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Synthesis, structural characterisation and nuclear magnetic resonance studies of cobalt complexes of pyridonate ligands†

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A series of heteroleptic cobalt(II) complexes of diimine and pyridonate ligands have been synthesized from cobalt(II) acetate, with the general stoichiometric formula $[Co(xhp)_2L]$ [xhp = 6-methyl- (mhp), 6-chloro- (chp), 6-bromo- (bhp) or 6-fluoro-2-pyridonate (fhp); L = 2,2′-bipyridyl (bipy), 4,4′-dimethyl-2,2′-bipyridyl (dmbipy), 1,10-phenanthroline (phen) or di-2-pyridylamine (Hdpa)]. Four have been characterised by X-ray crystallography. The compounds $[Co(mhp)_2(phen)]$, $[Co(chp)_2(Hdpa)]\cdot H_2O$ and $[Co(bhp)_2(dmbipy)]$ crystallise as mononuclear species containing six-co-ordinate cobalt sites. The co-ordination geometry of the metal is distorted due to the small bite angle of the chelating xhp ligands. The fourth complex, $[\{Co(\mu\text{-}fhp)(fhp)(dmbipy)\}_2]$, crystallises as a dinuclear unit with the cobalt atoms bridged by the exocyclic O atom of one fhp ligand. The Co ⋯ Co distance is 3.208(6) Å. A fifth complex, $[\{Co(\mu\text{-}bhp)(O_2CMe)(dmbipy)\}_2]$, has been characterised in which two cobalt atoms are bridged by the O atom from a bhp ligand, giving a Co ⋯ Co separation of 3.158(4) Å. The NMR studies of the complexes $[Co(xhp)_2(dmbipy)]$ revealed large paramagnetic shifts, especially for the 6,6′-protons of the dmbipy unit. The magnitude of the shift varies depending on the pyridonate ligand used, with the largest shifts found for fhp and the smallest for mhp. This shift correlates with the basicity of the N-donor atom of the xhp ligands and hence with the co-ordinative ability of the pyridonate ligands. The synthesis of 6-fluoro-2-pyridone (Hfhp) is reported for the first time.

Derivatives of 2-pyridone have been extensively used to bridge second- and third-row d-block metals,[1] but their chemistry with the first transition series is rather limited, with the exception of complexes of chromium[2–4] and copper.[5–10] We have been extending the number of complexes known with first-row transition metals and have reported some results for both nickel[11,12] and iron.[13,14] Earlier work by Clegg *et al.*[15] described some cobalt chemistry, including a fascinating dodecanuclear species $[Co_{12}(OH)_6(O_2CMe)_6(mhp)_{12}]$ (mhp = 6-methyl-2-pyridonate), but other than for this species no crystallographic results were reported. Here we report a series of heteroleptic cobalt complexes of pyridonate and diimine ligands and an interesting trend in their NMR spectra which appears to be related to the co-ordinative ability of the pyridonate groups.

Experimental

Cobalt salts, diimines, 2,6-dibromo- and 2,6-difluoro-pyridine and the pyridone derivatives Hmhp and Hchp (6-chloro-2-pyridone) were obtained from Aldrich. 6-Bromo-2-pyridone (Hbhp) and $[^2H_8]$2,2′-bipyridine were synthesised by published procedures.[16,17] Solvents were dried by standard procedures prior to use. Analytical data and yields for 6-fluoro-2-pyridone (Hfhp) and compounds **1**–**9** are given in Table 1.

Proton ($CDCl_3$), ^2H ($CHCl_3$), ^{19}F ($CDCl_3$) and ^{13}C NMR spectra in $CDCl_3$, referenced to $SiMe_4$, Cl_2 or $CFCl_3$, were recorded on a Bruker AM-360 MHz spectrometer. The magnetic moment of complex **4** in solution was calculated using the Evans method[18,19] in $CDCl_3$ containing 1% $CHCl_3$. Mass spectra were obtained by fast-atom bombardment of samples in a 3-nitrobenzyl alcohol matrix on a Kratos MS50 spectrometer, infrared spectra on a Perkin-Elmer Paragon 1000 FT-IR spectrometer as Nujol mulls. Analytical data were obtained on a Perkin-Elmer 2400 Elemental Analyser by the University of Edinburgh Microanalytical Service.

