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Synthesis and characterization of a novel metal complex Cobalt (III) with a tetradentate N,N,O,O-donor ligand and 2,2'-{propane-1,2-diyl-bis[nitrilo(E)methylidene]}bis(6-methoxyphenol)

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Abstract

Schiff bases have often been used as chelating ligands in the field of coordination chemistry, and their metal complexes have been extensively investigated due to their potential applications. It is known that reactions of N,N,O,O-donor Schiff bases ligands with transition metal ions have produced series of complexes with interesting structures and magnetic properties. A new complex prepared by the reaction of 2,2'-{propane-1,2-

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diyl-bis[nitrilo(E)methylidene]}bis(6-methoxyphenol) (**H_2L**) with Co(III) ion is reported in this paper. The bicompartmental ligand acts in a tetradentate fashion. The **H_2L** ligand is structurally characterized by elemental analysis, NMR and infrared spectroscopies, conductance and single X-ray diffraction.

The compound with Co(III) crystallizes in the monoclinic system in the space group $P2_1/c$ with the unit cell parameters a = 13.168(2) Å, b = 15.795(2) Å, c = 15.882(2) Å, α = 90°, β = 110.703(16)°, γ = 90°. The cobalt (III) ion has slightly distorted octahedral coordination geometry.

In the structure of the mononuclear complex, the Co(III) cation is coordinated by two imine nitrogen atoms, two phenoxo oxygen atoms, from deprotonated Schiff base ligand and two oxygen atoms of water. There is also neighboring two molecule of DMF and one perchlorate anion non coordinating.

1. Introduction

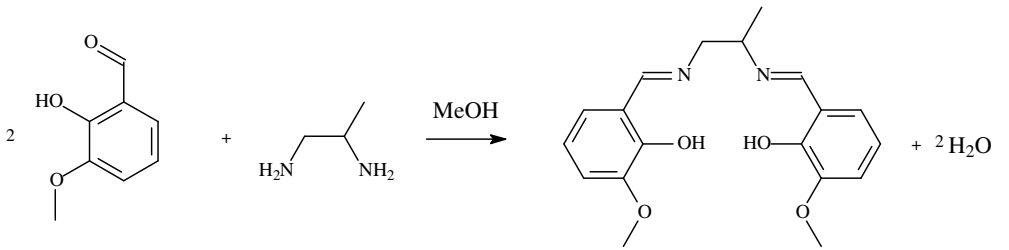
Since a long time, chelating agents derived from organic compounds containing N,S,O-donor as a functional group have a strong ability to form metal complexes and exhibit a variety of biological activities [1-8]. A number of studies have been done in the various Schiff bases complexes formed by the condensation of secondary amines with different aldehydes and ketones [9-12]. From the survey of existing literature, it appears that metal complexes of Schiff bases played a vital role in the development of coordination chemistry and their analytical utility in the determination of transition metal ions. Literature studies revealed that during the past decades, there has been a great deal of interest in the synthesis and structural elucidation of transition metal complexes containing N,N,O,O-donor.

In the present work, we described synthesis and characterization of new Schiff base 2,2'-{propane-1,2-diyl-bis[nitrilo(E)methylidene]}bis(6-methoxy phenol), derived from the condensation of ortho vanillin and 1,2 diaminopropane and its metal mononuclear complex obtained with Co(III).

2. Synthesis of 2,2'-{propane-1,2-diyl-bis[nitrilo(E)methylidene]}bis(6-methoxy phenol)(H_2L)

3.04g (20 mmol) of ortho vanillin was dissolved in methanol and then 0.9 mL (10 mmol) of 1,2-diaminopropane was added. The orange-yellow mixture obtained is heated

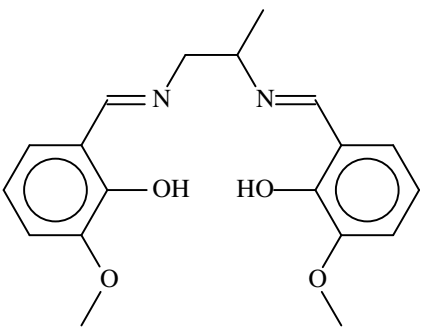
under reflux with magnetic stirring for 4 hours, then filtered and air-dried. A yellow-orange precipitate is obtained, which is washed with diethyl ether. The compound was thoroughly washed with ether and dried over P_4O_{10}. The yield is 65.5 %.



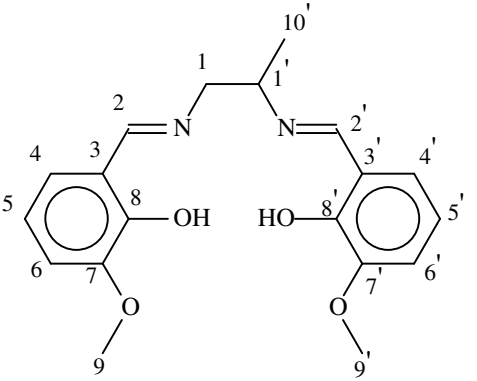
RMN ^{1}H : (δ, ppm) : 13.65 (s, 2H, Ar-O**H**), 8.30 (s, 2H, **H**C=N), 6.92-6.75 (m, 6H, Ar-**H**), 3.79-3.86 (m, H_1, H_1'), 3.71(s, 6H, -C**H$_3$**), 1.40 (3H-C**H$_3$**-CH).

RMN ^{13}C : (δ, ppm) : 65.20(C_1), 55,9 (C_1'), 166.5(C_2 ; $C_{2'}$), 148.08(C_3 ; $C_{3'}$), 123.14(C_4 ; $C_{4'}$), 118,28(C_5 ; $C_{5'}$), 118.00(C_6 ; C_6'), 151.40(C_7 ; $C_{7'}$), 154.6(C_8 ; $C_{8'}$), 64.49(C_9 ; $C_{9'}$), 20.25 (C_{10}').

