Synthesis of Heteroleptic Violurato Complexes of Co^{III}. Influence of the Co-ordinated Ligands on the Protonation–Deprotonation Reactions of Dihydrogenviolurate Anion. Crystal Structure of Potassium Dihydrogenviolurato(nitrilotriacetato)cobaltate(III) Dihydrate, $K[Co(H_2vi)(nta)]\cdot 2H_2O$†

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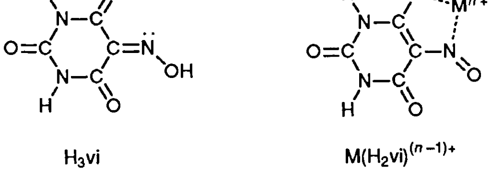
Six cobalt(III) heteroleptic violurato complexes of formula $[Co(Hvi)(trien)]Cl\cdot 4H_2O$, $K[Co(H_2vi)(nta)]\cdot 2H_2O$, $[Co(Hvi)(phen)_2]NO_3\cdot 5H_2O$, $[Co(H_2vi)_2(phen)]NO_3\cdot 4.5H_2O$, $Na[Co(Hvi)_2(phen)]\cdot 8H_2O$, and $[Co(H_2vi)(salen)]\cdot 4H_2O$ [H_3vi, trien, nta, phen, and salen being violuric acid (1*H*, 3*H*-pyrimidine-2,4,5,6-tetrone 5-oxime, triethylenetetramine, nitrilotriacetate(3−), 1,10-phenanthroline, and *N,N′*-ethylenebis(salicylideneiminate)(2−)] have been synthesized. The protonation and deprotonation constants of the violurato ligand in these complexes have been determined by potentiometry and the influence on them of the different co-ordinated ligands has been analyzed. The crystal structure of $K[Co(H_2vi)(nta)]\cdot 2H_2O$ was solved by direct methods. Crystals of $K[Co(H_2vi)(nta)]\cdot 2H_2O$ are monoclinic with $a = 21.705(5)$, $b = 9.930(3)$, $c = 7.451(2)$ Å, $\beta = 98.24(3)°$, space group $P2_1/n$, and $Z = 4$. The structure consists of $[Co(H_2vi)(nta)]^-$ anions, potassium cations, and water molecules of crystallization. The cobalt(III) ion is in a *trans*-N_2O_4 distorted octahedral environment. The H_2vi^- anion is co-ordinated to the metal ion as a bidentate ligand through the oxime nitrogen and one of the amide oxygens. The nitrilotriacetate anion is co-ordinated as a tetradentate ligand with the characteristic butterfly conformation.

Violuric acid, H_3vi (1*H*,3*H*-pyrimidine-2,4,5,6-tetrone 5-oxime), behaves as a weak triprotic acid in aqueous solution. Although the oxime group deprotonates easily ($pK_{a1} = 4.35$),[1] the NH groups are much weaker acids ($pK_{a2} = 9.64$, $pK_{a3} = 14.2$).[1,2] Dihydrogenviolurate anion, H_2vi^-, acts as a bidentate ligand co-ordinating to a metal ion through the nitrogen atom of the oxime group and an oxygen atom of a vicinal carbonyl group.[3] It behaves as a strong-field ligand, displaying a significant π-acceptor character. Thus H_2vi^- forms with Co^{II} a low-spin complex $[Co(H_2vi)_3]^-$, whereas even 1,10-phenanthroline (phen), a well known strong-field ligand, gives a high-spin species $[Co(phen)_3]^{2+}$.[4]

In previous work it has been demonstrated that H_2vi^- undergoes a great increase in its acidity constants when co-ordinated to a metal ion.[5,6] Thus, the dihydrogenviolurate ligands of $[Co(H_2vi)_3]$, the only reported cobalt(III) violurato complex, deprotonate easily to give $[Co(Hvi)_3]^{3-}$. This complex is the main species in aqueous solution at pH > 7. The pK_{a1} value is 3.4, *i.e.* 10^6 times greater than the value found for a free H_2vi^- anion. This effect is most remarkable considering the large distance between the metal ion and the hydrogen atom (four bonds).

On the other hand, some of us have observed the protonation of $[Cr(H_2vi)_3]$ in solution, yielding $[Cr(H_2vi)_2(H_3vi)]^+$, a complex which contains a violuric acid molecule as ligand.[7] This fact can be readily rationalized if it is considered that the protonation and co-ordination sites of the ligand (the oxygen and nitrogen atoms of the oxime group, respectively) are not the same.



Scheme.

This fact may be at the origin of the instantaneous acid dissociation process that the tris(violurato) species $[Fe(H_2vi)_3]^-$ exhibits in spite of being a low-spin iron(II) complex. Proton addition would involve the initial protonation of a H_2vi^- ligand yielding high-spin $[Fe(H_2vi)_2(H_3vi)]$ which would readily dissociate.[8]

In order to get further insight into the determining factors of these protonation–deprotonation reactions involving co-ordinated violurato ligands we have synthesized several mixed ligand cobalt(III) complexes and studied the influence on these equilibria of the different ligands that complete the co-ordination sphere of the metal ion. Cobalt(III) was chosen for its well known inertness towards ligand-substitution reactions.

