

The Crystal and Molecular Structure of Barium Diaquadi(*o*-phthalato)cuprate(II) Dihydrate. An Example of the Chelating Behaviour of the *o*-Phthalate Anion

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(Received 20 July 1977; accepted 14 September 1977)

The crystal structure of barium diaquadi(*o*-phthalato)cuprate(II) dihydrate has been determined from diffractometer data by Patterson and Fourier methods and refined by block-diagonal least squares to $R = 0.032$ for 1749 observed reflections. Unit-cell constants are: $a = 9.155$ (9), $b = 7.831$ (8), $c = 13.498$ (14) Å, $\beta = 95.1$ (1)°. The space group is $P2_1$ with $Z = 2$. In the structure, discrete $[\text{Cu}(\text{H}_2\text{O})_2(\text{C}_8\text{H}_4\text{O}_4)_2]^{2-}$ complex anions are present, containing two non-equivalent *o*-phthalate anions: one acting as a monodentate ligand, the other as a bidentate chelating ligand. The Cu complexes are held together by interactions with Ba^{2+} ions and by hydrogen bonds with water molecules. The coordination polyhedron of Cu is a square pyramid whose base is formed by one water molecule [$\text{Cu}-\text{O}_w = 1.971$ (10) Å], one O atom [$\text{Cu}-\text{O} = 1.946$ (8) Å] from the monodentate *o*-phthalate ligand and two O atoms [$\text{Cu}-\text{O} = 1.907$ (7), 1.972 (9) Å] from the chelating *o*-phthalate ligand. Another water molecule is at the apex of the pyramid [$\text{Cu}-\text{O}_w = 2.289$ (9) Å]. Ba^{2+} cations are surrounded by nine O atoms (three from the water molecules): the coordination polyhedron is a distorted trigonal prism with lateral centred faces. The Ba–O bond distances are in the range 2.670–3.055 Å.

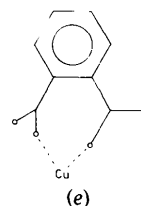
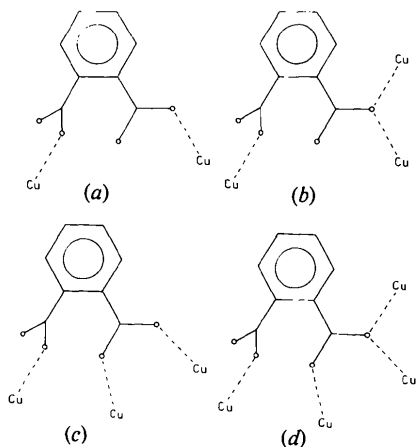
Introduction

Systematic studies of the crystal structures of Cu^{II} *o*-phthalate complexes showed that the *o*-phthalate (pht) ligand behaves in different ways, always acting as a bridging ligand: (i) when coordinating to metals through two O atoms, as shown in schemes (a) and (b), polymeric chains are formed as found in $\text{Li}_2\text{Cu}^{\text{II}}\text{pht}_2 \cdot 4\text{H}_2\text{O}$ and $\text{RbCu}^{\text{II}}\text{pht}_2 \cdot 2\text{H}_2\text{O}$ (Cingi, Lanfredi, Tiripicchio & Camellini, 1977), $\text{K}_2\text{Cu}^{\text{II}}\text{pht}_2 \cdot 2\text{H}_2\text{O}$ (Cingi, Lanfredi, Tiripicchio & Camellini, 1978*b*), and in $\text{Cu}^{\text{II}}(\text{NH}_3)_2\text{pht}$ (Cingi, Guastini, Musatti & Nardelli,

1970), (ii) when coordinating to metals through three O atoms, as shown in schemes (c) and (d), the chains are joined in layers as found in $\text{Cu}^{\text{II}}\text{pht} \cdot 2\text{H}_2\text{O}$ (Cingi, Lanfredi, Tiripicchio & Camellini, 1978*a*) and $\text{Cu}^{\text{II}}\text{pht} \cdot \text{H}_2\text{O}$ (Prout, Carruthers & Rossotti, 1971).

Water molecules can participate in the coordination to Cu when there are no metal cations in the structure showing a stronger tendency to interact with water.

