X-Ray Crystal Structures and Electron Spin Resonance Spectroscopic Characterization of Mixed-ligand Chromium(III) Complexes with L-Aspartate or Pyridine-2,6-dicarboxylate and 1,10-Phenanthroline or 2,2′:6′,2″-Terpyridyl†

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The crystal and molecular structure of two newly prepared chromium(III) complexes [Cr(L-asp)(phen)-$(H_2O)]NO_3\cdot 2H_2O$ **1** [L-asp = L-aspartate(2−), phen = 1,10-phenanthroline] and [Cr(terpy)(pydca)]-$[Cr(pydca)_2]\cdot 4H_2O$ **3** (pydca = pyridine-2,6-dicarboxylate, terpy = 2,2′:6′,2″-terpyridyl) were determined by means of X-ray diffraction. Crystals of **1** are triclinic, space group $P\bar{1}$, with a = 11.793(5), b = 10.507(5), c = 9.258(5) Å, α = 111.43(3), β = 86.44(3) and γ = 111.71(3)°. Crystals of **3** are triclinic, space group $P\bar{1}$, with a = 19.100(5), b = 12.874(5), c = 7.575(5) Å, α = 86.16(3), β = 95.10(3) and γ = 96.62(3)°. The co-ordination around the Cr atom in both **1** and **3** is distorted octahedral, the sixth position of **1** being occupied by a water molecule. Crystals of **3** are built up of two different ionic units. ESR spectra were run on magnetically dilute powders and frozen solutions, and the values of the spin-Hamiltonian parameters obtained by computer simulation. The similarity between these parameters for the chromium(III) species in powders and glasses suggests that the solution species possess the same kind of distortion found for the solid complexes.

It is well known that chromium(III) complexes, which, with some exceptions, are all six-co-ordinated, are kinetically inert. Hence, one can take advantage of this kinetic inertness and try to isolate complex species as solids in order to gain structural information by diffractometric methods. Thus there is not the usual limitation for other transition-metal ions that the species present in the solid state is not preserved in solution. In the case of chromium(III) complexes isolated as solids, there is a persistence of the complex species for a long time in solution even under conditions of thermodynamic instability.[1] As part of a research project on structural features of chromium(III) complexes with biological ligands, this paper deals with a diffractometric and spectroscopic study of the mixed-ligand chromium(III) complexes $[Cr(L\text{-}asp)(phen)(H_2O)]NO_3\cdot 2H_2O$ [L-asp = L-aspartate(2−), phen = 1,10-phenanthroline] and $[Cr(terpy)(pydca)][Cr(pydca)_2]\cdot 4H_2O$ (terpy = 2,2′:6′,2″-terpyridyl, pydca = pyridine-2,6-dicarboxylate). In particular, the possible application of ESR spectroscopy to the study of chromium(III) complexes from unknown samples like those from biological material is considered.

Experimental

ESR measurements were carried out by using a conventional X-band Bruker ER 200 D spectrometer equipped with standard low-temperature apparatus. A maximum magnetic field of 1 500 mT was reached by means of a 10 in pole gap electromagnet and a 12 kW (ER 083) power supply. The magnetic field was measured during each scan with an ER 035 M gauss-meter above 46 mT whereas the klystron frequency was calibrated using solid diphenylpicrylhydrazyl (dpph) (g = 2.0036) as standard. In order to get accurate spin-Hamiltonian parameters for the chromium(III) complexes with terpy and pydca, we endeavoured to prepare the corresponding cobalt(III) complexes which are suitable diamagnetic hosts. This allowed us to obtain magnetically dilute powders and took advantage of the narrower linewidths exhibited by solid samples. Unfortunately, little structural information is available for the cobalt(III) complexes used in this work; nonetheless, it is reasonable to assume that they are isostructural with the analogous chromium(III) complexes since the geometrical requirements of the terpy and pydca ligands impose a meridional configuration when they are co-ordinated to a metal ion. Magnetically dilute crystals were obtained by slow evaporation of concentrated aqueous solutions of the cobalt(III) compounds containing about 1% (mole ratio) of the same chromium(III) complex ion. Powder spectra were run both at low and room temperatures. Water–methanol (3:1) or water–methanol–dimethylformamide (1:1:4) mixtures were used as solvents for frozen-solution ESR spectra, the concentration of the complexes ranging from 5 up to 10 mmol dm^{-3} at 150 K. Spin-Hamiltonian parameters were obtained by means of a simulation computer program[2] based on the diagonalization of the Hamiltonian for $S = \frac{3}{2}$ systems [equation (1)].[3–5] Allowance was made for non-coincidence of

$$\mathscr{H} = \beta \sum_{i}^{x,y,z} g_i H_i S_i + D(S_z{}^2 - \tfrac{5}{4}) + E(S_{x'}{}^2 - S_{y'}{}^2) \quad (1)$$

g and D tensor directions in the xy plane.[6] All spectral simulations were performed on a VAX 11-750 computer.

Thermal gravimetric analysis (TGA) was performed by means of a Mettler TA 3000 system equipped with a Mettler TG 50 thermobalance at a heating rate of 2° min^{-1}. Optical data (UV–VIS) were obtained using a Perkin-Elmer 330 double-beam spectrophotometer. IR spectra were recorded on a Perkin-Elmer 684 spectrophotometer on CsBr discs.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Preparation of the Complexes.—The complexes K[Cr(pydca)$_2$] and [Cr(terpy)$_2$][ClO$_4$]$_3$·H$_2$O were prepared according to literature procedures.[7,8] Synthetic methods for complex **4** and the ammonium salt of [Co(pydca)$_2$]$^-$ have also been reported[9,10] but the procedures described here were found more convenient.

[Cr(L-asp)(phen)(H$_2$O)]NO$_3$·2H$_2$O **1**. Solid Cr(NO$_3$)$_3$·9H$_2$O (2.0 g, 5 mmol) was added to a suspension of phen·H$_2$O (0.99 g, 5 mmol) and L-H$_2$asp (0.67 g, 5 mmol) in water (30 cm^3). The reaction mixture was continuously stirred and its temperature maintained at 70 °C for 8 h. During this time KOH (0.56 g, 10 mmol) dissolved in water (4 cm^3) was gradually added. The red solution was concentrated to *ca.* 5 cm^3. On standing overnight in a refrigerator a red microcrystalline powder formed which was collected by filtration. After several days the filtrate produced more solid. The combined crude products were recrystallized from dilute nitric acid (pH *ca.* 3, 5 cm^3), yield after recrystallization 0.60 g (25%) (Found: C, 40.1; H, 4.10; Cr, 10.7; N, 11.8. C$_{16}$H$_{19}$CrN$_4$O$_{10}$ requires C, 40.1; H, 4.00; Cr, 10.85; N, 11.7%). IR: 563m, 499m, 440s, 420(sh), 397s, 374w, 350(sh), 297w, 243m and 221w cm^{-1}. TGA showed a weight loss of nearly 8% in the range 60–82 °C, corresponding to two molecules of water of crystallization (calc. 7.5%). A second weight loss of about 3.67%, observed in the range 160–185 °C, corresponded to one co-ordinated water molecule (calc. 3.76%).

[Cr(terpy)(pydca)]ClO$_4$ **2**. A suspension of terpy (0.47 g, 2 mmol) and H$_2$pydca (0.35 g, 2 mmol) in water (30 cm^3) was stirred and slowly heated until dissolved. 0.5 mol dm^{-3} Chromium(III) perchlorate (4 cm^3, 2 mmol) was added to the resulting pale yellow solution and the temperature raised to 70 °C. After a few minutes an orange microcrystalline powder separated, yield 0.34 g (70%). Recrystallization from a hot aqueous solution yielded red-orange plate-like crystals (Found: C, 47.8; H, 2.6; Cr, 9.1; N, 10.1. C$_{22}$H$_{14}$ClCrN$_4$O$_8$ requires C, 48.1; H, 2.6; Cr, 9.3; N, 10.2%). IR: 515w, 467s, 445w, 420w, 364s, 336m, 300w and 225w cm^{-1}.

[Cr(terpy)(pydca)][Cr(pydca)$_2$]·4H$_2$O **3**. A suspension of CrCl$_3$·6H$_2$O (0.53 g, 2 mmol) and H$_2$pydca (0.50 g, 3 mmol) in water (20 cm^3) was stirred and heated at *ca.* 70 °C for 1 h. Over this time KOH (0.34 g, 6 mmol) dissolved in water (3 cm^3) was gradually added. Terpyridyl (0.23 g, 1 mmol) dissolved in ethanol (3 cm^3) was added to the resulting violet solution. A small amount of violet crystals appeared and subsequently dissolved. The reaction was allowed to take place for another 45 min. The resulting dark red solution afforded fine brown needles on cooling, yield 0.72 g (80%). Dark brown crystals were obtained by recrystallizing from water (Found: C, 48.3; H, 3.2; Cr, 11.1; N, 9.4. C$_{36}$H$_{28}$Cr$_2$N$_6$O$_{16}$ requires C, 47.8; H, 3.1; Cr, 11.5; N, 9.3%). Dehydration as shown by TGA took place in two steps in the range 50–120 °C. A 7.83% weight loss was observed corresponding to four water molecules of crystallization (Calc. 7.96%).