Structural studies on violuratometal complexes are very

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† Potassium (nitrilotriacetato-κ,*O,O″,O‴*)(1*H*,3*H*-pyrimidine-2,4,5,6-tetrone-κO^4 5-oximato-κ*N*)cobaltate(III) dihydrate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

scarce. As far as we know, the crystal structures of only four have been reported: $[Cu(H_2vi)_2(H_2O)_2]\cdot 2H_2O$,[3] $NH_4[Fe(H_2vi)_3]\cdot xH_2O$,[9] $[H_3O][Ru(H_2vi)_3]\cdot 3H_2O$,[10] and $Ba[Ru(H_2vi)_3]_2\cdot 18H_2O$.[11] We also report here an *X*-ray diffraction study of $K[Co(H_2vi)(nta)]\cdot 2H_2O$ where nta^{3-} is the nitrilotriacetate anion.

Experimental

Materials and Measurements.—The salt $Co(NO_3)_2\cdot 6H_2O$, triethylenetetramine (3,6-diazaoctane-1,8-diamine) (trien), nitrilotriacetic acid (H_3nta), and phen were purchased from Merck and used as received. Violuric acid monohydrate ($H_3vi\cdot H_2O$),[12] *cis*-α-$[Co(trien)Cl_2]Cl$,[13] α-$K[Co(nta)(H_2O)(OH)]\cdot 2H_2O$,[14] and [Co(salen)][15] [salen = *N,N'*-ethylenebis(salicylideneiminate)] were synthesized as described in the literature.

E.m.f. measurements were carried out in 0.1 mol dm^{-3} KCl solution at 25 °C by using a previously described titration assembly.[16] The reference electrode was a Ag–AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen-concentration probe by titration of known amounts of HCl with CO_2-free NaOH and determining the equivalent point by Gran's method,[17] which gives the standard potential of the cell, $E^{\circ\prime}$, and the ionic product of water K_w [pK_w = 13.73(1)]. The acidity constants of the complexes were determined by potentiometric titration with NaOH of acidified solutions of the different isolated complexes (1.00×10^{-3}—5.00×10^{-3} mol dm^{-3}). The potentiometric study of the complex $[Co(H_2vi)(salen)]\cdot 4H_2O$ was carried out in water–dimethylsulphoxide (dmso) mixtures [70:30, 50:50 and 20:80 (w/w)], as solvent because the insolubility of this species in water; 0.1 mol dm^{-3} $KClO_4$ was used as background electrolyte. The solutions of this complex were acidified with $HClO_4$ and titrated with 6×10^{-2} mol dm^{-3} KOH. The measurements were performed as previously reported.[4] At least two different experiments were carried out for each system. The data sets for each system were merged and treated with the program SUPERQUAD[18] to obtain the acidity constants of the different metal complexes.

Synthesis of the Complexes.—$[Co(Hvi)(trien)]Cl\cdot 4H_2O$. The acid $H_3vi\cdot H_2O$ (0.52 g, 3 mmol) was added over 2 h to a solution of *cis*-α-$[Co(trien)Cl_2]Cl$ (1.40 g, 3 mmol) in water (50 cm^3). During the addition the solution was heated on a water-bath and stirred continuously. The resulting solution was filtered and allowed to stand overnight in a refrigerator after adjusting the pH to 4—5. The orange crystals which separated were washed with cold water and methanol and finally dried under vacuum (Found: C, 25.7; H, 5.75; N, 20.70. $C_{10}H_{17}CoClN_7O_8$ requires C, 25.60; H, 5.75; N, 20.90%).

$K[Co(H_2vi)(nta)]\cdot 2H_2O$. The acid $H_3vi\cdot H_2O$ (0.52 g, 3 mmol) was slowly added with stirring to a warm aqueous solution (50 cm^3) of α-$K[Co(nta)(H_2O)(OH)]\cdot 2H_2O$ (1.10 g, 3 mmol). On standing, red crystals separated in a few minutes. They were filtered off, washed with water and ethanol, and dried in a stream of air (Found: C, 24.40; H, 2.80; N, 11.05. $C_{10}H_{12}CoKN_4O_{12}$ requires C, 24.20; H, 2.80; N, 11.10%).

$[Co(Hvi)(phen)_2]NO_3\cdot 5H_2O$. The acid $H_3vi\cdot H_2O$ (0.52 g, 3 mmol) was dissolved in an aqueous solution (60 cm^3) containing $NaHCO_3$ (0.25 g). 1,10-Phenanthroline monohydrate (1.2 g, 6 mmol) dissolved in ethanol (15 cm^3) was added. The salt $Co(NO_3)_2\cdot 6H_2O$ (0.83 g, 3 mmol) dissolved in 2% H_2O_2 solution (6 cm^3) was added to the ligand, and the resulting solution quickly developed a very intense red colour. At the same time a black solid appeared that redissolved in a few minutes. The pH of the solution was then adjusted to 6 with dilute HNO_3. The orange solid which formed by slow evaporation was filtered off, washed with small portions of water and methanol, and finally dried in a stream of air (Found: C, 46.30; H, 3.75; N, 15.40. $C_{28}H_{27}CoN_8O_{12}$ requires C, 46.45; H, 3.75; N, 15.25%).

