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Extended Polymorphism in Copper(II) Imidazolate Polymers: A Spectroscopic and XRPD Structural Study

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Copper(II) bisimidazolate affords five different polymorphs; of these, one was structurally characterized 40 years ago by standard single-crystal X-ray diffraction (Jarvis, J. A. J.; Wells, A. F. *Acta Crystallogr.* **1960**, *13*, 1027), while the remaining four, *selectively* prepared as pure polycrystalline phases, have been now studied by X-ray powder diffraction (XRPD) methods. Of the four new (blue, green, olive-green, and pink) phases, three were solved by the ab initio XRPD technique and refined by the Rietveld method, and the fourth phase (pink) could not be structurally characterized. Crystal data for $[Cu(imidazolate)_2]_n$: blue phase, $a = 27.559(3)$ Å, $c = 5.3870(9)$ Å, trigonal, $R\bar{3}$, $Z = 54$; green phase, $a = 21.139(1)$ Å, $b = 19.080(1)$ Å, $c = 9.2842(8)$ Å, orthorhombic, *Ccca*, $Z = 20$; olive-green phase, $a = 11.7556(8)$ Å, $b = 23.422(2)$ Å, $c = 9.0727(9)$ Å, $\beta = 104.993(5)°$, monoclinic, $C2/c$, $Z = 12$. All polymorphs contain four-coordinate CuN_4 chromophores and (N,N′)-exobidentate imidazolate ligands, but show different spectroscopic and structural properties, the latter ranging from 2D to different 3D networks of the PtS, sodalite, and moganite archetypes. The intermediacy of the $[Cu(imidazole)_2CO_3]\cdot H_2O$ species in the synthesis of the blue polymorph has been confirmed by spectroscopic and thermal analyses. FTIR, Raman, and electronic spectra were correlated with the structural features revealed in the present work, and used to gain insight into the coordination geometry of copper(II) ions of the pink polymorph. In addition, the correct Raman spectrum for copper(II) bisimidazolate, common for all polymorphs, has been definitely determined.

Introduction

In the context of the well-established role played by the copper−imidazole bond in biological systems, the case of the bridging imidazolate anion is particularly interesting. For example, an imidazolate-bridged bimetallic moiety is contained in the active site of superoxide dismutase (SOD).[1] The formation of polynuclear complexes, where copper centers are linked by the deprotonated imidazolyl moiety, originally *hypothesized* at basic pH values for systems formed by copper(II) with histidine-containing oligopeptides,[2] has been recently demonstrated through spectroscopic evidence.[3] Interestingly, for such systems a biological activity analogous to that of SOD has been demonstrated[4] and pharmacological applications have been patented.[5]

Surprinsingly enough, copper(II) bisimidazolate $Cu(im)_2$ (imH = imidazole), the simplest model of the imidazolate-bridged Cu(II)−Cu(II) center, lacks in the literature an adequate structural and spectroscopic characterization.[6] However, several electrochemical studies on its (probable) formation have been very recently[7] published: in fact, $Cu(im)_2$ appears to form a strong anticorrosive layer on top of copper metal, when the latter is treated with imidazole (or its derivatives) in aerial conditions, and, as such, it has been proposed to possess relevant technological importance.[8] In addition, electrochemically generated $Cu(im)_2$ has been proven to be catalytically active in the oxidation of biologically available substrates.[9] For this compound, the existence of three polymorphs (of blue,[10] pink,[11] and green

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(1) Ohtsu, H.; Shinobu, I.; Nagatomo, S.; Kitagawa, T.; Ogo, S.; Watanabe, Y.; Fukuzumi, S. *Chem. Commun.* **2000**, 1051 and references therein.

(2) Morris, P. J.; Martin, R. B. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2913.

(3) Gajda, T.; Henry, B.; Delpuech, J. *J. Chem. Soc., Dalton Trans.* **1993**, 1301. Bruni, S.; Cariati, F.; Daniele, P. G.; Prenesti, E. *Spectrochim. Acta A* **2000**, *56*, 815. Bruni, S.; Cariati, F.; Daniele, P. G.; Galbiati, G.; Prenesti, E. In preparation.

(4) Ueda, J.; Ozawa, T.; Miyazaki, M.; Fujiwara, Y. *J. Inorg. Biochem.* **1994**, 123.

(5) Branca, A. PCT Int. Appl. WO 94 18,230, 1994. Sportoletti G.; Dal Pozzo, A. PCT Int. Appl. WO 94 03,482, 1994.

(6) Early work on the structure and magnetism of imidazolate and 2,2′-biimidazolate-bridged copper(II) complexes appeared in the following: Haddad, M. S.; Duesler, E. N.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 141−148.

(7) Richmond, W. N.; Faguy, P. W.; Weibel, S. C. *J. Electroanal. Chem.* **1998**, *448*, 237−244. Gašparac, R.; Martin, C. R.; Stupnišek-Lisac, E. *J. Electrochem. Soc.* **2000**, *147*, 548−551. Gašparac, R.; Martin, C. R.; Stupnišek-Lisac, E.; Mandic, Z. *J. Electrochem. Soc.* **2000**, *147*, 991−998.

(8) Sirtori, V.; Lombardi, L.; Redaelli, G. *J. Electron. Mater.* **1997**, *26*, 459−462. Gašparac, R.; Stupnišek-Lisac, E. *Corrosion* **1999**, *55*, 1031−1039.

(9) Aptekar, M. D.; Garnovskii, A. D.; Ismailov, Kh. M. *Sov. J. Coord. Chem.* (*Engl. Transl.*) **1983**, *9*, 288−292.

(10) Brown, G. P.; Aftergut, S. *J. Polym. Sci.* **1964**, *A2*, 1839−1845.

(11) Bauman, J. E., Jr.; Wang, J. C. *Inorg. Chem.* **1964**, *3*, 368−373. Xue, G.; Jiang, S.; Huang, X.; Shi, G.; Sun, B. *J. Chem. Soc., Dalton Trans.* **1988**, 1487−1488.

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color[12]) is briefly reported in the old literature. A single-crystal X-ray structure has been determined for the blue polymorph[13] and more extensively discussed elsewhere.[14] By contrast, the structures of the green and pink polymorphs have not been determined yet and, for the blue form, a powder diffraction pattern *only partially* corresponding to the single-crystal structure has been measured.[10] Also lacking is a thorough vibrational spectroscopic study of these compounds. A resonance Raman spectrum has been published,[15] again for (what was thought to be) the blue polymorph.

An investigation of copper(II) imidazolate by means of the Raman technique is of importance in the characterization of the active sites of metalloproteins and enzymes, and has been recently demonstrated for metal−oligopeptide complexes.[16]

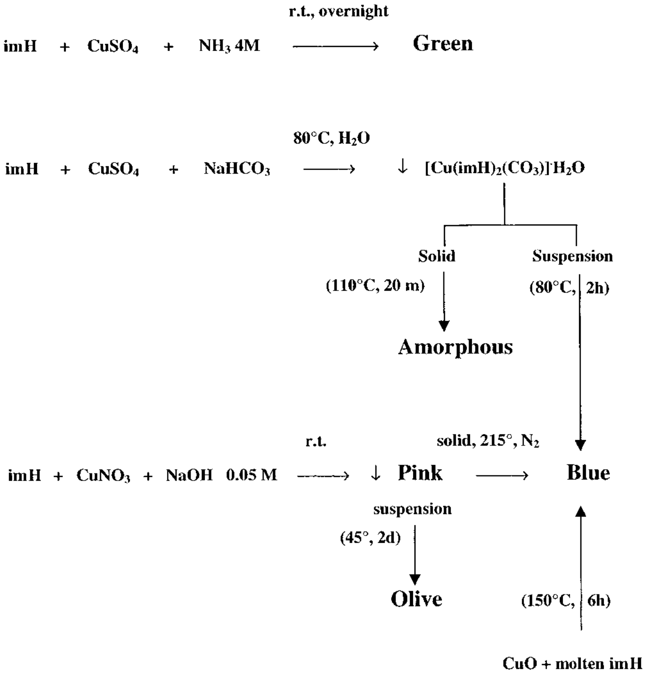
However, metal diazolates[17] and similar species[18] often afford intractable polymeric species, which, lacking thermal stability and solubility in common organic solvents, cannot be (re)crystallized from the melt or their solutions. If the complexity of such species is not too large, and if *monophasic* powders are available, then X-ray powder diffraction (XRPD) methods can be successfully employed to determine their crystal structures, even from conventional laboratory data.[19]

