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LETTERS TO THE EDITOR

Application of Acetone Cyanohydrin in the Synthesis of Cyanide Complexes of Transition Metals

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In the work [1] we have described the triad complexes $[(CO)_2ClRh(NC)RuPy_4(CN)RhCl(CO)_2]$, $[(Cod)ClRh(NC)RuPy_4(CN)RhCl(Cod)]$, and $[(Cod)\cdot ClRh(NC)RuPy_4(CN)RhCl(CO)_2]$ with ruthenium(II) complex *trans*-$[RuPy_4(CN)_2]$ (**I**) (Py is pyridine) as a central unit [2]. The desire to avoid inconveniences caused by the use of high-toxic KCN has resulted in our attempt to apply acetone cyanohydrin, $(CH_3)_2C\cdot(OH)(CN)$, as a source of cyanide ions in the synthesis of complex **I**. Testing this reagent in the cyanide process of gold oxidative dissolution has given encouraging results in due time [3]. We have obtained complex **I** with a satisfactory yield in experiments with application of a water–alkaline solution of acetone cyanohydrin instead of potassium cyanide.

$$[RuPy_4Cl_2] + 2(CH_3)_2C(OH)(CN) + 2KOH$$
$$\rightarrow [RuPy_4(CN)_2] + 2(CH_3)_2CO + 2KCl + 2H_2O.$$

We are inclined to assume that such modification of the procedure of synthesizing cyanide complexes of transition metals can appear sufficiently general. Our results on the synthesis of tetracyanide complexes of nickel subgroup metals support this assumption.

We adhered to procedures given in the manuals [4] (nickel and palladium) and [5] (platinum), replacing potassium and sodium cyanides by an alkaline acetone cyanohydrin solution. Nickel hydroxide readily reacts with acetone cyanohydrin aqueous solution under heterogeneous conditions to form the cyanide $Ni(CN)_2$ without adding alkaline reagents.

$$Ni(OH)_2 + 2(CH_3)_2C(OH)(CN)$$
$$\rightarrow Ni(CN)_2 + 2(CH_3)_2CO + 2H_2O.$$

We can expect that other metal hydroxides are also capable of such reactions.

The stretching frequencies of cyanide groups and the chemical shifts of the cyanide carbon for all synthesized complexes agree well with the published data [6] and [7].

***trans*-$[Ru(Py)_4(CN)_2]\cdot 2H_2O$** was obtained according to the procedure [2] with the replacement of KCN by an alkaline solution of acetone cyanohydrin. A solution of acetone cyanohydrin (0.8 ml) and KOH (0.4 g) in water (25 ml) was added to a suspension of *trans*-$[Ru(Py)_4(Cl)_2]$ (1 g) in pyridine (80 ml). The reaction mixture was boiled for 15 min. The golden solution was evaporated to dryness under reduced pressure at room temperature. The reaction product was purified by the chromatographic method [2]. Yield 0.71 g (76%). IR spectrum, ν, cm^{-1}: (CN) 2056 ($CDHCl_3$), 2062 (mull in mineal oil). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 168.3 (CN), 157.1, 134.8, 124.2 (Py). Found, %: C 52.35; H 4.37; N 16.47. $C_{22}H_{24}N_6O_2Ru$. Calculated, %: C 52.27; H 4.79; N 16.62.

$K_2[Ni(CN)_4]\cdot 0.3H_2O$. *a*. Acetone cyanohydrin (0.8 ml) and a solution of KOH (0.45 g) in water (2 ml) were added to a hot solution of $NiSO_4\cdot 7H_2O$ (1.0 g) in water (4 ml). A pale-blue precipitate of $Ni(CN)_2$ was formed. The precipitate was filtered off, washed with water, and dried in air. IR spectrum, ν, cm^{-1}: (CN) 2164. Resulting $Ni(CN)_2$ was added to an aqueous solution (2 ml) containing acetone cyanohydrin (0.8 ml) and KOH (0.45 g). The reaction mixture was heated with stirring to complete dissolution of the precipitate. The formed orange solution was evaporated on a water bath to appearance of orange-yellow crystals. After cooling to a room temperature the precipitate was filtered off, washed with alcohol and ether, and dried in vacuum. Yield 0.6 g (69%). IR spectrum, ν, cm^{-1}: (CN), 2126, 2120. ^{13}C NMR spectrum (D_2O), δ, ppm: 135.8 (CN). Found, %: C 19.52; N 22.73. $C_4H_{0.6}K_2N_4NiO_{0.3}$. Calculated, %: C 19.50; N 22.74.