$Na[Co(Hvi)_2(phen)]\cdot 8H_2O$. The acid $H_3vi\cdot H_2O$ (1.05 g, 6 mmol) was dissolved in an aqueous solution (80 cm^3) of $NaHCO_3$, (0.50 g) and 1,10-phenanthroline (0.6 g, 3 mmol) dissolved in ethanol (6 cm^3) was added. Cobalt(II) nitrate hexahydrate (0.83 g, 3 mmol) dissolved in 2% H_2O_2 solution (5 cm^3) was added (pH 6), and the resulting solution developed a very intense reddish colour. After a few seconds a black precipitate appeared which was redissolved by adjusting the pH to 7—8 by adding a few cm^3 of 1 mol dm^{-3} NaOH solution. Brown-red crystals were finally obtained by slow evaporation of this solution, washed with small portions of water, and dried in a stream of air (Found: C, 33.65; H, 3.65; N, 15.40. $C_{20}H_{26}CoNaN_8O_{16}$ requires C, 33.55; H, 3.65; N, 15.65%).

$[Co(H_2vi)_2(phen)]NO_3\cdot 4.5H_2O$. This complex was obtained as above except that the final solution was acidified to pH *ca.* 3 by adding 1 mol dm^{-3} HNO_3 (Found: C, 34.50; H, 3.00; N, 18.25. $C_{20}H_{21}CoN_9O_{15.5}$ requires C, 33.55; H, 3.05; N, 18.15%).

$[Co(H_2vi)(salen)]\cdot 4H_2O$. The complex [Co(salen)] (0.98 g, 3 mmol) was dissolved in refluxing methanol (150 cm^3) in a nitrogen atmosphere and $H_3vi\cdot H_2O$ (0.52 g) was added. The refluxing was stopped after 30 min and the solution exposed to the air. Its colour changed from deep green to deep brown. The volume was reduced to 15 cm^3 and the precipitate formed was filtered off and washed with methanol and water. It was dissolved in aqueous $NaHCO_3$ and the resulting solution filtered and carefully neutralized. Slowly, a crystalline precipitate quantitatively separated. Crystals were washed with water and dried over $CaCl_2$ (Found: C, 43.40; H, 4.35; N, 12.65. $C_{20}H_{24}CoN_5O_{10}$ requires C, 43.35; H, 4.20; N, 12.70%).

Crystal Structure Determination and Refinement.—A prismatic crystal (0.1 × 0.1 × 0.2 mm) of the complex $K[Co(H_2vi)(nta)]\cdot 2H_2O$ was selected and mounted on a Philips PW 1100 four-circle diffractometer. Diffraction data were collected at 293 K by using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). Unit-cell parameters were determined from automatic centring of 15 reflections ($4 < \theta < 12°$) and refined by least-squares methods. Data collection showed systematic absences (*h*0*l*, $h + l = 2n + 1$; 0*k*0, $k = 2n + 1$) which uniquely define the monoclinic space group $P2_1/n$. No significant intensity decay was observed for three standard reflections measured every 2 h as orientation and intensity control. Lorentz polarization but not absorption corrections were made. 1 727 Independent reflections with $I \geqslant 2.5\sigma(I)$ were used for the structure refinement.

The structure of the complex was solved by direct methods using the MULTAN 84 system of computer programs,[19] and refined by full-matrix least-squares methods with the SHELX 76 program.[20] The function minimized was $\Sigma w||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0.006|F_o|^2]^{-1}$; f, f', and f'' were taken from ref. 21. The positions of hydrogen atoms were obtained from a difference synthesis and refined with an overall isotropic thermal parameter. The refinement converged with values for R and R' listed in Table 1. Maximum and minimum peaks in the final Fourier difference map were 0.4 and −0.4 e $Å^{-3}$, respectively. The final atomic co-ordinates for all non-hydrogen atoms are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Synthesis of the Complexes.—The complex $[Co(H_2vi)_3]$ and

Table 1. Crystal data for $K[Co(H_2vi)(nta)]\cdot 2H_2O$

Formula	$C_{10}H_{12}CoKN_4O_{12}$
M	478.3
Space group	$P2_1/n$
a/Å	21.705(5)
b/Å	9.930(3)
c/Å	7.451(2)
β/°	98.24(3)
U/Å^3	1 589(1)
Z	4
D_c/g cm^{-3}	1.998
F(000)	968.0
Crystal size/mm	0.1 × 0.1 × 0.2
μ(Mo-K_α)/cm^{-1}	14.64
Scan width	1.0
Scan speed/mm s^{-1}	0.03
Reflections collected	2 134
Independent reflections [$I \geqslant 2.5\sigma(I)$]	1 727
No. of parameters refined	290
$R (= \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|)$	0.062
$R' [= (\Sigma w\|\|F_o\| - \|F_c\|\|^2/\Sigma w\|F_o\|^2)^{\frac{1}{2}}]$	0.070

Table 2. Final atomic co-ordinates with estimated standard deviations in parentheses for $K[Co(H_2vi)(nta)]\cdot 2H_2O$

