Spectroscopic and Magnetostructural Evidence for the Formation of \([\text{Cu}_0.5\text{Co}_0.5(\text{H}_2\text{Tea})\text{X}]\) Mixed-Crystal Compounds from Zerovalent Cu and Co Salts in the Presence of Triethanolamine (H\(_3\)Tea - Triethanolamine; \(X = \text{SCN}, \text{Cl}\))

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Mixed Crystals, Zerovalent Copper, Cobalt(II) Salts

Mixed crystals \([\text{Cu}_0.5\text{Co}_0.5(\text{H}_2\text{Tea})\text{X}]) (1), \([\text{Cu}_0.5\text{Co}_0.5(\text{H}_2\text{Tea})\text{Cl}]) (2) (\text{H}_3\text{Tea} = \text{triethanolamine}) have been obtained by the open-air reaction of metallic copper with cobalt(II) chloride/cobalt(II) thiocyanate and triethanolamine in non-aqueous solvents, like dmf, dmso, CH\(_3\)OH and CH\(_3\)CN. The simultaneous presence of copper and cobalt in the mixed crystals was unambiguously determined by atomic absorption, EPR and electronic spectroscopy. Details of 1 have been studied structurally, and a preliminary report of the structure of 2 is also given. The mononuclear species 1 and 2 contain crystallographically indistinguishable Cu(II) and Co(II) ions in virtually identical trigonal bipyramidal sites. The molecules are linked together by O-H...O hydrogen bonds to give chains. The values of the temperature independent \(\mu_{\text{eff}}\) of 3.50 and 3.48 \(\mu_{\text{B}}\) for 1 and 2 (in the range of \(T = 20 - 280\) K), respectively, agree with the 1:1 molar ratio of the metals in both samples.

Introduction

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 in air [1]. Employment of this approach to the synthesis of mixed-metal compounds has resulted in a number of novel tri- and tetranuclear Cu/Pb complexes prepared from zerovalent copper and lead halide in amino alcohol solutions in air [2]. The copper oxidation and complex formation were conditioned by the presence of a proton-donating agent (amino alcohol) and dioxygen from the air via the following reaction in which water was usually the only by-product:

\[
\begin{align*}
\text{Cu}^0 + \text{Pb}X_2 + 2\text{HL} + 1/2\text{O}_2 \xrightarrow{\text{Solv}} & \text{CuPb}X_2\text{L}_2 + \text{H}_2\text{O} \\
\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}; \text{Solv} = \text{dmf}, \text{dmso}, \text{CH}_3\text{CN}, \text{CH}_3\text{OH} \\
\end{align*}
\]

As part of our continuing research into a rational design of new mixed-metal Cu/M (M = Co, Ni, Zn) systems by employing zerovalent copper and a metal salt as starting materials in the presence of an amino alcohol, and to see whether it makes a large difference if metal ions are used which have related stereochemical requirements, we have used triethanolamine [H\(_3\)Tea, N\(^+\)\(\text{CH}_2\text{CH}(-\text{OH})\text{CH}_2\text{OH}\)] and cobalt(II) salts. The open-air reaction of copper powder with cobalt(II) chloride/cobalt(II) thiocyanate and triethanolamine in a non-aqueous solvent yielded mixed crystals \([\text{Cu}_0.5\text{Co}_0.5(\text{H}_2\text{Tea})\text{X}]\), \(X = \text{SCN}, \text{Cl}\)). Mixed-crystal systems offer a variety of interesting physical effects with the implication of technical application, for example, thermally-induced ferridistortive phase-transitions, spin-state interconversions, or crystallographic phase transitions [3].
Details of the syntheses, crystal structures, spectroscopic investigations as well as detailed magnetic studies of 1 and 2 are reported.