Preparation of compounds

6-Fluoro-2-pyridone. The synthesis was based on that reported for Hbhp.[16] Sodium metal (1 g) was dissolved in Bu^tOH (100 cm^3) with stirring. When all the sodium had dissolved 2,6-difluoropyridine (2 cm^3, 22 mmol) was added and the solution held at reflux for 8 h. The solvent was then removed under reduced pressure and ice-cold water (100 cm^3) was added. The solution was made slightly acidic using 3 mol dm^{-3} HCl. The product was then extracted from the aqueous solution using chloroform (2 × 100 cm^3 portions). The chloroform was then removed under reduced pressure, leaving a white solid. This was suitable for most purposes but can be purified by recrystallisation from methanol, or by sublimation under reduced pressure. IR: 1640s, 1597s, 1574s, 1494s, 1346s, 1242s, 1144m, 1070m, 1018s, 996s, 864w, 824w, 789s, 744s, 668w, 660w and 585w cm^{-1}. NMR: ^1H, δ 11.68 (s, 1 H), 6.45 (d, 1 H), 6.63 (d, 1 H) and 7.71 (q, 1 H); ^{13}C-$\{^1H\}$, δ 99.06, 107.08, 144.21, 159.45 and 163.36; ^{19}F-$\{^1H\}$, δ −75.71.

$[Co(mhp)_2(bipy)]$ 1. Under an atmosphere of nitrogen, anhydrous cobalt(II) acetate (0.35 g, 2 mmol) was mixed with Hmhp (0.55 g, 4.2 mmol) and the mixture heated to 160 °C for 15 min. During this time the mixture became purple. Excess of Hmhp and acetic acid formed during the reaction were then removed by heating under reduced pressure. The residual dark solid was dissolved in dichloromethane (20 cm^3) and the solution filtered. Solid 2,2′-bipyridyl (bipy) (0.31 g, 2 mmol) was slowly added while the solution was stirred. Over 3 h the solution changed from purple to orange. It was filtered and the solvent volume reduced to 2 cm^3. The product was isolated by diffusion of diethyl ether vapour into this solution. FAB mass spectrum (significant peaks, possible assignments): *m/z* 323 [Co(mhp)(bipy)], 215 [Co(bipy)] and 167 [Co(bipy)].

The following complexes were synthesized in a similar manner.

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† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

[Co(mhp)$_2$(dmbipy)] 2. With 4,4′-dimethyl-2-2′-bipyridyl (dmbipy) in place of bipy. FAB mass spectrum: *m*/*z* 351 [Co(mhp)(dmbipy)], 243 [Co(dmbipy)] and 167 [Co(mhp)].

[Co(mhp)$_2$(phen)] 3. With 1,10-phenanthroline (phen) in place of bipy. FAB mass spectrum: *m*/*z* 455 [Co(mhp)$_2$(phen)], 347 [Co(mhp)(phen)], 239 [Co(phen)] and 167 [Co(mhp)]. Crystals suitable for analysis by X-ray diffraction were grown by ether diffusion into a concentrated dichloromethane solution.

[Co(chp)$_2$(bipy)] 4. With Hchp in place of Hmhp. No significant peaks observed in FAB mass spectrum.

[Co(chp)$_2$([^{2}H$_8$]bipy)] 4d. With Hchp in place of Hmph and [^{2}H$_8$]bipy in place of bipy. No significant peaks observed in FAB mass spectrum.

[Co(chp)$_2$(dmbipy)] 5. With Hchp in place of Hmhp and dmbipy in place of bipy. FAB mass spectrum: *m*/*z* 500 [Co(chp)$_2$(dmbipy)], 372 [Co(chp)(dmbipy)] and 243 [Co(dmbipy)].

[Co(chp)$_2$(phen)] 6. With Hchp in place of Hmhp and phen in place of bipy. No significant peaks observed in FAB mass spectrum.

[Co(chp)$_2$(Hdpa)] 7. With Hchp in place of Hmhp and di-2-pyridylamine (Hdpa) in place of bipy. No significant peaks observed in FAB mass spectrum.

[Co(bhp)$_2$(dmbipy)] 8 and [{Co(bhp)(O$_2$CMe)(dmbipy)}$_2$] 9. Anhydrous cobalt(II) acetate (2 mmol, 0.354 g) was dissolved in MeOH (10 cm^3) and stirred as a solution of Na(bhp) (4.1 mmol, 0.80 g) in MeOH (10 cm^3) was added dropwise. After 3 h the solution had become dark purple and the solvent was then removed under reduced pressure. Extraction with dry CH_2Cl_2 (10 cm^3) gave a dark purple solution which was filtered. A solution of dmbipy (2 mmol, 0.368 g) in CH_2Cl_2 (5 cm^3) was added and stirred for 2 h, becoming red. The solution was then concentrated to *ca.* 3 cm^3 and filtered. Diethyl ether was allowed to diffuse into it giving dark red microcrystalline material. This could be redissolved in CH_2Cl_2 and crystallised by slow diffusion of ether, giving mainly complex **8** but also some **9**. Examination of the crystallisation in more detail showed that **9** crystallises first, and samples of both compounds which were pure by elemental analysis could be obtained by fractional crystallisation. Crystals suitable for X-ray diffraction analysis for both compounds were obtained by this procedure. FAB mass spectra: **8**, *m*/*z* 589 [Co(bhp)$_2$(dmbipy)], 415 [Co(bhp)(dmbipy)] and 243 [Co(dmbipy)]; **9**, *m*/*z* 705 [Co$_2$(bhp)$_2$(O$_2$CMe)(dmbipy)], 648 [Co(bhp)$_2$(O$_2$CMe)(dmbipy)], 589 [Co(bhp)$_2$(dmbipy)], 462 [Co(bhp)$_2$(O$_2$CMe)], 415 [Co(bhp)(dmbipy)], 289 [Co(O$_2$CMe)(dmbipy)] and 243 [Co(dmbipy)].