IR H_2L: ν(cm^{-1}) : 1625 (s) (C=N); 3196 (m) (HC=N); 3190(m)(OH), (1466 - 1358) (m) (C=C); 1249 (m) (C-O),2931 (m) (C-H).



$C_{19}H_{22}N_2O_4$
342.39
342.157957
C 66.65% H 6.48% N 8.18% O 18.69%



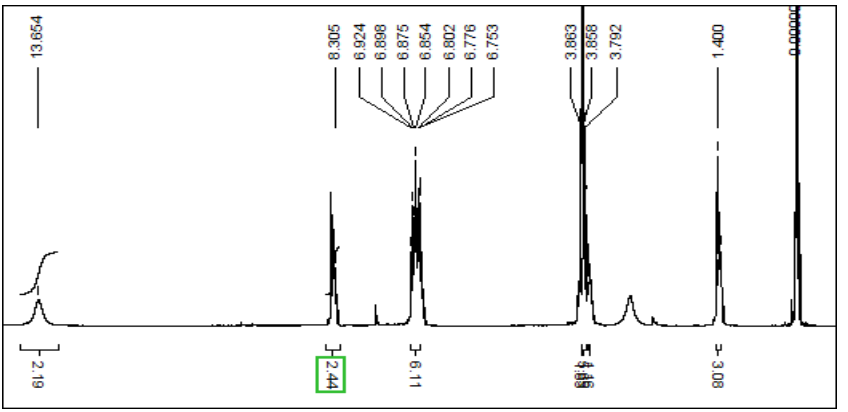


Figure 1. RMN of ^{1}H.

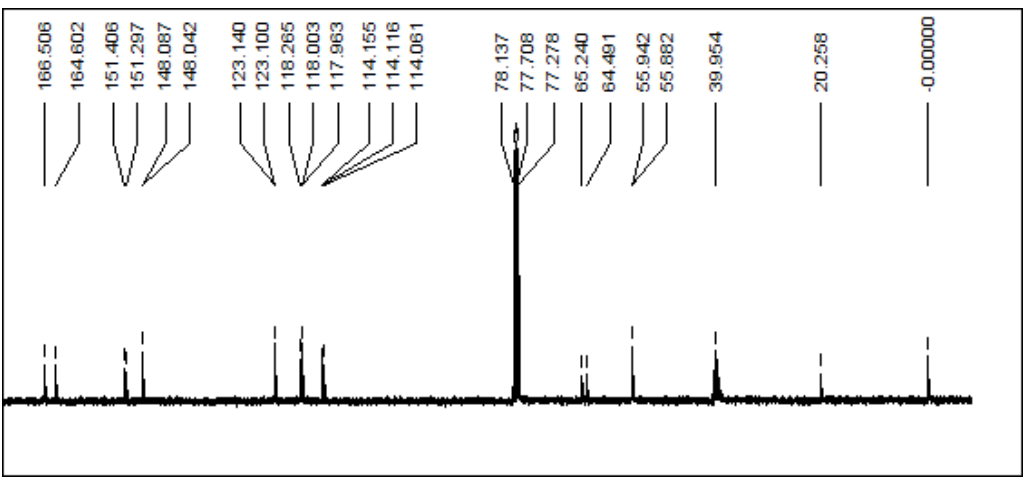


Figure 2. RMN of ^{13}C.

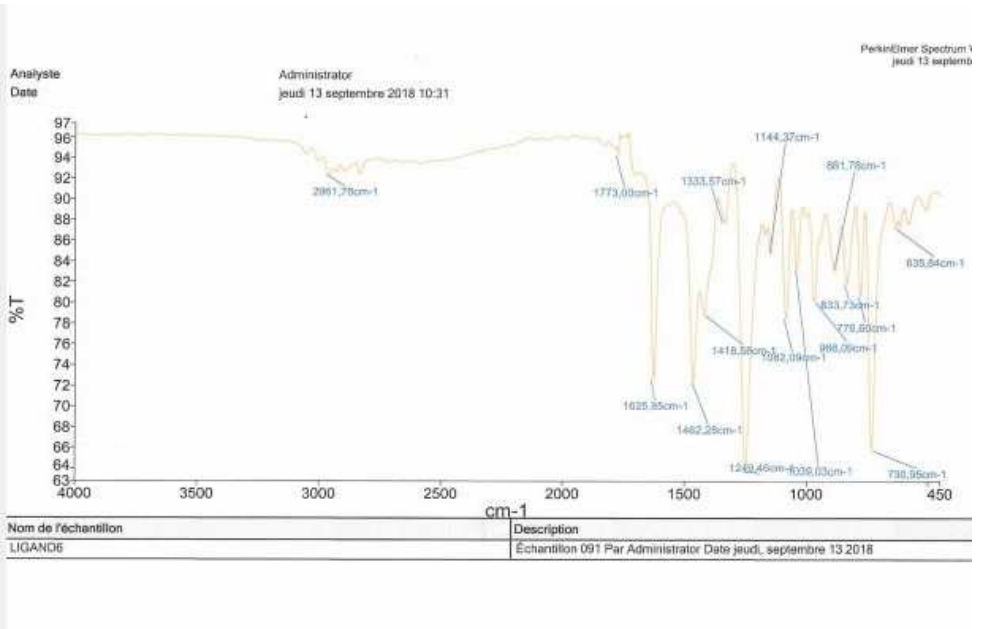
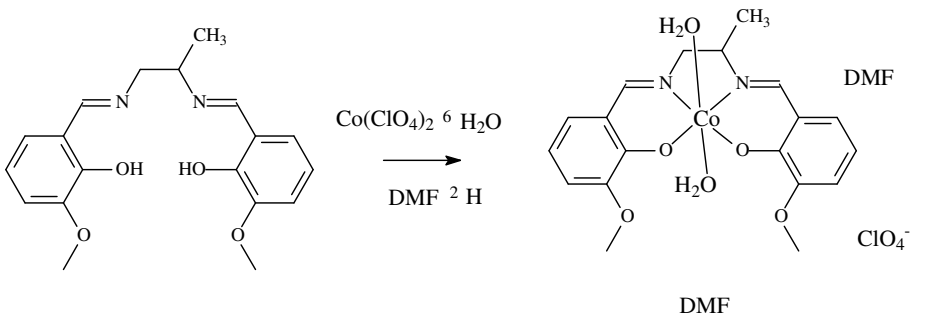


