Inorg. Chem. **1994,** *33,* 5535−5540 **5535**

(Dimethylviolurato)bis(phenanthroline)cobalt(II), a Novel Spin-Crossover Octahedral Co(II) Complex. Synthesis, Crystal Structure, and Magnetic Properties of $[Co(dmvi)(phen)_2]ClO_4\cdot 3H_2O$

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Received March 23, 1994[⊗]

The complex of formula $[Co(dmvi)(phen)_2]ClO_4\cdot 3H_2O$ (dmvi = $C_6H_6N_3O_4$, dimethylviolurate anion, and phen = $C_{12}H_8N_2$, 1,10−phenanthroline) has been synthesized, and its structure has been determined by X-ray crystallographic methods at two different temperatures, 294 and 92 K. Crystal data: triclinic system, space group $P\bar{1}$, with $a = 11.613(5)$ Å, $b = 12.390(4)$ Å, $c = 13.041(6)$ Å, $\alpha = 71.61(3)°$, $\beta = 83.67(3)°$, $\gamma = 79.09(3)°$, and $Z = 2$ at 294 K and $a = 11.29(1)$ Å, $b = 12.26(1)$ Å, $c = 13.08(2)$ Å, $\alpha = 72.26(9)°$, $\beta = 80.63(8)°$, $\gamma = 77.99(8)°$, and $Z = 2$ at 92 K. The structure was solved by direct methods. The perchlorate anion and the water molecules are disordered, and the latter could be located only in the low temperature structure. The structures were refined by the full-matrix least-squares method. The refinements, including 3374 (294 K) and 2244 (92 K) reflections converged at $R = 0.083$ and 0.107, respectively. The structure consists of $[Co(dmvi)(phen)_2]^+$ cations well separated from the ClO_4^- counterions and water of hydration. The metal ion exhibits a N_5O distorted-octahedral surrounding at room temperature. One phenanthroline ligand occupies two equatorial positions, with identical bond lengths to Co(II) of 2.00 Å, whereas the other is coordinated in a very asymmetric way, with one short equatorial (1.99 Å) and one long axial (2.11 Å) bonds. The dmvi anion also acts as a very asymmetrical chelating ligand, Co−N and Co−O bond lengths being 1.93 and 2.16 Å, respectively. The coordination sphere of the metal ion is very similar in the low temperature structure, the bond lengths being somewhat shorter. Average Co−N(equatorial) and Co−X(axial) (X = O, N) distances are 1.977 and 2.137 Å in the room temperature structure, while the corresponding values in the low temperature structure are 1.94 and 2.12 Å. Variable-temperature magnetic susceptibility measurements and EPR spectra, reveal that the complex exhibits a smooth and incomplete spin transition between $S = {}^{3}/_{2}$ and $S = {}^{1}/_{2}$ states which are separated by *ca.* 150 cm^{-1}.

Introduction

A variety of transition metal complexes exhibit transformations between different spin states which are induced by an external perturbation, usually a variation of temperature but also a variation of pressure or irradiation with light.[2] Most of them are Fe(II) (d^6), Fe(III) (d^5) and, to a lesser degree, Co(II) (d^7) complexes. The spin change can occur abruptly, in a narrow temperature range, or very gradually.[3] Although extreme examples of these two behaviors are known, it seems that most cases are intermediate between them. Although only a few novel examples of spin-crossover complexes have been reported in the last years, the interest in these compounds remains high. The general reasons why these complexes are being studied have been summarized recently.[4]

Magnetic susceptibility measurements and EPR spectroscopy have been the most widely used experimental techniques in these studies although heat capacity measurements and, for iron complexes, Mössbauer spectroscopy are also important.[5] The spin conversion results in a shortening of metal to ligand bonds, owing to the lower occupancy of antibonding orbitals in the low-spin forms, and is always accompanied by structural modifications of the coordination polyhedron. So, the characterization of a single compound by X-ray diffraction at two or more different temperatures is very important. At this respect, the first attempt was the determination of the structure of the iron(II) complex $[Fe(bpy)_2(NCS)_2]$, (bpy = 2,2′-bipyridine), at temperatures above and below the abrupt spin-state transition.[6] Nowadays, more than 20 metal complexes have been characterized in this form.[7]

Examples of spin-crossover dealing with cobalt(II) complexes are much less abundant than those concerning iron(II) and iron(III) complexes.[8] In these systems, cobalt(II) can be five- or six-coordinated and exhibits a $S = {}^{3}/_{2} \leftrightarrow S = {}^{1}/_{2}$ spin change. Two series of compounds $[Co(terpy)_2]X_2\cdot nH_2O$[9] and $[Co(H_2fsa_2en)L_2]$[8] (H_2fsa_2en = *N,N′-o*-ethylenebis(3-carboxysalicyl)-aldiminate and L = H_2O, py, substituted pyridines), have been most studied. Up to now, only three cobalt(II) complexes have been characterized by X-ray diffraction at two different temperatures, the five-coordinated $[Co(nnp)(NCS)_2]$, (nnp = *N*-[(diphenylphosphino)ethyl]-*N′*-diethylenediamine),[10] and [CoL-(mim)], [L = *N,N′*-bis(5−mercapto-3-methyl-1-phenylpyrazol-4-ylmethylene)-*o*-phenylenediamine; mim = *N*-methyl-

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1994.