Atom	X/a	Y/b	Z/c
Co	0.848 9(1)	0.229 1(1)	0.840 8(2)
K	0.800 4(1)	0.359 1(2)	1.262 9(3)
O(1)	0.929 2(3)	0.240 2(6)	0.758 4(10)
C(2)	0.946 1(4)	0.361 3(10)	0.758 7(13)
N(3)	1.003 5(4)	0.388 6(8)	0.716 1(12)
C(4)	1.024 3(5)	0.521 3(11)	0.703 0(15)
O(4)	1.075 8(3)	0.542 3(8)	0.654 4(12)
N(5)	0.988 0(4)	0.624 8(8)	0.749 3(12)
C(6)	0.927 4(6)	0.615 6(13)	0.808 5(15)
O(6)	0.900 6(4)	0.706 0(8)	0.852 0(14)
C(7)	0.907 9(4)	0.468 4(9)	0.808 8(14)
N(8)	0.853 8(4)	0.421 5(8)	0.852 7(10)
O(8)	0.815 4(3)	0.497 6(7)	0.914 9(10)
O(9)	0.890 5(3)	0.219 4(7)	1.080 4(9)
C(10)	0.920 8(5)	0.107 9(10)	1.111 8(14)
O(10)	0.960 7(4)	0.090 3(8)	1.249 0(11)
C(11)	0.909 6(4)	0.001 1(11)	0.967 7(15)
N(12)	0.851 3(4)	0.033 6(7)	0.842 0(11)
C(13)	0.794 9(5)	−0.013 4(10)	0.925 8(16)
C(14)	0.749 0(5)	0.101 2(10)	0.952 8(13)
O(14)	0.701 9(3)	0.077 8(8)	1.005 5(10)
O(15)	0.770 6(3)	0.222 8(7)	0.922 8(9)
C(16)	0.850 9(6)	−0.008 5(11)	0.652 0(14)
C(17)	0.817 4(5)	0.097 6(10)	0.525 1(14)
O(17)	0.800 8(4)	0.072 1(8)	1.364 5(10)
O(18)	0.810 4(3)	0.216 2(7)	0.595 6(9)
O(w1)	0.827 0(4)	−0.260 1(8)	1.207 7(12)
O(w2)	0.937 9(4)	−0.168 6(8)	1.395 0(12)

its deprotonated derivatives are the only violurato-containing cobalt(III) complexes which have been reported.[5] The choice of more appropriate synthetic procedures to obtain heteroleptic cobalt(III) violurato complexes was not obvious at first glance. However, it was soon observed that oxidation of cobalt(II) salts in the presence of the appropriate mixture of ligands led to the formation of $[Co(H_2vi)_3]$ because of its great stability. Therefore, ligand-substitution reactions of previously isolated cobalt(III) complexes were investigated. First, we tried the complex $[Co(NH_3)_4(CO_3)]^+$ because the carbonate ligand is labile while Co^{III}-NH_3 bonds are very inert.[22] Unfortunately, the reaction of violuric acid with this species produced $[Co(H_2vi)_3]$ as the final product too. Even $[Co(NH_3)_6]^{3+}$ reacts easily with violuric acid undergoing also complete substitution of the co-ordination sphere of the metal ion to yield $[Co(NH_3)_6][Co(Hvi)_3]$, an already known compound.[5] So, in order to avoid the complete substitution of the ligands by H_2vi^-, polydentate ligands were then used. This type of ligand, both from a thermodynamic and kinetic point of view, should be much more resistant to ligand-substitution reactions. A quantitative substitution of Cl^- for H_2vi^- occurred in the reaction between $[Co(trien)Cl_2]^+$ and H_2vi^- [equation(1)].

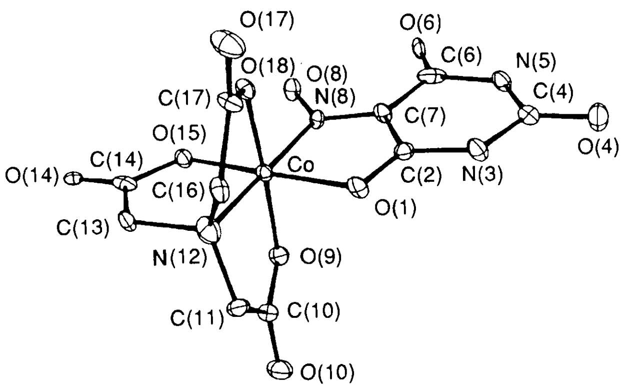

Figure 1. ORTEP view of the $[Co(H_2vi)(nta)]^-$ unit. Thermal ellipsoids are drawn at 25% probability. Hydrogen atoms have been omitted for clarity

$$[Co(trien)Cl_2]^+ + H_2vi^- \rightleftharpoons [Co(H_2vi)(trien)]^{2+} + 2Cl^- \quad (1)$$

Positive results were also obtained with nta^{3-}; $[Co(nta)(OH)(H_2O)]^-$ reacts quantitatively with H_3vi to yield $K[Co(H_2vi)(nta)]$ [equation (2)]. It has been pointed out that 1,10-phenanthroline and dihydrogenviolurato ligands exhibit a similar co-ordination behaviour.[23] Two mixed-ligand cobalt(III) phenanthroline–violurato complexes, $[Co(Hvi)(phen)_2]^+$ and $[Co(H_2vi)_2(phen)]^+$, were obtained by direct oxidation with H_2O_2 of cobalt(II) solutions containing the appropriate ligand ratio. The nature of the complexes obtained is controlled in this case by the initial composition of the solution.

$$[Co(nta)(OH)(H_2O)]^- + H_3vi \rightleftharpoons [Co(H_2vi)(nta)]^- + 2H_2O \quad (2)$$

Finally, we have obtained $[Co(H_2vi)(salen)]\cdot 4H_2O$ by air oxidation of methanolic solutions of the corresponding cobalt(II) complex formed *in situ* by the reaction of [Co(salen)] and violuric acid.