Experimental

All chemicals were of reagent grade and used as received. All experiments were carried out in air. Elemental analyses for metals were performed by atomic absorption spectroscopy, and for anions by standard titrimetric methods 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. UV/VIS spectra were recorded on a Perkin Elmer spectrophotometer using an ESR900 continuous-flow cryostat and a Drusch EAF 16 NC electromagnet, operating at a = 1.4 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Synthesis of [Cu\(_{0.5}\)Co\(_{0.5}\)(H\(_2\)Tea)(SCN)] (1)

Copper powder (0.32 g, 5 mmol), CoCl\(_2\)·6H\(_2\)O (1.19 g, 5 mmol), Me\(_2\)NC(O)H (10 cm\(^3\)) and H\(_2\)Tea·HCl (1.86 g, 10 mmol) were heated to 60 °C and magnetically stirred until total dissolution of Cu was observed (1 h). Purple crystals suitable for X-ray crystallography deposited in two weeks after the successive addition of isopropanol into the resulting green solution. Mass collected 1.0 g, yield 40%.

IR (KBr): \(\nu = 3600 - 3310, 3165, 2955, 2950, 2970, 2880, 2835, 1495, 1480, 1465, 1410, 1380, 1330, 1280, 1270, 1245, 1170, 1095, 1080, 1060, 1035, 1010, 940, 920, 900, 860, 750, 625, 590, 560, 555, 530, 435 cm\(^{-1}\). The compound is soluble in water and pyridine and sparingly soluble in common organic solvents.

The complexes are stable in air for periods of months.

Crystal structure determination of 1

C\(_{6}\)H\(_{13}\)Cu\(_{0.5}\)Co\(_{0.5}\)N\(_2\)O\(_4\)S, \(M = 267.51\), orthorhombic, \(a = 10.682(3), b = 7.963(2), c = 12.391(3)\) Å, \(U = 1054.0(5)\) Å\(^3\), \(T = 150\) K, space group \(Pnma\) (no. 62), \(Z = 4, \mu(\text{Mo-K}\alpha) = 2.031\) mm\(^{-1}\), \(T_{\text{min, max}}: 0.433, 0.862\), crystal dimensions: 0.37 × 0.14 × 0.10 mm, crystal habit: prism, 12300 reflections measured (\(\theta_{\text{max}} = 29.35°\)), 1444 unique (\(R_{\text{int}} = 0.055\)) and of these 1219 had \(F_o > 4.00\) \(\sigma(F_o)\) and were considered to be observed. The final \(R, R_w\) were 0.044, 0.052 for 88 parameters.

Diffraction experiments were performed on a Bruker SMART CCD diffractometer (\(\omega\) rotation scans with narrow frames) equipped with graphite monochromated Mo\(K\alpha\) radiation (\(\lambda = 0.71073\) Å). The data were corrected for Lorentz-polarization effects and for the effects of absorption (multi-scan), the non-hydrogen atoms refined anisotropically, hydrogen atoms included but not refined. The structure was solved by direct methods and refined by full-matrix least-squares methods on \(F\) using the XTAL3.4 program [4].

The crystallographic results of 1 represent an average of crystallographically indistinguishable copper(II) and cobalt(II) ions in identical trigonal bipyramidal sites, with the population of cobalt and copper atoms refined to 0.5. Other evidence for this mixed-metal formulation will be discussed below. From crystallographic considerations, the central metal atom, N\(_{H2Tea}\) and the ethanolate group must lie on a mirror plane and the two ethanolate groups are mirror related to each other. Due to disorder, C(13) is shifted away from the mirror plane and the single
carbon C(23) is disordered over two sites, namely C(23) and C(23'), all with occupancy of 0.5. The position of the OH proton in this compound was located in the difference Fourier map, but not refined.

Crystallographic data for compound 1 have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk), and are available on request quoting the deposition number CCDC 157215.

