Synthesis and Structural, Thermal and Electrical Properties of Piperazinium Iodocuprates(I)†

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The iodocuprate(I) systems $[H_2pipz]_2[Cu_2I_6]\cdot H_2O$ **1** and $[H_2pipz][Cu_2I_4]$ **2** (L = pipz = piperazine) have been prepared and their structural, thermal and electrical properties investigated. Compound **1** is monoclinic, space group $P2_1/n$, $a = 8.609(3)$, $b = 20.072(4)$, $c = 13.763(4)$ Å, $\beta = 101.3(1)^\circ$, $Z = 4$, $R = 0.050$. The crystal structure consists of organic cations, unco-ordinated water molecules and dimeric $[Cu_2I_6]^-$ anions composed of two CuI_4 tetrahedra sharing a common edge. Hydrogen bonds between organic counter cations and water molecules are present. Compound **2** is triclinic, space group $P\bar{1}$, $a = 7.559(3)$, $b = 7.465(3)$, $c = 6.826(3)$ Å, $\alpha = 68.1(1)$, $\beta = 69.1(1)$, $\gamma = 89.4(1)^\circ$, $Z = 1$, $R = 0.050$. The crystal structure consists of organic dications and infinite chains of $[CuI_2]^-$ units forming a one-dimensional polymer running along the [001] axis. The chains are composed of edge-sharing CuI_4 tetrahedra. Hydrogen-bond interactions between organic counter cations and inorganic chains are present and contribute to the crystal packing. Differential scanning calorimetry measurements did not show the presence of any structural phase transitions. Electrical measurements revealed an essentially ionic mechanism of conduction, especially at high temperature, protons involved in the hydrogen bonds being the charge carriers.

Copper(I) exhibits a wide variety in co-ordination numbers ranging from two to four, and in its structural chemistry, as is well illustrated by its halide complexes. In particular, two-co-ordinated species are found in the form of discrete monomers, usually linear, and of X–Cu–X units as part of infinite chains; the three-co-ordinated species are discrete, or vertex- or edge-sharing triangles; the four-co-ordinate ones, undoubtedly the most common in the solid state, present many structural motifs, among others dinuclear $[Cu_2X_6]^{4-}$ and polymeric with stoichiometry $[CuX_2]^-$.[1] No mononuclear $[CuX_4]^{3-}$ anions have been found to exist in the solid state.[2] The halogenocuprates(I) also exhibit very peculiar properties, of which the photoluminescent,[3] photochemical[4] and electrical[5] are the most interesting.

We are particularly interested in the structural chemistry of the d^{10} metal-ion compounds, and have previously investigated the synthesis and properties of polymeric one- and two-dimensional chlorocadmate systems. Our aim was to understand how the symmetry and thermal and electrical behaviour of these systems correlated with the factors controlling the stereochemistry and the polymeric nature of the metal(II) ion.[6–8] Based on their ability to form polymeric species and on their peculiar properties, copper(I) halides can be considered very suitable candidates for investigating the above correlations. In this paper we present the results of a study on the synthesis and structural and thermal characterization of two iodocuprates(I) of the piperazinium dication (H_2pipz^{2+}), of formula $[H_2pipz]_2[Cu_2I_6]\cdot H_2O$ **1** and $[H_2pipz][Cu_2I_4]$ **2**. Electrical characterization was performed for compound **2** and the results compared with those previously obtained for one-dimensional polymeric chloro-cadmate(II) and -cuprate(II) systems.[6,7,9,10]

Experimental

Synthesis of the Compounds.—Compound **1** was prepared by adding a solution of piperazine (6 mmol) in HI (57%, 20 cm^3) to a solution of CuI (6 mmol) in the same solvent (20 cm^3) (Found: C, 8.85; H, 2.45; N, 5.15. Calc. for $C_8H_{26}Cu_2I_6N_4O$: C, 8.85; H, 2.40; N, 5.15%). Compound **2** was prepared adding a solution of piperazine (6 mmol) in HI (57%, 20 cm^3) to a solution of CuI (30 mmol) in the same solvent (50 cm^3) (Found: C, 6.60; H, 1.70; N, 3.85. Calc. for $C_4H_{12}Cu_2I_4N_2$: C, 6.65; H, 1.65; N, 3.85%). By slow evaporation of the solutions, white crystals, suitable for X-ray single-crystal diffraction, precipitated.

