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Bis(triphenylphosphine)pyridine- and Pyrazine-carboxylatecopper(I) Complexes

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Several complexes obtained by the reaction of tetrahydroboratebis(triphenylphosphine)copper(I) with pyridine(py)- and pyrazine(pyz)-carboxylic acids have been obtained and characterized by infrared spectra. Crystal structures of the $L_2Cu(3\text{-}py(CO_2))$ and the $L_2Cu(2,3\text{-}py(CO_2)(COOH))$ (L = triphenylphosphine) complexes have been determined. The $L_2Cu(3\text{-}py(CO_2))$ complex has a polymeric structure in which each copper(I) atom is tetrahedrally coordinated to two molecules of triphenylphosphine and two nicotinate anions, one of which is bonded through the nitrogen atom and the other through the carboxylate group. The $L_2Cu(2,3\text{-}py(CO_2)(COOH))$ complex consists of tetrahedral monomeric units, in which the anion is coordinated through the nitrogen atom and the unidentate ortho *carboxylate group. The structures of the other complexes are proposed on the basis of their anlytical and infrared data.*

Introduction

Pyridine- and pyrazine-carboxylic acids have been found on the basis of the reported X-ray molecular structures to be interesting and versatile ligands. The nicotinic and isonicotinic acids act as ligands through the pyridine nitrogen atom [1, 2]. The picolinic and the 2-pyrazinecarboxylic acids act as bidentate ligands through the nitrogen atom and the unidentate carboxylate group [3–9].

The dipicolinic acid behaves as a terdentate ligand as it coordinates to metal ion through the pyridine nitrogen atom and two unidentate carboxylic groups [10–18]. The monoanions of the quinolinic acid and of the 2,3-pyrazinedicarboxylic acid coordinate to the metal ion through the nitrogen atom and one oxygen atom of the carboxylic group in *ortho* position [19–21]. The dianion of the 2,3-pyrazinedicarboxylic acid acts as bidentate ligand on two metal ions and forms complexes having polymeric structures [22–24]. Several complexes of copper(II) with pyridine- and pyrazine-carboxylic acids have been reported in the literature and their spectral properties used to establish their stereochemistry [21, 24–26]. For some of these complexes, *e.g.* $Cu(2\text{-}py(CO_2))_2$ [3], $Cu(2\text{-}py(CO_2))_2(H_2O)_2$ [4], $Cu(2,6\text{-}py(CO_2)_2)(H_2O)_2$ [11], $Cu(2,6\text{-}py(CO_2)(COOH))_2 \cdot 3H_2O$ [16], $Cu(2,6\text{-}py(CO_2)_2)(2,6\text{-}py(COOH)_2)$ [18] and $Cu(2,3\text{-}pyz(CO_2)_2) \cdot HCl$ [24] crystal and molecular structures have also been obtained by X-ray diffraction methods. In this paper we report the spectroscopic properties of 14 new tetrahedral complexes of copper(I) with pyridine- and pyrazine-carboxylic acids, and the preliminary X-ray structures for two of them. These complexes have been obtained by reaction of tetrahydroborate of bis(triphenylphosphine)copper(I) [25] with pyridine- and pyrazine-carboxylic acids. In fact it is well known that this compound reacts with acids [26] giving the corresponding bis(triphenylphosphine)copper(I) salts. The list of the complexes studied, their analytical results, melting points and molecular weights obtained are reported in Table I.

Experimental

Reagents

The acids (Ega-Chemie) were purified by recrystallization from water and dried under vacuum; their purity was checked by melting point and potentiometric titration. Pyrazine-2,5- and pyrazine-2,6-dicarboxylic acids were prepared according to Scohout *et al.* [27].

The tetrahydroboratebis(triphenylphosphine)copper(I) complex (hereafter indicated as L_2CuBH_4) was prepared according to the literature [25].

Preparation of the Complexes

The complexes of monocarboxylic acids were prepared by adding the solid acids to methylene chloride solutions of L_2CuBH_4 in the molar ratio acid/L_2CuBH_4 = 1/1; those of dicarboxylic acids were prepared using 1/1 or 1/2 molar ratios. The reaction with molar ratio 1/2 occurs only for 2,3-

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TABLE I. Analytical Data.