The title compound is the first example of a metal–pht complex containing bidentate chelating pht [scheme (e)] in addition to monodentate pht. Its structure consists of discrete $[\text{Cu}(\text{OH}_2)_2\text{pht}_2]^{2-}$ anions held together in the crystal by interactions with Ba^{2+} and hydrogen bonds.



Experimental

Light-blue crystals of the compound have been grown from an aqueous solution prepared by dissolving copper(II) carbonate hydroxide and barium carbonate in a warm solution of phthalic acid.

Crystal data

$C_{16}H_{16}BaCuO_{12}$, $M_r = 601.2$, monoclinic, $a = 9.155(9)$, $b = 7.831(8)$, $c = 13.498(14)$ Å, $\beta = 95.1(1)^\circ$, $V = 964(2)$ Å³, $D_c = 2.07$ g cm⁻³, $Z = 2$, $F(000) = 586$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 31.99$ cm⁻¹. Space group $P2_1$ from systematic absences and from the structure determination. Unit-cell parameters were determined from rotation and Weissenberg photographs and refined from diffractometer data.

Intensity data

Intensity data were collected on a Siemens AED single-crystal diffractometer, with Zr-filtered Mo $K\alpha$ radiation and the $\omega-2\theta$ scan technique. A prismatic crystal of dimensions ca $0.16 \times 0.05 \times 0.39$ mm was aligned with its [001] axis along the ϕ axis of the diffractometer and all reflections with $3 < \theta < 25^\circ$ were measured. Of 1858 measured independent reflections, 1749 having $I > 2\sigma(I)$ were used in the analysis. Corrections for Lorentz and polarization factors were made in the usual way, but no correction was applied for absorption effects. The first absolute scaling and the first overall isotropic temperature factor were obtained by Wilson's method.

Structure determination and refinement

The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares, at first with isotropic, then with anisotropic thermal parameters. Attempts at locating all the H atoms in a final ΔF map were unsuccessful. Unit weights were used in all stages of the refinement by analysing the variations of $|\Delta F|$ as a function of $|F|$. The final R index was 0.032 (observed reflections only). The atomic scattering factors for non-hydrogen atoms were taken from Cromer & Mann (1968). Final atomic coordinates are in Table 1.*

All calculations were carried out on the CYBER 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna), using the programs written by Immirzi (1967).

Discussion

The crystal structure (Fig. 1) consists of discrete diaquadi(*o*-phthalato)cuprate(II) anions, Ba^{2+} cations

* Lists of structure factors and anisotropic thermal parameters are available from the authors and have also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33017 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) with e.s.d.'s

	x	y	z
Ba	59 (1)	5219 (1)	574 (1)
Cu	3968 (1)	2494 (2)	1721 (1)
O _w (1)	4951 (7)	344 (13)	2148 (5)
O _w (2)	2107 (7)	7805 (10)	95 (5)
O _w (3)	563 (9)	5809 (13)	2800 (6)
O _w (4)	3401 (10)	1645 (11)	110 (6)
O(11)	3264 (8)	7466 (10)	1998 (5)
O(21)	3162 (7)	4734 (8)	1567 (5)
O(31)	5871 (7)	3415 (10)	1393 (5)
O(41)	7917 (7)	4771 (11)	1903 (5)
O(12)	-2857 (8)	-829 (12)	1219 (6)
O(22)	-546 (7)	-1603 (10)	1127 (5)
O(32)	480 (7)	1921 (9)	1249 (5)
O(42)	2355 (7)	1591 (10)	2409 (5)
C(11)	4676 (9)	5564 (12)	3035 (7)
C(21)	6048 (10)	4765 (13)	2996 (7)
C(31)	6933 (11)	4508 (16)	3881 (8)
C(41)	6473 (11)	4989 (20)	4784 (7)
C(51)	5131 (13)	5819 (17)	4819 (8)
C(61)	4244 (11)	6104 (17)	3935 (8)
C(71)	3656 (10)	5968 (13)	2124 (7)
C(81)	6657 (10)	4282 (13)	2039 (8)
C(12)	-1152 (9)	-233 (12)	2615 (6)
C(22)	31 (10)	827 (13)	2847 (7)
C(32)	345 (11)	1389 (16)	3821 (8)
C(42)	-503 (12)	832 (17)	4572 (8)
C(52)	-1671 (12)	-290 (16)	4328 (8)
C(62)	-1997 (10)	-813 (15)	3356 (8)
C(72)	-1532 (10)	-933 (13)	1584 (7)
C(82)	1010 (10)	1492 (12)	2103 (7)

