Conference paper

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Macrocyclic tetrakis-phosphines and their copper(I) complexes

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Abstract: A series of mono-, di- and tetranuclear copper(I) complexes with macrocyclic 14-, 16-, 18- and 20-membered tetrakis-phosphine ligands (P_4N_2) was obtained and fully characterized including single crystal X-ray diffraction. The 14-membered P_4N_2 macrocycles form very stable cationic mononuclear tetraphospha-coordinated copper(I) complexes, whereas their higher 16-, 18- and 20-membered homologues give neutral dinuclear $[Cu_2I_2L]$ complexes under the same conditions. An unusual tetranuclear complex with two three- and two four-coordinated copper(I) atoms was obtained from 16-$P^{Mes}{}_4N^{CH2CH2Py\text{-}2}{}_2$ and copper(I) iodide. This is the first example of N-coordination of cyclic aminomethylphosphines towards "soft" copper(I).

Keywords: copper; ICPC-21; macrocycles; metal complexes; tetrakis-phosphine.

Introduction

Crown ethers and aza-crown macrocycles are highly selective receptors (host molecules) for a variety of cations or anions, as well as for small or even huge (e.g. fullerenes) neutral organic molecules [1–4]. Incorporation of phosphorus atoms as donor atoms in the macrocyclic skeleton should result in specific properties and thus expand the possibilities [5]. Trivalent phosphorus donor centers are soft in contrast to the hard O and N counterparts and preferentially coordinate to soft metal ions. Furthermore, phosphine ligands play a major role in transition-metal based catalysis of various organic reactions; incorporation of the P and N donor atoms in a macrocycle could result in additional bonding of metal centers and/or (weak) interactions with organic substrates. Tetrakis-phosphine ligands are suitable for the complexation with most catalytically active transition metals, e.g. nickel(II), copper(I), palladium(II), or platinum(II). Nevertheless, there are only a few examples of macrocyclic tetrakis-phosphine complexes which mainly were obtained by cyclization of secondary phosphines on metal templates [6–15]. Even less examples of transition metal complexes with macrocyclic P_4-corands which were obtained by the complexation reactions of P_4-corands with metal salts were described [16–18]. There are some noticeable problems concerning the synthesis of tetrakis-phosphine macrocycles [18]. Our group has developed a synthetic self-assembly strategy for the preparation of macrocyclic

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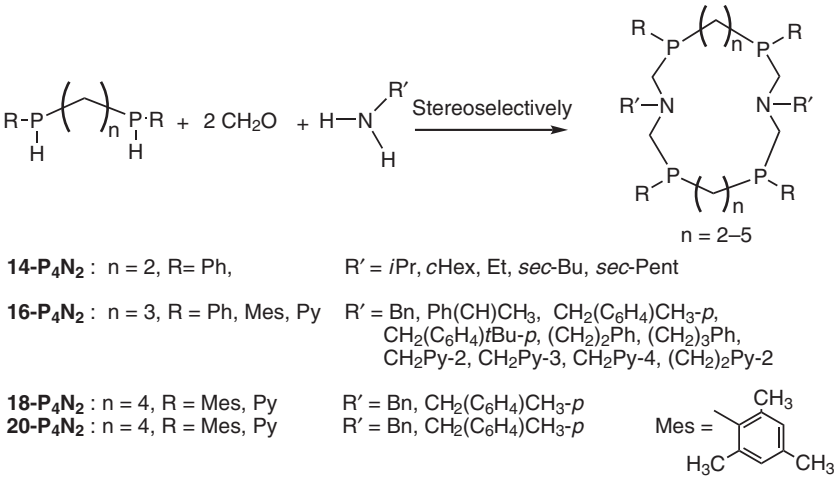


Scheme 1: Synthesis of P_4N_2 macrocycles.

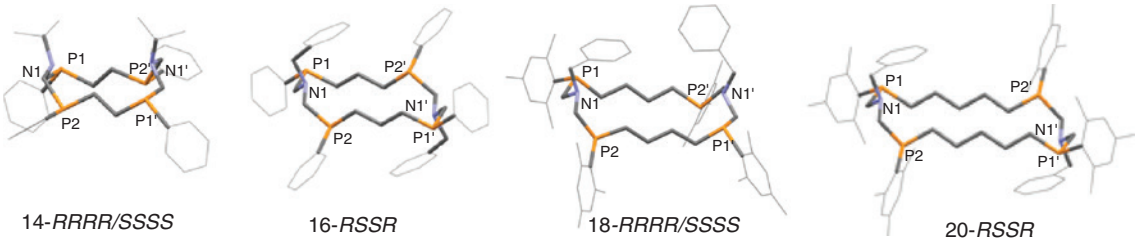


Fig. 1: Molecular structures of P_4N_2 macrocycles.

tetrakis-phosphines by which numerous 14-, 16-, 18- and 20-membered P_4N_2 macrocycles were obtained from various secondary α,ω-bis(phosphino)alkanes, formaldehyde and primary amines (Scheme 1) [19–27].

