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High-Energy-Capacity Cobalt(III) Tetrazolates

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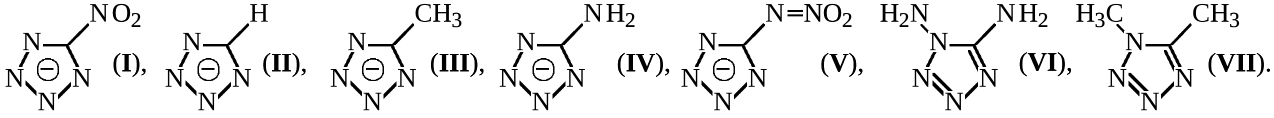
Abstract—Physicochemical and explosive properties of cobalt(III) tetrazolate perchlorate complexes were studied. The spectrophotometical properties of these complexes in the solid state and their sensitivity to laser radiation were examined.

Tetramminebis(5-nitrotetrazolato)cobalt(III) perchlorate **I** is used as an explosive in priming charges (PCs) initiated with a laser diode (λ = 800 nm, E_{beam} = 0.5 mJ) [1, 2]. Both **I** and its analogs are promising photosensitive compounds since they are safer than conventional primers used in laser detonators [3]. This study is concerned with a series of tetraminetetrazolato Co(III) perchlorates with the general formula

$$[\text{Co(NH}_3)_4(\text{Tz})_n](\text{ClO}_4)_m,$$

n = 2, m = 1 (**I–IV**); n = 1, m = 1 (**V**); n = 2, m = 3 (**VI, VII**);

Tz =


(**I**), (**II**), (**III**), (**IV**), (**V**), (**VI**), (**VII**).

Compounds **I**–**VII** were prepared by the reaction

$$[\text{Co(NH}_3)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_3 + n\text{Tz} \quad \textbf{VIII}$$

$$\xrightarrow[95^\circ\text{C, 4 h}]{\text{HClO}_4/\text{H}_2\text{O, pH} < 2,} [\text{Co(NH}_3)_4(\text{Tz})_n](\text{ClO}_4)_m + 2\text{H}_2\text{O}. \quad (1)$$

I–VII

The complexes are crystalline compounds soluble in water, DMSO, DMF and difficulty soluble in ethanol, isopropanol, and isobutanol. Their physicochemical and explosive characteristics are summarized in the table.

The densities of Co(III) tetramine complexes were calculated as sums of molecular increments of structural fragments with average error of ±0.04 g cm^{-3}. To determine the detonation rate of **I**–**VII**, their molecules were divided into active (perchlorate anion and the ligands) and inert (metal cation) parts. The detonation rate was calculated from these increments with average error of ±140 m s^{-1} [4].

Thermolysis of **I**–**VII** was studied under nonisothermal conditions at a heating rate of 5 deg min^{-1}. These compounds are relatively thermostable since their T_{oid} temperature is higher than 230°C. In the first stage of thermolysis of tetrazolatotetrammine cobalt(III) perchlorates, the inner coordination sphere of this complex degrades with elimination of ammonia. Then tetrazole ligands are thermally decomposed with their stepwise oxidation by outer-sphere perchlorate anions [5]. The thermal analysis curves of **I** and **VII** contain a broad exothermic peak corresponding to simultaneous occurrence of these steps. Clearly, in this case, the energy liberation is at a maximum and the energy loss, at a minimum. As a result, the combustion–detonation transition for **I** and **VII** is the fastest. For **II** and **IV**, the three thermolysis steps are separated in time. The total exothermic effect is lower owing not only to endothermic elimination of ammonia, but also to removal of the fuel from the reaction zone. A nonstoichiometric ratio of the fuel and oxidizing agent may result in

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Physicochemical and explosive characteristics of (tetramminetetrazolato)cobalt(III) perchlorates

Property	Compound						
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**
Density, ρ, g cm^{-3}	1.97*	1.86	1.75	1.81	1.90	1.85	1.90*
Detonation rate D^{ρ}, km s^{-1}	8.1	6.9	6.8	6.7	7.1	7.3	7.5
Onset temperature of intense decomposition T_{oid}, °C	234	239	252	242	238	233	234
Shock sensitivity H_{25}/cm, %**	8	64	–	14	10	32	8
Minimal priming charge (MIC), g	0.05	0.45	0.30	0.50	0.40	0.35	0.15

* Experimental values.

