# Potassium cobaltinitrite

**Article** *in* Russian Journal of Inorganic Chemistry · April 2011

DOI: 10.1134/S0036023611040267

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*ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2011, Vol. 56, No. 4, pp. 501–505. © Pleiades Publishing, Ltd., 2011.*
*Original Russian Text © A.G. Vendilo, N.E. Kovaleva, V.I. Chistov, V.M. Retivov, 2011, published in Zhurnal Neorganicheskoi Khimii, 2011, Vol. 56, No. 4, pp. 541–545.*

## SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

# Potassium Cobaltinitrite

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Received Septemper 20, 2010

**Abstract**—Potassium cobaltinitrite $K_3[Co(NO_2)_6]$ has been synthesized by three methods. The crystalline products have been characterized by scanning electron microscopy, X-ray powder diffraction, IR spectroscopy, and thermal and sedimentation analyses. A comparative analysis of the synthetic methods has been carried out. The highest yield, the smallest particle size, and the highest purity of the product are attained by reacting potassium nitrite with cobalt nitrate in an acid medium in the same way as in the synthesis of sodium cobaltinitrite: $2CH_3COOH + Co(NO_3)_2 + 7KNO_2 \longrightarrow K_3[Co(NO_2)_6]\downarrow + 2KNO_3 + 2CH_3COOK + NO\uparrow + H_2O$. All of the resulting potassium cobaltinitrite samples are hygroscopic. The water release and nitrite ion elimination temperature intervals have been determined.

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Sodium cobaltinitrite $Na_3[Co(NO_2)_6]$ has been known since 1885, and its properties and structure have been characterized properly [1]. This compound has found wide application in analytical chemistry, including organic analysis and the gravimetric determination of potassium and cobalt [1–4]. It is also used in nitration [1, 5] and catalysis [6]. It is widely manufactured as a reagent-grade chemical.

Potassium cobaltinitrite $K_3[Co(NO_2)_6]$ (potassium hexanitritocobaltate(III), Fischer's salt), as distinct from its sodium analogue $Na_3[Co(NO_2)_6]$, is little known, is poorly soluble in water, and has not been commercialized as a reagent. It is among the few poorly soluble potassium salts and is used as a component of smokeless powder [7], a component of curing compositions [8], and a dye [9]. State contract no. 02.740.11.0146 of June 15, 2009 [10] puts $K_3[Co(NO_2)_6]$ on the list of chemicals to be commercialized.

Potassium cobaltinitrite $K_3[Co(NO_2)_6]$ is a yellow crystalline solid poorly soluble in ethanol, diethyl ether, and acetic acid. Owing to the low water solubility of potassium cobaltinitrite, the hexanitritocobaltate ion is widely used in analytical chemistry for determination and gravimetric quantification of the potassium ion in solution. At 17°C, 1 g of potassium cobaltinitrite dissolves in 1120 g of water.

Potassium cobaltinitrite dissolves in strong mineral acids to yield nitrous acid ($HNO_2$), a very unstable substance, which decomposes readily, reducing the cobalt cation $Co^{3+}$ to $Co^{2+}$ [9]:

$$K_3[Co(NO_2)_6] + 6H^+ \longrightarrow 6HNO_2 + Co^{3+} + 3K^+,$$

$$2Co^{3+} + HNO_2 + H_2O \longrightarrow 2Co^{2+} + NO_3^- + 3H^+.$$

In an alkaline medium (pH >7), potassium cobaltinitrite decomposes totally, releasing dark brown cobalt hydroxide [11]:

$$K_3[Co(NO_2)_6] + 3NaOH \longrightarrow Co(OH)_3 + 3KNO_2 + 3NaNO_2.$$

Potassium cobaltinitrite formation is the key reaction in the most important method of determination of cobalt salts. In this method, the sample to be examined is placed in a solution consisting of potassium nitrite $KNO_2$, potassium chloride, and acetic acid (80–100%). If the sample contains cobalt chloride, heating this system will yield a yellow precipitate of potassium cobaltinitrite [11].

