A Dodecanuclear Copper(I) Complex Containing a Cubic $(CuS)_4$ Core Stabilized by a Tripodal (*N*,*N*,*P*)-Chelating Ligand

Margret M. Meinholz and Dietmar Stalke

Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstraße 4,
37077 Göttingen, Germany

Reprint requests to Prof. Dr. D. Stalke. Fax: (+)49-551-39-3459.
E-mail: dstalke@chemie.uni-goettingen.de

Z. Naturforsch. **2011**, *66b,* 981 – 984; received July 18, 2011

We present the structure elucidation of a copper(I) complex of a monoanionic phosphanylalkyl-diimido sulfonate ligand centered by a sulfur-copper cube. It has the formula $[\{Me_2PCH_2S(NSiMe_3)_2\}_4Cu_8\{CuS\}_4]$ (**2**) and is the first example of a copper(I) complex of this new ligand type.

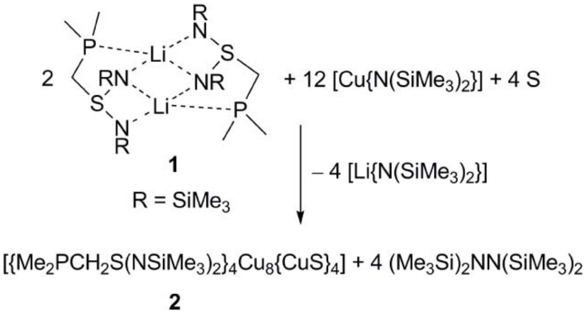
Key words: Copper, Sulfur, Phosphorus, Sulfur Diimide, Ligand Design

Introduction

Recently, we reported on main group metal complexes of tridentate polyimido sulfur ligands with a phosphorus [1] or a nitrogen [2, 3] side-arm. These monoanionic ligands have the general formulae $\{R^1{}_2PCH_2S(NR^2)_2\}^-$ (R^1 = Me, Ph; R^2 = *t*Bu, $SiMe_3$) and $\{R^1{}_2N(spacer)S(NR^2)_2\}^-$ (R^1 = Me; R^2 = *t*Bu, $SiMe_3$, spacer = 0, $(CH_2)_n$, C_6H_4). Metal complexes are accessible *via* salt elimination from the dimer $[Li\{Me_2PCH_2S(NR)_2\}]_2$ and $MgCl_2$. However, this route was so far only successful with $MgCl_2$, which is probably due to the diagonal relationship between lithium and magnesium. We now wanted to widen the route to other metal complexes by other reagents than metal halides. This is of great interest, because it is known that such halides can initiate S–N bond cleavage reactions in sulfur diimido compounds [4]. To prevent this ligand scrambling, the copper(I) amide $[Cu\{N(SiMe_3)_2\}]$ was employed in a transmetallation reaction.

Results and Discussion

The metal exchange reaction was conducted with the lithium dimer $[Li\{Me_2PCH_2S(NSiMe_3)_2\}]_2$ (**1**) as the starting material. The equimolar reaction of **1** and $[Cu\{N(SiMe_3)_2\}]$ yielded colorless crystals after several days. The composition was determined by single-crystal X-ray analysis. The origin of the sulfide S^{2-} dianions present in the product remains uncertain. Most probably they stem from ligand scrambling in the course of the reaction as the sulfur diimide starting material was purified vigorously before being employed. However, sulfur can always be a marginal contaminant of the starting material and cannot totally be excluded to be the source of the S^{2-} ions (Scheme 1).



Scheme 1. Proposed formation of **2**.

$[\{Me_2PCH_2S(NSiMe_3)_2\}_4Cu_8\{CuS\}_4]$ (**2**) crystallizes in the monoclinic space group $C2/c$ with half of the molecule in the asymmetric unit (Fig. 1), the second half generated by a two-fold axis. The crystal structure reveals that the metal exchange did indeed occurr quantitatively, and the original ligand is recovered in the structure. Nevertheless, four S^{2-} ions are incorporated in the structure (Fig. 2).

