



Dedicated to Professor Cristian Silvestru
on the occasion of his 65th anniversary

NEW MIXED-VALENCE DISK-LIKE [Co₇] CLUSTERS WITH AMINOALCOHOL LIGANDS^{**}

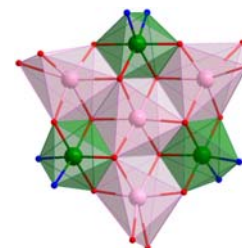
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Received March 2, 2020

Aerobic reactions of Co(AcO)₂·4H₂O with N-methyldiethanolamine (m-H₂dea) or N-ethyldiethanolamine (e-H₂dea), in the presence of NaClO₄, afford two new compounds, [Co^{II}₄Co^{III}₃(m-dea)₆(AcO)₃](ClO₄)₂·8H₂O (**1**), [Co^{II}₄Co^{III}₃(e-dea)₆(AcO)₃](ClO₄)₂ (**2**). Starting from Co(ClO₄)₂·6H₂O, diethanolamine (H₂dea) and pyridine-3-carboxylic acid (nicotinic acid = Hna) or pyridine-4-carboxylic acid (isonicotinic acid = Hina), two other mixed valence Co^{II}/Co^{III} complexes, [Co^{III}₃Co^{II}₄(dea)₆(na)₃](ClO₄)₂·CH₃CH₂OH·H₂O (**3**) and [Co^{III}₃Co^{II}₄(dea)₆(ina)₃](ClO₄)₂ (**4**), have been obtained. The four compounds have been characterized by single crystal X-ray diffraction, elemental analysis, IR and UV-VIS spectroscopy. The four new compounds are members of the family of homometallic mixed-valence Co^{II}/Co^{III} featuring a disk shape.



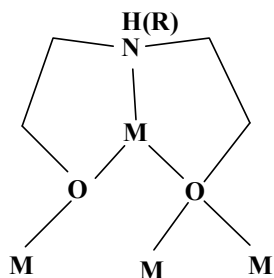
INTRODUCTION

Aminoalcohols are largely employed to generate homo- and heterometallic alkoxido-bridged clusters.^{1a-c} The aggregation of multimetallic complexes using such ligands is favored by their chelating behavior and, especially, by the ability of the alkoxido group to bridge two or three metal ions (Scheme 1). Numerous aminoalcohols, carrying one or more OH groups, have been employed, among these monethanolamine, monopropanolamine, diethanolamine, and triethanolamine being very popular.^{2a-f} The deprotonation of one or more OH groups can occur either spontaneously, or in the presence of a base, currently triethylamine. A plethora of clusters with various nuclearities has been

obtained through self-assembly processes involving aminoalcohols and 3d metal ions (cobalt, manganese, iron). The anions arising from the starting metal salts, the solvent molecules or other coligands play an important role on the nature of the resulting compounds (nuclearity, topology of the metal centers). This synthetic approach has been extended towards heterometallic clusters, containing either two different 3d metal ions,^{3a-d} or 3d and 4f metal ions.^{4a-d} An interesting synthetic approach leading to heterometallic alkoxido-bridged clusters has been developed by Nesterov, Vassilyeva, Kokozay *et al.*^{5a-d} It consists of one-pot reactions between metal salts, metal powders (most frequently copper) and aminoalcohols.

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** Supplementary information on <http://web.icf.ro/rrch/> or <http://revroum.lew.ro>



Scheme 1 – Deprotonated aminoalcohol ligand and its binding modes in polynuclear complexes.