Note that, under the potassium determination conditions, the formation of almost insoluble potassium cobaltinitrite may be accompanied by the formation of mixed, potassium–sodium salts of the hexanitrocobaltate ion:

$$2KCl + Na_3[Co(NO_2)_6] \rightleftharpoons K_2Na[Co(NO_2)_6] + 2NaCl,$$

$$2K^+ + Na^+ + [Co(NO_2)_6]^{3-} \rightleftharpoons K_2Na[Co(NO_2)_6].$$

Although the $K_3[Co(NO_2)_6]$ complex has long been known and is widely referred to in the scientific literature [9, 11], it is still unclear what methods are optimal for the synthesis and isolation of this compound. For example, it was reported that the isolation of $K_3[Co(NO_2)_6]$ yields the monohydrate $K_3[Co(NO_2)_6] \cdot H_2O$ along with the desired product [12], the complex

$[Co(NO_2)_6]^{3-}$ undergoes hydrolysis in aqueous solution at pH >7 [13], and the coordination polyhedron $[Co(NO_2)_6]$ isomerizes in aqueous solution in the presence of excess $NaNO_2$ so that part of the $NO_2^-$ ligands coordinate to the cobalt atom through the nitrogen atom rather than the oxygen atom [13]. There is no information concerning the size of, and the presence of impurities in, the resulting potassium cobaltinitrite crystals. Our patent search revealed no patent information on $K_3[Co(NO_2)_6]$ synthesis. For this reason, we undertook a comparative study of several potassium cobaltinitrite synthesis and isolation methods.

## EXPERIMENTAL

### *Potassium Cobaltinitrite Synthesis Methods*

In the synthesis of potassium cobaltinitrite, we relied on the methods used in the synthesis of sodium cobaltinitrite [14] and in the conversion of $Na_3[Co(NO_2)_6]$ into the potassium salt. Accordingly, we considered the following three synthetic procedures: exchange reaction

$$\begin{aligned} &Na_3[Co(NO_2)_6] + 3KNO_3 \\ &\rightarrow K_3[Co(NO_2)_6]\downarrow + 3NaNO_3, \end{aligned} \tag{1}$$

procedure similar to sodium cobaltinitrite synthesis from sodium nitrite and cobalt nitrate in an acid medium [14],

$$\begin{aligned} &2CH_3COOH + Co(NO_3)_2 + 7KNO_2 \\ &\rightarrow K_3[Co(NO_2)_6]\downarrow + 2KNO_3 \\ &+ 2CH_3COOK + NO\uparrow + H_2O, \end{aligned} \tag{2}$$

and the mixed procedure,

$$\begin{aligned} &4CH_3COOH + Co(NO_3)_2 + 9NaNO_2 + 4KNO_3 \\ &\rightarrow K_3[Co(NO_2)_6]\downarrow + 6NaNO_3 + NO_2 + 2NO\uparrow \\ &+ CH_3COOK + 3CH_3COONa + 2H_2O. \end{aligned} \tag{3}$$

**Procedure 1.** Sodium cobaltinitrite was dissolved in water at 55 ± 5°C and was combined with a 27 wt % potassium nitrite solution ($Na_3Co(NO_2)_6 : KNO_3 = 1 : 3$ mol/mol). The reaction was conducted under stirring at a rate of 400 ± 50 rpm. Copious precipitation of yellow crystals was observed. The precipitate was allowed to settle for 15–16 h. The resulting crystals were washed with distilled water four to eight times until pH ~4.5 (the mother liquor had pH ~4). Next, the solid was filtered and was dried in a Nabertherm L9/11/SKM drying oven at 90 ± 5°C for 32 h. Yield: 90%.

**Procedure 2.** A 22 wt % cobalt nitrate solution and a 27 wt % potassium nitrite solution were combined ($Co(NO_3)_2 : KNO_2 = 1 : 7$ mol/mol), and acetic acid was added ($Co(NO_3)_2 : CH_3COOH = 1 : 2$) at 70 ± 5°C under stirring. The mixture was stirred at a rate of 500 ± 50 rpm for 30 min. The reaction commenced before acetic acid was added, and the reaction mixture, initially brown, turned violet and then orange. The acidification of the mixture with 50 wt % acetic acid initiated the evolution of large amounts of nitrogen oxides, and the mixture turned orange quickly. As in procedure 1, the slurry was allowed to settle and the solid was washed with distilled water and was dried under the above-specified conditions. Yield: 97 %.

**Procedure 3.** The synthesis was carried out at 60 ± 5°C. Based on the corresponding chemical equations, the reactants were taken in the following stoichiometric ratios: $Co(NO_3)_2 : KNO_3 : NaNO_2 : CH_3COOH = 1 : 4 : 9 : 4$. A 25 wt % cobalt nitrate solution, a 22 wt % potassium nitrate solution, and a 40 wt % sodium nitrite were combined. The reaction mixture was stirred for 30–40 min at a rate of 500 ± 50 rpm and was then acidified with 50 wt % acetic acid. The addition of the acid was accompanied by the evolution of large amounts of nitrogen oxides, which were absorbed with a 20% alkali solution. After acetic acid was added over 5 min, the mixture changed its color from brownish red to yellow. This was evidence of a high reaction rate. The product was washed and dried in the same way as in procedures 1 and 2. Yield: 83%.