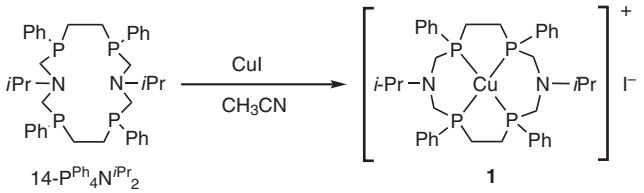
Molecular structures obtained of P_4N_2 macrocycles are generally very similar (Fig. 1). The macrocycles have crown conformation and a rectangular cavity. The shorter side of the rectangle is defined by the P1···P2 distance between the two phosphorus atoms of the P-CH_2-N(R)-CH_2-P moiety and is practically equal for all macrocycles independent of their size. The length of rectangle is defined by the P1···P2′ distance of the $P(CH_2)_nP$ moiety, i.e. the length of the alkylene chain, and increases from 14- to 20-membered macrocycles.

Both nitrogen atoms are directed toward the cavity and are located on the same side relative to the macrocyclic plane in the 14- and 18-membered macrocycles and on opposite sides in the 16- and 20-membered macrocycles. The zig-zag-like arrangement of the alkylene chain and the number of methylene groups determine the configuration at the phosphorus atoms. The configuration of the major isomer obeys the following empiric rule: if two chiral phosphorus centers in the macrocycle are linked by an odd number of methylene groups, the *RSSR* stereoisomer is adopted; if the phosphorus atoms in the macrocycle are linked by even number of methylene groups, the *SSSS/RRRR* isomer is formed [27].

The structural features of P_4N_2 macrocycles define their coordination abilities. In this work, we present the synthesis of copper(I) complexes of 14-, 16-, 18- and 20-membered macrocyclic tetrakis-phosphine ligands.

Results and discussion

P_4N_2 macrocycles have six potential donor centers – four soft phosphorus and two hard nitrogen atoms. It is noteworthy that no examples of N-coordination of cyclic aminomethylphosphines towards soft metal ions [copper(I), platinum(II), palladium(II), nickel(II)] are known. Only two representatives of N-coordination of



Scheme 2: Synthesis of the copper complex with 14-P_4N_2-ligand.

diazadiphosphacyclooctanes with hard chromium(III) and manganese(I) ions [28–30] are known, and one complex where copper(I) is chelated by two phosphorus atoms of a cyclic aminomethylphosphine and is located in close proximity to the nitrogen coordination center [31]. Therefore, it is permissible to consider the P_4N_2 macrocycles as P_4-ligands. Three representatives of 16-membered mononuclear copper(I) tetrakis-phosphine complexes and one example of 18-membered mononuclear copper(I) tetrakis-phosphine complex were obtained by cyclization of secondary bis-phosphines on a copper(I) template in 2016 by Swor [8]. The molecular structure of complex [Cu(16-P^{Ph}_4)]OTf was confirmed by X-ray analysis, and it was demonstrated that the phosphorus atoms in this complex have *RSRS* configuration [8].

The reaction of 14-$P^{Ph}_4N^{iPr}_2$ with copper(I) iodide in pyridine led to the macrocyclic mononuclear P_4-chelate complex **1** in good yield (Scheme 2).

The formation of [CuL]I (**1**) was confirmed by ESI mass spectrometry and elemental analysis. It is noteworthy that the mononuclear cationic complex **1** is formed even with excess of copper iodide. Complex **1** is very stable in organic solvents due to the macrocyclic effect and unlike the free ligand no dissociation is observed. Thus, only one slightly broadened signal at 9.8 ppm is observed in the $^{31}P\{^1H\}$ NMR spectrum of complex **1**. The $\Delta\delta$ value between the chemical shifts of coordinated and free ligand (ca. 42 ppm) is evidence of formation of a macrocyclic chelate complex. An X-ray structure analysis of crystals of **1** confirmed the proposed structure (Fig. 2).

