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P_4S_3 and P,P′ or N,N′ Donors as Competitive Building Blocks in Copper(I) Coordination Polymers

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The synthesis and characterization of hybrid polymers combining organic P,P′ (dppe) or N,N′ (pyrazine) ligands and inorganic donors (P_4S_3) as cross-linkers between copper(I) halide aggregates is described. As a simple model system the reaction of a mixture of P_4S_3, PEt_3, and CuX (X = Cl, Br, I) was studied. According to X-ray diffraction analysis, pseudotetrahedral monomers $[CuX(PEt_3)_2(P_4S_3)]$ (**1**–**3**) were formed, in which P_4S_3 coordinates through the apical phosphorus atom. Layering a mixture of P_4S_3, $Ph_2PCH_2CH_2PPh_2$ (dppe), and toluene with CuCl in MeCN under diffusion conditions gives 1D-[CuCl(dppe)(MeCN)] (**6**), which contains $(Cu_2Cl_2)_2$-(μ-dppe)$_2$ clusters linked by another dppe ligand. The analogous reaction with CuI gives 1D-$[CuI(P_4S_3)(dppe)]$ (**7**), which is built up of alternating *trans*-$(Cu_2I_2)(P_4S_3)_2$ units and dppe linkers. Hybrid polymers 2D-$[CuX(P_4S_3)(dppe)]$ [X = Br (**8**), I (**9**)] are formed if CH_2Cl_2 is used instead of toluene. The 2D structures of **8** and **9** may be derived from that of **7** by connecting neighboring (CuX)(dppe) strands with pairs of inversely coordinated P_4S_3 cages. Replacement of dppe by pyrazine (pyz) yields 3D-$[(CuCl)_4(P_4S_3)_2(pyz)]$ (**10**) and 3D-$[(CuBr)_3(P_4S_3)(pyz)]$ (**12**), respectively. The structure of **10** comprises a 3D network composed of alternating, linked 2D-$[(CuCl)_2(P_4S_3)]$ and 2D-[CuCl(pyz)] layers. The structure of **12** contains cradles built from opposing $(CuBr)_6$ rings and pairwise pyz and P_4S_3 bridges. These cradles are organized into a 3D framework by condensation of the $(CuBr)_6$ rings, and the layers formed are linked by additional pyz molecules. The resulting voids are occupied by toluene molecules. The behavior of P_4S_3 and P,P′ or N,N′ ligands as competitive building blocks is also expressed by the formation of binary P_4S_3/CuX or pyz/CuX polymers.

Introduction

Coordination polymers are a class of intensively studied solid-state materials with infinite structures constructed from metal ions and organic spacer ligands.[1] The combination of copper halide aggregates as inorganic connectors with bridging ligands by crystal engineering methods produces a wide range of discrete oligomers and 1-, 2-, and 3D architectures.[2] A particular role is devoted to bifunctional organic ligands, which, as secondary building units, offer new perspectives for the development of metal–organic frameworks (MOFs).[3] Common linkers in MOFs are polycarboxylates,[4] multidentate N-donor ligands, and combinations of both.[3] The tuneable flexibility of the coordination geometry and conformation make MOFs interesting for numerous applications, e.g. gas adsorption,[5] catalytic activity,[6] luminescent[7] and magnetic[8] materials, and templates for hosting nanoparticles.[9]

The supramolecular chemistry of multidentate ligands other than O and N donors is less developed.[10] Initial results obtained with bidentate bis(diphenylphosphane)alkanes and Ag^I or Cu^I compounds demonstrate the great structural flexibility of polymers with P,P′ donors.[11] Recent developments focus on the construction of organic–inorganic hybrid materials from bifunctional P,N or S,N ligands.[12,13] Inorganic polymers of a completely different nature have been developed using the multifunctional P,Q building block P_4Q_3 (Q = S,[14,15] Se[16]).

The combination of organic and inorganic donors as cross-linking ligands with copper halide aggregates has not yet been explored. In this context it is worthwhile to explore the potential of P_4S_3 as building block in MOFs. We report the stepwise formation of organic–inorganic hybrid polymers from mono- or bidentate phosphanes and P_4S_3 with CuX (X = Cl, Br, I) in competitive reactions and on the effects observed when replacing the conformational flexible dppe ligand with the rigid pyz linker.

Results and Discussion

The System P_4S_3, PR_3, and CuX (X = Cl, Br, I)

The reaction of a mixture of CuX (X = Cl, Br, I), triethylphosphane, and P_4S_3 (molar ratio 1:2.5:1) in acetonitrile/

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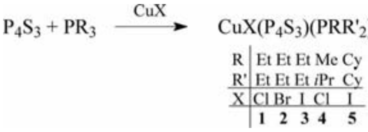
toluene at room temperature gave an orange-yellow solution, which after concentration and cooling gave colorless needles of **1**–**3** in 80% yield. The composition [$CuX(P_4S_3)(PEt_3)_2$] was confirmed by elemental analysis and X-ray crystallography.

Reaction of $PMe(iPr)_2$ with CuCl or PCy_3 (Cy = C_6H_{11}) with CuI under analogous conditions selectively gave [$CuCl(P_4S_3)\{PMe(iPr)_2\}_2$] (**4**) and [$CuI(P_4S_3)\{PCy_3\}_2$] (**5**), respectively [Equation (1)]. The homogeneity and composition of **4** and **5** were deduced from their ^{31}P NMR spectra (Table 1). Comparing the chemical shifts of **1**–**5** with those of the free P_4S_3 cage, the apical P atoms are more shifted towards low field than the basal atoms, probably as a consequence of copper coordination. It is striking that the halogens do not seem to contribute significantly to the shifts in **1**–**3**. $^{31}P^{31}P$-coupling between the trialkylphosphanes and P_4S_3 was not observed. A broadening of these signals may be explained by the quadrupole moments of the ^{63}Cu and ^{65}Cu nuclei.



(1)

Table 1. ^{31}P NMR chemical shifts (δ in ppm, C_6D_6) and coupling constants $^2J_{P,P}$ [Hz] of **1**–**5** and P_4S_3.