Compound **2** consists of four $\{Me_2PCH_2S(NSiMe_3)_2\}^-$ ligands that are N-bonded to two peripheral copper(I) ions each and P-bonded to the central $(CuS)_4$ distorted cube (Fig. 2). This monoanionic diimido sulfonate ligand consists of a central pyramidally coordinated S(IV) atom with a stereochemically active lone-

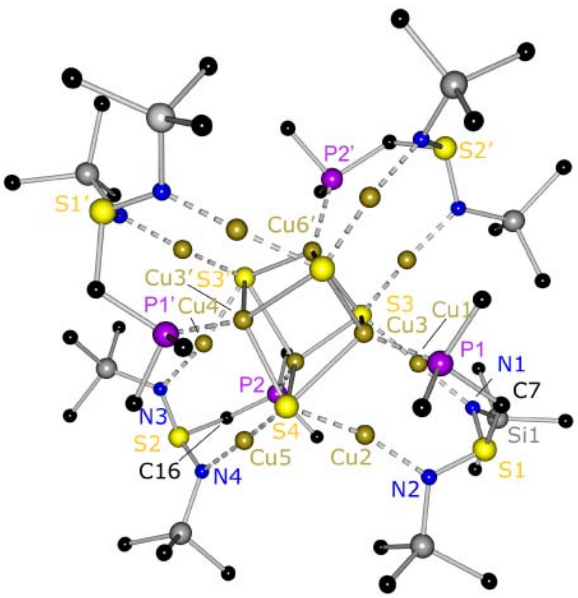


Fig. 1 (color online). Molecular structure of $[\{Me_2PCH_2S(NSiMe_3)_2\}_4Cu_8\{CuS\}_4]$ (**2**), hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu1–N1 1.8902(17), Cu2–N2 1.9077(17), Cu4–N3 1.9095(17), Cu5–N4 1.8783(18), Cu1–S3 2.1299(5), Cu2–S4 2.1630(5), Cu4–S3′ 2.1621(5), Cu5–S4 2.1135(6), average peripheral Cu–S 2.1421, Cu3–S4 2.7265(6), Cu3–S4′ 2.3390(5), Cu3–S3 2.4384(6), Cu6–S3 2.4010(5), Cu6–S4 2.5128(6), Cu6–S3′ 2.6630(5), average cube Cu–S 2.5134, Cu3–P1 2.2950(6), Cu6–P2 2.2817(5); N1–Cu1–S3 168.76(6), N2–Cu2–S4 162.08(6), N3–Cu4–S3′ 160.70(6), N4–Cu–S4 171.59(6). Symmetry transformations used to generate equivalent atoms labeled with (′): $-x+1$, y, $-z+3/2$.

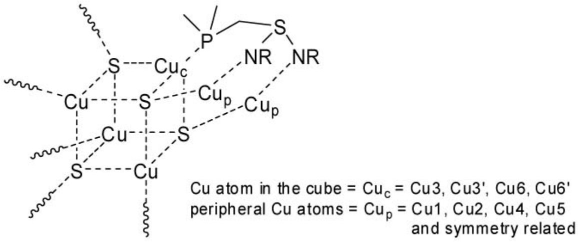


Fig. 2. Line drawing of the structural core of **2**.

pair and a P(III) donor atom in the side-arm. The twelve negative charges of the four ligands and the four sulfide anions S^{2-} are counterbalanced by twelve Cu(I) cations. It is remarkable that they exhibit two different coordination geometries in the same complex. The peripheral copper atoms Cu1, Cu2, Cu4 and Cu5 (Cu_p in Fig. 2) show nearly linear N–Cu–S coordination (160.70 to 171.59°) while the cube copper atoms Cu3 and Cu6 adopt tetrahedral S_3CuP coordination. In sulfur diimido compounds the twofold linear coordination would usually be favored [5–7]. However, the formation of cubes or prisms between copper(I) and chalcogens is a known coordination motif in cluster chemistry [8]. Usually, the cluster formation can be controlled by varying the employed phosphane ligands and/or reaction conditions [9]. Probably because of the mixed linear/tetrahedral coordination, the Cu1···Cu3 distance of 2.563 Å is very short [10]. However, this seems to be induced by the complex geometry of the tripodal ligand [7] and is not regarded a bond due to closed shell d^{10}-d^{10} interactions [11]. In contrast, Cu1 and Cu2 are 3.014 Å apart, which is also supported by the ligand due to the wide bite of the sulfur diimido moiety and the coordination of the central S^{2-} ions to Cu1 and Cu2. Consequently, the N1–Cu1–S3 angle of 168.76(6)° deviates considerably from 180°. This is different from other sulfur diimido copper complexes like $[Cu\{(SC_8H_5)S(N\textit{t}Bu)_2\}]_2$ (Cu···Cu: 2.7852(6) Å) [5] and has its origin in the central $(CuS)_4$ cube which influences the coordination angles of the outer ligands.