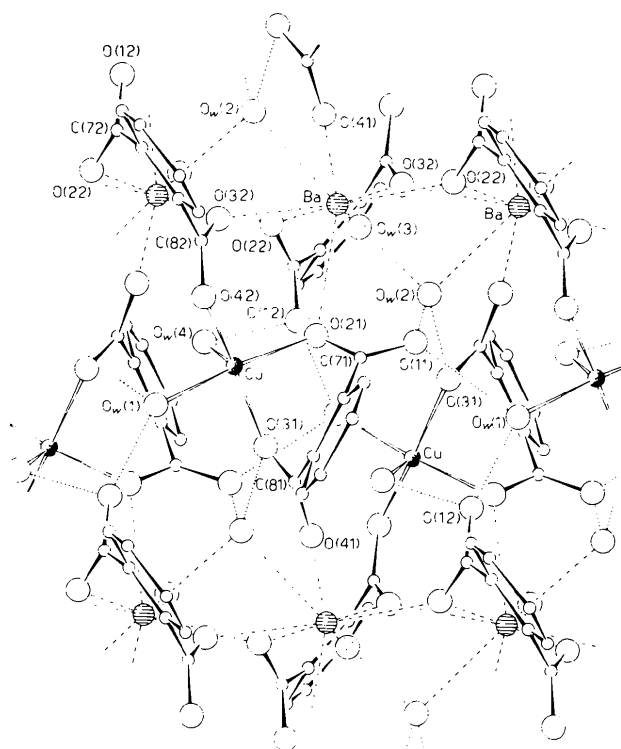


Fig. 1. Projection of the structure along [001].

Table 2. Bond distances (Å) and angles (°) in the barium compound

(a) In the coordination polyhedron

Cu—O _w (1)	1.971 (10)	Cu—O(31)	1.972 (9)	Cu—O _w (4)	2.289 (9)
Cu—O(21)	1.907 (7)	Cu—O(42)	1.946 (8)		
O _w (1)—Cu—O(42)	84.0 (3)	O(31)—Cu—O(42)	164.4 (3)	O _w (4)—Cu—O(21)	96.4 (3)
O _w (1)—Cu—O(31)	89.3 (3)	O _w (1)—Cu—O(21)	168.5 (3)	O _w (4)—Cu—O(31)	91.3 (3)
O(21)—Cu—O(42)	94.8 (3)	O _w (4)—Cu—O _w (1)	95.1 (3)	O _w (4)—Cu—O(42)	103.3 (3)
O(21)—Cu—O(31)	88.9 (3)				

