

First-principles study of energetic complexes (II): (5-cyanotetrazolato- N^2) pentaammine cobalt (III) perchlorate (CP) and Ni, Fe and Zn analogues

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Abstract First-principles methods using the TPSS density functional level of theory with the basis set 6-31G** were applied to study (5-cyanotetrazolato- N^2) pentaammine cobalt (III) perchlorate (CP) and Ni, Fe and Zn analogues in the gas phase. The optimized lowest-energy geometry of CP was calculated from reported experimental structural data using the TPSS method. The calculated values are in good agreement with those measured by X-ray diffraction. Ni, Fe and Zn analogues were constructed and calculated on the same basis. NBO results showed that the metal-ligand interactions have covalent character. Donor-acceptor analyses predicted that the delocalization energy E_2 decreases from Co to Zn, so the covalent nature of the complexes increases in the order $Co > Fe > Ni > Zn$. In addition, HOMO-LUMO composition was investigated to determine the stability of the title compounds.

Keywords (5-Cyanotetrazolato- N^2) pentaammine cobalt (III) perchlorate (CP) · Density functional theory · Donor-acceptor analyses · Electronic structure · Energetic coordinate compound

Introduction

Extensive research and development programs have been undertaken to develop safer explosive materials that can be initiated using a thermal source and that exhibit a rapid deflagration-to-detonation transition. The coordination compound (5-cyanotetrazolato- N^2) pentaammine cobalt (III) perchlorate (CP) [1] was first synthesized in 1968 by Sandia National Laboratories in the USA. In 1978, Searcy and Shanahan [2] studied the thermal decomposition of CP, which was developed for use in detonating components. They found that CP decomposition is a heterogeneous solid-to-gas type reaction that occurs in three stages. Later, Lieberman and Fronabarger synthesized CP using a conventional coordination preparative method and determined the structure using ^{15}N NMR spectroscopy and X-ray diffraction techniques. The powder has been qualified for detonator use and investigations revealed no corrosion or compatibility problems. The detonation parameters, characteristics of the transition to detonation and equations of state for the reaction products have also been determined [3]. Fronabarger studied several substituted CP analogs in a search for materials superior to CP [4]. Some of the analogs had lower electrostatic discharge sensitivity than CP, which indicated that selected compounds can be used to develop safer detonators; the analogs are mainly in the same impact sensitivity range as RDX, but less than PETN. Massis reported on the stability and compatibility of CP [5]. In 1983, the single-crystal structure was determined by Graeber [6]. The CP decomposition kinetics was then investigated. Approximation of the global decomposition mechanism as a two-stage procedure in which all energy emitted is related to ignition yields a predicted critical temperature in good agreement with experimental data [7].

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A review of chemical studies to develop explosive applications of CP has also been published [1]. Blachowski and Burchett reported that the use of CP and BNCP was expanded to US Navy missile and aircrew escape applications, and these materials were characterized and tested [8]. Based on Department of Energy performance and safety test data, certification of CP was granted. In 2004, a decomposition kinetics study was carried out for high-melting explosive (HMX) and CP separately and together [9]. At high thermal stress levels, the mixture decomposed more rapidly than the individual components. Thermal analysis data showed that the mixture has lower activation energy, in accordance with the amount of gas observed in long-term detonator aging experiments. The mixture is about 30 times more stable than expected for HMX by itself for 50 months at 100°C. Thus, it would take approximately 10,000 years to achieve 10% decomposition at 30°C. Weese and Burnham reported coefficients of thermal expansion for four specific temperature ranges, decomposition kinetics using linear and isothermal heating, and the reaction to impact, spark and friction stimuli [10].

Experimental studies have explored many properties of coordinate energetic materials, but few have investigated the relationship between the structure of energetic complexes and their explosive properties. In the absence of experimental data, quantum chemistry methods can be used not only to provide information about the preferred conformation, but also to identify the relationship between structure and properties for metal nitro-tetrazole coordination compounds. As common transition metal, the 3d orbitals of Ni, Fe and Zn are not fully occupied, which makes it easier for them to accept electrons. And the reaction products lead to less as potential lead-free. In 2005, Talawar has synthesized the analogues of bis-(5-nitro-2H-tetrazolato-N²)tetraammine cobalt(III) perchlorate (BNCP), whose central transition-metal was Ni/Cu/Zn. The performance results displayed that the analogues had excellent properties and could be applied as potential lead-free initiators [11]. Thus, we chose the Ni, Fe and Zn as central metal to study the analogues of CP theoretically.