Each ligand binds to three different copper atoms. N1 and N2 are coordinating Cu1 and Cu2 in an almost linear fashion. The N1–Cu1–S3 and N2–Cu2–S4 angles of 168.76(6)° and 162.08(6)°, respectively, underline this very clearly. The N1–Cu1 (1.8902(17) Å) and N2–Cu2 (1.9077(17) Å) bond lengths are comparable to the average values found in $[(thf)_2Cu_3Li_2I\{(N\textit{t}Bu)_3S\}_2]$ (Cu–N: 1.876(5) Å) [7] and $[Cu\{PhS(NSiMe_3)_2\}]_2$ (av. Cu–N: 1.874(2) Å) [6]. The Cu1–S3 bond of 2.1299(5) Å is somewhat longer which is expected as sulfur is larger and easier to polarize than nitrogen. The copper(I) ions in the central $(CuS)_4$ cube are fourfold coordinated by three S^{2-} ions and one phosphorus atom of the ligand side-arm in a distorted tetrahedral manner. The angles around Cu3 for instance range from 85.44(2)° to 124.94(2)°. The distortion is partly due to the different bond lengths inside the central cube; *e. g.* Cu3–S4 (2.7265(6) Å) is considerably longer than Cu3–S4′ (2.3390(5) Å). However, within the cube the Cu–S bonds are on average significantly longer (mean 2.5134 Å) than the bonds to the peripheral two-coordinated Cu(I) ions (2.1421 Å).

Due to different chemical environments in solution there is a signal doubling for the $NSiMe_3$, PMe_2 and CH_2 groups. In addition, the CH_2 protons show diastereotopic splitting and are thus coupled to each other (visible roof effect) as well as to the connecting phosphorus atom. Due to the higher dynamic and hence higher average symmetry of the flexible molecule in solution, the chemical shift of all phosphorus atoms is identical.

Conclusion

In summary, it has been shown in this paper that copper(I) complexes of the new *Janus* head ligand are feasible even if the very stable lithium dimers are employed in the synthesis. Still it is not clear whether the use of a metal amide as transmetalation reagent seems to prevent ligand scrambling and hence to be superior to metal halides. However, slight impurities of sulfur in the starting material seem to promote the formation of a central $(CuS)_4$ cube. Further investigations to employ various other metal amides are under way.

Experimental Section

All manipulations were performed in an inert gas atmosphere of purified dry argon with standard Schlenk techniques or in a glove box. The glassware was dried at 130 °C, assembled hot and cooled under vacuum. All solvents were dried over appropriate alkali metals, distilled and degassed prior to use. The NMR spectra were recorded on a Bruker Avance DPX 300 MHz spectrometer using TMS (^{1}H) and H_3PO_4 (^{31}P) as external reference and the protons of the deuterated solvents as internal standard. The spectra were measured at r. t.

[Li{Me₂PCH₂S(NSiMe₃)₂}]₂ (**1**) was synthesized according to literature protocols [1].

[{Me₂PCH₂S(NSiMe₃)₂}₄Cu₈{CuS}₄] (2)

$[Cu\{N(SiMe_3)_2\}]$ (0.20 g, 0.89 mmol, 2.0 eq.) was suspended in THF (15 mL). A solution of **1** (0.26 g, 0.45 mmol, 1.0 eq.) in pentane (15 mL) was slowly added at −78 °C. After stirring over night the solvent was removed *in vacuo* and the residue suspended in hexane (30 mL) and filtered over celite. The orange solution was reduced in volume and stored at 4 °C for two weeks, yielding colorless crystals, yield $< 5\,\%$. – ^{1}H NMR (300.13 MHz, C_6D_6): δ = 0.41 (s, 18 H, $NSi(CH_3)_3$), 0.42 (s, 18 H, $NSi(CH_3)_3$), 1.46 (d, 6 H, $^2J_{\text{P-H}}$ = 4.95 Hz, $P(CH_3)_2$), 1.53 (d, 6 H, $^2J_{\text{P-H}}$ = 3.99 Hz, $P(CH_3)_2$), 2.12 (dd, 2 H, $^2J_{\text{H-H}}$ = 13.50 Hz, $^2J_{\text{P-H}}$ = 4.15 Hz, PCH_2S), 2.28 (dd, 2 H, $^2J_{\text{H-H}}$ = 13.50 Hz, $^2J_{\text{P-H}}$ = 6.04 Hz, PCH_2S). – $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6): δ = −75.78.

