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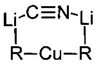
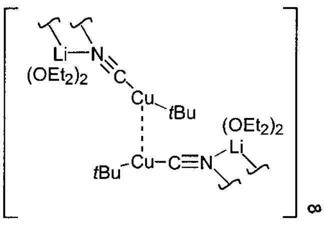
The Crystal Structures of a Lower Order and a "Higher Order" Cyanocuprate: [tBuCu(CN)Li(OEt$_2$)$_2$]$_\infty$ and [tBuCutBu{Li(thf)(pmdeta)}$_2$CN]**

Gernot Boche,* Ferdinand Bosold, Michael Marsch, and Klaus Harms

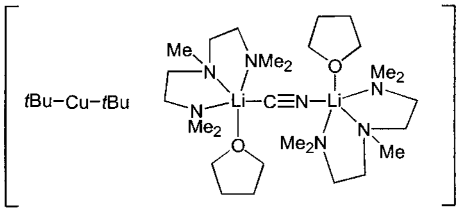
Cyanocuprates are an important class of cuprates because of their significance in organic synthesis.[1] On the basis of their different composition and reactivity they can be divided into two groups:[2] lower order cyanocuprates of the type RCu(CN)Li, with RLi and CuCN units in a 1:1 ratio, and "higher order" cyanocuprates of the type $R_2Cu(CN)Li_2$, with RLi and CuCN units in a 2:1 ratio. In recent years the structure of the latter has been the topic of much investigation and controversial discussion:[3] Do these compounds have a special reactivity due to a bis-anion character? EXAFS,[4] NMR,[5] and IR spectroscopic investigations[6] indicated that the major proportion of the Cu atoms (>90%) is not bonded to the cyanide ion, and thus $R_2Cu(CN)Li_2$ more likely exists as "RCuR-Li+LiCN" rather than with a three-coordinate Cu atom. This is consistent with quantum-chemical calculations which show **1** to be the most stable structure.[4c, 7] Recent cryoscopic investigations in tetrahydrofuran at −108 °C demonstrated that lower order cyanocuprates exist as a monomer [tBuCu(CN)Li] or as a dimer [(PhCu(CN)Li)$_2$]. For the higher order cyanocuprates $R_2Cu(CN)Li_2$, cryoscopy revealed monomeric species (R = Me,Ph); however, in the case of R = tBu there is the possibility of a fast equilibrium between a higher order and a lower order cyanocuprate.[8] While only a few solid-state structures of Gilman cuprates containing the free structural element R_2Cu^- exist,[9] no crystal structures of cyanocuprates have been described yet. Here we report on the crystal structures of [tBuCu(CN)Li·(OEt$_2$)$_2$]$_\infty$ (**2**), a lower order cyanocuprate, and [tBuCutBu{Li(thf)(pmdeta)$_2$CN}] (**3**, pmdeta = pentamethyldiethylenetriamine), a compound of the type $R_2Cu(CN)Li_2$.



1



2



3

Figure 1 shows a section of the crystal structure of **2**.[10a] The tBu group (Cu1 – C2 196.9(7) pm) and the cyanide ion (Cu1 – C1 187.8(8) pm) are bonded to the Cu atom. The N1 atom of the cyanide group (C1 – N1 115.9(9) pm) is coordinated to two Li cations (Li1 and Li1A), each of which is complexed by two diethyl ether molecules. By the formation of the four-membered ring N1-Li1-N1A-Li1A, an additional molecule is bound. The mutual arrangement of the two cyanocuprate units C2-Cu1-C1-N1 and C7-Cu2-C6-N2 is of particular interest. In both cuprates the angles C1-Cu1-C2 and C6-Cu2-C7 (170.0(3) and 168.0(3)°, respectively) are less than 180°, while the dihedral angles C1-Cu1-Cu2-C6 and C1-Cu1-Cu2-C7 are 84.8(3) and −94.9(3)°, indicating an almost perpendicular relative arrangement of the two cyanocuprates. The angle C1-Cu1-Cu2 (C6-Cu2-Cu1) amounts to 86.5(2)° (88.4(2)°), while that involving the tBu groups (C7-Cu2-Cu1

