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The syntheses and crystal structures of $Cs_2[Co_2(nta)_2(\mu\text{-}OH)_2]\cdot 4H_2O$ and $(C_{10}H_{10}N_3)_2[CoCl_4]$

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Abstract—The crystal structure of $Cs_2[Co_2(nta)_2(\mu\text{-}OH)_2]\cdot 4H_2O$ (nta = nitrilotriacetate) has been determined from three-dimensional X-ray diffraction data. Two hydroxo groups act as bridging groups between the two Co metal centres. The Co—OH bond distances are 1.899(5) and 1.897(5) Å, respectively and the Co—OH—Co bond angles 98.2(2)°. The nta ligand acts as a tetradentate ligand and bonds with a nitrogen as well as three oxygen atoms to the Co metal centre. The Co—N and Co—$O_{(av)}$ bonds are 1.922(6) and 1.895(5) Å, respectively. $(C_{10}H_{10}H_3)_2[CoCl_4]$ consists of discrete monoprotonated 2,2′-iminodipyridinium cations and $CoCl_4^{2-}$ anions. The anions assume a regular tetrahedral geometry, with the Cl—Co—Cl bond angles varying between 107.34(10) and 112.07(10)°. The Co—Cl bond distances are 2.270(2) and 2.282(2) Å, respectively. The two pyridine rings in the cation assume an almost planar orientation with a deviation of 7.7(6)° for the dihedral angle between the two ring systems. The planar orientation can be attributed to weak hydrogen bonding between the unprotonated nitrogen atom of the one pyridine ring and the proton bonded to the other nitrogen atom on the adjacent ring. © 1997 Elsevier Science Ltd

Keywords: syntheses; identification; crystal structures; cobalt(III)nitrilotriacetic acid dimer; tetrachlorocobaltate(II); 2,2′-iminodipyridinium cation.

It is well known that chromium(III), cobalt(III) and rhodium(III) complexes are relatively inert towards substitution reactions [1,2]. However, it became clear that the coordination of electron-donating ligands such as porphyrins to the above-mentioned cations can substantially increase the rate of substitution. The rate of aqua substitution in $[Co(TCPP)H_2O)_2]^{3-}$ [3] [TCPP = *meso*-tetrakis(4-carboxyphenyl)porhyrine] by NCS^- for example was determined as 4.45×10^2 M^{-1} s^{-1} compared with the 1.3×10^6 M^{-1} s^{-1} for the same reaction between $[Co(NH_3)_5(H_2O)]^{3+}$ [4] and NCS^-. High-pressure kinetic studies have also indicated a change in the substitution mechanism for the metal complexes. An activation volume of 18.8 cm^3 mol^{-1} which was obtained for the reaction between $[Co(TAPP)(H_2O)_3]^{5+}$ [5] (TAPP = *p*-trimethylammoniumphenyl porphyrine) and NCS^- clearly points to a dissociative mechanism (D) compared with the 1.2 cm^3 mol^{-1} which was obtained for the reaction between $[Co(NH_3)_5(H_2O)]^{3+}$ and NCS^- [6,7] and which is associated with an interchange mechanism (I_d).

In an attempt to gain more insight into the mechanistic aspects of the substitution reactions of these type metal complexes we decided to extend the study to other multidentate ligands such as nitrilotriacetate (nta). A study on the substitution kinetics of $[Cr(nta)(H_2O)_2]$ [8] also indicated an increase in substitution rate compared with the same reactions for $[Cr(NH_3)_5(H_2O)]^{3+}$.

It was decided to include the cobalt analogue in this study and this paper deals with the isolation and characterization of $Cs_2[Co_2(nta)_2(\mu\text{-}OH)_2]\cdot 4H_2O$ as well as $(C_{10}H_{10}N_3)_2[CoCl_4]$ which we obtained as product in our attempts to isolate the monomeric

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$[Co(nta)(H_2O)_2]$ or $[Co(nta)(OH)(H_2O)]^-$ complex.

