results and to Miss R. Juurik for the chemical analyses. This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by Army Research Missile Command, Redstone Arsenal, Huntsville, Ala., under Contract No. DA-30-069-ORD-2638.

Correspondence

The Isolation of Pentacyanonickelate(II) Salts

Sir:

Extensive and repeated investigations[1] have been made on the aqueous solution chemistry of the system Ni(II)–CN$^-$, and it now appears certain that the intense orange-red color of such solutions containing excess CN$^-$ is due to the species $Ni(CN)_5^{3-}$. However, it had not been possible to isolate compounds of this anion. For example, the statement is made,[1] "... no Ni(II) cyanides have been isolated containing more than four CN$^-$ per Ni(II); $K_2Ni(CN)_4$ is obtained from Ni(II) solutions saturated with KCN, even though the principal species in solution is $Ni(CN)_5^{3-}$." Assuming that this five-coordination persists in the solid state, we wish to report the isolation of salts of this anion. To the best of our knowledge this is the first time that a crystalline compound has been isolated of a five-coordinated Ni(II) complex containing only unidentate ligands.[2]

Before describing the rather simple syntheses of these salts, it may be worthwhile to mention the reasoning used to design these experiments. It is well recognized by coordination chemists that difficult-to-isolate complex ions can often be obtained by the use of large counterions. Almost always as a last resort, one can use $(C_6H_5)_4As^+$ and $(C_6H_5)_4B^-$ to isolate complex anions and cations, respectively. It is also known that greater success may be had if the large counterion one uses has a charge that is identical with that of the metal complex ion one wishes to isolate. For example, it is generally better to use PF_6^- to isolate monovalent complexes and SiF_6^{2-} to isolate divalent complexes. Dwyer[3] and his students have had considerable success using this simple approach for the resolution of optically active metal complexes. One can make the following empirical generalization: *metal complex ions that are difficult to isolate can often be isolated as salts of large ions having the same but opposite charge.*

Our first attempts to isolate salts of $Ni(CN)_5^{3-}$ were made using $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$, but these attempts failed. One of the difficulties was that in *ca.* 4 *M* CN$^-$ the Co(III) ammines react with the replacement of ammine by CN$^-$. From previous studies[4] on the mechanisms of reactions of Co(III) complexes, it appeared that this reactivity was due to the presence of catalytic amounts of Co(II) and/or that the base hydrolyses of Co(III) are very rapid. In contrast to this, the corresponding Cr(III) complexes were expected to be stable under these conditions because of the unfavorable potential for the formation of Cr(II) and because Cr(III) ammines are less susceptible to base hydrolysis.[5] This was borne out by an examination of the visible absorption spectrum of a solution of $[Cr(NH_3)_6]^{3+}$ in *ca.* 4 *M* CN$^-$, which does not change at room temperature over a period of 6 hr.

The compound $[Cr(NH_3)_6][Ni(CN)_5]\cdot 2H_2O$ was prepared five times, and the compound $[Cr(en)_3][Ni(CN)_5]\cdot 2H_2O$ was prepared three times. In each case the product obtained analyzed correctly for the dihydrate salt, and in each case it was possible to remove both molecules of water at room temperature under high vacuum over a period of 24 hr. Slight variations were made in all of these preparations, and the best results were obtained with $[Cr(en)_3]^{3+}$ because its salt is less soluble. Described here are optimum conditions for the isolation of the $[Cr(NH_3)_6]^{3+}$ compound.

To a solution containing 4.0 g of $K_2Ni(CN)_4\cdot H_2O$ and 15 g of KCN in 20 ml of water at room temperature was added 20 ml of a solution containing 4.0 g of $[Cr(NH_3)_6]Cl_3\cdot H_2O$. After stirring, the solution was placed in a refrigerator at *ca.* −5° and allowed to stand overnight. The orange-red crystals that separated were collected on a suction filter, and the mother liquor was carefully removed by suction, but the crystals were not washed. The air-dried product weighed 2.5 g (45% yield).

Anal. Calcd for $CrNiC_5H_{22}N_{11}O_2$: Cr, 13.73; Ni, 15.48; C, 15.84; H, 5.85; N, 40.64, O, 8.45. Found: Cr, 14.2; Ni, 15.1; C, 16.0; H, 5.80; N, 41.1; O, 8.1 (from weight loss assuming loss of H_2O). After the removal of the water of hydration, we have: *Anal.* Calcd for $CrNiC_5H_{18}N_{11}$: C, 17.51; H, 5.29. Found: C, 17.3; H, 5.1.

