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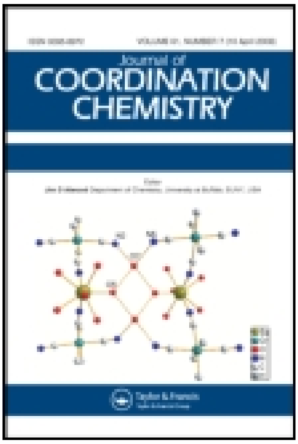

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Synthesis, spectroscopic, and thermal analyses of binuclear mixed ligand Co(II) and Ni(II) complexes

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Synthesis, spectroscopic, and thermal analyses of binuclear mixed ligand Co(II) and Ni(II) complexes

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Two isostructural mixed ligand binuclear metal complexes, $[Co_2(\mu_2\text{-}H_2O)(\mu_2\text{-}L_1)_2(L_1)_2(L_2)_2]0.5C_7H_8$ (**1**) and $[Ni_2(\mu_2\text{-}H_2O)(\mu_2\text{-}L_1)_2(L_1)_2(L_2)_2]0.5C_6H_6$ (**2**) ($L_1 = CCl_3COO^-$, $L_2 =$ *N*,*N*,*N*′,*N*′-tetramethylethylenediamine(tmen)), have been synthesized and structurally characterized by X-ray crystallography. Complex **1** crystallizes in orthorhombic system with space group *Pbcn* and **2** crystallizes in orthorhombic system with space group *Pbca*. L_1 has two different coordination modes, μ_2-bidentate bridging-(0,0′) and monodentate-(0); L_2 coordinates in chelating mode (*N*,*N*′) in both **1** and **2**. The coordination geometry around metals is highly distorted octahedral. The elemental, spectral (IR, diffused electronic spectra), physical (thermogravimetry, molar conductivity) and magnetic moment studies are reported. Molar conductance measurements of **1** and **2** in acetonitrile correspond to the non-electrolytic nature of the complexes.

Keywords: Cobalt(II); Nickel(II); Mixed ligand complexes; X-ray crystallography

1. Introduction

Organic, inorganic carboxylates and their derivatives are widely used in modern industrial, biological, and synthetic processes [1–17]. The universality of carboxylic acids as ligands and the binding of their acid residues (monodentate and bidentate either by chelation, or by forming bridges) favor the existence of a great variety of carboxylate-based complexes. The nature of carboxylate coordination in these complexes has been well explained [18, 19].

Transition metal carboxylate complexes, particularly with oxygen and nitrogen donors, are of special interest [20–24] because of their ability to possess unusual structures and their sensitivity to molecular environments. Excellent work has been devoted to new synthetic pathways and structural aspects of the resulting system, highlighting the role of coordinating ligands [25–27]. The topologies of such

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coordination complexes are mainly based on metal–ligand covalent bonds [28] and multiple weak non-covalent forces like hydrogen bonding [29, 30].

As part of an on-going study related to transition metal carboxylates, we report the preparation and structural characterization of mixed ligand complexes $[Co_2(\mu_2\text{-}H_2O)(\mu_2\text{-}L_1)_2(L_1)_2(L_2)_2]0.5C_7H_8$ (**1**) and $[Ni_2(\mu_2\text{-}H_2O)(\mu_2\text{-}L_1)_2(L_1)_2(L_2)_2]0.5C_6H_6$ (**2**). The skeletal structure of **1**, although reported by U. Turpeinen *et al.* [31] (space group $P2_1/c$) comes out to be different in this study where the complex crystallizes with distorted toluene in the orthorhombic system with space group *Pbcn* having different unit cell parameters. An attempt has been made to undertake complete characterization, including thermal studies which was lacking previously. Complexes **1** and **2** have been characterized by FT-IR spectroscopy, diffuse electronic spectroscopy, thermal analysis, elemental analysis, magnetic moment studies, molar conductivity, and single-crystal X-ray diffraction.

2. Experimental

2.1. *Materials*

Commercially available analytical grade reagents were used throughout this study without purification. Cobalt(II) trichloroacetate and nickel(II) trichloroacetate used in this research work were prepared according to the method described in the literature [32].