Compound[a]	N.	Colour	M.W.[b,c]	M.p., °C	Elemental Analysis[c]		
					C%	H%	N%
L$_2$Cu(2-py(CO$_2$))	1	white	714(710)	206	70.79(71.02)	4.80(4.79)	1.95(1.97)
L$_2$Cu(3-py(CO$_2$))	2	white	*	150	71.01(71.02)	4.72(4.79)	1.93(1.97)
L$_2$Cu(4-py(CO$_2$))	3	white	*	162	71.10(71.02)	4.78(4.79)	2.00(1.97)
L$_2$Cu(2,3-py(CO$_2$)(COOH))	4	yellow	789(754)	210	68.58(68.47)	4.54(4.50)	1.83(1.85)
L$_2$Cu(2,4-py(CO$_2$)(COOH))	5	yellow	767(754)	233	68.56(68.47)	4.48(4.50)	1.90(1.85)
L$_2$Cu(2,5-py(CO$_2$)(COOH))	6	yellow	[d]	244	68.27(68.47)	4.60(4.50)	1.84(1.85)
L$_2$Cu(2,6-py(CO$_2$)(COOH))	7	yellow	790(754)	212	68.42(68.47)	4.58(4.50)	1.81(1.85)
L$_2$Cu(3,4-py(CO$_2$)(COOH))	8	yellow	*	216	68.37(68.47)	4.45(4.50)	1.83(1.85)
L$_2$Cu(3,5-py(CO$_2$)(COOH))	9	yellow	*	237	68.35(68.47)	4.56(4.50)	1.87(1.85)
L$_2$Cu(2-pyz(CO$_2$))	10	pale-orange	740(711)	185	69.24(69.20)	4.58(4.64)	3.90(3.93)
L$_2$Cu(2,3-pyz(CO$_2$)(COOH))	11	orange	759(755)	210	66.79(66.75)	4.40(4.37)	3.68(3.70)
(L$_2$Cu)$_2$(2,3-pyz(CO$_2$)$_2$)	12	yellow	1320(1342)	183	69.58(69.79)	4.65(4.65)	1.98(2.08)
(L$_2$Cu)$_2$(2,5-pyz(CO$_2$)$_2$)	13	orange	1310(1342)	280	69.39(69.79)	4.59(4.65)	2.10(2.08)
L$_2$Cu(2,6-pyz(CO$_2$)(COOH))	14	yellow	758(755)	240	66.70(66.75)	4.41(4.37)	3.71(3.70)

[a] L = Triphenylphosphine, py = pyridine, pyz = pyrazine. [b] Osmometric determination in CHCl$_3$. [c] Calculated values in parentheses. [d] Not sufficiently soluble. *The values of polymeric compounds (see text) were of difficult interpretation.

pyrazine- and 2,5-pyrazine-dicarboxylic acids. In all the other cases the dicarboxylic acids react with L$_2$CuBH$_4$ only in the molar ratio 1/1. From the methylene chloride solutions, stirred until gas evolution was observed, precipitates were obtained by adding light petroleum. The precipitated complexes were filtered off and dried *in vacuo*.

Elemental Analysis

Nitrogen, carbon and hydrogen were analysed with a Perkin-Elmer 240 Elemental Analyzer.

Crystal Data

Compound (2). C$_{43}$H$_{34}$CuNO$_4$P$_2$, M = 754.24, triclinic, space group $P\bar{1}$, $a = 11.132(2)$, $b = 13.418(1)$, $c = 12.962(2)$ Å, $\alpha = 100.73(2)$, $\beta = 99.72(1)$, $\gamma = 75.56(2)°$, $V = 1826.9$ Å^3, $Z = 2$, $D_c = 1.37$ g cm^{-3}, μ(Mo-Kα) = 7.26 cm^{-1}.

Compound (4). C$_{42}$H$_{34}$CuNO$_2$P$_2$, M = 710.23, orthorhombic, space group Pna2$_1$, $a = 18.777(3)$, $b = 13.233(2)$, $c = 13.892(2)$ Å, $V = 3451.8$ Å^3, $Z = 4$, $D_c = 1.37$ g cm^{-3}, μ(Mo-Kα) = 7.61 cm^{-1}. Intensities for both samples were collected on a CAD-4 diffractometer by the ω-scan technique in the 2ϑ range 3–50°, and corrected for Lorentz and polarization effects. The observations used in the solution and refinement of the structures were limited to independent reflections having $I \geqslant 3\sigma(I)$ [4686 for compound (2), 3626 for compound (4)]. The structures were solved by usual Patterson and Fourier methods and partially refined by full-matrix least-squares down to R = 0.041 and 0.053, respectively. Principal bond parameters are reported in the captions of Figs. 1 and 2. Full details of these structure determinations will be reported elsewhere.