[Co(terpy)$_2$][ClO$_4$]$_3$ **4**. The salt CoCl$_2$·6H$_2$O (0.24 g, 1 mmol) and terpy (0.47 g, 2 mmol) were dissolved in water (5 cm^3). The deep brown solution was treated with concentrated HCl followed by dropwise addition of an excess (0.5 cm^3) of 35% H$_2$O$_2$. The reaction mixture was gently boiled for 5 min. A pale yellow microcrystalline solid precipitated upon addition of an excess of NaClO$_4$·H$_2$O (0.84 g, 6 mmol), yield 0.17 g (80%). The raw product was recrystallized from water (Found: C, 43.9; H, 2.8; Co, 7.00; N, 10.2. C$_{30}$H$_{22}$Cl$_3$CoN$_6$O$_{12}$ requires C, 43.7; H, 2.7; Co, 7.15; N, 10.2%). UV spectrum: λ_{max}(water) 435 nm (ε 300 dm^3 mol^{-1} cm^{-1}). This compound was previously[9] reported as having one water molecule of crystallization. TGA showed no weight loss in the range 30–200 °C.

[Co(terpy)(pydca)]ClO$_4$ **5**. A slurry of CoCl$_2$·6H$_2$O (0.238 g, 1 mmol) and KHCO$_3$ (0.21 g, 10 mmol) in water (1 cm^3) was treated with a few drops of 35% H$_2$O$_2$. Water (4 cm^3) was added followed by terpy (0.23 g, 1 mmol) dissolved in ethanol (2 cm^3). The green solution was heated at 60 °C for 3 min. Solid H$_2$pydca (0.25 g, 1.5 mmol) was added to the reaction mixture which was then heated for 10 min at 60 °C. On addition of HClO$_4$ or NaClO$_4$ an orange microcrystalline solid precipitated. The solid was washed with water to remove the coprecipitated KClO$_4$, yield 0.19 g (35%). It was recrystallized from hot water (Found: C, 47.7; H, 2.7; Co, 10.1; N, 10.1. C$_{22}$H$_{14}$ClCoN$_4$O$_8$ requires C, 47.5; H, 2.5; Co, 10.6; N, 10.1%). UV spectrum (water): λ_{max} 453 and 495 nm (ε 330 and 340 dm^3 mol^{-1} cm^{-1}).

M[Co(pydca)$_2$]·*n*H$_2$O (M = Na, *n* = 2, **6**; *or* M = Rb, *n* = 0, **7**). Solid Na$_3$[Co(CO$_3$)$_3$]·3H$_2$O[11] (1.81 g, 5 mmol) was slowly added (generation of CO$_2$) to a hot aqueous solution of H$_2$pydca (1.67 g, 10 mmol) and a slight excess of HNO$_3$ (*ca.* 12 mmol) in water (50 cm^3). The resulting deep purple solution was stirred and heated (70 °C) for 20 min. The reaction mixture was divided into two portions. One portion was concentrated (10 cm^3) and the precipitated crystals of **6** filtered off, yield 0.75 g (67%). The complex was recrystallized from water (Found: C, 37.7; H, 2.35; Co, 12.9; N, 6.4. C$_{14}$H$_{10}$CoN$_2$NaO$_{10}$ requires C, 37.5; H, 2.25; Co, 13.5; N, 6.25%). UV spectrum (water): λ_{max} 513 nm (ε 653 dm^3 mol^{-1} cm^{-1}) [lit.,[10] 510 nm (ε 630 dm^3 mol^{-1} cm^{-1})]. Dehydration took place between 90 and 115 °C causing a weight loss of about 7.9% corresponding to two water molecules of crystallization (calc. 8.0%). The second portion was poured into a Dowex 1X8 column (1.5 × 50 cm, 50–100 mesh) in the chloride form. Eluting with water, a small band descended which was discarded since it contained neutral or positive species. The absorbed violet band was eluted with 2 mol dm^{-3} RbCl and its volume reduced to *ca.* 10 cm^3. Dark purple crystals were removed. Yield 0.83 g (70%) (Found: C, 35.6; H, 1.30; Co, 12.4; N, 6.0. C$_{14}$H$_6$CoN$_2$O$_8$Rb requires C, 35.4; H, 1.25; Co, 12.4; N, 5.9%).

[Co(terpy)(pydca)][Co(pydca)$_2$]·2H$_2$O **8**. Compound **5** (0.28 g, 0.5 mmol) dissolved in water (400 cm^3) was converted into the much more soluble chloride by means of ion-exchange chromatography (Dowex 1X8, 50–100 mesh, chloride form). The eluate was reduced to *ca.* 10 cm^3 and mixed with a solution of complex **6** (0.23 g, 0.5 mmol) in water (10 cm^3). The volume was reduced to *ca.* 5 cm^3 and the solid collected by filtration, yield 0.40 g (90%). Large dark red crystals were obtained by recrystallization from water (Found: C, 49.1; H, 2.80; Co, 13.0; N, 9.5. C$_{36}$H$_{24}$Co$_2$N$_6$O$_{14}$ requires C, 49.0; H, 2.75; Co, 13.35; N, 9.5%). TGA showed a weight loss of nearly 4.06% corresponding to two water molecules of crystallization (calc. 4.08%).

Diffractometric Measurements of Complex **1**.—*Crystal data.* C$_{16}$H$_{19}$CrN$_4$O$_{10}$, M = 479, triclinic, space group $P\bar{1}$, a = 11.793(5), b = 10.507(5), c = 9.258(5) Å, α = 111.43(3), β = 86.44(3), γ = 111.73(3)°, U = 989 Å^3, D_c = 1.61 g cm^{-3}, Z = 2, μ(Mo-Kα) = 5.7 cm^{-1}, λ = 0.7107 Å, maximum crystal size = 0.2 mm.

Cell parameters were calculated from accurate settings of 25 medium-angle reflections on a PW 1100 Philips diffractometer with Mo-Kα radiation. Intensities for reflections up to θ = 25° were recorded with a scan speed of 2° min^{-1} and a conventional θ–2θ scan. Of the 3411 reflections, 2942 with $I > 3\sigma(I)$ were considered to be significantly above the background and were used in subsequent calculations. Corrections were made for Lorentz polarization.[12] No deterioration of crystals was observed during data collection. The structure was solved by standard methods and refined to the final conventional R of 0.080 when the largest parameter shifts were 0.8σ on the atom coordinates and 1.2σ on the thermal parameters. Refinement was carried out by full-matrix least squares, minimizing the function $\Sigma w(\Delta F)^2$ with w = 1. The nitrate ion is disordered. A careful inspection of the electron density map showed that the oxygen atoms are statistically distributed in two different positions. Refinement of the occupancy factors, with a fixed thermal parameter for these oxygens, resulted in values of approximately 70 and 30% respectively for the two models. Accordingly, O(6), O(7) and O(8) were introduced and refined with an occupancy factor of 30%. Maximum and minimum heights in the final Fourier difference map were 0.9 and −0.5

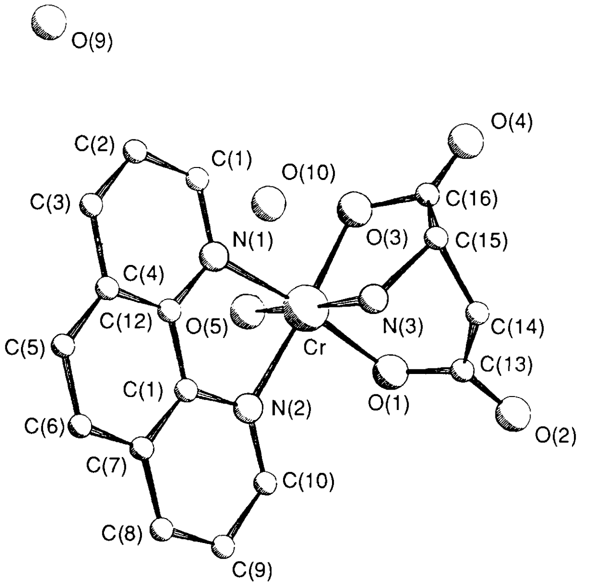

Fig. 1 Molecular structure and atom labelling of [Cr(L-asp)(phen)(H_2O)]NO_3·$2H_2O$ **1**. The disordered nitrate ion has been omitted.