	P_{apical}		P_{basal}		PR_3
	δ	$^2J_{P,P}$	δ	$^2J_{P,P}$	
P_4S_3	65.0	71	–126.0	71	
1	85.6	62	–115.9	62	–11.0
2	89.2	61	–115.0	61	–11.9
3	89.3	62	–115.9	62	–14.6
4	96.6	57	–109.8	57	–1.1
5	94.1	57	–111.8	57	12.6

Compound **1** crystallizes in the acentric orthorhombic space group $P2_12_12_1$. The central feature of the molecule is a tetrahedral copper atom bearing a P_4S_3, chloride and two triethylphosphane ligands. The cage is coordinated through its apical P atom (Figure 1). The geometry of the cage does not change significantly on coordination (Table 2). In the crystal structure of **1** there are disordered ethyl groups with an occupation factor of 70:30. In isostructural **2** and **3** only one phosphane ligand contains disordered ethyl groups with a ratio of 50:50. A comparison of the distances in **1**–**3**, particularly the P–Cu and the P–S bonds, does not indicate any significant influence of the halogen atoms.

In all complexes the basal P atoms of P_4S_3 should be accessible for attack by excess copper(I) halide. In a typical experiment diffusion of a solution of CuI in CH_3CN into the solution of **3** in toluene gave crystals of $(CuI)_3P_4S_3$[17] and [$(CuI)_4(PEt_3)_4$].[18] A related reaction of **3** with CuCl gave $(CuCl)_7(P_4S_3)_3$.[17] This means that in MeCN new binary compounds are formed after dissociation of **3** into the ligands and their subsequent reaction with the corresponding copper halide.

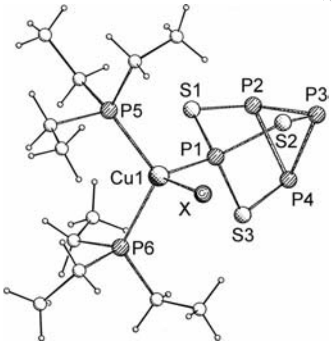


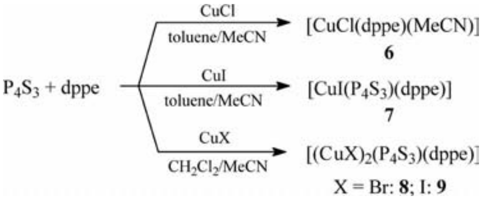
Figure 1. Molecular structure of [$CuX(P_4S_3)(PEt_3)_2$] [X = Cl (**1**), Br (**2**), I (**3**)]. The disorder of the ethyl groups is not shown (see text).

Table 2. Selected distances [Å] for **1**–**3**.

	1	**2**	**3**
S1–P1	2.096(2)	2.097(2)	2.102(2)
S1–P2	2.103(2)	2.099(2)	2.102(2)
S2–P1	2.095(2)	2.101(2)	2.104(2)
S2–P3	2.103(2)	2.097(2)	2.103(2)
S3–P1	2.103(2)	2.102(2)	2.106(2)
S3–P4	2.103(2)	2.096(2)	2.105(2)
P2–P4	2.238(2)	2.240(2)	2.245(2)
P2–P3	2.236(2)	2.248(2)	2.248(2)
P3–P4	2.249(2)	2.241(2)	2.246(2)
Cu1–X1	2.331(2)	2.479(1)	2.641(1)
Cu1–P1	2.266(2)	2.267(2)	2.260(2)
Cu1–P5	2.276(2)	2.267(2)	2.266(2)
Cu1–P6	2.275(2)	2.273(2)	2.272(2)

Coordination Polymers with dppe

Layering of a mixture of P_4S_3, dppe, and toluene with a solution of CuCl in acetonitrile gave colorless rods of 1D-[$CuCl(dppe)(CH_3CN)$] (**6**) along with crystals that could not be identified. The composition of **6** was determined by X-ray diffraction analysis. An analogous experiment, but with a threefold excess of copper(I) iodide gave bright yellow platelets of **7** after 5 d [Equation (2)]. These were analyzed with ^{31}P magic angle spinning (MAS) NMR spectroscopy and X-ray diffraction to give the composition [$CuI(P_4S_3)(dppe)$].



(2)

The diffusion reaction of an equimolar mixture of P_4S_3 and dppe in CH_2Cl_2 with CuX in acetonitrile gave yellow prisms of 2D-[$(CuX)_2(P_4S_3)(dppe)$] [X = Br (**8**), I(**9**)] [Equation (2)]. As by-products bright yellow, fine needles of $(CuBr)_7(P_4S_3)_3$[19] and $(CuI)P_4S_3$[17] were identified.

Compound **6** crystallizes in the triclinic space group $P\bar{1}$. The structure is characterized by two planar Cu_2Cl_2 rings as part of $(Cu_2Cl_2)_2(\mu\text{-dppe})_2$ clusters, which are linked by another dppe bridge. The resulting 1D ribbon (Figure 2) bears acetonitrile as an additional ligand. Related polymers from CuX, dppe, and MeCN are known, but the formation of a $(Cu_2Cl_2)_2(\mu\text{-dppe})_2$ cluster as part of a polymer seems to be unique.[11] Chelating coordination behavior of the dppe ligand has been observed in $[Cu_2(SePh)_2(dppe)(4,4'\text{-bipyridine})]$.[20]

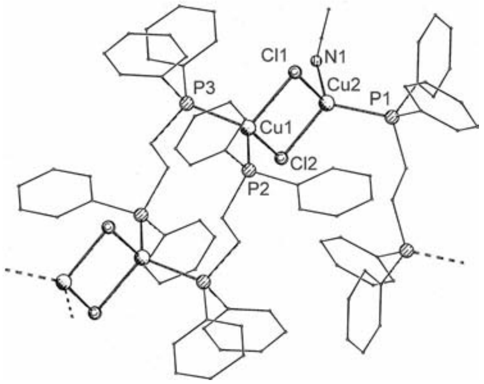


Figure 2. Section of the structure of **6**; H atoms omitted. Selected distances [Å]: Cu1–Cl1 2.419(1), Cu2–Cl1 2.385(1), Cu1–Cl2 2.400(1) Cu2–Cl2 2.370(1), Cu1–P2 2.254(1), Cu2–P1 2.212(1), Cu1–P3 2.256(1), Cu2–N1 2.047(3), Cu1···Cu2 3.149(1).