Physical Measurements

The infrared spectra were recorded with a Beckman 4250 spectrophotometer on powdered samples spread on KBr plates. Molecular weight data were carried out on a Hewlett-Packard 302 B osmometer.

Results

Molecular Structures

Crystals of satisfactory quality have been obtained only by slow diffusion of hexane through methylene solutions of L$_2$Cu(3-py(CO$_2$)) and L$_2$Cu(2,3-py(CO$_2$)(COOH)). Perspective views of the molecules are shown in Figs. 1 and 2. The L$_2$Cu(3-py(CO$_2$)) consists of Cu atoms linked to two molecules of triphenylphosphine and two nicotinate anions, one of which is bonded through the pyridinic nitrogen atom and the other through the unidentate carboxylate group. In the same way the isonicotinate anion is coordinated in the Mg(isonic)$_2$(H$_2$O) complex [28]. But our copper complex, unlike the magnesium one, presents a polymeric molecular structure. In fact the isonicotinate anion bonded to a bis(triphenylphosphine)copper(I) cation through the pyridinic nitrogen atom is bonded to another cation through the unidentate carboxylate group. Analogously, the isonicotinate anion bonded to the first copper atom through the carboxylate group is bonded to another metal atom through the pyridinic nitrogen atom. The molecule of the compound L$_2$Cu(2,3-py(CO$_2$)(COOH)) consists of discrete units in which the copper atom is in a tetrahedral coordination, being bonded to two molecules of triphenylphosphine and to one quinolinic monoanion which

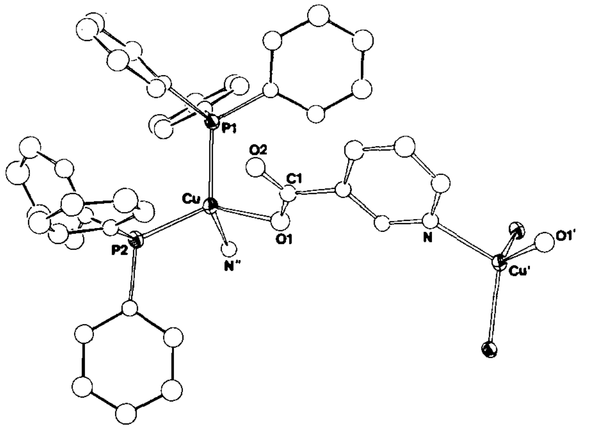


Fig. 1. Perspective view of $L_2Cu(3\text{-py}(CO_2))$ complex. Selected bond distances (Å) within the molecule are: Cu–P1 = 2.269(1); Cu–P2 = 2.258(1); Cu–N^{II} = 2.165(4); Cu–O1 = 2.135(3); C1–O1 = 1.241(5); C1–O2 = 1.237(5).

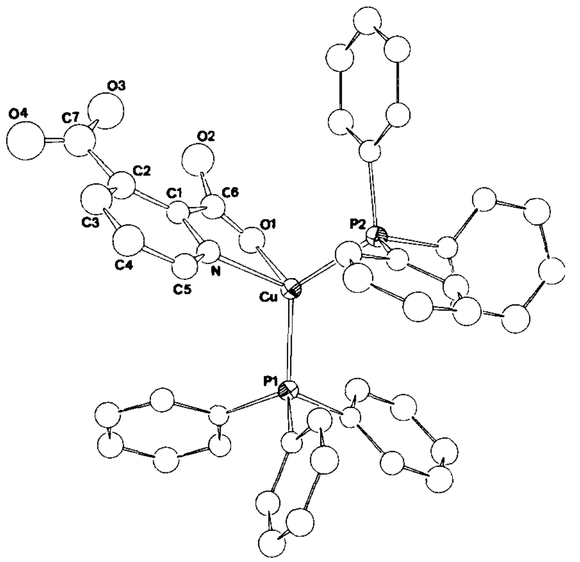


Fig. 2. Perspective view of $L_2Cu(2,3\text{-py}(CO_2)(COOH))$ complex. Selected bond distances (Å) within the molecule are: Cu–P1 = 2.237(1); Cu–P2 = 2.257(1); Cu–N = 2.109(2); Cu–O1 = 2.077(1); C1–N = 1.349(2); C1–C6 = 1.533(3); C6–O1 = 1.224(3); C6–O2 = 1.260(3); C7–O3 = 1.291(3); C7–O4 = 1.217(3).

is bonded through the pyridine nitrogen atom and the unidentate carboxylate group in an *ortho* position.