Physical Measurements.—Thermogravimetric and differential scanning calorimetric analyses were performed with a Mettler TG 50 thermobalance and a Perkin Elmer DSC-2C calorimeter equipped with an IBM PS 2/30 automatic data acquisition and processing system and sealed aluminium pans. Far-infrared spectra were recorded with an FT-IR Bruker 113-V spectrophotometer in polyethylene pellets in the range 500–60 cm^{-1}. Carbon, hydrogen and nitrogen were analysed with a Carlo-Erba model 1106 elemental analyser.

Crystal Structure Determination.—In Table 1 are reported the crystal data and parameters relative to data collection. The structure amplitudes were obtained after the usual Lorentz and polarization reduction and then converted on the absolute scale by the least-squares method. For compound **1** an empirical absorption correction was applied according to the method of Walker and Stuart,[11] while for **2** an empirical correction[12] by the ψ-scan method was applied. Both the compounds were unaffected by X-ray radiation. The structures were solved by the heavy-atom method and refined by full-matrix least-squares cycles with anisotropic thermal refinement for non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions in the final structure-factor calculation. In compound **1** the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Experimental data for crystallographic analysis *

Compound	1	2
Formula	$C_8H_{26}Cu_2I_6N_4O$	$C_4H_{12}Cu_2I_4N_2$
M	1082.84	722.86
Crystal symmetry	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	8.609(3)	7.559(3)
b/Å	20.072(4)	7.465(3)
c/Å	13.763(4)	6.826(3)
α/°	90	68.1(1)
β/°	101.3(1)	69.1(1)
γ/°	90	89.4(1)
U/A^3	2332(1)	330.3(5)
Z	4	1
D_c/g cm^{-3}	3.08	3.63
D_m/g cm^{-3} (by flotation)	3.00	3.68
F(000)	1944	320
Crystal size/mm	0.4 × 0.3 × 0.4	0.8 × 0.6 × 0.4
Diffractometer	Siemens	Philips
μ(Mo-Kα)/cm^{-1}	97.7	125.25
Scan speed/° min^{-1}	2.4	3
θ range/°	3–25	3–27
h, k, l range	−10 to 9, 0–23 0–16	−8 to 9, −8 to 9, 0–8
Standard reflections	4 1 4	−3 2 3
Scan mode	θ–2θ	ω–2θ
Measured reflections	2312	1353
No. of reflections used [$I > 2\sigma(I)$]	2225	1256
Minimum, maximum in final $\Delta\rho$/e Å^{-3}	−1.42, 1.43	−1.58, 2.96
Parameters	286	55
R	0.050	0.050
R'	0.057	0.056
K,g in $w = K/[\sigma^2(F_o) + gF_o^2]$	1.00, 0.013 789	1.00, 0.005 91

* Details in common: 293 K; scan width 1.20°; Mo-Kα radiation (λ = 0.7107 Å).

Table 2 Fractional atomic coordinates (×10^4) for non-hydrogen atoms of compound **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c
Cu(1)	3063(4)	3348(2)	1587(2)
Cu(2)	1968(4)	4085(2)	3020(2)
I(1)	359(2)	2982(1)	2137(1)
I(2)	4667(2)	4440(1)	2475(1)
I(3)	4993(2)	2338(1)	2057(1)
I(4)	2533(2)	3729(1)	−266(1)
I(5)	−153(2)	5019(1)	2513(1)
I(6)	2556(2)	3788(1)	4913(1)
N(1)	6822(19)	3661(9)	593(14)
N(2)	8152(22)	3844(11)	−1142(15)
N(3)	3284(24)	1124(10)	−988(16)
N(4)	1731(22)	1461(9)	602(14)
C(1)	6834(26)	4338(11)	116(17)
C(2)	8240(27)	4386(13)	−358(19)
C(3)	8177(26)	3155(11)	−654(17)
C(4)	6733(24)	3105(12)	−135(18)
C(5)	3399(28)	675(11)	−96(19)
C(6)	1964(27)	724(14)	310(21)
C(7)	1552(23)	1901(11)	−301(17)
C(8)	3062(27)	1823(12)	−703(16)
O	4730(22)	6223(9)	2557(13)

