Acta et Commentationes, Exact and Natural Sciences
Volume 21(1), 2026, Pages 29–38
UDC: 547.022.1/.4:579.84/.86

DOI: 10.36120/2587-3644.v21i1.29-38
ISSN: 2537-6284 E-ISSN: 2587-3644

Template synthesis, crystal and electronic structure of trinuclear Co(II) complex based on new 15-dentate macrocyclic Schiff base ligand

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Abstract. The new 15-dentate macrocyclic Schiff base ligand, derived from 2,6-diacetylpyridine and malonic acid dihydrazide, was synthesized using a template condensation approach. The deprotonation-protonation behaviour of this polydentate macrocyclic Schiff base in Co(II) coordination compounds was investigated and exploited as a strategy for the assembly of a novel trinuclear macrocyclic complex. The chemical composition and crystal structure of the resulting complex $[Co_3(H_6L)(H_2O)_6](ClO_4)_6 \cdot 8H_2O$ were elucidated by single-crystal X-ray diffraction, infrared spectroscopy, and elemental analysis. The TB2J python package and SIESTA code were used to analyse the magnetic exchange interactions in trinuclear macrocyclic Co(II) complex in the crystal.
Keywords: macrocyclic ligand, Co(II) complex, X-ray diffraction, 15-dentate.

Sinteza templată, structura cristalină și electronică a complexului trinuclear al Co(II) în baza ligandului macrociclic 15-dentat de tip bază Schiff

Rezumat. Prin metoda sintezei templată, a fost obținut un nou ligand macrociclic 15-dentat nou de tip bază Schiff, derivat din 2,6-diacetilpiridină și dihidrazida acidului malonic. A fost investigat comportamentul de deprotonare-protonare al ligandului macrociclic polidentat în compușii coordinativi ai Co(II), acesta fiind valorificat drept strategie pentru asamblarea unui nou complex macrociclic trinuclear $[Co_3(H_6L)(H_2O)_6](ClO_4)_6 \cdot 8H_2O$. Compoziția chimică și structura cristalină a complexului obținut, au fost determinate prin difracție cu raze X pe monocristal, spectroscopie în infraroșu și analiză elementală. Interacțiunile de schimb magnetic în complexul macrociclic trinuclear al Co(II) în stare cristalină au fost investigate utilizând pachetul software TB2J și programul Siesta.
Cuvinte-cheie: ligand macrociclic, complex de Co(II), difracţie de raze X, 15-dentat.

1. Introduction

Although the synthesis of macrocyclic compounds dates back nearly a century, recent studies indicate a renewed surge of scientific interest in coordination complexes incorporating macrocyclic ligands. This area of coordination chemistry remains at an early stage of systematic exploration [1].

Over the past decades, a large number of macrocyclic compounds have been synthesized and investigated, attracting the attention of specialists from various fields of science and technology due to their distinctive structural features and physicochemical properties. These characteristics form the basis for their application as catalysts, magnetic materials, semiconductors, dielectrics, analytical reagents, dyes, and medicinal applications.

Macrocyclic ligands and their metal complexes exhibit close similarities to certain natural biological systems such as vitamin B_{12}, hemoglobin, and chlorophyll. They emulate naturally occurring species, including the porphyrinic rings found in hemoglobin and chlorophyll, as well as the corrin macrocycle characteristic of vitamin B_{12}. For this reason, such ligands are classified as bioligands, and their corresponding metal complexes as biocomplexes. This structural and functional resemblance between natural and synthetic macrocyclic complexes provides these systems with a broad spectrum of potential applications.

At present, scientific interest in coordination compounds containing macrocyclic ligands is undergoing a marked increase. The diverse properties and broad applicability of macrocyclic complexes increasingly attract the attention of researchers from various fields of science and technology. Such interest is driven by their distinctive structural features and specific physicochemical properties, which underpin their application as catalysts, magnetic materials, semiconductors, dielectrics, analytical reagents, dyes, as well as compounds with promising potential in biotechnology [2], [3], [4].

Macrocyclic coordination compounds are notable for their significant pharmaceutical and biomedical properties. They are involved in the development of biosensors, the catalysis of RNA cleavage, and dopamine detection, and they display a wide range of biological activities, including antibacterial, antifungal, anticancer, antitumor, antioxidant, anti-inflammatory, and antifertility effects [5], [6], [7].

