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FULL PAPER

A thiocyanato-bridged layer structure composed of symmetrical, dithiocyanato(N,S)-bridged dimers of heterotrinuclear alkoxo-bridged Cu_2Pb units; synthesis from zerovalent copper, structural, spectroscopic and magnetic studies

Larisa A. Kovbasyuk,[a] Olga Yu. Vassilyeva,*,†,[a] Volodymyr N. Kokozay,[a] Wolfgang Linert,[b] Jan Reedijk,[c] Brian W. Skelton[d] and Allen G. Oliver[e]

[a] *Department of Inorganic Chemistry, Kyiv Shevchenko University, Volodimirska st, 64, Kyiv 252033, Ukraine*
[b] *Institute of Inorganic Chemistry, Vienna University of Technology, Getreidemarkt 9/153 A-1060 Vienna, Austria*
[c] *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands*
[d] *Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6907, Australia*
[e] *Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand*

A novel mixed-metal compound $[\{Cu_2Pb(SCN)_3L_3\}_2]$ has been prepared from zerovalent copper and lead thiocyanate in an acetonitrile solution of 2-dimethylaminoethanol (HL). The compound, which crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.5786(1)$, $b = 17.4145(2)$, $c = 10.5194(1)$ Å, $\beta = 105.11(1)°$ and $Z = 4$, has been characterized by a range of spectroscopic methods. The crystal structure contains symmetrical dimers of heterotrinuclear alkoxo-bridged Cu_2Pb units in which dimerization has occurred through bridging of NCS *via* the axial positions on the copper ions. The so-formed hexanuclear units are linked by Pb···S interactions between adjacent units to form layered supramolecular assemblies along the *b* axis of the crystal. The magnetic behaviour can be understood on the basis of the structure, and corresponds to that of a weakly antiferromagnetically coupled dinuclear unit. The small value of the antiferromagnetic coupling can be explained by the roof-shaped CuO_2Cu unit, which prevents the magnetic orbitals from undergoing significant overlap.

Mixed-metal complexes are common in the literature, both in magnetic materials and in bioinorganic (model) systems,[1] however the number of Cu/Pb complexes is rather small and those known generally utilize macrocyclic ligands.[2] Our aim has been to demonstrate the utility and the versatility of our synthetic approach to the preparation of co-ordination compounds[3] in the syntheses of novel mixed-metal complexes. We have recently reported the synthesis of a variety of mixed-metal Cu/Pb complexes with aminoalcohols.[4] The compounds were prepared from copper powder and lead halide in a non-aqueous solution of an aminoalcohol. Single-crystal X-ray studies have shown that in the solid state the compounds contain centrosymmetric tetranuclear units with similar structures, having a $Cu_2Pb_2O_4$ core and bridging halide atoms. While the $Cu_2Pb_2L_4$ (L = aminoethoxide group) unit is sufficiently rigid to retain structural similarity in these complexes irrespective of the nature of the halide atom and aminoalcohol, their molecular architectures are different.

When the lead halide is replaced by lead thiocyanate in the reaction with copper powder and 2-dimethylaminoethanol (HL), surprisingly, a compound is obtained which shows analytical data accounting for the presence of the two metals in a 2Cu : Pb stoichiometry and so suggests the formation of a mixed-metal species of empirical formula $Cu_2Pb(SCN)_3L_3$. We now report the first crystal structure of such a mixed-metal Cu/Pb complex containing dimeric units in which dimerization has occurred through bridging of NCS *via* the axial positions on the copper ions. The so-formed hexanuclear units are linked by Pb···S interactions between adjacent units to form two-dimensional sheets. The structure is discussed in relation to the magnetic properties.

Experimental

All chemicals were of reagent grade and used as received, all experiments were carried out in air.