Table 1 Fractional atomic coordinates for complex **1**

Atom	*X/a*	*Y/b*	*Z/c*
N(4)	1.0551(7)	1.1902(7)	0.8124(8)
O(6)	1.0011(10)	1.1257(19)	0.6805(10)
O(7)	1.1707(8)	1.2357(13)	0.8119(14)
O(8)	1.0027(20)	1.2068(23)	0.9299(17)
O(61)	1.0442(22)	1.1118(44)	0.6737(16)
O(71)	1.1489(20)	1.2394(42)	0.8996(27)
O(81)	0.9588(21)	1.2006(44)	0.8695(29)
Cr	0.7281(1)	0.7206(1)	0.6015(1)
O(1)	0.5635(4)	0.6761(5)	0.5224(6)
O(2)	0.4273(6)	0.7327(8)	0.4406(8)
O(3)	0.7192(4)	0.8688(5)	0.7968(5)
O(4)	0.6577(6)	1.0513(7)	0.9148(10)
O(5)	0.6706(4)	0.5672(5)	0.6950(6)
C(13)	0.5299(7)	0.7685(8)	0.4952(9)
C(14)	0.6309(16)	0.9231(10)	0.5289(14)
C(15)	0.7370(14)	1.0017(10)	0.6466(13)
N(3)	0.7790(9)	0.8882(10)	0.5209(12)
C(16)	0.6878(7)	0.9743(8)	0.7970(10)
N(1)	0.9098(4)	0.7585(5)	0.6436(6)
C(1)	0.9837(6)	0.8501(7)	0.7739(9)
C(2)	1.1085(7)	0.8736(9)	0.7813(10)
C(3)	1.1579(6)	0.8031(9)	0.6513(10)
C(4)	1.0803(3)	0.7030(4)	0.5126(4)
C(5)	1.1219(3)	0.6220(4)	0.3798(4)
C(6)	1.0401(3)	0.5222(4)	0.2502(4)
C(7)	0.9166(3)	0.5035(4)	0.2535(4)
C(11)	0.8750(3)	0.5844(4)	0.3863(4)
C(12)	0.9569(3)	0.6842(4)	0.5158(4)
C(8)	0.8273(8)	0.4007(8)	0.1268(9)
C(9)	0.7072(9)	0.3882(8)	0.1390(9)
C(10)	0.6725(7)	0.4754(8)	0.2786(9)
N(2)	0.7548(4)	0.5721(5)	0.3959(6)
O(9)	0.4263(7)	0.0953(10)	−0.1219(10)
O(10)	0.3940(10)	0.3751(12)	0.0165(10)

Table 2 Selected bond angles (°) for complex **1**. E.s.d.s refer to the last significant digit.

Co-ordination			
O(1)–Cr–N(1)	169.6(2)	N(1)–Cr–O(5)	92.5(2)
O(3)–Cr–N(2)	174.8(2)	N(1)–Cr–N(2)	79.8(2)
O(5)–Cr–N(3)	174.7(2)	N(1)–Cr–N(3)	90.2(2)
O(1)–Cr–O(3)	93.6(2)	O(3)–Cr–O(5)	90.8(2)
O(1)–Cr–N(2)	91.2(2)	O(3)–Cr–N(3)	84.3(2)
O(1)–Cr–N(3)	85.2(1)	N(2)–Cr–O(5)	91.1(2)
O(1)–Cr–O(5)	92.9(2)	N(2)–Cr–N(3)	93.9(2)
N(1)–Cr–O(3)	95.2(2)		
Ligands			
C(11)–N(2)–Cr	112.5(4)	O(1)–C(13)–O(2)	121.0(8)
C(12)–N(1)–Cr	112.7(3)	O(1)–C(13)–C(14)	115(1)
C(15)–N(3)–Cr	102(1)	O(2)–C(13)–C(14)	124(1)
C(13)–O(1)–Cr	124.1(5)	O(3)–C(16)–O(4)	121(1)
C(16)–O(3)–Cr	120.0(5)	O(3)–C(16)–C(15)	104(1)
C(14)–C(15)–C(16)	106(1)	O(4)–C(16)–C(15)	132(1)
Nitrate*			
O(6)–N(4)–O(7)	113(2)	O(61)–N(4)–O(71)	124(2)
O(6)–N(4)–O(8)	123(2)	O(61)–N(4)–O(81)	116(2)
O(7)–N(4)–O(8)	123(2)	O(71)–N(4)–O(81)	119(2)

* The oxygen atoms of the nitrate group are statistically distributed over two positions (see text).

Table 3 Selected bond distances (Å) for complex **1**. E.s.d.s refer to the last significant digit.

Co-ordination			
Cr–O(1)	1.944(5)	Cr–N(1)	2.064(5)
Cr–O(3)	1.936(5)	Cr–N(2)	2.067(5)
Cr–O(5)	1.986(5)	Cr–N(3)	2.034(5)
Ligands			
N(1)–C(1)	1.343(9)	C(13)–O(1)	1.28(1)
N(1)–C(12)	1.372(7)	C(13)–O(2)	1.21(1)
N(2)–C(10)	1.322(9)	C(10)–O(3)	1.29(1)
N(2)–C(11)	1.375(6)	C(16)–O(4)	1.22(1)
N(3)–C(15)	1.54(3)	C(13)–C(14)	1.55(2)
C(14)–C(15)	1.48(3)	C(15)–C(16)	1.56(3)
Nitrate			
N(4)–O(6)	1.24(2)	N(4)–O(61)	1.23(2)
N(4)–O(7)	1.27(2)	N(4)–O(71)	1.24(2)
N(4)–O(8)	1.20(2)	N(4)–O(81)	1.25(2)
Possible hydrogen bonds (e.s.d.s < 0.03 Å)			
O(5) ··· O(2$^{\mathrm{I}}$)	2.73	O(7) ··· O(10)	2.90
O(4) ··· O(9)	2.99	O(71) ··· O(10)	2.79
O(5) ··· O(10$^{\mathrm{I}}$)	2.64	O(10) ··· O(10$^{\mathrm{I}}$)	2.98
O(9) ··· O(10)	2.91	N(3) ··· O(61$^{\mathrm{I}}$)	2.67
O(4) ··· O(9$^{\mathrm{I}}$)	2.80	N(3) ··· O(7$^{\mathrm{I}}$)	2.99

Symmetry codes: none, x, y, z; I, $1 - x, 1 - y, 1 - z$.

e $Å^{-3}$. Scattering factors for Cr were from ref. 13, those for O, C and N being internally supplied by the SHELX program.[14] Final atomic parameters are listed in Table 1, bond angles and distances in Tables 2 and 3.

Diffractometric Measurements of Complex 3.—*Crystal data.* $C_{36}H_{28}Cr_2N_6O_{16}$, $M = 904$, triclinic, space group $P\bar{1}$, $a = 19.100(5)$, $b = 12.874(5)$, $c = 7.575(5)$ Å, $\alpha = 86.16(3)$, $\beta = 95.10(3)$, $\gamma = 96.62(3)°$, $U = 1\,840$ $Å^3$, $D_c = 1.63$ g cm^{-3}, $Z = 2$, μ(Mo-Kα) = 7.1 cm^{-1}, $\lambda = 0.710\,69$ Å, maximum crystal size = 0.2 mm.

Cell parameters were calculated from accurate settings of 25 medium-angle reflections on a PW 1 100 Philips diffractometer with Mo-Kα radiation. Intensities were recorded up to $\theta = 25°$ with a scan speed of 2° min^{-1} and the θ–2θ scan. 3065 Reflections with $I > 3\sigma(I)$ over the 6445 reflections were considered to be significantly above the background and used in subsequent calculations. Other details have already been mentioned. A Fourier difference synthesis revealed the presence of four independent water molecules of crystallization. Anisotropic refinement of the co-ordination polyhedrons and isotropic refinement of all non-hydrogen atoms converged at

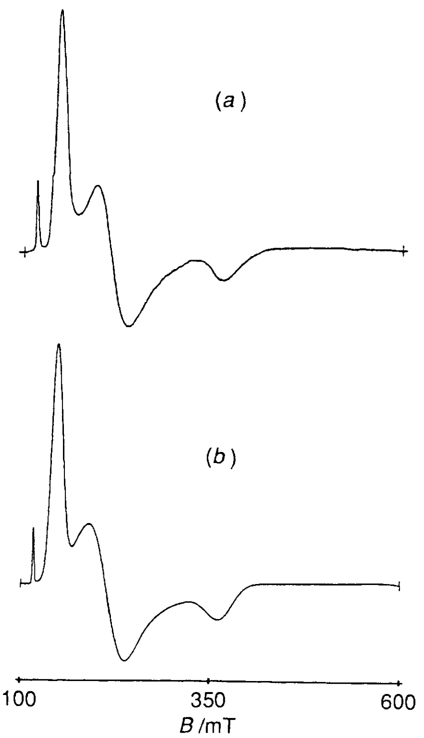

Fig. 2 Experimental (*a*) and simulated (*b*) ESR frozen-solution spectra, at 150 K and X-band frequency ν = 9.42 GHz, of $[Cr(L\text{-}asp)(phen)(H_2O)]^+$

the conventional R of 0.070 when the largest parameter shift was 0.1σ both for coordinates and thermal parameters. Maximum and minimum heights in the final Fourier difference map were 0.7 and −0.7 e Å^{-3}. Atomic scattering factors for Cr were taken from ref. 15 and corrected for anomalous scattering,[16] and those for H atoms from Stewart *et al.*[17] Final fractional parameters are reported in Table 4, bond lengths and angles in Tables 5 and 6.