Therefore, the purpose of this work is to investigate, in detail, the different polymorphs of copper(II) imidazolate, aiming toward selective syntheses of monophasic samples and toward the full characterization of their structures (via XRPD) and their spectroscopic features. In particular, we present a number of crystal structures, which correct a recently published, but rather implausible, structural model, which led to a clear misinterpretation of the magnetic behavior of these species, upon assuming infinite one-dimensional chains of (doubly μ-im bridged) copper ions.[20] The $Cu(im)_2$ polymorphs discussed in this paper will be labeled **B** (for blue), **G** (for green), **P** (for pink), and **O** (for olive). In order to avoid ambiguities stemming from this color code, the previously reported (second) blue phase[13] will be characterized by the letter **J**. An amorphous (green) phase was also prepared.

Experimental Section

General. Imidazole (imH, Fluka), $Cu(NO_3)_2{\cdot}3H_2O$ (Aldrich), and $CuSO_4{\cdot}5H_2O$ (Aldrich) were used as supplied. Thermogravimetric analyses were performed on a Perkin-Elmer TGA-7 system. DSC traces were obtained with the aid of a Perkin-Elmer DSC 7 calorimeter. Elemental analyses (C, H, N) were carried out using a Perkin-Elmer 2400 instrument.

Scheme 1



Spectroscopy. Raman spectra were recorded on samples diluted with NaCl and pressed into pellets, in order to reduce the absorption of the incident radiation. To obtain the spectra a multichannel JASCO TRS-300 spectrophotometer was employed, using, for the excitation, the 457.9 nm line of an Ar^+ laser, with an output power of 300 mW. IR spectra in the 4000−400 cm^{-1} frequency region were collected on NaCl pellets with a JASCO FT/IR 5300 spectrophotometer. FTIR spectra in the 500−80 cm^{-1} region were measured, using a Digilab FTS-40 instrument, on Nujol dispersions of the compounds placed between polyethylene windows. Electronic absorption spectra in the 350−2500 nm region were recorded in the diffuse reflectance mode on powdered samples by a JASCO V-570 spectrophotometer equipped with a sphere coated with barium sulfate.

Synthesis of the $Cu(im)_2$ Derivatives. Scheme 1 summarizes the detailed synthetic procedures.

Pink Modification. P was synthesized according to the method reported in the literature.[11] NaOH (0.1 M) was added to a solution prepared by dissolving 2 g of imidazole (29.4 mmol) in 50 mL of 0.05 M $Cu(NO_3)_2{\cdot}3H_2O$ (2.50 mmol), until the formation of a reddish-purple precipitate was observed. After filtering, the powder was washed with ethanol and dried in vacuo at 80 °C. Anal. Calcd for $Cu(C_3H_3N_2)_2$: C, 36.5; H, 3.1; N, 28.3. Found: C, 36.0; H, 3.2; N, 27.5.

Green Modification. G was prepared as reported in the literature[12] by dissolving 0.5 g of $CuSO_4{\cdot}5H_2O$ (2 mmol) in 3 mL of H_2O and bringing the volume up to 25 mL with 4 M NH_3. By addition of a solution of imidazole (0.25 g; 3.67 mmol) in water (15 mL) the quick formation of a brownish precipitate was observed. After filtering, the solution was left to stand overnight until the formation of a dark green powder was observed. The compound was filtered and dried in vacuo. Anal. Calcd for $Cu(C_3H_3N_2)_2$: C, 36.5; H, 3.1; N, 28.3. Found: C, 36.2; H, 2.9; N, 27.5

Blue Modification. B is quantitatively obtained by heating the **P** polymorph at 215 °C, under nitrogen atmosphere. Alternatively, **B** can be synthesized by a modification of the method reported by Brown and Aftergut.[10] In a 150 mL open two-necked flask a solution of 1.36 g of imidazole (20 mmol) and 6.6 g of $NaHCO_3$ (78.56 mmol) in 50 mL of H_2O was heated at 80 °C with a water bath for 3 h. To the hot solution was added dropwise 2.5 g of $CuSO_4{\cdot}5H_2O$ (10.1 mmol) in 12.5 mL of H_2O with stirring. The formation of a violet precipitate was immediately observed. By leaving the mixture under reaction conditions, the violet compound was gradually transformed into **B**, the blue modification of $Cu(im)_2$. After 2 h the blue compound was filtered

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(12) Inoue, M.; Kishita, M.; Kubo, M. *Inorg. Chem.* **1965**, *4*, 626−628.

(13) Jarvis, J. A. J.; Wells, A. F. *Acta Crystallogr.* **1960**, *13*, 1027−1028.

(14) Freeman, H. C. In *Advances in Protein Chemistry*; Anfinden, C. B., Jr., Anson, M. L., Edsall, J. T., Richards, F. M., Eds.; Academic Press: New York, 1967; p 257−424.

(15) Siiman, O.; Young, N. M.; Carey, P. R. *J. Am. Chem. Soc.* **1974**, *96*, 5583. Siiman, O.; Rivellini, R.; Patel, R. *Inorg. Chem.* **1988**, *27*, 3940.

(16) Casolaro, M.; Chelli, M.; Ginanneschi, M.; Laschi, F.; Muniz-Miranda, M.; Papini, A. M.; Sbrana, G. *Spectrochim. Acta A* **1999**, *55*, 1675. Bruni, S.; et al. In preparation.

(17) (a) Masciocchi, N.; Moret, M.; Cairati, P.; Sironi, A.; Ardizzoia, G. A.; LaMonica, G.; Cenini, S. *J. Am. Chem. Soc.* **1994**, *116*, 7668−7676. (b) Masciocchi, N.; Moret, M.; Cairati, P.; Sironi, A.; Ardizzoia, G. A.; La Monica, G. *J. Chem. Soc., Dalton Trans.* **1995**, 1671. (c) Masciocchi, N.; Ardizzoia, G. A.; Maspero, A.; La Monica, G.; Sironi, A. *Inorg. Chem.* **1999**, *38*, 3657.

(18) Masciocchi, N.; Corradi, E.; Moret, M.; Ardizzoia, G. A.; Maspero, A.; LaMonica, G.; Sironi, A. *Inorg. Chem.* **1997**, *36*, 5648−5650. Masciocchi, N.; Ardizzoia, G. A.; LaMonica, G.; Maspero, A.; Sironi, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 3366−3369.

(19) Masciocchi, N.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1997**, 4643−4650.

(20) Vecchio-Sadus, A. M. *Transition Met. Chem.* **1995**, *20*, 46−55.

