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Bis(dimethylviolurato)(phenanthroline)cobalt(II), a Low-Spin Octahedral Cobalt(II) Complex. Crystal Structure of [Co(dmvi)$_2$phen]·2CHCl$_3$

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The complexes of formula [Co(dmvi)$_2$phen]·2solv (dmvi, $C_6H_6N_3O_4$, dimethylviolurate anion; phen, $C_{12}H_8N_2$, 1,10-phenanthroline; and solv = H_2O, $CHCl_3$) have been synthesized, and the structure of chloroform solvate has been determined by X-ray crystallographic methods. Crystal data: monoclinic system, space group $C2/c$, a = 17.394(2) Å, b = 10.229(1) Å, c = 21.714(3), β = 117.4(1)°, Z = 4. Data up to θ = 25° (Mo Kα radiation) were collected at room temperature on a CAD-4 diffractometer. The structure was solved by Patterson methods and refined by least-squares methods to conventional agreement indices $R = R_w = 0.044$ with 1979 observed reflections $[I \geq 3\sigma(I)]$. The structure consists of [Co(dmvi)$_2$(phen)] neutral unities and chloroform molecules linked by van der Waals interactions. The metal ion exhibits a *trans*-N_4O_2 distorted-octahedral surrounding. The phenanthroline ligand occupies two equatorial positions in the coordination sphere of the metal ion (Co–N bond length, 1.97 Å). Dimethylviolurate ligands are coordinated to the metal ion through the oxime nitrogen atom (equatorial distance 1.89 Å) and one of the carbonyl oxygen atoms (axial distance 2.17 Å). Magnetic measurements, with μ_{eff} = 2.0 in the 80–300 K range, and EPR spectra, with $g_\perp$ = 2.23 and $g_\parallel$ = 2.02, prove that this octahedral Co(II) complex has a low-spin electron configuration at room temperature. Its electrochemical behavior was also investigated. Formation equilibria in aqueous solution of the mixed complexes in the Co(II)–dimethylviolurate–phenanthroline system have been studied and the stability constants determined.

Introduction

Low spin octahedral cobalt (II) complexes are very scarce.[2] This fact can be understood, keeping in mind two features of the cobalt (II) chemistry: (i) Very strong-field ligands are required to undergo spin pairing; for instance, ligands like phen and bipy form low-spin complexes with Fe(II) but not with Co(II); [Co(phen)$_3$]$^{2+}$ is an octahedral high-spin complex.[3–5] (ii) If the ligand field is strong enough to produce the spin pairing (electron configuration $t_{2g}{}^6e_g{}^1$), the Jahn–Teller effect allows the loss of some ligand to give four- or five- rather than six-coordinate complexes. The formation of the pentacyano complex [Co(CN)$_5$]$^{3-}$, instead of a hexacyano complex, exemplifies well this behavior.[6] Square-planar and five-coordinate low-spin Co(II) complexes are very numerous,[7] in contrast with six-coordinate species.

In the past, a number of Co(II) complexes were suggested to be low-spin six-coordinate on the basis of magnetic moment,[8–12] but it is clear that a rigorous distinction between five- and six-coordinate complexes cannot be made by magnetic measurements only. Combination of magnetic and EPR data should be more conclusive, but few cases have been reported.[13] [Co(NCPh)$_6$]$^{2+}$ was identified by its EPR spectrum in solutions with very high concentrations of phenyl isocyanide, but it was not isolated from them.[14] More recently, a thermodynamic, magnetic and EPR study of the formation of complexes of Co(II) with violuric acid (1*H*,3*H*-pyrimidine-2,4,5,6-tetraone 5-oxime), H$_3$vi, and its monomethyl (H$_2$mvi) and dimethyl (Hdmvi) derivatives in dimethyl sulfoxide–water (80:20)(w:w) clearly established that [Co(H$_2$vi)$_3$]$^-$, [Co(Hmvi)$_3$]$^-$, and [Co(dmvi)$_3$]$^-$ are low–spin octahedral complexes. The high-spin ↔ low-spin change occurs upon binding of the third ligand.[15]