Compound **7** crystallizes in the monoclinic space group *P*2_1/*c*. The structure is composed of 1D strands, which are formed by an alternating arrangement of planar Cu_2I_2 rings and *trans* coordinated dppe ligands. The coordination sphere around the Cu1 atoms is completed by apically coordinated P_4S_3 (Figure 3). No basal P atoms are involved in the coordination, which is in contrast to the structures observed for binary polymers formed from P_4S_3 and CuI.[17] The distances within the P_4S_3 ligand are only slightly affected by the coordination to copper. The parallel strands are organized in the crystal structure into stacks along the *a* axis.

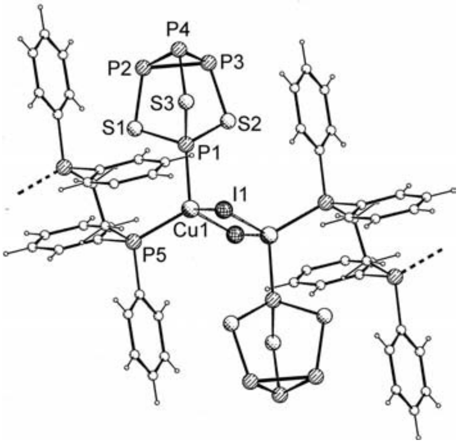


Figure 3. Section of the crystal structure of **7**. Selected distances [Å]: S1–P1 2.089(1), S1–P2 2.098(1), S2–P1 2.090(1), S2–P3 2.090(2), S3–P1 2.098(1), S3–P4 2.102(1), P2–P4 2.249(2), P2–P3 2.242(2), P3–P4 2.236(2), Cu1–P1 2.271(1), Cu1–P5 2.262(1), Cu1–Cu1a 2.875(1), Cu1–I1 2.637(1)–2.664(1).

The ^{31}P MAS NMR spectrum of **7** is shown in Figure 4. The multiplet at δ = 96.7 ppm ($^1J_{P,Cu}$ = 778 Hz) may be assigned to the apical P atom of the P_4S_3 cage, which is coordinated to copper as well as the P atoms of the bridging dppe ligand, which give rise to another multiplet at δ = –11.4 ppm ($^1J_{P,Cu}$ = 1473 Hz). The singlet at δ = –105.5 ppm is typical of the atoms of the P_3 base of P_4S_3.[17]

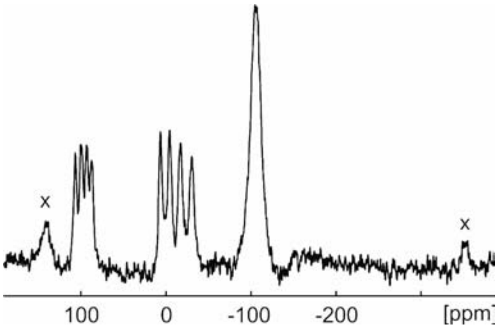


Figure 4. ^{31}P MAS NMR spectrum of **7**. Spinning side bands are marked by ×.

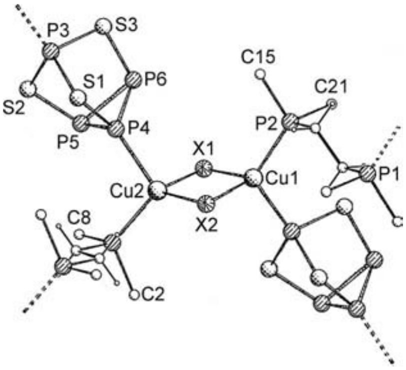


Figure 5. Section of the crystal structure of $[(CuX)_2(P_4S_3)(dppe)]$ [X = Br (**8**), I (**9**)]. Only the ipso C atoms of the phenyl groups are shown.

Table 3. Selected distances [Å] for **8** and **9**.

	8	**9**
S1–P3	2.104(1)	2.104(2)
S1–P4	2.101(1)	2.097(2)
S2–P3	2.099(2)	2.098(2)
S2–P5	2.097(1)	2.091(2)
S3–P3	2.089(1)	2.087(2)
S3–P6	2.094(1)	2.092(2)
P4–P5	2.242(2)	2.243(2)
P4–P6	2.239(1)	2.238(2)
P5–P6	2.226(2)	2.229(2)
Cu1–X1	2.484(1)	2.648(2)
Cu2–X2	2.455(1)	2.638(2)
Cu1–X2	2.500(1)	2.638(1)
Cu2–X1	2.489(1)	2.607(1)
Cu1–P2	2.262(1)	2.264(2)
Cu1–P3	2.279(1)	2.281(2)
Cu2–P1	2.244(1)	2.252(2)
Cu2–P4	2.373(1)	2.354(2)
Cu1–Cu2	3.115(1)	3.131(2)

The ratio of integrals of $P_{apical}/P_{dppe}/P_{basal}$ is 1:2:3, which is in agreement with the crystal structure determination.

Isostructural **8** and **9** crystallize in the triclinic space group $P\bar{1}$. Characteristic of both structures are planar Cu_2X_2 rings, which are *trans* connected by dppe ligands to form 1D strands (Figure 5). Contrary to the structure of **7**, two P_4S_3 ligands are coordinated through one of their apical atoms (P3) and one of the basal atoms (P4). The opposite phosphorus sites of the cage molecules coordinate to neighboring strands to give 2D networks. The distances within the P_4S_3 cage are only slightly affected by the coordination (Table 3).

The System P_4S_3, CuX (X = Cl, Br) and pyz

In the following experiments, the replacement of the conformational flexible dppe ligand by the rigid pyz ligand in the interdiffusion experiments was investigated. Layering a solution of P_4S_3 and pyz in CH_2Cl_2 with CuCl in CH_3CN gave a mixture of flat yellow and red prisms. The yellow prisms were identified by X-ray crystallography as a hybrid polymer of composition $[(CuCl)_4(P_4S_3)_2(pyz)]$ (**10**), whereas the red prisms were the P_4S_3-free coordination polymer [(CuCl)(pyz)].[21] Although an orange-red photoluminescence was observed for [(CuCl)(pyz)] upon irradiation at 254 nm, no emission was observed for **10**.

