Pyridine-Type Complexes of Transition-Metal Halides VIII[†] Preparation, Characterization and Single-Crystal Structure of Difluorotetrakis(3,5-dimethylpyridine)-cobalt(II)·n Hydrate [n ≈ 2.6(3)]

G. Kenessey,[a,*] K. Lashgari,[b] G. Machula[c] and G. Liptay[a,*]

[a]Department of Inorganic Chemistry, Technical University of Budapest, H-1521 Budapest, Hungary, [b]Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden and [c]Department of Inorganic and Analytical Chemistry, Attila József University, PO Box 440, H-6701 Szeged, Hungary

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A pyridine-type cobalt(II) complex containing fluoro ligands has been prepared from solution. The compound crystallizes in the tetragonal space group $P\ 4/mcc$, with $a = b = 9.352(2)$, $c = 17.264(4)$ Å and $Z = 2$. Refinement of its crystal structure against 1065 single-crystal X-ray diffraction data gave a final $Rw = 0.056$. The octahedral coordination around the Co is tetragonally distorted, Co–N = 2.186(4) Å and Co–F = 2.016(3) Å. The distorted D_{4h} symmetry is also apparent from the far-infrared spectrum. The observed effective magnetic moment (4.368 BM) is slightly lower than in the case of high-spin octahedral Co(II) complexes (5.2 BM at 300 K) because the ligand field departs from the octahedral. Thermal stability of the complex in a nitrogen atmosphere has also been studied.

In the last few decades considerable interest has been focused on the factors which may have an effect on the stability and the structure of pyridine type complexes containing halogen ligands.[1–9] The effect on the thermal stability, the electronic and infrared spectra and the magnetic moments of the different halides and pseudohalides have been discussed in detail.[8–20] Although the references mainly describe how a certain property depends on the halide, no information concerning fluoride complexes is available. In some previous works we reported the new solid–gas-phase preparation method and the application for obtaining fluoride complexes.[21–23] Because these compounds were microcrystalline and the recrystallization was impossible because of ligand changing processes, we have initiated preparation of fluoride complexes from solution.

Transition metals with d^7 electronic configurations are known to favour octahedral and tetrahedral coordination. The formation of [CoL₄X₂]-type compounds, where L is a sterically non-hindered ligand and X is a halide or pseudo-halide anion, has been found to depend mainly on the basicity of the anion.[12] On the basis of the splitting of the energy for absorption $^4T_{1g} \rightarrow {}^4T_{2g}(F)$, [CoL₄X₂]-type complexes, e.g. [Co(3,5-dimethylpyridine)₄Cl₂], were expected to have a tetragonally distorted D_{4h} environment[20] around the cobalt(II) atom.

We have earlier investigated the structural properties of some of the pyridine-type complexes with powder[24–29] and single-crystal[29–32] X-ray diffraction techniques. For complexes containing the same pyridine ligand, but different halides, we observed a linear relationship between the calculated density and molecular weight.[29] In the crystal structure of the dichlorotetrakis(3,5-dimethylpyridine)cobalt(II)[30] the central cobalt(II) ion has an octahedral environment, with Co–N distances of 2.188 Å and Co–Cl distances of 2.454 Å. The structure has orthorhombic symmetry, although the deviation in the cell parameters a and b ($a = 11.66$ Å and $b = 11.69$ Å) is small. The pyridine rings are tilted from the equatorial plane through 45°. There are more structural data available in the literature for pyridine, methylpyridine, halogenopyridine and aminopyridine complexes of different transition-metal halides.[33–41]

Experimental

Preparation of the complex. 0.01 mol of cobalt(II) fluoride dihydrate was dissolved in 20 cm³ of water, and 0.05 mol

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* To whom correspondence should be addressed.

of 3,5-dimethylpyridine (Fluka purum) was mixed with 20 cm³ of acetonitrile and added to the reaction mixture from a dropping funnel under stirring. The purple solution thus formed was allowed to crystallize overnight. Red–purple crystals with cubic shape were collected on a glass filter and dried over $CaCl_2$ in a desiccator.

Analysis. Carbon, hydrogen, nitrogen and oxygen content was determined by a Carlo Erba 1108 element analyzer. Results from the thermogravimetric measurements (see below) were used to check the stochiometry.

Thermal analysis. Simultaneous TG/DTG/DTA measurement was made in nitrogen atmosphere using Mettler 2 equipment with a sample weight of 15 mg and a heating rate of 2° min⁻¹. Platinum crucibles were utilized and 15 mg of α-Al_2O_3 was used as reference material.

