonamartini Corradi and L. Menabue, *Inorg. Chem.* 1983, **22**, 3251.
19. L. P. Battaglia, A. Bonamartini Corradi, L. Menabue, M. Saladini and M. Sola, *J. Chem. Soc., Dalton Trans.* 1987, 1333.
20. A. L. Abuhijleh and C. Woods, *Inorg. Chim. Acta* 1992, **194**, 9.
21. A. Corradi Bonamartini, S. Bruni, F. Cariati, L. P. Battaglia and G. Pelosi, *Inorg. Chim. Acta* 1993, **205**, 99.
22. D. Miernik, T. Lis, J. Palus and J. Reedijk, *Inorg. Chim. Acta* 1993, **205**, 231.
23. L. Antolini, L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, L. Menabue, G. C. Pellacani and M. Saladini, *Inorg. Chem.* 1982, **21**, 1391.
24. B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.* 1970, **5**, 143.
25. B. J. Hathaway, *Struct. Bonding (Berlin)* 1984, **57**, 55.