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0020-1669/94/1333-5535$04.50/0

imidazole],[11] and the six-coordinated $[\mathrm{Co(terpy)_2}]\mathrm{I_2}\cdot 2\mathrm{H_2O}$, (terpy = 2,2′:6′,2″-terpyridine).[9c]

Violurate anions (violuric acid, H$_3$vi, [1*H*,3*H*-pyrimidine-2,4,5,6-tetraone 5-oxime]) are strong-field bidentate ligands which are coordinated to the metal ions through two different donor atoms (N, O) and, hence, in an asymmetric way. They fulfill the requirements to stabilize low-spin octahedral Co(II).[12] Accordingly, $[\mathrm{Co(dmvi)_3}]^-$ (dmvi = dimethylviolurate anion), an anionic complex which was characterized in solution,[13] is a low-spin species. Substituting one of the dmvi anions by a phenanthroline molecule gives $[\mathrm{Co(dmvi)_2(phen)}]$. Very recently, the synthesis and full characterization in solid state and in solution of this complex has been reported.[12] This species is also a low-spin complex in spite of the high-spin nature of $[\mathrm{Co(phen)_3}]^{2+}$.[14] Substituting another dmvi anion by a second phenanthroline molecule leads to $[\mathrm{Co(dmvi)(phen)_2}]^+$, a species that we have proved to exist in solution together with $[\mathrm{Co(dmvi)_2(phen)}]$. $[\mathrm{Co(dmvi)(phen)_2}]^+$ is a very interesting complex because most likely it should exhibit a spin-equilibrium.[12]

We report here the synthesis, and variable-temperature EPR spectra and magnetic properties of the $[\mathrm{Co(dmvi)(phen)_2}]\mathrm{ClO_4}\cdot 3\mathrm{H_2O}$ complex, as well as its structural characterization by X-ray diffraction methods at two different temperatures, 92 and 294 K. All the experimental results show that this compound exhibits a spin equilibrium between $S = {}^3/_2$ and $S = {}^1/_2$ states, these two states being very close in energy.

Experimental Section

Materials. Dimethylvioluric acid monohydrate, was prepared and purified following a reported procedure.[15] 1,10−Phenanthroline monohydrate (Aldrich), cobalt(II) acetate tetrahydrate (Panreac), and all other reagents were used as received. Elemental analyses (C, H, N) were performed by the Servicio de Análisis Elemental de la Universidad Autónoma de Madrid, Madrid, Spain.

Synthesis of the Complex. A 0.25 mmol (50 mg) sample of $\mathrm{Hdmvi\cdot H_2O}$ and 0.5 mmol (100 mg) of phen were dissolved in 25 mL of methanol under inert atmosphere, and then a solution of 0.25 mmol (62 mg) of $\mathrm{CoAc_2\cdot 4H_2O}$ and 45 mg of $\mathrm{LiClO_4}$ in the least amount of water was added. When this solution was allowed to stand, a nearly black, microcrystalline precipitate of $[\mathrm{Co(dmvi)(phen)_2}]\mathrm{ClO_4}\cdot 3\mathrm{H_2O}$ slowly appeared. The solid was filtered, washed with methanol and dried in the air. Anal. Calcd for $\mathrm{C_{30}H_{28}CoClN_7O_{11}}$: C, 47.60; H, 3.69; N, 12.94. Found: C, 48.26; H, 2.97; N, 12.83.

The synthesis is carried out in methanol as solvent because a yellow precipitate of $[\mathrm{Co(phen)_3}]\mathrm{ClO_4}\cdot \mathrm{H_2O}$ instead of the desired complex is obtained by addition of perchlorate anions to an aqueous solution containing cobalt(II), dmvi, and phen in a 1:1:2 molar ratio. The distribution diagrams of the species in solution calculated from the stability constants previously reported[12] show that, under the more favorable conditions, $[\mathrm{Co(dmvi)(phen)_2}]^+$ coexists in aqueous solution, between other species, with significant amounts of $[\mathrm{Co(phen)_3}]^{2+}$, which forms a more insoluble perchlorate.

Single crystals for the X-ray crystallographic study were obtained following the same experimental procedure but in more diluted solutions.

Physical Techniques. Variable-temperature magnetic measurements were carried out on polycrystalline samples of $[\mathrm{Co(dmvi)(phen)_2}]\mathrm{ClO_4}\cdot 3\mathrm{H_2O}$ in the temperature range 4−300 K by means of a previously described pendulum-type apparatus.[16] The uncertainty in the data is lower than 0.1 K for temperatures and 2×10^{-5} cm^3 mol^{-1} for susceptibilities. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Experimental susceptibilities were corrected for diamagnetism of the constituent atoms by the use of Pascal's constants. Variable temperature X-band EPR spectra were recorded with a Brüker ER200D spectrometer equipped with a helium cryostat.