Strictly, proof that a complex contains low-spin octahedral Co(II) demands both structural and magnetic data. Up to now, only four of these compounds have been structurally characterized by X-ray crystallography: K$_2$Ba[Co(NO$_2$)$_6$],[16] [Co·hexathia-18-crown-6](picrate)$_2$,[17,18] [Co(trithiacyclononane)$_2$](BF$_4$)$_2$·2CH$_3$NO$_2$,[19,20] and [Co(trithianonane)$_2$] (BF$_4$)$_2$·CH$_3$NO$_2$.[18] In all of them, the metal ion exhibits a distorted octahedral coordination geometry, as expected. The CoN$_6$ octahedron shows a tetragonal elongation in the hexanitro complex whereas the related CoS$_6$ is compressed in the trithiacyclononane complex and elongated in the hexathia-18-crown-6 and the trithianonane complexes. The extent of distortion varies but is particularly strong in the last compound. The crystal structure of [Co(terpy)$_2$]Br$_2$·3H$_2$O has been also reported,[21] and although the low-spin form is predom-

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inant at room temperature, this compound clearly exhibits a spin equilibrium.[22]

Taking into account that $[Co(phen)_3]^{2+}$ is a high-spin complex with Δ_0 very close to the limiting value for the spin change[23] and that $[Co(dmvi)_3]^-$ is a low-spin complex, it seemed very interesting to investigate the formation and structure of Co(II)–dmvi–phen mixed complexes. The synthesis and properties of Co(III)–H_2-vi–phen mixed complexes were reported few years ago.[24] In this work we report the synthesis, crystal structure and electronic properties of $[Co(dmvi)_2phen]$, a six-coordinate low-spin Co(II) complex with a *trans*-N_4O_2 environment around the metal ion. The formation equilibria of the Co(II)–dmvi–phen mixed complexes have been also investigated in aqueous solution and the stability constants determined.

Experimental Section

Materials. Dimethylvioluric acid was prepared and purified following a reported procedure.[25] 1,10-Phenanthroline monohydrate (Aldrich), cobalt(II) acetate tetrahydrate (Panreac), and all other reagents were used as received. Elemental analyses (CHN) were performed by the Servicio de Análisis Elemental de la Universidad Autónoma de Madrid, Madrid, Spain.

Synthesis of the Complex. A 0.5-mmol (100-mg) sample of $Hdmvi{\cdot}H_2O$, 0.25 mmol (50 mg) of phen, and 0.25 mmol (62 mg) of $CoAc_2{\cdot}4H_2O$ were dissolved in 25 mL of water under inert atmosphere. On standing, a crystalline precipitate of $[Co(dmvi)_2phen]{\cdot}2H_2O$ slowly appeared. The dark-brown, nearly black crystals were filtered, washed with water and dried in the air. Anal. Calcd for $C_{24}H_{24}CoN_8O_{10}$: C, 44.81; H, 3.73; N, 17.41. Found: C, 44.36; H, 3.54; N, 17.07. This compound is insoluble in water, rather soluble in methanol, and soluble in chloroform, giving nonconducting solutions.

Single crystals for the X-ray crystallographic study were obtained following the same experimental procedure but from more dilute solutions. Unfortunately these crystals "died" on the diffractometer before the data collection was complete and the structure could not be solved. Eventually, the structure was determined on single crystals of the related chloroform solvate, $[Co(dmvi)_2phen]{\cdot}2CHCl_3$, which were obtained by careful addition of *n*-hexane to a chloroform solution of $[Co(dmvi)_2phen]{\cdot}2H_2O$.

Physical Techniques. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Variable-temperature magnetic measurements were carried out on polycrystalline samples of $[Co(dmvi)_2phen]{\cdot}2H_2O$ in the temperature range 80–300 K by means of a previously described pendulum-type apparatus.[26] 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 nitrogen cryostat.

Cyclic voltammograms were obtained with a Tacusel IMT-1 programmable function generator connected to a Tacusel PJT 120-1 potentiostat. The working electrode was platinum, with a saturated calomel reference electrode separated from the test solution by a salt bridge containing the solvent/supporting electrolyte. The auxiliary electrode was platinum wire. Tetrabutylammonium hexafluorophosphate and dichloromethane were used as supporting electrolyte and solvent, respectively, in the electrochemical experiences. The system was calibrated against ferrocene.

Emf measurements were carried out in a 0.1 mol dm^{-3} KNO_3 aqueous solution at 25 °C by using a previously described titration assembly.[27] The reference electrode was a Ag/AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen ion concentration probe by titration of known amounts of HNO_3 with CO_2-free NaOH and determining the equivalent point by Gran's method, which gives the standard potential of the cell, $E°$, and the ionic product of water K_w [pK_w = 13.73(1)]. Acidified aqueous solutions containing $Co(NO_3)_2{\cdot}6H_2O$, phen, and Hdmvi at different concentrations and molar ratios were titrated with NaOH and the data sets were merged and treated with the program SUPERQUAD[28] to obtain the stability constants of the mixed complexes. Reported values of the stability constants of the Co(II)–phen complexes[29] and that of the proton association constants of phen[29] and dmvi$^-$ [30] were used in the calculations. The program SPE[31] was used for the computation of species distributions.

