Inorganic – Organic Hybrid Polymers *via* Hydrothermal Syntheses: Tetraaquahexakis(pyrazine-2-carboxylato)pentacopper(4 +) Hexacosaoxooctamolybdate(4 –) Polymer ($\{[Cu_5(pzca)_6(H_2O)_4][Mo_8O_{26}]\}_n$; pzca = Pyrazine-2-carboxylate) and Dicopperdecaoxo(pyrazine)trimolybdenum Polymer ($[Mo_3Cu_2O_{10}(pz)]_n$; pz = pyrazine)

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Hydrothermal reactions of MoO_3, CuO, and pyrazine-2-carboxylic acid (Hpzca) resulted in two polymeric complexes, $\{[Cu_5(pzca)_6(H_2O)_4][Mo_8O_{26}]\}_n$ (**1**; pzca = pyrazine-2-carboxylate) and $[Mo_3Cu_2O_{10}(pz)]_n$ (**2**; pz = pyrazine). The former crystallized in the monoclinic space group $P2_1/c$ with $a = 10.805(3)$ Å, $b = 13.061(5)$ Å, $c = 13.337(10)$ Å, $\beta = 90.20(4)^\circ$, $V = 2729(2)$ Å^3, and $Z = 2$. The later crystallized in the orthorhombic space group *Pnma* with $a = 12.385(2)$ Å, $b = 7.6044(9)$ Å, $c = 12.7880(14)$ Å, $V = 1204.4(2)$ Å^3, and $Z = 4$. X-Ray diffraction analysis revealed that **1** possesses a two-dimensional wave-like structure, formed from a zigzag one-dimensional chain, and **2** is a three-dimensional network structure formed from a one-dimensional chain and a pz bridging ligand. The temperature-dependent magnetic behavior of **1** was studied.

1. Introduction. – Recently, inorganic-organic materials have become extremely interesting because they not only possess potential applications in catalysis, optical material, energy storage, molecular electronics, and ceramics [1][2], but also generate diversity of structure by adjusting the proportions of inorganic and organic components. In the course of reactions of the inorganic and organic parts, the synergistic interaction between the organic and inorganic composition [3] may lead to the formation of different one-, two-, and three-dimensional hybrid materials. This kind of interaction derives from the nature of the interface between the organic and inorganic components; synthetic and structural studies of the materials that exhibit such an interface will contribute to the development of structure-function relationships for these hybrid materials [4]. Metal oxides and multifunctional ligands were often used as inorganic and organic components, respectively. To construct inorganic-organic materials, three conditions should be met: *i*) appropriate starting materials, *ii*) optimal building subunits, and *iii*) suitable reaction conditions. Along this line, *Zubieta* and co-workers have synthesized a series of novel hybrid materials, using organic-amine ligands, by hydrothermal reaction [5–10]. Recently, the structure of the complex $(Me_4N)_2[Fe(H_2O)_6][Mo_8O_{26}]$ and $(Me_4N)_2[FeMo_6O_{20}]$ has been reported [11].

Our goal is to construct porous materials in which inorganic components are linked by organic species, and organic components coordinate to metal atoms, expecting the possibility of preparing hybrid materials with two-dimensional layer of three-dimensional network structures, to explore further the relationship between the structure of such materials and their functionality, and to study their possible application as magnetic materials, in catalytic activity, and in sorption. Syntheses of these materials not only enrich the contents of coordination chemistry, but also possibly change the physical and chemical property of the incorporated single-metal oxides because of the insertion of organic components. The initially performed reaction of metal salts (Na_2MoO_4, Cu^{II}, Zn^{II}, Gd^{III}, and so on) and organic carboxylic acid ligands containing an N-atom, such as H_2pydc (= pyridine-2,5-dicarboxylic acid) and Hpzca (= pyrazine-2-carboxylic acid), in organic solvent or water according to conventional solution methods has resulted in the formation of an uncharacterized insoluble precipitate (see [12]). A careful examination of the coordination mode of the employed organic ligands reveals that the reaction rate must be reduced to avoid quick polymerization and that an unusual synthetic method should be employed to obtain single crystals suitable for X-ray analysis. Indeed, the insoluble precipitates are induced by the high coordination ability of the carboxylate moiety of pzca or pydc, and the fast formation of the complexes impedes a convenient crystal growth. Thus, we have employed hydrothermal-synthesis techniques and changed the initially used reagents: by hydrothermal reactions of Gd_2O_3, H_2pydc, $Cu(OAc)_2$ or CuO, and H_2O, we have successfully obtained two polymeric complexes, $\{[Gd_2Cu_3(pydc)_6(H_2O)_{12}]\cdot 4\,H_2O\}_n$ with a one-dimensional chain structure and $\{[Gd_4Cu_2(pydc)_8(H_2O)_{12}]\cdot 4\,H_2O\}_n$ with a three-dimensional network structure [12].

In this paper, we describe the synthesis and structural characterization of two molybdenum oxide/(organic ligand)copper compounds, *i.e.*, of $\{[Cu_5(pzca)_6(H_2O)_4][Mo_8O_{26}]\}_n$ (**1**; pzca = pyrazine-2-carboxylate) possessing a two-dimensional wave-like structure formed from a one-dimensional zigzag chain and of $[Mo_3Cu_2O_{10}(pz)]_n$ (**2**; pz = pyrazine) having a three-dimensional network structure constituted of a one-dimensional chain and bridging pz ligands, and the magnetic properties of complex **1**.