[{Co(fhp)$_2$(dmbipy)}$_2$] 10. Anhydrous cobalt(II) acetate (1 mmol, 0.18 g) was dissolved in MeOH (10 cm^3) and stirred as a solution of Na(fhp) (2.1 mmol, 0.36 g) in MeOH (10 cm^3) was added dropwise. After 3 h the solution had become dark purple and the solvent was then removed under reduced pressure. The purple residue was dissolved in MeCN (10 cm^3) and a solution of dmbipy (0.2 mmol, 0.034 g) in CH_2Cl_2 (10 cm^3) was added and stirred for 3 h, becoming red. The solvent was then removed and the red-brown residue redissolved in CH_2Cl_2 (3 cm^3), filtered and crystallised by slow diffusion of ether vapour giving yellow crystals of complex **10** suitable for X-ray diffraction studies. FAB mass spectrum: *m*/*z* 823 [Co$_2$(fhp)$_3$(dmbipy)$_2$], 678 [Co$_2$(fhp)$_3$(dmbipy)(MeCN)], 638 [Co$_2$(fhp)$_3$(dmbipy)], 526 [Co$_2$(fhp)$_2$(dmbipy)], 467 [Co(fhp)$_2$(dmbipy)] and 355 [Co(fhp)$_2$(dmbipy)]. ^{19}F-{^{1}H} NMR: δ −140.

Crystallography

Crystal data and data collection and refinement parameters for compounds **3** and **7**–**10** are given in Table 2; selected bond lengths and angles in Tables 3 and 4.

Data collection and processing. Data were collected on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device[20] operating at 150.0(2) K, using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) ω–2θ scans and on-line profile fitting.[21] They were corrected for Lorentz-polarisation factors, and semiempirical absorption corrections based on azimuthal measurements were applied. No significant decay occurred during data collection.

Structure analysis and refinement. All structures were solved by direct methods using SHELXS 86[22] and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement. The hydrogen atoms were located in ΔF maps for complexes **2** and **7** and refined without constraints. For **8**–**10** they were included in idealised positions, allowed to ride on their parent C atoms (C–H 1.08 Å), and assigned isotropic thermal parameters [U(H) = 1.2U_{eq}(C) for aromatic H atoms, 1.5U_{eq}(C) for methyl H atoms]. All refinements were against F^2 and used SHELXL 93.[23]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/163.

Results and Discussion

Synthesis and structures

Compounds **1**–**7** were synthesized in a similar fashion derived from the work of Clegg *et al.*[15] Reaction of anhydrous cobalt(II) acetate with 2 equivalents of molten Hxhp (Hchp or Hmhp) under nitrogen leads to a purple paste from which acetic acid can be removed by heating under reduced pressure. The residue is extremely moisture sensitive but can be dissolved in CH_2Cl_2 and treated with diimines to give more stable complexes which analyse as [Co(xhp)$_2$L], where L = bipy, dmbipy, phen or Hdpa. Compounds **8**–**10** were made by the reaction of cobalt(II) acetate with 2 equivalents of Na(xhp) (xhp = bhp or fhp) in MeOH, which gives a purple solution. This was evaporated to dryness to give a similar purple paste to that formed in the previous reaction. Again extraction with CH_2Cl_2 or MeCN followed by addition of a diimine led to isolation of the products. The compounds synthesized are listed in Table 1, along with analytical data.

Several of these complexes have been characterised by X-ray single-crystal diffraction methods. The complex [Co(mhp)$_2$(phen)] **3** was crystallised from dichloromethane–diethyl ether and the structure solution shows a six-co-ordinate cobalt atom bound to 4N and 2O atoms from three chelating ligands, with the O atoms arranged *cis* (Fig. 1). The presence of three chelating ligands leads to a geometry far from octahedral. In particular the bite angle for the mhp ligand is narrow, with angles at Co between the N and O donors of *ca.* 63°. Four of the Co–X bond lengths fall in the range 2.106(3)–2.128(2) Å, with two bonds longer [Co–N(2) 2.149(3) and Co–O(21) 2.189(2) Å]. The two longest bonds are to donors *trans* to each other at Co.