Infrared spectra. Far-infrared spectrum was recorded with a Digilab FTS spectrophotometer, equipped with a TGS detector and 6 μm Hylar beam splitter. For sample preparation, a Nujol mull and polyethylene matrix were used.

Magnetic measurements. Variable-temperature, solid-state magnetic susceptibility data were measured with a series B-MB/7 susceptometer (Bruker Analytische Messtechnik GmbH) with BE 15 electromagnet. The susceptometer was operated at a magnetic field strength of 0.8 T. The susceptibility was measured by the Faraday method over the 85–300 K temperature range. The molar susceptibility

was corrected for ligand diamagnetism using Pascal's constants.[42] The experimental susceptibility was also corrected for temperature-independent paramagnetism (220×10^{-6} e.m.u. per Co^{2+}). The effective magnetic moment was calculated from the equation $\mu_{eff} = 2.828 \times [\chi'_M(T - \theta)]^{1/2}$, where χ_M is the atomic magnetic susceptibility, θ is the correction term (or Weiss constant) and T is the absolute temperature.[43]

X-Ray crystallography. A structural investigation based on X-ray diffraction data was carried out for the title compound.
X-Ray powder diffraction. Powder photographs were obtained using a Guinier–Hägg focusing camera with $CuK\alpha$ radiation. Silicon ($a = 5.430880$ Å) was added as internal

Table 2. Experimental conditions for crystal structure determination.

Formula (X-ray study)	$Co(N_4C_{28}H_{36})F_2 \cdot nH_2O$
	($n \approx 2.6$)
Formula weight/g mol⁻¹	572.09
Space group	$P4/mcc$ (No. 124)
Unit-cell dimensions	$a = b = 9.352(2)$,
	$c = 17.264(4)$
	$\alpha = \beta = \gamma = 90°$
Unit-cell volume, V/Å³	1509.8(6)
Formula units per unit cell, Z	2
Calculated density, D/g cm⁻³	1.26
Radiation	$MoK\alpha$
Wavelength, λ/Å	0.71073
Temperature, T/K	293
Crystal shape	Cubic
Crystal size/mm³	$0.20 \times 0.25 \times 0.18$
Diffractometer	Stoe four-circle
Determination of unit cell	
No. of reflections used	19
θ-range/°	20.9–26.6
Intensity data collection	ω–2θ scan technique
Maximum $\sin(\theta)/\lambda$/Å	0.70
Range of h, k and l	0–13, 0–13, 0–24
Standard reflections	3
Intensity instability (%)	3
Internal R	0.021
No. of collected reflections	2542
No. of unique reflections	1065
No. of observed reflections	527 (49%)
Criterion for significance	$I > 3\sigma(I)$
Absorption correction	Numerical integration
Linear absorption	
coefficient/cm⁻¹	6.08
Transmission factor range	0.89–0.91
Structure refinement	Full matrix least squares
Minimization of	$\Sigma w \Delta F^2$
Anisotropic thermal	
parameters	Co, N, C and F
Isotropic thermal parameters	O and H
No. of refined parameters	60
Weighting scheme	$[\sigma^2(F) + 0.0005 \,|F^2|]^{-1}$
Final R for observed refls.	0.041
Final Rw for observed refls.	0.047
Final Rw for all refls.	0.056
Final $(\Delta/\sigma)_{max}$(non-O	
and non-H)	0.014
Final $\Delta\rho_{min}$ and $\Delta\rho_{max}$/e Å⁻³	0.247 and 0.384

Table 1. Powder diffraction characteristics of [Co(3,5-dimethylpyridine)$_4$F$_2$]·nH$_2$O [$n \approx 2.6(3)$].

h	k	l	2θ obs./°	2θ calc./°	d/Å	I/I$_{max}$
1	0	0	9.464	9.450	9.33	73
0	0	2	10.227	10.227	8.64	100
1	0	1	10.655	10.748	8.29	30
1	0	2	13.953	13.942	6.34	15
2	0	0	18.972	18.965	4.674	8
2	1	0	21.225	21.228	4.182	64
2	1	1	21.838	21.848	4.066	88
2	1	2	23.634	23.615	3.761	8
3	0	0	28.636	28.314	3.114	9
3	1	0	30.205	30.198	2.956	37
3	0	2	30.386	30.461	2.939	13
3	1	1	30.653	30.647	2.914	6
0	0	6	31.072	31.019	2.875	10
3	1	2	31.971	31.961	2.797	20
3	2	0	34.531	34.555	2.595	8
3	2	2	36.134	36.129	2.4838	8
2	1	6	37.906	37.894	2.3717	9
4	0	0	38.492	38.476	2.3369	8
4	1	0	39.714	39.709	2.2677	13
4	1	1	39.998	40.064	2.2523	8
3	3	0	40.916	40.911	2.2039	9
4	1	2	41.105	41.113	2.1942	7
4	2	0	43.253	43.232	2.0901	7
4	2	2	44.552	44.545	2.0321	7
5	2	0	52.661	52.667	1.7367	14

