

08.2-16 NOVEL PCP SALTS CONTAINING TETRACHLOROMETAL-LATE(II) ANIONS: DICHLOROTETRAKIS[1-(1-PHENYLCYCLO-HEXYL)PIPERIDINIUM]TETRACHLOROCUPRATE(II) AND TETRACHLORONICKELATE(II). By Harold C. Nelson and Stanley H. Simonsen, Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

The structural investigations of these salts were carried out because of our interest in the geometry and environment of the tetrachlorocuprate(II) anion, the unusual composition of the salts, and the magnetic behavior of the copper salt. The copper and nickel salts are isomorphous, crystallizing in the tetragonal space group $P4_2/c$. The unit cell parameters of the copper and nickel salts are, respectively: $a = b = 15.840(3)$, $c = 13.006(2)$ Å, and $a = b = 15.740(3)$, $c = 13.179(3)$ Å. The metal atoms are on the $\bar{4}$ axis with a flattened, tetrahedral arrangement of chlorine atoms around them. Cu-Cl = 2.58(1) Å and Ni-Cl = 2.264(1) Å. There are four Cl-Cu-Cl angles of 99.3(1)° and two of 132.6(1)°. This is consistent with the solid state $d-d$ electronic absorption maximum at 8,820 cm^{-1} (R. L. Harlow, W. J. Wells, III, G. W. Watt & S. H. Simonsen, 1975, *Id*, 1768). The nickel salt subtends four angles of 103.4(1)° and two angles of 122.4(1)°. This represents, to our knowledge, the most severe flattening of the tetrachloronickelate(II) anion to date (tetramethylammoniumtetrachloronickelate(II), 112.8°, J. R. Wiesner, R. C. Srivastava, C. H. L. Kennard, M. DiVaira & E. C. Lingafelter, *Acta Cryst.* 1967, *23*, 565; tetraethylammoniumtetrachloronickelate(II), 110.81(7)°, *Acta Cryst.* 1967, *23*, 1064; bis(triphenylmethylarsonium)tetrachloronickelate, 109.5°, P. Pauling, *Inorg. Chem.* 1966, *5*, 1498).

The ionic chlorides are situated on a 2-fold axis and are hydrogen bonded to the PCP cation. In the copper salt the N---Cl distance is 3.18(4) Å. No interactions short enough to be considered as hydrogen bonds are observed between the tetrachlorocuprate(II) anion and the HN of the PCP cation.

The variable temperature bulk magnetic susceptibility data (300-4°K) of the copper salt conform to the Curie-Weiss Law ($r = 0.999$), $\chi = C/(T - \theta)$, with $C = 1.8197$ cgs units and $\theta = +3.914$ °K. The effective magnetic moment increases from 2.142 BM at room temperature to 3.214 BM at 4°K. This increase, together with the positive Weiss constant, suggests a significant degree of ferromagnetic interaction, which could be ascribed to through-space coupling of electronic spins. The solid state EPR signal is isotropic at room temperature, $g_{\text{iso}} = 2.163$ ($g_z = 2.363$ and $g_{xy} = 2.068$ at 77° K).

The authors thank the Robert A. Welch Foundation, Houston, Texas, for financial support, and Professor W. A. Baker and Dr. R. C. Dickinson (University of Texas at Arlington) for the susceptibility measurements. We also thank Ann F. Hoffschwelle, Welch Undergraduate Fellow for collecting and processing the data of the nickel salt.

08.2-17 $\text{K}_2\text{Ni}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$, $\text{CsNi}(\text{CN})_4$, $\text{Cs}_2\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$, AND $\text{SrNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$; PSEUDO-HEXAGONAL ISOTYPES. By S.F. Watkins and T.J. Delord, Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803 USA

Many alkali metal/alkaline earth tetracyanonickelates have been poorly characterized due to unrecognized twinning problems and/or variability of hydration. The crystal structures of some new compounds have been determined, and some previously studied structures have been redetermined: $\text{K}_2\text{Ni}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ crystallizes as (100) mirror twins, space group $I2/c$, $a=15.446(3)$, $b=7.932(1)$, $c=18.593(5)$ Å, $\beta=107.32(2)^\circ$ (partial resolution structure); $\text{CsNi}(\text{CN})_4$, reassigned to $I2/c$, $a=7.421(2)$, $b=13.969(5)$, $c=8.604(4)$ Å, $\beta=101.84(3)^\circ$, $R=0.0488$ with atoms shifting from previously reported values (*Inorg. Chem.* (1980). 19, 3400) less than 2σ ; $\text{Cs}_2\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$, $P6_1$ or $P6_5$, $a=9.556(1)$, $c=19.293(3)$ Å, $R=0.0257$ with hydrogens; $\text{SrNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ (Brasseur & Rassenfosse, *Bull. Soc. Roy. Sci. Liège* (1943). 522), $C2/m$, $a=10.358(1)$, $b=15.322(1)$, $c=7.251(1)$ Å, $\beta=98.67(1)^\circ$, $R=0.0192$ with hydrogens. These, and other well characterized tetracyanonickelate structures, deviate by varying amounts from a hexagonal archetype: square planar anions stack in columns, the columns pack in a hexagonal or quasi-hexagonal array, and the columnar interstices contain cations and variable amounts of H_2O . The anion column is characterized by the number of Ni atoms in the repeat unit (1, 2, or 6), the Ni-Ni distance(s), the nature of the column (straight, zigzag, spiral), and the relative tilt/twist angles of the anion planes. These structural features may be correlated with cation size, water content, and spectroscopic properties.