2. Results and Discussion. – 2.1. *Spectroscopies.* The IR spectrum of **1** exhibits a series of bands characteristic of deprotonated pyrazine-2-carboxylic acid in the range 1061 – 1618 cm^{-1} and typical bands of the coordinated H_2O (broad at 3438 and sharp at 1653 cm^{-1}). The absence of a band in the range 1690 – 1730 cm^{-1} (C=O of CO_2H) is in agreement with a carboxylate group. The bands at 796 and 860 cm^{-1} are typical absorptions of the Mo=O bond from the $[Mo_8O_{26}]^{4-}$ anion. The IR spectrum of **2** exhibits strong absorption bands between 849 and 899 cm^{-1} attributed to $\tilde{\nu}$(Mo=O), and a 746 – 850 cm^{-1} region for $\tilde{\nu}$(Mo–O–Mo). The absorptions at 1417, 1153, and 1061 cm^{-1} are characteristic of pyrazine.

The ESR spectrum of a powder sample of **1** shows a rhombic signal with $g_\parallel$ at 2.105 and $g_\perp$ at 2.005 with an average g value of 2.056 both at room temperature and at liquid-nitrogen temperature. The signal is ascribed to the Cu^{II} center with d^9 configuration.

2.2. *Structure Description.* X-Ray single-crystal diffraction analysis revealed that **1** adopts a two-dimensional wave-like structure constituted of the basic unit $\{[Cu_5(pzca)_6(H_2O)_4][Mo_8O_{26}]\}$, which is composed of a β-Mo_8O_{26} cluster anion and the $[Cu(pzca)(H_2O)]$ and $[Cu(pzca)_2]$ subunits, as shown in *Fig. 1.* In the cluster anion, the molybdate core consists of edge-sharing $[MoO_6]$ octahedrons in the compact β-molybdate geometry [13]. The coordination modes of the pzca ligands in **1** are shown in

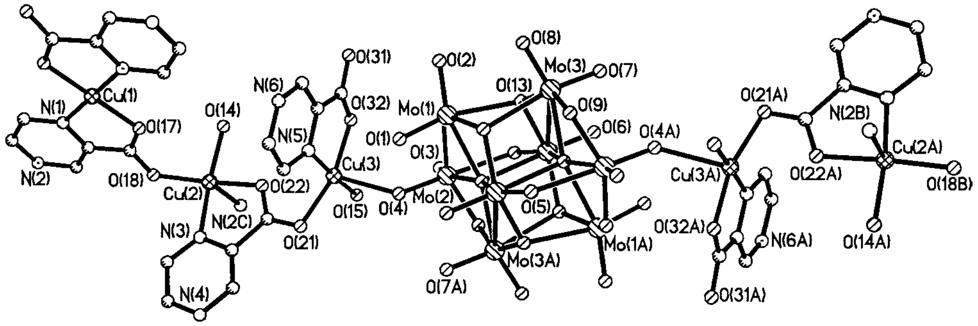

Fig. 1. *Building unit {[$Cu_5(pzca)_6(H_2O)_4$][Mo_8O_{26}]} of* **1**

Fig. 2, in which all N- and O-atoms of the pzca ligands certainly coordinate to Cu-atoms. In mode **a**, coordination to 1 Cu^{II} center occurs by 1 N- and 1 O-atom in a five-membered chelate ring; in mode **b**, pzca is coordinated to 2 Cu^{II} centers by 2 O- and 1 N-atom, both O-atoms of the carboxylate acting as donor atoms; in mode *c*, coordination to 3 Cu^{II} centers by 2 N- and 2-O-atoms is present. There are three coordination geometries of the Cu^{II} centers of **1**: Cu(1) is coordinated by 2 N- and 2 O-atoms of two pzca ligands to form a distorted square-planar [CuO_2N_2] geometry. Cu(2) is five-coordinated by O- and N-atoms of three different pzca ligands and a H_2O molecule. Cu(3) is coordinated by 1 N-atom of pzca and 4 O-atoms, of which 2 belong to carboxylate groups of different pzca ligands, 1 to a H_2O molecule, and 1 to the [Mo_8O_{26}] anion. Cu(1), Cu(2), and Cu(3) are connected by N- and O-atoms of pzca ligands forming an infinite structure, and a [Mo_8O_{26}] unit is inserted between 2 Cu(3) atoms through a Cu(3)–O(4) bond. Thus, the β-Mo_8O_{26} cluster anion and the [Cu(pzca)(H_2O)] and [$Cu(pzca)_2$] subunits are linked by Cu–O and Mo–O bonds forming a linear building unit. Such units link themselves head to tail through Cu–O and Cu–N bonds to form zigzag one-dimensional chain structures, which are further connected again by Cu(2)–N(2) and Cu–O_{pzca} bonds to generate an extended two-dimensional structure with a wave-like structure, as shown in *Fig. 3*.

