Novel Polymetallic Cobalt and Zinc Complexes formed with an Arsenic Sulphide Ligand. The X-Ray Structure Determination of Racemic Hexa-μ-dithiocacodylato-tetrazincsulphide $[SZn_4\{AsS_2(CH_3)_2\}_6]$

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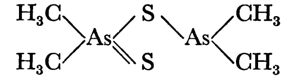
The reaction of the compound[1,2)]



with $M(ClO_4)_2\cdot 6H_2O$ ($M=Co$, Zn) in ethanol or acetone solution yields isomorphous hexagonal crystals, space group $P6_3$, unit cell dimensions ($M=Co$) $a=32.262$, $c=10.303$ Å, $D_m=2.05$ and stoichiometry (chemical and atomic absorption analyses) consistent with the formula $M_4As_6S_{13}C_{12}H_{36}$. Mixtures of the pure cobalt and zinc reactant or product molecules cause formation of isomorphous crystals with mixed metal stoichiometry. Recrystallization of the hexagonal crystals from dichloromethane solution yields isomorphous monoclinic crystals, space group $P2_1/n$, unit cell dimensions ($M=Zn$) $a=30.55$, $b=18.50$, $c=32.63$ Å; $\beta=95.7°$, $D_m=2.00$ and different stoichiometry. The title compound and its cobalt isomorph are minor recrystallization products.

The infrared spectra of all these compounds are strikingly similar in the range 1300—200 cm^{-1}, and similar to the spectra of dithiocacodylate complexes recently reported.[3)] The NMR spectra of the zinc compounds confirm the expected retention by arsenic of the methyl groups coordinated to it in the free ligand.

Solution molecular weight determinations and numerous physical measurements indicate large polynuclear transition metal structures abound. For example one crystalline product containing zinc has hexagonal unit cell dimensions $a=15.42$, $c=34.65$ Å.

Electronic spectral measurements on the cobalt hexagonal crystals indicate a tetrahedral environment around the cobalt ions. The magnetic moment over the temperature range 193—93K drops from 3.49 to 2.16 BM per cobalt suggesting spin coupling between the metal ions in the polynuclear structure. The coupling is retained in solution, but can be reduced by forming mixed solutions with the isomorphous zinc complex. A compound with the composition $[Co\{AsS_2(CH_3)_2\}_2]$ is also reported to show spin coupling.[4)]

The title compound was selected for initial X-ray analysis because it was ideally suited to locally available computing techniques.

Crystal Data. $Zn_4As_6S_{13}C_{12}H_{36}$, $M=1308.3$, Monoclinic, $a=11.586(8)$, $b=33.08(2)$, $c=11.996(8)$ Å, $\beta=117.39(1)°$, $U=4082$ Å^3, $D_m=2.12$ (by floatation), $Z=4$, $D_c=2.13$, $F(000)=2536$, Mo$K\alpha$ radiation, $\lambda=0.7107$ Å, $\mu(\text{Mo}K\alpha)=81.21$ cm^{-1}. Space group $P2_1/c$. 4520 independent intensity data ($0<\theta\leq 21°$) were collected on a Hilger and Watts 4-circle automatic diffractometer. After correction for LP and absorption effects, 2637 intensities exceeded 3 times their estimated standard deviations. The structure was solved by the symbolic addition procedure then refined using these data and full-matrix least-squares methods until $R=0.058$.

The structure consists of well separated neutral molecules one of which is shown in the figure. All non-hydrogen atoms are in approximately tetrahedral coordination environments and bond lengths lie in the ranges normally expected for the atoms concerned. The structure has topological similarity to basic beryllium acetate. In each structure a central non-metallic atom (S,O) is bonded to four metal atoms (Zn, Be) located at the corners of a tetrahedron. The six edges of this tetrahedron are bridged by polyatomic anionic ligands ($\{AsS_2(CH_3)_2\}^-$, $(CH_3CO_2)^-$). However the high symmetry (T-23) exhibited by basic beryllium acetate, and related oxy- compounds, is not developed in this sulphide which has only ana pproximate C_3 axis of symmetry.[5)] Figure 1 shows that the three six-membered SZnSAsSZn rings, which include the S and Zn atoms on the C_3 axis, have approximate chair conformations while the three which do not include the axial Zn atom have twist boat conformations. Models show no interactions precluding the existence of a molecule with the higher (T-23) symmetry and all twist boat ring conformations. This stereochemistry may be expected in some of the more complicated crystal modifications. Chirality of individual molecules has been demonstrated from the X-ray structural evidence, as well as studies of optical rotation.

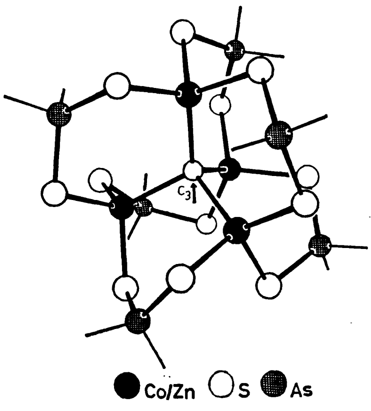


Fig. 1. Structure of $[SZn_4\{AsS_2(CH_3)_2\}_6]$
(Three top rings are chairs, three bottom rings are boats.)

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