Table 3 Fractional atomic coordinates (×10^4) for non-hydrogen atoms of compound **2** with e.s.d.s in parentheses

Atom	X/a	Y/b	Z/c
Cu	−31(2)	4 945(2)	2 523(2)
I(1)	1 154(1)	2 466(1)	536(1)
I(2)	−2 683(1)	3 440(1)	6 735(1)
N(1)	−3 724(11)	253(11)	12 715(12)
C(1)	−4 862(12)	1 825(12)	13 090(13)
C(2)	−3 315(14)	−941(14)	14 737(16)

hydrogens of the water molecules were not calculated. A few reflections, lower than 20, which may have been affected by errors, due to the irregular shape of the crystals, were excluded in the last refinement. Atomic coordinates are reported in Tables 2 and 3. The final R index was 0.050 for both compounds **1** and **2**. Atomic scattering factors corrected for anomalous dispersion were taken from ref. 13. Calculations were performed on the Gould 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. of the University of Parma, with SHELX 76,[14] PARST[15] and ORTEP[16] programs.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Electrical Measurements.—Fine powders, obtained by grinding crystals of compound **2**, were compacted under a pressure of 0.15 kN mm^{-2} in the form of disks (diameter 28 mm, up to 1 mm thickness). Electrical measurements could not be performed on **1** due to its extreme instability. The samples were then coated with gold by evaporation under vacuum thus providing a suitable three-terminal electrode configuration. Prior to any electrical measurement, samples were sintered in dry nitrogen for 8 h at 393 K. A three-terminal technique was used for both direct current (d.c.) and alternating current (a.c.) measurements, due to the rather low electrical conductivity exhibited by these compounds at room temperature. The voltmeter-ammeter method in d.c. and the Schering-bridge method in a.c. measurements (10^{-2} Hz to 1 MHz) were used with cells and instrumentation described elsewhere[17–19] according to the ASTM D 150 and D 257 standards. The d.c. charging currents, under an electric field of 100 V cm^{-1}, and discharging currents were also measured as a function of time by Fourier transform of the d.c. data to detect possible dielectric relaxation effects in the ultra-low-frequency range.[20] Measurements were also performed using different types of electrodes (Au, Ag); moreover, the constant electrical field of 100 V cm^{-1} was applied, in a nitrogen atmosphere, at high temperatures (433 K) up to 600 min, to evaluate the effect of voltage application on conductivity.

Results and Discussion

Both compounds are white, stable in air and easily soluble in water. Compound **1** shows a tendency to release iodine when suspended in organic solvents or pressed for the preparation of pellets for electrical measurements.

Crystal Structures.—The structures of both complexes are shown in Figs. 1 and 2, and selected bond distances and angles in Tables 4 and 5.

$[H_2pipz]_2[Cu_2I_6]\cdot H_2O$. The structure consists of dimeric $[Cu_2I_6]^{4-}$ anions, piperazinium dications and unco-ordinated water molecules. The anions are composed of two CuI_4 units, sharing an edge, in which both the copper atoms are surrounded by four iodine atoms in a tetrahedral arrangement. In particular, atoms I(1) and I(2) bridge the copper(I) ions, the co-ordination of which is completed by terminal iodine atoms, I(4) and I(3) for Cu(1) and I(5) and I(6) for Cu(2).