2.2. *Physical measurements*

Elemental microanalyses of recrystallized complexes for C, H, and N were carried out on an automatic Perkin–Elmer 2400 CHN elemental analyzer. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer RXFT-IR spectrophotometer from 4000 to $400\,cm^{-1}$. Solid-state diffuse reflectance spectra were recorded on a Hitachi-330 UV-Visible spectrophotometer equipped with a 150 mm DIA integrating sphere accessory. Conductance measurements were performed on a Pico conductivity meter (Model CNO4091201, Lab India). Magnetic susceptibility measurements were made on a Gouy Balance at R.T. The specifications of the apparatus used for magnetic susceptibility were: Pole face diameter, 10.2 cm; Pole gap, 4.0 cm; Current, 7.0 amp; Magnetic field, 6 kilogauss. The thermogravimetric (TG) analysis was carried out in a dynamic nitrogen atmosphere ($20\,mL\,min^{-1}$) with a heating rate of $5°C\,min^{-1}$ using a Perkin Elmer STA 6000 simultaneous thermal analyzer. Cobalt, nickel, and chlorine were determined gravimetrically by standard literature methods [33].

2.2.1. X-ray crystallography. Suitable crystals of $[Co_2(\mu_2\text{-}H_2O)(\mu_2\text{-}L_1)_2(L_1)_2(L_2)_2]$ $0.5C_7H_8$ (**1**) and $[Ni_2(\mu_2\text{-}H_2O)(\mu_2\text{-}L_1)_2(L_1)_2(L_2)_2]0.5C_6H_6$ (**2**) were mounted on glass fibers and used for data collection. Data were collected with a Bruker SMART APEX (Mo-Kα, 293 K) diffractometer. The data were processed with APEX2 [34] and corrected for absorption using SADABS [35]. The structures were solved by direct methods [36], which revealed the position of all non-hydrogen atoms, which were refined on F^2 by full-matrix least-squares using anisotropic-displacement parameters [37]. All hydrogens were located in difference Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 times those of the respective atom. For both **1** and **2**, the trichloromethyl of one μ_2-trichloroacetate is disordered over two positions with occupancies of 0.479(9) and 0.521(9) for **1** and 0.492(8) and 0.508(8) for **2**. The toluene in **1** is located on a two-fold axis and is disordered over two sites with equal occupancies. Geometric calculations were carried out with PLATON [38] and drawings were produced with PLATON [38] and MERCURY [39].

2.3. *Synthesis*

2.3.1. Synthesis of $[Co_2(\mu_2\text{-}H_2O)(\mu_2\text{-}L_1)_2(L_1)_2(L_2)_2]0.5C_7H_8$ (1). The complex was prepared by adding 250 mg (2.15 mmol) of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine to a suspension of 940 mg (1.07 mmol) cobalt(II) trichloroacetate in 20 mL dichloromethane. The contents were stirred for 15 min giving pink solution. Crude product was obtained by removing solvent under vacuum and crystals suitable for X-ray diffraction were obtained from toluene. The yield was 54.89% and melting point was 133–136°C.

2.3.2. Synthesis of $[Ni_2(\mu_2\text{-}H_2O)(\mu_2\text{-}L_1)_2(L_1)_2(L_2)_2]0.5C_6H_6$ (2). The complex was prepared by adding 159 mg (1.37 mmol) of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine to a suspension of 600 mg (0.685 mmol) nickel(II) trichloroacetate in 25 mL dichloromethane. The contents were continuously stirred for 15 min resulting in a green solution. Solvent was removed under vacuum and crude product was recrystallized from benzene after several unsuccessful attempts of recrystallization from toluene. Dark green transparent crystals suitable for X-ray diffraction were obtained over a period of 4 days by slow evaporation of solvent at room temperature. The yield was 65.21% and the melting point was 124–127°C.

3. Results and discussion

The binuclear complexes **1** and **2** are soluble in common organic solvents. Analytical and physiochemical data are given in table 1. The molar conductivities in acetonitrile indicate non-electrolytes. Magnetic moment data are found in the range corresponding to high spin distorted octahedral complexes.

3.1. *Infrared spectra*

FT-IR spectra of **1** and **2** are recorded as KBr pellets (Supplementary material). Almost identical spectra for the complexes suggest similar structures. In the IR spectrum, weak, broad bands at 3384 cm^{-1} in **1** and 3428 cm^{-1} in **2** are assignable to lattice water. The broadness and relatively low frequency indicates presence of the hydrogen bonding in the complexes [40]. Peaks from 3040 to 2800 cm^{-1} correspond to ν(CH) due to $-CH_2-$, $-CH_3-$ of tmen. $\nu_{as}(CO_2^-)$ at 1635 and 1663 cm^{-1} and $\nu_s(CO_2^-)$ at 1352 and 1472 cm^{-1},

Table 1. Physiochemical properties of **1** and **2**.

