DALTON
FULL PAPER

Coordination polymers of Co^{II} and 3,3′,5,5′-tetramethyl-4,4′-bipyrazolyl: a novel metal–organic three-dimensional network with four-coordinated planar vertices

Ishtvan Boldog,[a] **Eduard B. Rusanov,**[b] **Alexander N. Chernega,**[b] **Joachim Sieler**[c] **and Konstantin V. Domasevitch***[a]

[a] *Inorganic Chemistry Department, Kiev University, Volodimirska Street 64, Kiev 252033, Ukraine. E-mail: dk@anorgchemie.univ.kiev.ua*
[b] *Institute of Organic Chemistry, Murmanskaya St. 4, Kiev 253660, Ukraine*
[c] *Institut für Anorganische Chemie, Universität Leipzig, Linnéstraße 3, D-04103 Leipzig, Deutschland*

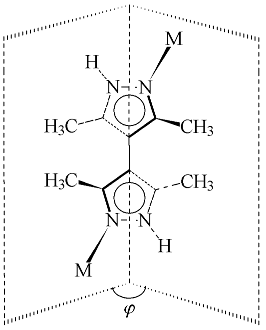
Received 5th September 2000, Accepted 23rd January 2001
First published as an Advance Article on the web 26th February 2001

The bitopic exodentate ligand 3,3′,5,5′-tetramethyl-4,4′-bipyrazolyl (4,4′-bpz), designed as an angular bridging unit capable of formation of a set of coordination and hydrogen bonds, gave the coordination polymers [Co(4,4′-bpz)$_2${C$_6$H$_5$CO$_2$}$_2$]·2C$_6$H$_5$Br **1** and [Co(4,4′-bpz){C$_6$H$_5$CO$_2$}{CH$_3$CO$_2$}]·2C$_6$H$_5$Br **2**. Complex **1** exhibits a 3-D structure containing rectangular channels. The topology of the array has no precedents in crystal engineering of linear spacer ligands of the 4,4′-bipyridine type and may be a prototype for engineering of a novel family of functional solids. Complex **2** exists as a hybrid coordination/hydrogen-bonded porous network which incorporates two guest bromobenzene molecules per metal atom.

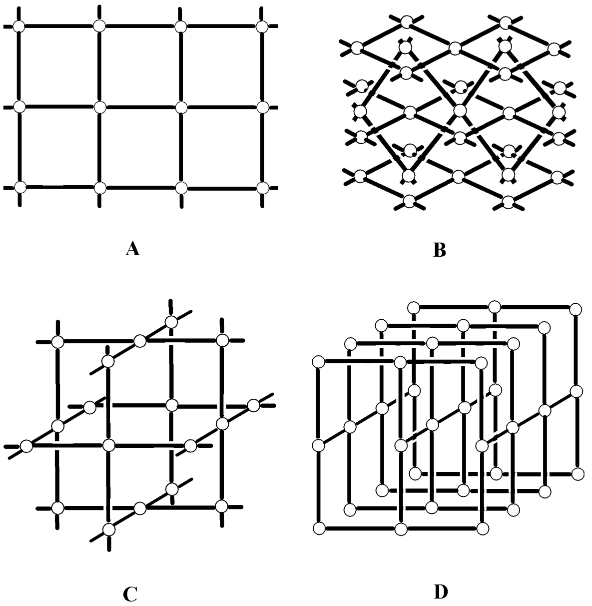
Introduction

Coordination polymers, often called metal–organic networks, are entities composed of metal centers bridged by organic connectors. Their design using principles of crystal engineering represents a new and growing area of inorganic, coordination and supramolecular chemistry,[1,2] which offers intriguing possibilities for developing novel functional materials with useful bulk properties. Different coordination polymers have the ability to afford controllable cavities that are suitable for enclathration of organic guest molecules.[1–3] Such aspects as the design of porous materials for separation of gases, liquids and solutes, chiral open structures as cost-effective alternatives to current methods of enantiomeric separations, new industrial heterogeneous catalysts and chemical sensors and directed inducement of supramolecular polarity or chirality (helical networks) as a key physical bulk property for a number of electrooptic applications have attracted attention and are extensively discussed.[2–5] Many types of coordination polymers were engineered under a strategy of supramolecular synthesis using a number of exodentate bitopic ligands (“spacers”) such as 4,4′-bipyridine and its extended analogues 1,2-bis(4-pyridyl)-ethane, -ethylene and -ethyne and square-planar or octahedral transition metal centers Co^{II}, Ni^{II}, Cu^{II}, *etc.*[1,5–7] The prominent property of such coordination polymers is their supramolecular isomerism and at least six supramolecular architectures [M(4,4′-bipy)$_{1.5}$(X)$_2$]$_n$ were reported recently (X = NO$_3$, RCO$_2$ or NCS).[7]