Results and Discussion

Based on our earlier findings we have used triethanolamine as ligand reported to be able to achieve control of the stoichiometry and geometry of mixed-metal species [5]. So we anticipated that it might be possible to synthesize mixed-metal Cu/Co complexes. The interaction of the amino alcohol with zerovalent copper and cobalt(II) chloride or thiocyanate in dmf, dmso, CH$_3$OH (except for Co(SCN)$_2$) and CH$_3$CN leads to the immediate formation of the insoluble coloured product in the reaction mixture. Only the methanol solution of cobalt(II) thiocyanate and H$_2$Tea did not show immediate signs of dissolution of copper powder; however, while kept during two months the metal gradually dissolved and the reaction mixture produced a large crop of crystals 1. In the case of 2 the use of H$_3$Tea·HCl instead of the pure ligand afforded the formation of a transparent solution in dmf from which the mixed crystals were easily grown. The simultaneous presence of copper and cobalt in compounds of formula M(H$_2$Tea)X, where X = Cl and SCN, was unambiguously determined by atomic absorption, EPR and electronic spectroscopy. The Cu to Co ratio in the products correlates with the metals ratio in the initial mixture. Noteworthy, mixed-metal crystals containing other halide anions if formed could not be isolated, probably because of the high solubility of the complexes in the solvents used.

Structure of [Cu$_{0.5}$Co$_{0.5}$)(H$_2$Tea)(SCN)] (1)

The geometry around the metal centers can be best described as an approximate trigonal bipyramid with two oxygen atoms from two ethanol groups and one from an ethanol group forming the basal plane with nitrogen atoms occupying the apical positions. The metal-N(0) and metal-N$_{SCN}$ bond distances of 2.049(4) and 1.949(4) Å, respectively, are normal and show strong coordinative interaction of the nitrogen atoms of the triethanolamine and thiocyanate ligands with cobalt / copper. The N(0)-M-N(1) angle of 174.7(2)° shows that the three atoms are nearly linear. The thiocyanate group lies in the plane of the metal atoms and forms a nearly linear coordination (Z M-N(l)-C(l): 170.0(4)°). The shortest metal-O(11) bond length (1.992(3) Å) is attributed to the negative charge on the oxygen atom in the C$_2$H$_4$O$^-$ group. The base angles of the equatorial plane are closed to 120°, thus approaching C$_3$ symmetry. The metal atom does not lie in the plane of the oxygen atoms but is shifted towards the N$_{SCN}$ atom, the deviation from the plane being 0.237(1) Å. The molecules are linked together in the solid state by relatively strong O-H···O hydrogen bonds to give chains parallel to the b axis [O(11) - O(21) {1 - x, 1 - y, 1 - z} and {1 - x, 1/2 + y, 1 - z} = 2.599(3), O(11) - H(21) {1 - x, 1 - y, 1 - z} and {1 - x, 1/2 + y, 1 - z} = 1.685(2) Å] (Fig. 2).
Structure of $[\text{Cu}_{0.5}\text{Co}_{0.5}(\text{H}_2\text{Tea})\text{Cl}]$ (2)*

A preliminary X-ray structural investigation of the mixed crystal shows that its structure is essentially identical with that of 1 with a five-coordinate trigonal bypiramidal metal centre, and a chloride anion as the apical ligand. The poor current refinement of this structure ($R = 0.10$), apparently as a result of twinning, limits the accuracy of bond length and angle data, but the metal center dimensions are comparable to those of 1 and the earlier reported $[\text{Co}(\text{H}_2\text{Tea})\text{Cl}]$ [6].

Spectroscopic measurements

The IR spectra of complexes 1 and 2 in the range 4000 - 400 cm\(^{-1}\) are quite similar and show all the characteristic ligand peaks, and bands due to O-H stretching [7]. In Nujol mull and KBr disk infrared spectra of 1 the very strong split $\nu$(CN) vibration (2090 and 2075 cm\(^{-1}\)) and the weak $\nu$(CS) absorption (845 and 835 cm\(^{-1}\)) of a thiocyanate group are easily identified [8]. The $\delta$(NCS) mode is obscured by other vibrations. The frequencies of the observed bands imply coordination of the NCS\(^-\) group through nitrogen [8], in accord with the crystal structure of 1. The splitting of the $\nu$(CN) mode is attributed to bonding of the thiocyanate group to different metals and the resulting lower symmetry.

