

Direct reaction of zerovalent copper with lead salts and an amino alcohol to form a heterotetranuclear mixed-anion polymeric complex

Larisa A. Kovbasyuk,^a Olga Yu. Vassilyeva,^{*a} Volodymyr N. Kokozay,^a Wolfgang Linert,^b
 Brian W. Skelton^c and Allen G. Oliver^d

^a Department of Inorganic Chemistry, Kiev Shevchenko University, Volodimirska st, 64, Kiev 252033, Ukraine

^b Institute of Inorganic Chemistry, Vienna University of Technology, Getreidemarkt 9/153, A-1060 Vienna, Austria

^c Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6907, Australia

^d Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand

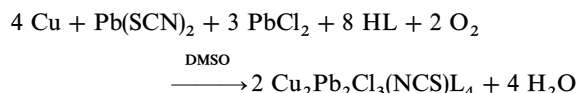
A direct reaction of zerovalent copper with PbCl₂, Pb(SCN)₂ and 2-dimethylaminoethanol (HL) in DMSO affords the heterotetranuclear mixed-anion polymeric complex [Cu₂Pb₂Cl₃(NCS)L₄]_n, the first example of a compound containing N-bonded thiocyanate-bridging heterometal atoms.

The potential use of mixed-metal compounds as advanced materials has encouraged extensive research on their design and synthesis during the last decade. Herewith extreme demands are placed on the efficiency and selectivity of the synthetic methods (and the purity of the synthetic reagents). Conventional synthesis involving a metal salt or organometallic precursor as a starting material is often rather sophisticated, tedious and possibly costly. Elaborate ligands may include impurities resulting from multi-stage syntheses. For this reason, attention has been focused on a quest for new synthetic routes to mixed-metal compounds.

We have previously shown that various metal complexes can be obtained easily through a one-pot reaction of a metal powder or metal oxide with a complex-forming agent in a non-aqueous solution.¹ Employment of this approach to the synthesis of mixed-metal compounds has resulted in a number of novel Cu–Pb aminoalkoxo complexes obtained from zero-valent copper and a lead salt.² Prior to this work only a few Cu–Pb complexes had been published, all of which contain macrocycles.³ Polyfunctional alcohols used as ligands have been reported to be able to achieve control of the stoichiometry as well as the geometry of mixed-metal species in chemical processing of ceramic materials.⁴ Following our extensions of the earlier studies we thought it of interest to examine the formation of mixed-metal species using a mixture of lead halide and lead pseudo-halide to more clearly define the role of the halide and to clarify any associated peculiarities.

We report here for the first time the synthesis and crystal structure† of a Cu–Pb mixed-anion complex. Copper powder (0.64 g, 10 mmol), PbCl₂ (1.39 g, 5 mmol), Pb(SCN)₂ (1.62 g, 5 mmol) and 2-dimethylaminoethanol (HL, 2 mL, 20 mmol) were heated in DMSO (15 mL) to 50–60 °C in air and stirred until total dissolution of the copper was observed (ca. 40 min). Blue-green crystals of the title compound were formed after several days at ambient temperature (2.57 g, 2.53 mmol,

73%).‡ Although the ratio of the initial lead salts was 1 : 1, a compound of empirical formula CuPbX₂L₂ was obtained (where X is total chloride and thiocyanate) with a Cl:NCS stoichiometry of 3 : 1. It is likely that the complex is one of the products with good crystal growing properties. Its preparation is summarized in the following equation:



The compound shows a sharp band for ν(CN) at 2030 cm^{−1} that is considered to be an indication of an asymmetric μ₂-