Table 1. Crystal Data, Details on Refinement, and Selected Structural Parameters for Four Cu(im)$_2$ Polymorphs (Esd's in Parentheses)

	blue, **J**	blue, **B**	green, **G**	olive, **O**
meth	single crystal	XRPD	XRPD	XRPD
syst	monoclinic	trigonal	orthorhombic	monoclinic
space group	$I2/c$	$R\bar{3}$	$Ccca$	$C2/c$
a, Å	11.75	27.559(3)	21.139(1)	11.7556(8)
b, Å	14.07	27.559(3)	19.080(1)	23.422(2)
c, Å	8.77	5.3870(9)	9.2843(8)	9.0727(9)
α, deg	90	90	90	90
β, deg	97.2	90	90	104.993(5)
γ, deg	90	120	90	90
Z	8	18	20	12
fw, g mol^{-1}	197.68	197.68	197.68	197.68
V, Å^3	1438	3543.3(7)	3744.6(5)	2413.1(4)
ρ_{calc}, g cm^{-3}	1.824	1.667	1.753	1.632
μ(Cu Kα), cm^{-1}		33.6	35.3	32.9
diffractometer	single crystal	Philips PW1820	Philips PW1820	Philips PW1820
T, K	rt	298(2)	298(2)	298(2)
2θ range, deg		16−105	15−105	13−105
N_{obs}		4450	4500	4600
N_{ref}		896	1067	876
R_{wp}, R_{p}[a]		0.055, 0.036	0.031, 0.023	0.034, 0.025
R_F		0.11	0.068	0.062
V/Z, Å^3	179.75	196.85	187.2	201

[a] $R_p = \sum_i |y_{i,o} - y_{i,c}| / \sum_i |y_{i,o}|$; $R_{wp} = [\sum_i w_i (y_{i,o} - y_{i,c})^2 / \sum_i w_i (y_{i,o})^2]^{1/2}$; $R_F = \sum_n ||F_{n,o}| - |F_{n,c}|| / \sum_i |F_{n,o}|$, where $y_{i,o}$ and $y_{i,c}$ are the observed and calculated profile intensities, respectively, and $|F_{n,o}|$ and $|F_{n,c}|$ are the observed and calculated structure factors. The summations run over i data points or n independent reflections. Statistical weights w_i are normally taken as $1/y_{i,o}$.

off, washed with water, and dried at 110 °C overnight in an oven. Anal. Calcd for Cu($C_3H_3N_2$)$_2$: C, 36.5; H, 3.1; N, 28.3. Found: C, 36.1; H, 3.5; N, 27.5.

In a parallel experiment, the intermediate violet species was separated by filtration, washed with H_2O, and characterized by infrared spectroscopy and elemental analyses. These are in agreement with the formation of [Cu(imH)$_2$(CO_3)]·H_2O. IR frequencies (cm^{-1}): H_2O, 3482 (m), 3350 (sh), 1635 (w); imH, 3140 (s), 3120 (s), 3040−2600, 1549 (m), 1330 (s), 1074 (s), 831 (s), 658 (s), 628 (m);[21] bidentate CO_3^{2-}, 1465 (vs), 1403 (vs), 842 (vs).[22] Raman frequencies (cm^{-1}): imH, 1550 (w), 1494 (w), 1448 (s), 1330 (vs), 1263 (vs), 1196 (s), 1157 (s), 1147 (s), 1105 (m), 1060 (w), 970 (w), 954 (w), 910 (w), 698 (w), 305 (w), 258 (w), 226 (w); CO_3^{2-}, 1074 (w). Anal. Calcd for [Cu(imH)$_2$(CO_3)]·H_2O: C, 30.5; H, 3.6; N, 20.3. Found: C, 30.4; H, 3.5; N, 20.1.

In addition, by heating solid [Cu(imH)$_2$(CO_3)]·H_2O at 110 °C for 20 min in an oven, the formation of a green, *but amorphous* (XRPD evidence), modification of Cu(im)$_2$ was observed. TGA monitoring confirmed the following decomposition reaction, corresponding to a 29% weight loss at 150 °C:

$$[\mathrm{Cu(imH)_2(CO_3)}]\cdot\mathrm{H_2O} \rightarrow \mathrm{Cu(im)_2} + 2\mathrm{H_2O} + \mathrm{CO_2}$$

Pure **B** can also be obtained by vigorously stirring a CuO suspension in molten imidazole (ca. 150 °C) for about 6 h, followed by removal of excess imidazole with hot acetone. Shorter reaction times may result in partial conversion.

Olive Modification. Imidazole (1 g; 14.7 mmol) was dissolved in 50 mL of 0.025 M Cu(NO_3)$_2$·3H_2O (1.25 mmol). The formation of a trace amount of a reddish precipitate was immediately observed. After filtering, 4 mL of NaOH 0.05 M was added to the solution, giving Cu(im)$_2$ (pink modification). By leaving the mixture at 45 °C for 2 days the gradual transformation of the color of the precipitate from pink to olive was observed. This compound (**O**) was isolated by filtration, washed with ethanol, and dried in vacuo. Anal. Calcd for Cu($C_3H_3N_2$)$_2$: C, 36.5; H, 3.1; N, 28.3. Found: C, 36.5; H, 3.2; N, 27.9.

J (Blue) Modification. In the original paper by Brown and Aftergut,[10] the synthesis of a "blue" phase was reported, but the X-ray diffraction features reported there, as well as our repeated attempts to obtain pure phase **J**, showed that only polyphasic powders could be obtained, mostly containing a mixture of the **J** and **B** polymorphs. The serendipitous occurrence of a single crystal of **J** (of unknown origin) in the hands of Jarvis and Wells[13] did not allow us to further substantiate its spectroscopic features.

X-ray Powder Diffraction Analysis of B, G, P, and O. The powders were gently ground in an agate mortar and then cautiously deposited in the hollow of an aluminum holder equipped with a zero background plate (supplied by The Gem Dugout, State College, PA) with the aid of glass slide. Diffraction data (Cu Kα, $\lambda = 1.5418$ Å) were collected on a vertical scan Philips PW1820 diffractometer, equipped with Soller slits, a secondary beam curved graphite monochromator, a Na(Tl)I scintillation detector, and pulse height amplifier discrimination. The generator was operated at 40 kV and 40 mA. Slits used: divergence 1.0°, antiscatter 1.0°, and receiving 0.2 mm. Nominal resolution for the present setup is 0.12° 2θ (fwhm) for the Si(111) peak at 28.44° (2θ). Long overnight scans were performed with $5° < 2\theta < 105°$, with $t = 10$ s and $\Delta 2\theta = 0.02°$.

Indexing, using TREOR,[23] of the low-angle peaks suggested, for **B**, **G**, and **O**, unit cells of approximate dimensions $a = 8.16$ Å, $b = 13.79$Å, $c = 5.40$ Å, $\beta = 102.9°$ [M(17)[24] = 21; F(17)[25] = 29 (0.017, 34), which could be later transformed into a rhombohedral lattice of $a = 27.56$ Å, $c = 5.40$ Å (hexagonal setting)], $a = 21.07$ Å, $b = 19.04$ Å, $c = 9.28$ Å [M(17) = 16; F(17) = 32 (0.007, 73), C-centered], and $a = 12.86$ Å, $b = 23.44$ Å, $c = 9.04$ Å, $\beta = 117.9°$ [M(12) = 30; F(12) = 56 (0.007, 29), I-centered, later transformed into the standard C setting]. Owing to the poor resolution of the broad peaks of the **P** phase, no successful unit cell determination could be attained. Systematic absences indicated (among others) $R\bar{3}$, $Ccca$, and $C2/c$ as the probable space groups for **B**, **G**, and **O**, respectively, later confirmed by successful solution and refinement.

Structure solutions of **B**, **G**, and **O** were initiated by EXPO,[26] which afforded all metal locations, as well as the position of a few other light atoms, which were initially excluded from the structure solution process. With the help of difference Fourier syntheses and geometrical modeling,

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(21) Cordes M., Walter, J. L. *Spectrochim. Acta, Part A* **1968**, *24A*, 237.