Figure 3. Spectre IR of ligand.

3. Synthesis of complex of Co(III) with cobalt perchorate and L^{2-}

In a 50 mL flask, the H_2L ligand (3 mmol, 0.1g) was dissolved in DMF. The solution of $Co(ClO_4)_2.6H_2O$ (0.3 mmol, 0.11g) in methanol is added. The mixture is heated with magnetic stirring for 2 hours, a dark brown solution is obtained and then filtered. One month of evaporation after, crystals of brown color are obtained which can be analyzed by X-ray.



IR: ν(C=N) =1617cm^{-1}; ν(Ar-C-O) =1239cm^{-1}; ν(H_2O) =2934 cm^{-1}

Λ (S.cm^2.mol^{-1}) : 106 and 23[13].

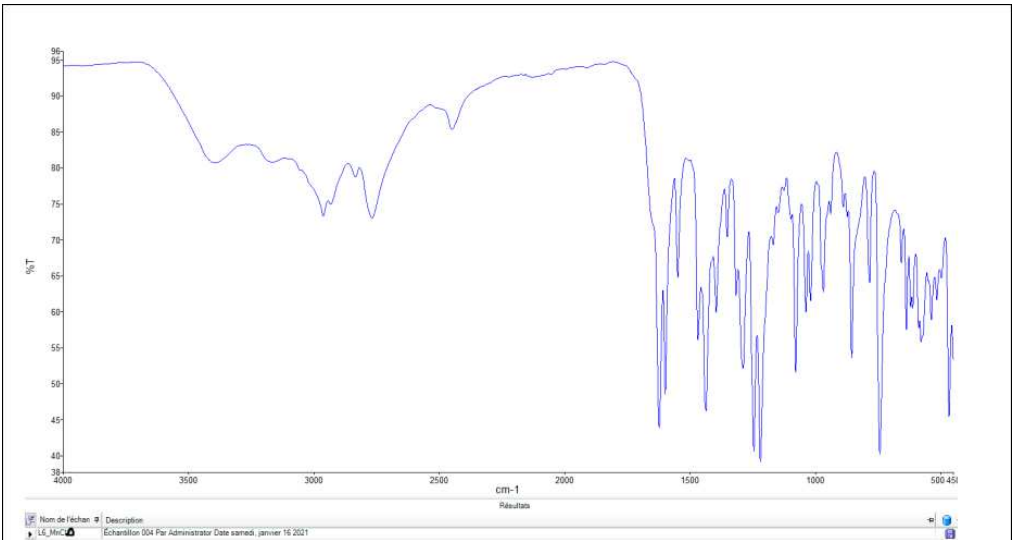


Figure 4. Spectre IR of complex with Co(III).

The complex crystallizes with two molecules of DMF and a perchlorate ion.

Table 1. Crystal data

Chemical formula	$C_{11}H_{10}Cl_{0.92}CoNO$
Mr	263.85
Density	1.843 Mg m^{-3}
Crystal system	Monoclinic
Space group	P21/c
Radiation	Mo Kα
λ	0.71073 Å
a	13.168 (2) Å
b	15.795 (2) Å

c	15.882 (2) Å
μ	2.03 mm^{-1}
T	293 K
β	110.703 (16)°
V	3090.0 (8) $Å^3$
Z	13
F(000)	1738

Table 2. Data collection.

R_{int}	0.120
θ_{max}	29.5°
θ_{min}	2.6°
h	−18 17
k	−21 20
l	−20 21
independent reflections	7399
measured reflections	18921
reflections with $I > 2\sigma(I)$	2272

Table 3. Refinement.

Refinement	on F2
Least-squares matrix	full
Hydrogen site location	mixed
$R[F^2 > 2\sigma(F^2)]$	0.094
$wR(F^2)$	0.330
w	$1/[\sigma^2(F_o^2) + (0.1465P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S	0.91
$(\Delta/\sigma)_{max}$	1.048
Reflections	7399
$\Delta\rho_{max}$	0.88 e Å^{-3}
$\Delta\rho_{min}$	–0.60 e Å^{-3}
Parameters	405
Extinction coefficient	0.0000 (8)