† Crystal data: C_{8.5}H₂₀N_{2.5}O₂PbCuCl_{1.5}S_{0.5}, *M* = 529.23, monoclinic, *a* = 7.9174(2), *b* = 15.3262(1), *c* = 13.0052(3) Å, β = 104.277(5)°, *U* = 1529.36(6) Å³ (by least-squares refinement on diffractometer angles from 6318 reflections, 3 < 2θ < 56°), *T* = 203(2) K, space group *P*2₁/*n* (no. 14 variant), graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, *Z* = 4, *D*_c = 2.298 Mg m^{−3}, *F*(000) = 996, blue-green prism with dimensions 0.10 × 0.22 × 0.25 mm, μ = 12.71 mm^{−1}, absorption correction by the multiscan method using the program SADABS, transmission factors 0.639–0.949; Siemens SMART diffractometer fitted with an area detector, 2θ ≤ 56.4°, −10 ≤ *h* ≤ 9, 0 ≤ *k* ≤ 20, 0 ≤ *l* ≤ 16, 9348 reflections measured, 3420 unique (*R*_{int} = 0.020) and of these 2726 had |*F*| > 4.00 σ(*F*) and were considered to be observed.

The structure was solved by direct methods and subsequent Fourier difference techniques and refined anisotropically (H atoms fixed), by full matrix least squares, on |*F*| (program XTAL3.4⁷). The weighting scheme was based on σ²(*I*) = σ²(*I*)_{diff} + 0.0004 σ⁴(*I*)_{diff}. The final *R*, *R*' were 0.032 and 0.026, respectively, for 173 parameters, goodness-of-fit = 1.804.

Bond distances and angles of L groups are normal and are given as supplementary material: CCDC reference number 440/058.

‡ Anal. calcd: C 19.3, H 3.8, N 6.6, Cu 12.0, Pb 39.2, Cl 10.0, S 3.0; found: C 19.0, H 3.8, N 6.8, Cu 11.7, Pb 39.9, Cl 10.0, S 3.1%. IR (KBr, strong bands only): 3600–3350, 2950, 2850, 1480, 1465, 1080, 1060, 1025, 1010, 945, 900, 780, 650, 470, 430 cm^{−1}. The X-band (9.45 GHz) powder EPR spectrum at ambient temperature shows signals at *g* = 2.09 and 2.29; the reflectance spectrum exhibits a broad band centred around 14 200 cm^{−1} in the range 30 000–12 000 cm^{−1}. This is typical for copper(II) ions in an axial symmetry.⁵ The compound is insoluble in water but soluble in DMF and DMSO.

* Fax: +380 44 296 2467; e-mail: vassil@inorg.chem.univ.kiev.ua

NCS⁻ bonding mode.^{6§} Given the low M : X : L ratio, the complex was expected to be an interesting polymer as is often the case with thiocyanate adducts.

It was rather a surprise that the compound appeared to be isomorphous with the Cu–Pb chloride [CuPbCl₂L₂]_n · $\frac{n}{2}$ H₂O, which was published earlier^{2c} with one Cl atom and the solvent water molecule replaced by disordered Cl/NCS, each with 0.5 population. The basic complex motif is a centrosymmetric dimer composed of two CuPbX₂L₂ units linked by alkoxo bridges of the L groups (Fig. 1). The Pb atom is six-coordinated in an irregular way by three alkoxo oxygen atoms from the three L groups and two chloride atoms; the sixth bonding position is occupied by the third chloride Cl(2') or N_{NCS} atoms, each with 0.5 population.

The coordination geometry around the Cu atom is distorted square pyramidal. The basal plane consists of two alkoxo oxygen and two amino nitrogen atoms from the two L groups while the axial coordination site is shared by the disordered Cl(2) and N_{NCS} atoms. Alkoxo oxygens form bridges between metal centres, resulting in lead–lead and lead–copper distances of 3.4338(6) and 3.8291(3) Å, respectively.

The tetranuclear mixed-metal units are further extended through μ -Cl(1) bridging between two Pb sites to form doubly bridged chains parallel to the *a* axis at *b* \approx 0 and \approx 0.5 (Fig. 1). These chains are considerably flattened staircase polymers with an angle between adjacent Pb₂O₂ and Pb₂Cl₂ planes of 32.99(4)°.