When Mn^{II} or Co^{II} salts are employed, the resulting homometallic clusters contain the metal ions in different oxidation states: Mn^{II} - Mn^{III} ,^{6a-d} Co^{II} - Co^{III} .^{7a-g} The basicity of the aminoalcohols favors the oxidation of the divalent metal ions, and their chelating ability prevents the formation of the corresponding oxides. Let us focus here on the particular case of cobalt, selecting several representative examples. The reaction between $CoCl_2$ and N,N-Bis(2-aminoethyl)ethanolamine, abbreviated as HL, in THF, affords a binuclear cobalt complex, $[Co^{III}(\mu-OH)Co^{III}(HL)](Co^{II}Cl_4)Cl$.^{7a} Hosseini *et al.* have reported heterocubane $Co^{II/III}$ compounds $[Co^{II}_2Co^{III}_2(tea)_2(py)_2(NO_3)_4] \cdot 2CH_3CN$, $[Co^{II}_2Co^{III}_2(\mu_3-OH)_2(Htea)_2(bpy)_4](NO_3)_4$, and $[Co^{II}_2Co^{III}_2(\mu_3-OH)_2(Htea)_2(phen)_4](NO_3)_4 \cdot 2CH_3CN \cdot 2CH_3OH$ (H_3tea = triethanolamine and py = pyridine, bpy = 2,2'-bipyridine and $phen$ = 1,10-phenanthroline).^{7b} Das and Shivashankar have synthesised two tetranuclear complexes, $[Co_4(teaH)_2(teaH_2)_2(OAc)_2] \cdot 2(CH_3)_2CO$ and $[Co_4(dea)_2(deaH_2)_2(AcO)_6] \cdot 3H_2O$ by reacting the acetone solution of $Co(AcO)_2 \cdot 4H_2O$ with triethanolamine and diethanolamine, respectively.^{7c} Scheurer and coworkers have obtained different types of Co^{II} cubanes: $[Co^{II}_4(Cl)_4(HL)_4]$ (HL = N-alkyl-substituted diethanolamine).^{7d} Other tetranuclear complexes have been reported by Siddiqi *et al.*, $[Co_4(\mu_3-OH)_2(\mu_2-dea)_2(AA)_4] \cdot 4Cl \cdot 8H_2O$, with a defect dicubane topology and two Co^{II} and two Co^{III} ions, where AA = bpy and $phen$, respectively.^{7e} A hexanuclear $Co^{II/III}$ cluster has been synthesised by Alley *et al.*, starting from $Co(OAc)_2$ and 2-amino-2-methyl-1,3-propanediol ($ampd$), in a mixture of solvents (methanol/water), the result being $[Co^{II}_4Co^{III}_2(H_2O)(MeOH)(AcO)_6(ampd)_4]$.^{7f} Another hexanuclear complex, $[Co^{II}_4Co^{III}_2(dea)_2(Hdea)_4(piv)_4](ClO_4)_2 \cdot H_2O$, has been reported by us.^{7g} Several other heptanuclear

cobalt complexes with a disk shape,⁸⁻¹² have been synthesized with cobalt ions in different oxidation states and a variety of ligands: Co^{II}_7 ,^{8a-j} $Co^{II}_6Co^{III}$,^{9a-d} $Co^{II}_5Co^{III}_2$,^{10a} $Co^{II}_4Co^{III}_3$,^{11a-e} and $Co^{II}_3Co^{III}_4$.¹²

In previous paper we have reported on a Co^{II}/Co^{III} heptanuclear cluster with diethanolamine and acetate as ligands, $[Co^{II}_4Co^{III}_3(dea)_6(AcO)_3](ClO_4)_{0.75} \cdot (AcO)_{1.75} \cdot 0.5H_2O$.^{11c} In this paper we report on four new mixed-valence heptanuclear Co^{II}/Co^{III} clusters, which are obtained using diethanolamine, diethanolamine derivatives (N-methyldiethanolamine = m-H₂dea, N-ethyldiethanolamine = e-H₂dea) and carboxylato coligands (nicotinato = na, isonicotinato = ina).

RESULTS AND DISCUSSION

Four new mixed valence Co^{II}/Co^{III} heptanuclear clusters have been obtained and characterized. The first two compounds, $[Co^{II}_4Co^{III}_3(m-dea)_6(AcO)_3](ClO_4)_2 \cdot 8H_2O$ (**1**) and $[Co^{II}_4Co^{III}_3(e-dea)_6(AcO)_3](ClO_4)_2$ (**2**), have been aggregated by the aerobic reaction of cobalt(II) acetate tetrahydrate and N-methyldiethanolamine (m-H₂dea) (**1**) and cobalt(II) acetate tetrahydrate and N-ethyldiethanolamine (e-H₂dea) for (**2**), in the presence of AcONa and NaClO₄. Compounds $[Co^{III}_3Co^{II}_4(dea)_6(na)_3](ClO_4)_2 \cdot CH_3CH_2OH \cdot H_2O$ (**3**) and $[Co^{III}_3Co^{II}_4(dea)_6(ina)_3](ClO_4)_2$ (**4**) have been obtained by reacting $Co(ClO_4)_2 \cdot 6H_2O$ with diethanolamine (H_2dea) and nicotinic acid (Hna) (**3**) and $Co(ClO_4)_2 \cdot 6H_2O$ with diethanolamine (H_2dea) and isonicotinic acid ($Hina$) (**4**), respectively. Their crystal structures have been solved. The four compounds contain 4 Co^{II} and 3 Co^{III} sites. The topology of the metal ions in compounds (**1**) - (**4**) is similar (Figures 1 and 2). The oxidation states of the cobalt ions were assigned on the basis of charge balance, the bond length considerations and BVS calculations (Table S1, Supporting Information). In all four clusters the aminoalkoxido and carboxylato ligands behave in an identical fashion. The ligands (aminoalcohols and carboxylato) surround the periphery of the cluster. Two deprotonated aminoalcohol molecules are coordinated to each Co^{III} ion. Three carboxylato ligands also support this core, acting as chelating ligands towards the peripheral Co^{II} ions. The seven cobalt centers are held together by six μ_3 - and six μ_2 -alkoxido groups arising from six aminoalcohol ligands. The crystal structure of (**1**) - (**4**) consists of heptanuclear cations, uncoordinated perchlorate ions, water molecules and solvent molecules in the particular case of (**3**).