The complex [Co(chp)$_2$(Hdpa)] **7** was crystallised in a similar manner and again a six-co-ordinate cobalt site is found, distorted from octahedral due to the acute bite angle of chp; the relevant O–Co–N angles are *ca.* 61° (Fig. 2). The bond lengths show a greater variation than in **3**. The N donors of Hdpa [N(1) and N(2)] have Co–N bonds of *ca.* 2.07 Å and this leads to the Co–X bonds *trans* to N(1) and N(2) having longer bonds of 2.291(3) and 2.214(2) Å [for N(11) and O(21) respectively] than those to the related mhp donor atoms which are not *trans* to Hdpa atoms.

The most obvious difference between complexes **3** and **7** is in the packing of the species (Fig. 2). The H atom of the amine nitrogen of Hdpa [N(3)] is involved in hydrogen bonding with a water molecule in the cell [all H atoms were located and refined freely; H(3n) • • • O(1w) 2.03(3) Å]. This water in turn bonds to O(21a) in a neighbouring molecule [H(2w) • • • O(21a) 1.94(5) Å] and to O(11b) in a second neighbour [H(1w) • • • O(11b) 1.91(5) Å] leading to a hydrogen-bonded two-dimensional polymer running through the crystal.

Table 1 Analytical data* and yields for Hfhp and compounds **1**–**10**

	Analysis (%)			
Compound	C	H	N	Yield (%)
Hfhp	53.1 (53.1)	3.6 (3.5)	11.9 (12.4)	74
1	60.0 (61.2)	3.8 (4.7)	12.4 (13.0)	63
2	62.7 (62.7)	5.7 (5.2)	12.1 (12.2)	52
3	64.0 (63.3)	4.9 (4.4)	11.6 (12.3)	71
4	52.2 (50.8)	3.7 (3.0)	11.1 (11.9)	55
5	53.2 (52.8)	3.6 (3.6)	10.8 (11.2)	59
6	53.2 (53.2)	3.5 (3.0)	11.0 (11.3)	47
7·H_2O	48.1 (47.5)	3.6 (3.4)	13.7 (13.9)	35
8·H_2O	43.3 (44.8)	3.1 (3.1)	9.1 (9.5)	41
9	48.7 (48.0)	3.3 (3.8)	9.1 (8.8)	21
10·CH_2Cl_2	51.3 (52.9)	3.7 (3.7)	10.3 (10.9)	25

* Calculated values in parentheses.

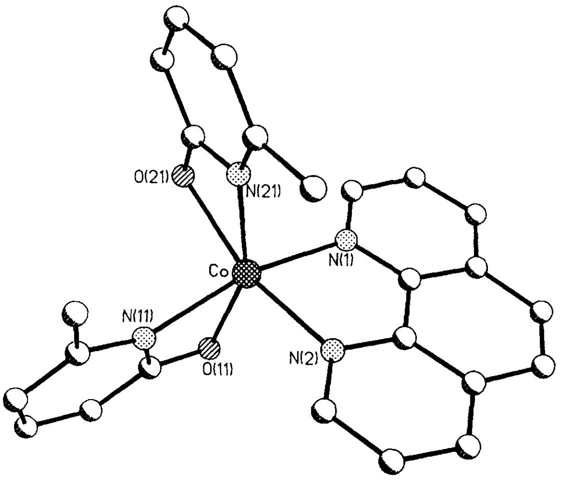

Fig. 1 Structure of complex **3** in the crystal showing the numbering scheme. The latter also applies to **8**

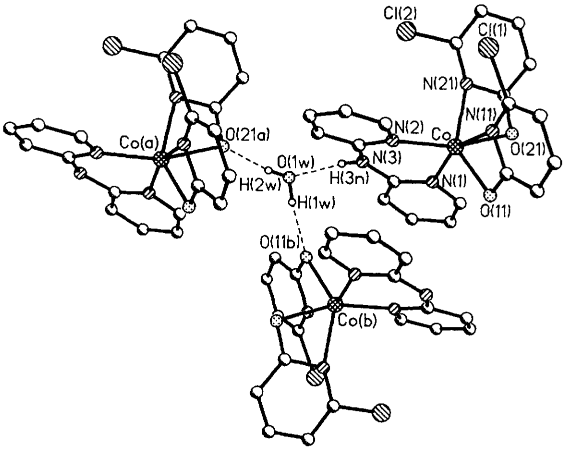

Fig. 2 Three molecules of complex **7**, showing the molecular structure in the crystal and the numbering scheme and illustrating the hydrogen bonding *via* a molecule of water leading to a weakly bound two-dimensional polymer

Both complexes **8** and **9** were crystallised from the reaction of Na(bhp) with cobalt(II) acetate, with **8** as the major product. They were separated by fractional crystallisation with **9** crystallising first. This procedure allowed analytically pure samples of both species to be produced. The complex [Co(bhp)$_2$(dmbipy)] **8** is again a mononuclear species containing a six-co-ordinate Co atom. As for **3** and **7** a small angle is found at Co between the N and O donors of the pyridonate ligand. For **8** the Co–X bond lengths vary from 2.075(4) to 2.210(5) Å with no obvious pattern. The bonds to the dmbipy N atoms are very similar, but the remaining four bonds vary in an unsystematic manner, and also differently to equivalent bonds in **3**.