Table 1. Crystallographic Data for $[\mathrm{Co(dmvi)(phen)_2}]\mathrm{ClO_4}\cdot 3\mathrm{H_2O}$ at 294 and 92 K

	room temp, 294 K	low temp, 92 K
chem formula	$\mathrm{CoClO_{11}N_7C_{30}H_{28}}$	$\mathrm{CoClO_{11}N_7C_{30}H_{28}}$
fw	756.98	756.98
space group	$P\bar{1}$	$P\bar{1}$
a/Å[a]	11.613(5)	11.29(1)
b/Å	12.390(4)	12.26(1)
c/Å	13.041(6)	13.08(2)
α/deg	71.61(3)	72.26(9)
β/deg	83.67(3)	80.63(8)
γ/deg	79.09(3)	77.99(8)
V/Å^3	1746(1)	1679(3)
Z	2	2
D_x/g cm^{-3}	1.440	1.497
λ/Å	0.710 63	0.710 63
μ/mm^{-1}	0.630	0.655
max, min transm factors	0.958, 0.895[b]	
R[c]	0.083	0.107
R_w[d]	0.108	0.127
S[e]	3.91	3.90

[a] Cell dimensions are calculated from a least-squares fit of the setting angles of 25 reflections with 2θ in the region 21−33°. [b] Absorption correction by the Gaussian integration method. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [e] $S = [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$. [f] $w = 4F_o^2/[\sigma_c^2 + (kF_o^2)^2]$, where σ_c is the standard deviation in F^2 based on counting statistics alone.

Crystallographic Data Collection and Structure Determination. Diffraction data were collected at 294 and 92 K with an Enraf-Nonius CAD4 diffractometer equipped with a liquid-nitrogen cooling device. Cell parameters were in each case determined from 25 reflections with 2θ angles between 21 and 33° (Mo Kα radiation, λ = 0.710 73 Å). Crystal parameters and refinement results are summarized in Table 1. Additional information on crystal data and experimental conditions are deposited as supplementary material (Table S1). A total of 4844 (294 K) and 4679 (92 K) reflections were recorded in the range $2 < \theta < 46°$. Three reference reflections were monitored and showed an average decrease of 5% and 13% for the room and low temperature data collections, respectively. The reflections had wide profiles and were in some cases clearly split. Although slow cooling of crystals was used, this problem was clearly most serious at low temperature. The usual corrections for Lorentz and polarization effects were carried out, as were corrections for linear decay. For the room temperature data, absorption correction was done by the Gaussian integration method.[17]

The intensity statistics clearly suggested a centrosymmetric space group for both sets of data. The structure was solved from the room temperature data by direct methods. The water of crystallization present according to the chemical analysis could not be located in the room temperature structure. Atomic coordinates as determined from room temperature data were used as starting point for the refinement of the low temperature structure. In this case three positions for water of crystallization were identified from residual peaks of electron densities 2.5−3.0 e/Å^3. The water molecules appear to be disordered, and occupancy parameters of 0.5 were used for these three atoms. Three additional residual peaks with electron densities 1.0−1.5 e/Å^3 may be due to water sites of low occupancies, but atoms were not included in these positions. The perchlorate ion is in each case disordered, two positions of occupancies 0.5 were refined. The structures were refined by the full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically in the room temperature structure. The oxygen atoms of water and one of the perchlorate ions had ill-defined

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Table 2. Atomic Coordinates and Isotropic Equivalent Displacement Parameters[a,b] for Non-Hydrogen Atoms of $[Co(dmvi)(phen)_2]ClO_4{\cdot}3H_2O$[c]