standard and used for the correction of the 2θ scale. The film strip was measured with an automatic film scanner,[44] yielding relative line intensities and geometrical positions. The powder diffraction characteristics were further evaluated with TREOR 90, a trial-and-error indexing program.[45,46] The indexed powder pattern with observed and calculated 2θ and d values is presented in Table 1.

Single-crystal diffraction studies. Details of data collection and structure refinement are summarized in Table 2. All calculations were carried out with the SHELX-76 program package.[47] The position of the cobalt atom was derived from interpretation of a calculated Patterson function. The positions of the remaining non-hydrogen atoms, but including H4, were obtained from subsequent least-squares refinements and difference electron density (Δρ) calculations. The initial hydrogen atom positions, except for H4, were obtained by assuming ideal geometry. The positions of the methyl hydrogen were then refined under the constraint that they had a common thermal parameter of 0.100 [distance C–H = 1.00(5), 1.00(6) and 1.00(7) Å]. The single-crystal X-ray study showed that approximately 5 water molecules were present in the unit cell. The water molecules in the unit cell were found to be disordered. The disorder was described by fractional occupancies (see discussion below) at their symmetry-independent positions ($z = ^{1}/_{4}$). Reliable hydrogen positions for the water molecules could not be derived. The final atomic coordinates and thermal parameters are presented in Table 3. The symmetry-related interatomic distances and bond angles are collected in Table 4.[48] The X-ray atomic scattering factors for neutral atoms were taken from Ref. 49.

Results and discussion

Analysis. Results of the elemental analysis and the thermogravimetry of C(%), H(%), N(%), O(%) and Δm(%) are for the title compound: Calc. 58.7, 7.3, 9.8, 7.3 and 83.1; Found 58.3, 7.3, 10.1, 6.8 and 81.1.

Table 3. Atomic coordinates and equivalent isotropic thermal parameters (U_{eq}) for [Co(3,5-dimethylpyridine)$_4$F$_2$]·nH$_2$O [$n \approx 2.6(3)$].

Atom	x	y	z	U_{eq}
Co	0.0000	0.0000	0.0000	0.0349(3)
F1	0.0000	0.0000	0.1168(2)	0.0465(7)
N1	0.2172(4)	−0.0864(4)	0.0000	0.041(2)
C2	0.2862(4)	−0.1151(4)	0.0661(2)	0.048(1)
C3	0.4232(4)	−0.1717(4)	0.0695(2)	0.052(1)
C31	0.4933(6)	−0.2015(5)	0.1461(2)	0.082(2)
C4	0.4896(7)	−0.1994(6)	0.0000	0.057(2)
OA	0.125(2)	0.125(2)	0.250	0.09(1)[a]
OB	0.0000	0.171(3)	0.250	0.14(2)[a]
OC	0.069(5)	0.174(4)	0.250	0.02(2)[a]

[a]Positional parameters for OA, OB and OC are 0.24(2), 0.28(2) and 0.06(1), respectively.

Table 4. Bond distances (in Å) and bond angles (in °) with e.s.d.s for [Co(3,5-dimethylpyridine)$_4$F$_2$]·nH$_2$O [$n \approx 2.6(3)$]. The atoms primed are generated by symmetry operation (x, y, $−z$).

CoF1	2.016(3)	C2C3	1.388(5)
CoN1	2.186(4)	C3C31	1.502(5)
N1C2	1.337(4)	C4C3	1.376(4)
F1CoN1	90.0	C2C3C31	120.8(3)
CoN1C2	121.5(2)	C2C3C4	116.8(4)
C2N1C2'	117.0(3)	C31C3C4	122.4(4)
N1C2C3	124.0(3)	C3C4C3'	121.4(5)

Thermal analysis. The title compound decomposes in two main steps. The DTG curve for the first process is split into two peaks (the DTG peak temperatures are 103 and 114°C). The weight losses corresponding to these overlapping steps are 41.4 and 16.1%, respectively. In the last decomposition process 23.6% of the original weight was released with a DTG maximum at 191°C. The intermediates formed during the decomposition could not be described as stochiometric compounds.