Compound **10** crystallizes in the monoclinic space group $P2_1/c$. The central structural features are castellated $(CuCl)_n$ chains running along the *c* axis (Figure 6), to which P_4S_3 cages and pyrazine molecules are coordinated. A more detailed inspection of the structure reveals that one of the $(Cu1Cl1)_n$ chains, which are twisted by 12°, is surrounded by P_4S_3 molecules, which connect neighboring pairs of $(CuCl)_n$ chains through their basal P1 and P4 atoms. The resulting $(CuCl)_2(P_4S_3)_2$ sheet is confined by the apical P2 atoms. Neighboring apical P atoms of the sheet are linked by slightly twisted (8°) $(Cu2Cl2)_n$ chains. Similar $(CuCl)_n$ chains are part of the structure of [CuCl(μ_2-2-Etpyz-*N*-*N'*)].[21] The coordination spheres of Cu2 are completed by pyz N atoms to accomplish a 3D network. In this way, organic and inorganic building blocks are organized into alternating planar layers orthogonal to the *ac* plane (Figure 7). The C atoms of the pyz ligands are disordered in a 68:32 ratio. Compared to free P_4S_3, only the P–P distances of the P_3 basis are slightly affected. Compound **10** can formally be described as a mixed polymer constructed from sections of 2D-$[(CuCl)_3(P_4S_3)_2]$[17] and 2D-[CuCl-$(C_4H_4N_2)$].[21]

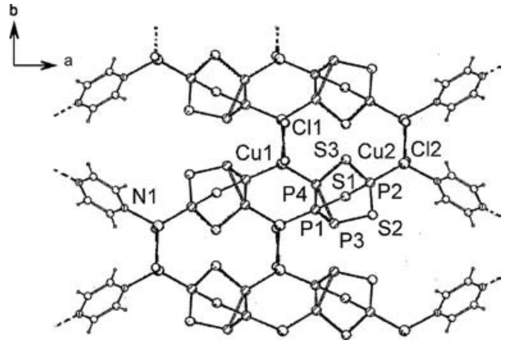


Figure 6. Section of the crystal structure of **10** viewed along the *c* axis. The C atoms of the pyz ligands are disordered, 68% occupancy is shown. Selected distances [Å]: S1–P1 2.092(2), S1–P2 2.108(2), S2–P3 2.101(2), S3–P4 2.082(2), S3–P2 2.096(2), P1–P3 2.250(2), P1–P4 2.217(2), P3–P4 2.267(2), Cu1–P1 2.267(2), Cu1–P4 2.300(2), Cu2–P2 2.177(2), Cu2–N1 2.053(3), Cu1–Cl1 2.287(2)–2.335(2), Cu2–Cl2 2.324(2)–2.335(2).

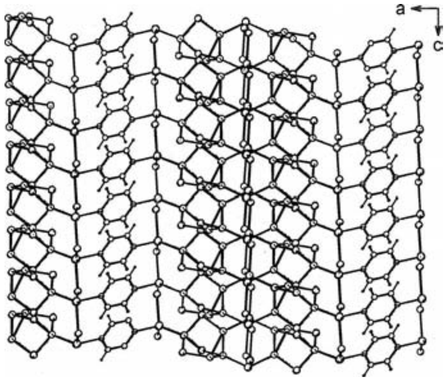


Figure 7. Section of the crystal structure of **10** projected on the *ac* plane.

The purity of **10** with respect to other phosphorus containing compounds was checked by ^{31}P MAS NMR spectroscopy. The spectrum contains two groups of signals. The multiplet at $\delta = 92.2$ ppm is typical of the apical atom P2,[17] the coordination to copper giving rise to a $^{31}P^{63,65}Cu$ coupling of 1102 Hz (Figure 8). The signals at $\delta = -72.5$ ($^1J_{P,Cu} = 1190$ Hz) and –83.4 ppm ($^1J_{P,Cu} = 894$ Hz) may be assigned to the atoms P1 and P4 of the P_3 base, both bound to copper. The singlet at $\delta = -97.1$ ppm is in agreement with P3 of the P_3 base. Thus, the spectrum supports the

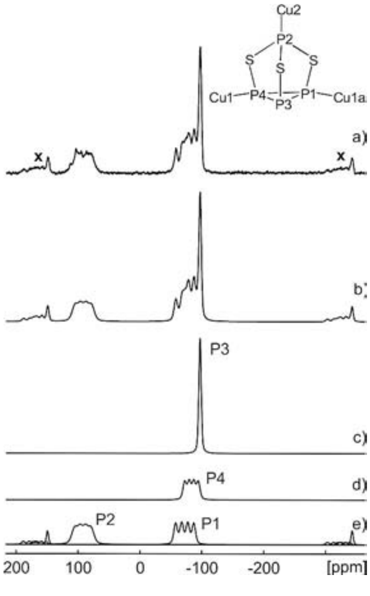


Figure 8. ^{31}P MAS NMR spectra of **10**. a) Experimental spectrum; b) sum of simulated spectra c–e) showing individual components. Spinning side bands are marked by x.

crystallographic result well, and other phosphorus containing species are not present.

The analogous reaction of CuBr with the mixture of P_4S_3, pyrazine, and CH_2Cl_2 gave the known binary polymers $(CuBr)_7(P_4S_3)_3$[19] and [CuBr(pyz)].[22] However, when a P_4S_3/pyz/toluene mixture was layered with CuBr/CH_3CN yellow rods of $(CuBr)_2(P_4S_3)_2$ (**11**), red prisms of [CuBr(pyz)],[22] and yellow-orange prisms of $[(CuBr)_3(P_4S_3)(pyz)]$ (**12**) crystallized, which were characterized by X-ray diffraction analysis. The products may be distinguished by the red luminescence of [CuBr(pyz)], whereas compounds **11** and **12** do not emit in the visible spectrum. Selective formation of **12** by modifying the concentrations or the ratios of the reactants could not be achieved. In the system P_4S_3/pyz/CuI only orange crystals of $(CuI)_3(P_4S_3)$ were found.[17]

Compound **11** crystallizes in the triclinic space group $P\bar{1}$. The structure is characterized by castellated $(CuBr)_n$ chains running along the *a* axis. Pairs of these chains are bridged by P6 and P7 of the tridentate P_4S_3 cage (P5–P8), and P5 of the same cage binds to Cu2 of the next ribbon. In this manner a layer parallel to *ab* is formed, which is confined by pendent monodentate P_4S_3 cages (P1–P4) (Figure 9). The 2D structure of **11** extends the known structures of the P_4S_3/CuBr system.[19]

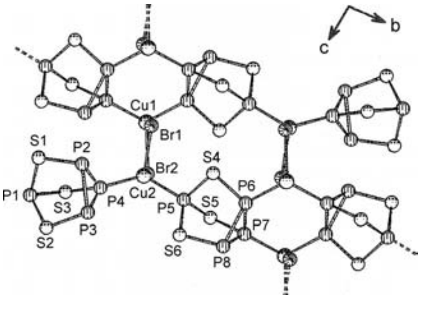


Figure 9. Section of the crystal structure of **11** viewed along the *a* axis. Selected distances [Å]: S–P 2.084(2)–2.110(2), P–P 2.215(2)–2.266(2), Cu–Br 2.417(1)–2.465(1).