Bond lengths and angles are in agreement with literature data. The Cu–I bridging distances [Cu(1)–I(1) 2.688(4), Cu(1)–I(2) 2.748(4), Cu(2)–I(1) 2.763(4) and Cu(2)–I(2) 2.675(4) Å] are longer than the terminal ones [Cu(1)–I(3) 2.620(4), Cu(1)–I(4) 2.615(4), Cu(2)–I(5) 2.614(4) and Cu(2)–I(6) 2.624(4) Å]. It is worth noting the short intradimer Cu • • • Cu separation

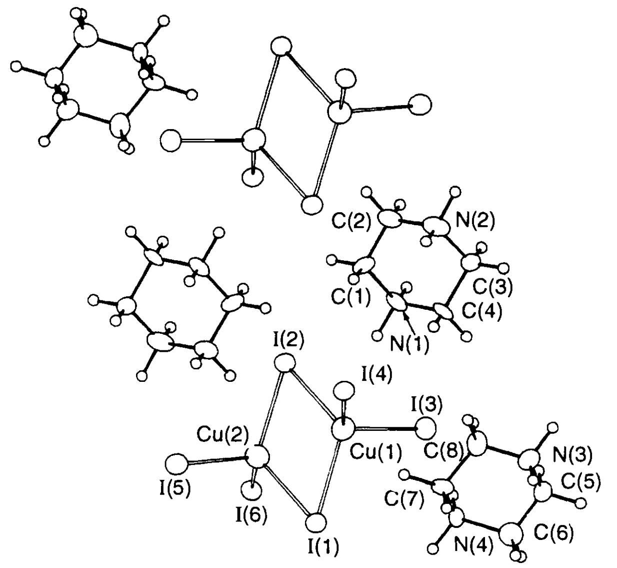

Fig. 1 Crystal structure of $[H_2pipz]_2[Cu_2I_6]\cdot H_2O$. For clarity water molecules are not shown

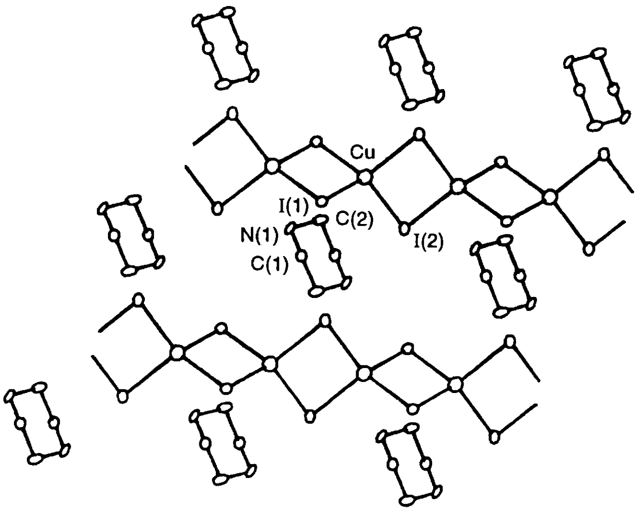

Fig. 2 Crystal structure of $[H_2pipz][Cu_2I_4]$. For clarity hydrogen atoms are not shown

[2.775(5) Å] is similar to that observed in the $Tl_4[Cu_2I_6]$ [2.612(3) Å].[21]

The crystal packing (Table 6) is determined by a network of contacts, involving the organic dications with the terminal and bridging iodine atoms of the inorganic anions and the water molecules, which can be considered as hydrogen bonds. In particular, atom N(1) interacts with the bridging I(1) and I(2) and with the terminal I(4); N(3) interacts with bridging I(1) and I(2). Other interactions involving nitrogen, iodine and oxygen atoms are to be considered van der Waals contacts.

$[H_2pipz][Cu_2I_4]$. The crystal structure consists of polymeric $[CuI_2]^-$ anions and piperazinium dications. Each copper atom is surrounded by four iodine atoms in a quite regular tetrahedral arrangement. The tetrahedra are joined by two centrosymmetrically related, alternately I(1) and I(2), bridging iodine atoms, giving rise to one-dimensional polymeric endless chains of edge-sharing metal iodide tetrahedra, running parallel along the [001] axis.