Complex	Molecular formula	Molecular weight (yield)	Color	Λ_m[a]	μ_{eff}[b]	Elemental analyses; Found (Calcd) %				
						C	H	N	Cl	M
1 $[Co_2(\mu_2\text{-}H_2O)(\mu_2\text{-}L_1)_2(L_1)_2(L_2)_2]0.5C_7H_8$	$C_{23.5}H_{38}Cl_{12}Co_2N_4O_9$	1063.84(54.89)	Pink	9.119	4.92	26.42 (26.50)	3.49 (3.57)	5.18 (5.26)	39.43 (40.03)	11.04 (11.07)
2 $[Ni_2(\mu_2\text{-}H_2O)(\mu_2\text{-}L_1)_2(L_1)_2(L_2)_2]0.5C_6H_6$	$C_{23}H_{37}Cl_{12}N_4Ni_2O_9$	1056.39(54.89)	Green	9.235	3.12	25.83 (26.12)	3.40 (3.50)	5.21 (5.30)	40.02 (40.32)	11.07 (11.11)

[a] Molar conductance (Λ_m), ($Scm^2\,mol^{-1}$) was measured in $10^{-4}\,mol^{-1}\,cm^{-1}$ in CH_3CN solvent.
[b] Magnetic moment, μ_{eff} (B.M.).

with a frequency difference ($\Delta\nu$ value) of 283 and 191 cm^{-1} for **1** and $\nu_{as}(CO_2^-)$ at 1635 and 1666 cm^{-1} and $\nu_s(CO_2^-)$ at 1354 and 1473 cm^{-1}, with a $\Delta\nu$ of 281 and 193 cm^{-1} for **2**, reflect the monodentate [41, 42] and bridging [43, 44] trichloroacetate. The band at 1685 cm^{-1} in free tmen shifts to ~1716 cm^{-1} in the complexes, indicating participation of nitrogens in coordination. The spectrum of the complexes are complicated from 1715 to 1025 cm^{-1}, due to simultaneous presence of ligands in variably coordinated modes (chelating tmen, bridging trichloroacetate, unidentate trichloroacetate, and bridging H_2O), which absorb in this region; thus many bands do not represent pure vibrations. The strong bands at 838 and ~800 cm^{-1} in **1** and **2** are assigned to C–Cl stretching vibrations in the complexes.

3.2. *Electronic spectra*

Diffuse reflectance spectra of **1** and **2** were recorded from 200 to 800 nm. The electronic spectra of both binuclear complexes are typical of a distorted octahedral environment about the metal in each case. The solid-state diffuse reflectance spectra of **1** and **2** show band maxima at 19,720 (21,056 sh), 16,200 sh cm^{-1} and at 29,890, 16,600, 14,100 sh cm^{-1}, respectively, in good agreement with known MN_2O_4 complexes having distorted octahedral geometry [45, 46]. Strong bands at 33,000 and 32,573 cm^{-1} in **1** and 42,550 and 44,220 cm^{-1} in **2** are attributed to charge-transfer bands.

3.3. *Magnetic susceptibility*

The room temperature magnetic susceptibilities (μ_{eff}) of **1** and **2**, 4.92 and 3.12 B.M., are within the ranges expected [47, 48]. These values are similar to known distorted octahedral cobalt(II) and nickel(II) coordination complexes [46].

3.4. *Molar conductance*

The conductances of **1** and **2** were carried out at 25°C in acetonitrile. The extrapolation of C to zero for both complexes gave insignificant values of Λ_m, 9.119 for 1 and 9.235 S cm^2 mol^{-1} for **2**, indicating non-ionic species [49] in solution as confirmed by the crystal structural studies.

3.5. *TG analyses*

Supplementary material shows the TG analyses performed on **1** and **2** under nitrogen atmosphere. Complex **1** is decomposed thermally in four successive decomposition steps from 36°C to 850°C. The curve in various steps indicate that the products formed at the end of each step are not stable and readily decompose further with increase in temperature. No reasonably flat plateau is obtained throughout the thermogram and almost continuous weight loss occurs, once the thermal decomposition begins. The first step (obs = 47.59%, Calcd = 47.46%) from 120°C to 154°C is accounted to loss of 0.5 C_7H_8, one bridging H_2O, one tmen, and two trichloroacetates. The second decomposition from 154°C to 382°C (obs = 26.14%, Calcd = 26.17%) may be attributed to liberation of one tmen and one trichloroacetate. Mass loss from 382°C to 592°C