** Load 2 kg, sample weight 20 mg.

additional heat loss and longer combustion–detonation transition, which is actually the case (see table). In thermolysis of **III**, **V**, and **VI**, the pattern is intermediate between those observed with **I**, **VII** and **II**, **IV**.

The kinetic parameters of thermolysis of **I**–**VII** at T_{oid} were calculated from the T–TG, T–DTG, and T–DTA curves. The preexponential factor in the Arrhenius equation, activation energy (kJ mol^{-1}), and reaction order are 18.5, 212.2, 0.5; 18.8, 228.6, 0.5; 16.7, 204.7, 1.0; 26.3, 293.3, 0.5; 17.6, 231.6, 1.0; 17.4, 204.6, 1.0; and 18.6, 218.3, 1.0, respectively. The fact that the reaction order of thermolysis is lower than unity ($n = 0.5$) is presumably due to occurrence of the reaction at the interface between sample and the reaction product and the influence of the crystal lattice on the diffusion of the reaction products [6]. The reaction order equal to 1.0 indicates that thermolysis is not hindered by diffusion factors.

The IR spectra of **I**–**VII** contain absorption bands associated with coordinated ammonia, substituents in the heterocyclic ring, tetrazole ring, and outer-sphere perchlorate anion.

The electronic absorption spectra of **I**–**VII** in aqueous solutions are typical of this type of compounds [7] and contain the *d*–*d* band of ${}^1T_{1g} \leftarrow {}^1A_{1g}$ transition. The other strong band (${}^1T_{2g} \leftarrow {}^1A_{2g}$) is overlapped by the absorption of the tetrazole ligand. Clearly, these complexes contain the octahedral chromophore CoN_6.

The ^{1}H NMR spectra of all the compounds except **III** contain signals of equatorial (in low field) and ax. (in high field) ammonia ligands in the range 3.4 –4.3 ppm. In the spectrum of **III**, the ammonia ^{1}H signal is not split, probably owing to *trans* configuration of the complex. The different chemical shifts of the equatorial and ax. ammonia molecules are consistent with coordination of the heterocyclic ligands via nitrogen atoms [8]. The splitting of these signals into a doublet is due to nonequivalence of the ammonia protons. This splitting is caused by coordination of the tetrazole ring via different atoms: N^1 and N^2 in **II** and **IV** [9], N^1 and O of one of the nitro groups in **V** (5-nitroaminotetrazole is coordinated in the bidentate manner) [10], and N^3 and N^4 in **VI** and **VII** [11]. The tetrazole ligands of **I** are coordinated only via the N^2 atom [12].

We also studied the sensitivity of pressed powders of the explosives to a single pulse of neodymium solid-state laser ($\lambda = 1.06$ μm, $\tau_q = 2$ ms, $E = 1.5$ J, $d_{beam} = 1$ mm). The results obtained are listed below.

Compound	Effect
I	Detonation
II	Combustion
III	Failure
IV	Detonation
V	Failure
VI	Detonation
VII	Failure

The modern concept of initiation of explosives with pulsed laser radiation is based on the ignition at centers formed upon hypothesis of radiation absorption by optical microheterogeneities in separate crystals [3]. In this context, a spectral study of the primers in the wavelength range used in industrial lasers (visible and near-IR region, ruby laser operating at 690 nm and neodymium laser operating at 1060 nm) is of not only theoretical, but also practical interest.

We recorded optical spectra of crystalline complexes **I**–**III** and **IV** (in pellets). First we recorded the spectra of **I** and **II**. Since the influence of the material brought in contact with primers in priming charges (PCs) is of practical interest, pellets of the compounds examined were placed on a copper support (Figs. 1, 2).