The ligand H_2vi^- deprotonates easily in all these complexes (see below). Thus, some of the isolated compounds contain the violurato ligand as Hvi^{2-}. In one case we have obtained the same complex in two different protonation degrees, $Na[Co(Hvi)_2(phen)]$ and $[Co(H_2vi)_2(phen)]NO_3$.

Molecular Structure of $K[Co(H_2vi)(nta)]\cdot 2H_2O$.—The structure consists of $[Co(H_2vi)(nta)]^-$ anions, K^+ cations, and water molecules of crystallization bound by electrostatic interactions and hydrogen bonds. A view of the complex anion with the atomic numbering scheme is shown in Figure 1. Selected bond distances and angles are given in Table 3. The metal ion exhibits *trans*-N_2O_4 distorted-octahedral surroundings, with N(8), O(9), N(12), and O(18) atoms in the basal plane and O(15) and O(1) atoms filling the apical positions. The largest deviation from the mean plane through N(8), O(9), N(12), and O(18) is 0.006 Å. The cobalt lies only 0.046 Å below this plane towards O(15). Equatorial distances vary between 1.884(6) and 1.942(7)

Table 3. Selected bond distances (Å) and angles (°) for non-hydrogen atoms of K[Co(H_2vi)(nta)]·2H_2O

Cobalt environment			
Co–O(1)	1.932(6)	Co–O(15)	1.889(6)
Co–N(8)	1.915(7)	Co–O(18)	1.902(7)
Co–N(12)	1.942(7)	Co–O(9)	1.884(6)
O(1)–Co–N(8)	84.9(3)	O(9)–Co–O(15)	91.3(3)
O(1)–Co–O(9)	88.4(3)	N(12)–Co–O(15)	89.4(3)
N(8)–Co–O(9)	89.5(3)	O(1)–Co–O(18)	89.5(3)
O(1)–Co–N(12)	91.9(3)	N(8)–Co–O(18)	97.2(3)
N(8)–Co–N(12)	174.8(3)	O(9)–Co–O(18)	172.8(3)
O(9)–Co–N(12)	86.3(3)	N(12)–Co–O(18)	86.8(3)
O(1)–Co–O(15)	178.6(3)	O(15)–Co–O(18)	90.9(3)
N(8)–Co–O(15)	93.7(3)		
Dihydrogenviolurato ligand			
C(2)–O(1)	1.257(11)	N(3)–C(2)	1.356(12)
C(7)–C(2)	1.430(13)	O(4)–C(4)	1.241(11)
N(5)–C(4)	1.368(13)	C(4)–N(3)	1.401(13)
C(6)–N(5)	1.449(14)	O(6)–C(6)	1.142(15)
C(7)–C(6)	1.522(14)	N(8)–C(7)	1.347(12)
O(8)–N(8)	1.262(9)		
Co–O(1)–C(2)	109.3(3)	O(1)–C(2)–N(3)	117.9(6)
O(1)–C(2)–C(7)	122.2(6)	N(3)–C(2)–C(7)	119.9(6)
C(2)–N(3)–C(4)	121.3(6)	N(3)–C(4)–O(4)	119.4(6)
N(3)–C(4)–N(5)	119.1(7)	O(4)–C(4)–N(5)	121.5(6)
C(4)–N(5)–C(6)	127.6(7)	N(5)–C(6)–O(6)	123.9(6)
N(5)–C(6)–C(7)	109.6(7)	O(6)–C(6)–C(7)	127.1(7)
C(2)–C(7)–C(6)	122.9(7)	C(2)–C(7)–N(8)	111.4(7)
C(6)–C(7)–N(8)	125.7(7)	Co–N(8)–C(7)	112.2(2)
Co–N(8)–O(8)	125.4(3)	C(7)–N(8)–O(8)	121.9(6)

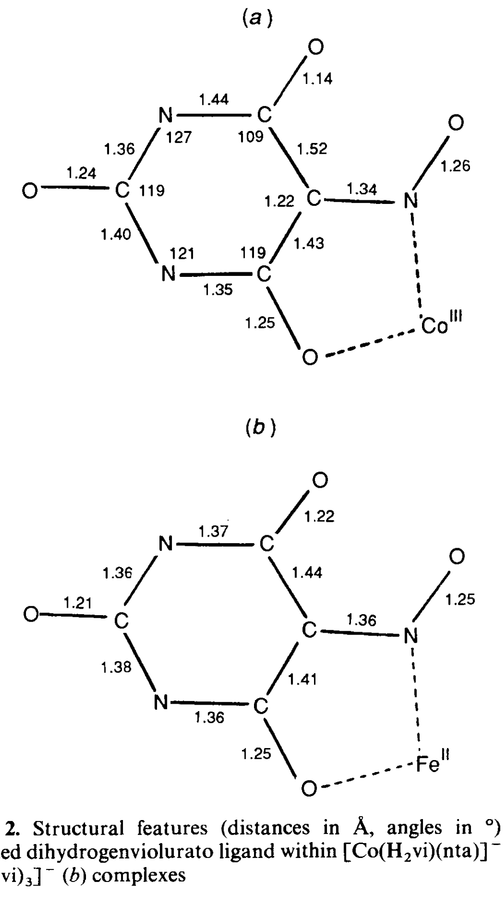

Figure 2. Structural features (distances in Å, angles in °) of co-ordinated dihydrogenviolurato ligand within [Co(H_2vi)(nta)]$^-$ (*a*) and [Fe(H_2vi)$_3$]$^-$ (*b*) complexes