To gain an understanding of the relation between the structure and properties of transition-metal cyano-tetrazole perchlorates, CP and its analogues were investigated using theoretical methods. Although the availability of density functional theory (DFT) and X-ray crystallography data, to the best of our knowledge this is the first systematic characterization of transition-metal cyano-tetrazole complexes. Using DFT methods, the structures of (5-cyanotetrazolato-N²) pentaammine cobalt (III)/nickel (III)/iron (III)/ zinc (III) perchlorate (CP/NCP/FCP/ZCP) and their relative stability were determined. Natural bond orbital (NBO) analysis was used to rationalize the origin of preferred conformations.

Computational methods

Calculations were carried out using Gaussian 03 [12] and the development version of Gaussian [13]. Total optimization of the geometries of the four metal complexes CP, NCP, FCP, and ZCP was performed using the self-consistent field (SCF) method at the Tao, Perdew, Staroverov, and Scuseria (TPSS) [14] density functional level of theory in combination with the 6-31G** [15, 16] basis set. The initial geometries of the four metal complexes were constructed using the graphics package Gaussview. The experimental X-ray structure of the CP molecule was taken as a starting point and used to generate the geometries of NCP, FCP and ZCP. The CP molecular geometry was generated using spin-restricted functions, while NCP, FCP and ZCP geometries were computed using the corresponding spin-unrestricted functions with the same basis set in the high-spin state. Their vibrational frequencies and NBO analyses [17] were studied at the same level.

Results and discussion

Geometric structure

Before further calculation, four typical functionals (PBE, B3LYP, SVWN5 and TPSS) were applied to CP as a test. Here the deviations are defined as $r_{\text{calc}} - r_{\text{exp}}$, the statistical analysis of the bond lengths is given in Table 1. However, all calculations show the structure parameters assigned by bond lengths are close to the experimental results. According

Table 1 Statistical assessment of the deviation and the selected bond length (Å) between calculated and experimental ones for the title compounds

Functional	PBE	B3LYP	SVWN5	TPSS	Experiment
Co ₁ -N ₂	1.961	1.976	1.907	1.962	1.987
Co ₁ -N ₃	1.957	1.971	1.902	1.959	1.987
Co ₁ -N ₄	1.980	2.000	1.918	1.983	1.984
Co ₁ -N ₅	1.888	1.928	1.827	1.893	1.921
Co ₁ -N ₆	1.969	1.975	1.916	1.967	1.959
Co ₁ -N ₇	1.950	1.960	1.901	1.950	1.991
N ₅ -N ₈	1.341	1.327	1.325	1.341	1.359
N ₈ -N ₉	1.327	1.318	1.315	1.342	1.370
N ₉ -C ₁₂	1.361	1.351	1.347	1.329	1.304
C ₁₂ -N ₁₀	1.355	1.343	1.346	1.360	1.367
N ₁₀ -N ₅	1.340	1.331	1.325	1.354	1.369
Δ _{max}	0.057	-0.052	-0.094	-0.041	-
MD	-0.015	-0.011	-0.052	-0.014	-
MAD	0.026	0.025	0.059	0.020	-
RMS	0.031	0.030	0.064	0.023	-

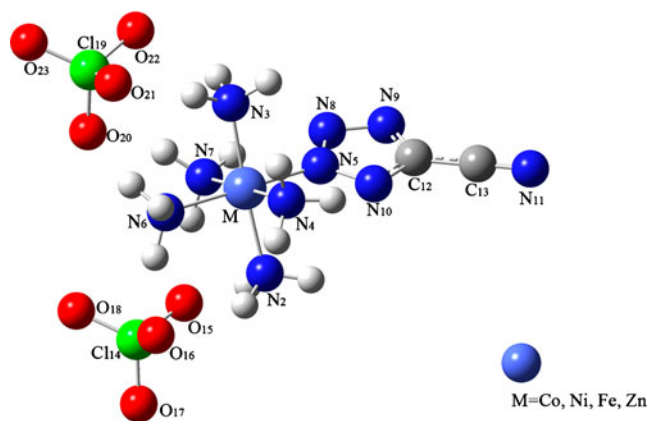


Fig. 1 The molecular structure of the title compounds

to the mean deviation values, the SVWN5 functional significantly over binds and produces bond lengths shorter than experiment data. In conclusion, the accuracy of the four tested functionals for reproducing geometries of these complexes is TPSS>B3LYP>PBE>SVWN5. Thus in further study, we use the TPSS function for the other three analogues, which may be expected to gain more dependable predictions of the structure.