Table I. Crystallographic Data for $[Co(dmvi)_2phen]{\cdot}2CHCl_3$

chem formula	$CoC_{26}H_{22}N_8O_8Cl_6$	Z	4
fw	846.16	T, °C	20
space group	$C2/c$	λ, Å	0.710 73
a, Å	17.394(2)	ρ_{calcd}, g cm^{-3}	1.64
b, Å	10.229(1)	μ, cm^{-1}	10.46
c, Å	21.714(3)	$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.043
β, deg	117.4(1)	$R_w{}^a = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.043
V, Å^3	3431		

[a] Unit weights.

Crystallographic Data Collection and Structure Determination. Diffraction data on a 0.4 × 0.4 × 0.2 mm prismatic crystal were collected at 293 K with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The cell parameters were determined from least-squares refinement of 25 well-centered reflections in the range $12 < \theta < 20°$. Crystal parameters and refinement data are summarized in Table I. Complete crystal data and experimental details are deposited as supplementary material (Table S1). A total of 3285 reflections were collected in the range $0 < 2\theta < 50°$. The calculated transmission factors varied between T_{min} = 0.8714 and T_{max} = 0.9711. Three reference reflections monitored throughout data collection showed no significant sign of crystal deterioration. The usual corrections for Lorentz and polarization effects were carried out. The absorption coefficient was μ = 10.46 cm^{-1}, and an empirical absorption correction using the ψ-scan was applied.[32]

The structure was solved by Patterson methods and refined by the full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from a difference synthesis and refined with an overall isotropic thermal parameter. The final full-matrix least-squares refinement, minimizing $\Sigma[w(F_o - F_c)^2]$ and including 1979 reflections with $I \geq 3\sigma(I)$, each reflection being assigned a unity weight, converged at $R = R_w = 0.044$. f, f' and f'' were taken from ref 33. All calculations were performed by using SHELX 86,[34] SHELX 76,[35] and SCHAKAL[36] programs.

The refined final coordinates for non hydrogen atoms and selected bond distances and angles are listed in Tables II and III, respectively. Tables of anisotropic temperature parameters, hydrogen coordinates, remaining bond distances and angles, and least-squares planes are deposited as supplementary material (Tables S2–S5).

Results and Discussion

Molecular Structure of $[Co(dmvi)_2(phen)]{\cdot}2CHCl_3$. The crystal structure of this compound consists of $[Co(dmvi)_2(phen)]$ neutral unities and chloroform molecules linked by van der Waals interactions. A view of this complex with the atomic numbering scheme is shown in Figure 1. The metal ion exhibits a *trans*-N_4O_2 distorted-octahedral surrounding (C_2 symmetry) with N(4), N(4)^i, N(5), and N(5)^i atoms in the basal plane and O(2) and O(2)^i atoms filling the axial positions. This basal plane is

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Table II. Atomic Coordinates and Thermal Parameters[a,b] for Non-Hydrogen Atoms of [Co(dmvi)$_2$phen]·2CHCl$_3$

atom	x/a	y/b	z/c	10^2U_{eq}, Å^2
Co	0.0000	0.15878(7)	0.2500	3.21
O(2)	0.1409(2)	0.1655(3)	0.3010(1)	4.19
O(3)	−0.0433(2)	0.3491(3)	0.3201(2)	5.50
N(4)	0.0041(2)	0.0147(3)	0.3118(2)	3.19
N(5)	0.0176(2)	0.2905(3)	0.3167(2)	3.81
C(6)	0.1018(2)	0.3193(4)	0.0082(2)	3.51
C(8)	0.1621(2)	0.0003(4)	0.0090(2)	3.47
O(9)	0.3564(2)	0.3663(4)	0.4854(2)	6.47
C(10)	0.2788(3)	0.3535(4)	0.0108(2)	4.64
N(11)	0.2492(2)	0.2636(3)	0.3939(2)	4.14
O(13)	0.0803(2)	0.4797(3)	0.0208(2)	6.04
C(14)	0.0023(2)	−0.1055(4)	0.2834(2)	3.27
C(15)	0.0021(3)	−0.3419(5)	0.2817(2)	5.44
C(16)	0.0089(3)	−0.2149(5)	0.3830(2)	4.66
N(17)	0.2190(2)	0.4245(4)	0.4573(2)	4.70
C(18)	0.0067(3)	0.0166(4)	0.3738(2)	4.30
C(20)	0.0044(3)	0.0028(4)	0.0079(2)	3.98
C(21)	0.1274(3)	0.4137(4)	0.4176(2)	4.30
C(23)	0.0083(3)	−0.0963(5)	0.4099(2)	5.00
C(24)	0.3127(3)	0.1909(6)	0.3824(3)	5.98
C(25)	0.2516(4)	0.5256(6)	0.5118(3)	7.13
C(30)	−0.2973(4)	−0.2807(6)	0.1686(3)	8.43
Cl(1)	−0.2203(1)	−0.1568(2)	0.1955(1)	9.51
Cl(2)	−0.3651(2)	−0.2650(3)	0.0798(1)	16.36
Cl(3)	−0.2462(2)	−0.4302(2)	0.1900(1)	18.68