The structure of **2** is a three-dimensional polymer $[Mo_3Cu_2O_{10}(pz)]_n$, which consists of a $[Mo_3O_{10}]^{2-}$ anion chain with incomplete cube-like packing and $[Cu_2(pz)]^{2+}$, as shown in *Fig. 4*. The anion chain in **2** is composed of incomplete cube-like [Mo_3O_4] units, which are linked by edge-sharing Mo-atoms. All molybdenum sites show [MoO_6] octahedral geometry, each of which has two terminal molybdyl (Mo=O) groups and three O-atoms that share the [CuO_3N] tetrahedron and/or the [MoO_6] octahedron. In

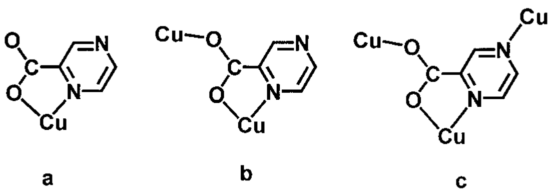

Fig. 2. *Coordination modes* **a**–**c** *of the pzca ligand*

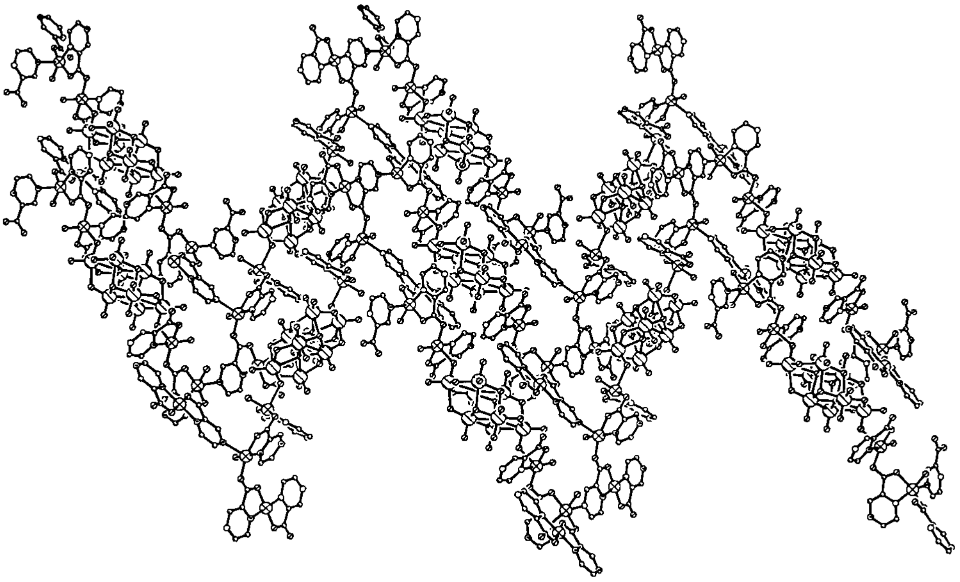

Fig. 3. *Two-dimensional network structure of* **1**

$[Cu_2(pz)]^{2+}$, the Cu-atom is coordinated by 1 N-atom of the pz ligand and 3 terminal O-atoms of two different $[Mo_3O_{10}]$ chains to give rise to a distorted tetrahedral geometry. Along different directions, the Cu-atoms, like a triangle pincer, tightly clutch the $[Mo_3O_{10}]$ chains. Thus, different $[Mo_3O_{10}]$ units are linked by a $[Cu_2(pz)]$ unit to form a three-dimensional network (*Fig. 5*). This structure is quite different from the previously reported one of $[Co(2,2'\text{-bpy})Mo_3O_{10}]$ [14].

To obtain more Mo–Cu inorganic-organic hybrid polymers with different ratios Mo/Cu, the reactions of MoO_3, CuO, Hpzca, and H_2O in different molar ratios Mo/Cu/Hpzca were carried out; however, the polymer **1** was always obtained. By changing the reaction temperature, **2** was isolated in high yield. It is interesting to note that, in the preparation of **2**, the starting Cu^{II} reagent was reduced to a Cu^{I} species by the organic pzca ligand under the hydrothermal reaction conditions, thus generating a repository of a reduced metal species for further aggregation [15]. In this reduction, pzca was decarboxylated to give pz. Since the reaction generated one-dimensional molybdenum-oxide chains, which are a recurring theme in oxide structural chemistry [16], and appropriate (ligand) metal subunits $[Cu_2(pz)]$, it is beneficial to make one-dimensional molybdenum-oxide chains turn into three-dimensional inorganic-organic hybrid materials by bridging O-atoms.