Since the four clusters display essentially identical structures, we will limit our discussion to compound **(3)**. There are seven independent cobalt ions in **(3)**, labeled Co1-Co7. The seven cobalt ions display distorted octahedral geometries. The stereochemistry of Co1 (Co^{II}) is the more regular, involving six oxygen donor atoms derived from six μ_3 -alkoxido groups, with O-Co-O angles in the range of 78.65(15) - 98.06(16)° (Table 2) and Co-O bonds ranging between 2.071(4) and 2.104(4) Å (Table 1). The other Co^{II} ions (Co2, Co6 and Co7) have bond lengths varying between 1.975(4) and 2.203(5) Å. The bond lengths of Co^{III} ions (Co3,

Co4 and Co5) are shorter: Co-N bonds fall in the range 1.940(6)-1.960(5) Å and Co-O range between 1.875(4) and 1.915(4) Å. The intramolecular distances between the central cobalt atom (Co1) and the peripheral ones (Co2, Co3, Co4, Co5, Co6, Co7) are Co1 - Co2 = 2.992, Co1 - Co3 = 2.992, Co1 - Co4 = 2.997, Co1 - Co5 = 2.991, Co1 - Co6 = 3.162, Co1 - Co7 = 3.180 Å (Table 1 and Table S2).

A summary of the important interatomic distances and angles is provided in Tables 1, 2 and S2, S3 (Supporting Information).

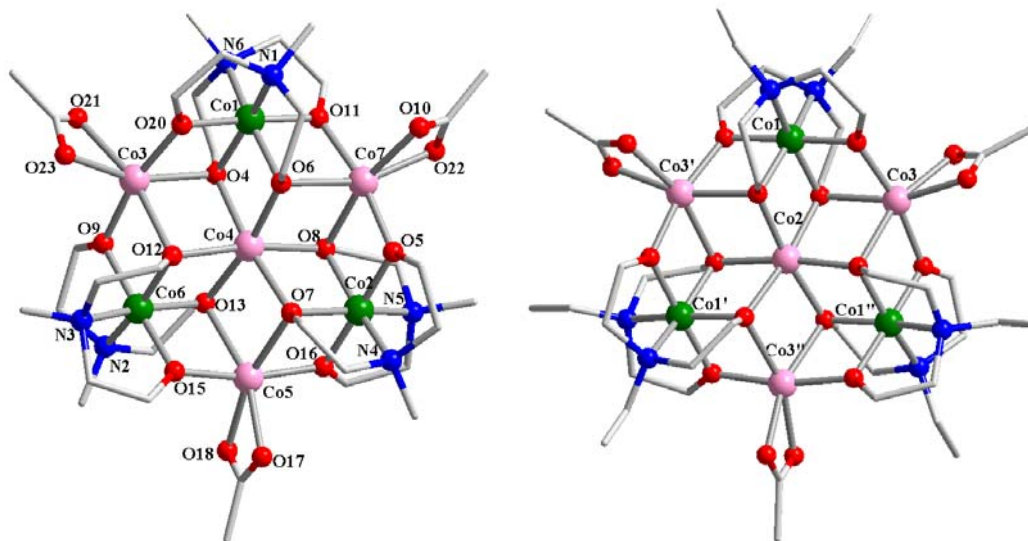


Fig. 1 – Perspective views of the heptanuclear cations in **(1)** and **(2)** (': 1-y, 1+x-y, z, '': -x+y, 1-x, z).