A particularly promising tool in control of the overall structure of coordination polymers is retrosupramolecular synthesis, *e.g.* design of the spacer ligands, their size, donor properties and conformations and thus programming of the desired topology of the coordination network at the molecular level.[1,6] A number of ligand systems, closely related to 4,4′-bipyridine, offer new possibilities for the crystal engineering of coordination, hydrogen-bonded and hybrid coordination/hydrogen-bonded networks. As an especially attractive target in this context we consider the 4,4′-bipyrazolyl family that represent exclusively flexible structural units for the construction of extended solids. Thus, (1) bipyrazolyls presumably may generate supramolecular arrays in neutral, mono- and di-cationic and mono- and di-anionic forms allowing design of a broad range of neutral, anionic or cationic coordination networks; (2) they possess a set of effective hydrogen-bond donor (NH) and acceptor (N) sites for the formation of hydrogen bonds; (3) for M(L)$_n$(anion)$_m$·nGuest systems, NH (pyrazole)–O,N (anion) hydrogen bonding may play a significant function for stabilization of a coordination core around the metal atom thus stabilizing the structure of the coordination network and preventing collapse of the porous array with elimination of guest moieties; (4) the conformation of bipyrazolyls may be controlled by varying the substituents in four 3,3′,5,5′ positions of the ligand. The planar bipyrazolyl core is a linear spacer unit, while the non-planar structure of the ligand constrained by steric repulsion of the substituents will effect angular disposition of two N–M vectors and the desired angle φ may be designed at the molecular level.

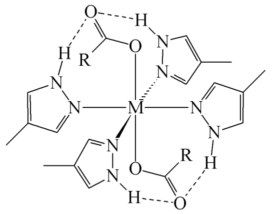


This is contrary to 4,4′-bipyridine and related systems, which usually act only as rigid rod-like spacers.[1,2] Such flexibility presumably may allow design of a variety of new extended solids even for the most simple and uniform metal–organic systems like $[M(L)_2]_n$ with planar four-coordination of the metal atoms. Actually only two known basic supramolecular archetypes (Scheme 1)[6,8] are exemplified by two-dimensional square grids



Scheme 1 Topology of frameworks that are observed for coordination polymers based upon octahedral or square-planar metal centers and 2 equivalents of linear bridging ligands: **A**, square grid planar network; **B**, 3-D structure by inclined interpenetration of square grids; **C**, 3-D network of NbO type; **D**, 3-D network of $CdSO_4$ type.

(**A**)[1,2] and three-dimensional NbO-like structures (**C**)[9] together with their variations, interpenetrating square grids (**B**)[2a] and $CdSO_4$-related networks (**D**).[6,9b,10] In this contribution we report the engineering of a novel metal–organic $[M(L)_2]_n$ topology by exploitation of the peculiarities of the geometry of a new ligand for supramolecular synthesis, 3,3′,5,5′-tetramethyl-4,4′-bipyrazolyl (4,4′-bpz), and a tetrakispyrazolato bis-carboxylate supramolecular synthon observed earlier for tetrakis(4-methylpyrazole)bis(trifluoroacetate)copper complex,[11] that appeared to be a suitable molecular prototype for polymeric M–4,4′-bpz systems.