However, it is well established that the synthesis of macrocyclic compounds depends on multiple factors, including the nature of the reactants and metal ions, as well as the reaction conditions and medium. The synthesis of cyclic compounds, especially those containing more than seven atoms in the ring, has always posed challenges for organic synthesis. The origin of these difficulties is attributed to the unfavorable entropy of the

reaction, resulting from the low probability that the two ends of the chain will come into contact to form a ring. Intermolecular reactions are more favourable and tend to predominate in such systems.

In many cases, cyclization reactions are not straightforward, since the presence of polyfunctional coordinating agents can give rise to competing polycondensation processes, resulting in the formation of acyclic polymers or oligomers. Another challenge arises from achieving cyclization at identical molar ratios but different stoichiometric combinations (e.g., [1+1], [2+2], [3+3], etc.) (Figure 1), as well as from the possibility of self-condensation of a single precursor molecule [8].

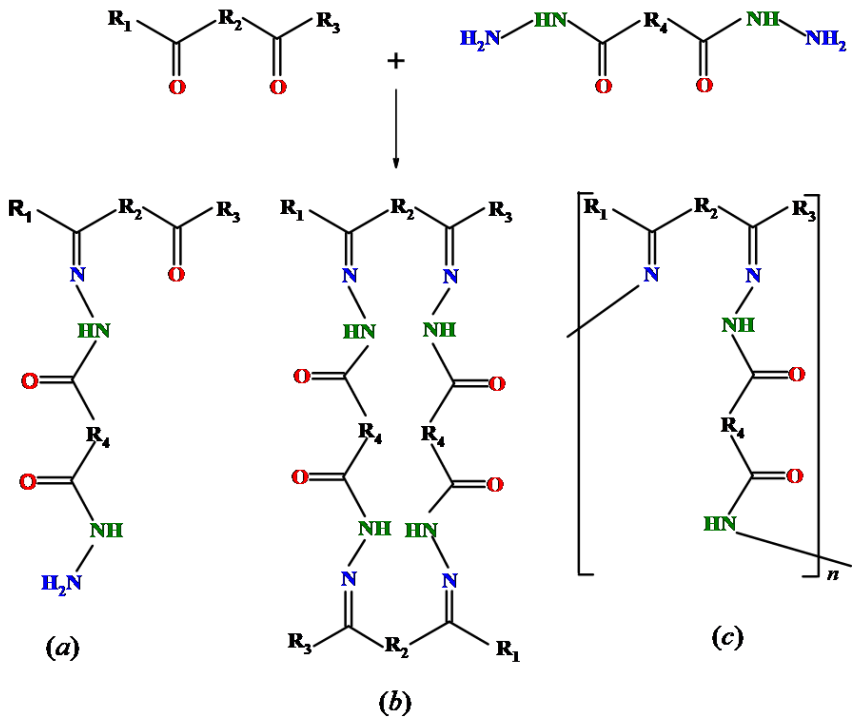

Figure 1. Scheme for the synthesis of Schiff base–type ligands *via* the condensation reaction of dicarbonyl compounds with dihydrazides in various proportions: [1+1] – monomeric ligand (*a*), [2+2] – macrocyclic ligand (*b*), and $[1+1]_n$ – oligomer (*c*)

Secondary processes may also occur, caused by the condensation of the already formed macrocyclic compound with the initial reactants. Such processes cannot be employed for the synthesis of modified macrocycles, as mixtures of products are obtained. These processes may arise when the valence of at least one of the heteroatoms exceeds two or when the molecules of the condensed reactants contain additional functional groups.

Template processes are those in which a metal ion or another centre possessing a defined stereochemistry and electronic state serves as a template, mold, or matrix for the assembly of products from appropriate building blocks, the synthesis of which is difficult or impossible under other conditions [1]. In the presence of the metal ion, the reactants are oriented in such way that the functional groups are positioned favorably for intramolecular interaction. Moreover, as a result of coordination, as indicated above, activation of the reactive groups occurs, and the process may proceed even in cases where its realization in the absence of the template ion would be impossible. Owing to template methodology, the synthesis and investigation of macrocyclic compounds have evolved from a chemical curiosity into a major field of contemporary chemistry. Template-directed assembly of coordinating agents on the metal-ion matrix remains one of the classical and most effective approaches for the synthesis of macrocyclic complexes.