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

Results and Discussion

Diffractometric and Spectroscopic Results for $[Cr(L\text{-}asp)(phen)(H_2O)]NO_3{\cdot}2H_2O$ **1**.—A labelled diagram of the molecular structure of complex **1** is shown in Fig. 1. The Cr atom is six-co-ordinated in an octahedral environment, the charges of the metal ion being neutralized by the bianionic aspartato ligand and by one nitrate group. Ring constraints and steric hindrance influence the geometry of the molecule, the configuration of the chromium atom being distorted by up to 10.2° from ideal angles. The Cr–N bond distances ranging from 2.06 Å (for phen) to 2.03 Å (for L-asp) are in agreement with the sum of the atomic radii (Cr–N 2.05 Å)[18] and confirm the values found in $[Cr(bipy)_2(H_2O)_2][NO_3]_3$[19] and in $[Cr(bipy)_2(H_3O_2)]I_4{\cdot}2H_2O$ (bipy = 2,2′-bipyridyl).[20] The Cr–O bond distances are of two types: that involving the neutral water oxygen (1.99 Å) is in agreement with the sum of atom radii (Cr–O 2.00 Å) and with values previously found for Cr–O(water) bonds (1.98–2.01 Å),[15,19,21] while those with carboxylato oxygens are significantly shorter (1.94 Å), as expected. Bond lengths in the ligands are normal. In particular, the C–O distances concerning the co-ordinated oxygens of the aspartato anion are of the same order as the longer bond in carboxylic acids and esters, whereas the double-bond character is well localized in the C=O bonds with the external oxygens. As the O • • • O contact distances, reported in Table 3, between the potential hydrogen-bond donors and acceptors largely fall into the range of accepted values, the structure appears to be stabilized by a network of hydrogen bonds between the water molecules and the oxygen atoms of the ligand and of the ionic nitrate.

The visible optical spectrum of an aqueous solution of $[Cr(L\text{-}asp)(phen)(H_2O)]^+$ shows one major band which can be attributed to the first spin-allowed electronic transition ($^4T_{2g} \longleftarrow {}^4A_{2g}$). It has its maximum at λ = 504 nm (ε 84 dm^3 mol^{-1} cm^{-1}) and a pronounced shoulder at λ = 483 nm. The second band ($^4T_{1g} \longleftarrow {}^4A_{2g}$) is clearly split even if it is partially obscured by charge-transfer absorptions and appears at λ = 420 nm (ε 44 dm^3 mol^{-1} cm^{-1}) and λ = 387 nm. No difference is shown between the absorption spectrum in solution and the reflectance spectrum run on the solid powdered compound, suggesting that the solid-state co-ordination is preserved in solution.

The ESR frozen-solution spectrum (Fig. 2) presents a group of well resolved lines in the low-field region (100–400 mT) while broad and ill resolved peaks were hardly detected in the high-field region (400–1500 mT). As a consequence it was possible only to determine the g values and the E/D ratio, D being in the range 0.6–0.8 cm^{-1}.[2,22] The ESR spectrum is described by a practically isotropic g and a rhombic D tensor (see Table 7). The large D value suggests that a ligand field with a strong axial perturbation is created by both ligands. This perturbation may play an important role in determining this unusual splitting in the ligand-field spectrum, which is uncommon for chromium(III) complexes. The non-zero E value is associated with the distortion of the overall co-ordination polyhedron. A comparison with the diffractometric data above shows that the co-ordination polyhedron is far from being symmetrical. The departure from octahedral symmetry due to the bidentate and tridentate nature of the phen and L-asp ligands, respectively, accounts for these results.

Diffractometric and Spectroscopic Results for $[Cr(terpy)(pydca)][Cr(pydca)_2]{\cdot}4H_2O$ **3**.—The molecular structure of the ionic complex **3**, with atomic nomenclature, is shown in Fig. 3, where only the molecules of water of crystallization are omitted for clarity. Both distorted-octahedral chromium ions are six-co-ordinated. Distortions from the idealized geometry around the metal ions are mainly localized to bond angles and appear to be determined by the geometrical constraints of both the tridentate ligands: in both ions, angles [subtended at the metal by adjacent donors from the same chelating group as, for instance, the angle O(1)–Cr(1)–N(4)] are at least 10° less than 90°, all being in the narrow range 77.9–79.6°.

Both the Cr–O (mean 1.98 Å) and the Cr–N bond lengths (mean 2.06 Å) with the peripheral N atoms N(1) and N(3) of the terpy molecule compare well with the sum of the atomic radii[18] (Cr–O 2.00 and Cr–N 2.06 Å). These values also agree with those [Cr–O 1.99 (mean), Cr–N 2.05 Å (mean)] found in $[Cr(bipy)_2(H_2O)_2][NO_3]_3$.[19] On the contrary, the Cr–N distances with the inner pyridine N atoms (mean 1.97 Å) are significantly shorter, irrespective of whether the ligand is the bianionic pydca or the neutral terpy. This feature, which is otherwise contradictory, could be related to the fact that, in both types of ligand, co-ordination of the central N atoms is favoured by the peculiar position they occupy in the tridentate ligands. The crystal and molecular structure of $Rb[Cr(pydca)_2]$ has been reported.[23] The data found in this work for the unit $[Cr(pydca)_2]^-$ compare well with those of the previous report, especially for the short Cr–N bond, which was attributed to the meridional co-ordination achieved by pydca. The Cr–O distances are somehow different in the two crystals. In $Rb[Cr(pydca)_2]$ a mean distance of 2.000 Å was found for both Cr–O(1) and Cr–O(2) bonds, whereas the unit $[Cr(pydca)_2]^-$ in **3** shows Cr–O lengths ranging from 1.975(7) to 1.998(7) Å.

The crystal and molecular structure of $[Cr(terpy)_2][ClO_4]_3{\cdot}H_2O$ has been reported[24] and the co-ordination polyhedron shows a mean Cr–N distance of 2.03 Å. On the contrary in the ternary complex $[Cr(terpy)(pydca)]^+$ the short distance Cr–