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}, Å^2	atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}, Å^2
(a) At 294 K									
Co	0.3010(1)	0.2855(1)	0.2207(1)	3.96(3)	C(15)	−0.062(1)	0.307(1)	0.186(1)	10.3(5)
O(1)	0.2954(7)	0.5238(6)	0.1275(5)	6.2(2)	C(16)	0.0466(9)	0.2918(9)	0.232(1)	6.6(3)
O(2)	0.2349(6)	0.2746(5)	0.3846(5)	4.6(2)	C(17)	0.128(2)	0.393(1)	−0.1649(9)	12.7(5)
O(3)	0.1028(8)	0.5124(6)	0.5895(6)	7.5(2)	C(18)	0.031(2)	0.383(1)	−0.102(1)	14.5(6)
O(4)	0.2306(7)	0.6740(5)	0.2446(6)	6.6(2)	C(19)	0.5280(9)	0.3253(8)	0.2853(9)	6.2(3)
N(1)	0.2746(6)	0.4462(6)	0.2126(6)	4.4(2)	C(20)	0.634(1)	0.287(1)	0.337(1)	7.7(3)
N(2)	0.1695(7)	0.3923(6)	0.4882(6)	4.3(2)	C(21)	0.676(1)	0.169(1)	0.380(1)	7.6(4)
N(3)	0.1666(7)	0.5932(6)	0.4153(6)	4.7(2)	C(22)	0.6057(9)	0.0926(9)	0.3711(9)	6.1(3)
N(4)	0.3460(8)	0.3205(7)	0.0533(6)	5.9(2)	C(23)	0.5016(8)	0.1376(8)	0.3173(8)	4.6(3)
N(5)	0.1409(7)	0.3060(6)	0.1701(6)	4.9(2)	C(24)	0.4313(8)	0.0628(8)	0.3042(7)	4.6(3)
N(6)	0.4619(7)	0.2524(6)	0.2756(6)	4.9(2)	C(25)	0.4675(9)	−0.0538(8)	0.3413(9)	6.2(3)
N(7)	0.3302(7)	0.1146(6)	0.2508(6)	4.6(2)	C(26)	0.400(1)	−0.1215(9)	0.317(1)	8.0(4)
C(1)	0.2326(8)	0.4721(7)	0.3040(7)	3.6(2)	C(27)	0.301(1)	−0.0717(8)	0.261(1)	7.4(3)
C(2)	0.2138(8)	0.3752(7)	0.3921(7)	4.0(2)	C(28)	0.2660(9)	0.0474(8)	0.2304(8)	5.6(3)
C(3)	0.1450(9)	0.5025(8)	0.5013(8)	5.3(3)	C(29)	0.637(1)	−0.030(1)	0.415(1)	7.5(4)
C(4)	0.2113(8)	0.5857(8)	0.3157(7)	4.7(3)	C(30)	0.571(1)	−0.0979(9)	0.399(1)	7.7(4)
C(5)	0.149(1)	0.2917(9)	0.5844(8)	6.0(3)	Cl(A)	0.500	0.500	0.500	6.4(1)
C(6)	0.149(1)	0.7072(9)	0.4356(9)	7.2(3)	Cl(B)	0.000	0.000	0.500	7.8(1)
C(7)	0.447(1)	0.3285(9)	−0.0033(9)	7.9(3)	O(5)	0.469(2)	0.533(2)	0.395(1)	9.7(6)
C(8)	0.446(2)	0.361(1)	−0.123(1)	13.5(5)	O(6)	0.394(2)	0.508(2)	0.563(1)	11.4(7)
C(9)	0.346(2)	0.382(1)	−0.179(1)	15.4(7)	O(7)	0.555(2)	0.592(2)	0.511(2)	13.8(7)
C(10)	0.240(2)	0.3737(9)	−0.1176(9)	9.9(5)	O(8)	0.567(3)	0.411(2)	0.521(2)	20(1)
C(11)	0.243(1)	0.3425(7)	0.0001(8)	6.7(3)	O(9)	0.046(1)	−0.110(1)	0.551(2)	9.5(6)
C(12)	0.134(1)	0.3324(8)	0.0657(9)	6.0(3)	O(10)	−0.108(2)	0.027(2)	0.551(2)	12.6(7)
C(13)	0.025(1)	0.3508(9)	0.011(1)	8.4(4)	O(11)	0.070(2)	0.080(2)	0.480(2)	18.3(9)
C(14)	−0.073(1)	0.334(1)	0.080(1)	10.7(5)	O(12)	−0.028(3)	0.007(3)	0.394(2)	19(1)
(b) At 92 K									
Co	0.2956(3)	0.2787(2)	0.2281(2)	2.42(6)	C(17)	0.191(3)	0.386(2)	−0.168(2)	8.3(8)
O(1)	0.283(1)	0.5149(9)	0.1376(9)	3.7(3)	C(18)	0.079(2)	0.390(2)	−0.126(2)	8.1(7)
O(2)	0.217(1)	0.2670(8)	0.3936(8)	2.7(3)	C(19)	0.522(2)	0.320(2)	0.294(2)	5.0(6)
O(3)	0.096(1)	0.507(1)	0.612(1)	4.5(4)	C(20)	0.632(2)	0.282(2)	0.343(2)	5.6(6)
O(4)	0.224(1)	0.667(1)	0.261(1)	4.7(4)	C(21)	0.674(2)	0.166(2)	0.381(2)	6.5(7)
N(1)	0.265(1)	0.437(1)	0.225(1)	2.8(4)	C(22)	0.604(2)	0.084(2)	0.375(2)	5.4(6)
N(2)	0.158(1)	0.385(1)	0.505(1)	2.7(4)	C(23)	0.495(2)	0.130(1)	0.322(1)	3.5(5)
N(3)	0.161(1)	0.588(1)	0.430(1)	3.1(4)	C(24)	0.426(2)	0.055(1)	0.305(1)	3.1(5)
N(4)	0.365(1)	0.308(1)	0.067(1)	4.6(5)	C(25)	0.464(2)	−0.061(1)	0.337(2)	4.1(6)
N(5)	0.143(1)	0.303(1)	0.168(1)	3.5(4)	C(26)	0.391(2)	−0.129(2)	0.312(2)	5.4(7)
N(6)	0.454(1)	0.247(1)	0.285(1)	3.8(4)	C(27)	0.294(2)	−0.080(2)	0.256(2)	4.8(6)
N(7)	0.325(1)	0.109(1)	0.254(1)	2.8(4)	C(28)	0.260(2)	0.041(1)	0.232(1)	3.2(5)
C(1)	0.220(1)	0.466(1)	0.318(1)	2.0(4)	C(29)	0.637(2)	−0.039(2)	0.412(2)	6.0(7)
C(2)	0.198(2)	0.365(1)	0.406(1)	2.9(5)	C(30)	0.573(2)	−0.103(2)	0.393(2)	5.2(7)
C(3)	0.138(2)	0.498(1)	0.520(1)	3.9(5)	Cl(A)	0.500	0.500	0.500	3.7(2)
C(4)	0.204(1)	0.577(1)	0.332(1)	2.4(4)	Cl(B)	0.000	0.000	0.500	3.4(2)
C(5)	0.137(2)	0.287(2)	0.603(1)	3.7(5)	O(5)	0.465(3)	0.530(2)	0.400(2)	4.8(8)
C(6)	0.145(2)	0.703(1)	0.453(2)	5.0(6)	O(6)	0.386(2)	0.507(2)	0.576(2)	4.0(7)
C(7)	0.473(2)	0.315(2)	0.011(2)	6.6(7)	O(7)	0.558(2)	0.588(2)	0.515(2)	5.7(9)
C(8)	0.493(2)	0.340(2)	−0.107(2)	11.5(7)	O(8)	0.566(3)	0.401(3)	0.538(3)	9(1)
C(9)	0.394(4)	0.372(2)	−0.163(2)	13(1)	O(9)	0.037(3)	−0.098(2)	0.583(2)	5.5(7)*
C(10)	0.283(3)	0.364(1)	−0.112(2)	7.8(8)	O(10)	−0.114(3)	0.032(2)	0.553(2)	6.4(8)*
C(11)	0.279(2)	0.333(1)	0.002(1)	4.7(6)	O(11)	0.078(3)	0.073(3)	0.468(3)	9(1)*
C(12)	0.153(2)	0.330(1)	0.060(2)	5.1(6)	O(12)	−0.037(2)	−0.049(2)	0.424(2)	5.0(7)*
C(13)	0.053(2)	0.348(2)	0.001(2)	6.7(6)	O(W1)	0.109(3)	0.826(2)	0.097(2)	5.1(7)*
C(14)	−0.058(2)	0.343(2)	0.059(2)	9.0(8)	O(W2)	0.767(3)	0.082(3)	0.098(3)	7.2(9)*
C(15)	−0.069(2)	0.307(2)	0.174(2)	8.3(8)	O(W3)	0.024(3)	0.013(2)	0.798(2)	6.2(8)*
C(16)	0.034(2)	0.289(1)	0.228(2)	4.2(5)					