This study describes the synthesis and a detailed spectral and structural characterization of a trinuclear macrocyclic complex of Co(II), derived from a 15-dentate macrocyclic Schiff base ligand, obtained from 2,6-diacetylpyridine and malonic acid dihydrazide, using the template synthesis method. A survey of the relevant literature and an examination of the Cambridge Structural Database (CSD) [9] reveal that, to date, macrocyclic Co(II) complexes incorporating Schiff base–type ligands have not been reported. The available data are limited to tetranuclear Co(II) complexes containing dihydrazide-based ligands [10], as well as a single example of a tetranuclear Co(II) complex with a macrocyclic architecture constructed from a 20-dentate Schiff base–type ligand and a tetranuclear Co(II) complex with a macrocyclic structure, obtained on the basis of a 20-dentate Schiff base–type ligand [11].

2. Results and discussion

In this paper, we describe the synthesis, crystal, and electronic structure of new macrocyclic trinuclear coordination compound of Co(II).

Following a strategy similar to recently reported synthetic approaches [11], a macrocyclic coordination compound of Co(II) was successfully obtained based on a macrocyclic ligand, resulting from the condensation of 2,6-diacetylpyridine (Dap) and malonic acid dihydrazide (DAM). The initial procedure for obtaining the trinuclear [3+3] type macrocyclic compound involved the template condensation of Dap and DAM in the presence of $Co(SCN)_2 \cdot 3H_2O$ (molar ratio 3:3:3) under reflux in an alcoholic medium, applying a protonation-deprotonation process of the macrocyclic ligand, achieved by treating the mixture with a 25% NH_4OH solution until a persistent ammonia odour was detected.

Subsequent treatment of the obtained product with a methanolic solution of perchloric acid allowed the synthesis of the macrocyclic complex $[Co_3(H_6L)(H_2O)_6](ClO_4)_6 \cdot 8H_2O$.

The chemical composition, molecular structure, and crystalline structure of macrocyclic complex were determined and confirmed by single-crystal X-ray diffraction, IR spectroscopy, and elemental analysis.

IR spectrum (ν, cm^{-1}): 3474 m, 3228 m, 2988 m, 2974 m, 2902 m, 1631 s, 1523 s, 1464 w, 1437 w, 1417 w, 1393 w, 1378 w, 1302 w, 1272 m, 1210 m, 1176 m, 1072 s, 1066 s, 1057 s, 1050 s, 925 m, 850 w, 809 m, 738 m, 722 m, 670 w, 622 w, 512 w, 455 w (where ***s*** – strong, **m** – medium and **w** – weak).

Elemental analysis for $C_{36}H_{62}Cl_6Co_3N_{15}O_{44}$.

Calculated, %: C 24.04; H 3.47; N 11.68.

Found, %: C 24.10; H 3.55; N 11.59.

The X-ray analysis established that the investigated compound crystallizes in the monoclinic space group $P2_1/m$ (Table 1).

Table 1. Crystallographic data and structure refinement details for $[Co_3(H_6L)(H_2O)_6](ClO_4)_6 \cdot 8H_2O$

CCDC number	**2526922**
Empirical formula	$C_{36}H_{62}Cl_6Co_3N_{15}O_{44}$
Crystal system	monoclinic
Space group	$P2_1/m$
a, Å	11.8354(4)
b, Å	20.9093(7)
c, Å	14.6001(7)
β, º	98.304(4)
V, $Å^3$	3575.2(2)
Z	2
D_c (g/cm^{-3})	1.671
Crystal size (mm^3)	0.38 x 0.18 x 0.15
Reflections collected/unique	12510/6788 [R(int) = 0.0339]
Parameters	520
GOF on F^2	1.007
R_1, wR_2 $[I > 2\sigma(I)]$	0.0905, 0.2568
R_1, wR_2 (all data)	0.1310, 0.3061

The asymmetric unit of the unit cell contains two metal atoms (one of which is located on the symmetry plane), two perchlorate $(ClO_4)^-$ anions in general positions, and two in special positions, with the central chlorine atoms situated on the symmetry plane, ½ of the neutral organic ligand H_2L, four water molecules coordinating to the metal atoms, two of which lie on a mirror plane, and 12 water molecules with varying occupancy factors (ranging from 0.5 to 0.2). As a result, the formula of the compound is $[Co_3(H_6L)(H_2O)_6](ClO_4)_6 \cdot 8H_2O$.

The central atom (Co1, Co2) in macrocyclic complex is heptacoordinated, with the coordination geometry of the Co(II) ion being a centrosymmetric pentagonal bipyramid. The coordination environment is $[CoN_3O_4]$, involving the Schiff base-type macrocyclic ligand and the oxygen atoms of the water molecules coordinated in the apical positions (Table 2).