Results and discussion

In the benzoate complex $[Co(4,4'\text{-bpz})_2\{C_6H_5CO_2\}_2]\cdot 2C_6H_5Br$ **1** the metal atoms and pyrazolyl and benzoate ligands constitute a three-dimensional open network (Figs. 1, 2). This network possesses rectangular channels in all three directions filled with guest bromobenzene molecules (two equivalents per metal atom). The resulting porosity of the network, however, is not high as can be seen from its space-filling representation, Fig. 3. The calculated[12] volume of the coordination net is 5574.1 $Å^3$ per unit cell (53.2%). The cobalt atoms occupy centers of inversion and are coordinated in slightly distorted octahedron with four nitrogen atoms of pyrazolyl ligands situated in the equatorial plane and two oxygen atoms of benzoate groups in axial positions. Bond distances within the coordination polyhedron are Co–N 2 × 2.186(3) and 2 × 2.189(3) Å, Co–O 2 × 2.103(3) Å (Table 1) and the Co–N separations are somewhat longer than those seen for $Co(3\text{-Me-5-t-Bu-pz})_4(BF_4)_2$ (2.092–2.135 Å).[13] The mutual orientation of the pyrazolyl and benzoate ligands is stabilized by strong hydrogen bonds N–H···O as shown in Fig. 1: N(2)···O(2) 2.783(5), N(4)···O(2) 2.828(5) Å; N(2)–H(1)···O(2) 168(5), N(4)–H(2)···O(2) 172(5)°.

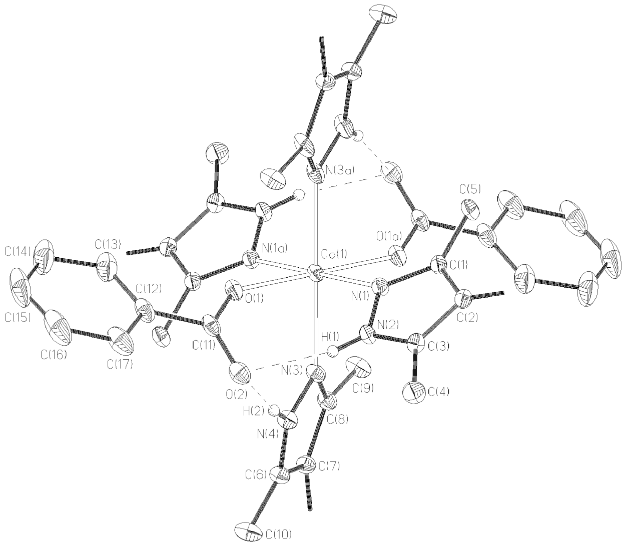


Fig. 1 Perspective view, with 30% probability ellipsoids, of the octahedral coordination environment of the metal atom in structure **1** and the atom labeling scheme. C–H hydrogen atoms are omitted for clarity.

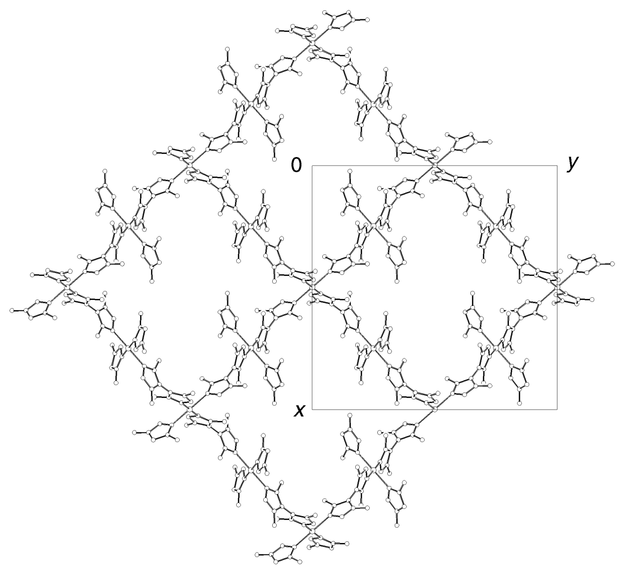


Fig. 2 Fragment of the coordination network in structure **1**, corresponding to the central bold-lined plane on Scheme 2. Projection on the *xy* plane. Coordinated benzoate groups are omitted for clarity.

The coordination portion of the compound exhibits a three-dimensional array with a topology of the coordination network unprecedented for porous metal–organic polymers. Although examination of the Cambridge Crystallographic Database revealed one simple prototype $[M(py)_2(N_3)_2]_n$ (M = Cd or Mn),[14] no structures having the present topology have been engineered using 4,4′-bipyridine or any of its extended analogs and it is interesting to query why such an unusual architecture is possible for 4,4′-bpz derivatives. As can be seen from Fig. 2, the unit of the network, the square constituting eight metal atoms and eight spacer ligands at first glance is similar to that for well known structures of the NbO type,[6,9] and all vertices and edges, but not all angles of the networks, are related by symmetry. Thus both architectures are uninodal quasiregular networks.[6] In both types eight-metal squares form