(22) Nakamoto K. *Infrared spectra of inorganic and coordination compounds*, 2nd ed.; Wiley-Interscience: New York, 1963.

(23) Werner, P. E.; Eriksson, L.; Westdahl, M. *J. Appl. Crystallogr.* **1985**, *18*, 367−370.

(24) De Wolff, P. M. *J. Appl. Crystallogr.* **1968**, *1*, 108−113.

(25) Smith, G. S.; Snyder, R. L. *J. Appl. Crystallogr.* **1979**, *12*, 60−65.

(26) Altomare, A.; Burla, M. C.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G. *J. Appl. Crystallogr.* **1995**, *28*, 842−846. Altomare, A.; Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, G.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Rizzi, R. *J. Appl. Crystallogr.* **1999**, *32*, 339−340.

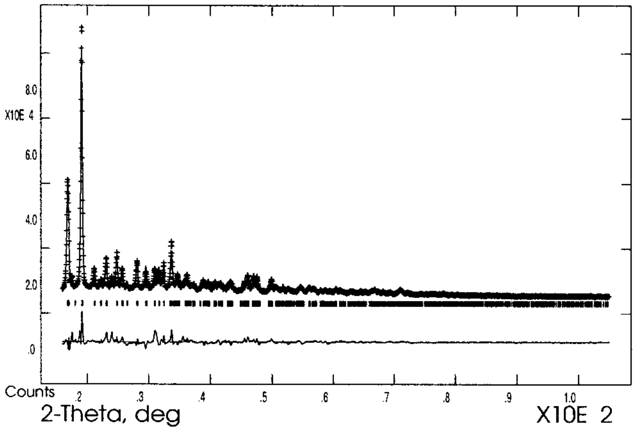
approximate coordinates for the remaining non-hydrogen atoms were later obtained. Additional optimization of the resulting stereochemistries was performed by minimizing the overall (intramolecular + packing) steric energy by a locally developed molecular mechanics program (based on MM3 and capable of dealing with crystal lattices and polymeric systems[27]).

The final refinements were performed with the aid of the GSAS suite of programs,[28] by imposing steric restraints to the rigid imidazolate rings, which were idealized with average literature values (C−C and C−N, 1.36 Å; all internal angles set at 108°). Soft restraints were also applied to Cu−N distances (2.00 Å) and to (some of the) Cu−C interactions, in order to maintain plausible Cu−N−C angles. The peak shapes were best described by the Thompson/Cox/Hastings formulation[29] of the pseudo Voigt function, with GV and LY set to zero. The experimental background was modeled by a cosine Fourier series, while systematic errors were corrected with the aid of sample-displacement angular shifts and preferred orientation corrections [with (001), (100), and (110) poles, for **B**, **G**, and **O**, respectively]. Metal atoms were given a refinable isotropic displacement parameter [U_{iso}(M)], while lighter atoms' U's were arbitrarily given [U_{iso}(M) + 0.02] Å^2 values. The contribution of the hydrogen atoms to the scattered intensity was neglected. Scattering factors, corrected for real and imaginary anomalous dispersion terms, were taken from the internal library of GSAS. Final R_p, R_{wp}, and R_F agreement factors, together with details of the data collections and analyses for the three crystal phases, can be found in Table 1. Figure 1 shows the final Rietveld refinement plots. Final fractional coordinates and full lists of bond distances and angles are supplied as Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 159161, 159162, and 159163. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223 336−033; e-mail, deposit@ccdc.cam.ac.uk).

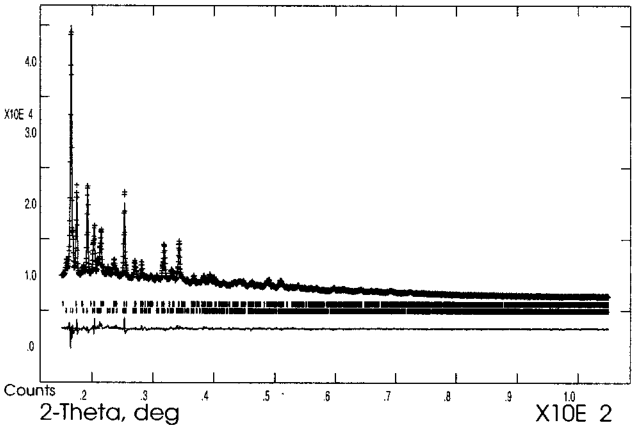
Results

Crystal Structure of the Blue Polymorph. Crystals of **B** contain a crystallographically unique copper atom and two independent imidazolate fragments, bridging copper atoms which are 5.98−6.00 Å apart. The coordination at the metals is "close" to square planar, but a significant bending toward a flattened tetrahedral geometry (trans N−Cu−N angles of ca. 140° and 155°) is also observed. The overall framework generated by the four-connected metals and the space group symmetry is topologically equivalent to the sodalite archetype,[30] with fused four- and six-membered rings in a *three-dimensional* net (see Figures 2 and 3). It is noteworthy that rather large tunnels (of 90 Å^3 each *per unit cell period*, with shortest centroid-to-C atom contact of 3.84 Å), aligned with *c*, are present (accounting for ca. 7.5% of the cell volume); they could host, at least in principle, water molecules, the presence of which was, however, ruled out by analytical, spectroscopic, and diffraction evidence.

Crystal Structure of the Green Polymorph. As shown in Figures 3 and 4, crystals of **G** are slightly more complex: they contain two crystallographically unique copper atoms (one on a 222 site and the other in a general position), two fully independent imidazolate fragments, and, finally, an imidazolate ligand bisected by a crystallographic 2-fold axis (aligned with *a*), thus leading to the unusual $Z = 20$ value. Also in this case, copper atoms show tetrahedrally distorted square-planar coordination (trans N−Cu−N angles of 154° for Cu1 and 142° and 138° for Cu2), and are bridged by the imidazolate ligands at Cu···Cu separations of 5.92−5.94 Å. The overall connectivity generates infinite *two-dimensional* slabs of Cu(im)$_2$, about 10 Å thick, which are stacked in the *a* direction. Only H···H contacts exist between these (very slightly) interdigitated slabs, thus accounting for the cleavage or morphology effects evidenced by the extreme tendency toward preferred orientation along the (100) pole. Moreover, the high-symmetry Cu1 atom and one of the 2 and $^1/_2$ crystallographically independent imidazolates are buried within the slabs, while "surface" copper atoms (Cu2) are also bound to the remaining imidazolate ligands, which are then involved in weak *interslab* interactions.



Blue



Green

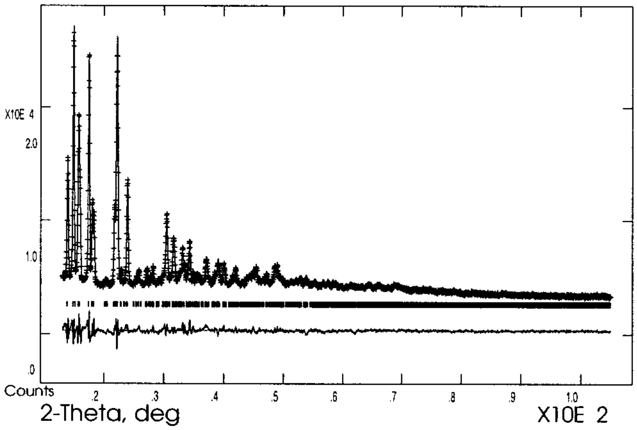


Figure 1. Rietveld refinement plots for the **B**, **G**, and **O** polymorphs. Difference plots and peak markers are at the bottom.

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(27) Mercandelli, P. L.; Moret, M.; Sironi, A. *Inorg. Chem.* **1998**, *37*, 2563−2569.