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}\mathbf{a}_i{\cdot}\mathbf{a}_j$. [c] Values marked with an asterisk denote atoms that were refined isotropically.

anisotropic thermal parameters in the low temperature structure and were thus refined isotropically. Hydrogen atoms attached to sp^2-hybridized carbon atoms were included at calculated positions, but they were not refined. The refinements, including 3374 (294 K) and 2244 (92 K) reflections converged at $R = 0.083$ and 0.107, respectively. These high R values may be due to both disorder and mixture of high- and low-spin forms (*vide infra*). One posible reason for the higher R value of the low temperature form may be that the crystals cracked somewhat when cooled, the reflections being very broad.

All calculations were carried out on a MICRO-VAX II computer with the Enraf-Nonius Structure Determination Program.[18] The scattering curves, with anomalous scattering terms included, were those of Cromer and Mann.[19]

The refined final coordinates for non-hydrogen atoms and selected bond distances and angles are listed in Tables 2 and 3, respectively. Tables of anisotropic thermal parameters of non-hydrogen atoms, hydrogen coordinates, remaining bond distances and angles, and least-squares planes are deposited as supplementary material (Tables S2–S6).

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(18) Frez, B. A. *The SDP-Users Guide*, (SDPVAX V.3), Enraf-Nonius, Delft, The Netherlands, 1985.

(19) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1974; Vol. IV, p 99 (Table 2.2B).

Table 3. Selected Bond Lengths (Å) and Angles (deg)[a] for $[Co(dmvi)(phen)_2]ClO_4{\cdot}3H_2O$

(a) At 294 K			
Co−O(2)	2.160(6)	Co−N(5)	1.986(9)
Co−N(1)	1.926(8)	Co−N(6)	1.997(8)
Co−N(4)	2.114(8)	Co−N(7)	1.997(7)
O(2)−Co−N(1)	79.7(3)	O(2)−Co−N(4)	170.9(2)
O(2)−Co−N(5)	92.6(3)	O(2)−Co−N(6)	86.9(3)
O(2)−Co−N(7)	93.1(3)	N(1)−Co−N(4)	93.0(3)
N(1)−Co−N(5)	89.2(3)	N(1)−Co−N(6)	94.8(3)
N(1)−Co−N(7)	172.2(3)	N(4)−Co−N(5)	81.8(3)
N(4)−Co−N(6)	99.3(3)	N(4)−Co−N(7)	94.4(3)
N(5)−Co−N(6)	175.7(3)	N(5)−Co−N(7)	94.3(3)
N(6)−Co−N(7)	81.5(3)		
(b) At 92 K			
Co−O(2)	2.17(1)	Co−N(5)	1.94(2)
Co−N(1)	1.89(1)	Co−N(6)	1.97(2)
Co−N(4)	2.07(2)	Co−N(7)	1.97(1)
O(2)−Co−N(1)	79.5(5)	O(2)−Co−N(4)	174.1(5)
O(2)−Co−N(5)	96.5(6)	O(2)−Co−N(6)	85.7(6)
O(2)−Co−N(7)	92.4(5)	N(1)−Co−N(4)	94.7(6)
N(1)−Co−N(5)	89.0(7)	N(1)−Co−N(6)	94.0(7)
N(1)−Co−N(7)	171.6(5)	N(4)−Co−N(5)	82.2(6)
N(4)−Co−N(6)	95.9(7)	N(4)−Co−N(7)	93.5(5)
N(5)−Co−N(6)	176.6(6)	N(5)−Co−N(7)	94.3(7)
N(6)−Co−N(7)	83.0(6)		

[a] Estimated standard deviations in the last significant digits are given in parentheses.