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] $U_{eq} = {}^1/_3(\text{trace } U)$.

Table III. Selected Bond Lengths (Å) and Angles (deg)[a,b] for [Co(dmvi)$_2$phen]·2CHCl$_3$

Co–O(2)	2.178(2)	O(2)–Co–N(4)	89.9(1)
Co–N(4)	1.973(3)	O(2)–Co–N(4)^i	92.8(2)
Co–N(5)	1.897(3)	O(2)–Co–N(5)	80.8(1)
N(4)–Co–N(4)^i	83.1(3)	O(2)–Co–N(5)^i	96.4(2)
N(4)–Co–N(5)	94.0(1)	O(2)–Co–O(2)^i	176.4(2)
N(5)–Co–N(5)^i	89.4(2)	N(4)–Co–N(5)^i	173.3(2)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] Roman numeral superscripts refer to the following equivalent positions relative to x, y, z: (i) $-x$, y, $0.5 - z$.

somewhat ruffled, being N(4) and N(5)^i 0.1 Å below and N(4)^i and N(5) 0.1 Å above the mean plane which contains the metal ion. Equatorial distances vary between 1.89 and 1.97 Å while the axial distance is 2.17 Å. Bond angles are close to the ideal values for a regular octahedron except those associated with the bite of the three bidentate ligands: 83.1° for the phen ligand, (N(4)-Co-N(4)^i) and 80.8° for the dmvi ligand, (O(2)–Co–N(5)). Although the symmetry of the environment of the metal ion is strictly C_2, it can be effectively described as D_{4h} (elongated octahedron), as shown by the electronic spectrum and EPR data (vide infra).

The phenanthroline ligand, which occupies two equatorial positions in the coordination sphere of the metal ion, is planar, the greatest deviation from the mean plane being 0.016 Å for C(16). The metal ion lies exactly in this plane. The intraligand bond lengths and angles are very similar to those found in other phenanthroline complexes.[5] However the bond length to Co(II) (1.97 Å) is significantly shorter than in [Co(phen)$_3$]$^{2+}$ (average value 2.12 Å) supporting the low-spin nature of the present complex. Accordingly, the bite angle N(4)–Co–N(4)^i (83°) is greater than in [Co(phen)$_3$]$^{2+}$ (78.1°).[5]

Both dimethylviolurate ligands are equivalent by symmetry and are coordinated to the metal ion through the oxime nitrogen N(5) and the carbonyl oxygen O(2) atoms. They are planar, the greatest deviation from the mean plane defined by their non-hydrogen atoms being 0.047 Å (O(2)). Deviation of Co(II) from this plane is 0.057 Å. These features are common to other reported structures of violurato-containing metal complexes.[24] The dihedral angle formed between the planes of dmvi and phen is 87.23°.

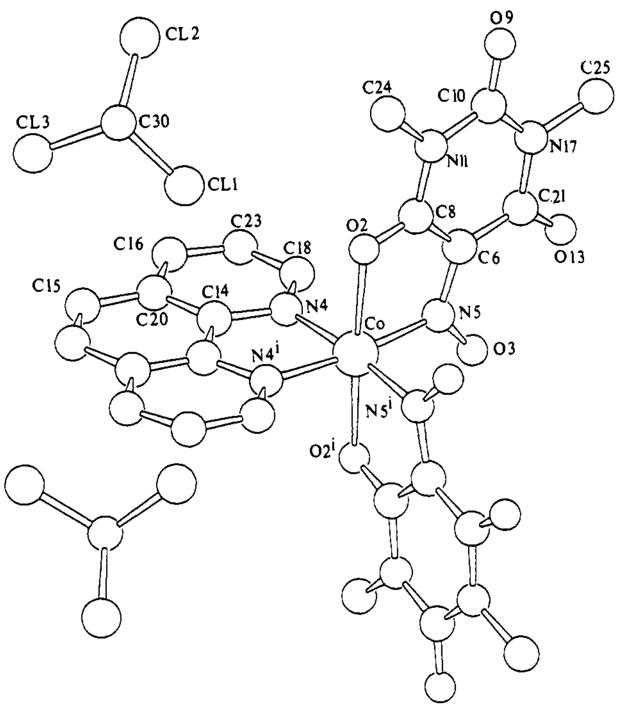

Figure 1. Perspective drawing of [Co(dmvi)$_2$(phen)]·2CHCl$_3$ with the atom numbering scheme used. Hydrogen atoms are omitted for clarity.