Optimized structures for a series of CP derivatives were calculated at the level of TPSS/6–31G**; all of the harmonic vibrational frequencies are real, which confirms that the geometries are true minima. These coordination modes are shown in Fig. 1. The geometric structures are similar in coordinate mode: all the central metal atoms coordinate with one 5-nitro-tetrazole ring and five NH₃ molecules through the nitrogen atoms, forming a hexacoordinated distorted

octahedral complex. The optimized geometric parameters for CP are summarized in Table 2. The results reveal that the bond lengths and angles are in agreement with standard values reported in the literature [6]. Computed metal-ligand bond lengths, selected bond angles and the relative energy of the three complexes are summarized in Table 3. The data show that the structures of the four compounds are very close. The bond length is greater for M–N (ring) than for M–NH₃, indicating that the latter bond is tighter. Second, the N–M–N bond angle is close to 90°, indicating that the structure resembles a regular octahedron.

Electronic structure

The natural population analysis was evaluated in terms of natural atomic orbital occupancies. Data on the natural atom charge for each metal atom, nitrogen atoms in the 5-cyano-tetrazole ring directly bonded to the metal, and perchlorate anions, the natural electron configuration (NEC) for the central metal atom and the Wiberg bond index (WBI) [18, 19] for M–N are listed in Table 4. It is notable that the effective valence for the metal atoms lies in the range 1.389–1.700, which is much smaller than 2. Moreover, the natural charge on each perchlorate ion in the complexes is close and is also less than –2. Thus, the metal–ligand interactions have covalent character. The charges of coordinated N atoms in the four complexes are in the range from –0.711 to –0.770, which is more negative than the NEC of –0.246 for the free 5-cyano-tetrazole ligand, indicating that charge is transferred when the molecules coordinate with the central metal atom.

Table 2 Comparison of calculated and experimental optimized parameters of CP (Å, °)

Bond	Length/Å		Angle	Degree/°	
	Computed	Experiment		Computed	Experiment
Co ₁ -N ₂	1.962	1.987	N ₂ -Co ₁ -N ₄	88.14	90.78
Co ₁ -N ₃	1.959	1.987	N ₂ -Co ₁ -N ₅	87.93	87.49
Co ₁ -N ₄	1.983	1.984	N ₂ -Co ₁ -N ₆	91.75	90.62
Co ₁ -N ₅	1.893	1.921	N ₂ -Co ₁ -N ₇	91.56	89.94
Co ₁ -N ₆	1.967	1.959	N ₃ -Co ₁ -N ₄	90.31	89.46
Co ₁ -N ₇	1.950	1.991	N ₃ -Co ₁ -N ₅	88.62	90.52
N ₅ -N ₈	1.341	1.359	N ₃ -Co ₁ -N ₆	91.73	91.37
N ₅ -N ₁₀	1.342	1.370	N ₃ -Co ₁ -N ₇	90.01	89.75
N ₈ -N ₉	1.329	1.304	N ₅ -N ₈ -N ₉	108.10	111.40
N ₉ -C ₁₂	1.360	1.367	N ₈ -N ₉ -C ₁₂	105.03	102.40
C ₁₂ -N ₁₀	1.354	1.369	N ₉ -C ₁₂ -N ₁₀	112.60	115.80
C ₁₂ -C ₁₃	1.424	1.486	C ₁₂ -N ₁₀ -N ₅	102.20	99.76
C ₁₃ -N ₁₁	1.172	1.115	N ₁₀ -N ₅ -N ₈	112.02	110.60
			N ₉ -C ₁₂ -C ₁₃	124.30	123.96
			N ₁₀ -C ₁₂ -C ₁₃	123.10	120.20
			C ₁₂ -C ₁₃ -N ₁₁	179.50	179.30

Table 3 Selected bond lengths (Å), bond angles (°) and energies for the study complexes^a

Compounds	M-NH ₃ /Å	M-N(ring) /Å	Cl-O/Å	N-M-N/°	E/(a.u.)
FCP	2.003	1.921	1.519	90.01	-3418.23
CP	1.964	1.893	1.519	90.01	-3537.27
NCP	2.017	1.890	1.519	90.01	-3662.74
ZCP	2.160	2.074	1.514	89.93	-3933.60

^a Values are averaged

The formal electron configurations of Fe, Co, Ni and Zn are listed in Table 4. It is evident that the 4s populations decrease, while almost all the 4p and 3d populations increase, except for ZCP, for which the 3d population decreases slightly. This is because the 3d valence orbitals of Zn are already so full that it is hard to accept more electrons. This also explains why the greatest number of electrons remains in the 4s valence orbitals of Zn.

