

[NHMe₃][Cu(CS₄)]: a two-dimensional network involving an unprecedented $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2$ coordination mode of perthiocarbonate to copper(I)

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The new complex [NHMe₃][Cu(CS₄)], which was obtained by solvothermal synthesis, contains a two-dimensional $2_{\infty}[\text{Cu}(\text{CS}_4)]^-$ network consolidated by an unprecedented $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2$ coordination mode of the perthiocarbonate dianion.

The reaction of transition metal chelate polysulfides with carbon disulfide to form metal perthiocarbonates was first reported by Coucouvanis and Draganjac in 1982,¹ and up to now the few known examples in the literature include [Ni(CS₄)₂]²⁻,² [MoS(CS₄)₂]²⁻,^{1,3} [(CS₄)Mo₂S₄(CS₄)]²⁻,^{1,3} [(CS₄)Mo₂O₂S₂(CS₄)]²⁻,³ [Mn(CO)₃(CS₄)]²⁻,⁴ [Mn(CS₄)₂Cl]³⁻,⁵ and [Zn(CS₄){Me₂NCH₂CH₂N(Me)CH₂CH₂NMe₂}].⁶ These compounds are now generally synthesized by (i) the reaction of metal polysulfides with CS₂,^{1,2b,3-6} (ii) the reaction of metal salts with K₂CS₄,^{2a} or (iii) the oxidation of metal thiocarbonates with iodine or sulfur.^{2a} Recently we employed the hydro(solvo)thermal technique to synthesize transition metal polychalcogenides using K₂E_n (E = S, Se and Te; *n* = 2–6) as mineralizers,⁷ and herein we report the crystal structure of [NHMe₃][Cu(CS₄)],[†] which was obtained in an analogous way.

The common coordination mode of the perthiocarbonate anion to a metal ion is bidentate, forming a nearly planar five-membered chelate ring [Fig. 1(a)], except for [Mn(CO)₃(CS₄)]²⁻ in which each CS₄²⁻ ligand chelates to one Mn atom to form a planar five-membered ring with its perthio sulfur atom further coordinated to the other Mn atom to generate a discrete dimeric anion [Fig. 1(b)]. Single-crystal X-ray analysis has shown that the perthiocarbonate ligand in the present [NHMe₃][Cu(CS₄)] complex exhibits an unprecedented $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2$ coordination mode, which bridges adjacent copper ions along the $[-1\ 1\ 1]$ and $[-1\ 1\ -1]$ directions to form a two-dimensional network (Fig. 2).[‡] To our knowledge, hitherto in all known metal perthiocarbonates only two terminal sulfur atoms of the CS₄²⁻ ligand bond to metal atom(s), but in [NHMe₃][Cu(CS₄)] the third terminal sulfur atom has been found to be involved in metal coordination for the first time.

The anionic network $2_{\infty}[\text{Cu}(\text{CS}_4)]^-$ can be regarded as constructed from a basic building unit, namely the centrosymmetric Cu₂(CS₄)₂ dimer as illustrated in Fig. 1(b). The unit cell contains two crystallographically independent dimers, which

cross-link each other through interaction between the non-chelating, third terminal sulfur atom of each CS₄²⁻ ligand and an adjacent copper atom to form a puckered network as shown in Fig. 2. The network has two non-equivalent, though similar, irregular polygonal openings with wall-to-wall interatomic distances ranging from 5.4 to 10.3 Å. The crystal structure of [NHMe₃][Cu(CS₄)] consists of a parallel stacking of these two-dimensional networks, with an interlayer separation of 7.83 Å, to form channels running along the $[1\ 0\ 0]$ direction, in each of which the ordered NHMe₃⁺ cations are arranged in a zigzag column (see corresponding figure in the Table of Contents).

Each copper atom exhibits distorted tetrahedral coordination geometry, with Cu–S bond distances in the range 2.265(1)–2.4517(9) Å that vary according to the coordination mode of the sulfur atom: S (chelate) < S (bridging) < perthio S (chelate) < perthio S (bridging). There are two kinds of nearly planar rings in the Cu₂(CS₄)₂ dimer, namely five-membered CuSCS₂ and four-membered Cu₂S₂, which make a dihedral angle of 71.2°. In $\beta\text{-}[\text{Cu}(\text{S}_4)]_n^{n-}$ the basic construction unit that generates a chain-like structure, namely a Cu₂(S₄)₂ dimer,⁸ is structurally analogous to the present Cu₂(CS₄)₂ dimer but, unlike the CS₄²⁻ ligand, the S₄²⁻ ligand symmetrically chelates the copper atom