EXPERIMENTAL

Synthesis of $Cs_2[Co_2(nta)_2(\mu\text{-}OH)_2]\cdot 4H_2O$

The $Cs_2[Co_2(nta)_2(\mu\text{-}OH)_2]\cdot 4H_2O$ complex was prepared by the method described by Mori [9] for the preparation of α-K[Co(nta)(H$_2$O)(OH)] · 2H$_2$O. $CoCl_4\cdot 6H_2O$ (5 g, 21 mmol) and nitrilotriacetic acid (4g, 21 mmol) was added to potassium bicarbonate solution (25 cm^3, 2.5 M). 30% H_2O_2 (1 cm^3) was added to this solution and the mixture was placed on an ice-bath and a blue precipitate separated after *ca* 5 h. The precipitate was filtered and washed several times with cold water. The product was then redissolved in hot water which contained potassium acetate and was recrystallized. The product was then washed with ethanol and diethylether and air dried. The blue precipitate was redissolved in water, an excess of CsCl was added and blue/purple $Cs_2[Co_2(nta)_2(\mu\text{-}OH)_2]\cdot 4H_2O$ crystals, suitable for X-ray data collection, were obtained after 24 h.

Synthesis of $(C_{10}H_{10}N_3)_2[CoCl_4]$

$Cs_2[Co_2(nta)_2(\mu\text{-}OH)_2]\cdot 4H_2O$ (0.3 g) was dissolved in water (10 cm^3) and a few drops of concentrated HCl and an excess of $C_{10}H_{17}N_3$ (2,2′-dipyridylamine) were added to this solution. Blue $(C_{10}H_{10}N_3)_2[CoCl_4]$ crystals, suitable for X-ray diffraction data collection, were obtained after 4 days.

Spectroscopic studies

Routine IR spectra were recorded as KBr discs on a Hitachi (Model 270-50) spectrophotometer. The electronic spectra were recorded on a Hitachi (Model 150-20) and a GBC (UV–vis 916) spectrophotometer at room temperature using distilled water as solvent. $[Co_2(nta)_2(\mu\text{-}OH)_2]^{2-}$: λ_{max}, 226 nm, ε_{226}, 3.6×10^4 M^{-1} cm^{-1}; $[Co(nta)(H_2O)_2]$: λ_{max} 227 nm, ε_{227}, 1.55×10^4 M^{-1} cm^{-1}; $[Co(nta)(OH)(H_2O)]^-$: λ_{max}, 236 nm, ε_{236}, 1.70×10^4 M^{-1} cm^{-1}.

Crystal data

The density of the compounds was determined by flotation in an iodomethane/benzene mixture. Lorentz, polarization and absorption corrections were applied to both sets of data. The structures were solved with the heavy-atom method and all the other atoms were located and their positions refined by successive Fourier calculations. The hydrogen-atom positions were calculated riding on the adjacent carbon, nitrogen and oxygen atoms [d(C—H) = 0.92 and d(N—H) = 0.86 Å] using an overall isotropic thermal parameter. Atomic scattering factors were obtained from Cromer and Mann [10]. The SHELXS86 [11] and SHELXL93 [12] programs were used for all the calculations. A final difference-Fourier for both structures showed no sign of disorder or residual peaks. The crystallographic data are listed in Table 1.

RESULTS AND DISCUSSION

Identification of different Co-nta *species in solution*

The blue product, α-K[Co(nta)(H$_2$O)(OH)] · 2H$_2$O, synthesized according to the method described by Mori, was dissolved in water and the UV–vis spectrum was record [214 (sh), 224 (s) and 303 nm (w)]. Subsequently, $Cs_2[Co_2(nta)_2(\mu\text{-}OH)_2]\cdot 4H_2O$ crystals were dissolved and the spectrum recorded [216 (sh), 226 (s) and 303 (w) nm]. These two spectra were identical and we conclude that the $[Co_2(nta)_2(\mu\text{-}OH)_2]^{2-}$ anion is synthesized using the Mori method and not α-[Co(nta)(H$_2$O)(OH)]$^-$ as was originally intended. Close inspection also reveals that results from a chemical analysis of the different Co-nta complexes (α-[Co(nta)(H$_2$O)(OH)]$^-$, β-[Co(nta)(H$_2$O)(OH)]$^-$ and $[Co_2(nta)_2(\mu\text{-}OH)_2]^{2-}$) were almost identical. A different number of moles of crystal waters was associated with each complex and identification of the different compounds using these results could not have been very accurate.