Compound **12** crystallizes in the triclinic space group $P\bar{1}$. The outstanding structural feature is a cradle composed of two nearly planar (torsion angle Cu2–Br2/Cu3–Br3 = 16°) twelve-membered Cu_6Br_6 rings bridged by two opposing pyz and two P_4S_3 ligands. Neighboring Cu_6Br_6 units are connected by four-membered Cu_2Br_2 rings (Cu3Br3). Such a $(CuBr)_n$ substructure is unprecedented.[2] Each ring is *trans*-annular spanned by the basal atoms P2 and P3 of a P_4S_3 cage, and the apical atom P1 of the same cage is bound to the next ring. Another cage molecule serves as linker in the opposite direction. Two pyz molecules bridge opposing, slightly displaced Cu_6Br_6 rings through the N2 atom (Figure 10). A cage-like substructure is formed in this manner.

The sequence of cradles and condensed Cu_6Br_6 rings forms layers parallel to the *ab* plane. As these layers are linked by "N1" pyz molecules, a 3D framework is built up (Figure 11). The shortest distance between parallel "N1" pyz molecules is ca. 9 Å, and that between P_4S_3 molecules of neighboring layers is ca. 5 Å. The resulting cavities are occupied by toluene molecules.

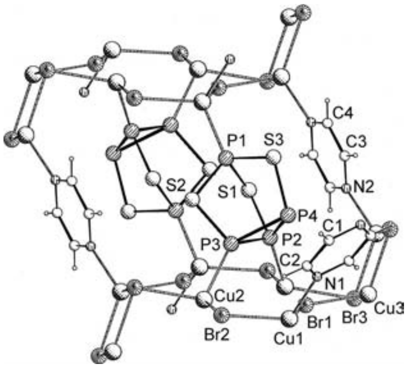


Figure 10. Section of the crystal structure of **12**. Three of the "N1" pyrazine rings are omitted for the sake of clarity. Selected distances [Å]: S1–P1 2.101(2), S1–P2 2.088(2), S2–P3 2.088(2), S3–P1 2.109(2), S3–P4 2.107(2), P2–P4 2.271(2), P2–P3 2.219(2), P3–P4 2.263(2), Cu1–Br1 2.460(1), Cu1–Br2 2.425(1), Cu2–Br2 2.423(1), Cu2–Br3 2.478(1), Cu3–Br3 2.453(1)–2.508(1), Cu1–P1 2.191(2), Cu2–P2 2.308(2), Cu2–P3 2.293(2), Cu1–N1 2.048(3), Cu3–N2 2.005(4), Cu3···Cu3a 2.875.

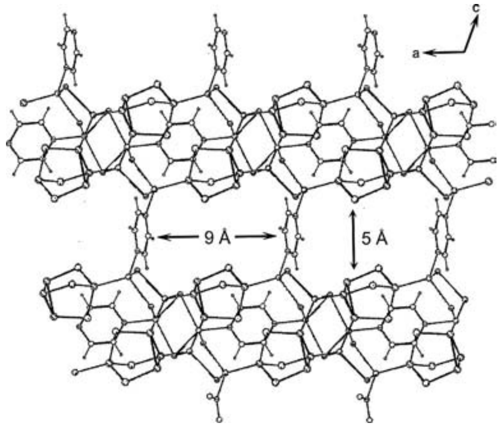


Figure 11. Section of the crystal structure of **12** projected on the *ac* plane. The solvent molecules are omitted for the sake of clarity.

Conclusions

Access to a new class of hybrid polymers by combining organic P,P′ or N,N′ donors and a multidentate inorganic cage molecule as cross-linkers with copper(I) halide aggregates of variable size has been described. The nature of the products, which range from mononuclear complexes to 3D frameworks, depends on the size and steric requirements of the organic ligands. The role of the P_4S_3 ligand may be characterized by its nearly spherical geometry, which allows reorientational coordination around the C_3 axis of the cage. In spite of the already well known tendencies of P_4S_3 or pyz to form binary polymers with copper(I) halides, the simultaneous coordination of P,P′ or N,N′ donors and P_4S_3 is shown to possess an important synthetic potential. If one considers the enormous variety of multifunctional organic donor ligands numerous and exciting new polymeric architectures may be expected.

Experimental Section

General: All manipulations were carried out under nitrogen and with dry solvents. Diffusion experiments were carried out in Schlenk tubes of 3.0 cm diameter. P_4S_3 was synthesized according to literature methods.[23] ^1H and ^{31}P NMR spectra were recorded with Bruker Avance 300 and Avance 400 spectrometers. ^{31}P MAS NMR spectra were recorded with a Bruker Avance 300 (121.495 MHz) spectrometer using a double resonance 2.5 mm MAS probe. All spectra were acquired at a MAS rotation frequency of 30 kHz, a 90° pulse length of 2.3 µs and with a relaxation delay of 450 s. For spectrum simulation the program DMFIT was used.[24]

[CuX(P$_4$S$_3$)(PRR′$_2$)$_2$] [R = R′ = Et, X = Cl (1), Br (2), I (3); R = Me, R′ = *i*Pr, X = Cl (4); R = R′ = Cy: X = I (5)]: A mixture of CuX (0.454 mmol), phosphane (1.135 mmol), and CH_3CN (10 mL) was combined with a solution of P_4S_3 (100 mg, 0.454 mmol) in toluene (50 mL) and stirred for 12 h at room temperature. After evaporation of the solvent, the oily residue was dissolved in toluene (3 mL) and cooled to –20 °C. Compounds **1**–**3** crystallized as colorless needles in 80% yield, compounds **4** and **5** were obtained as oils.

1: $C_{12}H_{30}ClCuP_6S_3$ (555.35): calcd. C 25.95, H 5.44, S 17.32; found C 26.14, H 5.47, S 16.60. ^1H NMR (300 MHz, C_6D_6): δ = 1.00 (m, 3 H), 1.38 (m, 2 H) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ = 85.6 (q; $^2J_{P,P}$ = 62 Hz), –11.0 (s), –115.9 (d; $^2J_{P,P}$ = 62 Hz) ppm.