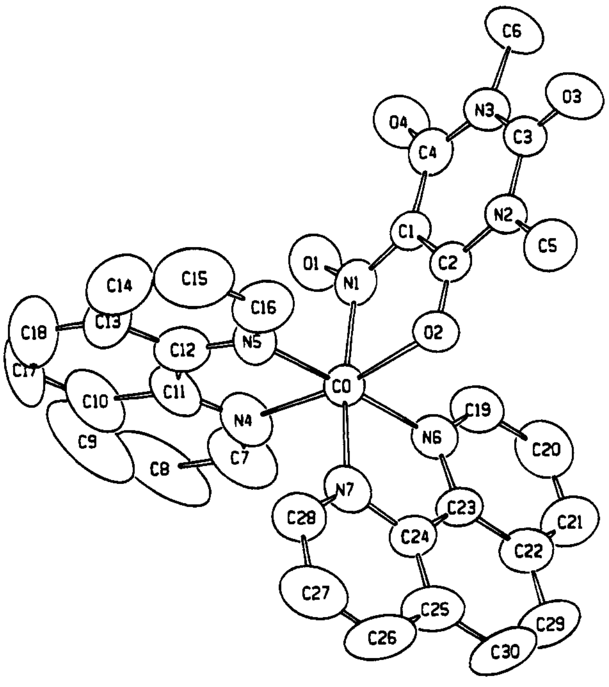

Figure 1. Complex unit, $[Co(dmvi)(phen)_2]^+$, at room temperature with the atom numbering used. Thermal ellipsoids are plotted at 50% probability level.

Results and Discussion

Molecular Structure of $[Co(dmvi)(phen)_2]ClO_4{\cdot}3H_2O$. The crystal structure of this compound consists of $[Co(dmvi)(phen)_2]^+$ cations well separated from the ClO_4^- counterions and water of hydration. A view of this complex with the atom numbering scheme is shown in Figure 1 and the crystal packing diagram in Figure 2. The metal ion exhibits a N_5O distorted-octahedral surrounding with N(1), N(5), N(6), and N(7) atoms in the basal plane and O(2) and N(4) atoms filling the axial positions. One phenanthroline ligand occupies two equatorial positions and the other two bidentate ligands, (the second phen molecule and the dimethylviolurate anion), one equatorial and one axial positions each one.

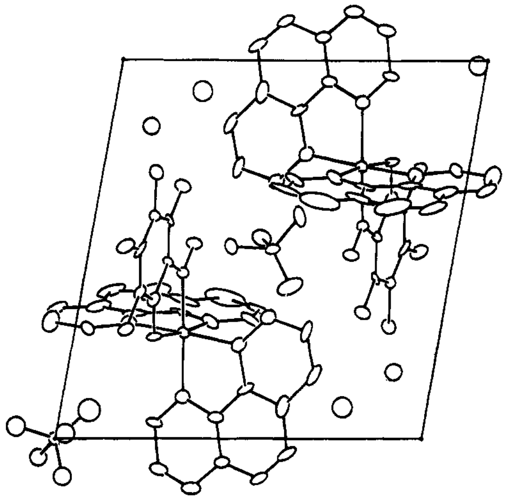

Figure 2. Crystal packing diagram projected along the *c*-axis. The origin of the unit cell is in the lower left hand corner with the *a*-axis running horizontally. Low temperature structure, including water of hydration, is shown.

In the room temperature structure, the equatorial and axial distances vary in the ranges 1.93−2.00 and 2.11−2.16 Å, respectively. The basal plane is slightly ruffled, N(5) and N(6) atoms being 0.05 Å below and N(1) and N(7) 0.05 Å above the mean plane. Co is displaced by 0.069 Å from this plane towards the axial N atom. Bond angles associated with the bite of the three bidentate ligands show the most pronounced deviation from the ideal value for a regular octahedron: 81.5° (N(6)−Co−N(7)) and 81.8° (N(4)−Co−N(5)) for the two phen ligands and 79.7° for the dmvi ligand, (O(2)−Co−N(1)).

The phenanthroline ligand which occupies two equatorial positions in the coordination sphere of the metal ion is bound in a symmetrical way, with a bond length to Co(II) of 2.00 Å. This bond is significantly shorter that found in the high-spin $[Co(phen)_3]^{2+}$ (average value 2.12 Å)[14c] but somewhat longer than reported for $[Co(dmvi)_2(phen)]$ (1.97 Å),[12] a low-spin complex. Accordingly, the bite angle N(6)−Co−N(7) (81.5°) is greater than in $[Co(phen)_3]^{2+}$ (78.1°) but smaller than in $[Co(dmvi)_2(phen)]$ (83°). On the other hand, the other phen ligand is coordinated in a very asymmetric way, with one short equatorial (1.98 Å) and one long axial (2.11 Å) bonds. This result, unprecedented for Co(II)−phen complexes, finds its equivalent in the structure of $[Cu(phen)_3]^{2+}$ (four short metal-nitrogen bonds at 2.04 Å and two longer bonds at 2.32 Å)[20] and is indicative of a Jahn−Teller distortion as expected for an octahedral low-spin Co(II) complex. The coordination of dmvi ligand to cobalt (II) is very asymmetrical, Co−N(1) and Co−O(2) bond lengths being 1.93 and 2.16 Å, respectively. Again, the Co(II)−N bond is longer that found in $[Co(dmvi)_2(phen)]$ (1.89 Å). All these data evidence that a mixture of high- and low-spin forms occurs in $[Co(dmvi)(phen)_2]ClO_4{\cdot}3H_2O$ at room temperature.

The high standard deviations in molecular dimensions of the low temperature (92 K) structure limit a detailed comparison with the high temperature structure. However, the following trends are evident: The coordination sphere of the metal ion is very similar in the two structures, the average bond lengths being somewhat shorter in the low temperature structure. The average Co−N(equatorial) and Co−X(axial) (X = O, N) distances are 1.977 and 2.137 Å in the room temperature structure, while the

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(20) Anderson, O. P. *J. Chem. Soc., Dalton Trans.* **1973**, 1237.