2.3. *Magnetic Properties.* The magnetic behavior of compound **1** was studied, and the $\chi_M T$ *vs.* T plots of the magnetic susceptibility for **1** is shown in *Fig. 6*. The observed $\chi_M T$ value is 2.216 cm^3 K mol^{-1} at 299 K and remains essentially constant down to 75 K. It then slightly increases and, upon further lowering the temperature, reaches a value of 3.31 cm^3 K mol^{-1} at 5.01 K, which indicates the presence of a ferromagnetic interaction between the Cu^{II} ions. The experimental effective magnetic moment (μ_{eff}) is 4.21 μ_B at

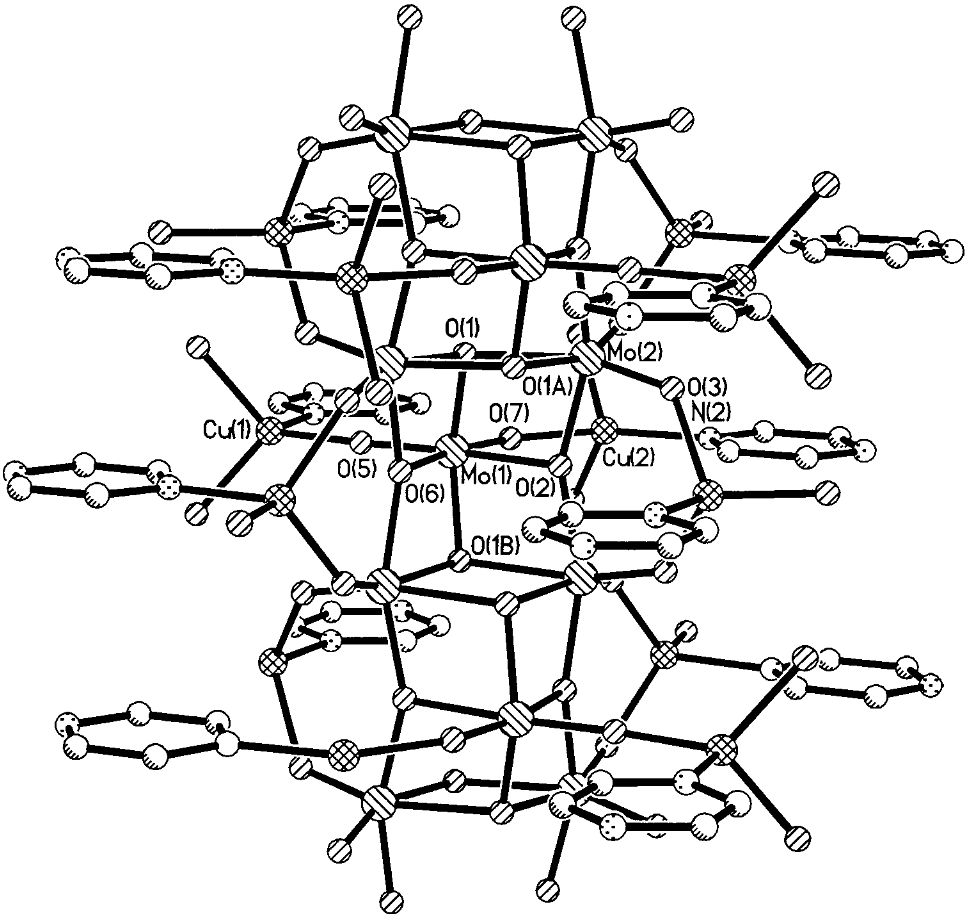

Fig. 4. *Chain structure of* **2**

room temperature, which is slightly higher than the theoretical value of 3.87 μ_B (five Cu^{II}), establishing a weak magnetic exchange interaction between the Cu^{II} ions. The $1/\chi_M$ *vs.* T plot, assuming that the Cu-unit obeys the *Curie-Weiss* law ($\chi_M = C/(T - \theta)$) with *Weiss* constant $\theta = 2.41(18)$ K and $C = 2.218(3)$ K cm^3 mol^{-1}, suggests that compound **1** is most likely a weak ferromagnetic material. However, because of the complicated structure of the compound, no satisfactory fit to a model could be derived. The magnetic behavior of **1** differs from those of discrete- or infinite-structure complexes of Cu^{II}, which normally show antiferromagnetic interactions [17][18].

3. Conclusion. – Two inorganic-organic hybrid coordination polymers were synthesized by the hydrothermal reaction of MoO_3, CuO, and pzca at 130–170°. Under the different reaction conditions, the pzca ligand decomposed at elevated temperatures; the same starting reagents resulted in the formation of different structure types, *i.e.* of complex **1** and **2**. The former possesses a two-dimensional wave-