The DTG peak temperature of the first decomposition step is at significantly lower temperature than for the other halide analogues:[16]

$$F(103°C) < Cl(150°C) < Br(175°C) < 185°C)$$

The cobalt–nitrogen distances for the fluoride (2.186 Å) and the chloride[30] (2.188 Å) are equal within the standard deviation. We assume that this value does not differ strongly on the halide, so the Co–N bond lengths are about 2.19 Å in the other two (bromide and iodide) analogues. The thermal stability slightly decreases from the iodide to the chloride compound; however, the DTG peak of the first decomposition step for the fluoride complex is almost 50°C lower than in the chloride analogue. We suggest that this low thermal stability is because of the different structure in the latter compound.

Far-infrared spectra. In addition to the ring deformation vibrations several metal–ligand bands were observed in the far-infrared region. On the basis of D_{4h} symmetry one metal–fluoride and one metal–nitrogen streching vibrations are expected, which were assigned at 345 and 220 cm^{-1}, respectively. The δ(F–Co–F) (228 cm^{-1}) and the δ(F–Co–N) (182 cm^{-1}) deformation vibrations accompany the ν(Co–N) band and can be seen as shoulders. The very weak band at 140 cm^{-1} was assigned as δ(N–Co–N) deformation mode. A band which arose at 59 cm^{-1} with medium intensity was assigned as lattice mode.

The metal–ligand streching vibrations were assigned for the lighter halide members of this series.[19] Both the cobalt–nitrogen and the cobalt–halogen vibration wavenumbers (212,212; 205,190 and 205,185 cm^{-1} for the chloride, bromide and iodide complexes, respectively) are lower than in the case of the fluoride complex. Taking into consideration the supposition that a stronger bond

yields a band at a higher wavenumber in the case of stretching vibrations, the decreasing order of the cobalt–halogen bonds from the fluoride to the iodide is supported by the cobalt–halogen bond length, which increases in the same order (see discussion below). No difference in cobalt–nitrogen distances could be found between the fluoride and chloride analogues, but the Co–N band is at a significantly lower wavenumber in the spectrum of the chloride compound.

Magnetic measurements. The solid-state magnetic susceptibility measurements was carried over the 85–300 K temperature range. The experimental data were evaluated with a local computer program, using a least-squares procedure, leading to an effective magnetic moment, as well as Curie and Weiss constants. The reliability of evaluation is reflected by the linear correlation coefficient (0.9936).

A high-spin octahedral cobalt(II) complex ($^4T_{1g}$ ground term) should have a magnetic moment of about 5.2 BM at 300 K, or probably somewhat lower if the symmetry of the ligand field departs from the octahedral. The spin-only value characteristic of three unpaired electrons (d^7 configuration) is 3.88 BM. In a high-spin tetrahedral cobalt(II) complex the ground term is $^4A_2$ and the magnetic moment should be about 4.4–4.8 BM at 300 K.

On the basis of the measured effective magnetic moment (4.368 ± 0.058 BM), Curie (2.365 ± 0.063 cm^3 mol^{-1} K) and Weiss constant ($- 1.57 ± 3.856$ K) we may suggest a deformed octahedral symmetry with high spin, and very weak antiferromagnetic interactions between the metal ions; consequently the structure is mononuclear. The observed low magnetic moment is probably due to the distorted octahedral symmetry and the orbital coupling which is negative in the case of ions with a d^6–d^{10} electronic configuration. The orbital coupling is more pronounced in the fluoride complex than in the chloride (μ_{eff} = 5.02 BM)[10] analogue.

X-Ray powder diffraction. The experimental X-ray powder pattern was indexed and yielded cell dimensions of $a = b = 9.351(2)$ and $c = 17.284(2)$ Å. The results of the calculations were supported with $M(20) = 11^\dagger$ and $F(20) = 16.*$ The close agreement of these cell parameters (cf. Table 2) and those obtained for the selected crystal by least-squares fitting of θ values for 19 selected and well centered reflections ensures that the single crystal used for collecting diffraction data was a proper representative of the specimen.