(b) In the phthalate anions

C(11)—C(21)	1.408 (13)	C(51)—C(61)	1.400 (16)	C(71)—O(21)	1.282 (12)
C(21)—C(31)	1.397 (14)	C(11)—C(61)	1.377 (14)	C(21)—C(81)	1.500 (14)
C(31)—C(41)	1.377 (15)	C(11)—C(71)	1.510 (13)	C(81)—O(41)	1.244 (12)
C(41)—C(51)	1.394 (17)	C(71)—O(11)	1.234 (13)	C(81)—O(31)	1.276 (12)
C(61)—C(11)—C(21)	119.8 (9)	C(21)—C(31)—C(41)	121.2 (9)	C(11)—C(71)—O(21)	118.7 (9)
C(61)—C(11)—C(71)	116.7 (8)	C(31)—C(41)—C(51)	119.8 (9)	O(11)—C(71)—O(21)	123.6 (9)
C(21)—C(11)—C(71)	123.5 (8)	C(41)—C(51)—C(61)	119.4 (1.0)	C(21)—C(81)—O(41)	118.0 (9)
C(11)—C(21)—C(31)	118.9 (9)	C(11)—C(61)—C(51)	120.8 (1.0)	C(21)—C(81)—O(31)	119.5 (8)
C(11)—C(21)—C(81)	123.0 (8)	C(11)—C(71)—O(11)	117.6 (9)	O(41)—C(81)—O(31)	122.5 (9)
C(31)—C(21)—C(81)	117.9 (9)				
C(12)—C(22)	1.378 (13)	C(52)—C(62)	1.382 (15)	C(72)—O(22)	1.253 (12)
C(22)—C(32)	1.392 (15)	C(12)—C(62)	1.394 (13)	C(22)—C(82)	1.498 (13)
C(32)—C(42)	1.400 (16)	C(12)—C(72)	1.507 (13)	C(82)—O(42)	1.266 (12)
C(42)—C(52)	1.401 (17)	C(72)—O(12)	1.271 (12)	C(82)—O(32)	1.256 (12)
C(62)—C(12)—C(22)	120.6 (8)	C(22)—C(32)—C(42)	120.3 (1.0)	C(12)—C(72)—O(22)	119.3 (8)
C(62)—C(12)—C(72)	116.5 (8)	C(32)—C(42)—C(52)	119.1 (1.0)	O(12)—C(72)—O(22)	122.7 (9)
C(22)—C(12)—C(72)	122.8 (8)	C(42)—C(52)—C(62)	120.4 (1.0)	C(22)—C(82)—O(42)	115.2 (8)
C(12)—C(22)—C(32)	119.8 (9)	C(12)—C(62)—C(52)	119.9 (9)	C(22)—C(82)—O(32)	120.2 (8)
C(12)—C(22)—C(82)	124.2 (8)	C(12)—C(72)—O(12)	118.0 (8)	O(42)—C(82)—O(32)	124.6 (9)
C(32)—C(22)—C(82)	116.0 (9)				

(c) Around the barium cation

Ba—O _w (2)	2.872 (8)	Ba—O(32)	2.754 (8)	Ba—O _w (2 ⁱⁱⁱ)	2.829 (8)
Ba—O _w (3)	3.034 (9)	Ba—O(41 ⁱ)	2.795 (9)	Ba—O(22 ^{iv})	2.773 (7)
Ba—O(21)	3.055 (10)	Ba—O(22 ⁱⁱ)	2.670 (8)	Ba—O(32 ^{iv})	2.803 (7)

(d) Probable hydrogen bonds

O _w (1)⋯O(11 ^v)	2.730 (12)	O _w (2)⋯O(11)	2.703 (10)	O _w (4)⋯O(12 ^{iv})	2.687 (12)
O _w (1)⋯O(12 ^{iv})	2.625 (12)	O _w (2)⋯O(31 ^{vii})	2.890 (11)		

Asymmetric units

(i)	−1 + x, y, z	(iv)	−x, $\frac{1}{2}$ + y, −z	(vi)	1 + x, y, z
(ii)	x, 1 + y, z	(v)	x, −1 + y, z	(vii)	1 − x, $\frac{1}{2}$ + y, −z
(iii)	−x, − $\frac{1}{2}$ + y, −z				

and water molecules linked by hydrogen bonds. Bond distances and angles are given in Table 2. The coordination polyhedron of Cu (Fig. 2) is a square pyramid whose base is formed by the water molecule O_w(1), by the oxygen atom O(42) from a pht anion behaving as a monodentate ligand and by two oxygen atoms, O(21) and O(31), from a pht anion acting as a chelating bidentate ligand. The Cu—O_w(1) distance and the three Cu—O(pht) bond lengths in the basal plane correspond well to the values usually found in similar configurations. The four atoms forming the base of the pyramid show a slight tetrahedral distortion from the

mean plane through them and the Cu atom is displaced from this plane towards the apex of the pyramid by 0.22 Å (Table 3). The apex of the pyramid is occupied by the O_w(4) water molecule at a distance (2.289 Å) longer than those in the basal plane. The sixth octahedral site of the coordination polyhedron is completely free.