$Cs_2[Co_2(nta)_2(\mu\text{-}OH)_2]\cdot 4H_2O$ crystals were dissolved in water (pH *ca* 6) and the UV–vis spectrum recorded. $NaHCO_3$ was added to this solution (pH *ca* 7) and the spectrum recorded. No change in absorption maxima at 226 and 303 nm was observed. A fresh $Cs_2[Co_2(nta)_2(\mu\text{-}OH)_2]\cdot 4H_2O$ solution was again prepared and its spectrum recorded, **1** in Fig. 1. A few drops of 1.0 M HCl were added to this solution (pH *ca* 1) and the spectrum immediately changed with the disappearance of the peak at 303 nm (**2**). The addition of base to this solution (pH *ca* 7) resulted in the immediate change of the spectra with an absorption maxima at 236 nm (**3**). After the addition of acid to this solution (pH 1) the spectrum changed to the original spectrum with an absorption maxima at 226 nm (**4**). These results clearly point to a stable $[Co_2(nta)_2(\mu\text{-}OH)_2]^{2-}$ complex in slightly alkaline solution, but when protonated, immediately forms the *cis*-diaqua complex, which by the addition of base forms the oxohydroxo complex and that this protonation reaction is reversible. The rapid change in spectra with the addition of HCl is only attributed to protonation of the hydroxo groups in $[Co_2(nta)_2(\mu\text{-}OH)_2]^{2-}$ and not to the substitution of an aqua ligand by Cl$^-$ ions since these reactions are traditionally slow. These results are summarized by the following reaction:

$$[Co_2(nta)_2(\mu\text{-}OH)_2]^{2-} \xrightarrow{H^+} 2[Co(nta)(H_2O)_2]$$

$$\underset{H^+}{\overset{OH^-}{\rightleftharpoons}} 2[Co(nta)(H_2O)(OH)]^-$$

Table 1. Crystal data and structure refinement of $Cs_2[Co_2(nta)_2(\mu\text{-}OH)_2]\cdot 4H_2O$ (**I**) and $(C_{10}H_{17}N_3)_2][CoCl_4]$ (**II**)

	I	**II**
Identification code	coces	codip
Empirical formula	$C_{12}H_{22}Co_2Cs_2N_2O_{18}$	$C_{20}H_{20}Cl_4CoN_6$
Formula weight	866.00	545.16
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073 (Mo)	1.542 (Cu)
Diffractometer	Enraf–Nonius CAD4	Syntex P-1
Crystal system	Tetragonal	Monoclinic
Space group	$I4_1/a$	$C2/c$
Unit cell dimensions	$a = 19.640(2)$ Å, $\alpha = 90°$ $b = 19.640(2)$ Å, $\beta = 90°$ $c = 12.581(2)$ Å, $\gamma = 90°$	$a = 14.569(3)$ Å, $\alpha = 90°$ $b = 11.178(2)$ Å, $\beta = 101.26°$ $c = 14.632(4)$ Å, $\gamma = 90°$
Volume ($Å^3$)	4852.9(10)	2337.0(9)
Z	8	4
Density (calculated) ($Mg\ m^{-3}$)	2.371	1.549
Absorption coefficient (mm^{-1})	4.411	10.134
$F(000)$	3328	1108
Crystal size (mm)	$0.30 \times 0.30 \times 0.22$	$0.12 \times 0.06 \times 0.04$
Theta range for data collection (°)	1.92–24.97	5.02–55.06
Index ranges	$0 \leqslant h \leqslant 23$ $-15 \leqslant k \leqslant 16$ $0 \leqslant l \leqslant 14$	$0 \leqslant h \leqslant 15$ $0 \leqslant k \leqslant 11$ $-15 \leqslant l \leqslant 15$
Reflections collected	1246	1178
Independent reflections	1246 ($R_{int} = 0.0000$)	1178 ($R_{int} = 0.0000$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1244/0/164	1175/0/142
Goodness-of-fit on F^2	0.839	0.925
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0322$, $wR_2 = 0.0854$	$R_1 = 0.0555$, $wR_2 = 0.1492$
R indices (all data)	$R_1 = 0.0325$, $wR_2 = 0.0879$	$R_1 = 0.0561$, $wR_2 = 0.1567$
Largest difference peak and hole (e $Å^{-3}$)	1.195 and −1.034	0.654 and −0.403