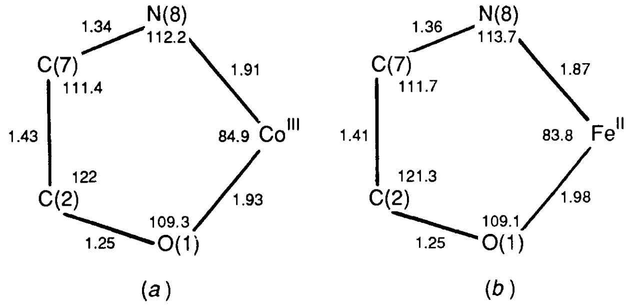

Figure 3. Schematic drawing showing the relevant structural features (distances in Å, angles in °) within MNC_2O chelate rings [M = Co^{III} (*a*) or Fe^{II} (*b*)]

Å while apical distances are 1.889(6) [Co–O(15)] and 1.932(6) Å [Co–O(1)]. The angle O(1)–Co–O(15) [178.6(3)°] is very close to the ideal value (180°), while the bond angles within the equatorial plane show greater distortions [89.5(3), 86.3(3), 86.8(3), and 97.2(3)°, for N(8)–Co–O(9), O(9)–Co–N(12), N(12)–Co–O(18), and O(18)–Co–N(8), respectively].

The dihydrogenviolurate anion is co-ordinated to the metal ion as a bidentate ligand through the oxime nitrogen [N(8)] and one of the amide oxygens [O(1)]. The ligand H_2vi^- is planar, the greatest deviation from the mean plane defined by its non-hydrogen atoms being 0.064 Å for N(3). Deviation of Co^{III} from this plane is only 0.01 Å. These features are common in other reported structures of violurato-containing complexes such as [Fe(H_2vi)$_3$]$^-$ and [Cu(H_2vi)$_2$(H_2O)$_2$].[4,9] Nevertheless, the H_2vi^- ligand is co-ordinated very asymmetrically, the M–N(8) and M–O(1) bond lengths being 1.84 and 1.95 Å for the iron(II) complex and 1.97 and 2.21 Å for the copper(II) one. This ligand is much more symmetric in our complex, the difference between these bond distances being only 0.017 Å.

It should be noted that the structural parameters of the violurato ligand are very sensitive to the polarization effects induced by the co-ordinated metal ion and the other cations present in the structure (see Figure 2). All C–C and C–N bond distances in [Fe(H_2vi)$_3$]$^-$ are intermediate between those of single and double bonds, showing that electron delocalization spreads to all the ring. The distances N(5)–C(6) and C(6)–C(7) in [Co(H_2vi)(nta)]$^-$ clearly correspond to single bonds and, consequently, electron delocalization within the ring is only partial. In agreement with these data, C(6)–O(6) is of the order of a C=O double bond. Atom O(6) is the only carbonyl oxygen atom that remains free, whereas O(1) is bound to Co^{III} and O(4) interacts with a K^+ ion. On the other hand there are only minor differences in the geometry of the $MNOC_2$ five-membered chelate ring in [Fe(H_2vi)$_3$]$^-$ and [Co(H_2vi)(nta)]$^-$ (see Figure 3).

The nitrolotriacetate anion is co-ordinated to the metal ion as a tetradentate ligand. The structure reveals two $CoONC_2$ five-atom chelate rings in envelope conformation related by a pseudo-mirror plane which is defined by the third flat ring. This butterfly structure occurs in all the published structures of octahedral transition-metal complexes containing a tetradentate nta^{3-} ligand.[24]

Deprotonation Equilibria.—The overall proton-association constants obtained in the potentiometric study of the complexes as well as the distribution diagrams for the existing species in solution are shown in Table 4 and Figure 4.

A great increase in the acidity of co-ordinated H_2vi^- with respect to the free ligand has been found for all the complexes studied herein. The pK_a values are in the range 2.6—5.6 (see Table 5). This phenomenon also occurs for the second deprotonation, $Hvi^{2-} \rightleftharpoons vi^{3-} + H^+$. Full deprotonation of

Table 4. Values of the overall proton association constants determined potentiometrically (25 °C, 0.1 mol dm^{-3} KCl)

Complex	log β_1	log β_2	log β_3
$[Co(vi)(nta)]^{3-}$	10.79(1)	15.24(2)	—
$[Co(vi)(trien)]$	10.58(1)	14.46(1)	—
$[Co(vi)(Hvi)(phen)]^{2-}$	10.49	15.21(5)	18.10(7)
$[Co(vi)(phen)_2]$	9.650(8)	12.27(2)	—
$[Co(Hvi)(salen)]^-$	5.40(1) *	7.80(1) *	—

* Determined in water–dmso (70:30 w/w) at 25 °C and 0.1 mol dm^{-3} $KClO_4$.