The infrared spectrum of solid $[Cr(NH_3)_6][Ni(CN)_5]$ in the C–N stretching region has three sharp absorption bands (2130 (m), 2100 (vs), and 2070 (s) cm^{-1}) which are in fair agreement with the bands (2123, 2103, and 2083 cm^{-1}) reported for the species in solution. The ultraviolet reflectance spectrum of the solid also appears to show the disappearance of the absorption band at 308 mμ due to $Ni(CN)_4^{2-}$, but the results are

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(1) J. S. Coleman, H. Peterson, Jr., and R. A. Penneman, *Inorg. Chem.*, **4**, 135 (1965), and references therein.

(2) J. A. Ibers, *Ann. Rev. Phys. Chem.*, **16**, 375 (1965); E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), in press.

(3) F. P. Dwyer and F. L. Garvan, *Inorg. Syn.*, **6**, 192 (1960).

(4) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 124, 328.

(5) J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 826 (1964).

not very satisfactory because of the strong absorption of the complex cation in this region of interest, 300–350 mμ. The compound $[Cr(NH_3)_6][Ni(CN)_5]\cdot 2H_2O$ is orthorhombic with lattice parameters of 11.72 ± 0.05, 11.65 ± 0.05, and 22.69 ± 0.05 A. It has eight molecules per unit cell and for a molecular weight of 379.0 it has an estimated density of 1.625 g/cm^3. The experimental density by flotation in methylene dibromide–toluene mixtures is 1.60 ± 0.03. The structure of $Ni(CN)_5^{3-}$ is being determined by means of X-rays by K. N. R. working with Professor J. A. Ibers.

Having had this much success, it will be of interest to attempt the isolation of $Co(CN)_5^{3-}$ (as the monomer[6]) and $HCo(CN)_5^{3-}$, both of which are believed to be present in solution,[7] but neither one has been isolated as a crystalline solid salt. We will also attempt the isolation of salts of $Pd(CN)_5^{3-}$, of $Pt(CN)_5^{3-}$, and, with a different cation, of $Au(CN)_5^{2-}$. None of these species exists in quantity in solution,[1] but perhaps the proper counterion will cause these to precipitate and shift the equilibria toward their formation. Investigations of this type are in progress.

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[6] A. W. Adamson, *J. Am. Chem. Soc.*, **73**, 5710 (1951).

[7] J. Kwiatek, I. L. Mador, and J. K. Seyler, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 201.

Book Review

Sauerstoff, System-Nummer 3, Lieferung 5, Gmelins Handbuch der anorganischen Chemie. [Oxygen, System Number 3, Section 5, Gmelins Handbook of Inorganic Chemistry.] Verlag Chemie, G.m.b.H., Weinheim/Bergstrasse. 1963. xviii + 548 pp. 17 × 25 cm. 104 Figures. In German. Clothbound $102.50.

Sauerstoff, System-Nummer 3, Lieferung 6, Gmelins Handbuch der anorganischen Chemie. [Oxygen, System Number 3, Section 6, Gmelins Handbook of Inorganic Chemistry.] Verlag Chemie, G.m.b.H., Weinheim/Bergstrasse. 1963. 363 pp. 17 × 25 cm. In German. Clothbound $69.50.

These two volumes are the fifth and sixth to appear dealing with oxygen, and essentially all of the two volumes is devoted to water. The literature coverage is complete through 1949, but one finds references to numerous papers published as late as 1963.

A significant fraction (324 pages) of Volume 5 is devoted to physical properties of water, but chemical properties are also covered in this volume. There are chapters on "Chemical Behavior of Water," "Behavior of Water as a Solvent," and "Behavior of Water on Irradiation."

Most of Volume 6 is devoted to "Isotopic Kinds of Water." This volume also contains chapters on "Water Ions" (including recent references pertaining to $H_9O_4^+$), "Electrochemical Behavior of Water," and "Systems of Water with Organic Solvents."

A short review cannot describe the many topics covered in these volumes, the high quality of which support the solid reputation of Gmelins Handbook.

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MIHALY T. BECK, Editor. "Proceedings of the Symposium on Coordination Chemistry." (Tihany, Hungary, 1964.) Akademiai Kiado Publishing House, Budapest, Hungary. 1965. 11 + 484 pp. $15.00.

R. COLTON. "The Chemistry of Rhenium and Technetium." John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1966. v + 185 pp. $8.50.

P. G. DE GENNES. "Super-Conductivity of Metals and Alloys." W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1966. ix + 274 pp. $12.50.

GEORGE I. SACKHEIM. "Atomic and Molecular Orbitals." Stipes Publishing Co., 10–12 Chester St., Champaign, Ill. 1965. 65 pp. $1.40 (paperback).

P. A. S. SMITH. "Open-Chain Nitrogen Compounds." W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1966. vii + 531 pp. $35.00.

WESLEY W. WENDLANDT and HARRY G. HECHT. "Reflectance Spectroscopy." John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1966. v + 298 pp. $12.00.