Crystal structure. The coordination octahedron around the central cobalt(II) is tetragonally distorted (Fig. 1). The Co–N distances are 2.186 Å, which are equal within the standard deviation to those observed for the chloride (2.188 Å) analogue.[30] As expected, the Co–F distances
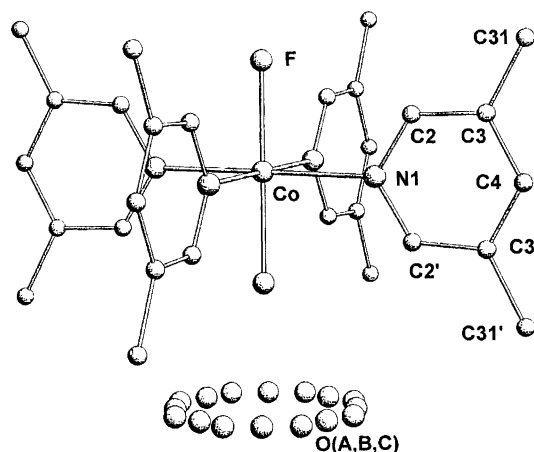
† *J. Appl. Crystallogr.* 1 (1968) 108.
$*$ *J. Appl. Crystallogr.* 12 (1979) 60.

Fig. 1. The [Co(3,5-dimethylpyridine)$_4$F$_2$]·nH$_2$O [$n \approx$ 2.6(3)] molecule. Hydrogen atoms are omitted.

(2.016 Å) are significantly shorter than the Co–Cl bond lengths (2.454 Å). On the basis of the X-ray powder diffraction data we estimated the cobalt(II)–halogen distances for the bromide and iodide analogues[28] to be 2.63 and 2.88 Å, respectively. These bond lengths are close to the sum of the ionic radii of the cobalt(II) and the appropriate halide ions (the sums are: 2.10, 2.55, 2.69 and 2.90 Å for the fluoride, chloride, bromide and iodide ions, respectively).

This effect can be explained by taking into account the electronic distribution of the molecules. In the case of pyridine type complexes, the back donation of electrons from the d-orbital of the cobalt to the non-bonding p-orbital of the nitrogen is well known, although this π-type interaction is greatly influenced by the electronic behaviour of the substituent and the place of substitution in the pyridine ring. In the case of electron-releasing substituents, such as methyl groups, the substitution in the β-position (third and fifth carbon atoms) increases the electron density in the *ortho-* and *para-*positions of the ring. The back-donated electrons are mainly localized at these atoms, so in the case of 3,5-dimethylpyridine (3,5-lutidine) the back donation is doubly hindered because of electronic interactions. While the cobalt(II) ion can not decrease its electron density via back donation, the increasing polarizability of the halide ions from the fluoride to the iodide plays only a minor role in the stability and the structure of 3,5-lutidine complexes.

The increasing ionic radius of the anions is more important from a structural point of view. In the fluoride complex the pyridine rings are coplanar and perpendicular to the plane formed by the four nitrogens and the cobalt. Because of the greater space requirement of the larger halide ion, the neighbouring pyridine rings are tilted 60° away from each other and approximately with 45° from the equatorial plane in the chloride analogue. We suggest that this deformation will be caused by all the larger halides. Because of the different preparation procedure, approximately 2.6 molecules of water per formula

unit was built into the crystal structure. The two complex molecules are separated by disordered water molecules, giving a sandwich-like structure in the unit cell. This structural feature was not found in the chloride analogue.[30] It seems possible that the strongly electronegative fluoride ion is responsible for stabilizing this structure. The disordered water molecules (OA, OB and OC) are located approximately on a circle with a radius of about 1.65 Å. The occupancies of the two 8-fold positions (OA and OB) were 0.24(1) and 0.28(2), respectively, and that of the 16-fold position (OC) was 0.06(2). The distances between the fluorine and the alternative positions (OA, OB and OC), which range from 2.81 to 2.89 Å, indicate that the water molecules are hydrogen-bonded to the fluorine atoms. The observed deformation from the ideal 120° of the bond angles in the aromatic ring agrees within two e.s.d.s with those predicted from the deformation parameters given by Norrestam and Schepper.[50]

Although the chloride, bromide and iodide analogues have orthorhombic symmetry the values of the parameters a and b differ only in the case of the chloride complex[30] (11.66 and 11.69 Å); the bromide and the iodide compounds are pseudotetragonal ($a = 11.86$ and 12.13 Å, respectively). The cobalt–halogen bond lengths, in the direction of the z-axis, increase from the fluoride to the iodide compound, but the value of c decreases in the same order (10.61, 10.34 and 10.21 Å for the chloride, bromide and iodide complex, respectively). The fluoride compound has significantly larger c-value (17.264 Å from powder diffraction studies). The differences in the structural parameters occur, i.e. because of the water content of the fluoride analogue.

In the unit cell of the fluoride complex the molecules are lined along the z-axes and separated by disordered water molecules (Fig. 1). The unit-cell volumes increase from the chloride to the iodide compounds (1448, 1454 and 1503 Å³) as expected. Because of the water content the fluoride complex deviates from this trend (1510 Å³).

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