Table 5. Acidity constants of co-ordinated H_2vi^-

Complex	pK_a	Ref.
$[Co(H_2vi)(phen)_2]^{2+}$	2.62	This work
$[Co(H_2vi)_2(phen)]^+$	2.89	This work
$[Co(H_2vi)_3]$	3.6	5
$[Co(H_2vi)(trien)]^{2+}$	3.9	This work
$[Co(H_2vi)(nta)]^-$	4.46	This work
$[Co(Hvi)(H_2vi)_2]^-$	4.6	5
$[Co(Hvi)(H_2vi)(phen)]$	4.72	This work
$[Co(H_2vi)(salen)]$	5.4 *	This work
$[Co(Hvi)_2(H_2vi)]^{2-}$	5.6	5
H_2vi^- (free)	9.64	1

* Conditions as in Table 4.

Table 6. Acidity constants of co-ordinated Hvi^{2-}

Complex	pK_a
$[Co(Hvi)(phen)_2]^+$	9.65
$[Co(Hvi)_2(phen)]^-$	10.49
$[Co(Hvi)(trien)]^+$	10.64
$[Co(Hvi)(nta)]^{2-}$	10.79
Hvi^{2-} (free)	14.2 *

* Value determined spectrophotometrically at 18 °C.[2]

the free ligand is hardly observed in aqueous solution (pK_a = 14.2); however, the corresponding pK_a values for our complexes are in the range 9.65—10.8 (see Table 6). Such a strong effect is rather surprising since the deprotonable NH is far away from the metal ion. It is evident that polarization effects are propagated to a great distance, although tautomeric equilibria[9] could be also involved in this effect.

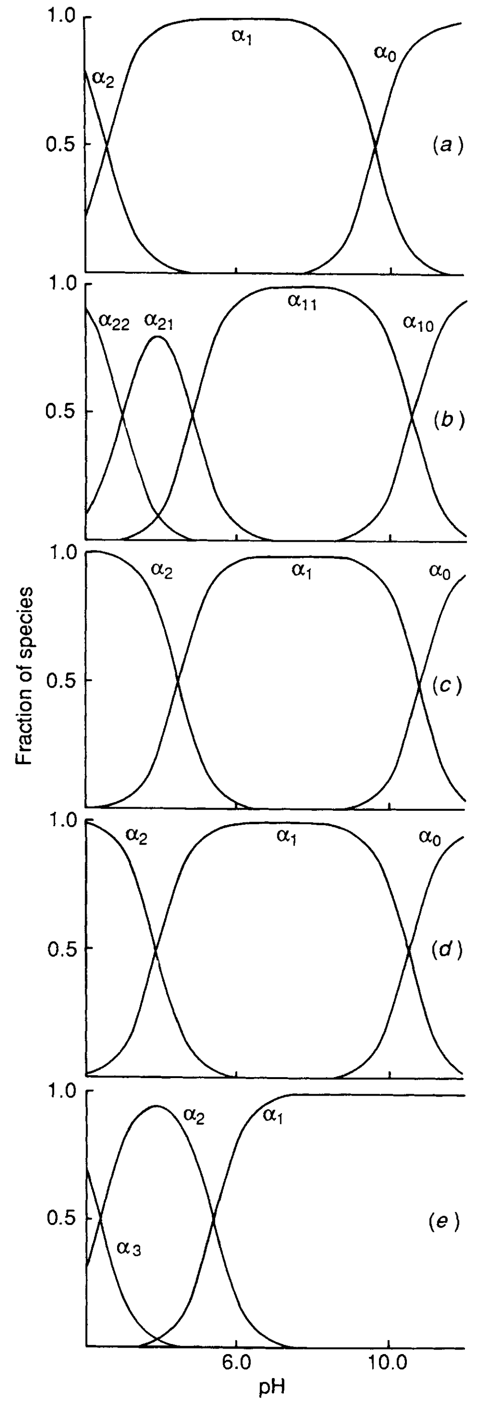

Figure 4. Distribution diagrams of the equilibrium species in solution for the systems: (*a*) $[Co(H_nvi)(phen)_2]^{n+}$, $\alpha_2(n = 2)$, $\alpha_1(n = 1)$, $\alpha_0(n = 0)$; (*b*) $[Co(H_nvi)(H_mvi)(phen)]^{(n+m-3)}$, $\alpha_{22}(n = 2, m = 2)$, $\alpha_{21}(n = 2, m = 1)$, $\alpha_{11}(n = 1, m = 1)$, $\alpha_{10}(n = 1, m = 0)$; (*c*) $[Co(H_nvi)(nta)]^{(n-3)-}$, $\alpha_2(n = 2)$, $\alpha_1(n = 1)$, $\alpha_0(n = 0)$; (*d*) $[Co(H_nvi)(trien)]^{n+}$, $\alpha_2(n = 2)$, $\alpha_1(n = 1)$, $\alpha_0(n = 0)$; and (*e*) $[Co(H_nvi)(salen)]^{(n-2)+}$, $\alpha_3(n = 3)$, $\alpha_2(n = 2)$, $\alpha_1(n = 1)$.