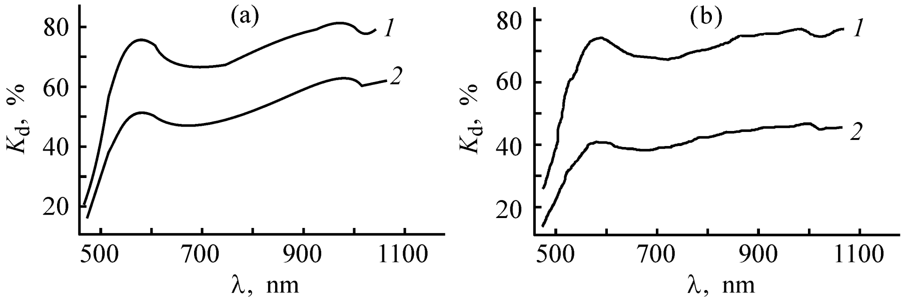

Fig. 1. Diffuse reflectance spectra of (a) **I** and (b) **II**. (K_d) Diffuse reflectance coefficient and (λ) wavelength. (*1*) No support and (*2*) on a support; the same for Fig. 2.

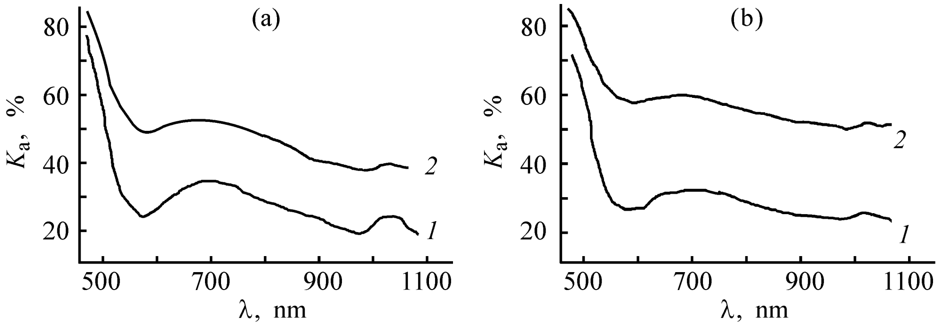

Fig. 2. Electronic absorption spectra of (a) **I** and (b) **II** (K_a) Absorption coefficient and (λ) wavelength.

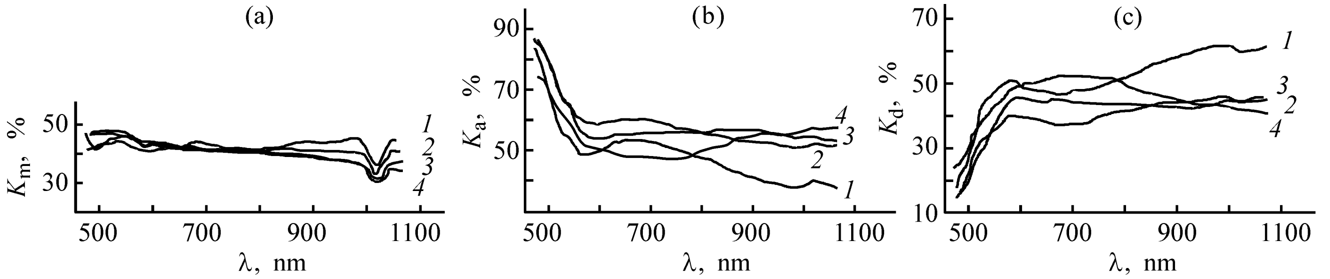

Fig. 3. (a) Mirror reflectance, (b) absorption, and (c) diffuse reflectance spectra of (*1*) **I**, (*2*) **II**, (*3*) **III**, and (*4*) **VI** on a support. (K_m, K_a, K_d) Coefficeints of mirror reflectance, absorption, and diffuse reflectance, respectively; (λ) wavelength.

As seen from Figs. 1 and 2, compounds **I** and **II** behave similarly under exposure to radiation in the whole spectral range, including the wavelength of the neodymium laser (1060 nm). In all cases, the copper support affects the spectral properties. To confirm this result, we also recorded the spectra of **III** and **VI** (Figs. 3a–3c).