The copper(I) atom is coordinated in a tetrahedral fashion by four phosphorus atoms (Cu–P1 2.2147(6) Å and Cu–P2 2.2251(7) Å). The five- and six-membered chelate rings have twist and chair conformations, respectively. The ligand has retained its conformation and *RRRR*/*SSSS* configuration of the phosphorus atoms.

The 16-, 18- and 20-membered P_4N_2 macrocycles have longer spacers between the phosphorus atoms than the 14-membered P_4N_2 macrocycle which could obstruct the formation of mononuclear tetrakis-phosphine copper(I) complexes. Indeed, according to ESI mass spectrometry and elemental analysis only binuclear complexes **2–5** of composition [Cu_2I_2L] were obtained from the respective ligands independent of the stoichiometry used (Scheme 3).

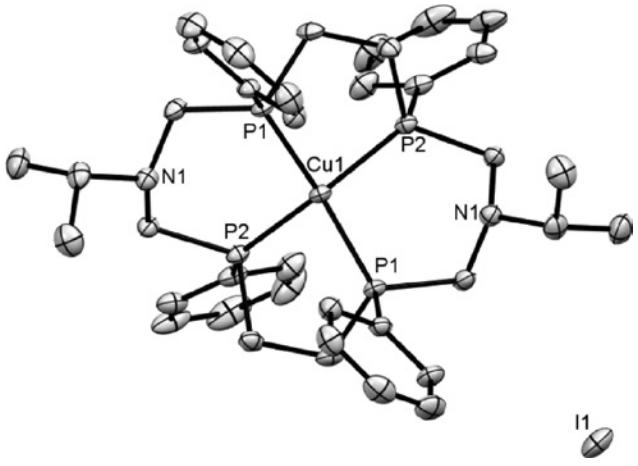
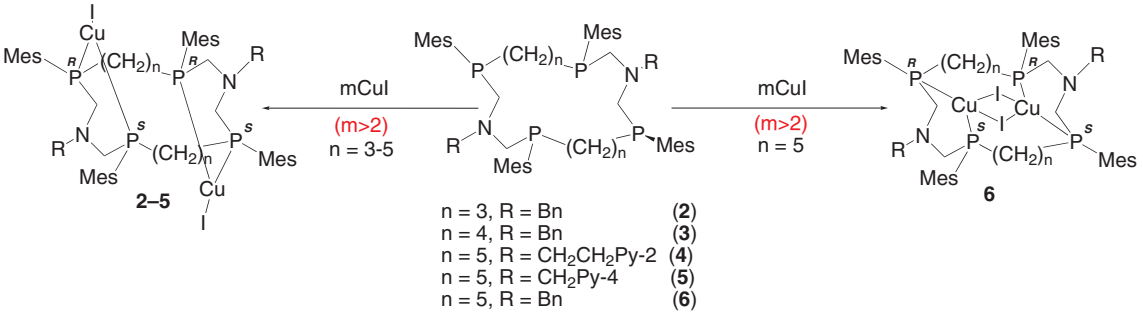


Fig. 2: Molecular structure of complex **1** (hydrogen atoms are omitted for clarity).



Scheme 3: Synthesis of copper complexes with 16-, 18- and 20-P_4N_2 ligands.

The neutral dinuclear complexes **2–5** are poorly soluble in most organic solvents excluding DMF and pyridine where dissociation occurs, resulting in not informative NMR spectra. However, the structures of complexes **2–5** could be established by X-ray analysis (Figs. 3–6).

The molecular structures of the dinuclear copper complexes **2–5** are similar; regardless of the initial phosphorus configuration of the free ligand (*RSSR* for 16- and 20-membered macrocycles or *RRRR/SSSS* for the 18-membered macrocycle), the dinuclear complexes are obtained as *RRSS* isomers. This change of configuration of the phosphorus atoms on complexation indicates kinetic lability of the P_4N_2 macrocycles [26]. The 20-membered P_4N_2 macrocycles are more flexible than their 16- and 18-membered homologues and form various conformers whose structures differ in the arrangement of the very flexible pentylene chains between the phosphorus atoms. Thus, complex **5** crystallized as a mixture of two conformers, **5a** and **5b** (Fig. 6).