Table 2. Crystal data and structure refinement parameters for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{23.5}H_{38}Cl_{12}Co_2N_4O_9$	$C_{23}H_{37}Cl_{12}N_4Ni_2O_9$
Formula weight	1063.84	1056.39
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbcn*	*Pbca*
Unit cell dimensions (Å, °)		
a	32.631(2)	11.6154(9)
b	11.6991(7)	22.6377(17)
c	22.8020(14)	32.427(2)
α	90	90
β	90	90
γ	90	90
Volume (Å^3), *Z*	8704.7(9), 8	8526.4(11), 8
Calculated density (g cm^{-3})	1.624	1.646
F(000)	4296	4280
Crystal size (mm^3)	0.16 × 0.12 × 0.11	0.18 × 0.14 × 0.08
θ range for data collection (°)	1.85–25.20	1.26–25.00
Reflections collected	45,735	43,964
Independent reflections	7823	7505
Max. and min. transmission	0.7456 and 0.6045	0.7454 and 0.6243
Goodness-of-fit on F^2	1.037	1.018
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0574$, $wR_2 = 0.1408$	$R_1 = 0.0587$, $wR_2 = 0.1257$

corresponds to fragments of trichloroacetate without donor atoms (obs = 11.93%, 12.26%). The residual ligand is removed in the last step from 592°C to 850°C (obs = 2.76%, Calcd = 3.01%). The total mass loss (obs = 88.43%, Calcd = 88.92%) suggests metallic cobalt as residue.

The TG curve of **2** represents four steps of decomposition from 37°C to 850°C. The first (obs = 47.70%, Calcd = 47.14%), occurring between 92°C and 127°C, corresponds to removal of 0.5 C_6H_6, one H_2O, two trichloroacetates, and one tmen. The second and third decomposition steps (obs = 19.77%, Calcd = 18.67%); (obs = 8.16%, Calcd = 7.69%) from 127°C to 285°C and 285°C to 342°C may be attributed to successive losses of 0.5 trichloroacetate, one tmen, and another 0.5 trichloroacetate. Between 342°C and 534°C is decomposition of coordinated trichloroacetate (obs = 14.82%, Calcd = 15.38%) with formation of nickel metal as the final product. The total mass loss observed up to 850°C (90.42%) agrees well with the theoretical value (88.89%) calculated by considering metallic nickel as residue.

3.6. *X-ray studies*

Crystal data for **1** and **2** are shown in table 2. Selected bond lengths and angles are listed in table 3. Both structures are formed from dimers and solvent (figure 1). Each bimetallic center is assembled by water and two carboxylate bridges. The coordination sphere of each metal is further coordinated by a monodentate carboxylate and two tmen N-donors, forming two equivalent distorted MN_2O_4 octahedra. The bimetallic molecule lies on a pseudo two-fold axis passing through the bridging water oxygen. Intramolecular H-bonding involving the bridging water and the two monodentate carboxylates stabilize the dimeric structures. In both complexes, the two five-membered

Table 3. Selected interatomic bonds lengths (Å) and *trans* angles (°) in **1** and **2**.

1			
Co1–O11	2.048(3)	O11–Co1–O21	178.31(15)
Co1–O21	2.062(4)	O1–Co1–N41	173.85(17)
Co1–O1	2.103(4)	O10–Co1–N46	176.83(16)
Co1–O10	2.176(3)		
Co1–N46	2.185(5)		
Co1–N41	2.211(5)		
Co2–O3	2.058(3)	O3–Co2–O31	177.51(13)
Co2–O31	2.067(3)	O13–Co2–N51	172.57(16)
Co2–O13	2.079(4)	O10–Co2–N56	179.27(15)
Co2–O10	2.176(3)		
Co2–N56	2.182(4)		
Co2–N51	2.201(4)		
2			
Ni1–O11	2.034(4)	O11–Ni1–O21	177.36(17)
Ni1–O21	2.042(4)	O1–Ni1–N41	174.24(19)
Ni1–O1	2.063(4)	O10–Ni1–N46	177.32(19)
Ni1–O10	2.128(3)		
Ni1–N46	2.130(5)		
Ni1–N41	2.151(5)		
Ni2–O3	2.028(4)	O3–Ni2–O31	177.15(15)
Ni2–O31	2.061(4)	O13–Ni2–N51	173.18(17)
Ni2–O13	2.049(4)	O10–Ni2–N56	178.75(16)
Ni2–O10	2.122(3)		
Ni2–N56	2.143(5)		
Ni2–N51	2.139(4)		