The second product from this reaction, [{Co(μ-bhp)(O$_2$CMe)(dmbipy)}$_2$] **9**, was unexpected, with the presence of the carboxylate ligand indicating incomplete substitution of this ligand by the bhp ligand occurred in the first step of the reaction. The structure shows two six-co-ordinate Co atoms bridged by the exocyclic O atoms of two bhp ligands (Fig. 3). The cobalt co-ordination geometry is again distorted from octahedral with the smallest *cis* angle of 61° now observed between the two donor atoms from the chelating acetate ligand. The longest Co–X bonds also involve the two carboxylate oxygens. As for **8** the variation in Co–X bond length, from 2.024(6) to 2.201(8) Å, does not appear dependent on any obvious factor with the shortest bond being to a bridging bhp oxygen. The bhp nitrogen atom is not involved in bonding to the metal. The intramolecular Co • • • Co distance is 3.158(4) Å.

The complex [{Co(μ-fhp)(fhp)(dmbipy)}$_2$] **10** also crystallises as a dinuclear species bridged by an exocyclic pyridonate oxygen, but a chelating fhp ligand takes the place of the acetate ligand in **9** (Fig. 4). The six-co-ordinate cobalt site is similar to that in the previous four structures; distorted from octahedral chiefly due to the bite angles of the chelating ligands. As in **9** the shortest Co–X bonds are to the bridging O atoms at 2.057(3) and 2.073(3) Å. This observation for both **9** and **10** suggests that strain within the chelate rings is lengthening the Co to pyridonate bonds in these structures, and where the O donor is not part of a chelate ring the bond shortens slightly. The Co • • • Co distance is 3.208(6) Å, slightly longer than in **9**.

As has been mentioned there are few obvious bond-length trends within the individual structures, and equally no reliable trends can be derived from comparison of structures. We have previously noted in copper–pyridonate chemistry that the

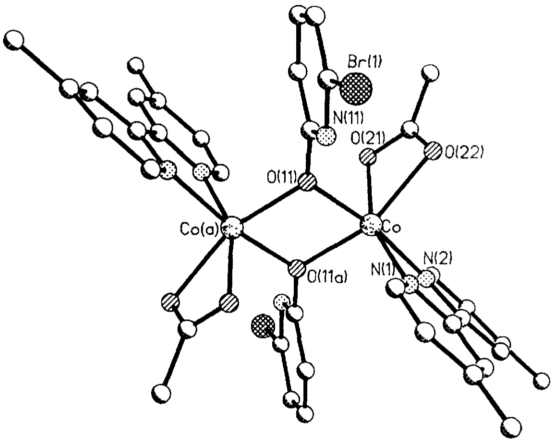

Fig. 3 Structure of complex **9** in the crystal showing the numbering scheme

Table 2 Experimental data for the X-ray diffraction studies of compounds **3** and **7–10**

	3	**7**	**8**	**9**	**10**
Formula	$C_{24}H_{20}CoN_4O_2$	$C_{20}H_{15}Cl_2CoN_5O_2{\cdot}H_2O$	$C_{22}H_{18}Br_2CoN_4O_2{\cdot}H_2O$	$C_{38}H_{36}Br_2Co_2N_6O_6{\cdot}2CH_2Cl_2$	$C_{44}H_{36}Co_2F_4N_8O_4{\cdot}CH_2Cl_2$
M	455	477	607	1120	1020
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	11.917(6)	8.493(5)	9.003(9)	9.46(2)	20.56(2)
b/Å	8.658(4)	9.369(5)	10.050(9)	10.19(2)	11.319(12)
c/Å	20.196(9)	14.346(12)	14.507(14)	13.47(3)	21.47(2)
α/°		89.01(6)	96.64(8)	110.26(13)	
β/°	98.20(3)	88.20(6)	100.03(8)	93.1(2)	119.10(6)
γ/°		65.64(4)	113.56(8)	106.20(14)	
U/Å^3	2063	1039	1160	1154	4365
Z	4	2	2	1^a	4^a
D_c/g cm^{-3}	1.467	1.509	1.739	1.613	1.551
Crystal size/mm	0.5 × 0.25 × 0.25	1.0 × 0.50 × 0.16	0.82 × 0.25 × 0.19	0.38 × 0.12 × 0.10	0.23 × 0.19 × 0.16
Crystal shape and colour	Orange lath	Pink plate	Red block	Red block	Yellow tablet
μ/mm^{-1}	0.861	1.106	4.217	2.733	0.954
Unique data	2697	3652	4013	4407	2848
Observed data [$I > 2\sigma(I)$]	2233	3340	2957	2252	2009
Parameters	360	348	297	274	296
Maximum Δ/σ ratio	0.001	0.001	0.002	0.010	0.003
$R1$, $wR2^b$	0.0248, 0.0697	0.0292, 0.0871	0.0437, 0.1140	0.0723, 0.1875	0.0467, 0.1101
Weighting scheme, $w^{-1\,c}$	$\sigma^2(F_o^2) + (0.0269P)^2 + 2.10P$	$\sigma^2(F_o^2) + (0.0380P)^2 + 0.88P$	$\sigma^2(F_o^2) + (0.0581P)^2 + 1.61P$	$\sigma^2(F_o^2) + (0.0714P)$	$\sigma^2(F_o^2) + (0.0397P)^2 + 5.25P$
Goodness of fit	0.974	1.092	1.040	0.989	1.065
Largest residuals/e Å^{-3}	0.21, −0.24	0.37, −0.52	0.75, −0.56	0.86, −0.75	0.33, −0.32