Table 1 Selected bond distances (Å) and angles (°) for cobalt complexes **1** and **2**

$[Co(4,4'\text{-bpz})_2\{C_6H_5CO_2\}_2]\cdot 2C_6H_5Br$ **1**^{a}			
Co(1)–O(1)	2.103(3)	O(1)–Co(1)–N(1a)	87.9(1)
Co(1)–N(3)	2.186(3)	N(3)–Co(1)–N(1a)	84.4(1)
Co(1)–N(1)	2.189(3)	C(11)–O(1)–Co(1)	144.0(3)
		C(1)–N(1)–Co(1)	134.9(3)
O(1)–Co(1)–N(3)	90.0(1)	N(2)–N(1)–Co(1)	119.7(2)
O(1)–Co(1)–N(1)	92.1(1)	N(4)–N(3)–Co(1)	121.4(3)
N(3)–Co(1)–N(1)	95.6(1)	C(8)–N(3)–Co(1)	131.7(3)
$[Co(4,4'\text{-bpz})\{C_6H_5CO_2\}\{CH_3CO_2\}]\cdot 2C_6H_5Br$ **2**			
Co(1)–O(1)	1.951(3)	O(1)–Co(1)–N(2)	107.7(2)
Co(1)–O(3)	1.976(4)	O(3)–Co(1)–N(2)	102.3(2)
Co(1)–N(4)	2.016(4)	O(3)–Co(1)–N(4)	118.3(2)
Co(1)–N(2)	2.036(4)	N(4)–Co(1)–N(2)	104.4(2)
		C(11)–O(1)–Co(1)	121.9(3)
O(1)–Co(1)–O(3)	110.4(2)	C(13)–O(3)–Co(1)	102.6(3)
O(1)–Co(1)–N(4)	112.7(2)	N(1)–N(2)–Co(1)	117.1(3)

^{a} Symmetry transformations used to generate equivalent atoms: a $-x$, $1 - y$, $-z$.

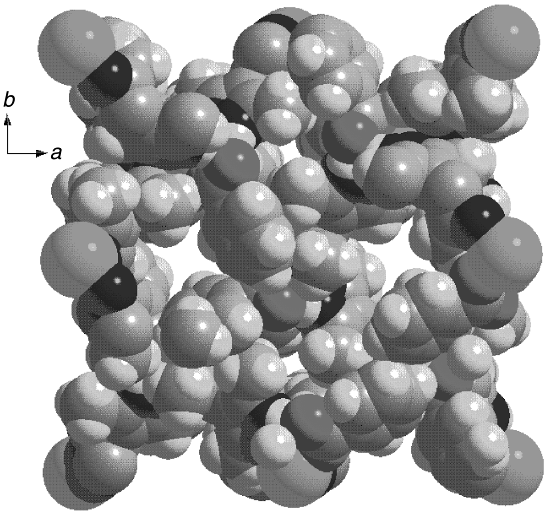
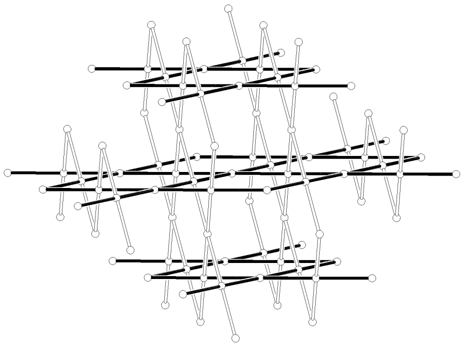


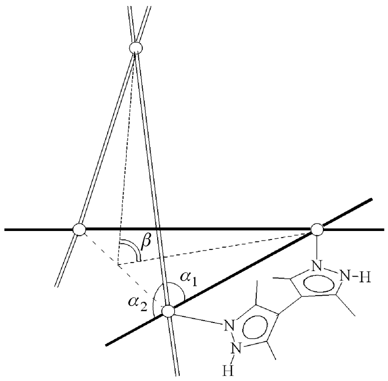
Fig. 3 Space filling diagram of the coordination network in structure **1** showing channels running down the *c* axis and how the bulky phenyl substituents and methyl groups minimize the space available for the guest species.

flat layers, but the principles of extension of the structure in the third dimension are dramatically different. In structures of the NbO topology the smallest circuit is a non-planar six membered ring, four of six angles (each 90°) at a vertex corresponding to two hexagonal circuits and the remaining two (each 180°) to two octagonal circuits (vertex symbol $6_2\cdot6_2\cdot6_2\cdot6_2\cdot8_2\cdot8_2$).[6] A diagram of the polymer in structure **1** is given in Scheme 2. In the present case the smallest circuit of the network is a quadrangle and the vertex symbol is $4\cdot4\cdot8_4\cdot8_4\cdot8_4\cdot8_4$.