WBI results were obtained by manipulation of the density matrix in the orthogonal natural atomic orbital basis set derived from natural population analysis. WBI expresses the sum of squares of density matrix elements and is closely related to the bond character: a greater WBI corresponds to stronger covalent character. Moreover, the greater the electronic cloud overlap of bonding atoms, the more stable the bond. Thus, it is widely accepted that WBI describes the bond order and can be used as an indicator of bond strength [20]. As shown in Table 4, WBI values are smallest for Zn and greatest for Co among the four complexes. The covalent character increases in the order Zn<Ni<Fe<Co, while the bond length decreases in the order Zn>Ni>Fe>Co. This conclusion is in accordance with the geometry structure results. Meanwhile, e_{occ} for the Co–N bonding orbital is 1.991 and there are no metal–ligand bonding orbitals for the other complexes. Thus, the interaction between the other three metal atoms and coordinated N atoms is ionic. This also demonstrates that Co–N has the strongest covalent character.

Donor–acceptor interactions

The electronic structure analysis implies that a certain amount of electronic charge is transferred from a proton

acceptor to a proton donor. Furthermore, there is a rearrangement of electron density within each monomer. NBO E_2 values were used to determine the origin of the electron density donated to the metal atom. E_2 values are a measure of the interaction strength between a donor NBO and an acceptor NBO, as defined by [21, 22] (Eq. 1):

$$E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}, \quad (1)$$

where $F(i,j)$ are the off-diagonal Fock matrix elements, $\varepsilon_j - \varepsilon_i$ is the energy difference between the NBOs, which is then weighted by q_i , the occupancy of the donor NBO.

NBO analysis results, including the maximum stabilization energy (E_2) associated with delocalization from N–N and N–H bond orbitals to lone-pair antibonding orbitals of the central metal atom ($\sigma_{N-N} \rightarrow n_M^*$ and $\sigma_{N-H} \rightarrow n_M^*$), at the TPSS/6-31G** level of theory are listed in Table 5. The NBO results predict that E_2 decreases according to the order Co>Fe>Ni>Zn. Thus, we can conclude that the charge transfer in ZCP is less than in NCP, FCP and CP. The more electrons transferred between N–N/N–H bonds and the metal atom, the more electrons can be shared between the coordinated N atoms and the central metal atom. Likewise, the stronger covalent character they will have. This result agrees with our electronic structure conclusion.

HOMO and LUMO analyses

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important for theoretical chemistry. They can be used to determine the way in which a molecule interacts with other

Table 4 Natural charges on each metal atom, coordinated N atoms; electron configuration of the metal atom; and WBI of M–N bonds for the studied compounds

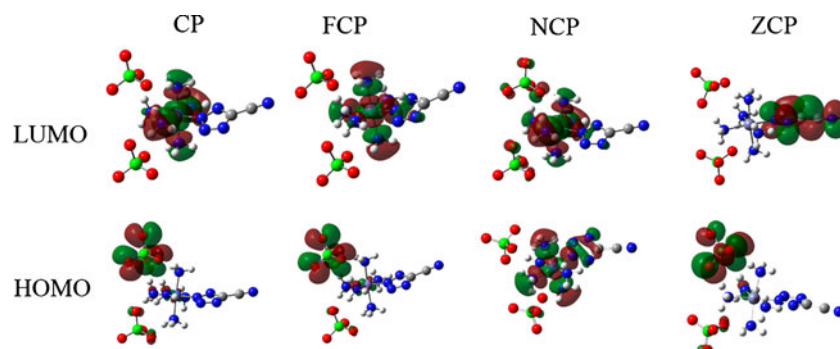
Species	Formal electron configurations	Natural charge		Atom	Electron configuration			M–N		M–N(ring)	
		M	ClO ₄		N-ring	ns	np	(n-1)d	Length/ Å	WBI	Length/ Å
FCP	3d ⁶ 4s ²	1.474	-1.641	-0.729	0.33	0.01	6.18	2.003	0.386	1.921	0.401
CP	3d ⁷ 4s ²	1.389	-1.650	-0.732	0.33	0.01	7.26	1.964	0.408	1.893	0.408
NCP	3d ⁸ 4s ²	1.511	-1.644	-0.711	0.36	0.01	8.11	2.017	0.287	1.890	0.362
ZCP	3d ¹⁰ 4s ²	1.700	-1.299	-0.770	0.43	0.03	9.83	2.160	0.140	2.074	0.143

Table 5 The maximum stabilization energies (in $\text{kJ}\cdot\text{mol}^{-1}$) associated with delocalizations of $\sigma_{N-N} \rightarrow n_M^*$ and $\sigma_{N-H} \rightarrow n_M^*$ for the study coordinate compound