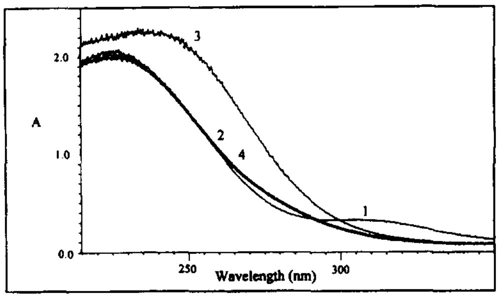

Fig. 1. Spectrum of the different Co-nta species in solution. **1** $[Co_2(nta)_2(\mu\text{-}OH)_2]^{2-}$, pH 5–7; **2**: $[Co_2(nta)_2(\mu\text{-}OH)_2]^{2-} + H^+$, pH ~ 1; **3**: $[Co(nta)(H_2O)_2] + HCO_3^-$, pH ~ 7; **4**: $[Co(nta)(OH)(H_2O)]^- + H^+$, pH ~ 1.

Crystal structure of $Cs_2[Co_2(nta)_2(\mu\text{-}OH)_2]\cdot 4H_2O$

The most relevant bond lengths and angles are reported in Table 2. The numbering scheme of the $[Co_2(nta)_2(\mu\text{-}OH)_2]^{2-}$ anion is shown in the perspective drawing in Fig. 2.

The two cobalt centres have regular octahedral geometries and are surrounded by the four nta atoms [N, O(2), O(4) and O(6)] and the two bridging OH groups [O(1) and O(1′)]. The Co—O bond distances are, within experimental error, the same, while the Co—N bond distance is 1.922(6) Å. All the N—Co—O bond angles deviate from 90° and the angles range between 85.2(2) and 88.1(2)°, while the N—Co—OH and O(6)—Co—OH bond angles are 177.6(2) and 93.9(2)°, respectively.

The Co—N bond distance in the current structure corresponds well with only one of the Cr—N bond distances in $K_2[Cr(nta)(\mu\text{-}OH)(\mu\text{-}acetate\text{-}O,O)Cr(nta)]\cdot 4H_2O$ [13] [2.060(5) and 1.936(4) Å, respectively]. The Co—O bond distances in $[Co_2(nta)_2(\mu\text{-}OH)_2]^{2-}$ are in general longer than the corresponding bond distances in $K_2[Cr(nta)(OH)(acetate\text{-}O,O)Cr(nta)]\cdot 4H_2O$, which range between 1.9449(5) and 1.982(4) Å, while the Co—OH bond distance of 1.899(5) Å in the current structure is shorter than the 1.936(4) and 1.925(4) Å in the above-mentioned structure. The M—O—M bond angle in the two structures also differ significantly [98.2(2) and 129.6(3)° for Co and Cr, respectively]. The N—C and C—O bond distances within the nta ligand correspond favourably with those obtained in both $Ca(nta)\cdot 2H_2O$ [14] and Hnta [15] (Hnta = nitrilotriacetic acid).

Table 2. Selected bond lengths (Å) and angles (°) for $Cs_2[Co_2(nta)_2(\mu\text{-}OH)_2 \cdot 4H_2O$