Synthesis of $[\{Cu_2Pb(SCN)_3L_3\}_2]$

Copper powder (0.63 g, 10 mmol), $Pb(SCN)_2$ (3.23 g, 10 mmol), CH_3CN (15 cm^3) and 2-dimethylaminoethanol (3.0 cm^3, 30 mmol) were heated to 60 °C and stirred until total dissolution of Cu and $Pb(SCN)_2$ was observed (30–35 min). The resulting clear green solution was allowed to stand at room temperature for 24 h during which a light white powder precipitated, which was found to be lead(II) oxide hydrate of a non-stoichiometric composition. It was filtered out and subsequently green crystals separated from the solution in 24 h. The overall reaction (1) is

$$4Cu + 3Pb(SCN)_2 + 6HL + 2O_2 \xrightarrow{CH_3CN} 2Cu_2Pb(SCN)_3L_3 + PbO\cdot 3H_2O \quad (1)$$

proposed. The crystals were filtered off, washed with dry Pr^{i}OH and finally dried *in vacuo* at room temperature. Mass collected 2.82 g, yield 73% (Found: C, 23.2; H, 4.0; Cu, 15.9; N, 10.6; Pb, 26.3; SCN, 22.8. $C_{15}H_{30}Cu_2N_6O_3PbS_3$ requires C, 23.3; H, 3.9; Cu, 16.45; N, 10.8; Pb, 26.8; SCN, 22.5%). IR (cm^{-1}): 3600–3350 (br), 3000w, 2970m, 2950m, 2910 (sh), 2890m, 2860m, 2840m, 2790w, 2110vs (CN), 2060vs (CN), 1630 (br), 1460m,

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† E-Mail: vassil@inorg.chem.univ.kiev.ua

1410w, 1380w, 1350w, 1280w, 1260w, 1180w, 1100w, 1060s, 1040 (sh), 1030m, 1010m, 950s, 890s, 820w (CS), 780m, 775 (sh) (CS), 625m, 610m, 595 (sh), 510m, 460s and 430m. The compound is insoluble in water and sparingly soluble in common organic solvents.

Physical measurements

Elemental analyses were performed by standard titrimetric methods (for Cu, Pb and SCN) and with a Carlo Erba Strumentazion Analyzer (for C, H and N) by the Institute of Organic Chemistry, National Academy of Sciences of Ukraine microanalytical service. Infrared spectra were recorded as KBr discs and in Nujol mulls on a UR-10 spectrophotometer in the 4000–400 cm^{-1} region using conventional techniques, electronic reflectance and dmso/dmf solution spectra on a Specord M40 spectrophotometer, X-band dmso/dmf solution and solid EPR spectra at 293 and 77 K using a Radiopan PS100.X spectrometer and X-band dmso/methanol solution and solid EPR spectra at 293 and 77 K on a JEOL RE2x spectrometer using an ESR900 continuous-flow cryostat. Magnetic susceptibility was measured in the temperature range 4–300 K with a fully automated Manics DSM-8 susceptometer equipped with a TBT continuous-flow cryostat and a Drusch EAF 16 NC electromagnet, operating at *ca.* 1.4 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal constants.

Crystallography

Crystal data. $C_{15}H_{30}Cu_2N_6O_3PbS_3$, $M = 772.93$, monoclinic, space group $P2_1/c$ (no. 14), $a = 14.5786(1)$, $b = 17.4145(2)$, $c = 10.5194(1)$ Å, $\beta = 105.11(1)°$, $U = 2578.4(1)$ $Å^3$, $T = 203(2)$ K, $Z = 4$, μ(Mo-Kα) = 9.22 mm^{-1}, 16 056 reflections measured, 5799 unique ($R_{int} = 0.0303$) and of these 4798 had $F > 6.00\sigma(F)$ and were considered to be observed. The final R, R' were 0.061, 0.086.

CCDC reference number 186/1046.

See http://www.rsc.org/suppdata/dt/1998/2735/ for crystallographic files in .cif format.

Results and Discussion

Spectroscopic measurements

In the IR spectrum of the compound two very strong ν(CN) vibrations (2110 and 2060 cm^{-1}) and two weak ν(CS) absorptions (820 and 775 cm^{-1}) of thiocyanate groups can be identified easily.[5] The position of ν(CN) and ν(CS) absorptions are quite similar to those of copper(II) 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine thiocyanates.[6] The reported compounds were considered to be thiocyanate-bridged copper(II) dimers with two types of thiocyanate groups present in their structures, with bridging functions and bonding through the nitrogen atom.