The products obtained via procedures 1–3 were characterized by elemental analysis, thermogravimetry, X-ray powder diffraction, sedimentation analysis, scanning electron microscopy, and IR spectroscopy. The most important characteristics of the products are presented in the table.

**Thermogravimetry.** Thermal analysis was carried out in air on a Q-1500 D thermoanalytical system (F. Paulik, J. Paulik, L. Erdey, MOM, Hungary). The sample size was 100–140 mg (weighing error of ±0.4 mg). The temperature was measured with a Pt/Pt–Rh thermocouple (PP-1) up to 600°C accurate to ±2°C. The heating rate was 5 K/min. Quartz crucibles were used.

**X-ray diffraction.** X-ray diffraction patterns were obtained on a DRON-4-13 automated diffractometer ($CuK_\alpha$ radiation, $2\theta = 5°–55°$ increments, counting time of 5 s per point). Phase analysis was carried out using the PDF2 database. Unit cell parameters were refined using the POWDER2 and QUANTO programs.

**IR spectroscopy.** IR spectra were recorded as mineral-oil mulls between NaCl plates on an Infralyum FT-02 Fourier-transform spectrometer (Lumeks) and as pellets between KBr glass plates on a PerkinElmer IR spectrometer.

**Sedimentation analysis.** The gravity sedimentation of powders in water was carried out via a standard procedure using a torsion balance. Three replica experiments were done for each powder to make sure that the measurements are reproducible. All measurements were taken at 25°C over 3 h. The dispersed phase concentration in the suspensions was 0.23 wt %. Immediately before measurements, the suspensions were ultrasonicated for particle disaggregation in an ultra-

Properties of potassium cobaltinitrite crystals synthesized via procedures 1–3

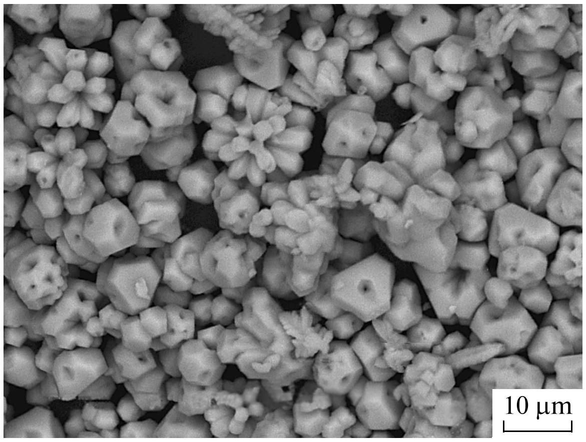
| Property | Potassium cobaltinitrite | | |
|---|---|---|---|
| | procedure 1 | procedure 2 | procedure 3 |
| Yield of the target product, % | 90 | 97 | 83 |
| Content, wt %: | | | |
| Co, found | 12.78 | 12.91 | 13.02 |
| calculated | 13.05 | 13.05 | 13.05 |
| N, found | 16.47 | 16.55 | 16.30 |
| calculated | 18.6 | 18.6 | 18.6 |
| Water content (thermogravimetric data), % | 1.73 | 1.97 | 1.46 |
| Na content, wt % | 0.10 | 0.08 | 0.40 |
| Crystal lattice (X-ray diffraction data) | Cubic cell, $a = 10.492(7)$ Å | Cubic cell, $a = 10.498(7)$ Å | Cubic cell, $a = 10.468(6)$ Å |
| Water release temperature interval, °C | 25–120<br>Loss of 1.73 wt % | 25–120<br>Loss of 1.97 wt % | 25–120<br>Loss of 1.46 wt % |
| Decomposition temperature interval, °C | 180–265 | 185–265 | 180–265 |
| Fundamental vibration frequencies, $cm^{-1}$ [20]: | | | |
| $\nu_{as}(NO_2)$ 1386 | 1389 | 1391 | 1384 |
| $\nu_s(NO_2)$ 1332 | 1332 | 1332 | 1331 |
| $\delta(ONO)$ 827 | 829 | 829 | 829 |
| $\rho_w(NO_2)$ 637 | 633 | 632 | 632 |
| $\nu(CoN)$ 416 | 410 | 412 | 408 |
| $P_r(NO_2)\alpha$ 293 | 295 | 297 | 302 |
| Crystal size (sedimentation data), μm: | | | |
| minimum | 0.8 | 2 | 5 |
| mean | 1.2 | 4 | 8 |
| maximum | 3 | 7 | 12 |
| Crystal size (electron microscopy data), μm: | | | |
| minimum | 0.5 | 1 | 4 |
| mean | 1.2 | 2.5 | 10 |
| maximum | 3 | 7 | 13 |