The most salient feature of the array is that these quadrangles are not planar. Under planar four-coordination of the vertices (points of the net are at centers of inversion) the angle β of intersection of corresponding planes (bold and open lines in Scheme 2) and the angles α_1 and α_2 between the nodes of the net are related as $\tan(\frac{1}{2}\alpha_1) = \sin(\frac{1}{2}\beta)$ and $\alpha_2 = 180 - \alpha_1$. Thus in the case of orthogonal intersection (that is, when $\beta = 90°$) the angles at a vertex are restricted to the values 2 × 70.5 and 2 × 109.5°, deviating from the regular values of 90° by *ca.* 20°. This is consistent with the observed geometry (2 × 72.1, 2 × 107.9°). Hence the present topology cannot be sustained with regular square planar coordination of the vertices. Such significant distortion required for a vertex coordination seems to be a critical factor limiting, if not even precluding, the possibility of engineering of this architecture using linear rod-like bridges of the 4,4′-bipy type and square-planar or octahedral metal centers like Ni^{II}, Co^{II}, Zn^{II}, *etc.* In complex **1** the coordination around the cobalt atom is actually octahedral with maximum deviations of bond angles from their regular values not exceeding 6° (*cf.* N(3)–Co(1)–N(1) 95.6(1)°), which still does not meet the requirements for formation of a $4\cdot4\cdot8_4\cdot8_4\cdot8_4\cdot8_4$ net. The present disposition of the net nodes, that made possible the assembly of the unusual 3-D array, is clearly the consequence of the structure of bipyrazolyl ligand. The interplanar angle φ in the 4,4′-bpz molecule (*ca.* 69.1°), which is responsible for mutual orientation of the Co–N bonds, almost exactly satisfies the demands of the $4\cdot4\cdot8_4\cdot8_4\cdot8_4\cdot8_4$ net.



Scheme 2 Diagram of the structure of novel metal–organic polymer **1**. Nodes of the net correspond to bridging 4,4′-bpz molecules. Note that the topology of the network requires significant distortion of the square planar four-coordination of the vertices.



The minor co-product of interaction in the system $Co(CH_3CO_2)_2$–$PhCO_2H$–4,4′-bpz has the composition $[Co(4,4'\text{-bpz})\{C_6H_5CO_2\}\{CH_3CO_2\}]\cdot 2C_6H_5Br$, **2**. This is the first mixed-carboxylate cobalt(II) complex examined structurally. It also possesses a porous structure which is of interest in the context of the present work as an illustration of a 2-D array formed by combination of two principal bipyrazolyl functions, metal coordination and formation of relatively strong hydrogen bonds (see Figs. 4, 5). The complex exists as a hybrid coordination/hydrogen-bonded porous network which incorporates two guest bromobenzene molecules per metal atom. The cobalt atoms adopt fourfold tetrahedral coordination comprising two nitrogen atoms of pyrazolyl groups (Co–N 2.016(4), 2.036(4) Å) and oxygen atoms of acetate (Co–O 1.951(3) Å) and benzoate ions (1.976(4) Å). These bond lengths are slightly shorter than those observed for complex **1**, which is a consequence of a lower coordination number (Table 1). The Co–N bond lengths and N–Co–N angle of 104.4(2)° are comparable with related parameters observed for the tetrahedral $Co(3,5\text{-}Me_2pz)_2Cl_2$ complex (2.011 Å and 105.9°).[15] The present configuration at the metal atom is stabilized by hydrogen bonding involving acetate and pyrazolyl moieties: N···O 2.752(6) Å, N–H···O 154(5)° (Fig. 4).