[a] The molecule lies on an inversion centre. [b] $R1$ based on observed data, $wR2$ on all unique data. [c] $P = \frac{1}{3}[\max(F_o^2, 0) + 2F_c^2]$.

Table 3 Selected bond lengths (Å) and angles (°) for mononuclear compounds **3**, **7** and **8**

	3	**7**	**8**
Bonds to chelating xhp ligands			
Co–N(11)	2.122(2)	2.291(3)	2.210(5)
Co–O(11)	2.128(2)	2.064(2)	2.075(4)
Co–N(21)	2.114(2)	2.149(2)	2.170(5)
Co–O(21)	2.189(2)	2.214(2)	2.120(5)
Bonds to chelating diimine ligand			
Co–N(1)	2.106(3)	2.064(2)	2.079(5)
Co–N(2)	2.149(3)	2.080(3)	2.086(5)
Angles between N and O donors of chelating xhp ligands			
N(11)–Co–O(11)	63.40(10)	61.22(8)	62.4(2)
N(21)–Co–O(21)	62.71(10)	61.09(8)	62.4(2)
Angle between two N donors of chelating diimine ligand			
N(1)–Co–N(2)	77.93(11)	89.17(9)	78.2(2)
Other *cis* angles			
N(1)–Co–N(21)	96.02(9)	109.73(9)	103.2(2)
N(21)–Co–N(11)	102.21(8)	90.00(9)	96.8(2)
N(1)–Co–O(11)	99.27(8)	96.81(9)	99.3(2)
N(21)–Co–N(2)	103.50(9)	99.79(9)	99.7(2)
N(11)–Co–N(2)	97.84(9)	97.36(8)	97.0(2)
O(11)–Co–N(2)	97.14(8)	113.03(8)	102.8(2)
N(1)–Co–O(21)	94.68(9)	89.71(8)	95.5(2)
N(11)–Co–O(21)	93.44(8)	91.45(8)	95.1(2)
O(11)–Co–O(21)	98.13(7)	87.87(8)	97.5(2)
trans angles			
N(1)–Co–N(11)	161.77(8)	157.92(8)	160.0(2)
N(21)–Co–O(11)	156.47(8)	137.91(8)	150.9(2)
N(2)–Co–O(21)	163.93(8)	159.05(7)	159.5(2)

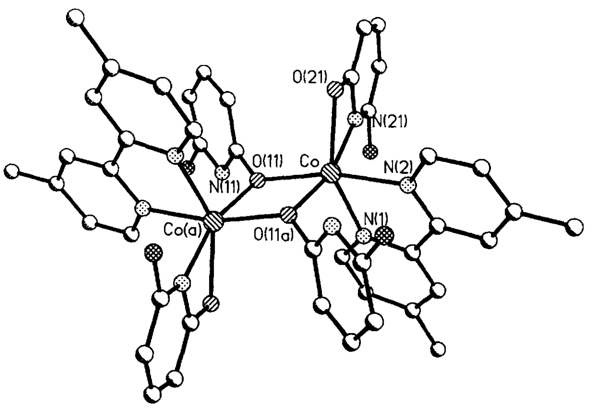

Fig. 4 Structure of complex **10** in the crystal showing the numbering scheme

Table 4 Selected bond lengths (Å) and angles (°) for dinuclear compounds **9** and **10**