Table 1. Crystal structure data for **2**.

Formula	$C_{36}H_{104}Cu_{12}N_8P_4S_8Si_8$
M_r	2016.83
Crystal size, mm^3	$0.18 \times 0.10 \times 0.02$
Crystal system	monoclinic
Space group	$C2/c$
a, Å	31.087(3)
b, Å	9.4333(8)
c, Å	29.451(3)
β, deg	112.4610(10)
V, Å^3	7981.4(12)
Z	4
D_{calcd}, g cm^{-3}	1.68
$\mu(\text{Mo}K_\alpha)$, cm^{-1}	3.6
$F(000)$, e	4096
Refl. measured / unique / R_{int}	40145 / 8166 / 0.0393
Param. refined	372
$R1$ $(F)^a$ / $wR2$ $(F^2)^b$ (all refl.)	0.0236 / 0.0499
GoF $(F^2)^c$	1.020
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	0.67 / −0.60

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] $\text{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

X-Ray structure determination

The X-ray data set was collected at 100(2) K on an INCOATEC Mo microfocus source [12] with mirror-monochromatized MoK_α radiation (λ = 0.71073 Å) in ω scan mode. The single crystal was mounted in inert oil under argon atmosphere by applying the XTEMP-2 device [13]. The structure was solved by Direct Methods with SHELXS. An absorption correction with SADABS [14] was applied and the structure refined by full-matrix least-squares methods on F^2 for all data with SHELXL [15]. Non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were placed in calculated positions and refined using a riding model. Crystallographic data can be found in Table 1.

CCDC 829018 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

We acknowledge funding from the DFG *Priority Programme 1178*, the DNRF funded *Centre of Materials Crystallography* and the doctoral programme *Catalysis for Sustainable Synthesis*, provided by the Land Niedersachsen.

[1] M.M. Meinholz, S.K. Pandey, S.M. Deuerlein, D. Stalke, *Dalton Trans.* **2011**, *40*, 1662.

[2] M. M. Meinholz, M. Klemmer, E. Kriemen, D. Stalke, *Chem. Eur. J.* **2011**, *17*, 9412.

[3] M. M. Meinholz, E. Carl, E. Kriemen, D. Stalke, *Chem. Commun.* **2011**, *47*, 10948.

[4] a) R. Fleischer, D. Stalke, *Organometallics* **1998**, *17*, 832; b) D. Hänssgen, R. Steffens, *Z. Anorg. Allg. Chem.* **1983**, *507*, 178.

[5] C. Selinka, S. Deuerlein, T. Häuser, D. Stalke, *Inorg. Chim. Acta* **2004**, *357*, 1873.

[6] S. Freitag, W. Kolodziejski, F. Pauer, D. Stalke, *Dalton Trans.* **1993**, 3479.

[7] B. Walfort, T. Auth, B. Degel, H. Helten, D. Stalke, *Organometallics* **2002**, *21*, 2208.

[8] a) D. Fenske, H. Krautscheid, S. Balter, *Angew. Chem.* **1990**, *102*, 799; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 796; b) D. Fenske, J.-C. Steck, *Angew. Chem.* **1993**, *105*, 254; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 238; c) J.-P. Lang, H. Kawaguchi, K. Tatsumi, *Chem. Commun.* **1999**, 2315.

[9] D. Fenske, H. Krautscheid, M. Müller, *Angew. Chem.* **1992**, *104*, 309; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 321.

[10] a) A. Heine, D. Stalke, *Angew. Chem.* **1993**, *105*, 90; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 121; b) A. Heine, R. Herbst-Irmer, D. Stalke *J. Chem. Soc., Chem. Commun.* **1993**, 1729.

[11] a) P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597; b) H. L. Hermann, G. Boche, P. Schwerdtfeger, *Chem. Eur. J.* **2001**, *7*, 5333.

[12] T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelsen, M. Ruf, G.M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* **2009**, *42*, 885.

[13] a) D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171; b) T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615.

[14] G. M. Sheldrick, SADABS 2008/1, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany), **2008**.

[15] a) G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112; b) G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467; c) P. Müller, R. Herbst-Irmer, A. L. Spek, T. R. Schneider, M. R. Sawaya in *Crystal Structure Refinement – A Crystallographer's* Guide to SHELXL, IUCr Texts on Crystallography, Vol. 8 (Ed.: P. Müller), Oxford University Press, Oxford, **2006**.