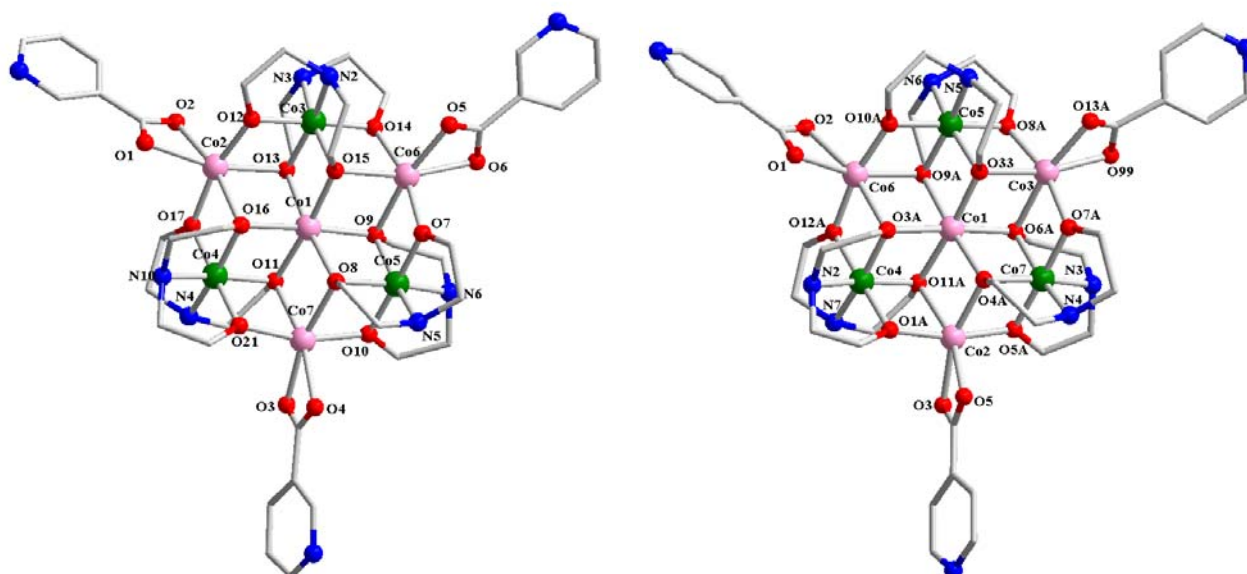


Fig. 2 – Perspective views of the heptanuclear cations in **(3)** and **(4)**.

Table 1

Selected bond lengths (Å) in compound (3)

(3)								
Co1	O13	2.104(4)	Co4	O11	1.915(4)	Co7	O11	2.183(4)
Co1	O15	2.089(4)	Co4	O16	1.911(4)	Co7	O8	2.189(4)
Co1	O9	2.075(4)	Co4	O17	1.875(4)	Co7	O21	1.983(5)
Co1	O11	2.094(4)	Co4	O21	1.876(4)	Co7	O10	1.993(5)
Co1	O8	2.100(4)	Co4	N4	1.943(5)	Co7	O3	2.141(5)
Co1	O16	2.071(4)	Co4	N10	1.941(5)	Co7	O4	2.203(5)
Co2	O13	2.163(4)	Co5	O9	1.906(4)	Co1	Co2	2.992
Co2	O12	1.982(4)	Co5	O8	1.911(4)	Co1	Co3	2.992
Co2	O16	2.186(4)	Co5	O10	1.879(4)	Co1	Co4	2.997
Co2	O17	1.978(4)	Co5	O7	1.881(4)	Co1	Co5	2.991
Co2	O2	2.116(4)	Co5	N5	1.940(6)	Co1	Co6	3.162
Co2	O1	2.191(4)	Co5	N6	1.952(6)	Co1	Co7	3.180
Co3	O13	1.908(4)	Co6	O15	2.173(4)			
Co3	O15	1.909(4)	Co6	O9	2.186(4)			
Co3	O12	1.889(4)	Co6	O14	1.983(4)			
Co3	O14	1.881(4)	Co6	O7	1.975(4)			
Co3	N3	1.944(5)	Co6	O5	2.133(4)			
Co3	N2	1.960(5)	Co6	O6	2.164(5)			

Table 2

Selected angles (°) in compound (3)