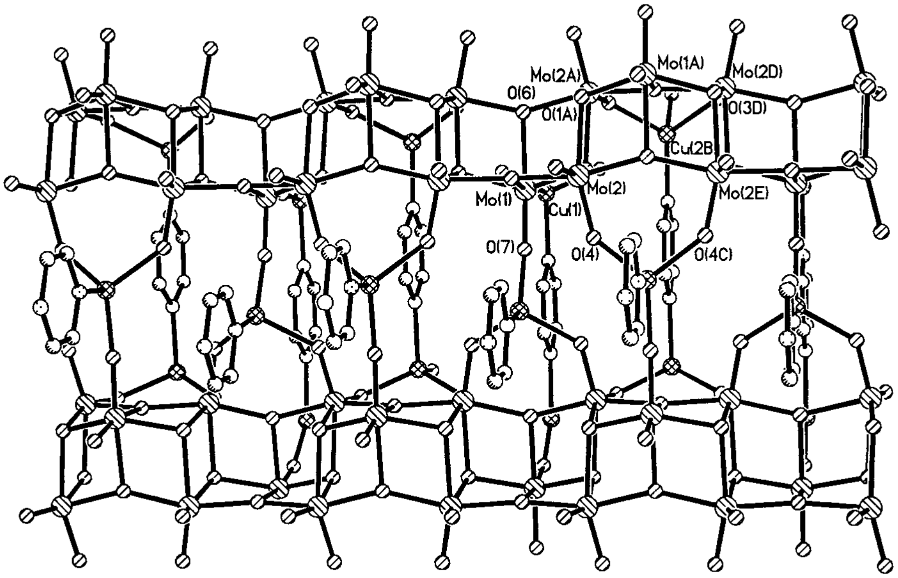

Fig. 5. *Three-dimensional network formed from chain structure* $[Mo_3Cu_2O_{10}]_n$ *and connecting pz bridges*

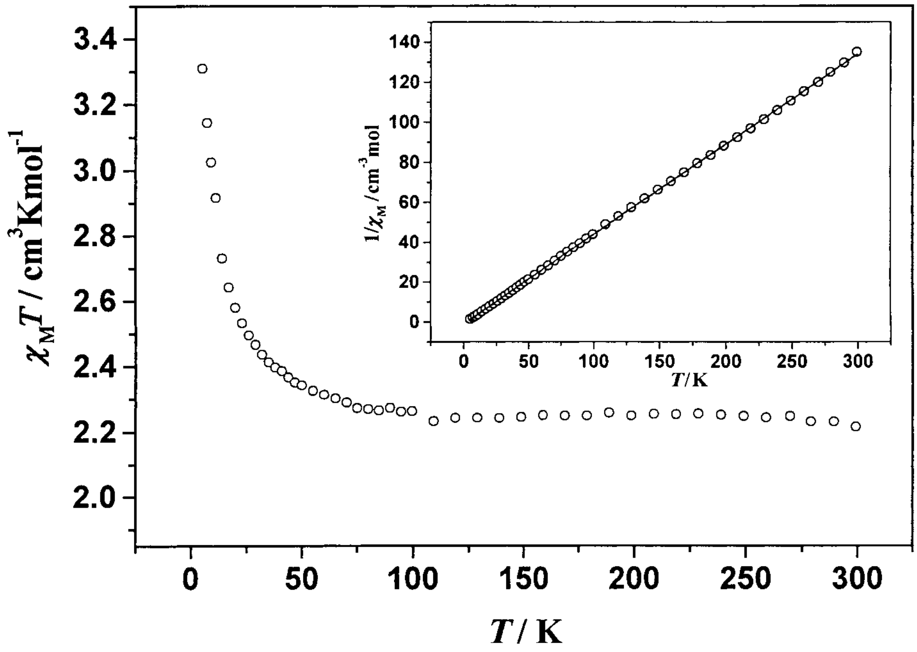

Fig. 6. *Experimental* χ_MT vs. T *curves for complex* **1**

like structure that consists of zigzag inorganic-organic chains. The later is a three-dimensional network structure made up of molybdenum oxide inorganic chains and simple $[Cu_2(pz)]^{2+}$ units, and adjacent inorganic chains are further linked by $[Cu_2(pz)]^{2+}$ units. The syntheses of **1** and **2** provide a new approach to prepare inorganic-organic hybrid materials, *i.e.* inorganic-organic coordination compounds, which we currently study further by changing the organic ligand.

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Experimental Part

General. All reagents were commercially available and used without further purification. IR Spectra: *Magna 750-FT-IR* spectrophotometer; KBr pellets; 4000 – 400 cm^{-1} region; in cm^{-1}. Magnetic susceptibility data of **1**: *Quantum-Design PPMS-6000* magnetometer, external field 10 KG, temp. range 5 – 300 K, polycrystalline samples; data corrected for experimentally determined diamagnetism of the sample holder and the diamagnetism of the samples calculated from *Pascal*'s constants [19]. ESR Spectra: *Bruker 420* spectrophotometer. Elemental analysis of C, H, N was carried out in our institute.

Tetraaquahexakis(pyrazine-2-carboxylato)pentacopper(4+) Hexacosaoxooctamolybdate(4−) Polymer ($[\{Cu_5(pzca)_6(H_2O)_4\}(Mo_8O_{26})]_n$; **1**). A mixture of MoO_3 (144 mg), CuO (80 mg), pyrazine-2-carboxylic acid (124 mg), and H_2O (16.0 ml) was sealed in a *Teflon*-lined stainless-steel reactor, heated to 130° at 10°/h and then at constant temp. for 72 h. Subsequent slow cooling to r.t. at 5°/h gave block-shaped green crystals of **1** (77%). IR (KBr): 3438*s* (br.), 1653v*s*, 1618v*s*, 1589*s*, 1416*m*, 1352v*s*, 1292*m*, 1174*m*, 1163*m*, 1061*s*, 1047*m*, 860*m*, 796*m*,