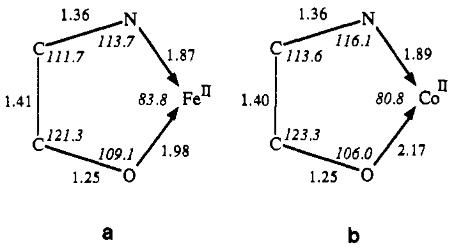

Figure 2. Schematic drawing showing the relevant structural features (distances in Å, angles in deg) concerning the metal ion–violurate ligand chelate ring: (a) [Fe(H$_2$vi)$_3$]$^-$; (b) [Co(dmvi)$_2$(phen)].

The coordination of dmvi ligand to cobalt (II) is very asymmetrical, Co–N(5) and Co–O(2) bond lengths being 1.89 and 2.17 Å, respectively. Although dmvi is inherently an asymmetric bidentate ligand, these bond lengths reflect the Jahn–Teller distortion expected for low-spin Co(II). A comparison between the geometry of the MNOC$_2$ five-membered chelate ring in the present compound and in [Fe(H$_2$vi)$_3$]$^-$ [37] reveals only minor differences in all the structural parameters except for the M-O bond length which is 0.19 Å shorter in the low-spin Fe(II) complex (electronic configuration t_{2g}^6) (see Figure 2).

Electronic Spectra. The UV–vis spectrum of [Co(dmvi)$_2$(phen)] in chloroform solution displays a broad and intense absorption band with a well-defined maximum at 26 000 cm^{-1} ($\epsilon = 7.8 \times 10^3$ dm^3 mol^{-1} cm^{-1}) and a shoulder at 21 000 cm^{-1} ($\epsilon = 4 \times 10^3$ dm^3 mol^{-1} cm^{-1}). This band, which can be assigned to a metal to ligand charge transfer electronic transition, masks nearly completely the visible d–d transitions. Only two slight shoulders at 19 000 and 17 000 cm^{-1} could be attributed to the spin-allowed d-d transitions of lower energy.

The reflectance spectrum of the solid complex shows a weak and broad band at 10 000 cm^{-1}, not observable in the solution spectrum. It corresponds to the transition within the octahedral ^2E_g ground state, which is split by the Jahn–Teller effect and the tetragonal ligand field, ($^2A_{1g} \rightarrow {}^2B_{1g}$). This electronic transition has been previously observed in the reflectance spectrum of [Co-

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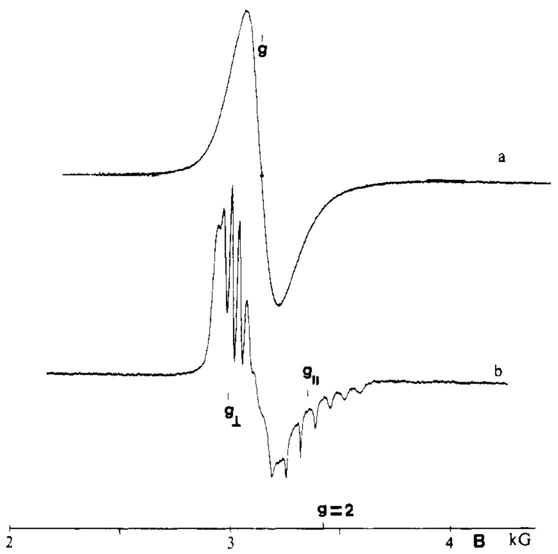

Figure 3. X-Band EPR spectra of $[Co(dmvi)_2phen]\cdot 2H_2O$ at 100 K: (a) powder spectrum; (b) frozen dichloromethane solution spectrum.