In complexes **2–5**, the copper atoms are in a distorted trigonal-planar environment (the sum of bond angles at copper is about 355–357°). The two copper atoms are located on opposite sides of the macrocyclic plane. The six-membered CuPCNCP metallacycles exhibit a distorted "half-chair" conformation and are almost perpendicular to the macrocyclic plane. In complexes **2** and **5a**, the bisphosphinoalkylene fragments have a zig-zag conformation, and the carbon atoms are located in the P_4 plane. In complex **3**, the butylene spacers also exhibit a zig-zag conformation, but here the carbon atoms are alternatingly located above and below the P_4 plane. In the pentylene spacers of complexes **4** and **5b**, the central carbon atoms are coplanar with the four phosphorus atoms whereas the other four carbon atoms are alternatingly located above and below the P_4 plane. The substituents on the nitrogen atoms are in axial and the lone pair of electrons in equatorial positions. The main difference between the molecular structures of **2**, **4**, **5b** and **3**, **5a** is the location of the aminomethyl fragments. In complexes **2**, **4**, **5b** they are directed outward with respect to the macrocyclic cavity, whereas in **3** and **5a** they are directed inward. The P···P distances (3.562(5) Å) and P–Cu–P bond angles (105.11(2)°) in **3** (18-membered macrocycle) are noticeably smaller than in the complexes with

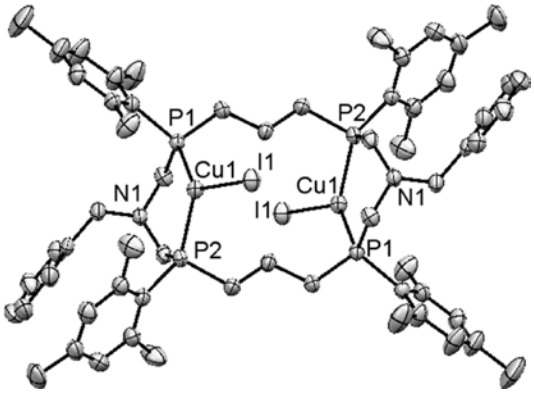


Fig. 3: Molecular structure of complex **2**.

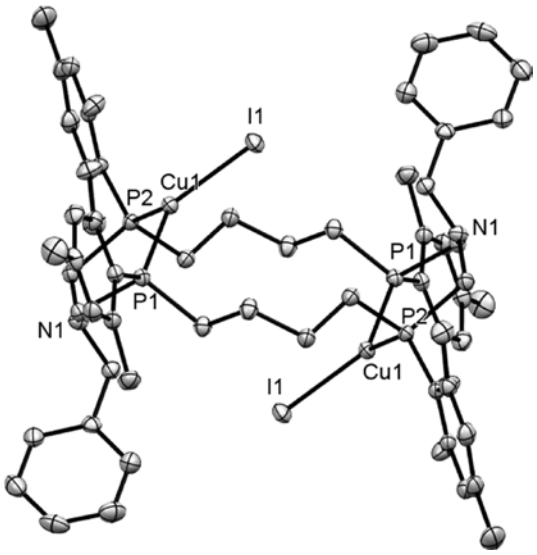


Fig. 4: Molecular structure of complex **3**.

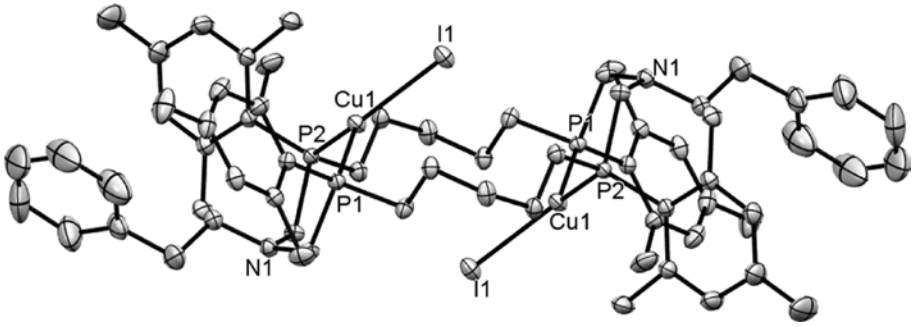


Fig. 5: Molecular structure of complex **4**.