08.2-18 CRYSTAL CHEMISTRY OF SOME SELENO-CYANATE COPPER(I)-COPPER(II) COMPLEXES. By V. Vrabel and J. Garaš, Department of Analytical Chemistry, Slovak Technical University, Bratislava, Czechoslovakia.

From the system Cu^{2+} -ethylenediamine(en)- $\text{SeCN}^- \cdot \text{H}_2\text{O}$ several new cuprous-cupric and cupric crystal compounds have been prepared. The crystal structures of three complexes were determined: $\text{Cu}_5\text{en}_2(\text{SeCN})_2(\text{CN})_2 \cdot \text{H}_2\text{O}$ (I), $\text{Cu}_3\text{en}_2(\text{SeCN})(\text{CN})_3 \cdot \text{H}_2\text{O}$ (II) and $[\text{Cuen}_2(\text{NO}_3)]\text{SeCN}$ (III) (Vrabel, *Acta Cryst.* (1979) *B35*, 357).

The structures of compounds (I) and (II) consist of polymeric $[\text{Cu}_2(\text{SeCN})_2(\text{CN})_2]_{\infty}^{2-}$ and $[\text{Cu}_2(\text{SeCN})(\text{CN})_3]_{\infty}^{2-}$ anions composed of a three-dimensional array of copper(I) ions linked tetrahedrally by SeCN and CN groups to form a cage-like array. The holes in this array are occupied by discrete $[\text{Cuen}_2 \cdot \text{H}_2\text{O}]^{2+}$ cations. The structure of compound (III) consists of infinite cation chains $[\text{Cuen}_2(\text{NO}_3)]_{\infty}^{+}$ where the NO_3 group forms a bridging unit between two $[\text{Cuen}_2]^{2+}$ cations.

X-ray analysis results of selenocyanate complexes have shown that SeCN group is bonded to the Cu(II) atom monodentately by N or Se atoms (Pajunen, *Suom. Kemistilehti* (1973) *E46*, 139; Kivekas, *Finn. Chem. Lett.* (1978)

71), in the compounds (I) and (II) as a bridge, linking Cu(I) atoms. In the complex (III) 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-CSe 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 $C_2NO...N(en)$ and $SeCN...N(en)$ suggest the presence of hydrogen bonds.

08.2-19 THE DISTRIBUTION OF Cu ATOMS IN THE STRUCTURE OF Cu_8BiS_5 . By M. Ohmura, N. Yamada, Institute of Materials Science, University of Tsukuba, Sakura, Ibaraki, Japan, and K. Tameoka, Department of Geology, Arizona State University, Tempe, Arizona, U.S.A.

In the chemical studies of mixtures of Cu_2S and Bi_2S_3 , a new compound with a ratio Cu:Bi:S=8:1:5 has been synthesized. The material was examined by X-ray diffraction. The hexagonal cell $a = 23.61 \text{ \AA}$, $c = 13.323 \text{ \AA}$, $P6_322$, contains $12 Cu_{19}Bi_{2.5}S_{12}$. Since the reflections corresponding to $h = 6n$, $k = 6n$, and $l = 2n$ (n is any integer) are stronger than the rest, the structure can be regarded as a modulated structure of the smaller cell: $a' = 3.94 \text{ \AA}$, $c' = 6.66 \text{ \AA}$, $P6_3/mmc$. The structure analysis of the latter (the subcell) revealed that the arrangement of the S and Cu atoms is similar to that in $\beta-Cu_2S$ (Sadanaga et al., Min. Jour. (1965) 4, 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 Eu_2O_3 - ZrO_2 BINARY SYSTEM. By I. F. Ferguson and A. Williams, Springfields Nuclear Power Development Laboratories, United Kingdom Atomic Energy Authority (Northern Division), Preston, PR4 ORR, United Kingdom

An investigation of the europia-zirconia binary system has been made to parallel one already reported for the europia-hafnia system (I. F. Ferguson and (Miss) L. Hammonds (1978) Acta Cryst. A34, S154-S155).

Mixed oxides were prepared as follows. The mixed 'hydroxides' were precipitated by the addition of excess ammonium hydroxide to mixed aqueous solutions containing 0.05 g/ml made up from Specpure zirconyl chloride octahydrate dissolved in dilute hydrochloric acid and Specpure europia dissolved in concentrated Analar 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 XDC focussing camera set for pure $CuK\alpha_1$ 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 FIRESTAR (G. Astle and I. F. Ferguson (1970) UKAEA Report TRG 1812). 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 about 5 mole % zirconia when its cube cell edge, a , decreased to 10.834 \AA . Between 9.6 and 39.8 mole % zirconia a two phase region containing b.c.c. and f.c.c. (pseudofluorite) phases occurred. The cell edge of the f.c.c. phase was about 5.338 \AA .

Between 39.8 and 84.8 mole % zirconia a range of f.c.c. solid solutions existed with cell edges which decreased continuously from 5.331 to 5.165 \AA . However, some evidence was obtained for the existence of ordered structures as reported for the europia-hafnia system (I. F. Ferguson and (Miss) L. Hammonds).

At 89.2 and 90.6 mole % zirconia both the f.c.c. phase and a phase based on tetragonal zirconia, with $a = 5.088 \pm 0.004 \text{ \AA}$, $c = 5.1836 \pm 0.006 \text{ \AA}$, 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 a 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 \AA as well as 3.73 , 2.62 , 2.14 , 1.85 and 1.65 \AA . Time did not allow a full investigation to be made of these 'contaminants' but they were not the H1 and H2 phases reported by Kiparisov et al (S. S. Kiparisov et al (1976) Izvestiya Akad. Nauk SSSR, Neorganicheskie Materialy, 12 (9) 1693-1694).