A Mixed-metal Mixed-halide Complex Prepared from Zerovalent Copper and Lead Salts: Solution and Solid-state Chemistry†

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The mixed-metal mixed-halide complex $[CuPbBrIL_2]_2$ has been prepared by the direct interaction of zerovalent copper with lead halides and 2-dimethylaminoethanol (HL) in dmso and has been characterized by X-ray crystallography; the structure shows a layer arrangement of the tetranuclear metal units through the μ_3-halogen bridging.

Mixed-metal complexes have been of general interest in connection with the potential application of the expected metal–metal interactions to give materials possessing useful electronic, magnetic and electrochemical properties.[1] As part of our continuing research into the rational design of new mixed metal Cu/M (M = Pb, Co, Ni, Zn) compounds by employing zerovalent copper and a metal salt as starting materials,[2] a novel Cu/Pb mixed-halide (Br/I) complex containing dimethylaminoethanol (HL) has been synthesized and structurally characterized.

The compound was prepared by the reaction of copper powder with an equimolar mixture of lead halides in a dmso solution of the aminoalcohol. We believed that coordinatively unsaturated copper aminoalkoxide generated *in situ* could easily interact with other metal species present in solution to afford formation of a mixed-metal compound due to the established ability of aminoalcohols to form polynuclear metal complexes. The overall reaction scheme is summarized in eqn. (1)

$$2Cu + 2PbX_2 + 4HL + O_2 \xrightarrow{dmso} [CuPbX_2L_2]_2 + 2H_2O$$
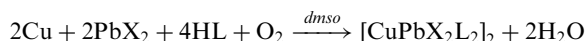
where X is total iodide and bromide.

The exact composition was established from the X-ray crystallographic study at 180(2) K. The compound appeared to be isostructural with the Cu/Pb iodide $[CuPbI_2L_2]_2$,[3] but possessed substantially shorter Pb–halogen distances [3.153(2) and 3.189(1) Å for the Br/I compound *cf.* 3.1966(9) and 3.2381(8) Å for the pure iodide]. The model on which the refinement was based assumed that halide ligands could be treated as 60% I + 40% Br for the first halogen site and 60% Br + 40% I for the second. Subsequent refinement of the data justified this assumption.

The basic structural motif of the complex is a centrosymmetric dimer composed of two $CuPbX_2L_2$ units with an approximate square-planar coordination geometry at the Cu atom and a highly irregular five-coordination of the Pb atom (Fig. 1). Alkoxo oxygens form bridges between lead and copper centres, resulting in Cu···Pb separations of 3.343(2) and 3.726(3) Å. The $Pb_2Cu_2O_4$ core displays a step-like configuration with the $PbCuO_2$ planes each folded by *ca.* 70(1)° with respect to the strictly planar Pb_2O_2 plane. The tetranuclear mixed-metal units are

further extended through μ_3-halogen(1) bridging between two Pb sites and one Cu site of adjacent heterometallic units to form a layer parallel to the *bc* plane (Fig. 2).
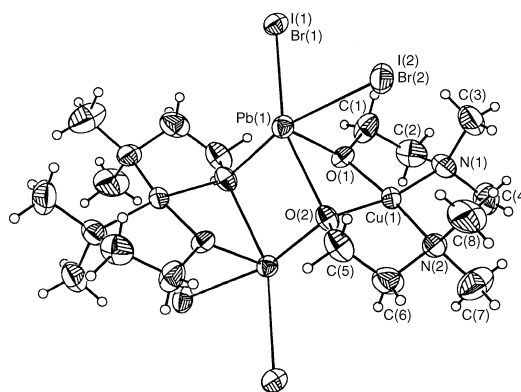

Fig. 1 ORTEP plot of the dimeric $[CuPbBrIL_2]_2$ molecule. The non-hydrogen atoms are shown as 50% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1Å. Bond distances to Pb are: O(1) 2.338(9), O(2) 2.58(1), O(2′) 2.532(9), Br(1) 3.189(1), Br(2) 3.135(2) Å [where primed atoms are related to their unprimed equivalents by the symmetry operation −x, −y, 1 − z]. Bond distances to Cu are: N(1) 2.06(1), N(2) 2.07(1), O(1) 1.93(1), O(2) 1.93(1) Å. Bond angles around Pb range from 61.2(3) to 166.2(2)°, and around Cu from 81.2(4) to 166.9(5)°, respectively.
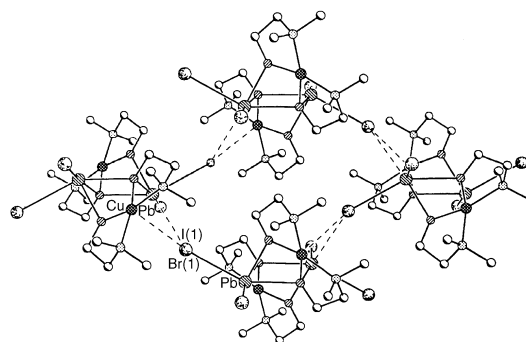

Fig. 2 Projection of part of the layer present in the crystal structure of $[CuPbBrIL_2]_2$ onto the *bc* plane (hydrogen atoms are omitted for clarity, the additional interactions are shown as dashes). I/Br(1) contacts to Cu {*x*, −0.5 − *y*, −0.5 + *z*} and Pb {−*x*, −0.5 + *y*, 0.5 − *z*} are of 3.585(3) and 3.520(3) Å, respectively.