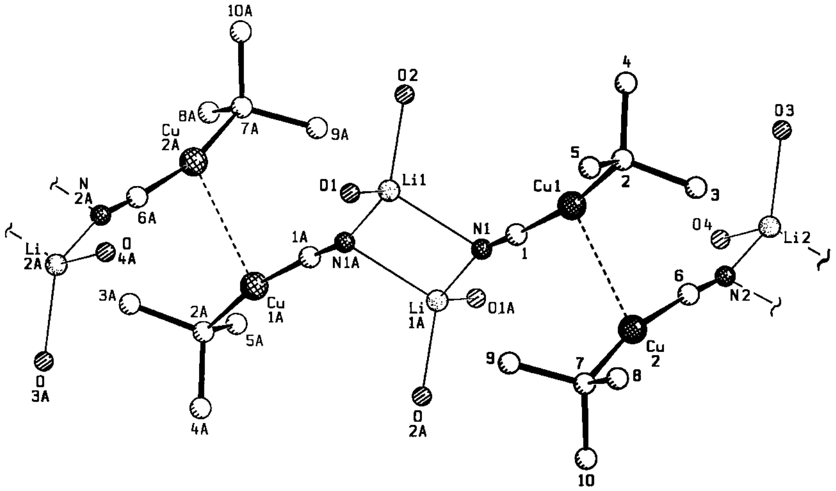


Figure 1. Section of the crystal structure of **2**. The ethyl groups of the diethyl ether molecules have been omitted for clarity.

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103.5(2)°, C2-Cu1-Cu2 103.4(2)°) is clearly larger than 90°. The cuprate units are thus bent towards one another at the Cu atoms. The Cu1 – Cu2 distance is 271.3(1) pm. This raises the question of whether in the case of **2** a Cu(d^{10}) – Cu(d^{10}) bond exists even in a free dimer, that is, not in a complex in which the Cu atoms are brought into close proximity through ligand complexation. After earlier quantum-chemical investigations by Hoffmann et al.,[11] both R. Ahlrichs et al.[12] and more recently P. Pyykkö et al.[13] made comprehensive studies of the weak d^{10} – d^{10} interactions of Cu compounds. Pyykkö et al. also compared these with interactions in similar compounds of Ag and Au. As models he used free metal – metal dimers of the type $(ClCu(Ag,Au)PH_3)_2$ with a perpendicular arrangement of the components, as found experimentally in the gold species.[14] Although the Cu – Cu interactions (Cu – Cu 313.2 pm) are energetically 48 % less favorable than the Au – Au interactions,[15] they are sufficient for dimer formation. These model calculations thus demonstrate that the structure containing a perpendicular arrangement of two lithium cyanocuprate molecules, as for **2,** provides the first experimental indication for a Cu(d^{10}) – Cu(d^{10}) bond in a free dimer.[16, 17]

A section of the crystal structure of [*t*BuCu*t*Bu{Li(thf)(pmdeta)}$_2$CN] (**3**)[10b] is shown in Figure 2. The essential difference between the structures of **2** and **3** is that in **3** the *t*BuCu*t*Bu$^-$ anion is completely detached from the LiCNLi$^+$ cation (Cu1 – Li1 747.4, Cu1 – Li1A 1062.3 pm). Consequently the cyanide ion also exhibits no contact with the Cu1 atom (C5 and N1 cannot be distinguished from one another in the X-ray crystal structure[10b]). In the linear cuprate anion (C1-Cu1-C1A 180.0°) the C – Cu1 bonds are 195.7(4) pm long. Both Li1 and Li1A are surrounded by three N atoms of the pmdeta ligand and by the O atom of a THF molecule; they also form bonds with atoms C5 and N1A (210.5(7) pm) of the cyanide ion. The arrangement of the cyanide ion and the two Li$^+$ ions is practically linear (C5b-N1-Li1 178.3(6)°). The structural situation in **3** corresponds essentially to that recently observed for a compound of the type $[Ar_2Cu(CN)Li_2(thf)_4]_\infty$ (Ar = C_6H_4-2-CH_2NMe_2).[18] A Gilman cuprate anion R_2Cu^- is found also in this structure beside a solvated cation LiCNLi$^+$. These solid-state structures are in agreement with most of the findings in solution.[3–6]