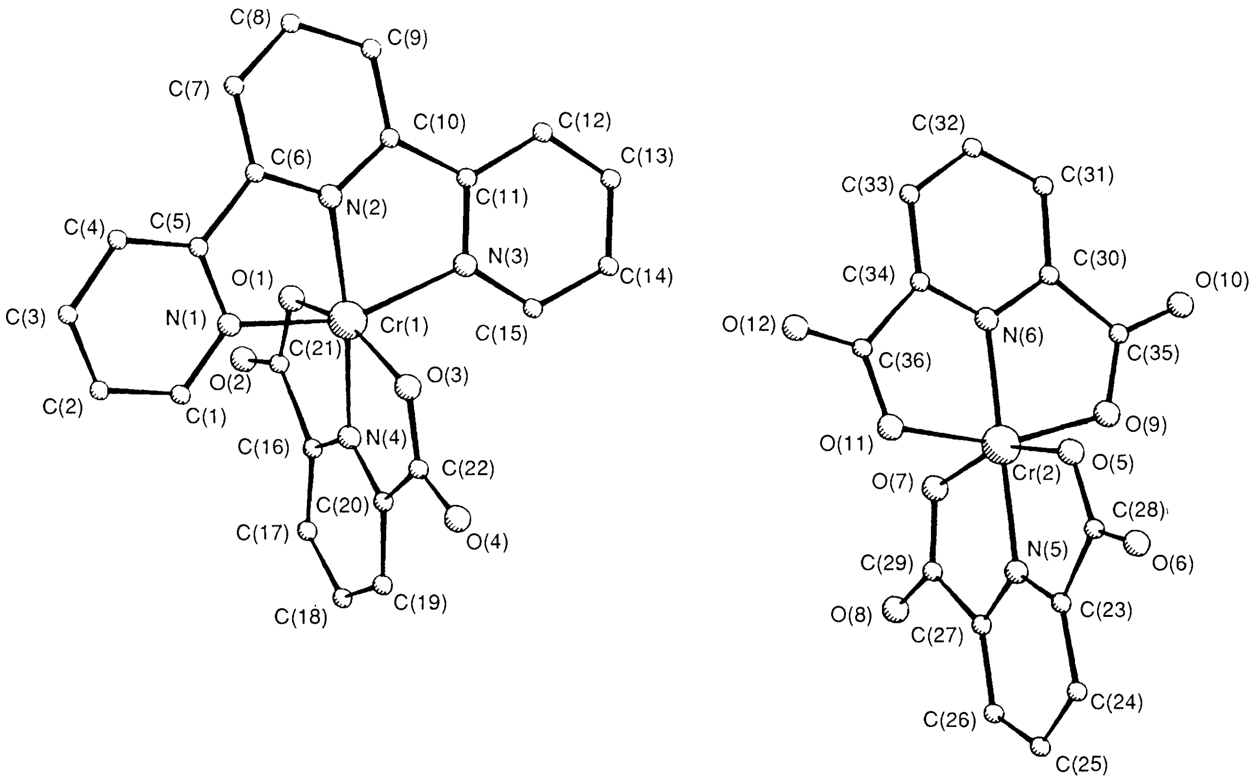

Fig. 3 Perspective view and atomic numbering scheme of the two ionic units of $[Cr(terpy)(pydca)][Cr(pydca)_2]\cdot 4H_2O$ **3**; molecules of water of crystallization have been omitted for clarity

Table 4 Fractional atomic coordinates for complex **3**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
The cation $[Cr(terpy)(pydca)]^+$			
Cr(1)	0.3636(1)	0.8144(1)	0.8376(2)
O(1)	0.3187(3)	0.8338(4)	0.5973(8)
O(2)	0.2796(5)	0.7538(6)	0.3512(12)
O(3)	0.4115(3)	0.7399(5)	1.0441(8)
O(4)	0.4492(5)	0.5884(6)	1.1478(11)
N(1)	0.2675(4)	0.7949(5)	0.9438(9)
N(2)	0.3507(4)	0.9597(5)	0.8878(10)
N(3)	0.4589(4)	0.8951(6)	0.7722(10)
N(4)	0.3639(4)	0.6731(5)	0.7513(10)
C(1)	0.2281(5)	0.7029(8)	0.9677(14)
C(2)	0.1626(5)	0.6875(8)	1.0306(13)
C(3)	0.1370(6)	0.7868(8)	1.0731(14)
C(4)	0.1782(5)	0.8821(8)	1.0521(13)
C(5)	0.2434(5)	0.8826(7)	0.9836(12)
C(6)	0.2898(5)	0.9796(7)	0.9442(12)
C(7)	0.2734(6)	1.0796(8)	0.9538(14)
C(8)	0.3213(6)	1.1617(9)	0.8973(15)
C(9)	0.3843(6)	1.1409(8)	0.8383(14)
C(10)	0.3987(5)	1.0381(7)	0.8330(13)
C(11)	0.4612(5)	0.9993(7)	0.7764(13)
C(12)	0.5224(6)	1.0631(8)	0.7305(14)
C(13)	0.5778(6)	1.0151(9)	0.6860(15)
C(14)	0.5771(6)	0.9114(9)	0.6856(15)
C(15)	0.5129(6)	0.8499(8)	0.7303(14)
C(16)	0.3339(5)	0.6549(7)	0.5883(13)
C(17)	0.3293(6)	0.5568(8)	0.5290(15)
C(18)	0.3573(6)	0.4902(9)	0.6358(16)
C(19)	0.3892(5)	0.4998(8)	0.8054(14)
C(20)	0.3903(5)	0.5993(7)	0.8585(13)
C(21)	0.3084(5)	0.7528(8)	0.4992(14)
C(22)	0.4202(5)	0.6428(8)	1.0333(14)
The anion $[Cr(pydca)_2]^-$			
Cr(2)	0.8891(1)	0.7443(1)	0.4650(2)
O(5)	0.9446(3)	0.7439(5)	0.6989(9)
O(6)	0.9962(4)	0.6429(6)	0.9114(10)
O(7)	0.8355(4)	0.6848(5)	0.2493(9)
O(8)	0.8025(5)	0.5353(6)	0.1143(11)
O(9)	0.9742(3)	0.7936(5)	0.3384(9)
O(10)	1.0343(4)	0.9354(6)	0.2142(10)
O(11)	0.8003(3)	0.7521(6)	0.5765(10)
O(12)	0.7257(4)	0.8624(8)	0.6437(13)
N(5)	0.8998(4)	0.5952(5)	0.5131(10)
N(6)	0.8790(4)	0.8944(5)	0.4283(9)
C(23)	0.9364(5)	0.5636(7)	0.6596(12)
C(24)	0.9474(5)	0.4604(7)	0.6930(13)
C(25)	0.9188(5)	0.3899(8)	0.5692(13)
C(26)	0.8815(5)	0.4250(7)	0.4172(13)
C(27)	0.8720(5)	0.5284(7)	0.3898(13)
C(28)	0.9625(5)	0.6554(7)	0.7706(13)
C(29)	0.8334(6)	0.5853(8)	0.2361(14)
C(30)	0.9292(5)	0.9558(7)	0.3450(12)
C(31)	0.9244(5)	1.0609(8)	0.3219(13)
C(32)	0.8687(6)	1.0995(8)	0.3892(14)
C(33)	0.8181(6)	1.0365(8)	0.4778(14)
C(34)	0.8257(5)	0.9319(7)	0.4908(13)
C(35)	0.9835(5)	0.8930(7)	0.2933(13)
C(36)	0.7783(6)	0.8437(9)	0.5788(16)
The water oxygen atoms			
O(13)	0.4866(6)	0.3051(8)	0.5659(14)
O(14)	0.8865(5)	0.8844(7)	0.9442(12)
O(15)	0.7249(5)	0.6066(8)	0.8078(13)
O(16)	0.4189(5)	0.3745(7)	0.2402(13)

Table 5 Bond lengths (Å) for complex **3**

$[\mathrm{Cr(terpy)(pydca)}]^+$

Co-ordination

Cr(1)–O(1)	1.955(6)	Cr(1)–N(2)	1.981(7)
Cr(1)–O(3)	1.988(6)	Cr(1)–N(3)	2.073(7)
Cr(1)–N(1)	2.052(7)	Cr(1)–N(4)	1.974(7)

Ligands

C(1)–N(1)	1.34(1)	C(7)–C(8)	1.39(2)
C(1)–C(2)	1.37(2)	C(8)–C(9)	1.38(2)
C(2)–C(3)	1.37(2)	C(9)–C(10)	1.39(1)
C(3)–C(4)	1.39(1)	C(10)–C(11)	1.46(1)
C(4)–C(5)	1.39(1)	C(10)–N(2)	1.35(1)
C(5)–N(1)	1.33(1)	C(11)–N(3)	1.34(1)
C(5)–C(6)	1.48(1)	C(11)–C(12)	1.40(1)
C(6)–N(2)	1.33(1)	C(12)–C(13)	1.36(2)
C(6)–C(7)	1.37(1)		
C(13)–C(14)	1.33(2)	C(19)–C(20)	1.37(1)
C(14)–C(15)	1.40(1)	C(20)–C(22)	1.51(1)
C(15)–N(3)	1.31(1)	C(20)–N(4)	1.32(1)
C(16)–C(21)	1.50(1)	C(21)–O(1)	1.31(1)
C(16)–N(4)	1.34(1)	C(21)–O(2)	1.20(1)
C(16)–C(17)	1.36(2)	C(22)–O(3)	1.29(1)
C(17)–C(18)	1.36(2)	C(22)–O(4)	1.21(1)
C(18)–C(19)	1.40(2)		

$[\mathrm{Cr(pydca)_2}]^-$

Co-ordination

Cr(2)–O(5)	1.983(7)	Cr(2)–O(11)	1.975(7)
Cr(2)–O(7)	1.998(7)	Cr(2)–N(5)	1.961(7)
Cr(2)–O(9)	1.981(7)	Cr(2)–N(6)	1.963(7)