(3)											
O15	Co1	O13	78.65(15)	O16	Co4	O11	88.09(17)	O8	Co7	O11	81.99(15)
O9	Co1	O13	92.48(11)	O17	Co4	O11	96.17(18)	O21	Co7	O11	73.48(16)
O9	Co1	O15	137.30(12)	O17	Co4	O16	82.45(17)	O21	Co7	O8	93.06(18)
O11	Co1	O13	97.92(16)	O21	Co4	O11	82.38(19)	O10	Co7	O11	94.96(18)
O11	Co1	O15	174.87(16)	O21	Co4	O16	97.00(19)	O10	Co7	O8	73.59(17)
O11	Co1	O9	97.64(16)	O21	Co4	O17	178.5(2)	O10	Co7	O21	163.68(18)
O8	Co1	O13	174.40(16)	N4	Co4	O11	87.8(2)	O3	Co7	O11	108.72(17)
O8	Co1	O15	97.42(16)	N4	Co4	O16	166.3(2)	O3	Co7	O8	166.09(18)
O8	Co1	O9	78.66(17)	N4	Co4	O17	85.0(2)	O3	Co7	O21	98.5(2)
O8	Co1	O11	86.27(16)	N4	Co4	O21	95.4(2)	O3	Co7	O10	96.15(19)
O16	Co1	O13	86.40(15)	N10	Co4	O11	166.6(2)	O4	Co7	O11	166.01(18)
O16	Co1	O15	96.50(15)	N10	Co4	O16	87.4(2)	O4	Co7	O8	110.13(18)
O16	Co1	O9	175.77(16)	N10	Co4	O17	95.7(2)	O4	Co7	O21	98.3(2)
O16	Co1	O11	79.40(16)	N10	Co4	O21	85.7(2)	O4	Co7	O10	95.2(2)
O16	Co1	O8	98.06(16)	N10	Co4	N4	99.3(2)	O4	Co7	O3	60.6(2)
O12	Co2	O13	74.34(16)	O8	Co5	O9	87.75(17)	Co1	O16	Co2	95.84(16)
O16	Co2	O13	82.16(15)	O10	Co5	O9	96.07(19)	Co1	O13	Co2	95.57(16)
O16	Co2	O12	92.79(16)	O10	Co5	O8	82.93(19)	Co1	O15	Co6	95.75(16)
O17	Co2	O13	96.90(16)	O7	Co5	O9	83.22(18)	Co1	O9	Co6	95.76(16)
O17	Co2	O12	164.79(17)	O7	Co5	O8	95.57(19)	Co1	O11	Co7	96.04(17)
O17	Co2	O16	73.46(16)	O7	Co5	O10	178.37(19)	Co1	O8	Co7	95.70(16)
O2	Co2	O13	106.96(16)	N5	Co5	O9	166.4(2)				
O2	Co2	O12	100.30(17)	N5	Co5	O8	87.7(2)				
O2	Co2	O16	165.64(16)	N5	Co5	O10	96.0(2)				
O2	Co2	O17	94.11(17)	N5	Co5	O7	84.5(2)				
O1	Co2	O13	163.63(16)	N6	Co5	O9	87.1(2)				
O1	Co2	O12	96.36(18)	N6	Co5	O8	166.4(2)				
O1	Co2	O16	112.18(16)	N6	Co5	O10	85.2(2)				
O1	Co2	O17	94.90(19)	N6	Co5	O7	96.3(2)				
O1	Co2	O2	60.76(17)	N6	Co5	N5	100.1(3)				
O15	Co3	O13	88.23(17)	O9	Co6	O15	81.87(15)				
O12	Co3	O13	82.72(17)	O14	Co6	O15	74.16(16)				
O12	Co3	O15	95.73(18)	O14	Co6	O9	93.32(17)				
O14	Co3	O13	94.58(18)	O7	Co6	O15	94.61(17)				
O14	Co3	O15	82.96(18)	O7	Co6	O9	74.19(16)				
O14	Co3	O12	177.05(18)	O7	Co6	O14	164.48(18)				
N3	Co3	Co1	130.70(17)	O5	Co6	O15	107.85(16)				

Table 2 (continued)

N3	Co3	O13	87.7(2)	O5	Co6	O9	169.42(16)
N3	Co3	O15	166.3(2)	O5	Co6	O14	93.40(18)
N3	Co3	O12	96.7(2)	O5	Co6	O7	100.34(18)
N3	Co3	O14	84.4(2)	O6	Co6	O15	165.05(17)
N2	Co3	O15	87.5(2)	O6	Co6	O9	109.79(17)
N2	Co3	O12	85.2(2)	O6	Co6	O14	95.31(19)
N2	Co3	O14	97.3(2)	O6	Co6	O7	97.6(2)
N2	Co3	N3	99.2(2)	O6	Co6	O5	61.42(18)

The crystallization water molecule (O1w) is hydrogen bonded to the carboxylate oxygen atom (O1) arising from the nicotinato ligand (Figure 3).