On co-ordination, changes in the absorption frequencies of 2-dimethylaminoethanol occur; namely, the strong mode found in spectra of the free alcohol[7] at 1040 cm^{-1} shifts 20 cm^{-1} to higher energy, the strong bands at 1270 and 1100 cm^{-1} are not observed and an intense band at 890 cm^{-1} appears. The electronic reflectance and solution spectra of the compound display one ligand field band at 14 200 and 14 600 cm^{-1}, respectively, consistent with the square-based bipyramidal geometries revealed in the crystal structure.[8]

The solution EPR spectra of the compound are temperature dependent. At ambient temperature a common four-line spectrum with $g_0 = 2.132$ and $A_0 = 72 \times 10^{-4}$ cm^{-1} is observed. At 77 K the spectrum shows a line shape characteristic of a complex with three different g values, a g_z signal with clear resolution of the four copper hyperfine lines (Fig. 1). Simulation of the spectra gave $g_x = 2.03$, $g_y = 2.07$, $g_z = 2.27$, $A_x = 9$, $A_y = 17$ and $A_z = 172$ (all A values $\times 10^{-4}$ cm^{-1}), thus indicating the presence of a $d_{x^2-y^2}$ ground state[8] for both copper(II) ions in solution. No triplet signals were detected, suggesting dissociation in solution. The solid-state EPR spectra, recorded at room and liquid-nitrogen temperatures, are quite similar. Unfortunately, solid-state measurements yielded little information, since the spectrum of the magnetically non-dilute solid consists of only a single line (Fig. 1). Neither hyperfine splitting nor any clear differentiation of copper(II) sites is observed on lowering the temperature. Also no signals for triplet spins are visible, which can be explained by relatively strong interdinuclear coupling, leading to line broadening.

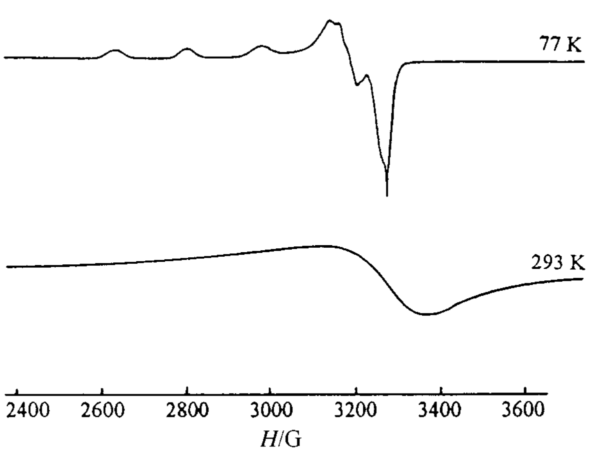

Fig. 1 X-Band frozen solution (77 K) and powder (293 K) EPR spectra of [$\{Cu_2Pb(SCN)_3L_3\}_2$]; G = 10^{-4} T

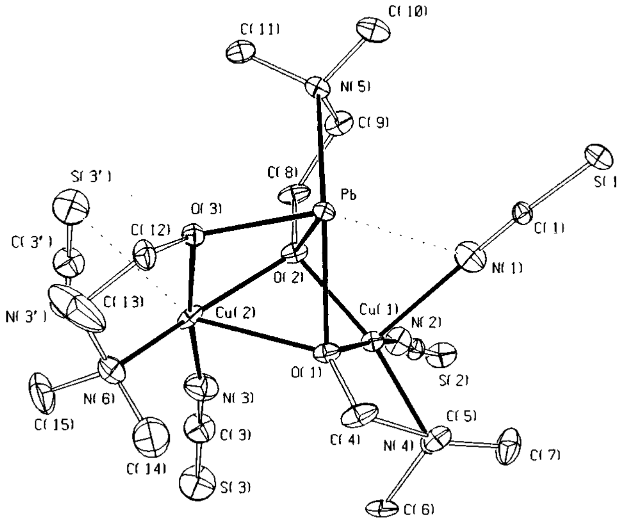

Fig. 2 A trinuclear unit in the crystal structure of [$\{Cu_2Pb(SCN)_3L_3\}_2$]. The thermal ellipsoids are drawn at the 20% probability level (hydrogen atoms are omitted for clarity)