The solid-state electronic spectra of 1 and 2 have a similar pattern. The energy level scheme for the cobalt ion in ligand fields with D\(_{3h}\) symmetry has been reported to lead to the four bands in the 470 - 2000 nm region [9a]. These are bands at 470 - 550, 550 - 625, 770 - 1000 and 1670 - 2000 nm that show the expected marked dependence on field strength [9]. Both 1 and 2 give rise to an intense multi-component band at ca. 550 nm and a broad asymmetric band of lower intensity in the range 1650 - 1700 nm that is absent in the reflectance spectrum of the copper complex $[\text{Cu}(\text{H}_2\text{Tea})\text{Cl}]$\(^b\) and therefore assigned to a five-co-ordinate, trigonal bipyramidal Co(II) center [10]. The two broad intense bands at 750 - 850 and 990 - 1020 nm are associated with both the cobalt(II) and copper(II) centres. The high-energy, much more intense band (284 nm) present in the spectra of 1 and 2 is assigned to a charge-transfer transition.

The frozen dmso-methanol solution EPR spectrum of 1 consists of well-resolved and easily identifiable parallel components of the hyperfine splitting. The perpendicular components are not resolved. The observed $g_{\perp} = 2.05$, $g_{\parallel} = 2.28$, $A_{\perp} = 160 \times 10^{-4}$ cm\(^{-1}\) are in accord with the $d_{x^2-y^2}$ orbital as the ground state [11] for a Cu(II) ion in solution. The signals due to Co(II) are known to be too broad to be observed at this temperature (relaxation). The solid-state EPR spectrum of 1 at room temperature shows an isotropic sig-

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*a* Crystal data for C\(_6\)H\(_{14}\)Cu\(_{0.5}\)Co\(_{0.5}\)NO\(_3\)Cl. $M = 244.88$, monoclinic, $a = 8.008(2)$, $b = 8.145(2)$, $c = 13.962(4)$ Å, $\beta = 90.083(3)^\circ$, $U = 910.7(4)$ Å\(^3\), $T = 150$ K, space group P2\(_1\)/n (no. 14), $Z = 4$, $\mu$(Mo-K\(_\alpha\)) = 2.040 mm\(^{-1}\), 17186 reflections measured, 2254 unique ($R_{int} = 0.035$), with 2113 having $F > 4.00\sigma(F)$.

*b* In the copper complex $[\text{Cu}(\text{H}_2\text{Tea})\text{Cl}]$ prepared in an independent synthesis the five-coordinate metal has crystallographically imposed C\(_3\)\(v\) symmetry.
nal \((g = 2.16)\), which becomes stronger and sharper upon cooling to 77 K \((g = 2.20)\), together with other features. The features can not be directly related to the copper pattern and comprise two low-field broad lines of low intensity \((g \approx 3 [room\ temperature], g \approx 4 \text{[77 K]}\) and \(g \approx 27\) at room temperature and 77 K). The study of this phenomenon requires high-field EPR and is left for future investigation.

**Magnetic properties**

Magnetic data for 1 and 2 are displayed in Fig. 3 as \(\mu_{\text{eff}}\) vs. \(T\) plots which show that in both cases the magnetic behaviour is paramagnetic. The drop of \(\mu_{\text{eff}}\) below 20 K indicates the onset of a weak antiferromagnetic coupling; this is not unexpected for systems in which H bond contacts are important.

Since magnetic moments for mononuclear high-spin Co(II) and mononuclear Cu(II) compounds are known to be 4.5 - 5.2 and 1.7 - 2.2 \(\mu_B\), respectively, \([13]\) the values of \(\mu_{\text{eff}}\) of 3.50 (1) and 3.48 \(\mu_B\) (2) (Fig. 3) indicate the presence of both Cu(II) and Co(II) in the samples. The measured values are close to that expected for a magnetically non-interacting \(\text{Cu}_{0.5} (s = 1/2) - \text{Co}_{0.5} (s = 3/2)\) mixed-spin system as estimated by the equation \(\mu_{M_{\text{eff}}} = \sum \mu_i^2\) (calculated value for \(\mu_{\text{eff}} = 3.47 \mu_B\) for \(g_{\text{Co}} = 2.35\) and \(g_{\text{Cu}} = 2.10\) \([14]\)).

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