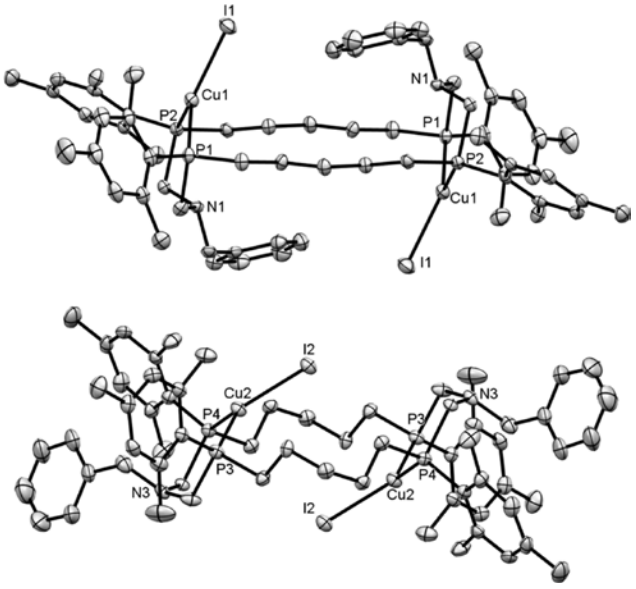


Fig. 6: Molecular structure of the two conformers of complex **5** (top: conformer **5a**, bottom: conformer **5b**).

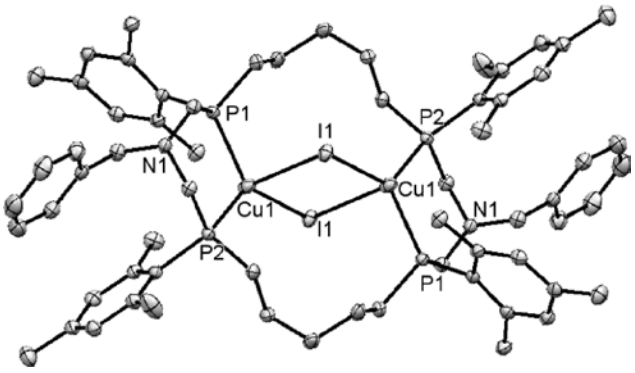


Fig. 7: Molecular structure of complex **6**.

16- and 20-membered macrocycles (**2**, **4** and **5**; 3.661(4)–3.739(3) Å and 107.89(4)–111.03(4)°, respectively). In the conformer **5a**, the copper–iodine bonds are almost orthogonal to the macrocyclic plane and are directed to opposite sides. In the other complexes, the copper–iodine bonds are pointing toward the macrocyclic cavity. The distance between the two parallel copper–iodine bonds decreases from **2** (16-membered) to **5b** (20-membered) with Cu···I′ distances are of 5.897 Å (**2**), 5.905 Å (**3**), 4.354 Å (**4**) and 4.454 Å (for **5b**). Finally, in complex **6**, an iodo-bridged $Cu_2(\mu\text{-}I_2)$ structure is formed (Fig. 7).

The molecular structure of the ligand in complex **6** is similar to those observed in complexes **2–5**, and the ligand conformation resembles that in complex **5b**. Unlike complexes **2–5**, the copper(I) atoms in **6** are coordinated in a tetrahedral fashion due to the additional coordination by the bridging iodo ligands.

We have previously already demonstrated the stereoconversion of P_4N_2 macrocycles in organic solvents [26]. This stereoconversion is also the reason for the formation of the minor isomer of the dicopper complex, **6-iso**, with *RSRS* configuration of the ligand 20-$P^{Mes}{}_4N^{Bn}{}_2$. The molecular structure of complex **6-iso** was also established by X-ray structure determination (Fig. 8).

Each of the two copper atoms is chelated by the two phosphorus atoms of the $N(CH_2PMes)_2$ fragments and has a trigonal-planar configuration. The copper–iodine bonds are directed to the same side of the macrocyclic plane. The two six-membered CuPCNCP metallacycles exhibit a distorted "half-chair" conformation. The substituents on the nitrogen atoms are in axial and the lone pair of electrons in equatorial positions. Only one of the aminomethyl fragments of the coordinated ligand is directed toward the center of the macrocycle. The P···P distances (3.597(6) and 3.642(4) Å) and P–Cu–P bond angles (105.43(6)° and 108.55(5)°) are significantly smaller than those in complexes **4–6**.