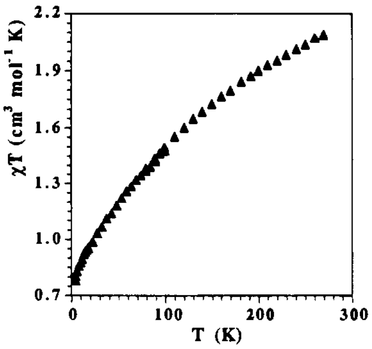

Figure 3. Magnetic properties of $[Co(dmvi)(phen)_2]ClO_4\cdot3H_2O$: χ_MT *vs* T plot.

corresponding low temperature distances are 1.94 and 2.12 Å. Such a contraction is in agreement with a spin transition. A smaller average change in the axial distances compared to the equatorial ones is to be expected due to the Jahn–Teller effect in the low spin species.

$[Co(terpy)_2]I_2\cdot2H_2O$[9c] is to our knowledge the only six-coordinated crossover Co(II) complex structurally characterized at two different temperatures. In this case the coordination geometry is a compressed octahedron and the changes observed in bond lengths for a 55% transition between the spin states are 0.030 Å (axial) and 0.021 Å (equatorial). This gives a extrapolated metal ligand bond lengths variations associated with a complete spin transition of 0.054 Å (axial) and 0.038 Å (equatorial). EXAFS studies on the series of complexes $[Co(H_2fsa_2en)L_2]$ give a variation of 0.09–0.13 Å for the complete transition in these compounds.[21] In the present compound the spin transformation between 294 and 92 K is only partial, ca. 35%, as estimated from magnetic data (*vide infra*). The average changes observed in equatorial bond lengths of the high and low temperature structures are therefore in full agreement with a change of ca. 0.10 Å for the complete spin transformation.

As the structure of both pure spin forms are unknown, it is not possible to calculate the composition of the spin mixture at 294 and 92 K from the crystallographic data. However, if the molecular dimensions obtained in this work are compared with those recently reported for the low-spin complex $[Co(dmv)_2(phen)]\cdot2CHCl_3$[12], it is found that the X-ray work suggest larger low-spin fractions at the given temperatures than those obtained from the magnetic data. This kind of discrepancy has been noted in other cases.[3] It may be due to the different nature of the sample, a single crystal of greater size for the crystallographic study and a microcrystalline powder for the magnetic measurements. It is well-known that a mild grinding of a spin crossover complex can have a dramatic impact on the transformation.[22]

Magnetic Properties and EPR Spectra. The thermal dependence of the molar magnetic susceptibility (χ_M) of $[Co(dmvi)(phen)_2]ClO_4\cdot3H_2O$, in the form of χ_MT *vs* T plot is shown in Figure 3. The magnetic measurements demonstrate that this metal complex exhibits a smooth and incomplete spin transition between high-spin ($S = {}^3/_2$) and low-spin ($S = {}^1/_2$) forms. At 270 K, χ_MT is 2.1. This value is clearly lower than that expected for high-spin Co(II). χ_MT decreases progressively with the temperature and a value of 0.74 is reached at 4 K. This behavior indicates that a significant amount of the high spin species remains at low temperatures.

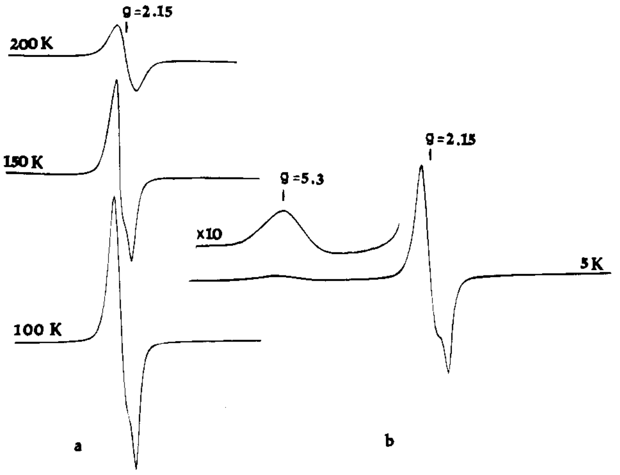

Figure 4. (a) Temperature variation of the powder X-band EPR spectrum of $[Co(dmvi)(phen)_2]ClO_4\cdot3H_2O$, (b) 5 K spectrum showing a weak high-spin signal at $g = 5.3$ in addition of the intense, $g = 2.15$, low-spin signal.

Electron paramagnetic resonance data confirm the existence of a spin transition in $[Co(dmvi)(phen)_2]ClO_4\cdot3H_2O$. The X-band powder EPR spectrum at room temperature, shows a weak and nearly symmetric signal at $g = 2.15$. The intensity of the signal increases significantly when decreasing the temperature (Figure 4a). Another weak signal at $g = 5.3$ appears (Figure 4b) at a very low temperature (5 K), supporting that the transition is not complete and that it remains a residual high-spin fraction.