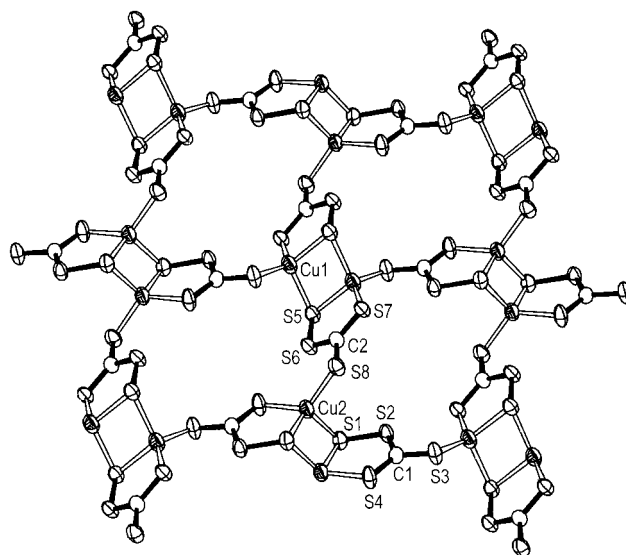


Fig. 2 Two-dimensional $2_{\infty}[\text{Cu}(\text{CS}_4)]^-$ network viewed along the $[1\ 0\ 0]$ direction. The thermal ellipsoids are drawn at the 70% probability level. Selected interatomic distances (Å), bond lengths (Å), and bond angles (°): Cu(1)⋯Cu(1)ⁱ 2.8438(9), Cu(1)–S(3)ⁱⁱ 2.2797(8), Cu(1)–S(5)ⁱ 2.3530(9), Cu(1)–S(5) 2.4517(9), Cu(1)–S(7)ⁱ 2.2681(9), Cu(2)⋯Cu(2)ⁱⁱⁱ 2.7361(8), Cu(2)–S(1) 2.4386(9), Cu(2)–S(1)ⁱⁱⁱ 2.3785(8), Cu(2)–S(4)ⁱⁱⁱ 2.265(1), Cu(2)–S(8) 2.3016(9), S(1)–S(2) 2.057(1), S(3)–C(1) 1.693(3), S(4)–C(1) 1.684(3), S(5)–S(6) 2.045(1), S(7)–C(2) 1.694(3), S(8)–C(2) 1.711(3); S(7)ⁱ–Cu(1)–S(3)ⁱⁱ 128.32(4), S(7)ⁱ–Cu(1)–S(5)ⁱ 95.79(3), S(3)ⁱⁱ–Cu(1)–S(5)ⁱ 111.75(3), S(7)ⁱ–Cu(1)–S(5) 107.67(3), S(3)ⁱⁱ–Cu(1)–S(5) 104.48(3), S(5)ⁱ–Cu(1)–S(5) 107.45(3), S(4)ⁱⁱⁱ–Cu(2)–S(8) 123.32(4), S(4)ⁱⁱⁱ–Cu(2)–S(1)ⁱⁱⁱ 94.36(3), S(8)–Cu(2)–S(1)ⁱⁱⁱ 113.95(3), S(4)ⁱⁱⁱ–Cu(2)–S(1) 107.89(4), S(8)–Cu(2)–S(1) 106.03(3), S(1)ⁱⁱⁱ–Cu(2)–S(1) 110.79(3). Symmetry codes: ⁱ $-x + 1, -y, -z + 2$; ⁱⁱ $x, y, z - 1$; ⁱⁱⁱ $-x, -y + 1, -z + 3$.

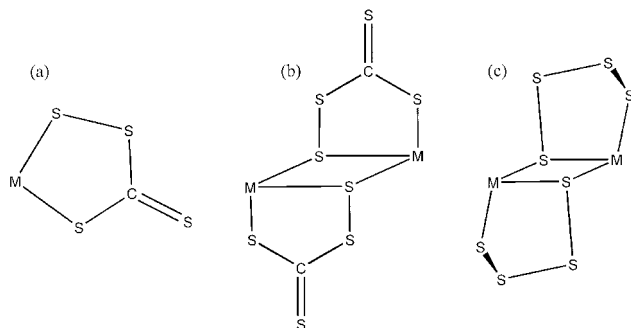


Fig. 1 Coordination modes of the perthiocarbonate dianion.

to form a puckered five-membered ring [Fig. 1(c)]. Obviously, the principal difference between the CS_4^{2-} and S_4^{2-} ligands is that the *exo* sulfur atom of a chelating CS_4^{2-} ligand is capable of binding to another metal atom, as found in the present $[\text{Cu}(\text{CS}_4)]^-$ anion. The average non-bonded $\text{Cu}\cdots\text{Cu}$ distance in $[\text{NHMe}_3][\text{Cu}(\text{CS}_4)]$ is 0.16 Å longer than that found in $[\text{Cu}(\text{S}_4)]_n^{n-}$.⁸