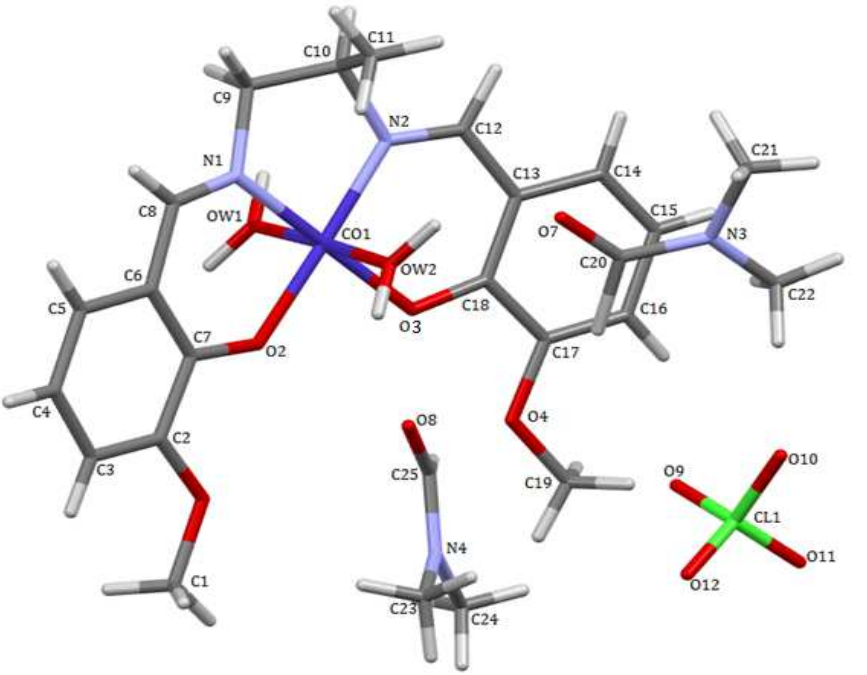


Figure 5. Crystal structure of the Co(III) complex.

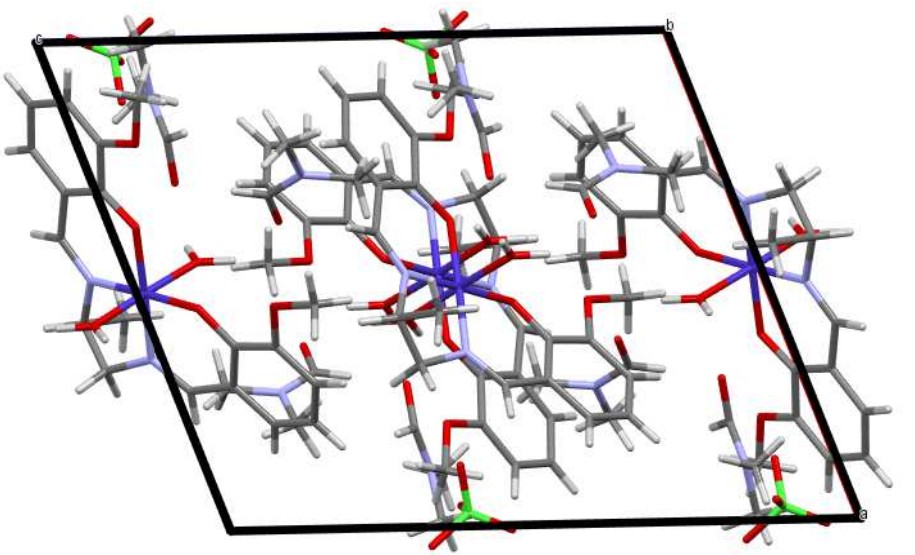


Figure 6. The packing of the compound in the crystal structure.

4. Results and Discussion

The ^{1}H NMR spectrum of **H_2L** (Figure 1) shows three singlets, one doublet and multiplets. The singlets at δ = 3.71 and δ = 13.65 ppm represent (C**H_3**-O) and Ar-O**H** respectively. The multiplet in the region 3.79-3.85 ppm represents H1, H1'. The aromatic protons appear as multiplets in the region 6.92-6.75 ppm.

The ^{13}C NMR spectrum of **H_2L** (Figure 2) show a signal at δ = 166.5 ppm which represent the carbon atom of the imine **C**=N. The peaks at δ = 151.40 and δ = 64.49 ppm represent respectively the aromatic Cipso of the OH of the phenol and the O-**C**H_3.

The IR spectrum of **H_2L** (Figure 3) show a strong band at 1625 cm^{-1} assigned to the ν(C=N) vibration [14]. Upon coordination the band due to C=N shift to low frequencies for both complexes. For compound the band of the C=N is pointed at 1560 cm^{-1}. The broad band of medium intensity that appear in the range 3190 cm^{-1} is due to the O–H stretching vibration of the phenolic and alcohol OH groups. The phenolic C–O stretching shift to low frequencies for complex at 1316 cm^{-1}.

The cobalt (III) ion has a slightly distorted octahedral coordination geometry. Co (III) is coordinated by two imine nitrogen atoms, N1 and N2, two phenoxo oxygen atoms, O2 and O3 from deprotonated Schiff base ligand and two oxygen atoms Ow1 and Ow2 of water. There is also neighboring two molecule of DMF and one perchlorate anion non coordinating. A deviation from 90° of the bond angles involving the chelation is observed N2—Co1—N1=84.4°; N2—Co1—O3=95.1° O2—Co1—N1=93.9°; O2—Co1—O3=86.6°). Relevant bonds distances are: *d*(Co1- N1)=1.883Å, *d*(Co1- N2)=1.870Å, *d*(Co1- O2)=1.876Å, *d*(Co1- O3)=1.909 Å, *d*(Co1- Ow1)=1.925Å, *d*(Co1- Ow2)=1.905 Å. Otherwise (N2-Co1-O2=178.3°; N1-Co1-O3=178.8°; Ow1-Co1-Ow2=177.4°) are different to 180° and (N2-Co1-Ow2=92.0°; O2-Co1-Ow2=88.2°; O2-Co1-Ow1=89.2°; N1-Co1-Ow2=90.8°; N1-Co1-Ow1=89.1°; O3-Co1-Ow2=90.3°; O3-Co1-Ow1=89.9°) are different to 90°.

The molar conductivity values of the freshly DMF (10^{-3} M) complex solution and fifteen days later are, respectively, 106 ($S.cm^2.mol^{-1}$) and 23 ($S.cm^2.mol^{-1}$) for complex.