2: $C_{12}H_{30}BrCuP_6S_3$ (599.84): calcd. C 24.03, H 5.04, S 16.04; found C 24.41, H 5.04, S 15.51. ^1H NMR (300 MHz, C_6D_6): δ = 0.98 (m, 3 H), 1.40 (m, 2 H) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ = 89.2 (q; $^2J_{P,P}$ = 61 Hz), –11.9 (s), –115.0 (d; $^2J_{P,P}$ = 61 Hz) ppm.

3: $C_{12}H_{30}CuIP_6S_3$ (646.80): calcd. C 22.28, H 4.67, S 14.87; found C 22.27, H 4.50, S 14.57. ^1H NMR (300 MHz, C_6D_6): δ = 0.97 (m, 3 H), 1.44 (m, 2 H) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ = 89.3 (q; $^2J_{P,P}$ = 62 Hz), –14.6 (s), –115.9 (d; $^2J_{P,P}$ = 62 Hz) ppm.

4: ^1H NMR (300 MHz, C_6D_6): δ = 0.91 (m, 12 H), 1.08 (m, 3 H), 1.63 (m, 2 H) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ = 96.6 (q; $^2J_{P,P}$ = 57 Hz), –1.1 (s), –109.8 (d; $^2J_{P,P}$ = 57 Hz) ppm.

5: ^1H NMR (300 MHz, C_6D_6): δ = 1.5 (m, 33 H) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ = 94.1 (q; $^2J_{P,P}$ = 57 Hz), 12.6 (s), –111.8 (d; $^2J_{P,P}$ = 57 Hz) ppm.

[CuCl(dppe)(CH$_3$CN)] (6): Layering a solution of P_4S_3 (50 mg, 0.227 mmol) and dppe (90 mg, 0.227 mmol) in toluene (10 mL, 22.7 mmol L^{-1}) with a solution of CuCl (36 mg, 0.368 mmol) in CH_3CN (10 mL, 36.8 mmol L^{-1}) gave colorless platelets of **6** and yellow needles of $(CuCl)_7(P_4S_3)_3$.

[CuI(P$_4$S$_3$)(dppe)] (7): A solution of P_4S_3 (50 mg, 0.227 mmol) and dppe (90 mg, 0.227 mmol) in toluene (10 mL, c = 45.4 mmol L^{-1}) was layered carefully with a solution of CuI (70 mg, 0.368 mmol) in CH_3CN (10 mL, 36.8 mmol L^{-1}). A few bright yellow platelets of **7** crystallized after about 5 d. ^{31}P MAS NMR: δ = 96.7 (m, $^1J_{P,Cu}$ = 778 Hz), –11.4 (m, $^1J_{P,Cu}$ = 1473 Hz), –105.5 (s) ppm.

[(CuX)$_2$(P$_4$S$_3$)(dppe)] [X = Br (8), I (9)]: P_4S_3 (50 mg, 0.227 mmol) and dppe (90 mg, 0.227 mmol) were dissolved in CH_2Cl_2 (10 mL, c = 45.4 mmol L^{-1}) and layered with a solution of CuX

Table 4. Crystal data and structure refinements for compounds **1**–**3** and **6**–**9**.

	1	**2**	**3**	**6**	**7**	**8**	**9**
Formula	$C_{12}H_{30}ClCuP_6S_3$	$C_{12}H_{30}BrCuP_6S_3$	$C_{12}H_{30}CuIP_6S_3$	$C_{41}H_{39}Cl_2Cu_2NP_3$	$C_{13}H_{12}CuIP_5S_3$	$C_{26}H_{24}Br_2Cu_2P_6S_3$	$C_{26}H_{24}Cu_2I_2P_6S_3$
M_w	555.39	599.81	646.80	836.64	609.74	905.38	999.38
Crystal size [mm^3]	0.16 × 0.08 × 0.06	0.22 × 0.15 × 0.07	0.16 × 0.07 × 0.04	0.17 × 0.03 × 0.02	0.130.09 × 0.05	0.21 × 0.12 × 0.09	0.07 × 0.05 × 0.02
Crystal system	orthorhombic	orthorhombic	orthorhombic	triclinic	monoclinic	triclinic	triclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	7.740(2)	7.698(1)	7.821(2)	13.462(1)	9.472(1)	9.684(1)	9.722(1)
b [Å]	16.617(1)	16.470(1)	16.301(1)	13.575(1)	18.782(1)	13.264(1)	13.355(1)
c [Å]	18.685(1)	19.141(1)	19.504(1)	13.808(1)	11.772(1)	14.070(1)	14.177(1)
α	–	–	–	103.2(1)	–	66.4(1)	66.8(1)
β	–	–	–	108.1(1)	109.3(1)	83.4(1)	82.5(1)
γ	–	–	–	111.2(1)	–	89.4(1)	88.0(1)
V [Å^3]	2403.3(1)	2426.6(2)	2486.6(1)	2062.4(2)	1976.5(2)	1643.2(2)	1676.8(2)
Z	4	4	4	2	4	2	2
$\rho_{calcd.}$ [g cm^{-3}]	1.535	1.642	1.728	1.347	2.049	1.830	1.979
μ [mm^{-1}]	8.488	9.323	16.964	3.777	20.573	9.139	20.621
λ (Å)	1.54178	1.54178	1.54178	1.54184	1.54178	1.54184	1.54180
Abs. corr.	empirical	empirical	analytical	analytical	–	–	analytical
Instrument	SuperNova	Gemini Ultra	SuperNova	SuperNova	SuperNova	SuperNova	SuperNova
Temp. [K]	123	123	123	173	123	295	123
Scan range	$3.56 < \Theta < -73.60$	$3.54 < \Theta < 72.75$	$3.53 < \Theta < 73.63$	$3.65 < \Theta < 62.18$	$4.62 < \Theta < 69.14$	$3.64 < \Theta < 71.36$	$3.42 < \Theta < 73.16$
Refl. collected / unique	4555 / 3785	4357 / 3939	6348 / 3830	17518 / 5318	9883 / 3255	17744 / 5658	17506 / 6051
Parameters	318	250	318	461	208	352	352
GOF in F^2	1.035	0.999	0.993	1.071	0.989	1.029	1.032
Residual density [e Å^{-3}]	0.542 / –0.316	0.542 / –0.354	0.717 / –0.582	0.818 / –0.509	0.330 / –0.353	0.930 / –0.710	1.052 / –0.784
R_1, wR_2 ($I > 2\sigma$)	0.033, 0.081	0.031, 0.076	0.027, 0.066	0.032, 0.086	0.019, 0.046	0.023/0.059	0.022, 0.055
R_1, wR_2 (all data)	0.038, 0.084	0.035/0.082	0.031, 0.066	0.038, 0.088	0.022, 0.047	0.025/0.060	0.025, 0.056
Flack parameter	0.48(4)	0.37(4)	–0.016(5)	–	–	–	–

Table 5. Crystal data and structure refinements for compounds **10**–**12**.