Table 2. Bond distances in the coordination polyhedron of Co(1) and Co(2) atoms in the macrocyclic complex $[Co_3(H_6L)(H_2O)_6](ClO_4)_6 \cdot 8H_2O$

Bond	**Distance, Å**	**Bond**	**Distance, Å**
Co(1)–O(1)	2.228(5)	Co(2)–O(3)	2.201(5)
Co(1)–O(2)	2.169(5)	Co(2)–N(7)	2.176(6)
Co(1)–N(2)	2.185(5)	Co(2)–N(8)	2.184(8)
Co(1)–N(3)	2.168(5)	Co(2)–O(3*w*)	2.087(7)
Co(1)–N(4)	2.198(5)	Co(2)–O(4*w*)	2.166(7)
Co(1)–O(1*w*)	2.113(5)	–	–
Co(1)–O(2*w*)	2.132(6)	–	–

Macrocyclic complex has an ionic crystalline structure composed of complex cation $[Co_3(H_6L)(H_2O)_6]^{6+}$, ClO_4^- anions, and crystallization water molecules in a molar ratio of 1:6:8. The Schiff base-type macrocyclic ligand (H_6L) is coordinated in the neutral mode and the keto form, so that the C=O bond lengths range from 1.208 to 1.249 Å (Figure 2).

In the crystal the complex cations $[Co_3(H_6L)(H_2O)_6]^{6+}$, as proton donors, inorganic ClO_4^- anions, crystallization and coordinated water molecules (O1*w*, O2*w*), as well as the =NH groups are connected through a complicated network of hydrogen bonds. The IR spectrum of macrocyclic complex $[Co_3(H_6L)(H_2O)_6](ClO_4)_6 \cdot 8H_2O$ shows a broad band of medium intensity at 3229 cm^{-1}, corresponding to ν(OH) coordinated water. A broad, intense band at 1631 cm^{-1} corresponds to $\nu(C{=}O)_{coord}$ + $\nu(C{=}N)_{azomethine}$ + $\nu(C{=}C)_{aromatic}$, indicating coordination of the macrocyclic ligand in the keto form.

An intense and broad band is observed at 1523 cm^{-1}, characteristic of the combined $\nu(C{=}C)_{aromatic}$ + $\delta(NH)$ vibrations.

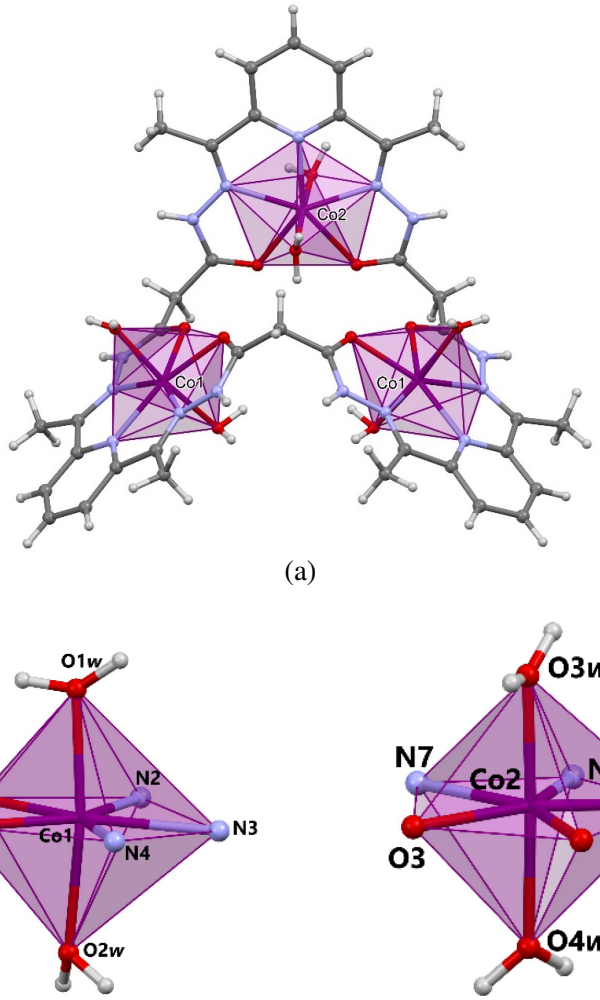

Figure 2. **(a)** Structure of the trinuclear macrocyclic complex cation $[Co_3(H_6L)(H_2O)_6]^{6+}$. **(b)** Coordination geometry of Co(II) ions with partial atom labelling scheme

The asymmetric and symmetric bending vibrations $\delta_{as}(CH_3)$ and $\delta_s(CH_3)$ appear at 1437 cm^{-1} and 1378 cm^{-1}, respectively. The most intense band in the spectrum of this macrocyclic complex appears in the 1072–1050 cm^{-1} region and it is attributed to the characteristic stretching vibrations of the perchlorate anion ($\nu(ClO_4^-)$). Out-of-plane δ(C–H) bending vibrations for three adjacent hydrogen atoms are observed at 809 cm^{-1}.

