

## Emission Mössbauer Study of “Cobalt Peroxide”

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**Abstract**—The product of the reaction of cooled alcohol solutions of cobalt(II) chloride with hydrogen peroxide, described in the literature as  $\text{CoO}_2$ , was studied by emission Mössbauer spectroscopy. It was shown that the dark green product obtained was actually cobalt(III) oxide.

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A considerable number of cobalt complexes are known in which cobalt is bound by the coordination bond to the dioxygen group [1–3]. These compounds are mixed-ligand complexes with the coordination sphere containing, in addition to the dioxygen group, other ligands completing the coordination polyhedron of the central atom to an octahedron. Depending on the number of complex-forming atoms involved in bonding to the dioxygen ligand, mononuclear complexes [4] and binuclear complexes (in which the O–O group act as a bridge [5]) are distinguished. In both cases, depending on the redistribution of electron density between the transition metal and dioxygen group, compounds are described as peroxy or superoxy compounds of cobalt(III) (for mononuclear complexes) and (III, III) or (III, IV) (for binuclear complexes) [1]. The only dioxygen compound of cobalt(II) with a “simple” composition is so-called cobalt peroxide obtained by treating a cooled water–alcohol solution of cobalt chloride and hydrogen peroxides with a sodium hydroxide solution [6, 7]. This procedure was repeatedly reprinted in the classical handbook on preparatory techniques [8–11]. Based on the thermal decomposition data, the dark green crystalline compound was identified as cobalt peroxide  $\text{CoO}_2$  [6, 7]. Such a compound is rather extraordinary taking into account the high mobility and donor properties of electrons in the antibonding orbitals of the peroxide ion [12, 13], which should increase the electron density at the cobalt(II) atom [14]. At the same time, this compound can be formally considered as cobalt(IV) oxide [15], which does not contradict the formula reported in [6, 7].

The charge state of the cobalt atom can be unambiguously judged from emission Mössbauer spectroscopy data [16], which demonstrated that, in iron–oxygen compounds, there is a correlation between the isomer shift and the oxidation state of iron atoms that form

upon the decay of cobalt atoms and retain their oxidation state [17]. Therefore, this study deals with the determination of the charge state of cobalt in this compound by emission Mössbauer spectroscopy.