	9	**10**
Bonds to chelating xhp (**10**) or acetate (**9**) ligands		
Co–N(21)	n.a.	2.158(4)
Co–O(21)	2.138(7)	2.156(4)
Co–O(22)	2.201(8)	n.a.
Bonds to chelating diimine ligand		
Co–N(1)	2.104(7)	2.106(4)
Co–N(2)	2.107(7)	2.131(4)
Bonds to bridging xhp ligands		
Co–O(11)	2.024(6)	2.073(3)
Co–O(11a)	2.080(6)	2.057(3)
Angles between donor atoms of chelating ligands		
N(21)–Co–O(21)	n.a.	62.0(2)
N(1)–Co–N(2)	77.7(3)	76.3(2)
O(21)–Co–O(22)	60.8(3)	n.a.
Other *cis* angles		
O(11)–Co–O(11a)	79.6(3)	78.08(14)
O(11a)–Co–N(1)	102.1(3)	99.7(2)
O(11)–Co–N(1)	96.1(3)	95.3(2)
O(11a)–Co–N(2)	94.4(3)	92.4(2)
O(11a)–Co–O(21)	98.1(3)	108.5(2)
O(11)–Co–O(21)	94.9(3)	104.06(14)
N(2)–Co–O(21)	93.3(3)	88.3(2)
O(11)–Co–N(21)	n.a.	92.7(2)
N(1)–Co–N(21)	n.a.	92.7(2)
N(2)–Co–N(21)	n.a.	98.5(2)
O(11)–Co–O(22)	93.2(3)	n.a.
N(1)–Co–O(22)	100.1(3)	n.a.
N(2)–Co–O(22)	95.1(3)	n.a.
trans angles		
O(11)–Co–N(2)	170.4(2)	166.2(2)
N(1)–Co–O(21)	158.5(2)	148.4(2)
O(11a)–Co–N(21)	n.a.	165.1(2)
O(11a)–Co–O(22)	157.3(2)	n.a.

n.a. = Not applicable.

C–O bond length in the xhp ligands is dependent on the 6-substituent,[8] which influences the position of the keto–enol tautomerism, and that the relative magnitudes of the Cu–N and Cu–O bond lengths can also be related to the pyridonate derivative used.[9] Unfortunately in this work use of differing diimine ligands was necessary to crystallise the various species, and this reduces the opportunity for comparisons. The absence of any significant trends illustrates how bond lengths to first-row metals are susceptible to minor changes in ligand environment. Here the nature of the diimine ligand, and possibly packing interactions, appears to override any preferences of the pyridonate ligands.

Spectroscopic studies

In some cases FAB mass spectral studies showed peaks for the molecular ion and also significant fragment peaks. For other compounds the technique was uninformative. Most information was gained from a study of the ^1H NMR spectra of these paramagnetic species. For reasons of solubility the dmbipy complexes **2**, **5**, **8** and **10** were examined in detail. Two of these have also been crystallographically characterised which was a further advantage. To clarify some aspects of the spectra $[Co(chp)_2(bipy)]$ **4** and $[Co(chp)_2([^2H_8]bipy)]$ **4d** were also examined. The results are in Table 5.

For complexes **2**, **5**, **8** and **10** six paramagnetically shifted peaks are seen in the spectrum which can be assigned to aromatic protons, and one peak at slightly negative chemical shift for the Me groups of dmbipy. For **2** an additional peak is seen at δ −19.7 which is due to the Me substituent of the mhp ligand. Although **10** crystallises as a dinuclear species, in solution it appears to be monomeric. This is confirmed by the single resonance observed in the ^{19}F NMR spectrum which shows that only one type of fhp ligand is present. Circumstantial support for this also comes from a study of related copper complexes,[8] where $[\{Cu(\mu\text{-chp})(chp)(bipy)\}_2]$ crystallised as a dimer but was shown by EPR spectroscopy to be monomeric in solution.

It is intriguing that although all spectra display paramagnetic

Table 5 Chemical shifts (δ) for complexes **2**, **4**, **4d**, **5**, **8** and **10** (^{1}H unless otherwise stated)

	Complex						
Assignment	**4**	**4d**	**4d** (^{2}H NMR)	**2**	**5**	**8**	**10**
bipy or dmbipy	154.0	n.o.	146.9	88.8	152.8	137.0	196.4
bipy or dmbipy	69.8	n.o.	68.5	77.3	66.7	69.5	58.2
xhp	56.1	56.1	n.o.	62.8	56.1	59.4	52.3
xhp	48.5*	49.8	n.o.	51.8	50.3	48.9	48.6
bipy or dmbipy	48.5*	n.o.	46.9	35.7	46.6	44.3	43.0
4,4′-H of bipy	12.6	n.o.	13.2	n.a.	n.a.	n.a.	n.a.
xhp	9.0	9.0	n.o.	14.4	9.4	12.4	5.9
Me of dmbipy	n.a.	n.a.	n.a.	−4.1	−1.2	−1.1	−1.2
Me of mhp	n.a.	n.a.	n.a.	−19.7	n.a.	n.a.	n.a.

n.o. = Not observed, n.a. = not applicable. * Not resolved from neighbouring peak.