Table 1. *Crystal-Structure Determination of* **1** *and* **2**

	1	**2**
Empirical formula	$C_{30}H_{26}Cu_5Mo_8N_{12}O_{42}$	$C_4H_4Cu_2Mo_3N_2O_{10}$
M_r	2311.85	655.00
Space group	$P2_1/c$	*Pnma*
a/Å	10.805(3)	12.385(2)
b/Å	13.061(5)	7.6044(9)
c/Å	19.34(1)	12.788(1)
α/°	90	90
β/°	90.20(4)	90
γ/°	90	90
V/Å^3	2729(2)	1204.4(2)
Z	2	4
ρ_{cal}/g cm^{-3}	2.814	1.806
T/K	293(2)	293(2)
μ/mm^{-1}	3.801	3.283
λ/Å (Mo$K\alpha$)	0.71073	0.71073
F(000)	2214	612
2θ range/°	2.76 – 50.06	4.58 – 50.06
Reflections measured	13744	3434
Independent reflections	4816	1141
Observed reflection	4799	1140
Variables	439	115
$R(F_o)$	0.0587	0.0491
R_w (F_o)	0.0893	0.0999
S	1.093	1.112
Largest difference peak and hole/e · Å^{-3}	1.140, − 1.102	1.835, − 1.347

Table 2. *Bond Lengths* [Å] *and Angles* [°] *for* **1**[a])

Mo(1)–O(1)	1.705(8)	Mo(4)–O(6)	1.689(7)
Mo(1)–O(2)	1.712(7)	Mo(4)–O(12)	1.749(7)
Mo(1)–O(10)	1.896(8)	Mo(4)–O(5)	1.952(7)
Mo(1)–O(5)#1	1.979(8)	Mo(4)–O(13)	1.960(7)
Mo(1)–O(11)	2.367(7)	Mo(4)–O(11)#1	2.131(8)
Mo(1)–O(13)	2.376(7)	Mo(4)–O(11)	2.423(7)
Mo(2)–O(3)	1.710(8)	Cu(1)–O(17)	1.953(7)
Mo(2)–O(4)	1.722(8)	Cu(1)–N(1)	1.987(9)
Mo(2)–O(9)#1	1.899(7)	Cu(2)–O(18)	1.929(7)
Mo(2)–O(10)	1.933(7)	Cu(2)–O(22)	1.966(8)
Mo(2)–O(12)	2.274(7)	Cu(2)–O(14)	1.966(7)
Mo(2)–O(11)	2.451(8)	Cu(2)–N(3)	2.000(10)
Mo(3)–O(7)	1.694(8)	Cu(2)–N(2)#3	2.327(9)
Mo(3)–O(8)	1.707(7)	Cu(3)–O(32)	1.937(8)
Mo(3)–O(9)	1.922(8)	Cu(3)–O(15)	1.967(8)
Mo(3)–O(13)	1.988(8)	Cu(3)–O(21)	1.974(8)
Mo(3)–O(11)#1	2.291(7)	Cu(3)–N(5)	1.988(10)
Mo(3)–O(5)#1	2.369(7)	Cu(3)–O(4)	2.401(8)
Mo(3)–Mo(4)	3.197(2)		
O(1)–Mo(1)–O(2)	105.5(4)	O(10)–Mo(2)–O(11)	74.7(3)
O(1)–Mo(1)–O(10)	101.4(4)	O(12)–Mo(2)–O(11)	70.0(3)
O(2)–Mo(1)–O(10)	101.3(4)	O(7)–Mo(3)–O(8)	104.4(4)
O(1)–Mo(1)–O(5)#1	98.7(4)	O(7)–Mo(3)–O(9)	100.3(4)
O(2)–Mo(1)–O(5)#1	101.3(3)	O(8)–Mo(3)–O(9)	101.2(4)
O(1)–Mo(1)–O(11)	93.3(3)	O(7)–Mo(3)–O(13)	98.8(4)
O(10)–Mo(1)–O(11)	77.4(3)	O(8)–Mo(3)–O(13)	99.8(3)
O(5)#1–Mo(1)–O(11)	72.3(3)	O(7)–Mo(3)–O(11)#1	95.6(3)
O(2)–Mo(1)–O(13)	89.2(3)	O(9)–Mo(3)–O(11)#1	77.4(3)
O(10)–Mo(1)–O(13)	81.5(3)	O(13)–Mo(3)–O(11)#1	74.1(3)
O(5)#1–Mo(1)–O(13)	71.6(3)	O(8)–Mo(3)–O(5)#1	87.6(3)
O(11)–Mo(1)–O(13)	71.8(2)	O(9)–Mo(3)–O(5)#1	84.1(3)
O(3)–Mo(2)–O(4)	103.3(4)	O(13)–Mo(3)–O(5)#1	71.7(3)
O(3)–Mo(2)–O(9)#1	100.7(4)	O(11)#1–Mo(3)–O(5)#1	72.3(2)
O(4)–Mo(2)–O(9)#1	101.4(3)	O(6)–Mo(4)–O(12)	104.7(4)
O(3)–Mo(2)–O(10)	104.0(3)	O(6)–Mo(4)–O(5)	101.3(3)
O(4)–Mo(2)–O(10)	97.5(3)	O(12)–Mo(4)–O(5)	96.1(3)
O(3)–Mo(2)–O(12)	91.8(3)	O(6)–Mo(4)–O(13)	102.4(3)
O(9)#1–Mo(2)–O(12)	76.8(3)	O(12)–Mo(4)–O(13)	96.5(3)
O(10)–Mo(2)–O(12)	77.1(3)	O(5)–Mo(4)–O(13)	149.3(3)
O(4)–Mo(2)–O(11)	95.0(3)	O(6)–Mo(4)–O(11)#1	100.4(4)
O(9)#1–Mo(2)–O(11)	73.8(3)	O(5)–Mo(4)–O(11)#1	78.3(3)
O(13)–Mo(4)–O(11)#1	78.4(3)	O(21)–Cu(3)–O(4)	102.5(3)
O(12)–Mo(4)–O(11)	79.3(3)	N(5)–Cu(3)–O(4)	95.9(4)
O(5)–Mo(4)–O(11)	77.1(3)	Mo(2)–O(4)–Cu(3)	126.7(4)
O(13)–Mo(4)–O(11)	78.0(3)	Mo(4)–O(5)–Mo(1)#1	110.7(3)
O(11)#1–Mo(4)–O(11)	75.6(3)	Mo(4)–O(5)–Mo(3)#1	110.0(3)
O(17)–Cu(1)–N(1)	83.6(3)	Mo(1)#1–O(5)–Mo(3)#1	104.2(3)
O(17)#2–Cu(1)–N(1)	96.4(3)	Mo(2)#1–O(9)–Mo(3)	116.9(4)
O(17)#2–Cu(1)–N(1)#2	83.6(3)	Mo(1)–O(10)–Mo(2)	116.4(4)
O(18)–Cu(2)–O(14)	92.2(3)	Mo(4)#1–O(11)–Mo(3)#1	92.5(3)
O(22)–Cu(2)–O(14)	89.0(3)	Mo(4)#1–O(11)–Mo(1)	91.7(3)
O(18)–Cu(2)–N(3)	94.5(4)	Mo(3)#1–O(11)–Mo(1)	163.6(4)
O(22)–Cu(2)–N(3)	82.3(4)	Mo(4)#1–O(11)–Mo(4)	104.4(3)