As seen from Figs. 3a–3c, the initiation threshold of the crystalline primers is independent of the wavelength of the initiating light. However, it is necessary to study the influence of the particle size distribution and the type of interparticle cohesion on initiation of these explosives. Laser initiation of the complexes was performed with assistance of V.V. Blagoveshchenskii.

Thus, the (tetraminetetrazolato)cobalt(III) perchlorates can be used as primers both in conventional priming charges and in optically initiated priming charges of high safety.

EXPERIMENTAL

The IR spectra of crystalline **I**–**VII** (Nujol or fluorinated oil mulls between KBr windows) were recorded on a Perkin–Elmer M457 spectrometer.

The UV spectra were recorded on a Perkin–Elmer LAMBDA 40 spectrometer in 1-cm quartz cells (analytical concentration 10^{-1}–10^{-2} M).

The ^{1}H NMR spectra were recorded on a Bruker AC (300 MHz) spectrometer using DMSO-d_6 as solvent and hexamethyldisiloxane (HMDS) as internal reference.

Synthesis of **I**–**VII** was monitored by thin-layer chromatography on Silufol UV-254 plates, using 3%

sodium perchlorate as eluent. A thermal gravimetric analysis was performed on an MOM derivatograph (Hungary) in the range 20–500°C at a heating rate of 5 deg $\min^{-1}$. The onset temperature of intense decomposition, T_{oid}, was determined on a thermograph at a heating rate of 5.3 deg $\min^{-1}$. The sensitivity to shock was determined by the pile-driving procedure performed in accordance with GOST (State Standard) 1944–80. The minimal primer charge (MPC) of the complexes was determined with respect to hexogen in the geometry of detonating cap (DC) no. 8 (compaction pressures P_c of the compound and hexogen were 121 and 363 kg cm^{-2}, respectively).

The optical properties of the solid compounds were studied on SPEFOT spectrophotometric unit described in [13].

Diaquatetramminecobalt(III) perchlorate **VIII** prepared by the procedure described in [14] was used in further synthesis without isolation from the solutions.

Tetramminebis(5-nitrotetrazolato)cobalt(III) perchlorate I and **tetramminebis(1-methyl-5-aminotetrazole)cobalt(III) perchlorate VII** were prepared by the procedure described in [15] in 54 and 51% yields, respectively. Compound **I**. IR spectrum, cm^{-1}: 1588 m, 1316 m (NH_3, Tz), 1076 m (ClO_4), 1540 m (NO_2). UV spectrum, $\lambda_{\max}$ = 456 nm, ε = 74 l cm^{-1} mol^{-1}. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.79, 4.29 (12H, NH_3).

Found, %: C 4.8, H 2.3, N 42.6.

$C_2H_{12}ClCoN_{14}O_8$.

Calculated, %: C 5.3, H 2.7, N 43.1.

Compound **VII**. IR spectrum, cm^{-1}: 3316 m, 1334 m (NH_3, Tz), 1118 m (ClO_4), 1628 m (C=N), 3236 w, 1616 w (NH_2), 2830 w (CH_3). UV spectrum, $\lambda_{\max}$ = 466 nm, ε = 77 l cm^{-1} mol^{-1}. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.85, 3.90 (9H, NH_3 eq.); 3.75, 3.80 (3H, NH_3 ax.); 7.12 (2H, NH_2–Tz, ax.), 7.52 (2H, NH_2–Tz eq.); 4.03 (3H, CH_3–Tz ax.), 4.22 (3H, CH_3–Tz eq.).

Found, %: C 7.8, H 3.3, N 31.9.

$C_4H_{22}Cl_3CoN_{14}O_{12}$.

Calculated, %: C 7.7, H 3.6, N 31.5.

Published procedures were used to prepare tetrazole [16], 5-methyltetrazole [17], 5-nitroaminotetrazole [18], 5-aminotetrazole [19], and 1,5-diaminotetrazole [20]. The physicochemical properties of the compounds agreed with published data.