$(terpy)_2]^{2+}$,[22] $K_2Ba[Co(NO_2)_6]$,[38] and $[Co(1\text{-oxa-}4,7\text{-diazacyclononane})_2]I_2$[39] appearing at 7500, 8000, and 13 600 cm^{-1}, respectively. The existence of this band gives definite evidence for the presence of a lower symmetry ligand field component.[22]

Magnetic Properties and EPR Spectra. Magnetic susceptibility measurements on polycrystalline samples of $[Co(dmvi)_2phen]\cdot 2H_2O$ reveal that the complex is a low-spin ($S = {}^1/_2$) system. It has a magnetic moment of 2.0 μ_B which remains constant in the 80–300 K temperature range. As far as we are aware, it is the first CoN_4O_2 complex with a low spin state at room temperature. Two other Co(II) complexes with the same environment, $[Co(1\text{-oxa-}4,7\text{-diazacyclononane})_2]I_2$[39] and $[Co(H_2fsa_2en)(py)_2]$[40] (H_2fsa_2en = *N,N'-o*-ethylenebis(3-carboxysalicylaldiminate), exhibit a spin transition, being low-spin at low temperatures.

Electron paramagnetic resonance data confirm the low-spin formulation of $[Co(dmvi)_2phen]\cdot 2H_2O$. The X-band powder EPR spectrum at 100 K shows an intense and symmetric signal at $g = 2.17$ (Figure 3a). The intensity of the signal shows no significant change at greater temperatures. The other isolated solvate, $[Co(dmvi)_2phen]\cdot 2CHCl_3$, has the same behavior. Two signals appear at $g_{\perp} = 2.23$ ($A_{\perp} = 32$ G) and $g_{\parallel} = 2.02$ ($A_{\parallel} = 64$ G) in the frozen dichlorometane solution spectrum at the same temperature (Figure 3b). This indicates a d_{z^2} ground state ($^2A_{1g}$) for the complex, which is consistent with the axial elongation observed in its molecular structure. The agreement between the EPR spectra of both solvates in the solid state and in solution shows that the crystallization solvent molecules have no significant influence on the electronic structure of the complex.

The analysis of the EPR data gives a detailed information of this electronic structure. The expected g values are given by eqs 1 and 2,[39,41,42] with $u_{2,4} = -k^2\zeta/E_{4,2}$, where $E_{4,2}$ is the quartet–

$$g_{\parallel} = g_0 + 2u_{2,4}^{\ 2} \tag{1}$$

$$g_{\perp} = g_0 + 6u + 2u_{2,4}^{\ 2} \tag{2}$$

doublet energy gap. Introducing the g values from the frozen solution EPR spectrum in the equations and considering $\zeta = 540$ cm^{-1} (free ion spin–orbit coupling constant) and $k = 0.8$, we obtain $E_{4,2} = -3500$ cm^{-1} (a negative value indicates that the doublet is the ground term) and $u = 0.035$. The quartet–doublet gap does not allow the thermal occupation of the quartet term, and accordingly, the metal complex is low spin at room temperature. Taking into account the doublet–doublet separation obtained from the reflectance spectrum, $4E_{JT} = 10\,000$ cm^{-1}, it is apparent that the low spin state is stabilized by the tetragonal distortion (Figure 4). This result was established for the first time by Reinen, some years ago, in the study of $K_2Ba[Co(NO_2)_6]$[38] and it seems that applies to all the octahedral low-spin Co(II) complexes reported up to now. Δ_0 can be estimated from the eq 3.[39] Assuming a B value between 700 and 750 cm^{-1} and C/B =

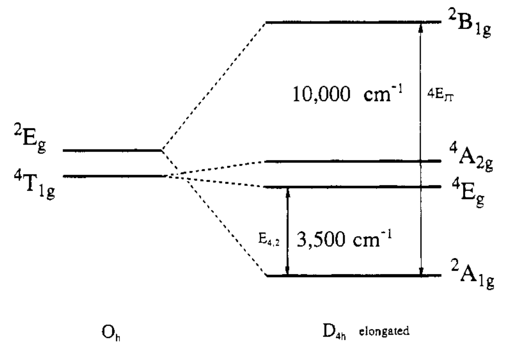

Figure 4. Energy levels diagram for $[Co(dmvi)_2phen]$. The low-spin ground state is stabilized by the tetragonal ligand field and the Jahn–Teller effect.

$$E_{4,2} \approx 4B + 4C - \Delta_0 - 2E_{JT} \tag{3}$$

4.3, a value of $\Delta_0 \approx 14\,000$ cm^{-1} is obtained.[43] Thus, the electronic structure of $[Co(dmvi)_2phen]\cdot 2H_2O$ is close to that of $K_2Ba[Co(NO_2)_6]$. The splitting of the octahedral term is somewhat greater in $[Co(dmvi)_2phen]\cdot 2H_2O$ because it is caused not only by the Jahn–Teller effect but also by the asymmetric bidentate character of the dmvi ligand (donor atoms N and O).