Table 2 (cont.)

O(18)–Cu(2)–N(2)#3	103.9(3)	Mo(3)#1–O(11)–Mo(4)	97.6(3)
O(22)–Cu(2)–N(2)#3	91.7(3)	Mo(1)–O(11)–Mo(4)	96.7(3)
O(14)–Cu(2)–N(2)#3	92.3(3)	Mo(4)#1–O(11)–Mo(2)	164.3(4)
N(3)–Cu(2)–N(2)#3	94.5(4)	Mo(3)#1–O(11)–Mo(2)	86.7(2)
O(32)–Cu(3)–O(15)	92.2(3)	Mo(1)–O(11)–Mo(2)	85.0(2)
O(15)–Cu(3)–O(21)	93.4(3)	Mo(4)–O(11)–Mo(2)	91.3(3)
O(32)–Cu(3)–N(5)	83.4(4)	Mo(4)–O(12)–Mo(2)	119.4(4)
O(21)–Cu(3)–N(5)	90.1(4)	Mo(4)–O(13)–Mo(3)	108.1(3)
O(32)–Cu(3)–O(4)	93.2(3)	Mo(4)–O(13)–Mo(1)	110.9(3)
O(15)–Cu(3)–O(4)	86.7(3)	Mo(3)–O(13)–Mo(1)	103.6(3)

[a]) Symmetry transformations used to generate equivalent atoms: #1 $-x+2$, $-y+1$, $-z$; #2 $-x+1$, $-y+3$, $-z$; #3 $-x+1$, $y-1/2$, $-z+1/2$; #4 $-x+1$, $y+1/2$, $-z+1/2$.

Table 3. *Bond Lengths* [Å] *and Angles* [°] *for* **2**[a])