Ligands

C(23)–C(28)	1.51(1)	C(30)–C(35)	1.48(1)
C(23)–N(5)	1.32(1)	C(30)–N(6)	1.34(1)
C(23)–C(24)	1.37(1)	C(30)–C(31)	1.36(1)
C(24)–C(25)	1.38(1)	C(31)–C(32)	1.38(2)
C(25)–C(26)	1.38(1)	C(32)–C(33)	1.38(2)
C(26)–C(27)	1.36(1)	C(33)–C(34)	1.37(1)
C(27)–C(29)	1.52(1)	C(34)–C(36)	1.52(2)
C(27)–N(5)	1.34(1)	C(34)–N(6)	1.31(1)
C(28)–O(5)	1.30(1)	C(35)–O(9)	1.30(1)
C(28)–O(6)	1.21(1)	C(35)–O(10)	1.24(1)
C(29)–O(7)	1.29(1)	C(36)–O(11)	1.30(1)
C(29)–O(8)	1.23(1)	C(36)–O(12)	1.21(2)

Possible hydrogen bonds (e.s.d.s < 0.03 Å)

O(16) · · · O(15$^{\mathrm{I}}$)	2.77	O(8) · · · O(15)	2.84
O(4) · · · O(13$^{\mathrm{I}}$)	2.80	O(11) · · · O(15)	2.86
O(4) · · · O(13)	2.81	O(16) · · · O(13)	2.88
O(3) · · · O(16)	2.81	O(10) · · · O(14$^{\mathrm{I}}$)	2.88

Symmetry code: I $-x, -y, -z$.

Table 6 Bond angles (°) for complex **3**

$[\mathrm{Cr(terpy)(pydca)}]^+$		$[\mathrm{Cr(pydca)_2}]^-$	
Co-ordination			
O(1)–Cr(1)–O(3)	157.5(2)	O(5)–Cr(2)–O(11)	90.5(3)
N(1)–Cr(1)–N(3)	155.7(2)	O(7)–Cr(2)–O(9)	93.4(3)
N(2)–Cr(1)–N(4)	169.8(3)	N(5)–Cr(2)–N(6)	177.4(2)
O(1)–Cr(1)–N(1)	91.7(2)	O(5)–Cr(2)–O(7)	157.5(2)
O(1)–Cr(1)–N(2)	90.8(2)	O(5)–Cr(2)–O(9)	92.1(2)
O(1)–Cr(1)–N(3)	93.2(3)	O(5)–Cr(2)–N(5)	77.9(3)
O(1)–Cr(1)–N(4)	79.4(2)	O(5)–Cr(2)–N(6)	99.7(3)
O(3)–Cr(1)–N(1)	92.4(3)	O(11)–Cr(2)–O(7)	92.2(2)
O(3)–Cr(1)–N(2)	111.1(2)	O(11)–Cr(2)–O(9)	158.4(3)
O(3)–Cr(1)–N(3)	91.8(2)	O(11)–Cr(2)–N(5)	99.8(3)
O(3)–Cr(1)–N(4)	78.9(2)	O(11)–Cr(2)–N(6)	79.1(2)
N(1)–Cr(1)–N(2)	77.9(3)	O(7)–Cr(2)–N(5)	79.6(2)
N(1)–Cr(1)–N(4)	99.3(3)	O(7)–Cr(2)–N(6)	102.8(3)
N(3)–Cr(1)–N(2)	78.3(3)	O(9)–Cr(2)–N(5)	101.7(3)
N(3)–Cr(1)–N(4)	104.9(2)	O(9)–Cr(2)–N(6)	79.3(3)
Ligands			
Cr(1)–O(1)–C(21)	117.7(6)	Cr(2)–O(5)–C(28)	118.5(6)
Cr(1)–O(3)–C(22)	118.7(6)	Cr(2)–O(7)–C(29)	116.8(6)
Cr(1)–N(4)–C(16)	117.9(6)	Cr(2)–N(5)–C(23)	120.0(6)
Cr(1)–N(4)–C(20)	119.3(6)	Cr(2)–N(5)–C(27)	118.0(6)
Cr(1)–N(1)–C(5)	115.3(6)	Cr(2)–O(9)–C(35)	116.4(6)
Cr(1)–N(3)–C(11)	113.9(6)	Cr(2)–O(11)–C(36)	117.5(7)
Cr(1)–N(2)–C(6)	119.4(6)	Cr(2)–N(6)–C(30)	118.0(6)
Cr(1)–N(2)–C(10)	118.3(7)	Cr(2)–N(6)–C(34)	119.5(6)
O(1)–C(21)–O(2)	124.2(9)	O(5)–C(28)–O(6)	126.1(9)
O(1)–C(21)–C(16)	114.2(8)	O(5)–C(28)–C(23)	113.2(9)
O(2)–C(21)–C(16)	121.6(9)	O(6)–C(28)–C(23)	120.7(8)
C(21)–C(16)–N(4)	110.6(8)	C(28)–C(23)–N(5)	110.3(8)
C(21)–C(16)–C(17)	130.0(9)	C(23)–N(5)–C(27)	122.0(8)
N(4)–C(16)–C(17)	119.4(9)	N(5)–C(27)–C(29)	110.9(8)
O(3)–C(22)–O(4)	125.7(10)	O(7)–C(29)–O(8)	125.8(10)
O(3)–C(22)–C(20)	113.4(8)	O(7)–C(29)–C(27)	114.7(9)
O(4)–C(22)–C(20)	120.9(9)	O(8)–C(29)–C(27)	119.5(9)
C(22)–C(20)–N(4)	110.7(8)	C(30)–N(6)–C(34)	122.4(8)
C(16)–N(4)–C(20)	122.7(8)	O(9)–C(35)–O(10)	123.8(10)
N(1)–C(5)–C(6)	115.0(8)	O(9)–C(35)–C(30)	115.7(8)
C(5)–C(6)–N(2)	111.9(8)	O(10)–C(35)–C(30)	120.5(9)
N(2)–C(10)–C(11)	112.3(8)	O(11)–C(36)–O(12)	125.9(11)
C(10)–C(11)–N(3)	116.0(8)	O(12)–C(36)–C(34)	120.2(11)
		O(11)–C(36)–C(34)	113.9(10)

N(pydca) 1.974 Å imposed by the pydca dianion causes shortening of the bond distance between the chromium atom and the central nitrogen of the terpy molecule [Cr–N(terpy) 1.981 Å]. The length of the C–N bonds (1.31–1.35, mean 1.33 Å) closely agrees with 1.340(1) Å found in free pyridine.[25] The shorter bonds of the carboxylato groups (1.20–1.24, mean 1.22 Å) and the longer bonds (1.29–1.31, mean 1.30 Å) are normal and compare well with the values reported by Sutton.[26] As shown in Table 4 the structure is strongly stabilized by a complicated network of hydrogen bonds between the water molecules of crystallization and the external oxygens of the complex ions.

Clearly, this ionic crystal breaks up in solution, leaving the complexes $[\mathrm{Cr(terpy)(pydca)}]^+$ and $[\mathrm{Cr(pydca)_2}]^-$ present as ionic species. An ESR spectrum run on a frozen solution of complex **3** showed exactly the same transitions as those due to the single units when they are considered separately. A chromium(III) 'dimer' species would have exhibited a completely different ESR spectrum, in which the interactions between chromium(III) pairs play a fundamental role. Hence, the spectroscopic study was carried out on the separate complex ions which were obtained independently, in order to avoid overlap between the visible or ESR spectra due to the single units. We also considered the complex $[\mathrm{Cr(terpy)_2}][\mathrm{ClO_4}]_3\cdot\mathrm{H_2O}$ to compare the spectroscopic properties of $[\mathrm{Cr(terpy)(pydca)}]^+$ with those of the parent compounds $[\mathrm{Cr(terpy)_2}]^{3+}$ and $[\mathrm{Cr(pydca)_2}]^-$. The optical data pertaining to the latter have already been reported.[27] Our data confirm what was previously ascertained: absorption bands at λ = 553 and 420 nm (ε 234 and 52 dm^3 mol^{-1} cm^{-1}). The former compound exhibits an optical spectrum complicated by the overlap of vibrational components; our UV–VIS data are in agreement with those previously reported.[28,29] The mixed-ligand complex $[\mathrm{Cr(terpy)(pydca)}]^+$ shows the first spin-allowed band at λ = 508 nm (ε 178 dm^3 mol^{-1} cm^{-1}) and three vibrational components ($\lambda_{\max}$ 458, 428 and 401 nm) centred at λ = 428 nm (ε 705 dm^3 mol^{-1} cm^{-1}); this vibrational structure is also shown by analogous complexes containing bipy and terpy.[29]

The ESR frozen-solution spectra of $[\mathrm{Cr(terpy)_2}]^{3+}$ and $[\mathrm{Cr(terpy)(pydca)}]^+$ were characterized by peaks of large linewidth. Nevertheless, the resolution of some spectral features allowed the estimation of the spin parameters even if imprecisely. In the case of the former complex the fit of the experimental spectrum was poor and did not improve even