(28) Larson, A. C.; Von Dreele, R. B. *LANSCE, MS-H805*; Los Alamos National Laboratory: Los Alamos, NM, 1990.

(29) Thompson, P.; Cox, D. E.; Hastings, J. B. *J. Appl. Crystallogr.* **1987**, *20*, 79−83.

(30) O'Keeffe, M.; Eddaoudi, M.; Li, H.; Reineke, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3−20.

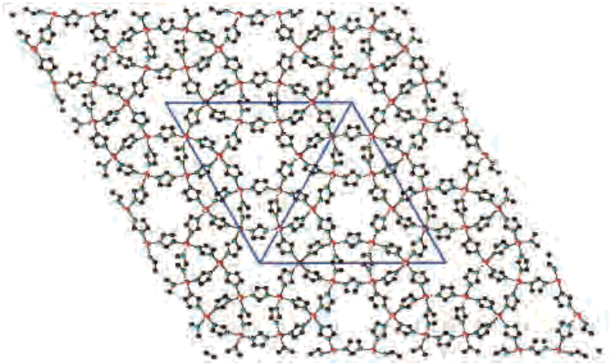

Figure 2. Drawing of the crystal structure of Cu(im)$_2$, **B** polymorph, viewed down *c*.

Crystal Structure of the Olive-Green Polymorph. Crystals of **O** contain two crystallographically unique copper atoms, one on a 2-fold axis and the other in a general position; three fully independent imidazolate fragments, bridging copper atoms which are 5.91−6.03 Å apart, complete the overall structure (see Figures 3 and 5). Again, the coordination at the metals is not regular, with the higher symmetry copper atom more distorted than the other (with flattened tetrahedral geometry and trans N−Cu−N angles of ca. 140° for the first and 146° and 157° for the latter). The overall framework generated by the four-connected metals and the space group symmetry is topologically equivalent to the moganite archetype,[30] (again) with fused four- and six-membered rings in a *three-dimensional* net. Also in this case large, *but closed*, cavities (four per cell, of 65 Å^3 each, ca. 11% of the total volume) are found, affording the least dense packing among all polymorphic species.

Crystal Structure of the Blue J Polymorph. Since its atomic coordinates are not published in the original paper, nor are they deposited in the Cambridge Data File, we have included, within Figure 3, a schematic drawing of the topology of the **J** phase (PtS[30]), derived from the crystallographic data reported in ref 14, which contains a more detailed description of this polymorph.

As mentioned earlier, powders of the pink polymorph, **P**, gave highly reproducible XRPD patterns, which, however, owing to their complexity and broad peak features, did not afford, so far, a reliable indexing, nor, obviously, any structural model. From the above analyses and spectroscopic evidence, it seems however highly probable that, in contrast to recent observations for the pyrazolate anion (which has been found to afford a variety of exotic coordination modes[31]), imidazolates behave as exo-bidentate ligands, bridging Cu···Cu atoms which are (slightly less than) 6.0 Å apart. It is also possible that, given the quantitative transformation of the **P** phase into the **B** one (if heated, under nitrogen atmosphere, above 215 °C, vide supra), these two phases share a partial, but still unknown, structural resemblance.

Isomorphous species which could shed some light on the structural features of **P** include two other M(im)$_2$ species, characterized by conventional single-crystal methods: the cobalt[32] and zinc[33] derivatives, which, in spite of sharing similar lattice parameters and the same Bravais lattice (tetragonal I), have been unambiguously assigned to different space groups with different structures, with only vague relations between each other. In these compounds, all metals are nearly tetrahedral, which may suggest that further, still unknown, Cu(im)$_2$ polymorphs may adopt one of these structures, if severe distortions from square-planar coordination (which copper can indeed sustain) occur. However, it appears that the **P** polymorph does not match any of these known structures.

Table 2. Synoptic Collection of Metal Diazolate and Pyrimidinolate Phases of General Formula ML$_2$

phase	metal stereochem		L	network topology	smallest circuits	ref
Co(im)$_2$	*Co*[a]	T[b]	im	3D-tetranodal	4, 8	32
Cu(im)$_2$ **J**	*Cu*	see text	im	3D-PtS[30]	4, 6	13
Cu(im)$_2$ **B**	Cu	see text	im	3D-sodalite[30]	4, 6	*e*
Cu(im)$_2$ **G**	Cu	see text	im	2D-complex	5	*e*
Cu(im)$_2$ **O**	Cu	see text	im	3D-moganite[30]	4, 6	*e*
Cu(im)$_2$ **P**	Cu	n/a	im	unknown	n/a	*e*
Zn(im)$_2$	*Zn*	T	im	3D-banalsite[47]	4, 6	33
Co(pymo)$_2$	Co	T	pymo	3D-diamond	6	40
Ni(pymo)$_2$	Ni	DT[c]	pymo	3D-diamond	6	40
Zn(pymo)$_2$	Zn	T	pymo	3D-diamond	6	40
Co(pz)$_2$	Co	T[d]	pz	1D-chain[d]	2	48
Cu(pz)$_2$	*Cu*	DT	pz	1D-chain	2	49
Zn(pz)$_2$	Zn	T	pz	1D-chain	2	17c

[a] Species with italicized symbols have been studied by conventional single-crystal techniques. [b] T = tetrahedron; DT = heavily distorded tetrahedron. [c] Neglecting ancillary Ni···O interactions. [d] Inferred from temperature-dependent magnetic susceptibility and morphologic evidence. [e] This work.

FTIR and Raman Spectra. For all the polymorphs of Cu(im)$_2$ synthesized in this work, both IR and Raman spectra, in the 1700−400 cm^{-1} region, are completely coincident, since all vibrational bands observed in this frequency range can be assigned to the μ-imidazolate ligands (see Table 4); consequently, they also match the IR spectrum reported for the related, but not isostructural,[32] cobalt complex Co(im)$_2$.[34] Bands in similar positions have also been recognized in the vibrational spectra of a series of copper imidazolate complexes with ancillary ligands.[3c]

Accordingly, the observed infrared frequencies correspond well to those reported in ref 7 for “blue” Cu(im)$_2$, probably a mixture of **B** and **J** (see above). On the contrary, the only Raman spectrum ever presented in the literature[12] for Cu(im)$_2$, namely, for the supposed-to-be polymorph **J**, shows a pattern completely different from those obtained in this work. Instead, it closely resembles the Raman spectrum of the intermediate of the synthesis of the polymorph **B**, [Cu(imH)$_2$(CO$_3$)]·H$_2$O (see Experimental Section), that, being itself blue/violet-colored, was probably confused with the imidazolate complex.

In the low-frequency region below 400 cm^{-1}, the Raman spectra of the polymorphs of Cu(im)$_2$ show only one band corresponding to a Cu−N stretching mode, situated at 370−360 cm^{-1}. The better resolved IR spectra allow one to detect significant differences between the polymorphs, related to the changes in their structure. In these spectra, a varying number of bands are observed between 350 and 320 cm^{-1}, quite a high-frequency value for Cu−N stretching modes, probably related to the high basicity of the imidazolate ligand.[35]

The multiplicity of the bands appears to be mainly related to the number of different environments of copper ions, rather than to the distortion from regular geometries. Indeed, both for a regular tetrahedral and for a regular square-planar molecule a

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(31) Deacon, G. B.; Gitlits, A.; Roesky, P. W.; Bürgstein, M. R.; Lim, K. C.; Skelton, B. W.; White, A. H. *Chem. Eur. J.* **2001**, *7*, 127−138 and references therein.

(32) Sturm, M.; Brandel, F.; Engel, D, Hoppe, W. *Acta Crystallogr.* **1976**, *B31*, 2369−2378.

(33) Lehnert, R.; Seel, F. *Z. Anorg. Allg. Chem.* **1980**, *464*, 187−194.

