In the compounds (I) and (II) as a bridge, linking Cu(I) atoms. In the complex (II) the SeCN group is out of the ligand sphere. The bond angles M-Se-CN deviate only slightly from 90°, the bond angles M-N-CoSe are close to 180°. The deviations from linearity of the SeCN groups have an average value of 5°.

Neutral molecules (diamines, water) in all above mentioned selenocyanate compounds are bonded only to the Cu(II) atoms. In mixed valence complexes (I) and (II) the Cu(II) atom has square pyramidal coordination. In copper(II) selenocyanate complexes central atoms are surrounded by a distorted octahedron. The calculated interatomic distances \( C_2 \mathrm{NO}_2 \cdots N(\text{en}) \) and SeCN...N(\text{en}) suggest the presence of hydrogen bonds.

08.2.19 THE DISTRIBUTION OF Cu ATOMS IN THE STRUCTURE OF CuOBlS \(_2\). By N. Ohashi, N. Yamada, Institute of Materials Science, University of Tsukuba, Sakura, Japan, and K. Tominaka, Department of Geology, Arizona State University, Tempe, Arizona, U.S.A.

In the chemical studies of mixtures of CuO and Br\(_2\)S\(_2\), a new compound with a ratio CuO:Br\(_2\)S\(_2\):81:1:5 has been synthesized. The material was examined by X-ray diffraction. The hexagonal cell \( a = 21.81 \) Å, \( c = 13.393 \) Å, \( P6 \_2 \_2 \_2 \). Since the reflections corresponding to \( h = 6n \), \( k = 6n \), and \( l = 2n \) (\( n \) is any integer) are stronger than the rest, the structure was regarded as a modulated structure of the smaller cell: \( a' = 3.94 \) Å, \( c' = 6.66 \) Å, \( P6_3/mmc \). The structure analysis of the latter (the subcell) revealed that the arrangement of the S and Cu atoms is similar to that in \( \beta \)-CuS (Sadanaga et al., Min. Jour. (1965) 2, 275).

The Bi atoms occupy centers of the octahedra of S atoms. The intensity distribution of the reflections around the subcell reflections gives the following feature: the intensity of the inner reflection is stronger than that of the outer ones. If an octahedron is occupied by a Bi atom, the octahedron has a larger scattering power and a larger size than an empty one. The characteristic intensity distribution can therefore be attributed to a 'synchronized' effect of the modulation of the scattering power and the modulation of the size of the octahedron.

08.2.20 THE EuO-BiO\(_2\) BINARY SYSTEM. By I. P. Ferguson and A. Williams, Springfield Nuclear Power Development Laboratories, United Kingdom Atomic Energy Authority (Northern Division), Preston, FY2 6NN, United Kingdom

An investigation of the europia-zirconia binary system has been made to parallel one already reported for the europia-hafnia system (I. P. Ferguson and Miss L. Hammonds (1978) Acta Cryst. A34, 8154-8155).

Mixed oxides were prepared as follows. The mixed 'hydroxides' were precipitated by the addition of excess ammonium hydroxide to a solution containing 0.05 g/ml made up from Spepure zirconyl chloride octahydrate dissolved in dilute hydrochloric acid and Spepure europia dissolved in concentrated nitric acid. Excess ammonia was removed by boiling, while the volume of solution was maintained constant by the addition of demineralised water. The precipitate was filtered off, dried at 110°C, lightly ground, transferred to an alumina boat, heated to 900°C for 10 h in air, then to 1300°C for a further 10 h in air and cooled slowly to room temperature. A portion was then removed for X-ray powder diffraction analysis. The remainder was reheated to 1550°C for 10 h and allowed to cool slowly to room temperature. The resultant mixed oxides were examined using an XRD focusing camera set for pure CuO radiation. A duplicate sample was examined similarly but with added NBS standard silicon as an internal standard. Lattice parameter measurements were made using a Hilger and Watts measuring rule and all computations made using a Fortran version of the program FINSTAR (G. Astle and I. P. Ferguson (1970) UKAEA Report FN4 1512). All sample compositions were determined by X-ray fluorescence analysis and are correct to ±1 mole %.

In samples prepared at 1300°C it was found that b.c.c. europia could dissolve up to 5 mole % zirconia when its cube cell edge, a, decreased to 10.834 Å. Between 9.6 and 39.8 mole % zirconia a two phase region containing b.c.c. and f.c.c. (pseudo-fluorite) phases occurred. The cell edge of the f.c.c. phase was about 5.338 Å.

Between 39.8 and 84.8 mole % zirconia a range of f.c.c. solid solutions existed with cell edges which decreased continuously from 5.338 to 5.165 Å. However, some evidence was obtained for the existence of ordered structures as reported for the europia-hafnia system (I. P. Ferguson and Miss L. Hammonds).

At 89.2 and 90.6 mole % zirconia both the f.c.c. and a phase based on tetragonal zirconia, with \( a = 5.088 \pm 0.004 \) Å, \( c = 5.1836 \pm 0.006 \) Å, were present. However, at 93.6 mole % zirconia the only phases present were indistinguishable from tetragonal and monoclinic zirconia.

Results obtained on samples heated to 1550°C were essentially the same as those reported above except that there seemed to be a greater tendency for the formation of ordered f.c.c. structures based upon the fluorite lattice. This ordering was evidenced by the same value occurring in samples which differed in composition by 5 or even 15 mole %. In addition some samples heated at 1550°C displayed faint additional diffraction lines which indicated contamination of the f.c.c. phases by one of two phases characterised by d spacings of 6.1, 2.39, 2.00 and 1.76 Å as well as 3.75, 2.02, 2.14, 1.85 and 1.65 Å. Time did not allow a full investigation to be made of these 'contaminants' but they were not the BiI and BiII phases reported by Kiparisov et al. (8, 8, Kiparisov et al. (1976) Izvestiya Akad. Nauk SSSR, Neorganicheskii Materialy, 12 (3) 1653-1654).