Molecular Helicity in Inorganic Complexes; Double Helical Binuclear Complexes of 2,2′:6′,2″:6″,2‴:6‴,2⁗-Quinquepyridine (L): Crystal Structures of $[Cu_2L_2(O_2CMe)][PF_6]_3{\cdot}H_2O$ and $[Cu_2L_2][PF_6]_3{\cdot}2MeCN$ †

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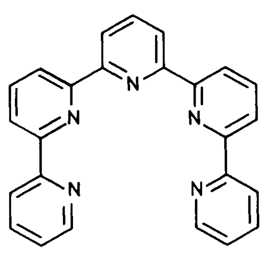
The potentially pentadentate ligand 2,2′:6′,2″:6″,2‴,2⁗-quinquepyridine (L, quinquepy) forms complexes with first row transition-metal cations of 2:2 stoicheiometry. Crystallographic studies of the complexes $[Cu_2L_2(O_2CMe)][PF_6]_3{\cdot}H_2O$ and $[Cu_2L_2][PF_6]_3{\cdot}2MeCN$ reveal a double helical arrangement of the ligands about the metals.

Helicity is a widespread phenomenon in natural systems,[1] although examples of this geometry in inorganic co-ordination compounds are relatively rare.[2,3] We have been interested in the preparation of binuclear complexes of transition-metal ions as models for metalloenzymes incorporating two cations at the active site.

Binuclear complexes incorporating copper are of particular interest as models for Type III cuproproteins (Cu ••• Cu), superoxide dismutase (Cu ••• Zn), and cytochrome oxidases (Cu ••• Fe).[4] Preliminary studies indicated that quinquepyridine should act as a polynucleating ligand of unusual structural adaptability.[5] We recently made a preliminary report describing a binuclear complex of 2:2 stoicheiometry between 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (quinquepy) and copper(II), and demonstrated a double helical arrangement of the ligands in $[Cu_2L_2(O_2CMe)][PF_6]_3{\cdot}H_2O$ (L = quinquepy).[3] We have now demonstrated the double helical arrangement of quinquepy ligands to be a common and robust feature of its transition-metal complexes, and report herein the preparation and characterisation of a range of such complexes, and describe the crystal and molecular structures of $[Cu_2L_2(O_2CMe)][PF_6]_3{\cdot}H_2O$ (**1**) and $[Cu_2L_2][PF_6]_3{\cdot}2MeCN$ (**2**).

Experimental

Quinquepy[6] and $[Cu(MeCN)_4][PF_6]$[7] were prepared by literature methods. Electrochemical experiments were performed with a Princeton Applied Research model 170 electrochemistry system, or a Metrohm E506 Polarecord and Metrohm E612 VA Scanner connected to a home-built OTTLE cell mounted in a Pye-Unicam 8800 spectrophotometer; all experiments were conducted using purified acetonitrile as solvent[8] with 0.1 mol dm^{-3} $[NBu^n{}_4][BF_4]$ as supporting electrolyte. For the cyclic voltammetry experiments, platinum beads were used as working and auxiliary electrodes with a silver wire or an Ag–AgCl electrode as reference; in all cases, ferrocene was added at the end of the experiment as an internal reference. Bulk electrolyses were performed using a cylindrical platinum gauze as working electrode, with a smaller coaxial platinum gauze as auxiliary electrode; an Ag–AgCl electrode was used as reference, calibrated against internal ferrocene at the end of each experiment. Electronic spectra were recorded using a Pye-Unicam 8800 spectrophotometer; i.r. spectra were recorded using a Perkin-Elmer 1710 FT spectrometer with the compound in compressed KBr pellets. E.s.r. spectra were recorded on a Varian E109 spectrometer as powders, or in acetonitrile glasses at 4 or 77 K. Fast-atom bombardment (f.a.b.) mass spectra were measured using a Kratos MS-50 spectrometer, and were loaded using acetonitrile as solvent with 3-nitrobenzyl alcohol as supporting matrix.


Quinquepy, L

Preparation of $[M_2L_2]^{4+}$ (M = Co *or* Cu) *and* $[M_2L_2(O_2CMe)]^{3+}$ (M = Ni, Cu, *or* Zn).—Quinquepy (100 mg, 0.26 mmol) was added to a solution of the appropriate metal(II) acetate (0.3 mmol) in boiling methanol (20 cm^3). The solution was heated until all of the ligand had dissolved, treated with $[NH_4][PF_6]$, and cooled, when the metal complex precipitated as a microcrystalline powder (60—80%). The products were recrystallised by the diffusion of diethyl ether vapour into an acetonitrile solution. Microanalytical results for the complexes are reported in Table 1.