Thus, higher order cyanocuprates $R_2Cu(CN)Li_2$, or better: cyano – Gilman cuprates,[19] do not appear to be strongly different from normal Gilman cuprates, at least in the anionic portion. Perhaps it is significant that in the solid-state structures of Gilman cuprates Li$^+$ is bonded to R – Cu – R$^-$ except if Li$^+$ is complexed by a crown ether.[1e] Certain differences in reactivity and selectivity between these cuprates might therefore be due to differences in anion – cation interactions as well as different complexing solvents ligands, and the cyanide anion.[19] From the structure of **3** it can also be seen that enantioselective syntheses with chiral cyano – cuprates should be successful only if the moiety X* that contains the chiral information remains bonded to the Cu atom. If complexes of X* with Li$^+$ are formed, or if heterocuprates RCuX*Li are transformed into homocuprates RCuRLi and X*CuX*Li, the distance from X* to the reaction site is rather large.[20] The fact that cyanocuprates of the type $R_2Cu(CN)Li_2$ have not been shown to be dimers by both cryoscopic measurements and determinations of solid-state structures could be a result of the smaller tendency of the R_2Cu^- anion to form Cu – Cu bonds.[16] The distinctly different reactivities and selectivities of compounds of the types RCu(CN)Li and $R_2Cu(CN)Li_2$ are consistent with the completely different cuprate structures which have been revealed for **2** and **3**.

Experimental Section

2: CuCN (45 mg, 0.50 mmol) was heated under high vacuum, purged with argon, and layered with diethyl ether (2.2 mL). At 203 K 1.6 M *tert*-butyllithium in *n*-pentane (0.32 mL, 0.50 mmol) was added, and, while maintaining this temperature, the mixture was shaken vigorously until all CuCN had dissolved. After 24 h at 195 K crystals suitable for X-ray structure analysis had formed; yield: 83 mg (79 %).

3: CuCN (45 mg, 0.50 mmol) was heated under high vacuum, purged with argon, and layered with THF (1 mL). At 233 K 1.6 M *tert*-butyllithium in *n*-pentane (0.63 mL, 1.00 mmol) was added, and, while maintaining this temperature, the mixture was shaken vigorously until all CuCN had dissolved. The mixture was warmed to 273 K and pmdeta (0.1 mL, 172 mg, 1.00 mmol) was added. After six days at 195 K crystals suitable for X-ray structural analysis had formed; yield: 290 mg (41 %).

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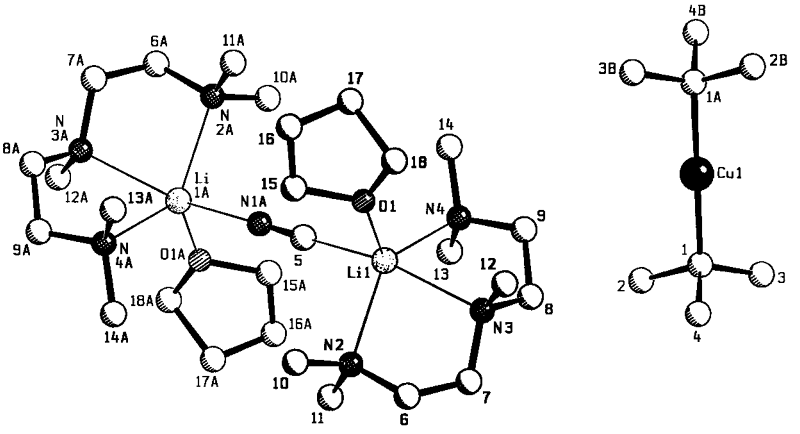

Figure 2. Section of the crystal structure of **3**.