5. Conclusion

This work allowed us to synthesize and characterize a new isolated bicompartmental ligand as well as its cobalt (III) complex. From spectroscopies methods we were able to

demonstrate the formation of ligand. We also determined structure of complex of Co(III) by X-ray diffraction. The structure reveals tetradentate coordination of the ligand via two nitrogen atoms and two deprotonated phenolicoxygen atoms. In this complex the central metal center is hexacoordinated. This complex is characterized by spectroscopic studies (IR, NMR), molar conductivity and X-ray diffraction.

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SUPPLEMENTARY MATERIALS

	x	y	z	Uiso*/Ueq
Co1	0.48651 (8)	0.14663 (7)	0.01226 (6)	0.0559 (4)
Cl1	1.0282 (2)	0.1458 (2)	0.3860 (2)	0.1029 (9)
N1	0.3524 (5)	0.2031 (4)	−0.0178 (4)	0.0686 (18)
N2	0.5151 (5)	0.2264 (4)	−0.0635 (4)	0.0661 (17)
N3	0.8879 (6)	0.3180 (6)	0.1465 (5)	0.089 (2)
N4	0.7212 (6)	0.0207 (5)	0.3339 (5)	0.085 (2)
OW1	0.4223 (4)	0.0717 (3)	−0.0881 (3)	0.0558 (13)
HW1A	0.418887	0.087639	−0.145467	0.067*
HW1B	0.394810	0.019583	−0.079332	0.067*
OW2	0.5477 (4)	0.2175 (3)	0.1149 (3)	0.0691 (14)
HW2A	0.575799	0.270199	0.108738	0.083*
HW2B	0.549388	0.199411	0.171075	0.083*
O1	0.4550 (5)	−0.0427 (4)	0.2075 (3)	0.0771 (16)
O2	0.4536 (4)	0.0680 (3)	0.0873 (3)	0.0590 (13)
O3	0.6217 (4)	0.0887 (3)	0.0401 (3)	0.0557 (12)
O4	0.7907 (4)	−0.0070 (4)	0.0919 (4)	0.0723 (16)
O7	0.7102 (6)	0.3147 (5)	0.1302 (5)	0.117 (3)

O8	0.6278 (6)	0.1363 (4)	0.2690 (4)	0.093 (2)
O9	0.9613 (15)	0.1168 (10)	0.3072 (10)	0.331 (11)
O10	1.0421 (8)	0.2344 (6)	0.3785 (8)	0.178 (4)
O11	1.1240 (11)	0.1100 (8)	0.4021 (13)	0.270 (8)
O12	0.9918 (18)	0.1201 (15)	0.4441 (12)	0.363 (12)
C1	0.4573 (8)	−0.1056 (7)	0.2732 (6)	0.096 (3)
H1A	0.517894	−0.142828	0.282035	0.145*
H1B	0.464492	−0.078486	0.329096	0.145*
H1C	0.391174	−0.137731	0.252488	0.145*
C2	0.3733 (7)	0.0167 (6)	0.1858 (5)	0.065 (2)
C3	0.2961 (8)	0.0208 (7)	0.2255 (6)	0.093 (3)
H3	0.295246	−0.018669	0.268672	0.112*
C4	0.2188 (8)	0.0855 (9)	0.1995 (8)	0.111 (4)
H4	0.167368	0.089281	0.227135	0.133*
C5	0.2163 (7)	0.1425 (7)	0.1361 (6)	0.090 (3)
H5	0.162662	0.183906	0.119444	0.108*
C6	0.2950 (6)	0.1397 (6)	0.0946 (5)	0.069 (2)
C7	0.3754 (6)	0.0765 (5)	0.1217 (5)	0.063 (2)

C8	0.2861 (7)	0.1980 (6)	0.0237 (6)	0.070 (2)
C9	0.3306 (9)	0.2580 (8)	−0.0968 (8)	0.122 (4)
H9A	0.293030	0.225747	−0.150870	0.147*
H9B	0.283761	0.304166	−0.093337	0.147*
C10	0.4266 (9)	0.2908 (8)	−0.1021 (10)	0.127 (5)
H10	0.419219	0.309136	−0.162986	0.153*
C11	0.4373 (14)	0.3692 (8)	−0.0334 (8)	0.163 (6)
H11A	0.501326	0.401294	−0.027501	0.245*
H11B	0.374582	0.404926	−0.056477	0.245*
H11C	0.442322	0.347566	0.024441	0.245*
C12	0.6010 (7)	0.2299 (5)	−0.0850 (5)	0.067 (2)
C13	0.6947 (6)	0.1755 (6)	−0.0496 (5)	0.066 (2)
C14	0.7845 (8)	0.1920 (7)	−0.0752 (6)	0.088 (3)
H14	0.781232	0.237938	−0.112632	0.106*
C15	0.8748 (8)	0.1443 (7)	−0.0480 (8)	0.103 (3)
H15	0.932644	0.155844	−0.066957	0.124*
C16	0.8784 (7)	0.0764 (7)	0.0101 (7)	0.089 (3)
H16	0.940218	0.042693	0.030618	0.107*