The analysis of the packing diagram (Figure 4) reveals the formation of supramolecular dimers

supported by π - π stacking interactions (3.35 Å) established between two pyridyl fragments arising two neighboring clusters. Only one out of the three pyridyl fragments from each cluster is involved in these interactions.

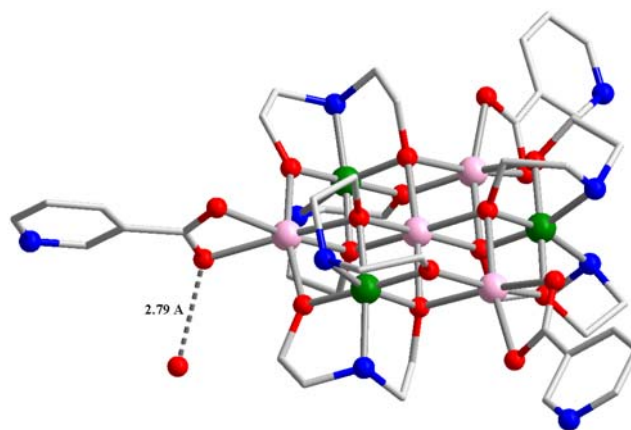


Fig. 3 – Hydrogen bond established between the water molecule and one carboxylate oxygen atom in compound (3).

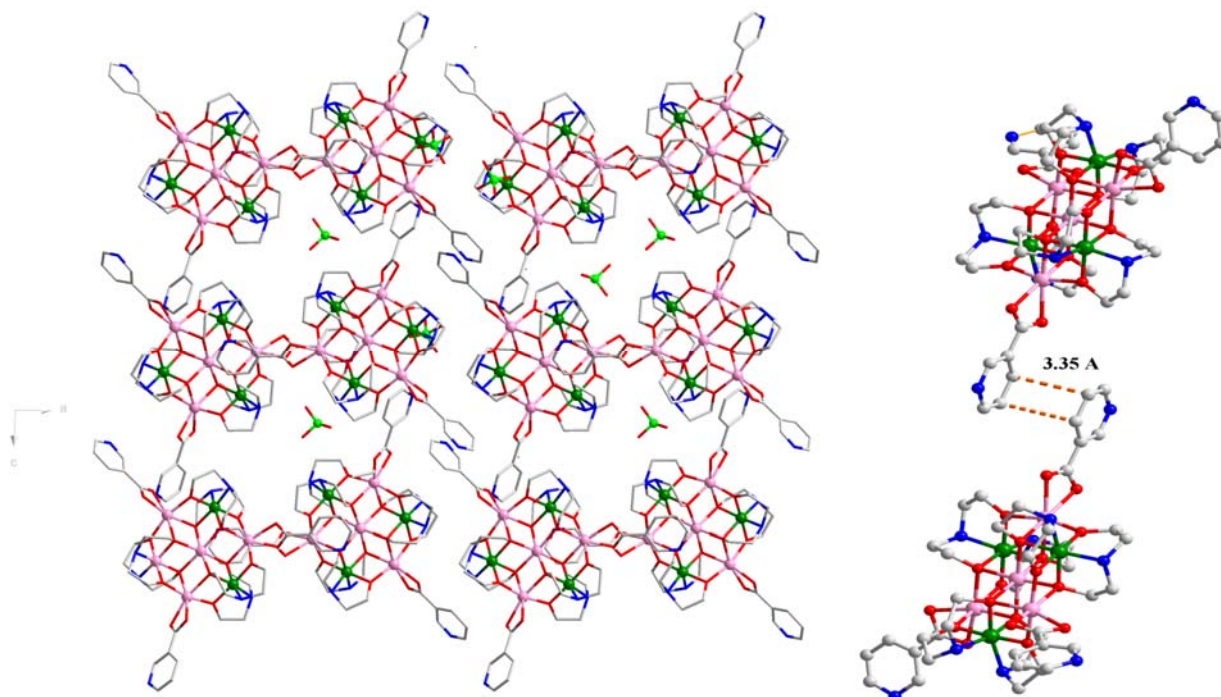


Fig. 4 – Packing diagram in crystal (3) showing the π - π staking interactions between the pyridyl rings (left: view along the crystallographic *b* axis).