Bridging bipyrazolyl groups and cobalt ions form zigzag chains of a coordination polymer extending along the *y*

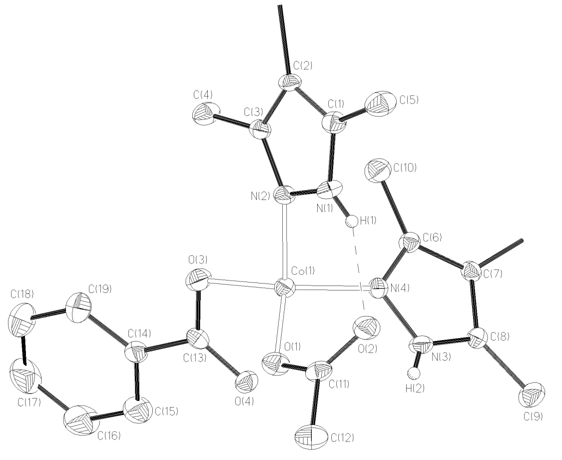


Fig. 4 Tetrahedral coordination environment of the cobalt atom and atom labeling scheme in structure **2**. Thermal ellipsoids are shown at the 40% probability level and C–H hydrogen atoms are omitted for clarity.

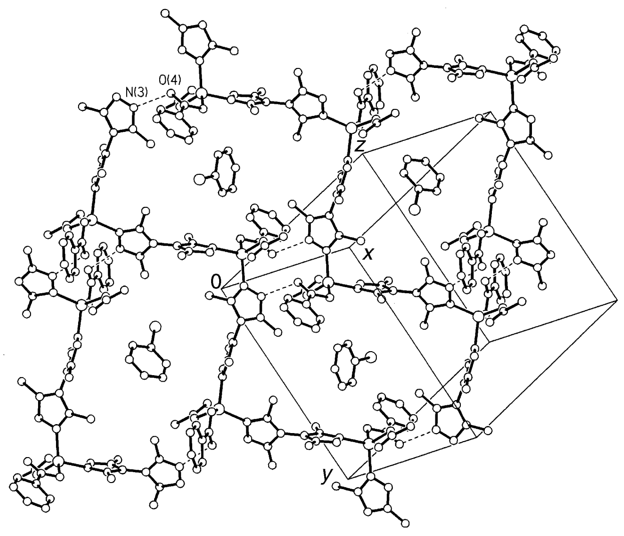


Fig. 5 Zigzag coordination chains in structure **2** held by NH···O hydrogen bonds and the packing forming a pseudo square grid network. Each large rectangular cavity incorporates a bromobenzene molecule.

crystallographic direction. These chains are held together by relatively strong hydrogen bonding between NH fragments of pyrazole and benzoate groups $(1 - x, -y, -z)$ (N···O 2.815(6) Å, N–H···O 162(5)°) producing a two-dimensional pseudo square-grid structure with large rectangular cavities (compare with supramolecular motif **A**, Scheme 1). Thus the points of this flat net are the dinuclear cobalt(II) fragments generated by the centrosymmetric paired pyrazole/benzoate hydrogen-bonding interactions (Fig. 5). Each of the cavities formed is populated with a bromobenzene molecule (guest : Co ratio 0.5 : 1), which is involved in edge-to-face stacking interactions with pyrazolyl rings (shortest distances C···N are *ca.* 3.49 Å) (Fig. 5). These guest molecules fit perfectly inside the rectangular cavities which allows the postulation of a special templating effect of bromobenzene on the assembly of the overall structure. In the same way, $[M(bipy)_2(NO_3)_2]_n$ square grid polymers (M = Co or Ni) incorporate even larger naphthalene molecules.[4c] The coordination/hydrogen-bonded layers $[Co(4,4'\text{-bpz})\{C_6H_5CO_2\}\{CH_3CO_2\}(C_6H_5Br)_{0.5}]$ pack one on the top of another with relatively large interlayer separations of *ca.* 11.6 Å *versus* the usual values of 7.5–8.0 Å for bipyridine coordination polymers.[4] Additional guest molecules (1.5 equivalents per metal atom) are located between the layers.