C17	0.7934 (6)	0.0590 (6)	0.0369 (5)	0.066 (2)
C18	0.6961 (6)	0.1092 (5)	0.0087 (5)	0.0577 (18)
C19	0.8854 (7)	−0.0578 (6)	0.1238 (7)	0.099 (3)
H19A	0.875130	−0.101928	0.161528	0.148*
H19B	0.899116	−0.082418	0.073582	0.148*
H19C	0.946124	−0.023336	0.157798	0.148*
C20	0.7987 (10)	0.2801 (8)	0.1451 (7)	0.098 (3)
C21	0.8907 (9)	0.4070 (10)	0.1341 (9)	0.146 (5)
H21A	0.962164	0.423441	0.137196	0.220*
H21B	0.839011	0.422092	0.076240	0.220*
H21C	0.872926	0.435664	0.180357	0.220*
C22	0.9891 (8)	0.2728 (9)	0.1600 (8)	0.135 (5)
H22A	1.043858	0.312342	0.158702	0.203*
H22B	1.012191	0.244583	0.217235	0.203*
H22C	0.977745	0.231779	0.112972	0.203*
C23	0.7116 (12)	0.0375 (10)	0.4185 (8)	0.163 (6)
H23A	0.745628	−0.007268	0.459731	0.244*
H23B	0.746559	0.090227	0.441532	0.244*

H23C	0.636259	0.040764	0.411370	0.244*
C24	0.7848 (9)	−0.0537 (8)	0.3291 (8)	0.131 (4)
H24A	0.806496	−0.083453	0.385454	0.197*
H24B	0.741533	−0.090365	0.281811	0.197*
H24C	0.848069	−0.036220	0.317037	0.197*
C25	0.6809 (8)	0.0728 (7)	0.2681 (7)	0.085 (3)
H12	0.612 (5)	0.280 (4)	−0.124 (4)	0.06 (2)*
H8	0.225 (11)	0.228 (9)	0.014 (9)	0.20 (6)*
H25	0.690 (5)	0.045 (5)	0.218 (5)	0.06 (2)*
H20	0.809 (7)	0.204 (6)	0.175 (5)	0.10 (3)*

Atomic displacement parameters (Å2)

	U11	U22	U33	U12	U13	U23
Co1	0.0499 (6)	0.0525 (7)	0.0694 (7)	0.0041 (5)	0.0261 (5)	0.0036 (5)
Cl1	0.0775 (16)	0.107 (2)	0.130 (2)	−0.0048 (16)	0.0426 (15)	−0.0179 (18)
N1	0.071 (4)	0.058 (5)	0.080 (4)	0.013 (4)	0.031 (4)	0.013 (4)
N2	0.051 (3)	0.063 (5)	0.086 (4)	0.005 (3)	0.026 (3)	0.013 (3)
N3	0.067 (5)	0.091 (6)	0.097 (5)	0.007 (5)	0.016 (4)	−0.008 (5)
N4	0.075 (5)	0.087 (6)	0.085 (5)	0.003 (4)	0.020 (4)	0.001 (5)
OW1	0.061 (3)	0.053 (3)	0.053 (2)	−0.003 (2)	0.020 (2)	0.005 (2)

OW2	0.082 (4)	0.051 (3)	0.075 (3)	0.000 (3)	0.027 (3)	−0.003 (3)
O1	0.084 (4)	0.078 (4)	0.076 (3)	−0.003 (3)	0.037 (3)	0.015 (3)
O2	0.053 (3)	0.063 (4)	0.067 (3)	0.007 (2)	0.029 (2)	0.000 (2)
O3	0.049 (3)	0.047 (3)	0.078 (3)	0.005 (2)	0.031 (2)	0.005 (2)
O4	0.048 (3)	0.070 (4)	0.097 (4)	0.015 (3)	0.023 (3)	0.012 (3)
O7	0.074 (4)	0.122 (6)	0.161 (7)	−0.015 (5)	0.048 (4)	−0.028 (5)
O8	0.110 (5)	0.077 (5)	0.085 (4)	0.018 (4)	0.024 (4)	−0.012 (3)
O9	0.36 (2)	0.269 (17)	0.216 (12)	−0.179 (16)	−0.082 (13)	0.056 (12)
O10	0.151 (8)	0.085 (7)	0.271 (12)	−0.012 (6)	0.042 (8)	−0.025 (7)
O11	0.174 (11)	0.140 (10)	0.55 (3)	0.015 (9)	0.201 (15)	0.039 (14)
O12	0.49 (3)	0.44 (3)	0.323 (19)	0.04 (2)	0.34 (2)	0.053 (18)
C1	0.099 (7)	0.111 (8)	0.089 (6)	0.001 (6)	0.044 (5)	0.040 (6)
C2	0.080 (5)	0.066 (6)	0.064 (4)	−0.017 (5)	0.043 (4)	0.000 (4)
C3	0.108 (8)	0.106 (8)	0.088 (6)	0.007 (7)	0.064 (6)	0.012 (6)
C4	0.085 (7)	0.148 (11)	0.124 (8)	−0.010 (8)	0.068 (6)	−0.025 (8)
C5	0.080 (6)	0.108 (9)	0.106 (7)	0.025 (6)	0.061 (5)	0.014 (6)
C6	0.050 (4)	0.082 (7)	0.083 (5)	0.011 (4)	0.035 (4)	−0.011 (5)
C7	0.061 (5)	0.068 (6)	0.067 (4)	0.000 (4)	0.033 (4)	−0.009 (4)
C8	0.056 (5)	0.075 (7)	0.080 (5)	0.017 (5)	0.026 (4)	0.005 (5)