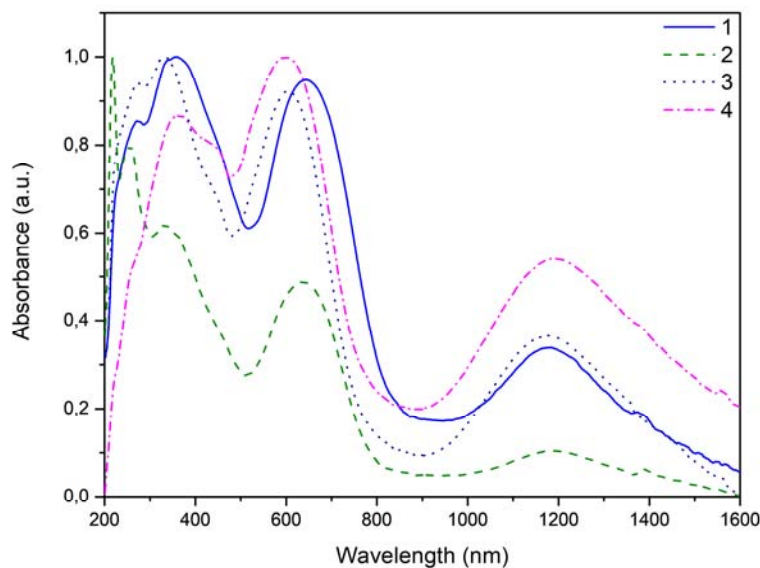


Fig. 5 – Diffuse reflectance spectra for compounds (1) - (4).

The UV-VIS spectra of the four compounds are displayed in Figure 5 and result from the superposition of the *d-d* transitions of the Co^{II} and Co^{III} chromophores.¹³ The four spectra have the same features. The bands located at around 1200 nm for (1) – (4), are ascribed to the ${}^4T_{1g} \rightarrow {}^4T_{2g}$ transition of hexacoordinated cobalt(II).

EXPERIMENTAL

Materials and methods

All the chemicals used were purchased from commercial sources and used without further purification. Elemental analyses (C, H, N) were performed on an EuroEA Elemental Analyzer.

[Co^{IV}Co^{III}₃(m-dea)₆(AcO)₃](ClO₄)₂·8H₂O (1). An ethanolic solution (10 mL) of sodium acetate (0.0246 g, 0.3 mmol) and cobalt(II) acetate tetrahydrate (0.0747 g, 0.3 mmol) was mixed with an ethanolic solution (10 mL) of N-methyldiethanolamine (0.0714 g, 0.6 mmol) and triethylamine (0.166 mL, 1.2 mmol) and an ethanolic solution (10 mL) of sodium perchlorate (0.0421 g, 0.3 mmol). The mixture was stirred for two hours and then filtered off. The resulting green solution was allowed to evaporate in the open air for four weeks, after which green crystals were collected. Elemental chemical analysis: 26.44% C, 5.61% H, 5.14% N (calcd.); 25.97 % C, 6.03 % H, 5.59 % N (found). IR (cm⁻¹, KBr): 3432(s), 2932(w), 2865(w), 1549(s), 1456(s), 1420(m), 1145(vs), 1088(vs), 1027(vs), 626(m).

[Co^{IV}Co^{III}₃(e-dea)₆(AcO)₃](ClO₄)₂ (2). An ethanolic solution (10 mL) of sodium acetate (0.0246 g, 0.3 mmol) and cobalt(II) acetate tetrahydrate (0.0747 g, 0.3 mmol) was mixed with an ethanolic solution (10 mL) of N-ethyl-diethanolamine (0.0799 g, 0.6 mmol) and triethylamine (0.166 mL, 1.2 mmol), and an ethanolic solution (10 mL) of sodium perchlorate (0.0421 g, 0.3 mmol). The mixture was stirred for two hours and then filtered off. The resulting green solution was allowed to evaporate in the open air for four weeks, after which green crystals were collected.

Elemental chemical analysis: 32.01% C, 5.58% H, 5.33% N (calcd.); 32.46% C, 5.04% H, 5.59% N (found). IR (cm⁻¹, KBr): 3430(s), 2924(w), 2860(w), 1548(s), 1452(m), 1145(vs), 1099(vs), 1034(vs), 624(m).

[Co^{III}Co^{IV}₄(dea)₆(na)₃](ClO₄)₂·CH₃CH₂OH·H₂O (3). An ethanolic solution (10 mL) of Co(ClO₄)₂·6H₂O (0.5 mmol; 0.183 g) was reacted with H₂dea (1 mmol; 0.105 g) dissolved in 10 mL of methanol and triethylamine (2 mmol; 0.202 g, 0.278 mL). To the resulting dark green solution, a methanolic solution (10 mL) of nicotinic acid (1 mmol, 0.123 g) and triethylamine (1 mmol, 0.139 mL). The final mixture was stirred for 2 h and then it was filtered off. The resulting dark green solution was allowed to evaporate in the open air for two weeks. Dark green single crystals appeared after a week by slow evaporation of the solution at room temperature. Elemental chemical analysis: 31.60% C, 4.10% H, 7.54% N (calcd.); 31.00% C, 4.22% H, 7.84% N (found). IR (cm⁻¹, KBr): 3421(s), 3268(m), 2938(m), 2872(m), 1595(m), 1542(s), 1433(s), 1410(s), 1284(w), 1200(w), 1100(vs), 1068(vs), 1043(vs), 1000(vs), 900(w), 698(m), 624(m).