Cyclic Voltammetry Study. The electrochemical behavior of $[Co(dmvi)_2phen]\cdot 2H_2O$ has been investigated by cyclic voltammetry and rotating disk electrode (RDE). The experiments were carried out at room temperature in the presence of $[n\text{-}Bu_4N][PF_6]$ as supporting electrolyte and using CH_2Cl_2 as solvent. All potentials were measured relative to the saturated calomel electrode but have been referred to the normal hydrogen electrode (NHE) by addition of 244 mV. Cyclic voltammogram shows only an oxidation peak (E_{p_a}) at 390 mV and the corresponding reduction peak (E_{p_c}) at 318 mV, when the sweep is reversed. The couple Co(III)/Co(II) is completely reversible with a separation peak of 72 mV (ferrocene gives an ΔE_p of 77 mV in the same conditions) and with an anodic and catodic intensities ratio equal to the unity. The formal potential $E_f = (E_{p_a} + E_{p_c})/2 = 354$ mV exactly agrees with the semiwave potential obtained from RDE experiences. Plots of i_d versus $w^{1/2}$ (from RDE experiences; i_d = diffusion intensity and w = angular velocity of rotating disk electrode) or i_p versus $v^{1/2}$ (from cyclic voltammetry experiences; i_p = anodic peak intensity and v = scan rate) indicate that the chemical oxidation is controlled by diffusion.

This result is similar to those reported with other well characterized hexacoordinate low-spin Co(II) complexes with thioether ligands. In these cases the values of E_f are very high, 864, 844 and 680 mV for $[Co(trithianonane)_2]^{2+}$, $[Co\cdot hexathia\text{-}18\text{-}crown\text{-}6]^{2+}$,[17,18] and $[Co(trithiacyclononane)_2]^{2+}$ [19,20] respec-

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(43) Unfortunately a B value cannot be obtained from the visible espectrum. Values of 800, 750, and 650 cm^{-1} have been reported for $[Co(1\text{-oxa-}4,7\text{-diazacyclononane})_2]^{2+}$, $[Co(terpy)_2]^{2+}$, and $K_2Ba[Co(NO_2)_6]$, respectively. B should be closer to 700 than 800 for $[Co(dmvi)_2(phen)]$, due to the π-acceptor character of the ligands. Assuming a B value between 700 and 750 cm^{-1}, a Δ_0 value between 13 500 and 14 500 cm^{-1} is obtained.

Table IV. Overall Stability Constants of Ternary and Binary Metal Complexes in the Co(II)–dmvi–phen System

complex[a]	log β	ref
$Co(dmvi)(phen)^+$	9.91(1)	this work
$Co(dmvi)_2(phen)$	13.65(1)	this work
$Co(dmvi)(phen)_2^+$	17.10(1)	this work
$Co(phen)^{2+}$	7.02	29
$Co(phen)_2^{2+}$	13.72	29
$Co(phen)_3^{2+}$	20.10	29

[a] All the complexes are six-coordinate. Water molecules have been omitted for the sake of simplicity.

tively, indicating a great stabilization of the Co(II). The E_f value for [Co(dmvi)$_2$phen] is smaller but significantly greater than that of most low-spin Co(II) complexes. It can be oxidized in solution, but it is indefinitely stable as a solid in the air.

Formation Equilibria in Solution. Previously acidified aqueous solutions of cobalt(II) nitrate, phen and Hdmvi ($c_M = (1-3) \times 10^{-3}$ mol dm^{-3}, $c_{phen}/c_M = 0.5-2$, and $c_{Hdmvi}/c_M = 1-5$) were titrated with NaOH (0.1 mol dm^{-3}) in order to investigate the formation of mixed-metal complexes. Data processing by the program SUPERQUAD of the experimental points showed the formation of the three possible complexes, [Co(dmvi)(phen)]$^+$, [Co(dmvi)$_2$(phen)] and [Co(dmvi)(phen)$_2$]$^+$ in the pH range 3–6. The stability constants of these species and those of the binary complexes are gathered in Table IV. From these data, the equilibrium constants for the stepwise binding of dmvi ligands to the Co(phen)$^{2+}$ moiety can be easily obtained (eqs 4–5). The

$$Co(phen)^{2+} + dmvi^- \rightleftharpoons Co(dmvi)(phen)^+ \qquad \log K_1 = 2.89 \quad (4)$$

$$Co(dmvi)(phen)^+ + dmvi^- \rightleftharpoons Co(dmvi)_2(phen) \qquad \log K_2 = 3.74 \quad (5)$$

inverted sequence in the stability constants, $K_2 > K_1$, is a thermodynamic proof of the low-spin nature of [Co(dmvi)$_2$(phen)].[15] On the other hand, the equilibrium constant of the formation reaction of Co(dmvi)(phen)$_2^+$ from Co(phen)$_2^{2+}$ (eq 6), greater than K_1 but lower than K_2, suggests a spin equilibrium for the electronic structure of this complex.

