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ESTIMATION OF DENSITY AND DETONATION VELOCITY OF TETRAZOLE Co(III) COMPLEXES

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ABSTRACT The densities of Co(Ⅲ) amminates are calculated by additive method using molar volume increments of structural fragments with average error of ±1.2g/cm³. Their detonation velocity are estimated by dividing the coordination complexes into an "active" (anion-oxidizer and ligands) and an "inert" (metal center cation and water) parts and then by calculation method using increments of chemical bonds and structural fragments with average error of ±140m/s.

KEY WORDS tertrazole Co(Ⅲ) coordination complex, density, detonation velocity, calculation method.

Pentaamine Co (III) perchlorates with 5-substituted tetrazoles as ligands are well known as safety explosives for detonators[1]. The reaction of substitution of coordinated water in $[Co(NH_3)_5 \cdot H_2O]$ cation for 5-R-tetrazole molecules has been studied in our laboratory[2,3], and some tetrazole complexes were synthesized. Properties of the perchlorate complexes are given in Table 1.

Table 1 Properties of $[Co(NH_3)_5R-C-N_4](ClO_4)_2$ complexes

R	Density (calc.) (g/cm³)	Density (exp.) (g/cm³)	Decomp. T/(℃)	D/(km/s)		
				ρ/(g/cm³)	calc.	exp.
H	1.97	1.970	280	1.97	7.14	——
NH_2	1.96	1.95	270	1.624	6.14	6.50
NH_3	1.90	1.88	282	1.900	6.94	——
NO_2	2.01	2.03	265	1.613	6.30	6.65
CN[7]	1.97	1.96	288	1.750	7.14	7.18

The general utility of explosives may be assessed on the basis of calculation of their explosive and physicochemical properties. In this article the densities of Co (III) amminates are calculated by the additive method using increments of structural fragments (Table 2).

The densities of the complexes are calculated according to the equation:

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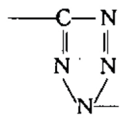
$$\rho = \frac{M}{\sum V_i} \tag{1}$$

Table 2　Increments of structural fragments

Fragment	V_i	Fragment	V_i
Co^{3+}	2.89	$(C_{Het.})-H$	11.876
ClO^{4-}	34.89	$(C_{Het.})-CH_3$	25.963
NH_3	19.83	$(C_{Het.})-NH_2$	19.75
	28.37	$(C_{Het.})-NO_2$	29.697

Where V_i stands for a partial molar volume of the fragment; M is the molecular mass of the complex.

The calculated densities of the complexes lie close to experimental values (Table 1). The average error of the method is $\pm 0.2 g/cm^3$.

The idea of calculation method for detonation velocity (D) assesment of Co (III) amminates with outer-sphere anions as oxidizers consists of dividing the complex into an "active" (anion-oxidizer and ligands) and an "inert" (metal cation and water) parts. Indeed, this method is boiled down to the calculation method using increments of chemical bonds and structural fragments[4] and the corresponding method for explosive mixtures with inert additives[5]. In this case cobalt cation plays the part of ultradispersed inert metal additive. The average error of this method is ±140m/s.

The first step of the method consists of the calculation of D of the "explosive" part in the complex at the density of $1.7 g/cm^3$ (see eqn. (2)[4]).

$$D_{e.p.} = 2.77 + \frac{\rho}{M_{e.p.}}\left(\sum n_i F_i + \sum n_j N_j\right) \tag{2}$$

Here $M_{e.p.}$ stands for the molar mass of the "explosive" part; ρ is density of the "explosive" part, $1.7 g/cm^3$; F_i is increment of fragment; n_i is the number of identical fragments; N_j is increment of bond; n_j is the number of identical bonds.

The increments of structural fragments and bonds are given in Table 3.

Then the value of D of the "explosive" part is calculated as its partial density in a charge (ρ_n).

$$D\rho_n = D_{1.7} - m(1.7 - \rho_n) \tag{3}$$

Where m is a coefficient depending on the structure of "explosive" part on the basis of its elemental composition, $C_aH_bO_cN_dF_eCl_f$[4]

$$m = \frac{1.1a - K_2 b + 7.6c + 8.1d + 7.2f}{0.1 M_{e.p.}} \tag{4}$$

Table 3 Increments of chemical bonds and structural fragments for the calculation of detonation velocity of the "explosive" part of the complexes.