shifts the size of these varies enormously between spectra. For example, for complex **10** the most shifted peak occurs at δ 196.4 while for **2** the equivalent peak is found at δ 88.8. Given that the structures are likely to be identical in solution such differences must be due to differences in the through-bond contact shift within the species, rather than due to the pseudo-contact contribution to the shift. Therefore it appears that the spectra are giving information about the bonding in these co-ordination complexes. As the complexes contain Co^{II} there was a possibility that the shift indicated that the complexes are showing spin-crossover behaviour, for example **10** might be high spin and **2** low spin, however this possibility was eliminated by measuring the magnetic moment of **4** in solution using the Evans method.[18,19] This gave a value of 4.93 μ_B per molecule, which is consistent with high-spin Co^{II} in an octahedral environment as a large orbital contribution to the moment is inevitable.[24]

To assign the aromatic peaks to either diimine or pyridonate species we synthesized a complex containing an 80% deuteriated bipy ligand.[17] The results are decisive with seven paramagnetically shifted aromatic peaks seen for [Co(chp)$_2$(bipy)] **4**, while in the ^{1}H NMR spectrum of **4d** only three major peaks are observed, with very weak signals for the residual 20% non-deuteriated bipy. In the ^{2}H NMR spectrum of **4d** the four peaks which are present for **4** but not **4d** are seen (Fig. 5). This allows assignment as given in Table 5, with assignment of the spectra of complexes **2**, **5**, **8** and **10** based on that for **4**.

It is clear that the most shifted peaks in the NMR spectra are due to the diimine ligand, and that these also show the greatest variation between the compounds. This result was not expected, however the trend in the chemical shifts, certainly of the most shifted peak, can be related to the relative strength of the cobalt–ligand interactions. We assume that the most shifted peak is due to the 6,6′-protons within the bipy or dmbipy as these are the only protons *ortho* to the bound N atoms.

The basicity of the ring nitrogen atom in 2-pyridones is dependent on the substituent in the 6 position of the ring.[1] If this substituent is electron withdrawing, *e.g.* F or Cl, then the nitrogen has low basicity. The converse is true if the substituent is electron donating. This factor influences whether the neutral species is present as the enol (essentially the case for Hchp or Hfhp) or the keto-form (essentially the case for Hmhp). In the NMR spectra reported here we are seeing this effect in the chemical shifts of a 'reporter' coligand, in this case dmbipy. For the fhp ligand, where we have the least basic and hence least strongly binding ring nitrogen, the cobalt interaction with dmbipy is correspondingly the strongest, leading to the largest paramagnetic shift. For the mhp ligand the cobalt–pyridonate interaction is greater and hence the Co–dmbipy interaction is weaker leading to a smaller paramagnetic shift for the dmbipy protons.

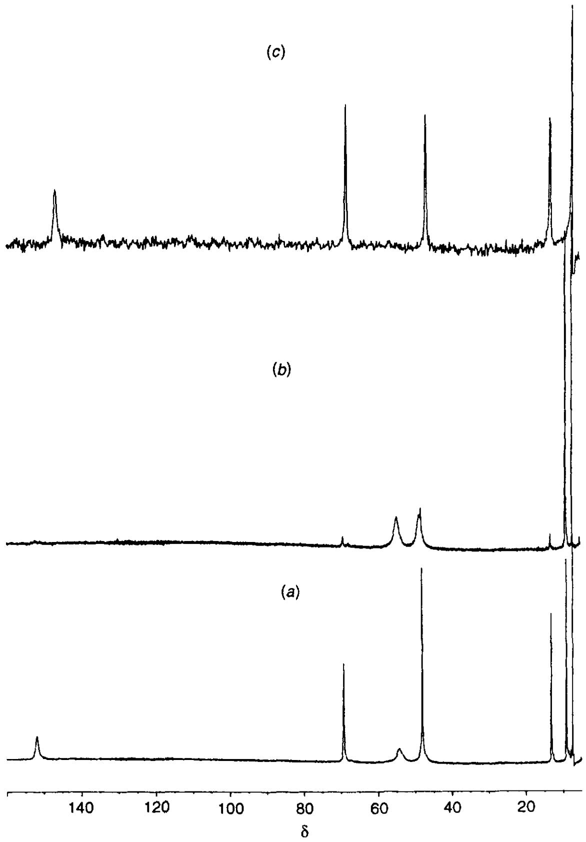

Fig. 5 The NMR spectra of complexes **4** and **4d**: (*a*) ^{1}H of **4** showing the seven aromatic proton resonances; (*b*) ^{1}H of **4d** showing the three proton resonances due to chp; (*c*) ^{2}H of **4d** showing the four deuterium resonances due to [^{2}H$_8$]bipy

This observation confirms that the nature of the substituents on the pyridonate ligands affects the electronic properties of the resulting complex, even where that effect is not noticeable in the structural chemistry. Perhaps more generally it illustrates that a 'reporter' ligand, in this case dmbipy, attached to a paramagnetic metal can be used to probe the co-ordinative ability of a second ligand, in this case the pyridonates. In essence, the greater the paramagnetic shift found for the 'reporter' ligand protons, the weaker the interaction between the metal and the ligand being investigated.

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