The binding mode of thiocyanate is worthy of note, although it is not overly novel. No more than 20 structures with *N*-bridging thiocyanate have been published, with approximately half of these containing alkali metals.[¶] Bridging different metals through the thiocyanato nitrogen only is highly unusual and the present compound is the first case

involving copper and lead atoms in this way. This study also seems to reaffirm that the band at 2030 cm⁻¹ is due to an asymmetric μ_2 -NCS bonding mode, although it is indeed true that a direct correlation between ν (NCS) stretching frequencies and NCS⁻ bonding modes may be too simplistic.^{6a} Thus, in the compound [Cu₂Pb(SCN)₃L₃]₂^{2e} the N_{NCS} atom occupying the axial bonding position in the coordination environment of one of the copper atoms makes an additional contact with the lead atom. The distances Cu–N and Pb–N [2.32(1) and 3.05(1) Å, respectively] are comparable with the corresponding distances for the complex under consideration but no detection of *N*-bridging thiocyanate is revealed in the IR spectrum of compound [Cu₂Pb(SCN)₃L₃]₂. It could be presumed that a significant difference between the Cu–N–C and Pb–N–C angles [168(1) and 114.5(9)°, respectively] could be the reason. However, the highly asymmetric bridging is not necessary to prevent a low CN stretching frequency from being observed. For solid [LiNCS · Me₂N(CH₂)₃NMe₂]₂, in which two Li⁺ cations are bridged by the N centres of two NCS⁻ anions with four Li–N–C angles being significantly different [115(1) and 109(1)° in the case of the more acute angles and 160(1) and 167(1)° in the case of more open ones], this band does appear at 2033 cm⁻¹.^{6a}

Acknowledgements

We thank Professor J. Reedijk for valuable discussion. Thanks are due to the International Soros Program of Support of Education in the Field of Natural Sciences (ISSEP) for the grant GSU 053068 (L.A.K.) and to the Fonds zur Förderung der wissenschaftlichen Forschung in Österreich (projects 10818-CHE and 11218-CHE).

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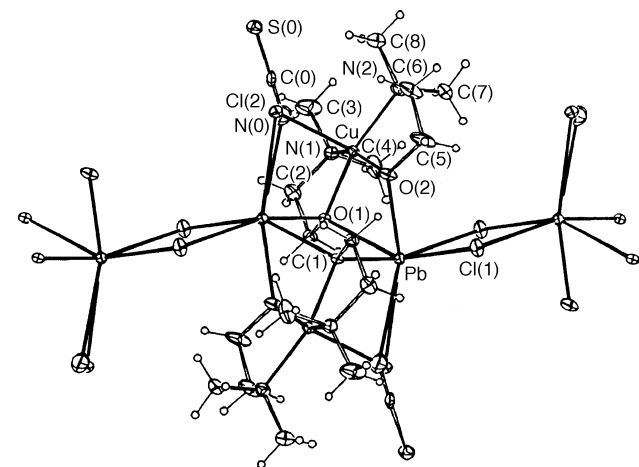


Fig. 1 ORTEP plot of a part of the [Cu₂PbCl₃(NCS)L₄]_n chain. The non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å. Bond distances to Pb are: Cl(1) 2.801(2), O(1) 2.603(3), O(2) 2.310(4), Cl(2') 3.02(1), O(1') 2.404(3), N(0') 2.99(5), Cl(1'') 3.111(2) Å. Bond distances to Cu are: N(1) 2.085(5), N(2) 2.089(5), O(2) 1.941(4), O(1) 1.987(4), N(0) 2.27(4), Cl(2) 2.53(1) Å. Bond angles around Pb range from 62.6(1) to 165.26(8)° and around Cu from 81.6(2) to 155.5(2)°. The bridging angle Cu–N(0)–Pb' is 83(1)°, the M–N(0)–C(0) angles are 129(3) and 137(4)° for the lead and copper atoms, respectively (where ' and '' refer to the symmetry operations 1 – *x*, 1 – *y*, 1 – *z* and 2 – *x*, 1 – *y*, 1 – *z*, respectively).

§ The weaker band at 2080 cm⁻¹ was assigned to bromide–thiocyanate exchange in the KBr disc preparation. Also the compound appears to decompose in Nujol to give a weak band at 2110 cm⁻¹.

¶ Search of the Cambridge Structural Database (version October 1997), University of Cambridge.

Received in Montpellier, France, 6th May, 1998;
Letter 8/03428A