Medium-to-weak intensity bands at 511 cm^{-1} and 455 cm^{-1} are assigned to ν(Co–N) and ν(Co–O) vibrations, respectively.

It is known that high spin Co(II) complexes, with a spin S=3/2 ground state, usually demonstrate the weak antiferromagnetic interactions in such system as dinuclear and layered systems. Therefore, in the framework of Density Functional Theory, the TB2J python package [12] and SIESTA code [13] were used to analyse the magnetic exchange interactions in trinuclear macrocyclic Co(II) complex in the crystal, containing both cations and anions, joined by extensive net of hydrogen bonds. The calculated spin-polarized density of states (DOS) and projected DOS (Figure 3) revealed that in studied complex both spin-up and spin-down spin channels are the spin-gapless channels.

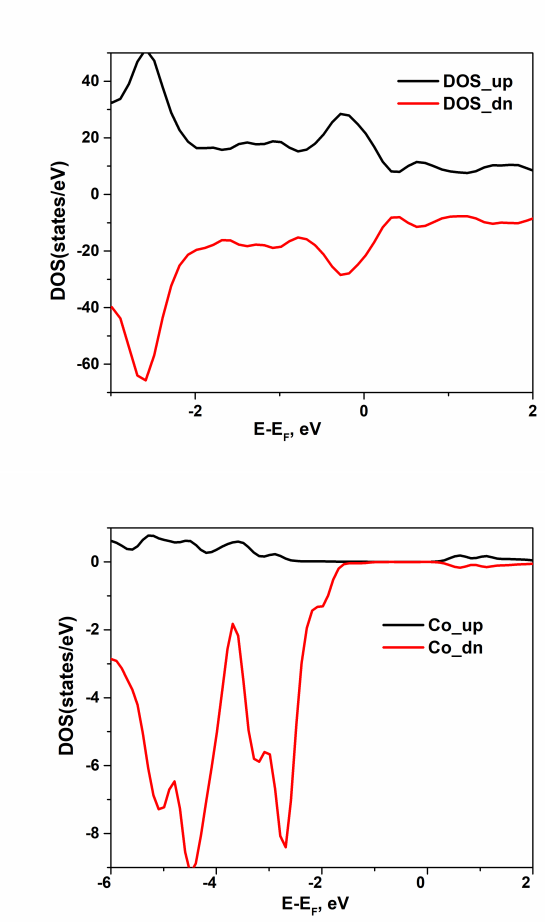

Figure 3. Spin-up and spin-down density of states and projected DOS of studied compound

The spin-up and spin-down states of Co(II) ions are delocalized and such hybridization between metals and ligands atoms could provide the magnetic exchange between ions.

The weak ferromagnetic interaction (0.018 cm^{-1}) is observed for atoms Co1...Co2, while for Co1...Co1' and Co1...Co1' (neighboring complex) there is antiferromagnetic coupling with -0.005 and -0.003 cm^{-1}, the corresponding distances are equal to 6.481, 6.939 and 8.700 Å.

3. Conclusions

The trinuclear macrocyclic complex $[Co_3(H_6L)(H_2O)_6](ClO_4)_6 \cdot 8H_2O$ was synthesized and characterized by applying the template condensation strategy of 2,6-diacetylpyridine and malonic acid dihydrazide on a Co(II) matrix.

This compound has an ionic structure, in which the 15-dentate macrocyclic ligand is stabilized in the ketone form.

The absence of these types of compounds in BDSC, as well as in the specialized literature, highlights the innovative nature and originality of the macrocyclic complex obtained in this study.

The isotropic exchange parameters between Co(II) ions were calculated using the Heisenberg model from Density Functional Theory and it was observed both weak ferro- and antiferromagnetic coupling.

The obtained results contribute significantly to the deepening and expansion of knowledge on the coordination chemistry of Co(II), especially in the context of designing macrocyclic supramolecular structures with potential applications in fields such as catalysis and the development of advanced functional materials.

Acknowledgements. *The authors are grateful to subprograms financed by the Ministry of Education and Research of Republic of Moldova: 010602 and 011202.*

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Received: March 26, 2026 *Accepted: July 01, 2026*

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