Preparation of $[Cu_2L_2][PF_6]_3{\cdot}2MeCN$ (**2**).—Quinquepy (100 mg, 0.26 mmol) was added to a solution of $[Cu(MeCN)_4][PF_6]$ (113 mg, 0.3 mmol) in methanol (25 cm^3) and the mixture heated to reflux for 2 h in air, after which period the brown solid was collected by filtration (60—70%). Recrystallisation from acetonitrile gave brown crystals of the title complex.

Crystal Structure Determinations of $[Cu_2L_2(O_2CMe)][PF_6]_3{\cdot}H_2O$ (**1**) *and* $[Cu_2L_2][PF_6]_3{\cdot}2MeCN$ (**2**).—Suitable single crystals of (**1**) were obtained as olive green blocks by the slow diffusion of diethyl ether vapour into an acetonitrile

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† 2-Acetato-*O*-di-μ-[2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine-*NN′N″*-(Cu^1),*N‴N⁗*(Cu^2)]-dicopper(II) tris(hexafluorophosphate) monohydrate and di-μ-[2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine-*NN′N″*-(Cu^1),*N‴N⁗*(Cu^2)]-dicopper(I)(II) tris(hexafluorophosphate)–acetonitrile (1/2).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: B.M. = 9.274×10^{-24} J T^{-1}.

Table 1. Microanalytical data (%) for the complexes

	Found				Calc.			
Complex	C	H	N	M	C	H	N	M
(**2**) $[Cu_2L_2][PF_6]_3{\cdot}2MeCN$ (brown)	44.5	2.7	10.9	9.3	45.7	2.8	11.8	9.0
(**1**) $[Cu_2L_2(O_2CMe)][PF_6]_3{\cdot}H_2O$ (olive green)	43.3	2.6	9.7	9.8	44.2	2.8	9.9	8.9
$[Cu_2L_2][PF_6]_4{\cdot}MeCN$ (yellow-green)	41.0	2.5	9.9	8.6	41.0	2.4	10.1	8.4
$[Ni_2L_2(O_2CMe)][PF_6]_3{\cdot}2H_2O$	43.4	2.7	10.0	8.2	43.9	2.9	9.8	8.3
$[Zn_2L_2(O_2CMe)][PF_6]_3{\cdot}H_2O$	43.8	2.4	9.8		44.0	2.9	9.8	
$[Co_2L_2][PF_6]_4{\cdot}2MeCN{\cdot}2H_2O$	40.7	3.1	10.9		40.8	2.8	10.6	