Crystal structure

A trinuclear unit in the crystal of the compound is shown in Fig. 2. Selected bond distances and bond angles are given in Table 1. The asymmetric unit comprises two copper atoms, Cu(1) and Cu(2), and one lead atom, which occupy general positions. The two copper sites are chemically distinct. The co-ordination geometry of Cu(1) is distorted square pyramidal. The copper atom is 0.171(2) Å above the least-squares basal plane formed by O(1), O(2), N(2), N(4) atoms [the maximum deviation of oxygen and nitrogen atoms from the plane is not greater than 0.05(1) Å]. The Cu–N_{ax} bond distance is approximately 0.4 Å longer than that of Cu–N_{eq}, which is rather common for copper(II)–thiocyanate complexes.[9] While the thiocyanate group located in the equatorial plane is co-

Table 1 Selected bond distances (Å) and angles (°)

Cu(1)–O(1)	1.937(8)	Cu(2)–N(3)	1.81(1)
Cu(1)–O(2)	2.004(8)	Cu(2)–N(6)	1.97(2)
Cu(1)–N(1)	2.32(1)	Pb–O(1)	2.440(7)
Cu(1)–N(2)	1.93(1)	Pb–O(2)	2.460(6)
Cu(1)–N(4)	2.03(1)	Pb–O(3)	2.264(9)
Cu(2)–O(2)	2.148(8)	Pb–N(5)	2.693(9)
Cu(2)–O(3)	2.030(7)		
O(1)–Cu(1)–O(2)	78.5(3)	O(2)–Cu(2)–N(3)	92.8(5)
O(1)–Cu(1)–N(1)	93.4(4)	O(2)–Cu(2)–N(6)	158.9(4)
O(1)–Cu(1)–N(2)	167.8(4)	O(3)–Cu(2)–N(3)	172.1(6)
O(1)–Cu(1)–N(4)	85.1(4)	O(3)–Cu(2)–N(6)	84.1(5)
O(2)–Cu(1)–N(1)	91.3(4)	N(3)–Cu(2)–N(6)	102.3(6)
O(2)–Cu(1)–N(2)	98.9(4)	O(1)–Pb–O(2)	61.2(2)
O(2)–Cu(1)–N(4)	162.7(4)	O(1)–Pb–O(3)	80.0(3)
N(1)–Cu(1)–N(2)	98.7(4)	O(1)–Pb–N(1)	67.9(3)
N(1)–Cu(1)–N(4)	95.4(4)	O(1)–Pb–N(5)	127.8(2)
N(2)–Cu(1)–N(4)	95.8(4)	O(2)–Pb–O(3)	69.1(3)
O(1)–Cu(2)–O(2)	61.0(3)	O(2)–Pb–N(1)	67.5(3)
O(1)–Cu(2)–O(3)	78.6(3)	O(2)–Pb–N(5)	67.6(2)
O(1)–Cu(2)–N(3)	95.3(5)	O(3)–Pb–N(1)	134.5(3)
O(1)–Cu(2)–N(6)	102.4(4)	O(3)–Pb–N(5)	91.4(3)
O(2)–Cu(2)–O(3)	79.9(3)	N(1)–Pb–N(5)	84.4(3)