$$Co(phen)_2^{2+} + dmvi^- \rightleftharpoons Co(dmvi)(phen)_2^+ \qquad \log K = 3.38 \quad (6)$$

The formation degree of the mixed complexes is very dependent on the composition of the solution. The distribution diagram of the species in solution, for Co(II)–Hdmv–phen stoichiometric ratio of 1:2:1 and $c_M = 10^{-3}$ mol dm^{-3} is shown in Figure 5. The formation of [Co(dmv)$_2$(phen)] is not quantitative ($\alpha_{max} = 45\%$), but it is the main species in solution at pH > 5. In these conditions the two other mixed complexes only occur in a small extent. The formation of [Co(dmv)$_2$(phen)] is favoured in presence of an excess of Hdmvi ($\alpha_{max} = 80\%$ at a 1:5:1 reactants ratio) or by increasing the total concentration of the solution. From these results, it is apparent that the concentration of [Co(dmv)$_2$(phen)] in solution must be low in the conditions of the synthesis (see Experimental Section), allowing thus the precipitation of the insoluble [Co(dmvi)$_2$phen]·2H$_2$O in a crystalline form.

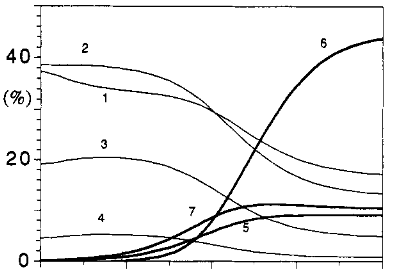

Figure 5. Distribution diagram for metal complexes in the Co(II)–Hdmvi–phen system, as a function of pH [$c_M = 10^{-3}$ mol dm^{-3} mol dm^{-3} and the Co(II):Hdmvi:phen molar ratio is 1:2:1]. Curves 1–7 refer to Co^{2+}, Co(phen)$^{2+}$, Co(phen)$_2^{2+}$; Co(phen)$_3^{2+}$, Co(dmvi)(phen)$^+$, Co(dmvi)$_2$(phen), and Co(dmvi)(phen)$_2^+$, respectively.

Concluding Remarks. The low-spin electronic configuration in octahedral Co(II) complexes, ($t_{2g}^6e_g^1$) is stabilized by a tetragonal distortion of the regular geometry. This distortion is intrinsic to the metal ion due to the Jahn–Teller effect, as evidenced in the structure of K$_2$Ba[Co(NO$_2$)$_6$],[16] but can be increased by the nature of the ligands. Violurate anions 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). Accordingly, [Co(dmvi)$_3$]$^-$, an anionic complex which was characterized in solution,[15] is a low-spin species. Formal substitution of a phenanthroline molecule for a dmvi$^-$ anion in the coordination sphere of the metal ion gives [Co(dmv)$_2$(phen)]. The synthesis and full characterization in the solid state and in solution of this complex is reported in this work. It is also a low-spin complex in spite of the high-spin nature of [Co(phen)$_3$]$^{2+}$. Substitution of another phenanthroline molecule for a dmvi$^-$ anion gives [Co(dmv)(phen)$_2$]$^+$, a species that we have proved to occur in solution, besides [Co(dmv)$_2$(phen)]. This is a very interesting complex because most likely it should exhibit a spin-equilibrium. Its synthesis and structural characterization are in progress.

Our results suggest there is no fundamental reason which justifies the paucity of the low-spin six-coordinate Co(II) complexes known up to now, and their number should be significantly increased in the next years. The synthesis of a series of complexes of formula [Co(dmvi)$_2$L$_2$], where L$_2$ is a bidentate or two monodentate strong field ligands can be proposed. Along this line, a preliminary study of [Co(dmvi)$_2$(HIm)$_2$] (HIm = imidazol) supports a low-spin formulation for this complex.[44]

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Supplementary Material Available: Tables S1–S5, giving crystal data and details of the structure determination, anisotropic thermal parameters, hydrogen atom locations, bond lengths, bond angles, and least-squares planes (6 pages). Ordering information is given on any current masthead page.

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