(34) Cordes, M.; Walter, J. L. *Spectrochim. Acta* **1968**, *24A*, 237.

(35) Ferraro, J. R. *Low-Frequency Vibrations of Inorganic and Coordination Compounds*; Plenum Press: New York, 1971; pp 202−204.

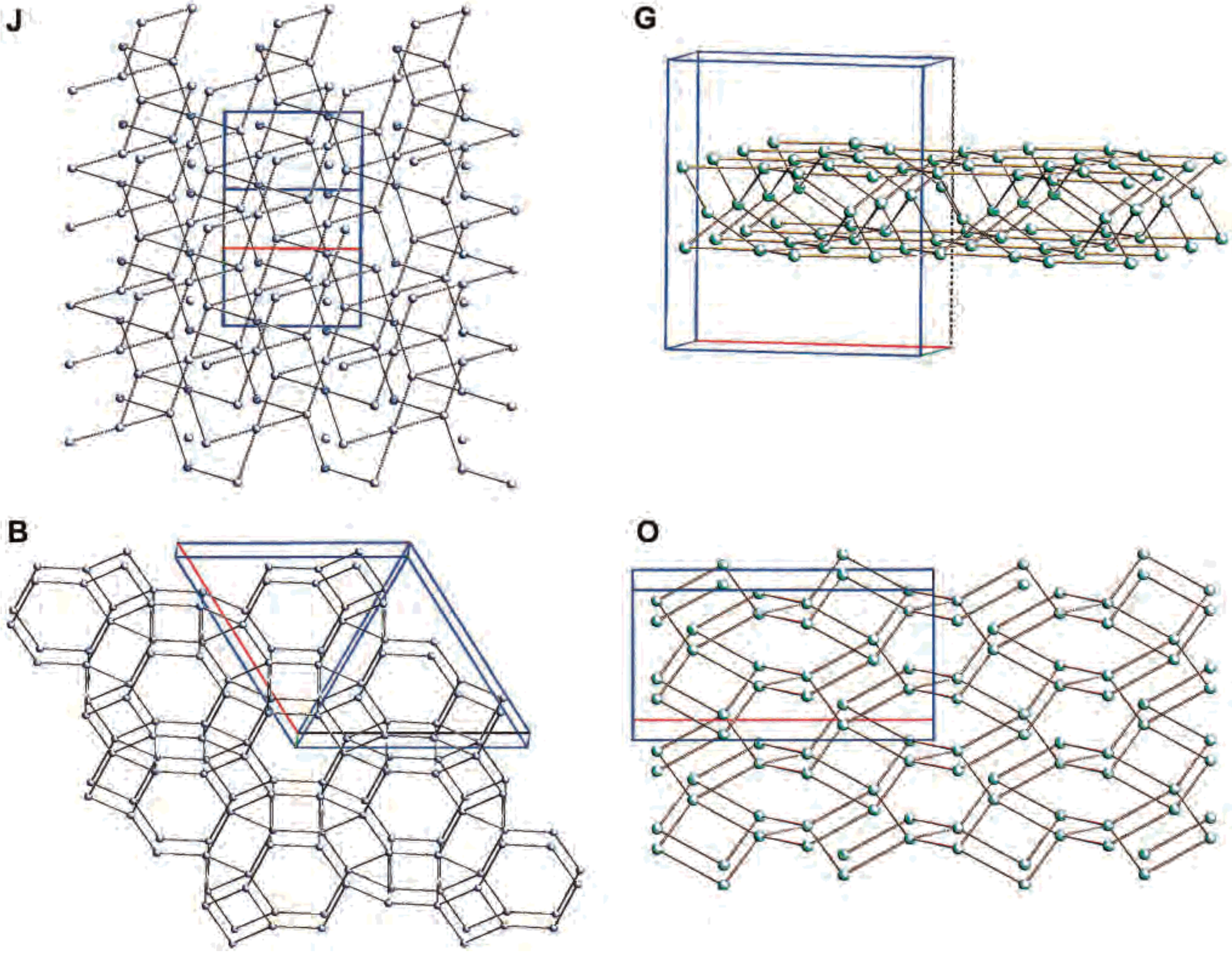

Figure 3. Schematic drawing of the overall topologies of **J**, **B**, **G**, and **O**, highligting Cu(μ-im)Cu interactions.

Table 3. Relevant Geometrical Parameters[a] for the Four Structurally Characterized Cu(im)$_2$ Polymorphs

	blue, **J**	blue, **B**	green, **G**	olive, **O**
site sym Cu1	[−1]	[1]	[222]	[2]
site sym Cu2	[2]		[1]	[1]
Cu1−Cu1′	5.888	5.978(7)−5.997(5)		
Cu1−Cu2	5.914		5.921(4)	5.939(5)−6.030(5)
Cu2−Cu2′			5.936(5)	5.907(5)
trans N−Cu1−N	180	139.6−154.8	154.0	140.8
trans N−Cu2−N	140		138.4−142.5	146.3−157.3
ω[b]	(1) 0 − (2) 54	44	(1) 37 − (2) 54	(1) 53 − (2) 40
topology[30]	3D-PtS	3D-sodalite	2D-slabs	3D-moganite

[a] Distances in angstroms and angles in degrees (esd's in parentheses). [b] ω is here defined as the [N$_2$]Cu[N$_2$] dihedral angle, ideally 0° for square-planar and 90° for tetrahedral CuN$_4$ chromophores.

single IR-active band is expected, corresponding to a mode of T$_2$ symmetry in the former case and to a mode of E$_u$ symmetry in the latter. This hypothesis is confirmed by the far-IR spectrum of the blue polymorph **B**, showing only one band located at 348 cm^{-1}, in agreement with the presence of just one site for all copper ions in the structure (Table 3). Similarly, in the case of **G**, a band, split into three components, at 350, 341, and 326 cm^{-1}, is observed and can be assigned to Cu−N stretching for copper ions of Cu2 type, i.e., those showing a higher distortion toward a tetrahedral geometry (as shown in Table 3, such a dihedral angle ω between the two CuN$_2$ coordination planes is 54°). Indeed, in the structure of **G**, copper ions of the Cu2 type are four times more abundant than those labeled as Cu1; this fact explains the predominance of the related band in the far-IR spectrum, the degeneracy of the band being partially removed by the low site symmetry (C_1). The far-IR spectrum of **O** shows two bands, a stronger one at 346 cm^{-1} and a less intense one at 320 cm^{-1}: following the proposed interpretative scheme, the former is here attributed to Cu2 ions, twice more abundant than Cu1 ions, to which the second, weaker, band is assigned. In **O**, the site symmetry of Cu2 ions, having a coordination geometry closer to square planar, is again C_1, but this does not seem to affect the multiplicity of the band. *In the absence of structural data for the pink polymorph*, we infer that **P**, for which two bands of similar intensity are observed in the region of the Cu−N stretching modes, should contain two different, but probably equiabundant, Cu(II) sites, with nearly square-planar geometries.

Visible Spectra. The diffuse-reflectance spectral patterns of polymorphs **B**, **G**, and **O** in the 350−2000 nm region (Figure

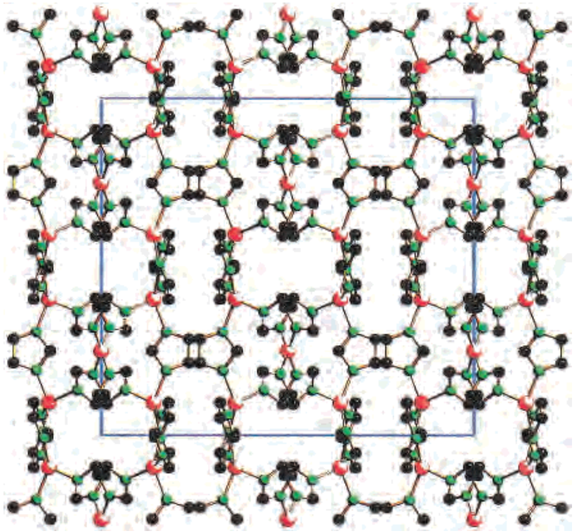

Figure 4. Drawing of the crystal structure of Cu(im)$_2$, **G** polymorph, viewed down *c*.