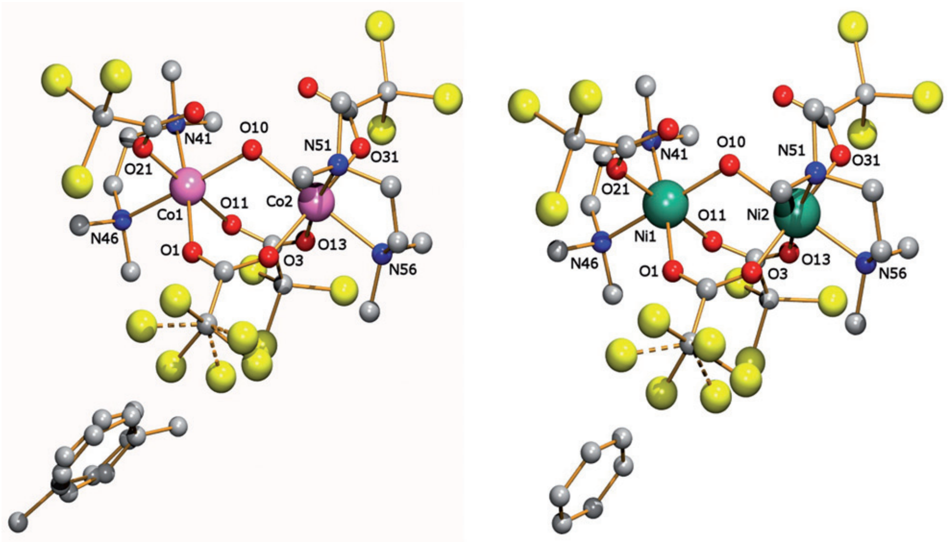

Figure 1. Asymmetric unit of **1** (left) and **2** (right) with the numbering of the coordination atoms.

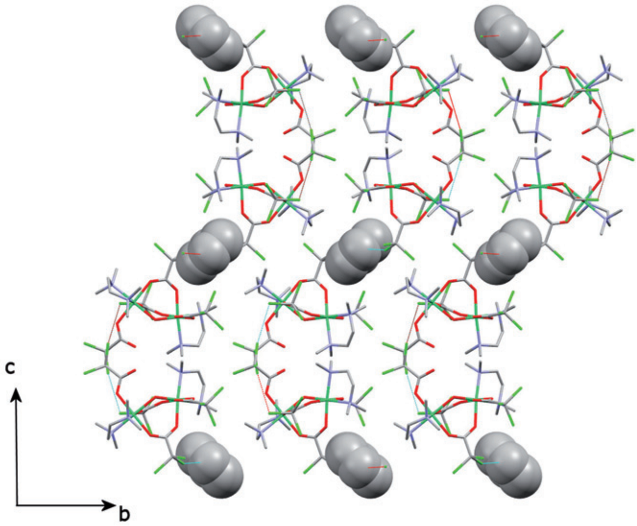

Figure 2. View in the *bc* plane of the 3D architecture in **2** showing hydrogen bonding and Cl···Cl interactions. Solvent molecules are represented as spacefills.

rings formed by the ethylenediamine fragment adopt twist conformation with puckering parameters [50] for **1**: ring Co1/N41/C44/C45/N46: $q^2 = 0.209(11)$ Å, $\varphi = 264.7(17)°$; ring Co2/N51/C54/C55/N56: $q^2 = 0.368(7)$ Å, $\varphi = 265.0(7)°$; for **2**: ring Ni1/N41/C44/C45/N46: $q^2 = 0.218(11)$ Å, $\varphi = 265.1(16)°$; ring Ni2/N51/C54/C55/N56: $q^2 = 0.434(7)$ Å, $\varphi = 264.4(6)°$. Molecules are linked via intermolecular C–H···Cl hydrogen bonds between solvent and dimeric units. In addition, intermolecular Cl···Cl interactions are observed (figure 2) falling in the typical range of halogen–halogen interactions [51, 52], resulting in a 3D architecture.

4. Conclusion

Here, we present the synthesis, crystal structure, physiochemical and spectroscopic studies of dimeric cobalt(II) and nickel(II) complexes with trichloroacetate and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine. Each dimeric unit consists of four monodentate trichloroacetates, two bridging trichloroacetates, two chelating tmen, and one bridging H_2O. The geometry of the complexes is distorted octahedral. The crystal packing of the complexes is a composite of intramolecular hydrogen-bonding interactions between bridging water and monodentate trichloroacetate and intermolecular Cl···Cl and C–H···Cl hydrogen-bonding interactions stabilizing the dimeric structures.

Supplementary material

CCDC 778291 and 778292 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/

conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk

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