

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).

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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: $\text{Cu}_2\text{en}_2(\text{SeCN})_2(\text{CN})_2 \cdot \text{H}_2\text{O}$ (I), $\text{Cu}_2\text{en}_2(\text{SeCN})(\text{CN})_3 \cdot \text{H}_2\text{O}$ (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)