Tetramminebis(trazolato)cobalt(III) perchlorate II, tetramminebis(5-methyltetrazolato)cobalt(III) perchlorate III, tetramminebis(5-aminotetrazolato)-cobalt(III) perchlorate IV, tetrammine-5-nitroaminotetrazolatocobalt(III) perchlorate V, and **tetramminebis(1,5-diaminotetrazole)cobalt(III) perchlorate VI**. Carbonatotetramminecobalt(III) perchlorate (0.5 g) prepared by the procedure described in [21] was dissolved in 5% perchloric acid (15 ml) until CO_2 evolution stopped. The solution was filtered. An appropriate tetrazole derivative was added in 60% excess to the filtrate. The reaction mixture was heated on a boiling water bath for 4 h, cooled to 15°C, and poured into propan-2-ol (100 ml). The precipitate was filtered off and washed with two portions of ethanol (2 × 5 ml). Yield (60–65 %). Compound **II**. IR spectrum, cm^{-1}: 3320 m, 1329 m (NH_3, Tz), 3050 m (CH), 1094 ws (ClO_4). UV spectrum, $\lambda_{\max}$ = 454 nm, ε = 87 l cm^{-1} mol^{-1}. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.00, 4.25 (9H, NH_3 eq.), 3.66, 3.85 (3H, NH_3 ax.), 6.90 (H, C–H, Tz ax.), 8.70 (H, C–H, Tz, eq.).

Found, %: C 6.7, H 4.1, N 45.7.

$C_2H_{14}ClCoN_{12}O_4$.

Calculated, %: C 6.6, H 3.9, N 46.1.

Compound **III**. IR spectrum, cm^{-1}: 3315 m, 1330 m (NH_3, Tz), 1101 s (ClO_4), 1450 s, 1370 s (CH_3). UV spectrum, $\lambda_{\max}$ = 455 nm, ε = 92 l cm^{-1} mol^{-1}. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.74, (12H, NH_3 eq.), 2.52 (6H, CH_3–Tz ax.).

Found, %: C 6.7, H 4.1, N 45.7.

$C_4H_{18}ClCoN_{12}O_4$.

Calculated, %: C 6.6, H 3.9, N 46.1.

Compound **IV**. IR spectrum, cm^{-1}: 3318 m, 1312 m (NH_3, Tz), 3426 w, 1596 w (NH_2) 1084 m (ClO_4). UV spectrum, $\lambda_{\max}$ = 463 nm, ε = 80 l cm^{-1} mol^{-1}. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.05, 4.25 (9H, NH_3 eq.), 3.45, 3.72 (3H, NH_3 ax.), 5.22 (2H, NH_2–Tz ax.), 6.87 (2H, NH_2–Tz, eq.).

Found, %: C 6.1, H 4.3, N 49.5.

$C_2H_{16}ClCoN_{14}O_4$.

Calculated, %: C 6.1, H 4.1, N 49.7.

Compound **V**. IR spectrum, cm^{-1}: 3320 s, 1308 m (NH_3, Tz), 1556 m (NO_2), 1340 m (C–N), 1110 s (ClO_4). UV spectrum, λ_{max} = 475 nm, ε = 63 $l\,cm^{-1}\,mol^{-1}$. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.10, 4.50 (6H, NH_3 eq.), 3.45, 3.75 (6H, NH_3 ax.).

Found, %: C 3.8, H 3.9, N 39.6.

$CH_{12}ClCoN_{10}O_6$.

Calculated, %: C 3.4, H 3.4, N 39.5.

Compound **VI**. IR spectrum, cm^{-1}: 3321 m, 1332 m (NH_3, Tz), 1095 s (ClO_4), 1630 m (C=N), 3232 w, 1610 w (NH_2). UV spectrum, λ_{max} = 470 nm ε = 80 $l\,cm^{-1}\,mol^{-1}$. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.00, 4.15 (9H, NH_3 eq.), 3.70, 3.78 (3H, NH_3 ax.), 6.20 [4H, $(NH_2)_2$–Tz ax.], 6.92 [4H, $(NH_2)_2$–Tz, eq.).