b. Water (3 ml) and acetone cyanohydrin (1.55 ml) were added to a weighted sample of $Ni(OH)_2$ (0.39 g). The reaction mixture was stirred at 70°C over 1 h. The color of the precipitate gradually changed from light green to pale blue as a result of $Ni(CN)_2$ formation. On addition of 2 ml of KOH (0.47 g) aqueous solution, the precipitate instantaneously dissolved to form an orange solution. The solution was evaporated on a water bath to the appearance of orange-yellow crystals. After cooling to a room temperature the precipitate was filtered off, washed with alcohol and ether, and dried in vacuum. Yield 0.89 g (88%). In spectral characteristics the reaction product coincides with the sample obtained in experiment *a*.

$K_2[Pd(CN)_4]\cdot H_2O$. A weighted sample of $PdCl_2$ (0.5 g) was dissolved in water (35 ml) acidified by hydrochloric acid (2 drops) with heating (~60°C) and stirring. Acetone cyanohydrin (0.5 ml) and a solution of KOH (0.32 g) in water (10 ml) were added to the hot solution. The solution became colorless. A yellow precipitate of $Pd(CN)_2$ was formed. The precipitate was filtered off, washed with water, transferred into a beaker, and a solution containing acetone cyanohydrin (0.55 ml) and KOH (0.35 g) in water (15 ml) was added. A dominating part of the precipitate was dissolved upon heating and stirring the reaction mixture. The solution was filtered and evaporated to a minimum volume. On cooling a colorless crystalline precipitate was formed, which was filtered off and dried in a desiccator above sulfuric acid. Yield 0.65 g (76%). IR spectrum, ν, cm^{-1}: (CN), 2142, 2130. ^{13}C NMR spectrum (D_2O), δ, ppm: 131.51 (CN). Found, %: C 15.58; N 18.22. $C_4H_2K_2N_4OPd$. Calculated, %: C 15.66; N 18.27.

$K_2[Pt(CN)_4]\cdot H_2O$. A solution of KOH (0.56 g) and acetone cyanohydrin (0.9 ml) in water (3 ml) was added to a suspension of $K_2[PtCl_4]$ (0.84 g) in water (2 ml). On heating (70°C) a transparent orange solution was formed, which became colorless during further heating. The solution was evaporated on a water bath and cooled in a refrigerator. After 4 h colorless needle-like crystals possessing a characteristic pleochroism were filtered off, washed with a small amount of ice water, and dried in a desiccator above sulfuric acid. Yield 0.7 g (88%). IR spectrum, ν, cm^{-1}: (CN) 2136, 2124. ^{13}C NMR spectrum (D_2O), δ, ppm: 125 [CN, ^1J(CPt) 1030 Hz]. Found, %: C 12.27; N 13.98. $C_4H_2K_2N_4OPt$. Calculated, %: C 12.15; N 14.17.

The IR spectra of samples in mulls in mineral oil suspensions were measured on a Specord-75IR spectrometer. The ^{13}C NMR spectra were measured on a DPX-300 spectrometer with working frequency of 75 MHz. Chemical shifts (δ scale) were measured in relation to internal references [$CDCl_3$, δ(^{13}C) 77.0 ppm; $(CH_3)_2CO$, δ(^{13}C) 30.9 ppm].

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REFERENCES

1. Varshavsky, Yu.S., Cherkasova, T.G., Galding, M.R., Khrustalev, V.N., Podkorytov, I.S., Gindin, V.A., Smirnov, S.N., and Nikol'skii, A.B., *J. Organomet. Chem.*, 2009, vol. 694, p. 2917.
2. Coe, B.J., Meyer, T.J., and White, P.S., *Inorg. Chem.*, 1995, vol. 34, pp. 593, 3600.
3. Lebedev, A.N. and Kakovskii, I.A., *Tsvet. Metall.*, 1965, no. 7, p. 17.
4. *Neorganicheskie sintezy* (Inorganic Syntheses), Ryabchikov, D.I., Ed., Moscow: Inostrannaya Literatura, 1951, pp. 220, 237.
5. *Handbuch der Praparativen Anorganischen Chemie*, Brauer, G., Ed., Stuttgart: Ferdinand Enke Verlag, 1980, vol. 5.
6. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 2009, part B, p. 110.
7. Monlien, F.J., Helm, L., Abou-Hamdan, A., and Merbach, A.E., *Inorg. Chem.*, 2002, vol. 41, p. 1717.