The Cu–I bond distances are very similar, being in a very restricted range [2.652(3)–2.677(3) Å]. This is similar to what is found for the structurally similar $[Me_2N{=}CH{-}N{=}CHNMe_2][CuI_2]$ compound [Cu–I 2.680–2.685(1) Å], while other iodocuprates(I), although presenting similar single chains, show different wide-ranging Cu–I distances.[22] As a consequence the intrachain Cu···Cu distances in our compound [Cu···Cu^{I} 3.397(3), $-x$, $-y+1$, $-z$; Cu···Cu^{II} 3.431(3) Å, $-x$, $-y+1$, $-z+1$] are very similar, as also observed for $[Me_2N{=}CH{-}N{=}CHNMe_2][CuI_2]$[22] [Cu···Cu 3.362(1) Å], while in the iodocuprates(I), presenting different Cu–I bond distances, the Cu···Cu separations appear to be very different [2.987–

Table 4 Bond distances (Å) and angles (°) for compound **1** with e.s.d.s in parentheses

Cu(1)–I(1)	2.688(4)	Cu(2)–I(1)	2.763(4)
Cu(1)–I(2)	2.748(4)	Cu(2)–I(2)	2.675(4)
Cu(1)–I(3)	2.620(4)	Cu(2)–I(6)	2.624(4)
Cu(1)–I(4)	2.615(4)	Cu(2)–I(5)	2.614(4)
Cu(1)···Cu(2)	2.775(5)		
N(1)–C(1)	1.51(3)	N(4)–C(6)	1.56(3)
N(1)–C(4)	1.49(3)	N(4)–C(7)	1.51(3)
N(2)–C(2)	1.52(3)	C(1)–C(2)	1.49(4)
N(2)–C(3)	1.53(3)	C(3)–C(4)	1.55(3)
N(3)–C(5)	1.51(3)	C(5)–C(6)	1.46(4)
N(3)–C(8)	1.48(3)	C(7)–C(8)	1.52(3)
I(3)–Cu(1)–I(4)	116.6(1)	I(6)–Cu(2)–I(5)	114.6(1)
I(2)–Cu(1)–I(4)	100.2(1)	I(2)–Cu(2)–I(5)	109.5(1)
I(2)–Cu(1)–I(3)	105.6(1)	I(2)–Cu(2)–I(6)	109.3(1)
I(1)–Cu(1)–I(4)	111.1(1)	I(1)–Cu(2)–I(5)	101.2(1)
I(1)–Cu(1)–I(3)	105.2(1)	I(1)–Cu(2)–I(6)	103.7(1)
I(1)–Cu(1)–I(2)	118.7(1)	I(1)–Cu(2)–I(2)	118.6(1)
Cu(1)–I(1)–Cu(2)	61.2(1)	Cu(1)–I(2)–Cu(2)	61.5(1)
C(1)–N(1)–C(4)	113(2)	N(2)–C(3)–C(4)	108(2)
C(2)–N(2)–C(3)	110(2)	N(1)–C(4)–C(3)	109(2)
C(5)–N(3)–C(8)	110(2)	N(3)–C(5)–C(6)	110(2)
C(6)–N(4)–C(7)	110(2)	N(4)–C(6)–C(5)	109(2)
N(1)–C(1)–C(2)	109(2)	N(4)–C(7)–C(8)	107(2)
N(2)–C(2)–C(1)	109(2)	N(3)–C(8)–C(7)	111(2)

Table 5 Bond distances (Å) and angles (°) for compound **2** with e.s.d.s in parentheses

Cu–I(1)	2.653(3)	Cu···Cu^{II}	3.431(3)
Cu–I(2)	2.657(5)	N(1)–C(1)	1.49(1)
Cu–I(1^{I})	2.652(3)	N(1)–C(2)	1.47(1)
Cu–I(2^{II})	2.677(3)	C(1)–C(2^{III})	1.54(1)
Cu···Cu^{I}	3.397(3)		
I(1)–Cu–I(2)	116.23(8)	C(1)–N(1)–C(2)	111.9(8)
Cu–I(1)–Cu^{I}	79.65(7)	N(1)–C(1)–C(2^{III})	110.0(7)
Cu–I(2)–Cu^{II}	80.04(7)		

Symmetry relations: I $-x, -y+1, -z$: II $-x, -y+1, -z+1$; III $-x, -y, -z$.