Found, %: C 3.8, H 3.6, N 35.9.

$C_2H_{20}Cl_3CoN_{16}O_{12}$.

Calculated, %: C 3.8, H 3.2, N 35.8.

REFERENCES

1. Merson, J.A., Salas, F.J., and Harlan, J.G., *Proc. Int. Pyrotech. Semin.*, 1994, vol. 19, pp. 191–206.
2. Fyfe, D.W., Fronabarger, J.W., and Bickes, R.W., Jr., *Proc. Int. Pyrotech. Semin.*, 1994, vol. 20, pp. 341–343.
3. Ilyushin, M.A., Tselinskii, I.V., and Chernai, A.V., *Ross. Khim. Zh.*, 1997, vol. 41, no. 4, pp. 81–88.
4. Ilushin, M.A., Smirnov, A.V., Kotomin, A.A., and Tselynsky, I.V., *Hanneng caliliao=Energ. Mater.*, 1994, vol. 2, no. 1, pp. 16–20.
5. Zhilin, A.Yu., Ilyushin, M.A., and Tselinskii, I.V., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 5, pp. 710–713.
6. Kukushkin, Yu.N., Budanova, V.F., and Sedova, G.N., *Termicheskoe prevrashchenie koordinatsionnykh soedinenii v tverdoi faze* (Thermal Transformations of Coordination Compounds in the Solid Phase), Leningrad: Leningr. Gos. Univ., 1981.
7. Fronabarger, J., Schuman, A., Chapman, R.D., *et al.*, *AIAA Pap.*, 1995, no. 2858, pp. 1–7.
8. Sheng, D., Ma, F., Sun, F., and Lu, Q., *Hanneng caliliao=Energ. Mater.*, 2000, vol. 8, no. 3, pp. 100–103.
9. Moore, D.S. and Robinson, S.D., *Adv. Inorg. Chem.*, 1988, vol. 32, pp. 171–239.
10. Subba Rao, N.S.V., Ganorkar, M.C., Mohan Murali, B.K., and Ramaswamy, C.P., *Bull. Acad. Polon. Sci.*, 1979, vol. 27, no. 1, pp. 21–28.
11. Shilin, A.Yu., Ilyushin, M.A., Tselinskii, I.V., *et al.*, *Zh. Prikl. Khim.*, 2002, vol. 75, no. 11, pp. 1885–1888.
12. Morosin, B., Dunn, R.G., Assink, R., *et al.*, *Acta Crystallogr.*, 1997, Sect. C, vol. 53, pp. 1609–1611.
13. RF Patent no. 1673928.
14. Ilyushin, M.A., Lukogorskaya, A.S., Tselinskii, I.V., and Brykov, A.S., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 3, pp. 449–451.
15. Zhilin, A.Yu., Ilyushin, M.A., Tselinskii, I.V., and Brykov, A.S., *Zh. Prikl. Khim.*, 2001, vol. 74, no. 1, pp. 96–99.
16. Gaponik, P.N. and Karavai, V.P., *Vestn. Belorus. Gos. Univ., Ser. 2*, (Minsk), 1980, no. 3, pp. 51–52.
17. Spear, R.J., *Aust. J. Chem.*, 1984, vol. 37, no. 12, pp. 2453–2468.
18. Mayants, A.G., *Khim. Geterotsikl. Soedin.*, 1969, no. 11, pp. 1569–1571.
19. Lavrenova, L.G., Larionov, S.V., Grankina, Z.A., and Ikorskii, V.N., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1983, nos. 2/1, pp. 81–86.
20. Gaponik, P.N. and Karavai, V.P., *Khim. Geterotsikl. Soedin.*, 1984, no. 12, pp. 1683–1686.
21. Novakovskii, M.S., *Laboratornye raboty po khimii kompleksnykh soedinenii* (Laboratory Works on Coordination Chemistry), Kharkov: Kharkov Univ., 1972.