### EXPERIMENTAL

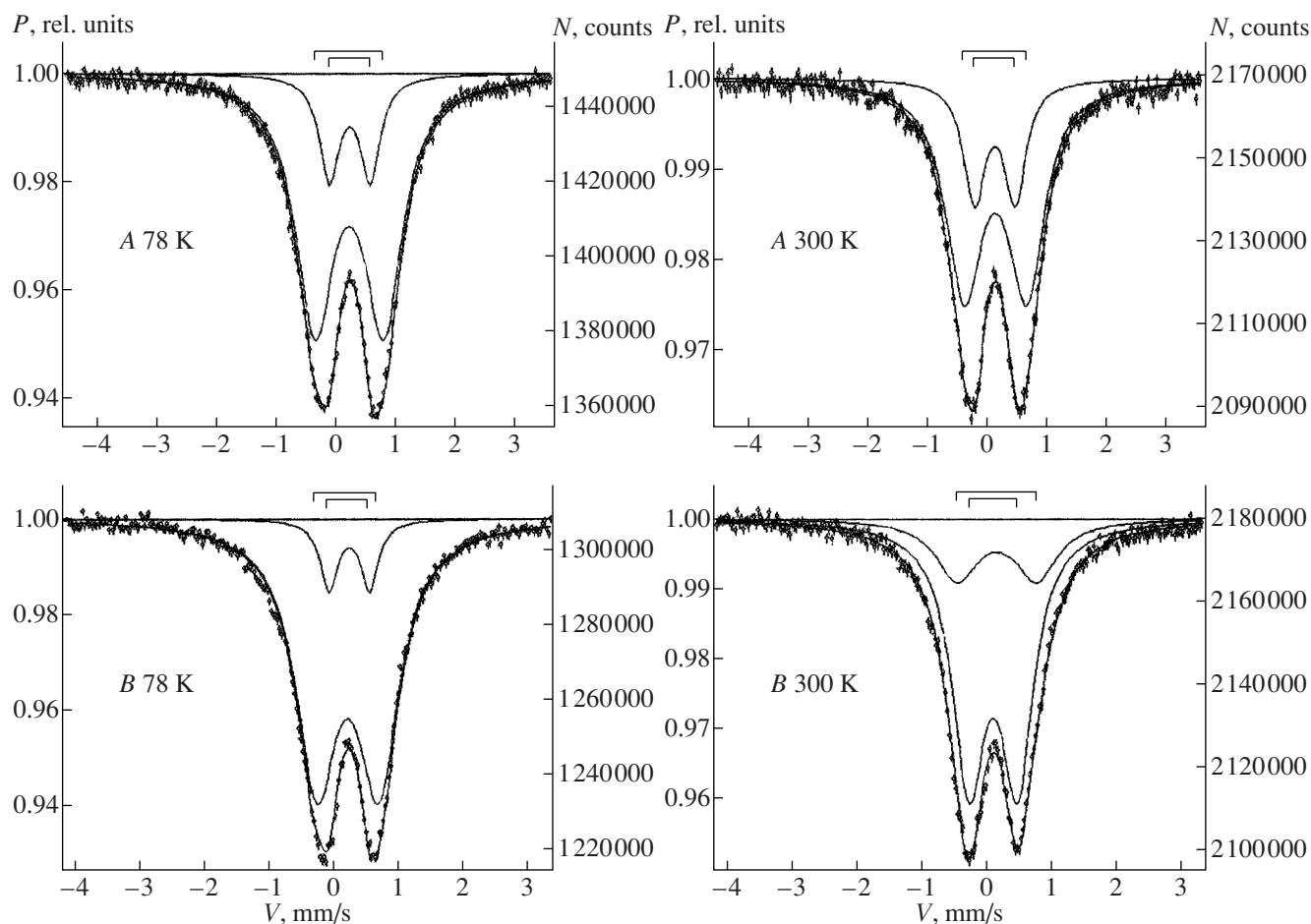
The compound was synthesized by a somewhat modified procedure described in [6–8]. To 20 mL of a 4%  $\text{CoCl}_2$  solution (containing  $^{57}\text{Co}$  in the amount corresponding to an activity of 1 mCi) in 96% alcohol cooled to  $-30$  to  $-35^\circ\text{C}$ , 10 mL of a 30% hydrogen peroxide was added. The resulting pink solution was cooled again, and 6 mL of 15%  $\text{Na}_2\text{CO}_3$  solution was added dropwise under vigorous stirring. The resulting dark green suspension was slowly heated avoiding rapid decomposition of hydrogen peroxide and, hence, a sharp increase in mixture temperature. After room temperature was achieved, the precipitate was separated from the mother liquor by centrifuging and successively washed with ethyl alcohol and acetone. The resulting dark green powder was finally dried in a vacuum desiccator over crystalline potassium hydroxide.

The compound obtained by the above procedure is stable at liquid nitrogen temperature at least for a month, whereas, at room temperature, the powder turns dark brown within 3–7 days.

All reagents used in the work were of pure for analysis or higher grade. An aqueous solution of cobalt(II) without a carrier in 0.1 M HCl was used as the cobalt-57 source. The reagents were cooled in a thermostat preliminarily cooled with aqueous ethylene glycol.

Emission Mössbauer spectra were recorded on an MS1101-E constant-acceleration spectrometer (MosTec, Rostov-on-Don) both at room temperature and liquid nitrogen temperature (with the use of a cryostat). The absorber (potassium ferrocyanide with a line width of 0.32 mm/s with the use of a standard  $^{57}\text{Co}/\text{Rh}$  source (Tsiklotron, Obninsk)) was at room temperature. The spectra were processed with the

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**Fig. 1.** Emission Mössbauer spectra of the same sample (A) immediately after preparation and (B) within 7 months after preparation and various temperatures.

Univem MS 4.02b software (Research Institute of Physics, Rostov-on-Don) by the least-squares method. The Mössbauer spectral parameters were referenced to  $\alpha$ -iron.

## RESULTS AND DISCUSSION

Preliminary studies showed that the procedure in [6–11] implying that the cooled alcohol mixture of hydrogen peroxide and cobalt chloride should be treated with a sodium hydroxide solution led to the formation of a black-brown rather than green precipitate, evidently, of cobalt(III) hydroxide [18]. The desired green precipitates were obtained only by treating the solutions with sodium carbonate.