Remarkable differences in the pK_a values of the co-ordinated H_2vi^- ligand are observed in this series of complexes in spite of their qualitative similar behaviour. The ligands in the co-ordination sphere of Co^{III} can modulate the acidity of co-ordinated violurate anions, particularly for H_2vi^-. Two factors can be invoked to explain this: (*i*) the ionic charge of the complex, and (*ii*) the nature of the metal–ligand bond. It can be readily understood that the greater the positive charge on the complex, the easier the proton will be lost and therefore cationic complexes should present lower pK_a values than anionic ones. Although this order is roughly followed for the complexes in Tables 5 and 6, it appears that this is not the main factor. The actual charge on the metal ion which is determined by the nature of the metal–ligand bond is more important than the net charge of the complex. The stronger the donation of electron density of ligands to Co^{III}, the smaller is the polarization effect of Co^{III} on violurate, resulting in a higher pK_a value. A comparison between $[Co(H_2vi)(phen)_2]^{2+}$ (pK_a = 2.62) and $[Co(H_2vi)(trien)]^{2+}$ (pK_a = 3.90) is very illustrative in this respect. Both complexes have the same charge and moreover phen and trien are N-donor ligands. However the former exhibits a greater acidity. Triethylenetetramine is only a σ-donor ligand whereas phen shows also a well known π-acceptor character and will afford smaller electron density to the metal ion. The π-acceptor character of H_2vi^- is illustrated by comparing $[Co(H_2vi)_3]$ (pK_a = 3.6) and $[Co(H_2vi)(salen)]$ (pK_a = 5.4). The substitution of the σ-donor salen ligand by two H_2vi^- groups enhances the acidity of the metal centre. A comparison between $[Co(H_2vi)(phen)_2]^{2+}$ and $[Co(H_2vi)_2(phen)]^+$ reveals once more the similar behaviour of H_2vi^- and phen as ligands.

Protonation Equilibria.—The protonation of H_2vi^- as a ligand, although possible at first sight, should not be easily observed in solution because its pK_a value is expected to be very small. In this regard, we recall that the pK_a value for free H_3vi is 4.35. The complex $[Cr(H_2vi)_3]$ is the only species where the protonation of a H_2vi^- has been reported (pK_a = 3.32).[7] For the cobalt(III) complexes the extent of protonation should be smaller.[7] Accordingly we have not found any clear evidence of protonation for the complexes herein reported at pH > 2.50 except for $[Co(H_2vi)(salen)]$. At lower pH values a better fit of the experimental data is obtained by considering the existence of protonation to yield the complexes $[Co(H_2vi)(H_3vi)]^{2+}$ (pK_a *ca.* 1.6), $[Co(H_3vi)(nta)]$ (pK_a *ca.* 1.8), and $[Co(H_3vi)(trien)]^{3+}$ (pK_a *ca.* 1.5). These values are only approximate because of the unreliability of e.m.f. measurements in such acidic media. The species $[Co(H_2vi)(salen)]$ undergoes an extensive protonation in acidic media corresponding to equation (3). In this case

$$[Co(H_2vi)(salen)] + H^+ \xrightleftharpoons{pK_a\,=\,2.4} [Co(H_3vi)(salen)]^+ \quad (3)$$

the reaction is favoured by the good donor properties of the phenolate groups of $salen^{2-}$ which decrease significantly the polarizing power of Co^{III} (see Table 5). The acid–base behaviour of $[Co(H_2vi)(salen)]$ can be also followed by spectrophotometry. The absorption spectrum of this complex in water–dmso (70:30) (w/w) solution displays a very intense band at 350 nm ($\varepsilon = 1.9 \times 10^4$ dm^{-3} mol^{-1} cm^{-1}). Addition of KOH produces a great increase in the absorption intensity and a slight shift of the peak towards higher wavelengths. On the other hand, acidification of the solution causes a progressive decrease in the band intensity. These changes are instantaneous and completely reversible.

Water–dmso Mixtures.—Protonation and deprotonation equilibria of the $[Co(H_2vi)(salen)]$ complex have been studied in water–dmso mixtures as solvent due to its insolubility in water. Since the results obtained in such a medium cannot strictly be compared with ones in aqueous solution, we have investigated the influence of the dmso contents on them. The results obtained can be summarized as follows: (*i*) For the first acidity constant of co-ordinated H_2vi^- the pK_a value is 6.3 (20:80), 5.7 (50:50), and 5.4 (70:30) (w/w). As the water content of the solvent mixture increases, the differences in the pK_a values are narrowing, and so, in pure water a pK_a value close to the last one should be expected. (*ii*) The protonation constant is nearly identical (2.4) for water–dmso mixtures containing more than 50% of water. Higher contents of dmso enhance the acidity of the salen complex and the potentiometric determination of this constant becomes troublesome. It is well known that cationic acids are stronger in dmso than in water whereas neutral or anionic ones are weaker.[25] These results allow us to state that the values obtained for $[Co(H_2vi)(salen)]$ in water–dmso (70:30) can be compared with those determined in water for the other complexes.

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