It is possible to calculate the molar fraction, c, of the high-spin species at each temperature from the magnetic measurements,[23] using eq 1. If the spin transition was complete the

$$c = [\chi_MT - (\chi_MT)_{ls}]/[(\chi_MT)_{hs} - (\chi_MT)_{ls}] \qquad (1)$$

values of χ_MT for the pure high-spin (hs) and low-spin (ls) forms should be directly obtained from the magnetic data, but this is not the case. However, $(\chi_MT)_{ls}$ can be evaluated from the EPR signal. In this case $g = 2.15$ and hence $(\chi_MT)_{ls} = 0.45$. For the high-spin value, only an approximate estimation can be made. The χ_MT values reported in the literature for high-spin six-coordinated Co(II) complexes vary between 2.5 and 3.0.[24] On this basis, the values of c can vary between 0.8 and 0.6 at room temperature and between 0.45 and 0.3 at 90 K. As the dimethylviolurate anion introduces an inherent asymmetry in the coordination polyhedron, it is reasonable that the value of $(\chi_MT)_{hs}$ for $[Co(dmvi)(phen)_2]ClO_4\cdot3H_2O$ occurs in the lower range. The variation of the high-spin fraction with the temperature assuming $(\chi_MT)_{hs} = 2.65$ is shown in Figure 5.

The thermodynamical parameters associated with the spin crossover process can be estimated from the ln K *vs* $1/T$ plot, where $K = (1 - c)/c$ is the formal constant for the $S = {}^3/_2 \leftrightarrow S = {}^1/_2$ equilibrium.[23] A linear dependence is obtained between 120 and 250 K for $[Co(dmvi)(phen)_2]ClO_4\cdot3H_2O$ (Figure 6). In this range of temperature we can apply eq 2.[23,25]

$$\ln K = -\Delta H/RT + \Delta S/R \qquad (2)$$

A least-squares fit of the experimental data yields $\Delta H = -1.7$ kJ mol^{-1} and $\Delta S = -16$ J mol^{-1} K^{-1}. As expected, the low spin form is enthalpically stabilized but disfavored by the

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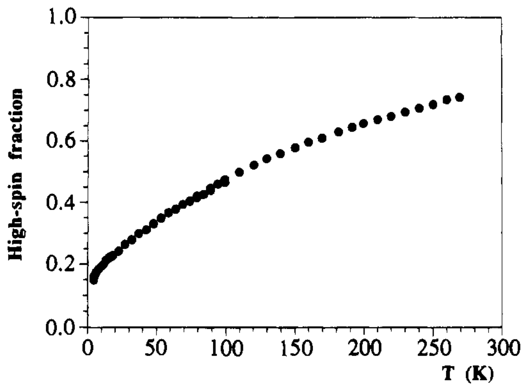

Figure 5. High-spin molar fraction as a function of temperature for $[Co(dmvi)(phen)_2]ClO_4{\cdot}3H_2O$.

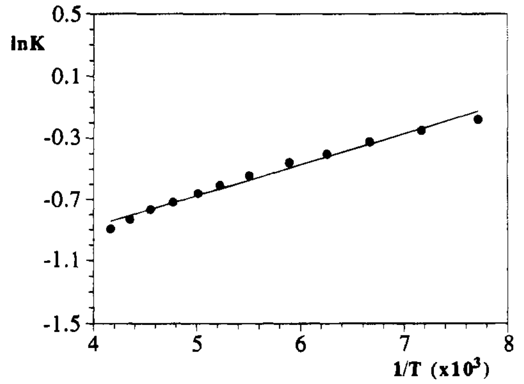

Figure 6. Plot of ln K *vs* T^{-1} for $[Co(dmvi)(phen)_2]ClO_4{\cdot}3H_2O$.

entropy variation. The enthalpy variation is close to the energy difference between the ground high- and low-spin states and thus can be evaluated as *ca.* 150 cm^{-1}. This value is very close to that found for the complexes $[Co(H_2fsa_2en)L_2]$ (120−200 cm^{-1})[8] and lower than those reported for $[Co(terpy)_2]X_2{\cdot}nH_2O$ (300−500 cm^{-1}).[9] The entropy variation is much larger than the expected value from the spin-multiplicity change alone, $\Delta S_{spin} = -5.8$ J mol^{-1} K^{-1}.[23,26] This reveals the existence of a significant vibrational contribution to the entropy variation, ΔS_{vib} *ca.* −11 J mol^{-1} K^{-1}, due to the structural changes associated to the spin transition. Again, this value is similar to that found for $[Co(H_2fsa_2en)L_2]$ complexes (5−17 J mol^{-1} K^{-1}).[8]

Concluding Remarks

The synthesis of $[Co(dmvi)(phen)_2]ClO_4{\cdot}3H_2O$, reported herein, completes the series of octahedral Co(II) complexes $[Co(dmvi)_x(phen)_{3-x}]^{(2-x)+}$. Whereas low-spin species result when $x = 3$ and 2 and a high-spin species when $x = 0$, a spin-crossover complex is obtained when $x = 1$, as is proved by variable-temperature magnetic susceptibility measurements, EPR spectra, and single-crystal X-ray diffraction studies at two different temperatures, 294 and 92 K, on $[Co(dmvi)(phen)_2]ClO_4{\cdot}3H_2O$.

Acknowledgment. This work was partially supported by the Dirección General de Ciencia y Tecnología (DGCYT) (proyecto PB91-0807-C02-01).

Supplementary Material Available: Tables S1−S6, giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, hydrogen atom locations, and least-squares planes (26 pages). Ordering information is given on any current masthead page.

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