It is likely that the reagent solutions used in [6, 7] were not protected from carbon dioxide, which formed upon the sublimation of artificial ice used as a refrigerant. Sodium hydroxide reacts with carbon dioxide to form sodium carbonate, which was responsible for the formation of a green precipitate described by the authors [6, 7] as cobalt peroxide. Therefore, we used a

sodium carbonate solution for precipitation since, only under these conditions the deposition of the green precipitate can be reproduced. The emission Mössbauer spectra of both freshly prepared samples (hereafter, sample A) and the samples stored for more than 7 months at room temperature (hereafter, sample B) differ only slightly from each other. Each of them represents a well-resolved doublet (Fig. 1). All spectra can be satisfactorily described as a superposition of two nested doublets (table). Taking into account that the isomer shifts of the doublets are close to each other and that only the quadrupole splittings and line widths are significantly different, we can assume that both sub-spectra correspond to the parent cobalt atoms in the same environment. The doublet with the small quadrupole splitting and line width corresponds to the atoms in a well-formed crystal lattice, whereas the subspectrum with the large quadrupole splitting and the larger line width corresponds to the amorphous part of the sample or to the atoms in the near-surface layer of crystallites. Taking into account nonequilibrium synthesis

## Parameters of emission Mössbauer spectra

Sample	Temperature, K	Doublet No.	Isomer shift $\delta$ , mm/s	Quadrupole splitting $\Delta$ , mm/s	Line width, $\Gamma_{\text{exp}}$ , mm/s	$S/S_0$ , %	$\chi^2$
A	78	1	$0.25 \pm 0.01$	$1.17 \pm 0.01$	$0.78 \pm 0.01$	$78 \pm 4$	1.6
		2	$0.26 \pm 0.01$	$0.68 \pm 0.01$	$0.41 \pm 0.01$	$21.8 \pm 0.9$	
	300	1	$0.14 \pm 0.01$	$1.04 \pm 0.20$	$0.74 \pm 0.04$	$75 \pm 4$	1.1
		2	$0.14 \pm 0.01$	$0.68 \pm 0.06$	$0.43 \pm 0.20$	$25 \pm 1$	
B model 1	78	1	$0.22 \pm 0.01$	$0.95 \pm 0.01$	$0.78 \pm 0.01$	$89 \pm 4$	2.3
		2	$0.25 \pm 0.01$	$0.62 \pm 0.01$	$0.32 \pm 0.01$	$11.0 \pm 0.4$	
	300	1	$0.17 \pm 0.01$	$1.22 \pm 0.04$	$0.77 \pm 0.04$	$23 \pm 6$	1.6
		2	$0.11 \pm 0.01$	$0.75 \pm 0.01$	$0.61 \pm 0.01$	$77 \pm 2$	
B model 2	300	1	$0.14 \pm 0.01$	$0.86 \pm 0.02$	$0.78 \pm 0.04$	$82 \pm 7$	1.4
		2	$0.14 \pm 0.01$	$0.63 \pm 0.01$	$0.37 \pm 0.05$	$15 \pm 3$	
		3	$-0.45 \pm 0.01$		$0.25 \pm 0.02$	$3.1 \pm 0.3$	

conditions, we may assume that the resulting compound has a high concentration of defects, which is confirmed by its X-ray diffraction analysis (only very weak broad lines are observed).

The isomer shift of the doublets at room temperature correspond to iron atoms (and, hence, to the parent cobalt atoms) in the oxidation state +3 in the tetrahedral oxygen environment [17]. Thus, the dark green substance prepared by the above procedure cannot be a cobalt(II) compound. Its peroxide nature is likewise improbable since only octahedral complexes are known for cobalt(III) peroxo compounds [1–3]. These conclusions are supported by the chemical analysis data for the products obtained by the above procedure, which demonstrated that these is one electron equivalent of the oxidant per cobalt(II) atom.

At first glance, the spectral parameters of the dark brown sample B differ slightly from those of the freshly prepared sample (table). The most clearly observed is the change in the quadrupole splitting, which corresponds to a higher symmetry of the central ion. Small changes in Mössbauer parameters are evidence of an insignificant change in the nearest environment of the cobalt atoms that accompanies the transformation of A to B (with a radical change in color) in the course of storage at room temperature.