C9	0.094 (8)	0.138 (11)	0.153 (9)	0.060 (8)	0.066 (7)	0.066 (8)
C10	0.079 (7)	0.107 (10)	0.207 (12)	0.032 (7)	0.063 (8)	0.081 (9)
C11	0.26 (2)	0.070 (8)	0.141 (10)	0.022 (10)	0.054 (11)	−0.018 (8)
C12	0.089 (6)	0.048 (5)	0.080 (5)	−0.002 (5)	0.048 (5)	0.008 (4)
C13	0.062 (5)	0.064 (6)	0.086 (5)	0.001 (4)	0.042 (4)	0.006 (4)
C14	0.098 (7)	0.083 (7)	0.110 (7)	−0.007 (6)	0.069 (6)	0.011 (6)
C15	0.085 (7)	0.095 (8)	0.160 (10)	0.016 (6)	0.081 (7)	0.004 (7)
C16	0.062 (5)	0.085 (7)	0.132 (8)	0.008 (5)	0.048 (5)	0.019 (6)
C17	0.055 (4)	0.072 (6)	0.079 (5)	−0.003 (4)	0.034 (4)	−0.006 (5)
C18	0.056 (4)	0.053 (5)	0.074 (5)	−0.002 (4)	0.036 (4)	−0.008 (4)
C19	0.073 (6)	0.088 (8)	0.129 (8)	0.022 (5)	0.026 (5)	0.036 (6)
C20	0.098 (8)	0.084 (8)	0.120 (8)	−0.029 (7)	0.050 (7)	−0.027 (7)
C21	0.091 (8)	0.143 (13)	0.176 (12)	0.000 (9)	0.012 (8)	0.012 (11)
C22	0.076 (7)	0.172 (13)	0.149 (9)	0.010 (8)	0.029 (7)	−0.025 (9)
C23	0.216 (16)	0.186 (15)	0.101 (8)	0.072 (13)	0.075 (9)	0.018 (9)
C24	0.108 (9)	0.142 (12)	0.137 (9)	0.044 (8)	0.035 (7)	0.000 (8)
C25	0.094 (7)	0.083 (8)	0.078 (6)	0.011 (6)	0.030 (5)	−0.013 (6)

Selected bond lengths (Å) and angles (°)			
Co1—N2	1.870 (6)	C5—C6	1.411 (11)
Co1—O2	1.876 (5)	C5—H5	0.9300
Co1—N1	1.883 (6)	C6—C7	1.407 (11)
Co1—OW2	1.905 (5)	C6—C8	1.427 (12)
Co1—O3	1.909 (4)	C8—H8	0.90 (14)
Co1—OW1	1.925 (4)	C9—C10	1.396 (14)
Cl1—O12	1.247 (12)	C9—H9A	0.9700
Cl1—O11	1.323 (12)	C9—H9B	0.9700
Cl1—O9	1.332 (12)	C10—C11	1.623 (17)
Cl1—O10	1.421 (9)	C10—H10	0.9800
N1—C8	1.268 (10)	C11—H11A	0.9600
N1—C9	1.468 (11)	C11—H11B	0.9600
N2—C12	1.294 (10)	C11—H11C	0.9600
N2—C10	1.505 (11)	C12—C13	1.445 (11)
N3—C20	1.310 (12)	C12—H12	1.05 (7)
N3—C21	1.423 (15)	C13—C18	1.393 (11)
N3—C22	1.459 (12)	C13—C14	1.404 (11)

N4—C25	1.288 (11)	C14—C15	1.344 (13)
N4—C23	1.418 (12)	C14—H14	0.9300
N4—C24	1.460 (12)	C15—C16	1.405 (13)
OW1—HW1A	0.9300	C15—H15	0.9300
OW1—HW1B	0.9300	C16—C17	1.359 (11)
OW2—HW2A	0.9300	C16—H16	0.9300
OW2—HW2B	0.9300	C17—C18	1.436 (10)
O1—C2	1.377 (10)	C19—H19A	0.9600
O1—C1	1.434 (9)	C19—H19B	0.9600
O2—C7	1.333 (8)	C19—H19C	0.9600
O3—C18	1.288 (8)	C20—H20	1.28 (9)
O4—C17	1.370 (9)	C21—H21A	0.9600
O4—C19	1.417 (9)	C21—H21B	0.9600
O7—C20	1.232 (13)	C21—H21C	0.9600
O8—C25	1.225 (11)	C22—H22A	0.9600
C1—H1A	0.9600	C22—H22B	0.9600
C1—H1B	0.9600	C22—H22C	0.9600
C1—H1C	0.9600	C23—H23A	0.9600
C2—C3	1.373 (11)	C23—H23B	0.9600

C2—C7	1.396 (10)	C23—H23C	0.9600
C3—C4	1.398 (14)	C24—H24A	0.9600
C3—H3	0.9300	C24—H24B	0.9600
C4—C5	1.342 (14)	C24—H24C	0.9600
C4—H4	0.9300	C25—H25	0.96 (7)

N2—Co1—O2	178.3 (2)	C10—C9—H9B	109.3
N2—Co1—N1	84.4 (3)	N1—C9—H9B	109.3
O2—Co1—N1	93.9 (3)	H9A—C9—H9B	108.0
N2—Co1—OW2	92.0 (3)	C9—C10—N2	108.1 (9)
O2—Co1—OW2	88.2 (2)	C9—C10—C11	96.2 (11)
N1—Co1—OW2	90.8 (3)	N2—C10—C11	111.8 (10)
N2—Co1—O3	95.1 (2)	C9—C10—H10	113.2
O2—Co1—O3	86.6 (2)	N2—C10—H10	113.2
N1—Co1—O3	178.8 (2)	C11—C10—H10	113.2
OW2—Co1—O3	90.3 (2)	C10—C11—H11A	109.5
N2—Co1—OW1	90.6 (2)	C10—C11—H11B	109.5
O2—Co1—OW1	89.2 (2)	H11A—C11—H11B	109.5
N1—Co1—OW1	89.1 (2)	C10—C11—H11C	109.5