Table 6 Crystal packing: bond distances (Å) and angles (°) for compound **1** with e.s.d.s in parentheses

N(1)···I(2)	3.81(2)	N(4)···I(6^{III})	3.57(2)
N(1)···I(4)	3.65(2)	I(1)···O^{IV}	3.56(2)
N(1)···I(1^{I})	3.62(2)	I(2)···O	3.58(2)
N(2)···O^{II}	2.84(3)	I(6)···O^{VI}	3.79(2)
N(3)···I(2^{III})	3.59(2)	H(9)···I(2)	2.97
N(4)···I(3)	3.58(2)	H(9)···I(4)	2.98
N(4)···O^{IV}	3.08(3)	H(10)···I(1^{I})	2.60
N(2)···I(4^{I})	3.73(2)	H(12)···O^{II}	1.77
N(2)···I(5^{II})	3.61(2)	H(21)···I(2^{III})	2.52
N(3)···I(5^{V})	3.52(2)	H(23)···I(3)	2.53
N(3)···I(6^{V})	3.65(2)	H(24)···O^{IV}	2.26
N(1)–H(9)···I(2)	134	N(3)–H(21)···I(2^{III})	167
N(1)–H(9)···I(4)	120	N(4)–H(23)···I(3)	161
N(1)–H(10)···(1^{I})	156	N(4)–H(24)···O^{IV}	131
N(2)–H(12)···O^{II}	166		

Symmetry relations: I $x+1, y, z$; II $-x+1, -y+1, -z$; III $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; IV $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; V $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; VI $-x+1, -y+1, -z+1$.

Table 7 Hydrogen-bond distances (Å) and angles (°) for compound **2** with e.s.d.s in parentheses

$N(1)\cdots I(1^{IV})$	3.593(9)	$H(1)\cdots I(1^{IV})$	2.77
$N(1)\cdots I(2^{V})$	3.71(1)	$H(2)\cdots I(2^{V})$	2.77
$N(1)-H(1)\cdots I(1^{IV})$	139	$N(1)-H(2)\cdots I(2^{V})$	157

Symmetry relations: IV $x, y, z + 1$; V $-x - 1, -y, -z + 2$.