On the other hand, in the spectrum recorded at 78 K, shoulders are clearly observed at the left wing of the doublet line. These shoulders are poorly described by the suggested model of two nested doublets (Fig. 1, B). In addition, these shoulders cannot be described by assuming the presence of the third doublet with a large

quadrupole splitting and isomer shift typical of iron(III) compounds. These shoulders can indicate the presence of resonance lines arising from iron atoms in higher (than +3) oxidation states. There is no way to reliably isolate these lines because of a low concentration of the corresponding atoms. In the spectrum of the same sample at room temperature, these lines are not observed, but their possible presence leads to an abrupt change in the proportion (reversal) between the areas of the doublets describing this spectrum and to a considerably difference between the corresponding isomer shifts (table, sample B, model 1).

If we assume that cobalt atoms have the same charge state and, by analogy with sample A, fix the isomer shifts of both doublets at 0.14 mm/s in simulation of room-temperature spectra, the spectrum can be most satisfactorily described by introducing a singlet with an area of about 3% (Fig. 2, table, model 2). The isomer shift of this singlet coincides with the corresponding value for an iron +5 compound [19] and, hence, corresponds to cobalt atoms in the oxidation state +5.

To explain the existence of this highly charged cobalt state, we can consider two hypotheses of radiation nature. On the one hand, the  $E$  capture by the  $^{57}\text{Co}$  nucleus, underlying the nuclear transformation of the latter, brings about a cascade of Auger processes resulting in ionization of cobalt atoms up to the charge +8 [20]. Further behavior of this highly charged ion is determined by its nearest environment and lifetime. If this metastable state persists longer than  $10^{-7}$  s, it can be detected by emission Mössbauer spectroscopy [21]. In this case, assuming that the cobalt atoms in samples A

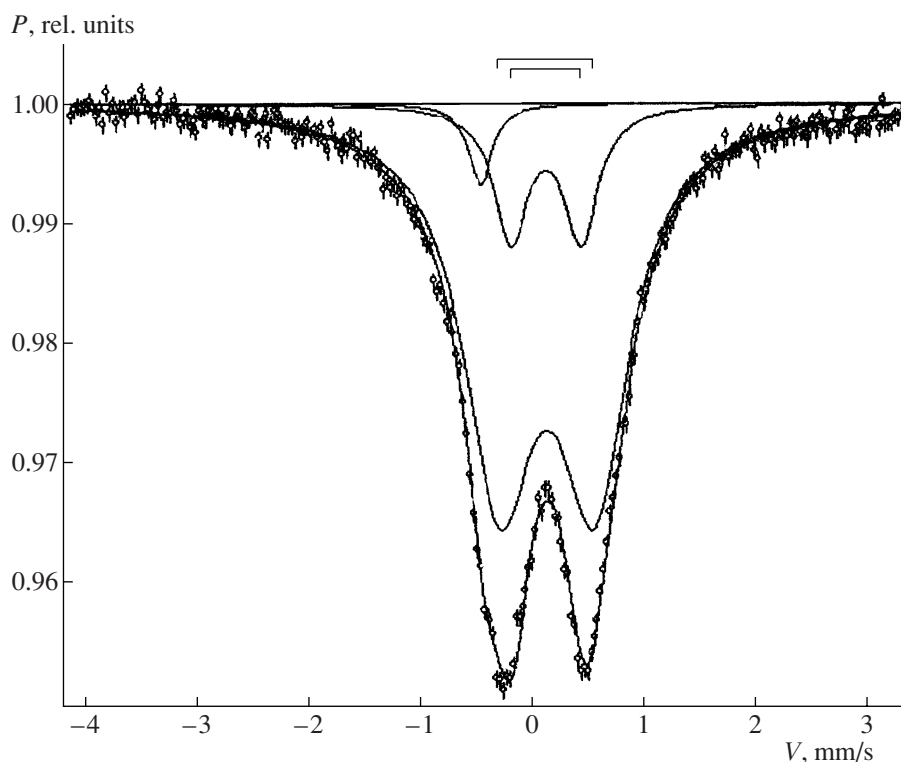


Fig. 2. Model 2 for the emission Mössbauer spectrum of sample B at 300 K.

and B have similar nature, the observed phenomenon should manifest itself in both samples. In addition, a short (if at all) lifetime of the ionized state should lead to a considerable broadening of the resonance line. On the other hand, the emergence of the narrow line only in the spectrum of sample B can be accounted for by the accumulation of radiation defects in the sample caused by radiolysis [22] followed by the electron density redistribution in the crystal and stabilization of a fraction of cobalt atoms in the oxidation state +5.