[Co^{III}Co^{IV}₄(dea)₆(ina)₃](ClO₄)₂ (4). An ethanolic solution (10 mL) of Co(ClO₄)₂·6H₂O (0.5 mmol, 0.183g) was reacted with H₂dea (1 mmol, 0.105g) dissolved in 10 mL of methanol and triethylamine (2 mmol, 0.202 g, 0.278 mL). The mixture was stirred for five minutes and then was mixed with a methanolic solution (10 mL) of isonicotinic acid (0.5 mmol, 0.062 g) with triethylamine (0.5 mmol, 0.069 mL). The final mixture was stirred for 2 h and then it was filtered off. The resulting dark green solution was allowed to evaporate in the open air for several days. Dark green single crystals appeared by slow evaporation of the solution at room temperature. Elemental chemical analysis: 31.72% C, 3.80% H, 7.93% N (calcd.); 31.41% C, 3.92% H, 7.97% N (found). IR (cm⁻¹, KBr): 3438, 3268(m), 2936(m), 2874(m), 1640(m), 1589(m), 1538(m), 1498(s), 1416(s), 1285(w), 1200(w), 1100(vs), 1070(vs), 1000(vs), 914(w), 626(m).

Physical Measurements

IR spectra (KBr pellets) were recorded on a Tensor 37 spectrophotometer in the 4000–400 cm⁻¹ region and UV-Vis spectra were recorded with a Jasco V-670 spectrophotometer, using MgO oxide as a reference.

Table 3

Crystallographic data, details of data collection and structure refinement parameters for compounds (1) - (4)

Compound	(1)	(2)	(3)	(4)
Chemical formula	Co ₇ C ₃₆ H ₉₁ O ₃₄ N ₆ Cl ₂	Co ₇ C ₄₂ H ₈₇ O ₂₆ N ₆ Cl ₂	Co ₇ C ₄₄ H ₇₄ O ₂₈ N ₉ Cl ₂	Co ₇ C ₄₂ H ₆₆ O ₂₆ N ₉ Cl ₂
<i>M</i> (g·mol ⁻¹)	1635.74	1575.76	1660	1596
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	trigonal	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>R</i> -3 <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	13.5105(2)	15.7120(6)	21.6144(3)	23.1182(3)
<i>b</i> (Å)	13.7641(3)	15.7120(6)	12.2760(4)	12.0379(4)
<i>c</i> (Å)	18.8263(4)	43.224(3)	24.3516(5)	23.9297(5)
α (°)	98.361(3)	90	90	90
β (°)	90.520(2)	90	92.309(6)	100.155(6)
γ (°)	117.406(4)	120	90	90.00
<i>V</i> (Å ³)	3063.45(16)	9241.0(9)	6456.2(3)	6555.2(3)
<i>Z</i>	2	12	4	4
<i>D</i> _c (g·cm ⁻³)	1.509	1.669	1.608	1.778
μ (mm ⁻¹)	1.961	2.008	0.915	1.592
<i>F</i> (0 0 0)	1435	4872	3132	3488
Goodness-of-fit (GOF) on <i>F</i> ²	1.0758	1.088	1.019	1.110
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0918, 0.2239	0.0390, 0.0731	0.0635, 0.1650	0.1279, 0.3532
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1978, 0.3029	0.0744, 0.0894	0.0729, 0.1695	0.1668, 0.3732
Largest difference in peak and hole (eÅ ⁻³)	-1.485, 1.566	-0.697, 0.525	-1.121, 2.500	-0.693, 2.050

X-ray crystallographic analysis

Crystals of (1) – (4) were measured on STOE IPDSII single crystal diffractometer, using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares techniques based on *F*². The non-H atoms were refined with anisotropic displacement parameters. A summary of the crystallographic data and refinement parameters for (1) – (4) is given in Table 3. The very small size of crystals 1 and 4 (needles shape crystals) and poor diffraction patterns were the reason of the significantly flattened thermal ellipsoids and the high *R*₁ parameters. CCDC reference numbers: 1986453-1986456.

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