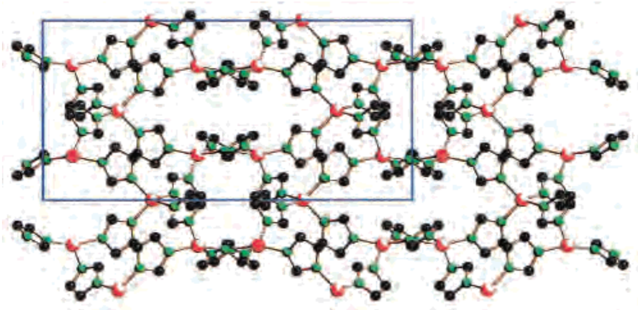

Figure 5. Drawing of the crystal structure of Cu(im)$_2$, **O** polymorph, viewed down [001].

Table 4. Vibrational Frequencies of the Polymorphs **B**, **G**, **O**, and **P** of Cu(im)$_2$ in the Range 1700−400 cm^{-1}

frequencies (cm^{-1})		
Raman	IR	assignment
	3140	ν(C−H)
	3111	
	1593	ν(C−C)
1491		ring stretching
	1473	
1320	1315	δ(C−H)
1287		ring vibrations
	1234	
1163	1168	“ring breathing”
	1084	δ(C−H)
965		
	949	ring bending
	846	
834		
767	764	γ(C−H)
	748	
669	665	Torsion

6) conform to the structural data, even if frequency assignments are complicated by overlapping of the bands. For a perfectly tetrahedral CuN$_4$ chromophore, an energy gap between d orbitals of 8000−5000 cm^{-1} is expected, while for the same chromophore with a perfect square-planar geometry, the energy difference should be around 20000 cm^{-1}.[36] For a CuN$_4$ chromophore with a geometry distorted from tetrahedral by a dihedral angle around 54°, as found for example in the case of the complex [Cu(2-pyridyl-2-pyrimidylamine)$_2$](ClO$_4$)$_2$, three bands are observed[37] at 15900, 10300, and 7500 cm^{-1} and one more is predicted at 13800 cm^{-1}. For the [Cu(2,2′-bipyridylamine)$_2$](ClO$_4$)$_2$ complex, in the visible absorption spectrum bands at 18400, 15700, 13500 and 10400 cm^{-1} are observed[32] and the stereochemistry was suggested to be square planar with a tetrahedral distortion (ω < 45°).

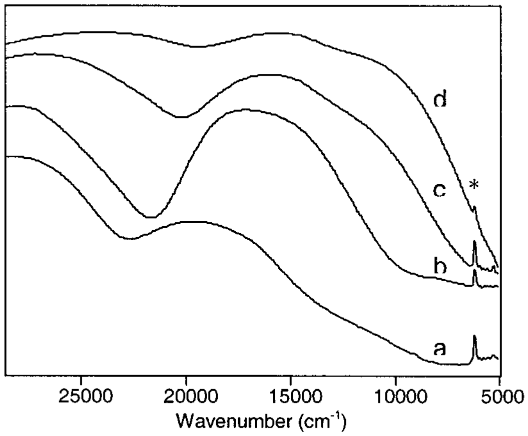

Figure 6. Diffuse-reflectance visible spectra of Cu(im)$_2$ polymorphs: (a) **P**; (b) **B**; (c) **O**; and (d) **G**. The band marked with an asterisk (same for all compounds) is due to an overtone of a vibrational mode.

On the basis of the literature data reported above, the visible spectra of **B**, **G**, and **O** are correlate with the local copper environments observed in the crystal structures, since (a) **B** shows a rather narrow absorption profile, when compared with the spectra of **G** and **O**; two components centered around 18400 and 14600 cm^{-1} are clearly detected, in agreement with the presence of a single coordination environment for copper ions with a value of 44° for ω; and (b) **G** and **O** show more complex spectra, characterized by an increasing absorption, particularly intense for **G**, at lower frequencies down to 5000 cm^{-1}; indeed both polymorphs contain copper ions in a distorted tetrahedral environment (ω = 54°), and this coordination geometry is presented by a greater fraction of copper ions in the structure of **G** than in **O**.

In addition, all polymorphs show an absorption band at frequencies higher than 20000 cm^{-1}, assigned to a charge-transfer transition. Its energy is higher for **B**, and this fact is responsible for the deep blue color of this species, to be compared with the green-colored **G** and **O**.

Finally, the pink polymorph **P** is expected to contain (more or less) square-planar reddish CuN$_4$ chromophores.[38] Nevertheless, the absorption band observed for **P** is broader than expected,[38] extending down to 10000 cm^{-1}, suggesting the presence of more than one type of crystallographically independent Cu(II) ions in the structure of this polymorph.

Discussion

In order to show the absence of any straightforward structural relationship between the different polymorphs, Figure 7 pictorially shows the *computed* traces for the five known Cu(im)$_2$ phases and for the two *known* structures of the cobalt and zinc analogues (except for the *pink* polymorph).

In the original blue phase (**J**), which did not require restrained refinements, “rigid” imidazolate ligands (planar to within 0.005 Å[14]) were found to bridge atoms which are about 5.90 Å apart,

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[36] Dudley, R. J.; Hathaway, B. J.; Hodgson, P. G. *J. Chem. Soc., Dalton Trans.* **1972**, 882.

[37] Gouge, E. M.; Geldard, J. F.; Sinn, E. *Inorg. Chem.* **1980**, *19*, 3356.

[38] Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; p 570.

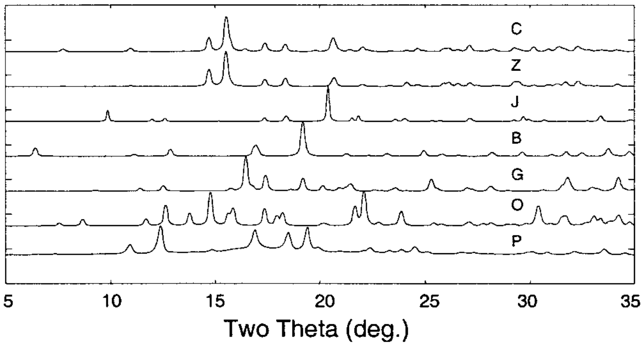

Figure 7. Top to bottom: computed XRPD patterns for Co(im)$_2$, Zn(im)$_2$, and Cu(im)$_2$ (**J**, **B**, **G**, **O** phases) and observed pattern of the P phase (5° $< 2\theta <$ 35° range).

with metals more than 0.5 Å off the best plane. **J** is the one showing the highest density (1.824 g cm^{-3}), while much lower values, down to 1.632 g cm^{-3} (**O** phase), are found for the other polymorphs. Such a 10% decrease, though not exceptional,[39] is relevant and is related to the presence of large cavities (as in **O**) or nanopores (**B** phase, see above). In the latter case, voids are estimated to account for about 15 Å^3 per Cu(im)$_2$ formula (vs ca. 22 Å^3 in **O**), thus resulting in the second least dense packing among all polymorphic species.