The conformations of the two independent pht anions are significantly different. In the monodentate ligand the carboxylate groups are rotated around their C—C bonds on the same side with respect to the benzene ring [the angles which the planes through C(12)C(72)-

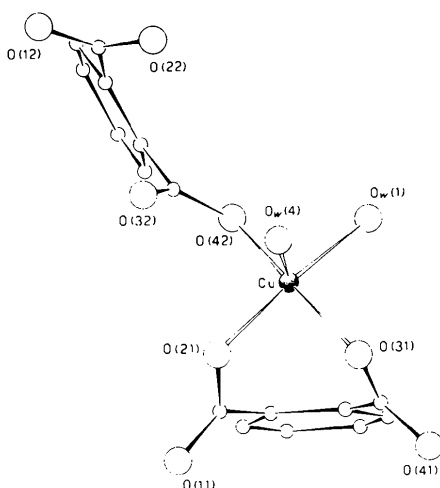


Fig. 2. Coordination around the Cu atom.

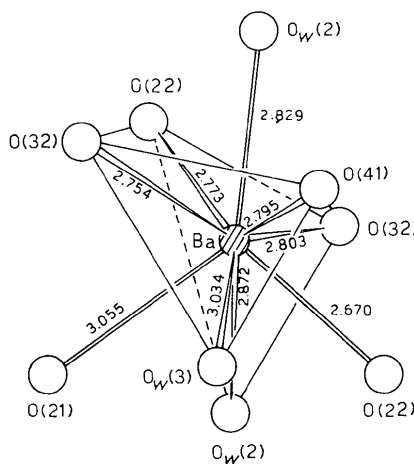


Fig. 3. Coordination around the Ba atom.

O(12)O(22) and C(22)C(82)O(32)O(42) form with the benzene plane are 51 and 39°) as in all the compounds where pht acts as a bridging ligand, while in the chelating pht anion they are rotated to opposite sides [57° for C(11)C(71)O(11)O(21) and -50° for C(21)C(81)O(31)O(41)]. This different orientation of the carboxylate groups with respect to the benzene ring in the bidentate pht makes it possible for O(21) and O(31) to chelate the Cu atom. The O(21)⋯O(31) distance is shorter [2.716 (12) Å] than O(22)⋯O(32) in the monodentate pht [2.915 (11) Å]. The conformation of the seven-membered coordination ring is boat, as shown by data collected in Table 4.

Table 3. Equations of least-squares planes in the form: $AX + BY + CZ = D$, where X , Y and Z are coordinates in Å referred to orthogonal axes and are obtained from fractional ones by applying the matrix: $//a,0,c \cos \beta/0,b,0/0,0,c \sin \beta//$

Deviations (Å) of relevant atoms from the planes are in square brackets.

	A	B	C	D
Plane 1: O _w (1), O(21), O(31), O(42)	-0.2386	-0.3189	-0.9173	-3.7856
[O _w (1) 0.031 (7), O(21) 0.025 (7), O(31) -0.028 (7), O(42) -0.028 (7), Cu 0.223 (1), O _w (4) 2.499 (8)]				
Plane 2: C(11), C(21), C(31), C(41), C(51), C(61)	0.4457	0.8888	-0.1068	5.1915
[C(11) -0.009 (9), C(21) 0.003 (10), C(31) 0.011 (12), C(41) -0.020 (15), C(51) 0.003 (13), C(61) 0.013 (13), C(71) 0.036 (10), C(81) 0.104 (10), O(11) 0.943 (8), O(21) -0.915 (6), O(31) -0.693 (8), O(41) 0.985 (8)]				
Plane 3: C(11), C(71), O(11), O(21)	0.8242	0.1323	-0.5506	1.5685
[C(11) -0.011 (9), C(71) 0.026 (9), O(11) -0.009 (7), O(21) -0.007 (7)]				
Plane 4: C(21), C(81), O(31), O(41)	-0.3361	0.8438	-0.4183	-0.2785
[C(21) 0.002 (10), C(81) -0.005 (10), O(31) 0.001 (8), O(41) 0.002 (8)]				
Plane 5: C(12), C(22), C(32), C(42), C(52), C(62)	-0.5936	0.7867	-0.1694	0.0619
[C(12) 0.011 (9), C(22) -0.015 (10), C(32) 0.008 (12), C(42) 0.008 (13), C(52) -0.010 (12), C(62) -0.003 (11), C(72) -0.052 (10), C(82) -0.021 (9), O(12) 0.789 (9), O(22) -0.929 (7), O(32) 0.665 (7), O(42) -0.739 (7)]				
Plane 6: C(12), C(72), O(12), O(22)	0.2310	0.8901	-0.3928	-1.8583
[C(12) -0.001 (9), C(72) 0.004 (10), O(12) -0.001 (9), O(22) -0.001 (8)]				
Plane 7: C(22), C(82), O(32), O(42)	0.1681	-0.9309	-0.3243	-1.8954
[C(22) -0.002 (10), C(82) 0.004 (9), O(32) -0.001 (7), O(42) -0.001 (8)]				