sonic bath operating at 25 kHz for 10 min. Particle size determination by gravity sedimentation means construction and analysis of a sedimentation curve, which is a plot of the sediment weight versus the sedimentation time. Cumulative and differential particle size distribution curves were derived from sedimentation curves using Tsurupa's analytical method [15]. In these calculations, we used the potassium cobaltinitrite density determined by the pycnometer method ($2.64 g/cm^3$).

**Elemental analysis.** Nitrogen was quantified on a Vario EL Cube CHNS analyzer with an accuracy of ~0.2%. Sodium was determined by ICP analysis on a Baird PS-3 spectrometer. The cobalt content was determined chelatometrically. The sample was dissolved in dilute nitric acid. The analysis was performed at pH 6 in the presence of xylenol orange.

**Electron microscopy.** Electron microscopic examinations were carried out on a JSM-5910LV (JEOL) scanning electron microscope. Microscopic data were processed manually by randomly selecting equal areas in different images and counting the particles of a given size in each image. A typical SEM image is shown in the figure.

The starting chemicals were glacial acetic acid (reagent grade), cobalt nitrate hexahydrate (pure



Electron micrograph of crystals obtained via procedure 3.

grade), potassium nitrite (pure grade), potassium nitrate (pure grade), and sodium nitrite (pure grade). The solvent was distilled water.

## RESULTS AND DISCUSSION

Elemental analysis demonstrated that all of the three samples have the composition $K_3[Co(NO_2)_6]$ and contain 1.5–2% water, which can be removed by heating the salt to 120°C. The presence of water in all samples is confirmed by weak absorption in the 3200–3700 $cm^{-1}$ range and by the elemental analysis data indicating the presence of approximately 0.5 wt % H.

It is noteworthy that the sample isolated from the solution containing an excess $NaNO_2$ concentration (procedure 3) contains 4 times more sodium ions than the two other samples. In this case, $Na_3[Co(NO_2)_6]$, $Na_2K[Co(NO_2)_6]$, or $NaK_2[Co(NO_2)_6]$ likely cocrystallizes with the target product, all of them having a cubic lattice and similar unit cell parameters [16–18]. The possibility of obtaining a mixed product is also indicated by a study of the successive substitution of potassium ions for sodium ions in an aqueous solution of $Na_3[Co(NO_2)_6]$ [19]. However, although X-ray and electron diffraction techniques and transmission electron microscopy were employed in that study, the individual phases were not identified. Again, this is likely due to the similarity of the unit cell parameters of these phases.

X-ray diffraction data indicate that all of the three products are single-phase. The X-ray diffraction patterns of $K_3[Co(NO_2)_6]$ are indexable on the basis of a cubic cell. The refined unit cell parameter is $a$ = 10.492(7) Å (sample obtained via procedure 1), $a$ = 10.498(7) Å (procedure 2), and $a$ = 10.468(6) Å (procedure 3). These data are in good agreement with X-ray crystallographic data [16, 18].

Our IR spectroscopic data confirm that the complex is an individual compound and check well with earlier spectroscopic data [19–21]. The thermoanalytical profiles of the samples are similar to one another and to those presented in the literature [22–25]. The decomposition of the $[Co(NO_2)_6]^{3-}$ anion commences at 180°C and is accompanied by a copious evolution of nitrogen dioxide gas.

Sedimentation analysis provided cumulative and differential particle size distribution curves. It was found that the synthesis via procedure 1 affords the finest powder with a mean particle size of 800 nm to 3 μm. Because the reaction takes place instantaneously, it produces abundant nuclei. Synthesis 2 yields a fine-powder product with a mean particle size of 2–7 μm. Synthesis 3 yields a coarser product with a mean particle size of 8–12 μm because the solid surface area is smaller and the product forms via nucleus growth. On the whole, the electron microscopic data confirm the sedimentation data.

Thus, procedure 2 affords the purest, fine-particle product in highest yield.

## ACKNOWLEDGMENTS

This study was carried out under state contract no. 02.740.11.0146 of June 15, 2009, “Synthesis of Potassium Cobaltinitrite with a Preset Composition and Particle Size.”

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