The CS_4^{2-} ligand in the title compound exhibits electron delocalization similar to that found in $[\text{Mn}(\text{CS}_4)_2\text{Cl}]^{3-}$,⁵ $[\text{Ni}(\text{CS}_4)_2]^{2-}$ ^{2b} and one of the two non-equivalent anions in $\text{K}_2\text{CS}_4\cdot\text{MeOH}$.⁹ The S–S bond distances in both delocalized and localized CS_4^{2-} ligands in transition metal complexes, with the possible exception of $[\text{Mo}_2(\text{S})_2(\mu\text{-S})_2(\text{CS}_4)_2]^{2-}$,^{1,3} are all longer than those found in $\text{K}_2\text{CS}_4\cdot\text{MeOH}$; this is attributable to M–S π bonding within the MCS_3 ring that results in weakening of the S–S bond, as is the case commonly found in metal complexes containing a chelating S_4^{2-} ligand.¹⁰ Generally, polychalcogeno complexes of d^2 and d^8 metals show a pronounced E–E bond alternation pattern within the ME_4 ($\text{E} = \text{S}, \text{Se}$ and Te) ring whereas d^{10} metal complexes do not. Thus lengthening of the S–S bond distance in $[\text{NHMe}_3][\text{Cu}(\text{CS}_4)]$, as compared to those in $\text{K}_2\text{CS}_4\cdot\text{MeOH}$,⁹ is consistent with additional binding of the perthio sulfur atom to the copper center. A similar case was found in $[\text{Mn}(\text{CO})_3(\text{CS}_4)]_2^{2-}$ ⁴ in which the S–S bond distance is longer than that in $[\text{Mn}(\text{CS}_4)_2\text{Cl}]^{3-}$.⁵

Recently it has been pointed out that the formation of carbon–heteroatom bonds in amines, ethers and sulfides by reductive elimination can be incorporated into a number of catalytic processes,¹¹ and interesting speculations as to the possible significance of C–S forming processes in the biosynthesis of metalloenzymes have been proposed.¹² The identity of the perthiocarbonate dianion in the title compound is firmly established, as the measured C–S distances are in good agreement with those of known perthiocarbonate complexes. However, the formation of C–S bonds to yield CS_4^{2-} in the synthesis of $[\text{NHMe}_3][\text{Cu}(\text{CS}_4)]$ is presumably much more complex under hydrothermal conditions, causing partial degradation of the tetramethylammonium ion to yield the trimethylammonium ion while providing the source of carbon. In this context it is noted that in $[\text{Mn}(\text{CO})_3(\text{CS}_4)]_2^{2-}$, the carbon atom of the CS_4^{2-} ligand arises from a carbonyl group in the reaction between $[(\text{CO})_5\text{MnMn}(\text{CO})_4\text{Br}]^-$ and S_8 in 4-methylpentan-2-one and not from the solvent.⁴

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Notes and references

† *Synthesis*: $[\text{NHMe}_3][\text{Cu}(\text{CS}_4)]$ was prepared by reacting CuCl (37.1 mg, 0.375 mmol), $\text{K}_2\text{S}_4^{7a}$ (232.0 mg, 1.125 mmol), NMe_4Br (115.4 mg, 0.75 mmol), and 0.4 mL EtOH in a Pyrex ampoule of ca. 7 mL capacity. The ampoule was flame-sealed under vacuum, heated in a furnace to 100 °C for 144 h, and then cooled to 60 °C at 6 °C h^{-1} . Dark red prismatic crystals were isolated and washed with ethanol (estimated yield ca. 10 %). The crystals are air-stable and insoluble in water and most organic solvents.

‡ *Crystal data*: $[\text{NHMe}_3][\text{Cu}(\text{CS}_4)]$, $\text{C}_4\text{H}_{10}\text{CuNS}_4$, $M = 263.91$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.254(1)$, $b = 10.737(1)$, $c = 10.887(1)$ Å, $\alpha = 78.62(1)$, $\beta = 74.18(1)$, $\gamma = 68.22(1)^\circ$, $U = 960.9(2)$ Å³, $T = 293$ K, $Z = 4$, $D_c = 1.824$ g cm^{-3} , $F(000) = 536$, $\mu(\text{Mo-K}\alpha) = 30.72$ cm^{-1} , absorption corrections applied using ABSCOR,¹³ relative transmission factors in the range 0.936–1.0. A total of 3210 reflections were collected in the 2θ range 4.0–53.5° ($-11 \leq h \leq 10$, $-13 \leq k \leq 0$, $-13 \leq l \leq 13$), 3095 of which with $I > 2\sigma(I)$ were considered as observed. The structure was solved by direct methods and the NHMe_3^+ and CS_4^{2-} ions, which exhibit normal molecular dimensions, were readily identified. Anisotropic refinement of all non-hydrogen atoms was carried out by full-matrix least squares on F^2 using the Siemens SHELXTL (PC Version)¹⁴ package of crystallographic software, 181 variables, $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0436$, $wR2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2} = 0.1146$, $\text{GOF} = 1.119$, min., max. residual electron density +0.522, -0.754 e Å⁻³. CCDC reference 182/1149.

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