While complex **4** showed no coordination of external pyridine, which was used in the reaction as a solvent, nor coordination of the flexible pyridylethyl substituent, this type of interaction was observed when the 16-membered P_4N_2 macrocycle containing an exocyclic pyridyl-2-ethyl fragment was reacted with excess of copper iodide in pyridine. Here, an unusual tetranuclear complex $[Cu_4I_4L]$ (**7**) was obtained. Complex **7** is poorly soluble in organic solvents; the structure was determined by X-ray crystallography (Fig. 9).

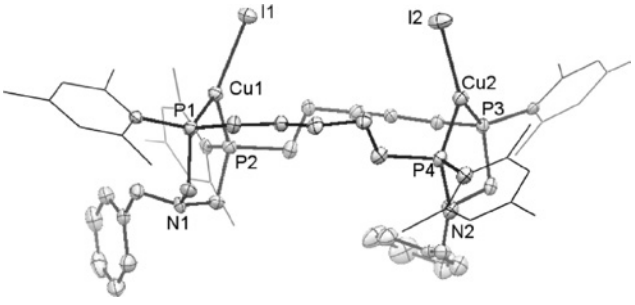


Fig. 8: Molecular structure of complex **6-iso**.

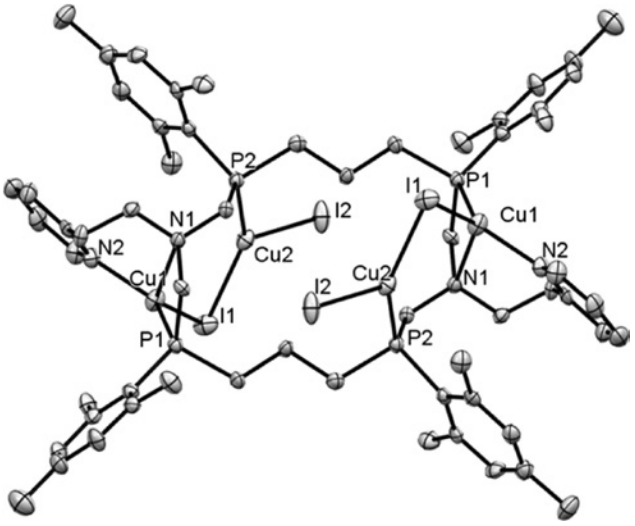


Fig. 9: Molecular structure of complex **7**.

The macrocyclic ligand in **7** is the *RRSS* isomer, and its conformation is similar to the conformation of the ligand in complex **2**. The four phosphorus atoms are coordinating alternatingly three- and four-coordinate copper(I) atoms which are bridged by iodo ligands. Two copper atoms are coordinated in a trigonal-planar fashion by one phosphorus atom and two iodo ligands (one bridging), and the other two copper(I) atoms are coordinated in a tetrahedral fashion by one phosphorus atom, the bridging iodo ligand and the exocylic and endocylic nitrogen atoms, resulting in a tricyclic structure at Cu1, which is formed by two six-membered and one four-membered metallacycles. This is the first example of N-coordination of cyclic aminomethylphosphines in a copper(I) complex. The terminal Cu–I bonds are directed toward the macrocyclic cavity, as it was also observed for complexes **2–5**.

Conclusions

Copper(I) complexes based on macrocyclic tetrakis-phosphines show large structural diversity. 14-Membered P_4N_2 macrocycles form very stable cationic mononuclear P_4-coordinated copper(I) complexes, whereas the 16-, 18- and 20-membered homologues give neutral binuclear $[Cu_2I_2L]$ complexes under the same conditions. The most flexible 20-membered P_4N_2 macrocycle with pentylene spacers form various conformers of dicopper(I) complexes with different arrangement of the alkylene chains as well as stereoisomers and isomers with different copper-iodide arrangements. An unusual tetranuclear complex with two three- (via P, $I_{terminal}$, and $I_{bridging}$) and two four-coordinated cooper(I) atoms (via P, $I_{bridging}$, N_{endo}, and N_{exo}) was obtained from 16-$P^{Mes}_4N^{CH2CH2Py\text{-}2}_2$ and copper(I) iodide. This complex is the first example of N-coordination of cyclic aminomethylphosphines towards soft copper(I).