The coordination polyhedron of Ba can be described as a distorted trigonal prism (Fig. 3) with lateral centred faces; it is similar to that found in the Ba salt of *N,N'*-dimethylisonitrosomalonamide (Raston & White, 1976). The six corners of the prism are occupied by two water molecules, O_w(2) and O_w(3), and by four O atoms belonging to three pht anions. One face is centred by one water molecule, the others by two O atoms, one belonging to the chelating ligand and the other to the monodentate ligand. Packing is determined by interactions between the Cu complex anions and the Ba ions and by hydrogen bonds (Table 2) involving water molecules and O atoms from the two different phthalate anions.

Table 4. *Conformation of the seven-membered coordination ring*

The authors thank Professor Mario Nardelli for helpful discussion.

Equation of least-squares plane through O(21)C(71)C(81)O(31) (see Table 3)

$$0.2095X + 0.6097Y - 0.7644Z = 1.2489$$

Displacements (Å) of relevant atoms from this plane

O(21) -0.032 (7), C(71) 0.066 (10), C(81) -0.075 (11), O(31) 0.041 (7), Cu -1.109 (1), C(11) -0.891 (9), C(21) -0.968 (10)

Torsion angles (°)

Cu-O(21)-C(71)-C(11)	12.0
O(21)-C(71)-C(11)-C(21)	-61.2
C(71)-C(11)-C(21)-C(81)	-2.0
C(11)-C(21)-C(81)-O(31)	51.2
C(21)-C(81)-O(31)-Cu	7.1
C(81)-O(31)-Cu-O(21)	-75.6
O(31)-Cu-O(21)-C(71)	61.7

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Acta Cryst. (1978). **B34**, 778-781

Structure Cristalline du Complexe Dinitrato Bis(méthylthio-2 méthyl-3 imidazole) Nickel(II)

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(Reçu le 17 juin 1977, accepté le 14 septembre 1977)

Dinitratobis(2-méthylthio-3-méthylimidazole)nickel(II) crystallizes in space group $P\bar{1}$, with $a = 12.614$ (5), $b = 9.145$ (5), $c = 8.533$ (5) Å, $\alpha = 114.5$ (1), $\beta = 86.7$ (1), $\gamma = 102.8$ (1)°. The cell contains two formula units. The structure determination, carried out with an automatic program producing multiple solutions (*MULTAN*), gave a final *R* factor of 0.07 and confirms the bidentate bonding of the NO₃ groups, as deduced from earlier infrared studies, and also shows their symmetric character, C_{2v} , (the metal atom being in a 'quasi-tetrahedral' environment). Furthermore, it shows the particular character of the Ni^{II} complex. Thus, depending on the nature of the ligand (particularly when replacing NO₃ groups by halogens, and the heterocycles by their imidazole isomers), Ni^{II} complexes show different symmetries involving four or six bonds, while homologous complexes of both Co^{II} and Zn^{II} keep the same tetrahedral symmetry.

Introduction

L'étude des complexes du nickel est intéressante par suite des nombreuses possibilités de leur stéréochimie. Ainsi, avec les dérivés imidazoliques ils peuvent

présenter une symétrie tétraédrique, octaédrique ou plan carré (Ellbeck, Holmes, Taylor & Underhill, 1968a,b; Taylor & Underhill, 1968; Petillon & Guerschais, 1971). La complexation par un halogénure, du méthylthio-2 méthyl-3 imidazole (*L*) et de la