Infrared Spectra

The values of the $\nu_{as}(COOH)$, $\nu_s(COOH)$, $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ stretching vibrations of the complex studied and of the sodium salts of pyridine- and pyrazine-carboxylic acids are listed in Table II. It is known from the literature [21, 29, 30] that the $\nu_{as}(COOH)$ and $\nu_s(COOH)$ stretching vibrations of pyridine- and pyrazine-carboxylic acids absorb at about 1700 and 1350 cm^{-1} respectively, the difference between the two stretching values being about 350 cm^{-1}. To obtain IR spectra, since the use of mulls between alkali halide plates or of potassium halide disks could result in anion exchange [31], we have operated on powdered samples spread on KBr plates. From the inspection of Table II it appears that the $L_2Cu(3\text{-py}(CO_2))$ complex exhibits $\nu_{as}(CO_2)$ at 1615 cm^{-1} and the $\nu_s(CO_2)$ at 1392 cm^{-1}, with $\Delta\nu = 213$ cm^{-1}. This difference, being greater than that of the corresponding sodium salt, is in accordance with the assumption that the unidentate coordination of a carboxylic group removes the equivalence of the two oxygen atoms [32] and produces both an increase of $\nu_{as}(CO_2)$ and a decrease of $\nu_s(CO_2)$ with respect to the sodium salt. The infrared spectrum of $L_2Cu(2,3\text{-py}(CO_2)(COOH))$ shows both the stretching frequencies of 'free' carboxylic and carboxylate groups. This agrees with the structural data which show that only the *ortho* carboxylic group is bonded to the metal ion.

Discussion

Taking into account the two determined molecular structures, the analytical data and the infrared spectra, it may be pointed out that:

1) In all the complexes studied in this paper the copper atom has tetrahedral coordination.

2) The 2-pyridine- and 2-pyrazine-monocarboxylic acids form monomeric complexes with five membered chelate rings being coordinated to the metal ion through the nitrogen atom and the unidentate carboxylic group.

3) The pyridinedicarboxylic acids having one carboxylic group in an *ortho* position with respect to the nitrogen atom form monomeric complexes with five membered chelate rings, leaving the second carboxylic group uncoordinated.

4) The pyridinemono- and di-carboxylic acids without carboxylic groups in *ortho* position with respect to the nitrogen atom form polymeric complexes.

5) The pyrazinedicarboxylic acids owing to the *ortho* positions of their carboxylic groups with respect to two different nitrogen atoms form dimeric complexes.

6) The 2,6-pyridine- and 2,6-pyrazine-dicarboxylic acids having two carboxylic groups in *ortho* positions with respect to the same nitrogen atom form monomeric complexes with five membered chelate rings leaving one carboxylic group not coordinated.

In fact from the values of the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ stretching vibrations it results that compounds labelled 1 and 10 in Tables I and II present the same type of coordination, the monoanion being

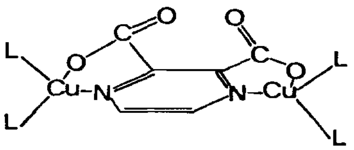
TABLE II. Infrared Carbon–Oxygen Stretching Frequencies (cm^{-1}).