Delocalization	Co	Fe	Ni	Zn
$\sigma_{N5-N8} \rightarrow n_M^*$	8.067	4.180	4.514	3.010
$\sigma_{N5-N10} \rightarrow n_M^*$	9.614	5.225	5.392	3.093
$\sigma_{N2-H30} \rightarrow n_M^*$	10.41	5.141	5.183	2.926
$\sigma_{N2-H31} \rightarrow n_M^*$	12.16	6.354	5.643	3.804
$\sigma_{N2-H32} \rightarrow n_M^*$	7.399	4.556	3.971	2.550
$\sigma_{N3-H36} \rightarrow n_M^*$	9.112	5.100	4.347	2.926
$\sigma_{N3-H37} \rightarrow n_M^*$	10.49	5.685	5.309	3.762
$\sigma_{N3-H38} \rightarrow n_M^*$	9.530	4.932	4.932	3.051
$\sigma_{N4-H33} \rightarrow n_M^*$	12.54	8.151	3.260	3.302
$\sigma_{N4-H34} \rightarrow n_M^*$	7.649	4.222	1.630	1.505
$\sigma_{N4-H35} \rightarrow n_M^*$	7.106	4.055	1.505	1.505
$\sigma_{N6-H27} \rightarrow n_M^*$	13.29	6.688	5.518	1.505
$\sigma_{N6-H28} \rightarrow n_M^*$	6.354	3.637	3.386	1.505
$\sigma_{N6-H29} \rightarrow n_M^*$	11.04	5.936	4.807	1.505
$\sigma_{N7-H24} \rightarrow n_M^*$	12.33	4.807	2.884	1.505
$\sigma_{N7-H25} \rightarrow n_M^*$	13.25	5.727	3.260	1.505
$\sigma_{N7-H26} \rightarrow n_M^*$	13.75	5.810	3.302	1.505

species; hence, they are called frontier orbitals. HOMO, which can be thought of as the outermost orbital containing electrons, tends to give electrons and is thus an electron donor. Conversely, LUMO can be thought of as the innermost orbital containing free places to accept electrons [23, 24]. The reaction mechanism for the complexes can be studied in terms of the interaction between HOMO and LUMO orbitals of the structure. Many studies have proved that the HOMO–LUMO energy gap is an important parameter characterizing the activity of energetic materials [25–30]. HOMO and LUMO 3D plots are shown in Fig. 2.

Figure 2 depicts representative differences in HOMO and LUMO orbitals for the coordinate compounds. For CP, FCP and ZCP, HOMOs comprise the perchlorate ion; this orbital is localized mainly on the isolated electron pair at the O atom in the perchlorate group. From the NBO results, the negative charge for each perchlorate ion is approximately -1 .

Fig. 2 HOMO and LUMO orbitals of the title compounds. First-principles study on energetic complexes (II): (5-cyanotetrazolato- N^2) pentaammine cobalt (III) perchlorate (CP) and its transition metal (Ni/Fe/Zn) perchlorate analogues**Table 6** The calculated eigenvalues of LUMO and HOMO and their energy gap for the title compounds

Energy/eV	CP	FCP	NCP	ZCP
E_{HOMO}	-6.981	-6.691	-6.376	-7.065
E_{LUMO}	-2.400	-4.080	-5.375	-2.400
ΔE	4.582	2.610	1.001	4.665

Therefore, in CP, FCP and ZCP, electron transit from HOMO to LUMO will lead to the formation of ClO_4 free radicals and then rapid decomposition or explosion. Both the NCP HOMOs are mainly around the central metal–ligand bond. Moreover, LUMOs for CP, NCP and FCP comprise the metal–ligand bond. However, the ZCP LUMO is centered on the cyano-tetrazole atoms.

The LUMO and HOMO eigenvalues and their energy gap for the title compounds are shown in Table 6. According to the calculation, the energy band gap ΔE (translation from HOMO to LUMO) for the molecules decreases in the order $\text{ZCP} > \text{CP} > \text{FCP} > \text{NCP}$. For NCP, both HOMO and LUMO are nearly composed of the same atoms, so electron transition is easy. The cyano-tetrazole ring that makes up the LUMO of ZCP is a π -conjugated system and electron transition is difficult, so the energy gap for this compound is the highest.

Conclusions

We used computational methods to clarify the characterization of CP and Ni, Fe and Zn analogues. Bond lengths and angles were calculated using the TPSS/6–31G** method and the results compared well with experimental values. Electronic structure analyses revealed that CP has the strongest covalent character and ZP has the weakest. HOMO and LUMO orbitals were also visualized. Atomic charges, donor–acceptor interactions and energy band gaps were determined. The calculated data and simulations provide useful information for the synthesis of coordinate compounds.

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