Table 2 Crystal data for $[Co(4,4'\text{-bpz})_2\{C_6H_5CO_2\}_2]\cdot 2C_6H_5Br$ **1** and $[Co(4,4'\text{-bpz})\{C_6H_5CO_2\}\{CH_3CO_2\}]\cdot 2C_6H_5Br$ **2**

	1	2
Formula	$C_{34}H_{38}CoN_8O_4\cdot 2C_6H_5Br$	$C_{19}H_{24}CoN_4O_4\cdot 2C_6H_5Br$
M	995.67	743.36
T/K	213	223
Crystal system	Tetragonal	Monoclinic
Space group	$I4_1/a$	$P2_1/n$
a/Å	22.3175(7)	14.1437(10)
b/Å		14.4751(11)
c/Å	21.0429(10)	16.4467(12)
β/°		97.733(1)
U/Å^3	10480.9(7)	3336.5(4)
Z	8	4
μ(Mo-Kα)/cm^{-1}	18.97	29.49
Measured/independent reflections	27250/4632	18668/6545
R_{int}	0.044	0.049
Data used/parameters refined	3811/306	5411/376
$R1$, $wR2$ $(I > 2\sigma(I))$	0.069, 0.185	0.069, 0.173
(all data)	0.121, 0.297	0.121, 0.238

Conclusion

Thus we may conclude that the conformational and functional features of bipyrazolyl ligands may be exploited as important tools for engineering of functional solids. Tetramethyl-substituted non-planar bipyrazolyl allows the assembly of a novel 3-D coordination network which has no analogy in the chemistry of 4,4′-bipyridine and related species and presumably cannot be engineered with their use.

Experimental

$Co(CH_3CO_2)_2\cdot 4H_2O$, benzoic acid and bromobenzene were commercial products of reagent grade (Khimlaborreaktiv, Ukraine), used without further purification. 3,3′,5,5′-Tetramethyl-4,4′-bipyrazolyl was prepared in accordance with the literature method.[16] The product was recrystallized from hot water. Reaction of cobalt(II) acetate and 4,4′-bpz (also in the presence of different aromatic species as potential guest molecules) in methanol solution did not afford crystalline products, while addition of benzoic acid effected crystallization of benzoate and mixed-carboxylate acetate–benzoate complexes. For the preparation of coordination polymers the following method was used.

In a typical synthesis, 0.249 g (1.0 mmol) of $Co(CH_3CO_2)_2\cdot 4H_2O$, 0.244 g (2.0 mmol) of benzoic acid and 0.380 g (2.0 mmol) of 4,4′-bpz were dissolved in 20 ml of methanol and 5 ml of bromobenzene. The mixture was allowed to evaporate slowly to 5 ml volume for about 30 days, after which crystalline solid (0.60 g) was removed from the solution. The product consists of a mixture of two complexes, $[Co(4,4'\text{-bpz})_2\{C_6H_5CO_2\}_2]\cdot 2C_6H_5Br$ **1**, light pink blocks, and $[Co(4,4'\text{-bpz})\{C_6H_5CO_2\}\{CH_3CO_2\}]\cdot 2C_6H_5Br$ **2**, pink prisms. The latter was the minor product (*ca.* 20%). Both carboxylate complexes are stable in the mother-liquor, but easily decompose in air with loss of guest molecules.

Crystallographic measurements were made using a Siemens SMART CCD area-detector diffractometer (graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), exposure 40 s per frame, empirical absorption corrections using SADABS).[17] The essential experimental conditions and crystal data are given in Table 2. The structures were solved by direct methods and refined in the anisotropic approximation using SHELXS 86 and SHELXL 93.[18] All N–H hydrogen atoms were located from the Fourier-difference syntheses and refined isotropically, whereas C–H hydrogen atoms were placed in calculated positions with their isotropic U values set at 0.08 Å^2. In structure **1** the guest moieties are badly disordered over three overlapping sites; each of these components shows two orientations of the heavy bromine atom. The disorder was resolved by imposing the standard geometry of the phenyl rings and the partial occupancies were 0.4, 0.4 and 0.2. Only sites of bromine atoms were refined anisotropically for the sake of overall convergence (U_{eq} 0.12–0.22 Å^2), while the carbon atoms left isotropic and the hydrogen atoms not included. Structure **2** involves three unique bromobenzene molecules, two of which are disordered over a center of inversion. Refinement of the disorder proceeded smoothly and therefore it was possible to refine all bromine and carbon atoms anisotropically and to include hydrogen atoms. Graphical representation of the structures was made using the programs XP and Diamond.[19]

CCDC reference number 186/2330.

See http://www.rsc.org/suppdata/dt/b0/b007183h/ for crystallographic files in .cif format.