Compound	N.	ν_{as}(COOH)	ν_s(COOH))	$\nu_{as}(CO_2)$	$\nu_s(CO_2)$	$\Delta\nu^a$
$L_2Cu(2\text{-}py(CO_2))$	1	–	–	1635vs	1352m	283
$L_2Cu(3\text{-}py(CO_2))$	2	–	–	1605vs	1392s	213
$L_2Cu(4\text{-}py(CO_2))$	3	–	–	1615s	1360s	255
$Na(2\text{-}py(CO_2))$		–	–	1605vs	1410vs	195
$Na(3\text{-}py(CO_2))$		–	–	1610vs	1410vs	200
$Na(4\text{-}py(CO_2))$		–	–	1590vs	1410vs	180
$L_2Cu(2,3\text{-}py(CO_2)(COOH))$	4	1700m	–	1625m	1362s	263
$L_2Cu(2,4\text{-}py(CO_2)(COOH))$	5	1705m	1340m,br	1610m	1385s	225
$L_2Cu(2,5\text{-}py(CO_2)(COOH))$	6	1705m	–	1620s	–	–
$L_2Cu(2,6\text{-}py(CO_2)(COOH))$	7	1700m	–	1602s	1360m	242
$L_2Cu(3,4\text{-}py(CO_2)(COOH))$	8	1705m,br	–	1600m	1355s	245
$L_2Cu(3,5\text{-}py(CO_2)(COOH))$	9	1715m	–	1650s	1375m	275
$Na_2(2,3\text{-}py(CO_2)_2)$		–	–	1640vs	1380m 1390m	255^b
$Na_2(2,4\text{-}py(CO_2)_2)$		–	–	1620vs,br	1387vs,br	233
$Na_2(2,5\text{-}py(CO_2)_2)$		–	–	1590vs	1405s	185
$Na_2(2,6\text{-}py(CO_2)_2)$		–	–	1610vs	1390vs	220
$Na_2(3,4\text{-}py(CO_2)_2)$		–	–	1615s	1425s	190
$Na_2(3,5\text{-}py(CO_2)_2)$		–	–	1615vs	1375vs	235
$L_2Cu(2\text{-}pyz(CO_2))$	10	–	–	1640vs	1350s	290
$Na(2\text{-}pyz(CO_2))$		–	–	1615vs	1420vs	195
$L_2Cu(2,3\text{-}pyz(CO_2)(COOH))$	11	1735s	1350s	1625s	1375m	250
$(L_2Cu)_2(2,3\text{-}pyz(CO_2)_2)$	12	–	–	1625vs	1350m	275
$Na(2,3\text{-}pyz(CO_2)(COOH))$		1715vs	1365vs	1620vs	1315vs	305
$Na_2(2,3\text{-}pyz(CO_2)_2)$		–	–	1635vs	–	–
$(L_2Cu)_2(2,5\text{-}pyz(CO_2)_2)$	13	–	–	1640s	1355m	285
$Na_2(2,5\text{-}pyz(CO_2)_2)$		–	–	1640vs	1392vs	248
$L_2Cu(2,6\text{-}pyz(CO_2)(COOH))$	14	1705m	–	1602m	1360m	242
$Na_2(2,6\text{-}pyz(CO_2)_2)$		–	–	1630vs	–	–

$^a\Delta\nu = \nu_{as}(CO_2) - \nu_s(CO_2)$. ^{b}Calculated using average values.

bonded to the metal through the nitrogen atom and one of the oxygen atoms of the carboxylate group. The infrared spectra of the compounds labelled 4, 5, 6, 7, 11, 14 show ν_{as}(COOH) at about 1700 cm^{-1} and $\nu_{as}(CO_2)$ at about 1600 cm^{-1}. Therefore complexes labelled 5, 6, 7, 11, 14 probably present the same structure as compound 4. Molecular structures of this type are reported in the literature for complexes of silver(II) [19, 20], zinc(II) and cobalt(II) [9, 21]. The compound $L_2Cu(4\text{-}py(CO_2))$ should present a polymeric molecular structure like that of the compound 2. Structures of these types are reported for complexes of cobalt(II), nickel(II), copper(II), and manganese(II) with isonicotinate anion as ligand [33].

The infrared spectra of compounds 8 and 9 present both the ν(COOH) and $\nu(CO_2)$ stretching vibrations and very probably they have polymeric molecular structures like that of compounds 2 and 3. The complexes labelled 12 and 13 whose infrared spectra do not show the ν(COOH) stretching vibrations, have probably molecular structures of the type presented here:



Molecular weight determinations (see Table I) agree with this hypothesis. It is worth noting that the dimeric molecular structures were found only for the complexes of 2,3- and 2,5-pyrazinedicarboxylic acids which have two carboxylic groups in equivalent *ortho* position with respect to the two nitrogen atoms of the heterocyclic ring. Even if the 2,6-pyridine- and 2,6-pyrazine-dicarboxylic acids present two equivalent carboxylic groups, they do not form dimeric complexes because they have only one nitrogen atom available for obtaining the five membered chelate ring that seems to represent a very stable structure for the complexes studied here. The carboxylic acid groups present in compounds 4–9 do not react with another molecule of L_2-$CuBH_4$. The reason for this behaviour in our opin-

TABLE III. pK_a Values for Pyridine- and Pyrazine-carboxylic Acids.[a]