Co—O(2)	1.892(5)	C(4)—C(3)	1.526(12)
Co—O(4)	1.893(6)	O(2)—C(1)	1.283(9)
Co—0(6)	1.902(5)	O(4)—C(4)	1.256(10)
Co—O(1)	1.899(5)	N(1)—C(3)	1.478(10)
Co—O(1′)	1.897(5)	N(1)—C(2)	1.488(9)
Co—N(1)	1.922(6)	N(1)—C(5)	1.503(9)
O(6)—C(6)	1.276(9)	C(5)—C(6)	1.509(11)
C(1)—C(2)	1.498(12)	C(6)—O(7)	1.221(9)
C(1)—O(3)	1.231(9)	C(4)—O(5)	1.250(11)
O(2)—Co—O(4)	172.0(2)	O(2)—Co—O(6)	89.6(2)
O(4)—Co—O(6)	91.9(2)	O(4)—Co—O(1)	95.9(2)
O(2)—Co—O(1)	91.8(2)	O(4)—Co—N(1)	85.2(2)
O(6)—Co—O(1)	93.9(2)	O(1)′—Co—N(1)	96.1(2)
O(2)—Co—N(1)	87.0(2)	O(4)—Co—Cs(1)	135.2(2)
O(6)—Co—N(1)	88.1(2)	Co′—O(1)—Co	98.2(2)
O(1)—Co—N(1)	177.6(2)	C(4)—O(4)—Co	111.7(5)
C(6)—O(6)—Co	114.9(5)	C(3)—N(1)—C(5)	110.3(6)
C(1)—O(2)—Co	113.5(5)	C(3)—N(1)—Co	103.9(4)
C(3)—N(1)—C(2)	115.7(6)	C(5)—N(1)—Co	107.2(4)
C(2)—N(1)—C(5)	112.3(6)	O(7)—C(6)—O(6)	125.4(7)
C(2)—N(1)—Co	106.6(5)	O(6)—C(6)—C(5)	116.1(6)
N(1)—C(5)—C(6)	112.1(6)	O(5)—C(4)—O(4)	124.4(8)
O(7)—C(6)—C(5)	118.6(7)	O(4)—C(4)—C(3)	116.7(7)
O(5)—C(4)—C(3)	118.9(8)	O(3)—C(1)—O(2)	122.2(8)
O(3)—C(1)—C(2)	120.7(7)	O(2)—C(1)—C(2)	117.0(7)
N(1)—C(2)—C(1)	109.9(6)	N(1)—C(3)—C(4)	107.8(6)

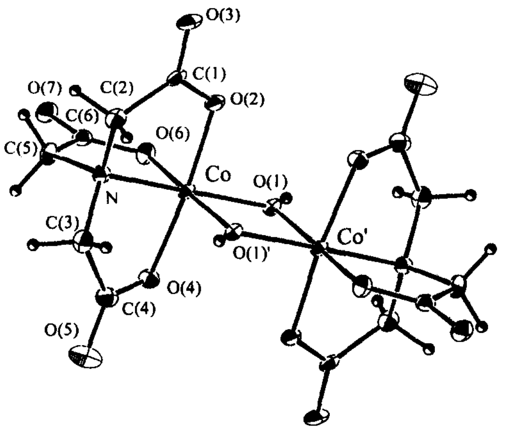

Fig. 2. Perspective view of $[Co_2(nta)_2(\mu\text{-}OH)_2]^{2-}$, indicating the atom labelling. Displacement ellipsoids are drawn at 30% probability level.

Crystal structure of $(C_{10}H_{10}N_3)_2[CoCl_3]$

The most relevant bonds lengths and angles are reported in Table 3. The monoprotonated 2,2′-iminodipyridium ion is illustrated in Fig. 3, while the packing of some of the cations and anions within the crystal is illustrated in Fig. 4. The two bridging N—C bond distances of 1.382(9) and 1.380(9) Å as well as the different N—C bond distances within the pyridine rings [average = 1.344(11) Å corresponds favourably with the same bonds in 2,2-iminodipyridine [16] and 2,2-iminodipyridinium tetrachlorocuprate(II) [12]]. The bridging C—N—C bond angle of 130.5(6)° in the current structure is exactly the same as the corresponding angle in 2,2-iminodipyridine, but differs from the 128.2(4)° obtained in 2,2-iminodipyridinium tetrachlorocuprate(II). The monoprotonated cation in the current structure has an almost planar orientation (7.6°) as was the case for 2,2′-iminodipyridine, while a twisted orientation for the two ring systems (45.7°) was observed for the diprotonated cation in 2,2′-iminodipyridinium tetrachlorocuprate(II). This planar orientation can be attributed to hydrogen bonding between the unprotonated nitrogen and the proton bonded to the other nitrogen atom with the $N \cdots H^+$ interaction of 1.93 Å. This interaction is also illustrated by the smaller than usual [N(11)—C(5)—N(1) and N(11)—C(10)—N(2)] bond angles [116.7(6) and 116.3(6)°, respectively] when compared with the same angles in 2,2-iminodipyridine [N(2)—C(5)—N(1) = 119.4 and N(2)—C(6)—C(7) = 124.2(4)°] and 2,2-iminodipyridinium tetrachlorocuprate(II) [N(1)—C(8)—N(9) = 119.9(5) and N(1)—C(2)—C(7) = 125.7(5)°].