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[10] a) Crystallographic data for **2** ($C_{26}H_{58}Cu_2Li_2N_2O_4$, $M_r = 603.7$): monoclinic, space group $P2_1/n$, $a = 1208.7(1)$, $b = 1497.9(1)$, $c = 1941.8(2)$ pm, $\beta = 91.10(1)^\circ$, $V = 3515.1(5) \times 10^{-30}$ m^3, $Z = 4$, $\rho_{calcd} = 1.141$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 1.237$ mm^{-1}. Data were collected with a STOE IPDS array detector with $Mo_{K\alpha}$ radiation and a graphite monochromator at $T = 120(2)$ K. Of 27126 reflections measured ($2 < \theta < 26^\circ$), 6427 were independent ($R_{int} = 0.0803$). The structure was solved by direct methods (SHELXS-97)[10c] and refined against F^2 with all reflections (SHELXL-97).[10d] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined with isotropic temperature factors. Parameters of the weighting scheme calculated by the program: 0.0449, 33.6513; $wR2 = 0.2052$, $R1 = 0.0756$ (for 4128 reflections with $I > 2\sigma(I)$), GOF = 1.073; in total 339 refined parameters; b) crystallographic data for **3** ($C_{35}H_{80}CuLi_2N_7O_2$, $M_r = 708.48$): monoclinic, space group $P2_1/c$, $a = 916.9(1)$, $b = 1498.5(1)$, $c = 1661.8(2)$ pm, $\beta = 100.95(1)^\circ$, $V = 2241.8(3) \times 10^{-30}$ m^3, $Z = 2$, $\rho_{calcd} = 1.050$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.521$ mm^{-1}. Data were collected with a STOE IPDS array detector with $Mo_{K\alpha}$ radiation and a graphite monochromator at $T = 190(2)$ K. Of 17246 reflections measured ($2 < \theta < 26^\circ$), 4324 were independent ($R_{int} = 0.0443$). The structure was solved by direct methods (SIR92)[10e] and refined against F^2 with all reflections (SHELXL-97).[10d] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined with isotropic temperature factors. Parameters of the weighting scheme calculated by the program: 0.1576, 0.4352; $wR2 = 0.2553$, $R1 = 0.0787$ (for 2804 reflections with $I > 2\sigma(I)$), GOF = 1.093; in total 242 refined parameters. The CN group is disordered about the center of symmetry. The disordered *tert*-butyl group was refined in two positions in the ratio 62:38. Unrefined disorder in the atoms of the solvent molecules is reflected in large thermal ellipsoids. All calculations were made on a DEC Alpha Station with the VMS operating system;[10f–h] c) G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Göttingen, **1997**; d) G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Göttingen **1997**; e) M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, D. Viterbo, *J. Appl. Crystallogr.* **1989**, *22*, 389–393; f) A. L. Spek, Platon 94, Program for Geometrical Analysis of Crystal Structures, Utrecht, **1994**; g) E. Keller, SCHAKAL-88B, A FORTRAN Program for the Graphic Representation of Molecular and Crystallographic Models, Freiburg, **1988**; h) crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101103. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[17] It is possible that the observations made with cryoscopy in THF[8] of RCu(CN)Li dimers are due to the same phenomenon. In THF, which solvates Li^+ much more favorably than diethyl ether (particularly at low temperature, $-108\,^\circ$C), the Li-N-Li-N four-membered ring, as found in **2,** could be cleaved by threefold coordination of THF to Li^+, whereas the Cu–Cu bonds remain unaffected.

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Unusual Five-Center, Four-Electron Bonding in a Rhodium–Bismuth Complex with Pentagonal-Bipyramidal Geometry**

Zhitao Xu and Zhenyang Lin*

Pentagonal coordinated molecules always provide very interesting bonding features. For example, in $[In\{Mn(CO)_4\}_5]^{2-}$ (**1**),[1] the indium atom and five manganese atoms lie almost in a plane. The bonding was elegantly described as an In^{3+} ion that binds the pentagonal Mn_5 ring.[2] In the pentagonal ring there are five two-center, two-electron bonds. Each manganese center satisfies the 18-electron rule. In the recently synthesized pentagonal $[Ni_5(\mu_5\text{-}S)(\mu_2\text{-}S t\text{Bu})_5]^-$ cluster (**2**),[3] the bonding has been described as having a six-center, ten-electron bond in the central $Ni_5(\mu_5\text{-}S)$ unit.[4] The cluster has a total of 70 valence electrons and actually conforms to the 16-electron rule. Very recently Ruck reported the synthesis and structural characterization of, and calculations on, a structurally remarkable ternary subhalide of bismuth containing the discrete rhodium–bismuth molecular complex $[\{RhBi_7\}Br_8]$ (**3**).[5] In this complex the seven bismuth atoms are bonded to the central rhodium atom in a regular pentagonal-bipyramidal arrangement. The eight bromine atoms bridge the apical and equatorial bismuth atoms in a

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