OW2—Co1—OW1	177.4 (2)	H11A—C11—H11C	109.5
O3—Co1—OW1	89.9 (2)	H11B—C11—H11C	109.5
O12—Cl1—O11	107.9 (13)	N2—C12—C13	125.2 (8)
O12—Cl1—O9	106.4 (13)	N2—C12—H12	121 (4)
O11—Cl1—O9	107.7 (13)	C13—C12—H12	114 (4)
O12—Cl1—O10	118.5 (12)	C18—C13—C14	121.2 (8)
O11—Cl1—O10	107.2 (7)	C18—C13—C12	121.0 (7)
O9—Cl1—O10	108.8 (8)	C14—C13—C12	117.8 (8)
C8—N1—C9	121.3 (7)	C15—C14—C13	122.9 (9)
C8—N1—Co1	126.5 (6)	C15—C14—H14	118.5
C9—N1—Co1	112.2 (5)	C13—C14—H14	118.5
C12—N2—C10	119.1 (8)	C14—C15—C16	117.3 (9)
C12—N2—Co1	126.4 (6)	C14—C15—H15	121.3
C10—N2—Co1	114.5 (6)	C16—C15—H15	121.3
C20—N3—C21	121.1 (10)	C17—C16—C15	121.3 (9)
C20—N3—C22	123.1 (11)	C17—C16—H16	119.3
C21—N3—C22	115.8 (10)	C15—C16—H16	119.3
C25—N4—C23	120.0 (10)	C16—C17—O4	124.3 (8)
C25—N4—C24	123.5 (9)	C16—C17—C18	122.3 (8)

C23—N4—C24	116.3 (9)	O4—C17—C18	113.4 (6)
Co1—OW1—HW1A	120.0	O3—C18—C13	127.8 (7)
Co1—OW1—HW1B	120.0	O3—C18—C17	117.2 (7)
HW1A—OW1—HW1B	120.0	C13—C18—C17	115.0 (7)
Co1—OW2—HW2A	120.0	O4—C19—H19A	109.5
Co1—OW2—HW2B	120.0	O4—C19—H19B	109.5
HW2A—OW2—HW2B	120.0	H19A—C19—H19B	109.5
C2—O1—C1	117.9 (6)	O4—C19—H19C	109.5
C7—O2—Co1	125.4 (5)	H19A—C19—H19C	109.5
C18—O3—Co1	124.3 (5)	H19B—C19—H19C	109.5
C17—O4—C19	116.2 (6)	O7—C20—N3	125.6 (12)
O1—C1—H1A	109.5	O7—C20—H20	117 (4)
O1—C1—H1B	109.5	N3—C20—H20	116 (4)
H1A—C1—H1B	109.5	N3—C21—H21A	109.5
O1—C1—H1C	109.5	N3—C21—H21B	109.5
H1A—C1—H1C	109.5	H21A—C21—H21B	109.5
H1B—C1—H1C	109.5	N3—C21—H21C	109.5
C3—C2—O1	123.9 (8)	H21A—C21—H21C	109.5
C3—C2—C7	120.7 (9)	H21B—C21—H21C	109.5

O1—C2—C7	115.4 (6)	N3—C22—H22A	109.5
C2—C3—C4	118.6 (9)	N3—C22—H22B	109.5
C2—C3—H3	120.7	H22A—C22—H22B	109.5
C4—C3—H3	120.7	N3—C22—H22C	109.5
C5—C4—C3	122.2 (9)	H22A—C22—H22C	109.5
C5—C4—H4	118.9	H22B—C22—H22C	109.5
C3—C4—H4	118.9	N4—C23—H23A	109.5
C4—C5—C6	120.1 (9)	N4—C23—H23B	109.5
C4—C5—H5	119.9	H23A—C23—H23B	109.5
C6—C5—H5	119.9	N4—C23—H23C	109.5
C7—C6—C5	118.4 (8)	H23A—C23—H23C	109.5
C7—C6—C8	122.9 (7)	H23B—C23—H23C	109.5
C5—C6—C8	118.6 (8)	N4—C24—H24A	109.5
O2—C7—C2	116.6 (7)	N4—C24—H24B	109.5
O2—C7—C6	123.5 (7)	H24A—C24—H24B	109.5
C2—C7—C6	119.8 (7)	N4—C24—H24C	109.5
N1—C8—C6	124.8 (8)	H24A—C24—H24C	109.5
N1—C8—H8	128 (9)	H24B—C24—H24C	109.5
C6—C8—H8	107 (9)	O8—C25—N4	125.9 (10)

C10—C9—N1	111.4 (9)	O8—C25—H25	129 (4)
C10—C9—H9A	109.3	N4—C25—H25	104 (4)
N1—C9—H9A	109.3		

Donor ---	H....Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
Ow1	--Hw1A....O1	[3655.01]	0.93	2.32	2.929(8)	123
Ow1	--Hw1B....O3	[3655.01]	0.93	1.86	2.766(7)	164
Ow1	--Hw1B....O4	[3655.01]	0.93	2.39	2.966(8)	120
Ow2	--Hw2A....O7	[1555.03]	0.93	1.82	2.574(10)	136
Ow2	--Hw2B....O8	[2645.04]	0.93	1.83	2.631(8)	143
C9	--H9B....O11	[4554.02]	0.97	2.48	3.42(2)	164
C12	--H12....O8	[3665.04]	1.05(6)	2.22(6)	3.248(10)	167(5)
C15	--H15....O10	[4654.02]	0.93	2.59	3.421(16)	149
C22	-H22B....O10	[1655.02]	0.96	2.46	3.344(17)	154

Translation of ARU-Code to CIF and Equivalent Position Code

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[3655.] = 1-x,-y,-z [2645.] =1-x,-1/2+y,1/2-z [4554.] = x,1/2-y,-1/2+z [3665.] = 1-x,1-y,-z [4654.] = 1+x,1/2-y,-1/2+z [1655.] =1+x,y,z