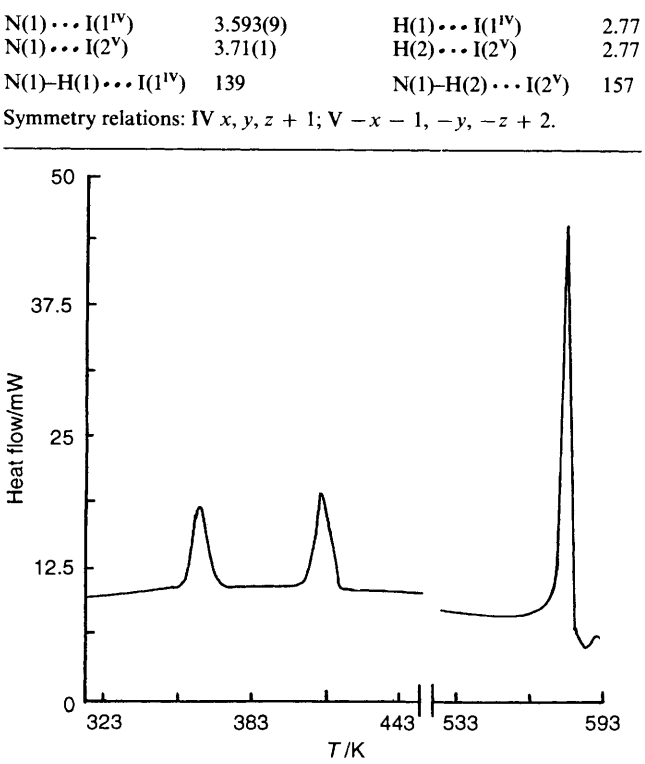

Fig. 3 The DSC thermogram of $[H_2pipz]_2[Cu_2I_6]\cdot H_2O$

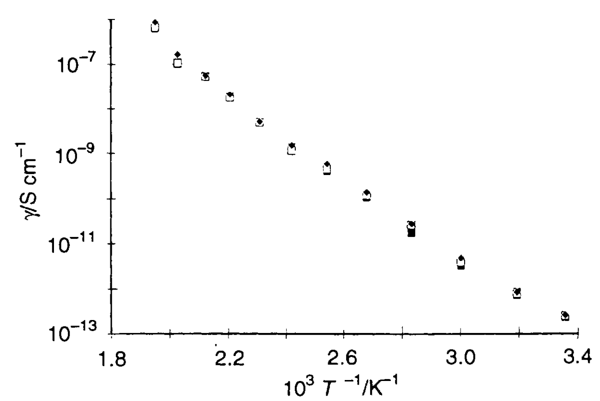

Fig. 4 Electrical conductivity γ of $[H_2pipz][Cu_2I_4]$ as a function of reciprocal absolute temperature at 1 (■), 10 (□) and 60 (◆) min after the voltage application

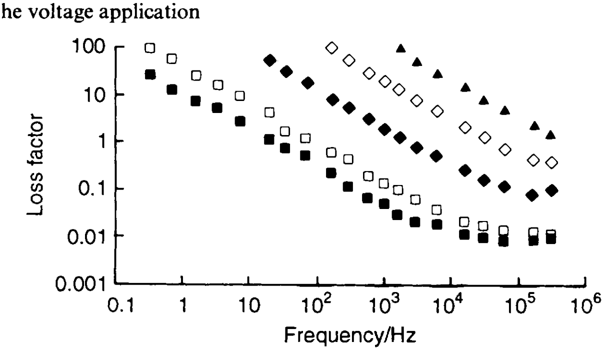

Fig. 5 Loss factor of $[H_2pipz][Cu_2I_4]$ *vs.* frequency at 298 (■), 323 (□), 373 (◆), 423 (◇) and 473 K (▲)

3.581,[23] 3.01(2)–3.54(3) Å[22]]. These distances are always comparatively greater than those observed in the dinuclear idocuprates(I) (see above).

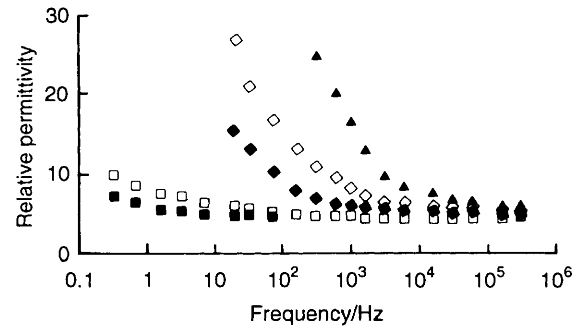

Fig. 6 Relative permittivity of $[H_2pipz][Cu_2I_4]$ *vs.* frequency. Temperatures as in Fig. 5

A network of long interactions between organic counter cations and inorganic chains, which can be considered as hydrogen bonds, links the chains; in fact the N(1) hydrogen atoms interact with I(1) and I(2) of two different chains. The bond distances and angles are reported in Table 7.

Thermal Results.—The thermal behaviour of the dinuclear compound **1** is very interesting, showing a two-step loss of the water molecule. The TG and DTG thermograms show a weight loss of 0.88%, corresponding to half a water molecule, between 293 and 373 K and of 0.82%, corresponding to half a water molecule, between 373 and 413 K. The total weight loss of 1.70% corresponds to the loss of one water molecule (calc: 1.6%). In the DSC thermograms (Fig. 3) the two-step loss of the water molecule is clearly shown by two sharp, well defined endothermic peaks at 353–373 and 398–423 K. The total heat of transformation, $\Delta H = 47$ kJ mol^{-1} is in good agreement with the value calculated for the dehydration heat of crystal hydrates ($\Delta H = 54$–59 kJ per mol H_2O).[24,25] A third sharp endothermic peak ($\Delta H = 66$ kJ mol^{-1}), corresponding to the melting point, begins at 563 K.