The Co—Cl bond distances of 2.270(2) and 2.282(2) Å as well as the Cl—Co—Cl bond angles obtained in the title complex compare well with those found in (Hist.H2)$CoCl_4$) [18] (Hist.H2 = diprotonated histidinium ion).

We attribute the isolation of this Co^{II}-chloro com-

Table 3. Selected bond lengths (Å) and angles (°) for $(C_{10}H_{10}N_3)_2[CoCl_4]$.

Co—Cl(1)	2.270(2)	C(10)—N(2)	1.345(8)
Co—Cl(2)	2.282(2)	C(10)—C(9)	1.369(9)
N(1)—C(5)	1.332(9)	C(4)—C(3)	1.361(10)
N(1)—C(1)	1.342(9)	N(2)—C(6)	1.373(9)
C(2)—C(3)	1.386(11)	C(7)—C(8)	1.379(11)
C(2)—C(1)	1.372(11)	C(9)—C(8)	1.364(11)
N(11)—C(10)	1.380(9)	C(5)—N(11)	1.382(9)
C(5)—C(4)	1.380(10)		
C(9)—C(10)—N(11)	122.4(6)	C(7)—C(6)—N(2)	121.5(7)
C(5)—C(4)—C(3)	118.6(7)	Cl(1)$^{\#1}$—Co—Cl(1)	107.34(10)
C(10)—N(2)—C(6)	118.7(6)	Cl(1)$^{\#1}$—Co—Cl(2)	109.43(7)
C(2)—C(3)—C(4)	120.3(7)	Cl(1)—Co—Cl(2)	109.23(7)
C(7)—C(8)—C(9)	119.7(7)	Cl(1)$^{\#1}$—Co—Cl(2)$^{\#1}$	109.23(7)
C(4)—C(5)—N(11)	121.8(6)	Cl(1)—Co—Cl(2)$^{\#1}$	109.43(7)
C(10)—N(11)—C(5)	130.5(6)	Cl(2)—Co—Cl(2)$^{\#1}$	112.07(10)
N(1)—C(1)—C(2)	121.7(7)	C(5)—N(1)—C(1)	119.7(6)
N(2)—C(10)—N(11)	116.3(6)	C(3)—C(2)—C(1)	118.1(7)
C(10)—C(9)—C(8)	119.4(7)	N(1)—C(5)—C(4)	121.5(6)
N(1)—C(5)—N(11)	116.7(6)		

(1) Symmetry related.

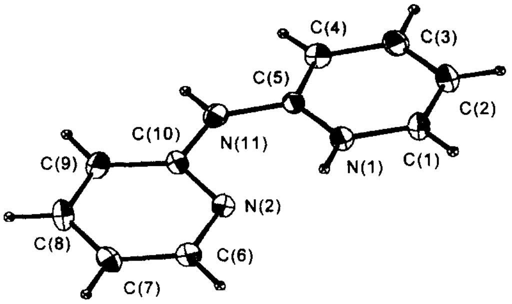

Fig. 3. Perspective view of the $(C_{10}H_{10}N_3)^+$ cation indicating the atom labelling. Displacement ellipsoids are drawn at 30% probability level.

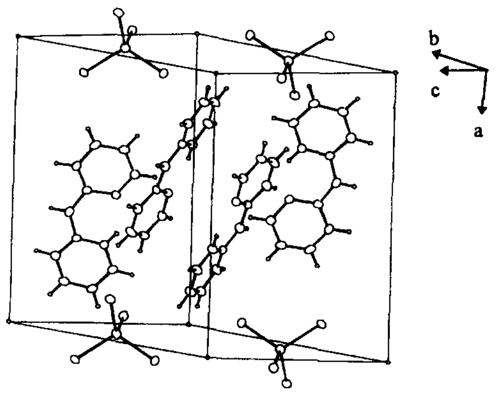

Fig. 4. Packing of $(C_{10}H_{10}N_3)_2[CoCl_4]$ within the unit cell.

plex to the incomplete oxidation of the Co^{II} ions, which were used as a starting material in the preparation of $[Co_2(nta)_2(\mu\text{-}OH)_2]^{2-}$. The $CoCl_4^{2-}$ complex was produced in the presence of the relatively high chloride ion concentration and with the addition of the 2,2′-iminodipyridyl in the high acid environment generated ideal conditions for this complex to crystallize.

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