As shown in Table 2, three different diazaaromatic anions have been coupled to M(II) ions, and their structures solved mainly from XRPD data. While one-dimensional chains are present in all known, but not necessarily isomorphous, M(pz)$_2$ phases (pzH = pyrazole) and 2D-diamondoid structures have been found for the pymo (pymoH = 2-hydroxypyrimidine, a 1,3-diazaaromatic ligand analogue of imidazole) derivatives, the data reported in this paper show that M(im)$_2$ species can attain much more complex topologies and afford a variety of polymorphs. Obviously, (exobidentate) pyrazolates can afford M(μ-pz)$_2$M fragments, while largers circuits are needed in the presence of 1,3-diazaaromatic ligands. However, why M(im)$_2$ phases of the diamondoid type are still unknown is not clear, particularly since *all* other known M(pymo)$_2$ belong to this structural class.[40]

Thus, the structural versatility of these Cu(im)$_2$ species can be related to the wider choice of [M(im)]$_n$ circuits available (n = 4, 5, 6, ...) in their crystalline phases. The topology of the different phases can be characterized by the size of the *smallest* [Cu(im)]$_n$ circuits found, as well as by the way they are fused together. For example, the green polymorph is unique not only because it shows a lower dimensionality than all others but also because it contains five-membered, i.e., [Cu(im)]$_5$, rings, fused about the Cu1 atom in the 222 position.

Such an extended polymorphism can hardly be related to different steric and electronic requirements of the metal or among the ligands in the solid; rather, it appears that the stereochemical relationships in the nucleation process favor one polymorph over the other upon minimal changes in the synthetic procedure. Accordingly, we suggest that these polymorphs, differing in the way the different atoms are interconnected, and *particularly* in the dihedral angles between neighboring imidazolate rings, are a manifestation of the presence in solution, *before* deprotonation, of different precursors (i.e., imH-containing, possibly polynuclear, Cu(II) complexes), stable in different environments (ligand and metal concentration, acidity or ionic strength). Since the imidazolate ligands appear to be free to rotate about the M−N bonds so as to adopt whatever orientation is most favorable for packing and minimization of ring strain), we can infer that little or no $d_\pi - p_\pi$ interaction is present.

In all known Cu(im)$_2$ polymorphs, copper atoms adopt a square-planar geometry (see Table 3), but significant distortions toward a flattened tetrahedral geometry (trans N−Cu−N angles as low as 138°) are also observed. In agreement with such observations, a very recent structure correlation[41] study on four-coordinate copper(II) ions revealed that such trans angles cluster near 180°, with an extended tail of their distribution reaching rather low values (but *rarely* close to tetrahedral) and a subsidiary less pronounced maximum near 140°, mostly attributed to steric interactions.

Calorimetric measurements showed that **P** quantitatively transforms into **B** at 215 °C with ΔH of −5.5 kJ mol^{-1}. The **B**, **G**, and **O** polymorphs (and the amorphous phase as well) possess a slightly higher, and similar, thermal stability, decomposing in vacuo above 240 °C to a glossy amorphous material ($\Delta H \approx$ 30 kJ mol^{-1}) and a colorless organic species, originally described as “im” [42] in its dimeric form [1*H*,1′*H*-(2,2′)-bisimidazolyl]; an unidentified product was also reported to form upon decomposition of the **J** phase.[10] GC−MS analysis of this material revealed the trimeric nature of “im” (molecular peak for $C_9H_9N_6$ at 198 Da (Da = dalton)), with a fragmentation pattern consistent with a polycyclic *s*-triazine derivative similar (or identical) to 1,3a,4,6a,7,9a-hexaazatrindene.[43] Inter alia, the (semi)quantitative formation of this species by this method may replace the rather complex sequence of organic reactions employed in its original synthesis.[44] The thermal decomposition of Cu(im)$_2$, generated in situ from Cu(imH)$_2$(acac)$_2$ (acac = acetylacetonate), shows a very similar TG curve and a multiple step degradation to what was originally interpreted as CuCN.[42] IR evidence, however, contradicts this observation, since the spectra (Nujol mulls) are rather flat in the 2500−1800 cm^{-1} region, thus excluding the presence of cyanides (by loss of CH_3CN) and (di)cyanamides.

Conclusions

This paper focuses on the structural versatility of a “simple” species, which, even if based upon a few “local” coordination rules (four-coordinate metal atoms and μ-im spacers), affords a variety of networks in the different polymorphic phases. A recent survey has shown that, among the current entries of the Cambridge Structural Database for purely organic species, ca. 300 polymorphic species can be found, none showing more than four different crystal phases. Accordingly, the very recent report of (conformational) hexamorphism of 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile sets the actual record for systems whose crystal structures have been determined.[45] For polymeric coordination compounds, “multiple” polymorphism is a much rarer occurrence; this is quite reasonable since, due to the low directionality of most *intermolecular* interactions,

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(39) Gavezzotti, A.; Filippini, G. *J. Am. Chem. Soc.* **1995**, *117*, 12299−12305.

(40) Masciocchi, N.; Ardizzoia, G. A.; La Monica, G.; Maspero, A.; Sironi, A. *Eur. J. Inorg. Chem.* **2000**, 2507−2515.

(41) Raithby, P. R.; Shields, G. P.; Allen, F. H, Samuel Motherwell, W. D. *Acta Crystallogr.* **2000**, *B56*, 444−454.

(42) Döring, M.; Ludwig, W.; Meinert, M., Uhlig, E. *Z. Anorg. Allg. Chem.* **1991**, *595*, 45−52.

(43) Or triimidazo[1,2-*a*;1′,2′-*c*;1″,2″-*e*][1,3,5]triazine in the following: Takeuchi, Y.; Kirk, K. L.; Cohen. *J. Org. Chem.* **1979**, *44*, 4243−4246.

(44) Kirk, K. L., Nagai, W.; Cohen, L. A. *J. Am. Chem. Soc.* **1973**, *95*, 8389−8392, and references therein.

(45) Yu, L.; Stephenson, G. A.; Mitchell, C. A.; Bunnell, C. A.; Snorek, S. V.; Bowyer, J. J.; Borchardt, T. B.; Stowell, J. G.; Byrn, S. R. *J. Am. Chem. Soc.* **2000**, *122*, 585−591.

we can expect a larger number of possible “supramolecular” arrangements in molecular systems than in extended polymeric frameworks, based on “directional” covalent interactions. Thus our system is an outlier among 2D/3D polymers.

The results presented in this paper should provide caution to “crystal engineers” because, even for a rather rigid exobidentate ligand (L = im), a simple complex stoichiometry (CuL_2), and one of the most studied transition metal atoms, a number of networks have been observed. The occurrence of polymorphs can be turned into a source of information if the selective synthesis of the different species is achieved.[17a,46] Further work can be anticipated aiming to discover the real nature of **P**, and to force truly square-planar geometries upon using d^8 ions.

Acknowledgment. We thank the Italian Consiglio Nazionale delle Ricerche and MURST for funding. Dr. D. M. Proserpio is also acknowledged for helpful discussions. We thank one referee for helpful suggestions.

Supporting Information Available: Full list of fractional atomic coordinates, bond distances, and bond angles for compounds **B**, **G**, and **O**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) Masciocchi, N.; Ardizzoia, G. A.; La Monica, G.; Moret, M.; Sironi, A. *Inorg. Chem.* **1997**, *36*, 449.

(47) Smith, J. V. *Am. Mineral.* **1978**, *63*, 960−968.

(48) Ehlert, M. K.; Rettig, S. J.; Storr, A.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1993**, *71*, 1412.

(49) Ehlert, M. K.; Rettig, S. J.; Storr, A.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1989**, *67*, 1970−1974. Ehlert, M. K.; Storr, A.; Thompson, R. C.; Einstein, F. W. B.; Batchelor, R. J. *Can. J. Chem.* **1993**, *71*, 331−334.