Compound **2** is thermally stable until about 573 K. At this temperature the DSC thermogram shows a sharp endothermic peak ($\Delta H = 15.7$ kcal mol^{-1}), corresponding to the melting point, after which the compound decomposes.

No structural phase transitions are observed for either of the compounds.

Electrical Results.—Fig. 4 shows the electrical conductivity γ of compound **2**, calculated at 1, 10 and 60 min after the voltage application, as a function of the reciprocal absolute temperature, in the temperature range 298–513 K. The d.c. behaviour in the Arrhenius plot is almost linear, small transient phenomena being present at intermediate temperatures (393–433 K) and over 473 K. Measurements were performed from room temperature to the highest allowed one (513 K); at higher temperatures degradation phenomena take place and the conductivity is no longer reproducible. The conductivity values span from those typical of insulating materials, at low temperatures, to those of semiconductors at the highest ones.

Measurements performed at room temperature after the absorption of a small amount of moisture (0.83%) showed a strong increase in conductivity (amost two orders of magnitude). The use of different types of electrodes gave no variations in conductivity and apparent activation energy; the prolonged application of electrical fields caused a small decrease in conductivity.

Dielectric measurements in the frequency range 10^{-1}–10^6 Hz at constant temperature showed no remarkable relaxation effects; Fig. 5 shows the loss factor, ε″, while Fig. 6 shows the relative permittivity, ε′. As can be seen, at constant temperature the loss factor and relative permittivity increase with decreasing frequency. The Fourier transform of the discharging current showed no relaxation processes of the Maxwell–Wagner–Sillars type. The apparent activation energy is 37 kJ mol^{-1}, a value close to those found for polymeric one-dimensional chlorocuprates(II).[9,10]

Compound **2** shows higher values of the conductivity and a lower apparent activation energy (37 compared to 52 kJ mol^{-1}) than those of the analogous chlorocadmates.[6,7] Many features hint at an ionic mechanism of conduction in this compound: (*a*) the slope of loss factor as a function of frequency in a log–log plot approaches unity at high temperatures; (*b*) the strong increase in conductivity after the absorption of a small amount of water; (*c*) the unchanged values of conductivity and activation energy when different kinds of electrodes are used; (*d*) the slight but systematic decrease in charging currents after prolonged application of an electrical field to the sample at high temperature, an effect commonly ascribed to the sweeping away of ionic charge carriers.[26,27]

The same mechanism of conduction found in chlorocuprates(II)[9,10] as well as in one-dimensional chlorocadmates[6,7] can thus be proposed, *i.e.* proton migration *via* hydrogen bonds. A possible electronic contribution to conduction due to the different oxidation number of the copper ions in the compounds and the increased polarizability of the iodine atom compared to chlorine could not be detected, but merits further investigation.

Conclusion

The ability to form more than one compound in the presence of the same cation is not unusual as already observed for copper(II) and cadmium(II) ions, and can easily be predicted by taking into account the structural flexibility of the cations. In our case the formation of one simple (dimeric) and one polymeric structural archetype may be tentatively explained by the type of hydrogen-bonding interactions in the two compounds. In the polymeric compound the network of hydrogen bonding, involving bridging counter cations, connects the columnar stacks of chains and stabilizes the whole crystal structure. In the dimer, one nitrogen atom of the counter cation is prevented from interacting with more than one inorganic anion by the presence of the water molecule; as a consequence the structural packing, corresponding to the lowest stabilization energy, requires the presence of the short-chain inorganic anions and results in a lower density than that of the polymeric compound.

Electrical measurements could not be performed on compound **1** due to its instability. Compound **2** exhibits an essentially ionic conduction, especially at high temperatures, protons engaged in hydrogen bonds being the charge carriers: a small electronic contribution cannot however be ruled out on account of the polarizability of the iodine atom. The whole electrical behaviour closely resembles that of the one-dimensional polymeric chlorocuprates(II)[9,10] previously studied.

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