Thus, emission Mössbauer spectroscopy showed that the substance obtained by the procedure in [6–11] cannot be cobalt(II) peroxide; rather, it is a cobalt(III) compound (evidently, hydrated oxide).

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#### REFERENCES

- Connor, J.A. and Ebsworth, E.A.V., *Adv. Inorg. Chem. Radiochem.*, 1964, vol. 6, p. 279.
- Vaska, L., *Acc. Chem. Res.*, 1976, vol. 9, p. 175.
- Bratushko, Yu.I., *Koordinatsionnye soedineniya 3d-perekhodnykh metallov s molekulyarnym kislorodom* (Complexes of 3d Transition Metals with Molecular Oxygen), Kiev, 1987.
- Valentine, J.S., *Chem. Rev.*, 1973, vol. 73, p. 235.
- Lever, A.B.P. and Gray, H.B., *Acc. Chem. Res.*, 1978, vol. 11, p. 348.
- Shcherbinin, V.A. and Bogdanov, G.A., *Zh. Fiz. Khim.*, 1958, vol. 32, p. 2761.
- Shcherbinin, V.A. and Bogdanov, G.A., *Zh. Neorg. Khim.*, 1959, vol. 4, p. 260.
- Klyuchnikov, N.G., *Rukovodstvo po neorganicheskomu sintezu* (Handbook on Inorganic Synthesis), Moscow, 1965.
- Klyuchnikov, N.G., *Praktikum po neorganicheskomu snitezu* (Practical Work on Inorganic Synthesis), Moscow, 1979.
- Klyuchnikov, N.G., *Neorganicheskiy sintez* (Inorganic Synthesis), Moscow, 1988.
- Gorichev, I.G., Zaitsev, B.E., Kipriyanov, N.A., Klyuchnikov, N.G., and Gromov, D.N., *Rukovodstvo po neorganicheskomu sintezu* (Handbook on Inorganic Synthesis), Moscow, 1997.
- Pankratov, D.A., *Cand. Sci. (Chem.) Dissertation*, Moscow, 1998.
- Pankratov, D.A., Komozin, P.N., and Kiselev, Yu.M., *Abstracts of Papers, XXIII Mezhdunarodnaya Chugaevskaya konf. po koord. khimii, 2007, Odessa* (XXIII

- International Chugaev Conference on Coordination Chemistry, 2007, Odessa), Kiev, 2007, p. 564.
14. Pankratov, D.A., Prikhodchenko, P.V., Perfil'ev, Yu.D., and Ippolitov, E.G., *Izv. Akad. Nauk, Ser. Fizich.*, 2001, vol. 65, p. 1030.
  15. Simmons, G.W., Vertes, A., Varsanyi, M.L., and Leidheisen, U., *J. Electrochem. Soc.*, 1979, vol. 126, p. 187.
  16. Goldanskii, V.I. and Herber, R.H., *Chemical Application of Mossbauer Spectroscopy*, New York, 1968.
  17. Menil, F., *J. Phys. Chem. Solids*, 1985, vol. 46, p. 763.
  18. *Handbuch der präparativen anorganischen Chemie*, Brauer, G., Ed., Stuttgart, 1975. Translated under the title *Rukovodstvo po neorganicheskomu sintezu*, Moscow, 1975.
  19. Byuffa, B., Demazo, Zh., Pushar, M., Furnes, L., Dans, Zh.M., Fabrichnyi, P.B., and Khagenmyuller, P., *Fiz. Tverd. Tela*, 1981, vol. 23, p. 2262.
  20. Pollak, H., *Phys. Status Solidi*, 1962, vol. 2, p. 720.
  21. Fontcuberta, J., Fernandes, A., and Goodenough, J.B., *Phys. Rev. Lett.*, 1986, vol. 57, p. 1931.
  22. Seregin, P.P., Nasredinov, F.S., and Vasilev, L.N., *Phys. Status Solidi A*, 1978, vol. 45, p. 11.