	10	**11**	**12**
Formula	$C_2H_2Cl_2Cu_2NP_4S_3$	$Br_2Cu_2P_8S_6$	$C_4H_4Br_3Cu_3N_2P_4S_3$, 0.5 C_7H_8
M_w	458.14	727.08	776.57
Crystal size [mm^3]	0.15 × 0.11 × 0.06	0.25 × 0.03 × 0.01	0.16 × 0.04 × 0.02
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	19.090(1)	6.310(1)	9.210(1)
b [Å]	11.122(1)	9.226(1)	9.288(1)
c [Å]	6.175(1)	15.505(1)	12.557(2)
α	–	99.6(1)	106.4(1)
β	94.1(1)	97.7(1)	108.9(2)
γ	–	106.3(1)	94.9(1)
V [Å^3]	1307.8(2)	838.6(1)	955.8(1)
Z	4	2	2
D $\rho_{\text{calcd.}}$ [g cm^{-3}]	2.327	2.880	2.698
μ [mm^{-1}]	16.579	22.753	17.423
λ [Å]	1.54184	1.54178	1.54184
Absorption correction	–	–	analytical
Instrument	SuperNova	Gemini Ultra	SuperNova
Temperature [K]	123	123	123
Scan range	$4.60 < \Theta < 73.07$	$5.11 < \Theta < 65.06$	$5.06 < \Theta < 70.86$
Reflections collected / unique	5015 / 2373	6872 / 2678	5991 / 3085
Parameters	128	163	209
GOF in F^2	1.113	1.040	0.961
Residual density [e Å^{-3}]	0.401 / –0.532	1.180 / –0.698	0.603 / –0.683
R_1, wR_2 ($I > 2\sigma$)	0.027, 0.070	0.025, 0.063	0.026, 0.067
R_1, wR_2 (all data)	0.030, 0.072	0.027, 0.064	0.032/0.069

(0.368 mmol) in CH_3CN (10 mL, 36.8 mmol L^{-1}). After 5 d yellow needles of **8** or **9** and yellow $(CuBr)_7(P_4S_3)_3$ and $(CuI)(P_4S_3)$, respectively, crystallized, which could not be separated quantitatively.

[(CuCl)$_4$(P$_4$S$_3$)$_2$(pyz)] (10): P_4S_3 (30 mg, 0.136 mmol) and $C_4H_4N_2$ (11 mg, 0.136 mmol) were dissolved in CH_2Cl_2 (10 mL, 27.2 mmol L^{-1}) and layered with a solution of CuCl (40 mg, 0.408 mmol) in CH_3CN (5 mL, 81.6 mmol L^{-1}). After 3 d flat yellow prisms of **10** and yellow needles of [CuCl(pyz)] crystallized, which were separated manually for crystallographic examination. ^{31}P MAS NMR: δ = 92.2 (m, $^1J_{P,Cu}$ = 1102 Hz), –72.5 (m, $^1J_{P,Cu}$ = 1190 Hz), –83.4 (m, $^1J_{P,Cu}$ = 894 Hz), –97.4 (s) ppm.

Reaction of P$_4$S$_3$/pyz with CuBr: A solution of P_4S_3 (30 mg, 0.136 mmol) and $C_4H_4N_2$ (22 mg, 0.272 mmol) in toluene (10 mL, 40.8 mmol L^{-1}) was layered with a solution of CuBr (59 mg, 0.408 mmol) in CH_3CN (5 mL, 81.6 mmol L^{-1}). Crystalline material appeared after 4 d consisting of yellow rods of $(CuBr)_2(P_4S_3)_2$ (**11**), red prisms of [CuBr(pyz)], and yellow-orange prisms of [$(CuBr)_3(P_4S_3)(pyz)\cdot 0.5C_7H_8$] (**12**), which were separated manually for X-ray diffraction analysis.

Crystal Structure Determination: Crystallographic data of the crystal structure determinations for **1**–**3** and **6**–**12** are given in Tables 4 and 5. The structures were solved by direct methods (SIR97 program)[25] and refined by full-matrix least-squares (SHELXL97 program)[26] with all reflections. The crystals of **6** and **12** contain solvent molecules. For **6** it was not possible to refine any reasonable molecule from the difference Fourier peaks, therefore the contribution of the heavily disordered solvent to the calculated structure factors was taken into account by the SQUEEZE[27] procedure. For **12** a toluene molecule could be found from difference Fourier peaks but it showed also some peculiarity: in the middle of the benzene ring is an inversion center of the symmetry framework, which does not fit to the molecular symmetry. The description of the crystal structure in the acentric space group $P\bar{1}$ was unsuccessful because all atoms apart from the solvent clearly follow centrosymmetric requirements. Hence the toluene molecule was necessarily refined with disorder.

CCDC-826120 (for **1**), -826121 (for **2**), -826122 (for **3**), -826123 (for **6**), -826124 (for **7**), -826125 (for **8**), -826126 (for **9**), -826127 (for **10**), -826128 (for **11**), and -826129 (for **12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] K. Biradha, A. Ramanan, J. J. Vittal, *Cryst. Growth Des.* **2009**, *9*, 2969–2970.

[2] R. Peng, M. Li, D. Li, *Coord. Chem. Rev.* **2010**, *254*, 1–18.

[3] A. S. Degtyarenko, P. V. Solntsev, H. Krautscheid, E. B. Rusanov, A. N. Chernega, K. V. Domasevitch, *New J. Chem.* **2008**, *32*, 1910–1918.

[4] D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O'Keeffe, O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1257–1283.