Table 7 Spin-Hamiltonian parameters for the chromium(III) complexes obtained by simulation of their ESR spectra[a]

Complex	T/K	g_z	g_x	g_y	D[b]	E[b]	Zero-field splitting[b]	E/D
Na[(Co,Cr)(pydca)$_2$]·2H$_2$O	298	1.975(3)	1.980(3)	1.980(3)	0.409 0(5)	0.0155(2)	0.820	
	150	1.975(3)	1.988(3)	1.988(3)	0.406 0(5)	0.0095(2)	0.813	
Rb[(Co,Cr)(pydca)$_2$]	298	1.966(3)	1.966(3)	1.966(3)	0.401(1)	0.0	0.802	
	150	1.965(3)	1.968(3)	1.968(3)	0.406(1)	0.0	0.812	
[Co(terpy)(pydca)][(Co,Cr)(pydca)$_2$]·2H$_2$O	150	1.976(3)	1.985(3)	1.985(3)	0.503(1)	0.0392(2)	1.015	
[(Co,Cr)(terpy)(pydca)]ClO$_4$	298	1.975(3)	1.990(3)	1.990(3)	0.261(1)	0.0060(2)	0.522	
	150	1.970(3)	1.980(3)	1.980(3)	0.280(1)	0.0085(2)	0.561	
[(Co,Cr)(terpy)(pydca)][Co(pydca)$_2$]·2H$_2$O	150	1.984(3)	1.992(3)	1.992(3)	0.359(1)	0.0800(2)	0.770	
[(Co,Cr)(terpy)$_2$][ClO$_4$]$_3$	298	1.950(5)	1.950(5)	1.950(5)	0.169(1)	0.025(1)	0.349	
	150	1.950(5)	1.950(5)	1.950(5)	0.154(2)	0.020(3)	0.300	
[Cr(pydca)$_2$]$^-$	150	1.965(5)	1.940(5)	1.940(5)	0.420(2)	0.012(1)	0.841	
[Cr(terpy)(pydca)]$^+$	150	1.92(2)	1.95(2)	1.95(2)	0.26(3)	*c*	0.52–0.60	0.096
[Cr(terpy)$_2$]$^{3+}$	150	1.95(2)	1.95(2)	1.95(2)	0.16(3)	*c*	0.28–0.34	<0.2
[Cr(L-asp)(phen)(H$_2$O)]$^+$	150	1.950(5)	1.950(5)	1.950(5)	0.6–0.8	*c*	1.2–1.6	0.128

[a] The errors in parentheses are given as the least parameter variation that causes an appreciable change in the peak positions of the simulated spectrum. [b] The units of D, E and zero-field splitting are cm^{-1}. [c] The value of E is determined by the ratio E/D.

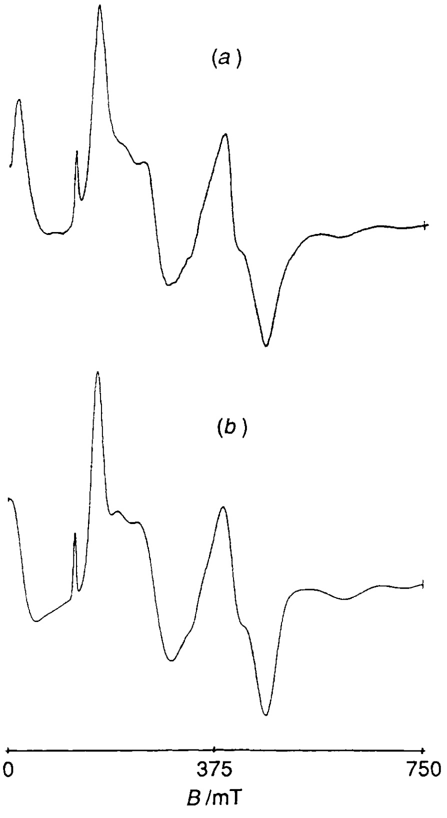

Fig. 4 Experimental (*a*) and simulated (*b*) room-temperature ESR powder spectra, at X-band frequency ν = 9.46 GHz, of [Cr(terpy)$_2$]$^{3+}$ doped in [Co(terpy)$_2$]$^{3+}$

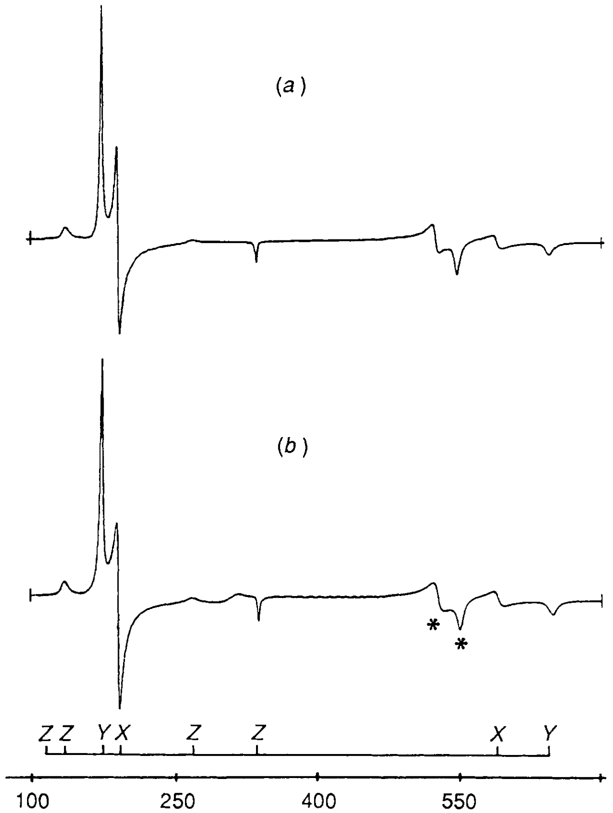

Fig. 5 Experimental (*a*) and simulated (*b*) ESR powder spectra, at 150 K and X-band frequency ν = 9.46 GHz, of [Cr(terpy)(pydca)]$^+$ doped in [Co(terpy)(pydca)]ClO$_4$. The peaks marked with an asterisk in the simulated spectrum are 'extra peaks' due to a looping transition while the spurious peak at nearly 320 mT and the rippling between 350 and 500 mT are due to computer noise.

when introducing non-coincidence between the g and D tensor directions in the xy plane. Experimental and simulated ESR powder spectra for the species [Cr(terpy)$_2$]$^{3+}$ and [Cr(terpy)(pydca)]$^+$ doped in the analogous cobalt(III) complexes are reported in Figs. 4 and 5. Fig. 6(*a*) shows the ESR frozen-solution spectrum of the [Cr(pydca)$_2$]$^-$ complex ion. Fig. 6(*b*) and (*c*) show the room-temperature ESR powder spectra of the latter complex doped in Na[Co(pydca)$_2$]·2H$_2$O and Rb[Co(pydca)$_2$] respectively. All the spin-Hamiltonian parameters are collected in Table 7. This ion [Cr(pydca)$_2$]$^-$ shows a D value higher than those of [Cr(terpy)$_2$]$^{3+}$ and [Cr(terpy)(pydca)]$^+$. This value can be interpreted in terms of the net tetragonal distortion (compression) along the N–Cr–N axis as shown by the structural studies. The ESR spectra of this complex ion, doped in Na[Co(pydca)$_2$]·2H$_2$O as well as in frozen solution, show a slightly rhombic D tensor. Unexpectedly, the same complex ion diluted in Rb[Co(pydca)$_2$] has a perfectly axial spectrum. In general, the E value may derive either from an intrinsic molecular anisotropy or lattice effects in powders,[30] whereas solvation may be important for the complex ions in solution. In this case, the zero E value can be explained as arising from a lattice contribution to the molecular structure of [Cr(pydca)$_2$]$^-$. The chromium co-ordination polyhedron in the case of Rb[Cr(pydca)$_2$] is more symmetrical than that found for the same ionic unit in complex **3**, as already stated when comparing the two structural results for [Cr(pydca)$_2$]$^-$ and