Mo(1)–O(7)	1.725(9)	Mo(2)–O(1)#2	2.185(7)
Mo(1)–O(5)	1.742(10)	Mo(2)–O(1)	2.204(6)
Mo(1)–O(1)	1.931(6)	Cu(1)–O(5)	1.962(10)
Mo(1)–O(6)	2.199(9)	Cu(1)–O(4)#3	1.991(6)
Mo(1)–O(2)	2.207(9)	Cu(1)–N(1)	2.053(13)
Mo(2)–O(3)	1.712(7)	Cu(2)–N(2)	1.980(13)
Mo(2)–O(4)	1.729(7)	Cu(2)–O(7)	2.024(9)
Mo(2)–O(6)#2	1.952(2)	Cu(2)–O(3)#5	2.100(7)
Mo(2)–O(2)	1.961(2)		
O(7)–Mo(1)–O(5)	103.9(5)	O(6)#2–Mo(2)–O(1)	90.2(3)
O(7)–Mo(1)–O(1)	102.7(2)	O(2)–Mo(2)–O(1)	74.0(3)
O(5)–Mo(1)–O(1)	102.6(2)	O(1)#2–Mo(2)–O(1)	74.5(3)
O(1)#1–Mo(1)–O(1)	138.3(4)	O(5)–Cu(1)–O(4)#3	120.8(3)
O(7)–Mo(1)–O(6)	166.6(4)	O(4)#3–Cu(1)–O(4)#4	99.0(4)
O(5)–Mo(1)–O(6)	89.4(4)	O(5)–Cu(1)–N(1)	101.4(5)
O(1)–Mo(1)–O(6)	73.8(2)	O(4)#3–Cu(1)–N(1)	107.0(3)
O(7)–Mo(1)–O(2)	87.1(4)	N(2)–Cu(2)–O(7)	130.9(5)
O(5)–Mo(1)–O(2)	169.0(4)	N(2)–Cu(2)–O(3)#5	113.9(3)
O(1)–Mo(1)–O(2)	74.5(2)	O(7)–Cu(2)–O(3)#5	98.0(3)
O(6)–Mo(1)–O(2)	79.5(3)	O(3)#5–Cu(2)–O(3)#6	95.7(4)
O(3)–Mo(2)–O(4)	103.8(4)	Mo(1)–O(1)–Mo(2)#2	105.2(3)
O(3)–Mo(2)–O(6)#2	100.7(4)	Mo(1)–O(1)–Mo(2)	104.5(3)
O(4)–Mo(2)–O(6)#2	91.1(3)	Mo(2)#2–O(1)–Mo(2)	105.5(3)
O(3)–Mo(2)–O(2)	91.5(3)	Mo(2)#1–O(2)–Mo(2)	153.1(5)
O(4)–Mo(2)–O(2)	101.2(3)	Mo(2)–O(2)–Mo(1)	103.3(3)
O(6)#2–Mo(2)–O(2)	160.1(4)	Mo(2)–O(3)–Cu(2)#7	134.8(4)
O(3)–Mo(2)–O(1)#2	93.0(3)	Mo(2)–O(4)–Cu(1)#8	135.0(4)
O(4)–Mo(2)–O(1)#2	159.4(3)	Mo(1)–O(5)–Cu(1)	171.2(6)
O(6)#2–Mo(2)–O(1)#2	73.7(3)	Mo(2)#2–O(6)–Mo(2)#9	152.0(5)
O(2)–Mo(2)–O(1)#2	90.2(3)	Mo(2)#2–O(6)–Mo(1)	103.9(3)
O(3)–Mo(2)–O(1)	160.5(3)	Mo(1)–O(7)–Cu(2)	158.0(6)
O(4)–Mo(2)–O(1)	92.0(3)		

[a]) Symmetry transformations used to generate equivalent atoms: #1 x, $-y+1/2$, z; #2 $-x+2$, $-y$, $-z+1$; #3 $-x+3/2$, $-y$, $z-1/2$; #4 $-x+3/2$, $y+1/2$, $z-1/2$; #5 $x-1/2$, y, $-z+3/2$; #6 $x-1/2$, $-y+1/2$, $-z+3/2$; #7 $x+1/2$, y, $-z+3/2$; #8 $-x+3/2$, $-y$, $z+1/2$; #9 $-x+2$, $y+1/2$, $-z+1$.

746*m*, 661*m* (br.), 592*m*. Anal. calc. for $C_{30}H_{26}Cu_5Mo_8N_{12}O_{42}$: C 15.58, H 1.13, N 7.27; found: C 15.47, H 1.07, N 7.13.

Dicopperdecaoxo(pyrazine)trimolybdenum Polymer ($[Mo_3Cu_2O_{10}(pz)]_n$; **2**). A mixture of MoO_3 (144 mg), CuO (80 mg), pyrazine-2-carboxylic acid (124 mg), and H_2O (16.0 ml) was sealed in a *Teflon*-lined stainless-steel reactor and heated to 170° for 72 h. Subsequent natural cooling to r.t. gave needle-shaped black crystals of **2** (65%). IR (KBr): 3385v*s* (br.), 1610*m*, 1417*m*, 1153*m*, 899v*s*, 887v*s*, 866v*s*, 791*s*, 663*m* (br.), 523*m* (br.). Anal. calc. for $C_4H_4Cu_2Mo_3N_2O_{10}$: C 7.33, H 0.62, N 4.28; found: C 7.18, H 0.53, N 4.13.

Crystallography. Single crystals with approximate dimensions 0.05 × 0.05 × 0.10 mm for **1** and 0.04 × 0.04 × 0.26 mm for **2** were used for data collections on a *Siemens Smart-CCD* diffractometer with graphite-monochromated Mo*Kα* radiation (λ 0.71073 Å) at 298 K. Empirical absorption corrections were applied for both compounds by means of the SADABS program for the *Siemens* area detector. The structures were solved by direct methods, and all calculations were performed on a *Legend* computer with the SHELXTL-PL version 5.10. For **1** and **2**, the coordinates of the heavy atoms were obtained from *E*-maps, successive difference *Fourier* syntheses gave all the coordinates of other atoms. Both structures were refined by full-matrix least-squares minimizations of $\Sigma(F_o - F_c)_2$ with anisotropic thermal parameters for all non-H-atoms. The positions of H-atoms were generated geometrically (C–H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent C-atoms before the final cycle of refinement. *Table 1* summarizes the important crystal data, and *Tables 2* and *3* list selected bond lengths and angles for **1** and **2**, resp. Crystallographic data for both structures have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC 158155 and 158156. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting information available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** and **2**.

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