Experimental

General

All reactions and manipulations were carried out under dry argon with standard vacuum line techniques. Solvents were purified, dried, deoxygenated and distilled before use. MALDI mass spectra were obtained on a Bruker ULTRAFLEX III mass spectrometer (laser Nd: YAG, λ 355 nm) in a linear mode, without accumulation

of mass spectra. ESI mass spectra were registered on an AmazonX mass spectrometer (Bruker Daltonics, Germany) in positive and negative mode. The mass spectra are given as m/z values and relative intensities (I_{rel}, %). ^{1}H NMR (400 MHz) and ^{31}P NMR (162 MHz) spectra were recorded on a Bruker Avance – DRX 400 spectrometer. Chemical shifts are given in parts per million relative to $SiMe_4$ (^{1}H, ^{13}C, internal solvent) and 85% H_3PO_4 (^{31}P, external). *J* values are given in Hz.

Synthesis and characterization of compounds 1–7

The synthesis, NMR data, mass spectrometry data and elemental analysis of complexes **1–7** are given in the Supporting Information.

X-ray structure determination

Data of complex **1**·EtOH and **6** were collected on a Bruker Smart Apex II CCD diffractometer using graphite monochromated Mo-K_α ($\lambda = 0.71073$ Å) radiation and ω-scan rotation. Data for **2** were collected on a Siemens CCD 1K-SMART diffractometer, **3**, **4**, **5**, **6-iso** and **7** on an Rigaku Gemini diffractometer, all of them equipped with a graphite-monochromated Mo-K_α radiation source ($\lambda = 0.71073$ Å). Data collection images for **1** and **6** were indexed, integrated, and scaled using the APEX2 data reduction package [32] and corrected for absorption using SADABS [33]. Data reduction for **2** was performed with SAINT-NT V5.0 [34] including the program SADABS, and for **3**, **4**, **5**, **6-iso** and **7** the program CrysAlis Pro [35] including the program SCALE3 ABSPACK [36] for empirical absorption correction was used. All structures were solved by direct methods (Sir-92) [37] or with SHELXS and refined using SHELXL programs [38]. With the exception of disordered solvent molecules (**5**, **6-iso**, **7**), all non-hydrogen atoms were refined anisotropically. H atoms were calculated on idealized positions and refined as riding atoms.

Crystal data and experimental details are given in Table S1 (Supporting Information). CCDC 1509561 (**1**), 1508688 (**2**), 1508689 (**3**), 1508690 (**4**), 1508691 (**5**), 1509562 (**6**), 1508692 (**6-iso**) and 1508693 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

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References

[1] J. W. Steed, J. L Atwood. *Supramolecular Chemistry*, John Wiley & Sons, Chichester (2000).
[2] B. König, J. Svoboda. "Azamacrocyclic systems with different supramolecular function", in *Macrocyclic Chemistry*, K. Gloe (Ed.), pp. 87–103, Springer, Netherlands (2005).
[3] R. G. Chapman, J. C. Sherman. *Tetrahedron* **53**, 15911 (1997).
[4] M. Caricato, C. Coluccini, D. Dondi, D. A. van der Griend, D. Pasini. *Org. Biomol. Chem.* **8**, 3272 (2010).
[5] A.-M. Caminade, J. P. Majoral. *Chem. Rev.* **94**, 1183 (1994).
[6] T. A. DelDonno, W. Rosen. *J. Am. Chem. Soc*. **99**, 8051 (1977).
[7] T. A. DelDonno, W. Rosen. *Inorg. Chem*. **17**, 3714 (1978).
[8] B. P. Nell, Ch. D. Swor, E. A. Henle, L. N. Zakharov, N. I. Rinehart, A. Nathan, D. R. Tyler. *Dalton Trans*. **45**, 8253 (2016).
[9] R. Bartsch, S. Hietkamp, S. Morton, O. Stelzer. *Angew. Chem. Int. Ed*. **21**, 375 (1982).
[10] T. Mizuta, A. Okano, T. Sasaki, H. Nakazawa, K. Miyoshi. *Inorg. Chem*. **36**, 200 (1997).
[11] B. Lambert, J. F. Desreux. *Synthesis* **12**, 1668 (2000).
[12] R. Bartsch, S. Hietkamp, S. Morton, H. Peters, O. Stelzer. *Inorg. Chem*. **22**, 3624 (1983).
[13] R. Bartsch, S. Hietkamp, H. Peters, O. Stelzer. *Inorg. Chem*. **23**, 3304 (1984).