[5] a) X. Lin, A. J. Blake, C. Wilson, X. Z. Sun, N. R. Champness, M. W. George, P. Hubberstey, R. Mokaya, M. Schröder, *J. Am. Chem. Soc.* **2006**, *128*, 10745–10753; b) X. Lin, I. Telepeni, A. J. Blake, A. Dailly, C. M. Brown, J. M. Simmons, M. Zoppi, G. S. Walker, K. M. Thomas, T. J. Mays, P. Hubberstey, N. R. Champness, M. Schröder, *J. Am. Chem. Soc.* **2009**, *131*, 2159–2171.

[6] a) A. M. Shultz, O. K. Farha, J. T. Hupp, S. T. Nguyen, *J. Am. Chem. Soc.* **2009**, *131*, 4204–4205; b) Y. K. Hwang, D.-Y.

Hong, J. S. Chang, S. H. Jhung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Férey, *Angew. Chem. Int. Ed.* **2008**, *47*, 4144–4148.

[7] a) R. Langer, L. Wunsche, D. Fenske, O. Fuhr, *Z. Anorg. Allg. Chem.* **2009**, *635*, 2488–2494; b) B. Chen, L. Wang, Y. Xiao, F. R. Fronczek, M. Xue, Y. Cui, G. Qian, *Angew. Chem. Int. Ed.* **2009**, *48*, 500–503; c) B. D. Chandler, J. O. Yu, D. T. Cramb, G. K. H. Shimizu, *Chem. Mater.* **2007**, *19*, 4467–4473; d) M. Knorr, A. Pam, A. Khatyr, C. Strohmann, M. M. Kubicki, Y. Rousselin, S. M. Aly, D. Fortin, P. D. Harvey, *Inorg. Chem.* **2010**, *49*, 5834–5844.

[8] a) W. Ouellette, A. V. Prosvirin, K. R. Whitenack, K. Dunbar, J. Zubieta, *Angew. Chem. Int. Ed.* **2009**, *48*, 2140–2143; b) Q. F. Zhang, Z. Yu, A. Rothenberger, D. Fenske, W. H. Leung, *Inorg. Chim. Acta* **2007**, *360*, 1568–1574.

[9] M. Meilikhov, K. Yusenko, D. Esken, S. Turner, G. Van Tendeloo, R. A. Fischer, *Eur. J. Inorg. Chem.* **2010**, 3701–3714.

[10] For pure P_n ligand complexes, see M. Scheer, *Dalton Trans.* **2008**, 4372–4386.

[11] a) C. Di Nicola, Effendy, F. Fazaroh, C. Pettinary, B. W. Skelton, N. Somers, A. H. White, *Inorg. Chim. Acta* **2005**, *358*, 720–734; b) A. Cingolani, C. Di Nicola, Effendy, C. Pettinary, B. W. Skelton, N. Somers, A. H. White, *Inorg. Chim. Acta* **2005**, *358*, 748–762; c) Effendy, C. Di Nicola, M. Fianchini, C. Pettinary, B. W. Skelton, N. Somers, A. H. White, *Inorg. Chim. Acta* **2005**, *358*, 763–795; d) Effendy, C. Di Nicola, C. Pettinary, A. Pizzabiocca, B. W. Skelton, N. Somers, A. H. White, *Inorg. Chim. Acta* **2006**, *359*, 64–80.

[12] a) H. Araki, K. Tsuge, Y. Sasaki, S. Ishizaka, N. Kitamura, *Inorg. Chem.* **2007**, *46*, 10032–10034; b) A. M. Kirillov, P. Smoleński, M. Haukka, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Organometallics* **2009**, *28*, 1683–1687; c) A. M. Kirillov, P. Smoleński, Z. Mha, M. F. C. Guedes da Silva, M. Haukka, A. J. L. Pombeiro, *Organometallics* **2009**, *28*, 6425–6431.

[13] a) J. J. M. Amoore, L. R. Hanton, M. D. Spicer, *Dalton Trans.* **2003**, 1056–1058; b) J. Wang, S.-L. Zheng, S. Hu, Y.-H. Zhang, M.-L. Tong, *Inorg. Chem.* **2007**, *46*, 795–800; c) S.-Q. Bai, L. L. Koh, T. S. A. Hor, *Inorg. Chem.* **2009**, *48*, 1207–1213; d) T. S. Lobana, S. Khanna, A. Castineiras, G. Hundai, *Z. Anorg. Allg. Chem.* **2010**, *636*, 454–456.

[14] a) A. Adolf, M. Gonsior, I. Krossing, *J. Am. Chem. Soc.* **2002**, *124*, 7111–7116; b) I. Raabe, S. Antonijevic, I. Krossing, *Chem. Eur. J.* **2007**, *13*, 7510–7522.

[15] J. Wachter, *Coord. Chem. Rev.* **2010**, *254*, 2078–2085.

[16] A. Biegerl, C. Gröger, H. Kalbitzer, A. Pfitzner, J. Wachter, R. Weihrich, M. Zabel, *J. Solid State Chem.* **2011**, *184*, 1719–1725.

[17] A. Biegerl, E. Brunner, C. Gröger, M. Scheer, J. Wachter, M. Zabel, *Chem. Eur. J.* **2007**, *13*, 9270–9276.

[18] M. R. Churchill, K. L. Kalra, *Inorg. Chem.* **1974**, *13*, 1899–1904.

[19] A. Biegerl, C. Gröger, H. R. Kalbitzer, J. Wachter, M. Zabel, *Z. Anorg. Allg. Chem.* **2010**, *636*, 770–774.

[20] M.-L. Fu, D. Fenske, B. Weinert, O. Fuhr, *Eur. J. Inorg. Chem.* **2010**, 1098–1102.

[21] a) C. Näther, I. Jeß, J. Greve, *Polyhedron* **2001**, *20*, 1017; b) C. Näther, I. Jeß, *J. Solid State Chem.* **2002**, *169*, 103–112.

[22] P. M. Graham, R. D. Pike, M. Sabat, R. D. Bailey, W. T. Pennington, *Inorg. Chem.* **2000**, *39*, 5121–5132.

[23] A. Stock, *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 150.

[24] D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calve, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan, G. Hoatson, *Magn. Reson. Chem.* **2002**, *40*, 70–76.

[25] *SIR97*, A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[26] *SHELXL-97*, G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

[27] P. van der Sluis, A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, 194–201.

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