Acknowledgements

The work was in part supported by a grant from Deutsche Forschungsgemeinschaft (J. S. and K. V. D.) and a visiting stipendium from Sächsische Staatsministerium für Wissenschaft und Kunst (K. V. D.), which are gratefully acknowledged.

References

1 P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 2638; S. Kitagawa and M. Kondo, *Bull. Chem. Soc. Jpn.*, 1988, **71**, 1739.

2 (*a*) S. R. Batten and R. Robson, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 1460; (*b*) O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474. Square and rectangular grids based upon 4,4′-bipyridine: K. Biradha, A. Mondal, B. Moulton and M. J. Zaworotko, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 3837 and refs. therein.

3 R. Robin, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Huskiness and J. Lieu, *Supramolecular Architecture*, ACS publications, Washington, DC, 1992, p. 256; M. Munakata, Liang Ping Wu and T. Kuroda-Sowa, *Adv. Inorg. Chem.*, 1999, **46**, 173.

4 (*a*) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; (*b*) K. Biradha, K. V. Domasevitch, B. Moulton, C. Seward and M. J. Zaworotko, *Chem. Commun.*, 1999, 1326; (*c*) K. Biradha, K. V. Domasevitch, C. Hogg, B. Moulton, K. N. Power and M. J. Zaworotko, *Crystal Eng.*, 1999, **2**, 37; K. V. Domasevitch, G. D. Enright, B. Moulton and M. J. Zaworotko, *J. Solid State Chem.*, 2000, **152**, 280.

5 J.-M. Lehn, *Comprehensive Supramolecular Chemistry*, Pergamon Press, Oxford, 1996 and refs. therein; G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989; O. M. Yaghi, G. Li and H. Li, *Nature* (*London*), 1995, **378**, 703; K. Biradha, C. Seward and M. J. Zaworotko, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 492; M. A. Withersby, A. J. Blake, N. R. Champness, P. A. Cooke, P. Hubberstey and M. Schröder, *New J. Chem.*, 1999, **23**, 573; A. J. Blake, N. R. Champness, A. Khlobystov, D. A. Lemenovskii, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 2027.

6 M. O'Keeffe, M. Eddaoudi, Hailian Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3.

7 H. Gudbjartson, K. Biradha, K. M. Poirier and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1999, **121**, 2599 and refs. therein; T. L. Hennigar, D. C. MacQuarrie, P. Losier, R. D. Rogers and M. J. Zaworotko, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 972; K. N. Power, T. L. Hennigar and M. J. Zaworotko, *New J. Chem.*, 1998, **22**, 177.

8 A. F. Wells, *Structural Inorganic Chemistry*, 5th edn., Clarendon Press, Oxford, 1986.

9 (*a*) K. N. Power, T. L. Hennigar and M. J. Zaworotko, *Chem. Commun.*, 1998, 595; (*b*) L. Carlucci, G. Ciani, P. Macchi and D. M. Prosperio, *Chem. Commun.*, 1998, 1837.

10 O. M. Yaghi, H. Li and M. O'Keeffe, *Mater. Res. Soc. Symp. Proc.*, 1997, **453**, 127.

11 T. Kogane, K. Harada, M. Umehara, R. Hirota and M. Nakahara, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2638.

12 Cerius^2, v. 3.8, Molecular Simulations Inc., San Diego, 1998.

13 J. W. Evan and K. H. Theopold, *Acta Crystallogr.*, *Sect. C*, 1990, **46**, 1013.

14 I. Agrell, *Acta Chem. Scand.*, 1970, **24**, 3575; M. A. S. Goher and F. A. Mautner, *Croat. Chim. Acta*, 1990, **63**, 559.

15 L. A. Safronova, N. T. Komyagin, A. I. Yanovskii, Yu. T. Struchkov and A. D. Shebaldova, *Koord. Khim.*, 1987, **13**, 1407; A. R. Oki, J. Sanchez, S. Hamilton and T. J. Emge, *J. Coord. Chem.*, 1995, **36**, 63.

16 W. L. Mosby, *J. Chem. Soc.*, 1957, 3997.

17 SADABS, Siemens X-Ray Instruments, Madison, WI, 1995.

18 G. M. Sheldrick, SHELXL 93, A system of computer programs for crystal structure determination, University of Göttingen, 1993; G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.

19 XP, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1990; K. Brandenburg, Diamond 2.1c, Crystal Impact GbR, Bonn, 1999.