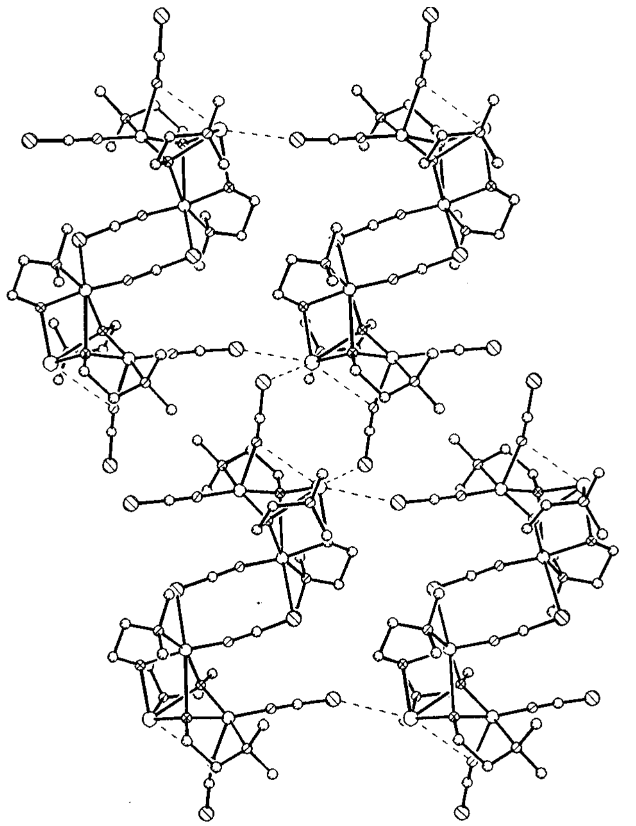

Fig. 3 Projection of part of the layer present in the crystal structure of [{$Cu_2Pb(SCN)_3L_3$}$_2$] onto the *ac* plane (hydrogen atoms are omitted for clarity)

ordinated in a nearly linear fashion [Cu(1)–N(2)–C(2) 173.3(9)°], Cu(1)–N(1)–C(1) 168(1)° indicates the axial thiocyanate is slightly bent.

The atoms O(2), O(3), N(3), N(6) form four strong bonds to Cu(2). The maximum deviation of oxygen and nitrogen atoms from the O(2), O(3), N(3), N(6) plane is 0.17(2) Å, while the copper atom is shifted from this plane by 0.163(4) Å. In addition Cu(2) is bonded to a sulfur atom from the bridging thiocyanate group at 3.027(6) and an oxygen atom at 2.682(9) Å, a distance also considered as semico-ordination, which implies that Cu(2) has a 4 + 2 co-ordination sphere. The Cu(2)–S(3) ($1 - x$, $2 - y$, $1 - z$) 'contact' agrees well with Cu–S_{ax} bond lengths of some other known copper(II)–thiocyanate systems which range from 2.698(5) to 3.286(9) Å.[9] Thiocyanate groups co-ordinated to the Cu(2) atom mutually link neighbouring co-ordination polyhedrons to form a dimer. The Cu(2)···Cu(2) ($1 - x$, $2 - y$, $1 - z$) distance in the dimer is 5.369(2) Å.

The lead atom is seven-co-ordinate but its environment is far from regular. The atoms O(1), O(2), O(3), N(5) complete the nearest unilateral co-ordination. The unsymmetrical co-ordination is caused by the presence of the stereochemically active lone pair in a hybrid orbital of the lead atom. Such an environment also has space vacant for weak lead–ligand specific intra- or inter-molecular contacts. In fact three interatomic separations are found considerably less than the sum of the van der Waals radii of the atoms under consideration[10,11] [Figs. 2, 3; *r*(Pb⟨van der Waals⟩) 2.3, *r*(N⟨van der Waals⟩) 1.6, *r*(S⟨van der Waals⟩) 1.85 Å]. For example, Pb···N(1) is 3.05(1), Pb···S(1) ($-x$, $2 - y$, $-z$) 3.260(3) and Pb···S(2) (x, y, $z - 1$) 3.426(3) Å.

The Cu(1), Cu(2) and Pb atoms are bridged by μ-alkoxo oxygens O(1), O(2) and O(3) resulting in Cu(1)···Cu(2) 3.183(2), Cu(1)···Pb 3.290(1) and Cu(2)···Pb 3.370(1) Å separations with Cu–O–Pb and Cu–O–Cu angles ranging from 82.2(3) to 103.3(4)° and the dihedral angle between the planes Cu(1), O(1), O(2) and Cu(2), O(1), O(2) of 123.7(3)°. The origin of this large deviation from planarity of the Cu_2O_2 unit is clearly the Pb atom, forming strong bonds with O(1) and O(2) atoms.