Fragment	F_i	Bond[2)]	N_j	Fragment	K_O	F_i
C[1)]	6.6	C—C	13.4	CN	—	181.2
CH	−12.1	C=N	39.6	NO_2	if $0.35 \leqslant K_O \leqslant 1.0$	175.8
CH_3		N—N	52.1		$1.0 \leqslant K_O \leqslant 1.45$	$175.8-66(K_O-1.0)$
if H>3.8%	11.5	N=N	49.8	ClO_4	if $K_O > 1.5$	227.2
if H<3.8%	1.5	C—N	4.4		$1.0 \leqslant K_O \leqslant 1.5$	269.2
N[1)]	8.8	—	—		$0.5 \leqslant K_O \leqslant 1.0$	278.7
NH_2	21.4	—	—		$0.2 \leqslant K_O \leqslant 0.5$	309.8
NH_3	34.8	—	—		$K_O \leqslant 0.2$	514.7

Notation: 1) The atom as a fragment of all structures; 2) Merely a bond (whithout atoms).

$$K_2 = 3.0 \quad \text{if } H \leqslant 3.5\%; \; K_2 = 1.3 \quad \text{if } H > 3.5\%;$$

$$\rho_n = \alpha_{e.p.}\rho_0 \tag{5}$$

Here ρ_0 is charge density of the explosive complex, g/cm^3; $\alpha_{e.p.}$ is mass fraction of "explosive" part in the complex.

$$\alpha_{e.p.} = \frac{M_{e.p.}}{M_{compl.}} \tag{6}$$

Here $M_{compl.}$ is molecular mass of the explosive complex.

At the last step of detonation velocity calculation of the charge ($D_{expl.}$) the influence of the "inert" part is calculated[5]:

$$D_{expl.} = D\rho_n + \sum \Delta D_{ad} \tag{7}$$

Here ΔD_{ad} is the change of D determined from "inert" fragments in the molecule of the explosive.

For crystalline or coordinated water D_{ad} can be calculated according to the equation[5]:

$$\Delta D_{H_2O} = A_{H_2O}\frac{\beta_{H_2O}\rho_0}{\rho_{H_2O}} \tag{8}$$

Here β_{H_2O} is the mass part of water in the explosive complex; ρ_{H_2O} is the density of water, g/cm^3.

The shock compression parameter A_{H_2O} may be expressed as followes[6]:

$$A_{H_2O} = 10 \times \frac{\sum n_i\delta_i}{M_{H_2O}}\rho_{H_2O} \tag{9}$$

The values of increments δ_i for hydrogen and oxygen atoms are 1.855, and 1.175 respectively[6].

The D_{ad} parameter is expressed as the following formula for metal cations[5]:

$$D_{ad} = a(b - \rho_{ad}) \frac{\beta \rho_0}{\rho_{ad}} \tag{10}$$

Here β and ρ_{ad} are the mass part and density of the "inert" additive respectively; a and b are coefficients for ultradispersed metals, their values are 1.125 $\frac{m/s}{g/cm^3}$ and 4.0 g/cm³ respectively.

Let us show the example of the calculation of ideal detonation velocity for cyanotetrazolatopentaamine Co (III) perchlorate (CP) at the density of charge ρ_0(1.86 g/cm³).

1. $C_2H_{15}O_8N_{10}Cl_2Co$

$$M_{compl.} = 437.037 \quad M_{e.p.} = 378.104$$

The oxygen coefficient of "explosive" part is:

$$K_0 = \frac{c + f/2}{2a + b/2} = 0.78$$

$$\alpha_{e.p.} = 0.865, \text{ see eqn. (6)}$$

$$\rho_n = 1.609, \text{ see eqn. (5)}$$

2. Divide the structural formula of CP into "explosive" and "inert" parts and further the "explosive" one into fragments and bonds connecting them (Table 4).

Table 4 The "fragments" and bonds of CP

Fragment	F_i	n_i	Bond	N_j	n_j
N	8.8	4	C—N	4.4	1
C	6.6	1	C—C	13.4	1
CN	181.2	1	C=N	39.6	1
NH_3	34.8	5	N—N	52.1	2
ClO_4	278.7	2	N=N	49.8	1

$$\sum n_i F_i + \sum n_j N_j = 1165.8$$

3. Calculate D of the "explosive" part of CP at density of 1.7g/cm³(see eqn. (2)):

$$D_{1.7} = 8.012\text{km/s}$$

4. Calculate coefficient M according to eqn. (4).

$$m = \frac{1.1 \times 2 - 3.0 \times 15 + 7.6 \times 8 + 8.1 \times 10 + 7.2 \times 2}{0.1 \times 378.104} = 3 \frac{km/s}{g/cm^3}.$$

5. Calculate D of the "explosive" part of CP at density ρ_n (see eqn. (3)).

$$D\rho_n = 7.739 \text{ km/s}$$

6. The last step of the method is calculation of detonation velocity of CP, which takes into account the "inert" part of the substance Co(III) cation:

$$\beta = \frac{58.938}{437.037} = 0.135$$

$$\Delta D_{ad} = -0.156 \text{ km/s, see eqn. (10)}$$

$$D_{1.86cal.} = 7.583 \text{ km/s, see eqn. (7)}$$

$$D_{1.86exp.} = 7.579 \text{ km/s}$$[7]

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