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† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

The powder EPR spectrum of the compound at room temperature shows a broad low intensity absorption which becomes stronger upon cooling to 77 K ($g \approx 2.09$ signal with line width of 240 G). This is consistent with the dimeric structure of the complex as revealed by the X-ray crystallographic results and suggests the presence of a weak exchange interaction.

The solution EPR spectra of the compound are temperature dependent. At ambient temperature a superposition of a common four line spectrum with a sharp line at the highest field and poorly defined lines at a lower field ($g_0 = 2.09$, $A_0 = 70$ G) and a broad near-isotropic signal is observed. When the temperature is lowered to 77 K a broad absorption centered around $g = 2.08$ with line width of 230 G is seen only.

The room temperature EPR spectrum of the reaction solution is very similar to the analogous solution spectrum of the complex and also shows a common four-line pattern with $g_0 = 2.09$ and $A_0 = 77$ G (only the lines at a higher field are clearly resolved) together with a broad near-isotropic absorption. Upon cooling to 77 K the spectrum shows a line shape characteristic of a copper(II) compound with two different g values, a $g_\parallel$ signal with clear resolution of the four copper hyperfine lines: $g_\parallel = 2.23$, $g_\perp = 2.02$, $A_\parallel = 170$ G, $A_\perp = 50$ G, thus indicating the presence of a $d_{x^2-y^2}$ ground state[4] for Cu(II) ions in solution. The similarity of EPR parameters leads to a tentative conclusion that the solid and solution coordination is similar.

Experimental

Elemental analyses were performed by standard titrimetric methods (for Cu and Pb), and for C, H and N analyses were performed by the Cambridge University microanalytical service. The IR spectrum was recorded as KBr disc on a UR-10 spectrophotometer in the 4000–400 cm^{-1} region using conventional techniques. X-Band dmso solution and solid EPR spectra were measured at 293 and 77 K using a Bruker ER 200 D spectrometer.

Synthesis of [CuPbBrIL$_2$]$_2$.—Copper powder (0.64 g, 10 mmol), PbBr$_2$ (1.84 g, 5 mmol), PbI$_2$ (2.31 g, 5 mmol) and 2-dimethylaminoethanol (2 mL, 20 mmol) were heated in dmso (10 mL) to 50–60 °C in air and stirred until total dissolution of copper was observed (*ca.* 20 min). Dark-green crystals of the title compound were formed after 12–15 h at ambient temperature (5.00 g, 77%) (Found C, 14.3; H 2.8; N, 4.2; Cu, 9.7; Pb 29.8. C$_8$H$_{20}$BrCuIN$_2$O$_2$Pb requires C, 14.0; H, 2.9; N, 4.1; Cu, 9.3; Pb, 30.2%). ν_{max}/cm^{-1} (KBr, strong bands only): 3600–3350, 2900, 2870, 2840, 1480, 1465, 1070, 1060, 1020, 1010, 945, 900, 780, 650, 510, 475.

Crystal Data.—C$_8$H$_{20}$BrCuIN$_2$O$_2$Pb, $M = 653.80$, monoclinic, $a = 12.316(5)$, $b = 8.380(2)$, $c = 15.312(2)$ Å, $\beta = 93.94(3)°$, $U = 1576.6(8)$ Å^3 (by least-squares refinement on diffractometer angles from 21 reflections, $7.5 < \theta < 10°$), $T = 180(2)$ K, space group $P2_1/c$ (no. 14), graphite-monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, $Z = 4$, $D_c = 2.754$ Mg m^{-3}, $F(000) = 1188$, dark-green plate with dimensions $0.20 \times 0.20 \times 0.05$ mm, $\mu = 16.496$ mm^{-1}, semi-empirical absorption correction, transmission factors 0.437–0.998; Rigaku AFC7R diffractometer mounted on a rotating anode generator, $5 \leq 2\theta \leq 49.9°$, $-3 \leq h \leq 14$, $0 \leq k \leq 9$, $-18 \leq 1 \leq 17$; 3464 reflections measured, 2570 unique ($R_{int} = 0.0610$) and of these 2017 had $|I| > 2.00\sigma(I)$ and were considered to be observed. The structure was solved by direct methods and subsequent Fourier difference techniques (TEXSAN[5]), and refined anisotropically (H atoms fixed), by full matrix least squares, on F^2 (SHELXL-93[6]). The final R, $wR2$ were 0.0480 and 0.1172, respectively, for 2017 observed reflections and 150 parameters, goodness of fit = 1.039, largest difference peak and hole 1.624 and -1.843 e Å^{-3}.

Bond distances and angles of the L groups are normal and are given in the supplementary material.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Research (S)*, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 423/28. See http://www.rsc.org/suppdata/jc/1999/670/ for crystallographic data in .cif format.

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