Additional intermolecular association in the structure occurs through the Pb···S interactions between S(1) and S(2) atoms of SCN groups and Pb atoms of adjacent complex molecules. As a consequence, a layered supramolecular assembly is evident along the *b* axis of the crystal. A section of such a layer is shown in Fig. 3. The layers are held together through van der Waals-type forces.

The 2-dimethylaminoethoxo groups act as bi- and tri-dentate chelating agents through an amino nitrogen and μ-alkoxo oxygen atoms. They form five-membered puckered rings with the *gauche* configuration. Bond distances and angles of L groups are normal. Thiocyanate groups [*d*(N–C) *ca.* 1.16(2)–1.21(2), *d*(S–C) *ca.* 1.59(1)–1.64(1) Å, N–C–S *ca.* 176(1)–180(2)°] are structurally normal.[10]

Magnetic susceptibility

The magnetic susceptibility for the compound recorded between 4 and 300 K shows a Curie–Weiss behaviour with $\theta = -15$ K. The complex shows a room-temperature magnetic moment per copper ($\mu_{eff} = 1.85\ \mu_B$; $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}) typical for an uncoupled copper(II) ion. When the temperature is lowered to 4 K, the μ_{eff} per Cu^{II} decreases to 1 μ_B, indicating a weak antiferromagnetic exchange. The obtained magnetic data were fitted by the Bleaney–Bowers equation (2) for a dinuclear

$$\chi_m = (2N\beta^2g^2/kT)[3 + \exp(-J/kT)]^{-1}(1 - \rho) + (N\beta^2g^2\rho/2kT) + 2N_\alpha \quad (2)$$

copper(II) system where the symbols have their usual meanings and N_α was fixed to -60×10^{-6} cm^3 mol^{-1}. The best fit was obtained below 180 K for $J = -5.0$ cm^{-1}, $g = 2.00$, $\rho = 0$ with $R = 5.34\%$. The susceptibility data were also modelled with the *g* value constrained to be 2.11 (as obtained from EPR measurements), which gave $J = -5.8$ cm^{-1}, but a slightly worse agreement factor.

The magnetic susceptibility data indicate that the magnetic exchange interaction between the copper ions is small. The bridging alkoxo groups may provide an effective pathway for the magnetic interaction between the two copper ions. However, this pathway did not appear to be effective in the case of the compound studied, due to the fact that not enough unpaired electron density is present on the bridging ligands.

The small antiferromagnetic interaction can be explained by the roof shape of the Cu_2O_2 unit.[12] A somewhat similar stereochemistry has been reported for the alkoxo-bridged dinuclear unit of the compound $[CuBr_2(Hea)_2][Cu_2(ea)_2Br_2]$ (Hea = 2-aminoethanol) with a roof angle between the two CuO_2 planes of 139.7°.[13] This case has only weak antiferromagnetism, $J = -5.3$ cm^{-1}, since the sharp dihedral angle prevents any significant overlap of the magnetic orbitals.[13] Non-planar Cu_2O_2 structures have also been reported for (2-dimethylaminoethanolato)thiocyanatocopper(II)[14] and bis[1,3-bis(dimethylamino)propan-2-ol]tetrachlorocopper(II)[15] with a dihedral angle between the two CuO_2 planes of 162.4° for the former and a dihedral angle between the two Cu_2O planes of 125.5° for the latter. The magnetic susceptibility of (2-dimethylaminoethanolato)thiocyanatocopper(II) shows a broad maximum at 200 K.[14]

Conclusion

A direct reaction of copper powder with lead thiocyanate in the acetonitrile solution of 2-dimethylaminoethanol has led to a novel mixed-metal compound, $[\{Cu_2Pb(SCN)_3L_3\}_2]$. Its crystal structure incorporates dithiocyanato-bridged dimers of heterotrinuclear alkoxo-bridged Cu_2Pb units. In spite of a seemingly favourable structure in which neighbouring magnetic ions are alkoxo- and dithiocyanato-bridged, no evidence for significant magnetic interaction between copper(II) ions in the heterotrinuclear units as well as between those in the dimers has been detected.

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