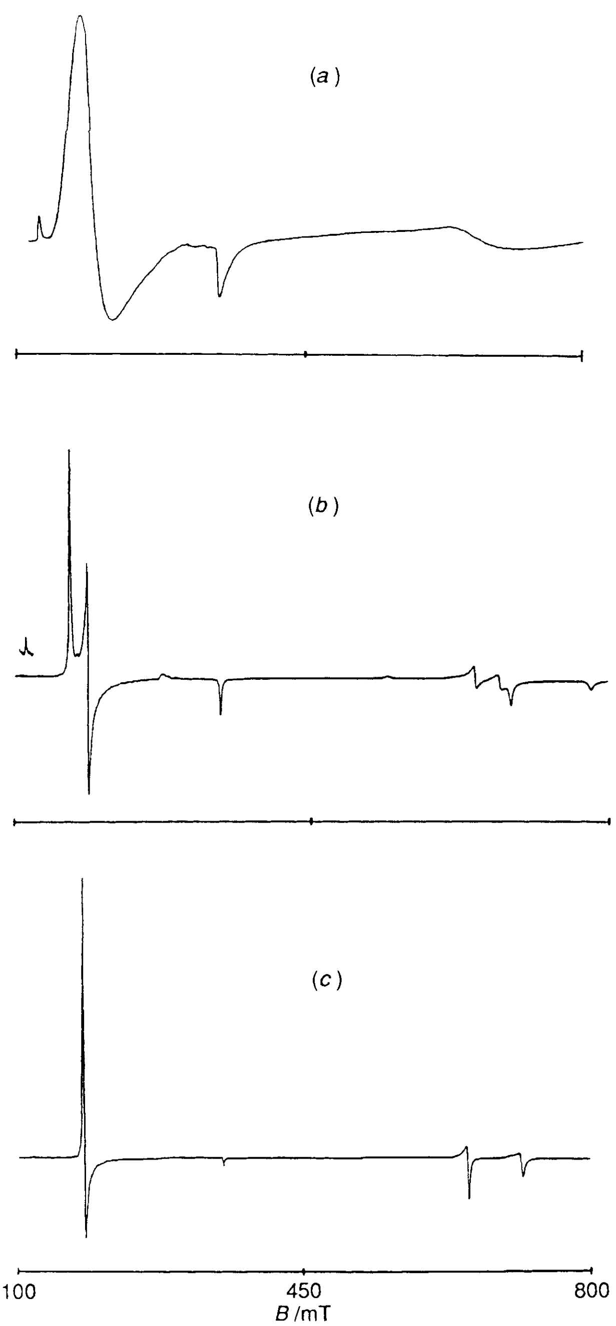

Fig. 6 Experimental ESR spectra of (*a*) a frozen solution of $[Cr(pydca)_2]^-$ (at 140 K and X-band frequency ν = 9.42 GHz), (*b*) $[Cr(pydca)_2]^-$ diluted in $Na[Co(pydca)_2]\cdot 2H_2O$ (at room temperature and X-band frequency ν = 9.79 GHz) and (*c*) $[Cr(pydca)_2]^-$ diluted in $Rb[Co(pydca)_2]$ (at room temperature and X-band frequency ν = 9.79 GHz)

$Rb[Cr(pydca)_2]$. The asymmetry present in the $[Cr(pydca)_2]^-$ unit of complex **3** should be present also in $Na[Cr(pydca)_2]\cdot 2H_2O$ as well as in the complex anion present in frozen solution, as suggested by the non-zero E value. Moreover, the analysis of ESR spectra (Fig. 7) recorded for the cobalt(III) complex $[Co(terpy)(pydca)][Co(pydca)_2]\cdot 2H_2O$ **8**, alternatively doped with $[Cr(pydca)_2]^-$ and $[Cr(terpy)(pydca)]^+$, yielded higher D and E values. As shown in Table 7, these magnetic parameters, which are only slightly temperature dependent, show higher E/D ratios, surely due to the influence of the peculiar crystal lattice on the molecular structure.

In the case of the mixed-ligand complex doped in $[Co(terpy)(pydca)]ClO_4$ it is interesting that the D value lies approximately between those found for the parent compounds doped in the cobalt(III) ones. This trend was also found from the analysis of the ESR frozen-solution spectra. The D values found for these ions in frozen solutions and powders are similar, while the E parameter seems to be more sensitive to the environment. The difficulty of simulating the ESR spectrum of the frozen solution containing $[Cr(terpy)_2]^{3+}$ is probably due to the distorted meridional geometry, which leaves this ion exposed to a greater solvation as suggested by Wickramasinghe *et al.*[24] Solvation could cause perturbation of the chromium(III) core, giving rise to a statistical distribution of D and E values.

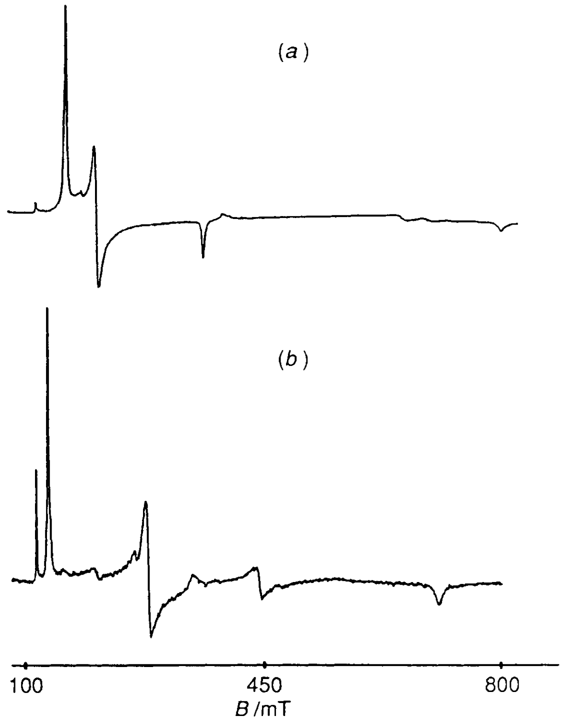

Fig. 7 X-Band (ν = 9.459 GHz) powder ESR spectra at 150 K of (*a*) $[Cr(pydca)_2]^-$ doped in $[Co(terpy)(pydca)][Co(pydca)_2]\cdot 2H_2O$ and (*b*) $[Cr(terpy)(pydca)]^+$ doped in the same cobalt(III) complex

Conclusion

The features of the experimental ESR spectra due to chromium(III) complexes are mainly determined by the D tensor of the Hamiltonian (1) which results from spin–orbit interaction. It has been pointed out that the dipole–dipole interaction may be a contributory factor in the case of distorted complex ions.[31] The D and E values are determined essentially by the nature of the ligands and by the perturbation of the ligand field around the metal ion. Many attempts have been made in the past to find a correlation between the zero-field splitting and the ligand-field strength. Hempel *et al.*[22] found a simple correlation in a series of *trans* disubstituted bis(ethylenediamine)chromium(III) complexes, in which the absolute value of the E parameter is proportional to the ligand strength of the *trans* ligand, the value of D being practically constant. A similar pattern was found by Andriessen[32] in a series of *trans* disubstituted bis(oxalato)-chromate(III) complexes, which showed very high D and E values; despite not knowing the reason for the magnitude of the zero-field splitting, these authors suggested that one important factor could be the deviation from octahedral symmetry. Also Pedersen and Toftlund[33] working on *trans* tetramine- and tetrapyridine-chromium(III) complexes found that the experimental value of D correlates with the tetragonal ligand field caused by the *trans* ligand. Andriessen and Groenewege[34] attributed a correlation between the magnitude of D and the ligand-field strength of the *cis* ligand for a series of *cis* bis(2,2′-bipyridyl)-, bis(1,10-phenanthroline)- and bis(oxalato)-chromium(III) complexes. When considering lower-symmetry chromium(III) complexes, it should be noted that it is not easy to find any correlation because the parameters influencing the zero-field splitting are too numerous. This implies that each such complex has its own D tensor, which is essentially a function of the relative ligand strengths, π-bonding ligand capabilities and co-ordination polyhedron distortions.[35] The example of the mixed-ligand complex $[Cr(terpy)(pydca)]^+$ is extremely instructive when compared with the bis parent compounds $[Cr(pydca)_2]^-$ and $[Cr(terpy)_2]^{3+}$: in a series of structurally correlated chromium(III) complexes the D value of the mixed-ligand complex falls between those observed for the bis parent compounds. No correlation at all can be found for the other complex, $[Cr(\text{L-asp})(phen)(H_2O)]^+$, which must be considered a separate case. The diffractometric data were extremely useful in characterizing these complexes and were a good guide in interpreting their spectroscopic properties. We would stress that, in the absence of crystal structure data, the correct interpretation of ESR spectra could be a valuable tool in inferring stereochemical features of chromium(III) complexes. Since the observed zero-field splitting is the resultant of a number of contributions it is impossible to deduce the type of donor atoms for an unknown complex directly from the D and E values. Hence, the ESR spectra of chromium(III) complexes only provide information on the symmetry of the co-ordination polyhedron. To know something about the kind of chromophore, the spectra of complexes under investigation should be compared with those of model complexes, the ESR spectra of which are clearly distinctive.

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