Acid	pK_{a_1}	pK_{a_2}	Ref.
2-py(COOH)	4.66	–	b
3-py(COOH)	4.30	–	c
4-py(COOH)	4.51	–	c
2,3-py$(COOH)_2$	2.36	4.72	d
2,4-py$(COOH)_2$	2.23	4.79	d
2,5-py$(COOH)_2$	2.17	4.58	e
2,6-py$(COOH)_2$	2.17	4.96	f
3,4-py$(COOH)_2$	2.70	5.00	g
3,5-py$(COOH)_2$	2.08	4.31	h
2-pyz(COOH)	2.92	–	i
2,3-pyz$(COOH)_2$	0.80	2.84	l
2,5-pyz$(COOH)_2$	0.60	2.54	this work
2,6-pyz$(COOH)_2$	0.90	3.24	this work

[a]When different values are reported we have considered those obtained by potentiometric method. [b]L. Campanella, E. Chiacchierini, G. De Angelis and V. Petrone, *Ann. Chimica, 67*, 385 (1977). [c]E. Chiacchierini, G. D'Ascenzo, A. Marino, G. De Angelis, *Ann. Chimica, 67*, 547 (1977). [d]M. Yasuda, K. Yamasaki, *Naturwiss., 45*, 84 (1958). [e]A. Napoli, *Talanta, 15*, 189 (1968). [f]V. D. Canic, *Glas. Hem. Drus., Beograd, 20*, 29 (1955). [g]C. Tissier, M. Agoutin, *Electroanal. Chem. Iterfac. Electrochem., 47*, 499 (1973). [h]G. D'Ascenzo, E. Chiacchierini, A. Marino, A. Magri, G. De Angelis, *Gazz. Chim. Ital., 104*, 607 (1974). [i]J. W. Sansville and P. E. Spoerri, *J. Am. Chem. Soc., 63*, 3153 (1941). [l]A. L. Magri, F. Balestieri, E. Chiacchierini, A. D. Magri and A. Panzanelli, *Ann. Chimica, 68*, 585 (1978).

ion is not the pKa_2 values of the corresponding acids. In fact these values (see Table III) are comparable to those of pK_{a_1} of pyridinemonocarboxylic acids. Probably the molecules of pyridinedicarboxylic acids after reacting with one molecule of L_2CuBH_4 and giving the five membered chelate rings of compound 4–9, do not react further because they have carboxylic acid groups and not nitrogen atoms available for coordination. This is in apparent disagreement with the behaviour of 4-pyridine-, 3-pyridine-, 3,4-pyridine- and 3,5-pyridine-carboxylic acids that give polymeric molecular structure, but these acids never are able to form five membered chelate rings. It is of interest to notice also that the pyridine- and pyrazine-carboxylic acids are never bonded to bis(triphenylphosphine)copper(I) cation via a symmetrical bidentate carboxylate group.

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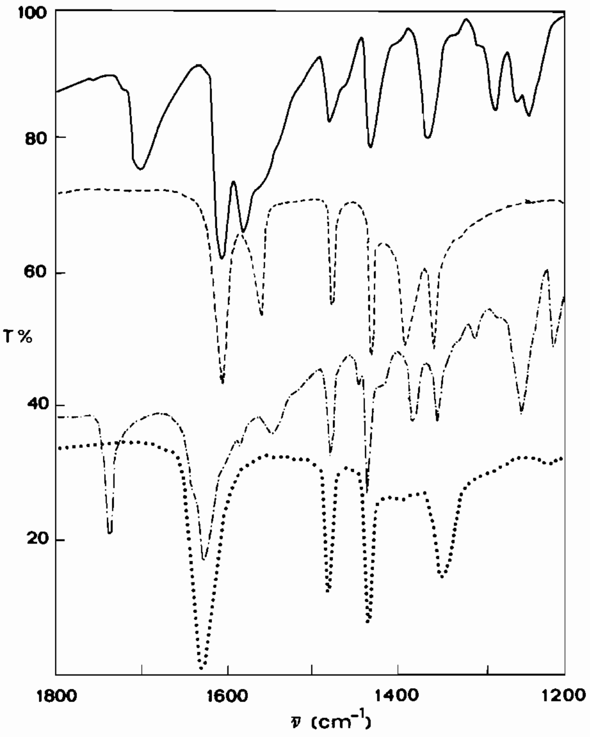

Fig. 3. Infrared spectra of powdered sample of $L_2Cu(2,6\text{-}py(CO_2)(COOH))$ (——); $L_2Cu(3\text{-}py(CO_2))$ (- - -); $L_2Cu(2,3\text{-}pyz(CO_2)(COOH))$ (– · –); $(L_2Cu)_2(2,3\text{-}pyz(CO_2)_2)$ (. . . .) spread on KBr plates.

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