[14] D. J. Brauer, T. Lebbe, O. Stelzer. *Angew. Chem. Int. Ed*. **27**, 438 (1988).
[15] D. J. Brauer, F. Dörrenbach, T. Lebbe, O. Stelzer. *Chem. Ber*. **125**, 1785 (1992).
[16] G. Q. Li, R. Govind. *Inorg. Chim. Acta*. **231**, 225 (1995).
[17] M. Ciampolini, N. Nardi, F. Zanobini. *Inorg. Chim. Acta*. **76**, 17 (1983).
[18] M. Ciampolini, N. Nardi, P. Dapporto, P. Innocenty, F. Zanobini. *J. Chem. Soc. Dalton Trans*. 575 (1984).
[19] A. A. Karasik, O. G. Sinyashin. "Phosphorus based macrocyclic ligands: synthesis and applications", in *Phosphorus Compounds Advanced Tools in Catalysis and Material Sciences*, M. Peruzzini, L. Gonsalvi (Eds.). pp. 375–444. Springer, Netherlands (2011).
[20] E. I. Musina, A. A. Karasik, O. G. Sinyashin, G. N. Nikonov. "Heterocyclic Phosphines with P-C-X Fragments (X = O, N, P)", in *Advances in Heterocyclic Chemistry*, 117, pp. 83–130, Academic Press, Waltham, USA (2015).
[21] A. A. Karasik, A. S. Balueva, O. G. Sinyashin, *C. R. Chimie*, **13**, 1151 (2010).
[22] R. N. Naumov, A. A. Karasik, K. B. Kanunnikov, A. V. Kozlov, Sh. K. Latypov, K. V. Domasevitch, E. Hey-Hawkins, O. G. Sinyashin, *Mendeleev Commun*. **18**, 80 (2008).
[23] R. N. Naumov, A. A. Karasik, O. G. Sinyashin, P. Lönnecke, E. Hey-Hawkins, *Dalton Trans*. 357 (2004).
[24] A. A. Karasik, D. V. Kulikov, A. S. Balueva, S. N. Ignat'eva, O. N. Kataeva, P. Lönnecke, A. V. Kozlov, Sh. K. Latypov, E. Hey-Hawkins, O. G. Sinyashin, *Dalton Trans*. 490 (2009).
[25] R. N. Naumov, E. I. Musina, K. B. Kanunnikov, T. I. Fesenko, D. B. Krivolapov, I. A. Litvinov, P. Lönnecke, E. Hey-Hawkins, O. G. Sinyashin. *Dalton Trans*. **43**, 12784 (2014).
[26] A. A. Karasik, R. N. Naumov, K. B. Kanunnikov, D. B. Krivolapov, I. A. Litvinov, P. Lönnecke, A. S. Balueva, E. I. Musina, E. Hey-Hawkins, O. G. Sinyashin. *Macroheterocycles* **7**, 181 (2014).
[27] E. I. Musina, T. I. Fesenko, I. D. Strelnik, F. M. Polyancev, Sh. K. Latypov, P. Lönnecke, E. Hey-Hawkins, A. A. Karasik, O. G. Sinyashin. *Dalton Trans*. **44**, 13565 (2015).
[28] M. T. Mock, Sh. Chen, R. Rousseau, M. J. O'Hagan, W. G. Dougherty, W. S. Kassel, D. L. DuBois, R. M. Bullock. *Chem. Commun*. **47**, 12212 (2011).
[29] E. B. Hulley, K. D. Welch, A. M. Appel, D. L. DuBois, R. M. Bullock. *J. Am. Chem. Soc*. **135**, 11736 (2013).
[30] E. B. Hulley, M. L. Helm, R. M. Bullock. *Chem. Sci*. **5**, 4729 (2014).
[31] A. A. Karasik, G. N. Nikonov, A. S. Dokuchaev, I. A. Litvinov. *Russ. J. Coord. Chem*. **20**, 282 (1994).
[32] APEX2 (Version 2.1), SAINTPlus. Data Reduction and Correction Program (Version 7.31A, Bruker Advanced X-ray Solutions, BrukerAXS Inc., Madison, WI (2006).
[33] G. M. Sheldrick, SADABS, Program for empirical X-ray absorption correction, Bruker-Nonis (1990–2004).
[34] SAINT: Area-Detector Integration Software. Version 6.01, Siemens Industrial Automation, Inc., Madison, WI (1999).
[35] CrysAlis Pro: Data collection and data reduction software package, Rigaku Inc. (2012).
[36] SCALE3 ABSPACK: Empirical absorption correction using spherical harmonics. (2010).
[37] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr*. **27**, 435 (1994).
[38] G. M. Sheldrick. *Acta Cryst*. **A64**, 112 (2008).

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