Table 2. Fractional atomic co-ordinates (10^4) for (**1**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	9 163(2)	8 030(2)	7 973(1)	N(71)	10 762(11)	7 380(12)	7 508(7)
N(01)	10 404(11)	8 948(14)	8 780(6)	C(72)	11 576(16)	8 209(17)	7 160(9)
C(02)	11 545(18)	9 776(18)	8 741(10)	C(76)	11 132(16)	6 635(17)	7 727(8)
C(03)	12 326(19)	10 169(22)	9 274(12)	C(73)	12 797(15)	8 324(20)	7 037(12)
C(04)	11 990(20)	9 713(23)	9 834(14)	C(74)	13 187(16)	7 604(20)	7 273(13)
C(05)	10 779(22)	8 816(21)	9 865(9)	C(75)	12 392(18)	6 804(22)	7 616(10)
C(06)	10 048(13)	8 469(14)	9 310(8)	N(81)	9 108(11)	4 996(12)	7 811(6)
N(11)	8 227(12)	7 178(12)	8 707(6)	C(82)	10 221(16)	5 752(16)	8 106(9)
C(12)	8 731(17)	7 509(15)	9 316(9)	C(83)	10 442(19)	5 754(21)	8 738(9)
C(13)	8 039(21)	7 001(22)	9 818(8)	C(84)	9 522(22)	5 014(22)	9 094(11)
C(14)	6 838(20)	6 146(21)	9 716(10)	C(85)	8 388(21)	4 259(23)	8 813(9)
C(15)	6 345(17)	5 803(17)	9 117(9)	C(86)	8 214(17)	4 258(16)	8 173(9)
C(16)	7 019(14)	6 352(13)	8 612(9)	N(91)	7 058(10)	3 606(13)	7 217(7)
N(21)	7 492(10)	6 410(11)	7 473(6)	C(92)	5 977(15)	3 001(15)	6 891(9)
C(22)	6 596(13)	6 075(14)	7 937(8)	C(93)	4 874(16)	2 383(22)	7 190(12)
C(23)	5 358(13)	5 593(15)	7 807(10)	C(94)	4 846(16)	2 361(20)	7 820(13)
C(24)	4 977(14)	5 360(16)	7 167(9)	C(95)	5 912(16)	2 951(16)	8 170(10)
C(25)	5 877(14)	5 714(18)	6 685(11)	C(96)	7 022(15)	3 551(17)	7 879(9)
C(26)	7 173(14)	6 159(12)	6 838(7)	O(100)	8 160(9)	3 246(12)	5 955(5)
N(31)	8 970(10)	5 890(11)	6 339(6)	C(101)	8 148(16)	2 259(18)	6 031(11)
C(32)	8 157(12)	6 398(14)	6 305(7)	O(102)	8 605(13)	2 171(12)	6 517(9)
C(33)	8 307(16)	7 073(16)	5 860(8)	C(103)	7 576(25)	1 200(21)	5 519(14)
C(34)	9 275(18)	7 242(17)	5 392(9)	P(1)	6 006(4)	2 498(5)	10 240(2)
C(35)	10 141(15)	6 776(16)	5 420(8)	F(11)	7 430(11)	3 142(19)	10 128(8)
C(36)	9 936(13)	6 118(17)	5 902(9)	F(12)	4 563(10)	1 848(16)	10 321(8)
N(41)	10 453(11)	4 824(13)	6 420(6)	F(13)	6 229(20)	1 667(21)	10 591(10)
C(42)	10 820(13)	5 547(14)	5 964(8)	F(14)	5 806(12)	3 413(15)	9 889(8)
C(43)	11 902(17)	5 739(19)	5 615(10)	F(15)	6 029(19)	1 784(16)	9 552(7)
C(44)	12 617(15)	5 146(18)	5 680(9)	F(16)	5 976(16)	3 300(18)	10 915(7)
C(45)	12 278(14)	4 408(17)	6 126(10)	P(2)	4 236(5)	2 375(5)	5 128(3)
C(46)	11 178(13)	4 259(16)	6 503(9)	F(21)	2 774(11)	1 822(15)	5 061(9)
Cu(2)	8 740(2)	4 409(2)	6 818(1)	F(22)	4 277(11)	3 554(12)	4 946(9)
N(51)	8 003(12)	8 994(13)	8 010(7)	F(23)	5 672(10)	2 985(15)	5 258(8)
C(52)	7 000(15)	8 938(17)	8 392(8)	F(24)	4 124(14)	1 230(13)	5 354(8)
C(53)	6 330(18)	9 579(20)	8 346(11)	F(25)	4 024(12)	2 887(15)	5 892(7)
C(54)	6 705(20)	10 264(19)	7 865(14)	F(26)	4 433(22)	1 926(22)	4 430(9)
C(55)	7 701(19)	10 293(19)	7 466(13)	P(3)	1 627(4)	2 989(5)	8 216(3)
C(56)	8 356(15)	9 659(15)	7 555(8)	F(31)	1 093(15)	3 489(18)	8 880(7)
N(61)	9 986(11)	8 986(12)	7 296(7)	F(32)	454(10)	2 788(13)	7 842(6)
C(62)	9 463(13)	9 689(15)	7 129(9)	F(33)	2 171(16)	2 515(23)	7 564(8)
C(63)	9 961(17)	10 337(18)	6 657(10)	F(34)	2 821(11)	3 194(14)	8 600(7)
C(64)	11 121(17)	10 296(17)	6 329(10)	F(35)	922(19)	1 771(18)	8 398(14)
C(65)	11 635(17)	9 646(17)	6 505(10)	F(36)	2 286(14)	4 274(17)	8 080(9)
C(66)	11 023(11)	8 920(16)	6 953(10)	O(W1)	4 597(60)	−221(63)	5 986(32)

solution of the complex. Suitable single crystals of (**2**) were obtained as dark brown needles by recrystallisation of the complex from acetonitrile.

Crystal data for (**1**). $C_{52}H_{39}Cu_2F_{18}N_{10}O_3P_3$, brown crystals, $M = 1\,413.1$, triclinic, $a = 11.829(8)$, $b = 12.575(11)$, $c = 20.917(22)$ Å, $\alpha = 103.0(1)$, $\beta = 82.9(1)$, $\gamma = 114.4(1)°$, $U = 2\,758.6$ Å^3, $F(000) = 1\,420$, space group $P1$ (no. 2), $Z = 2$, $D_m = 1.68$, $D_c = 1.70$ g cm^{-3}, Mo-K_α radiation ($\lambda = 0.710\,7$ Å), μ(Mo-K_α) = 10.1 cm^{-1}.

Crystal data for (**2**). $C_{54}H_{40}Cu_2F_{18}N_{12}P_3$, olive-green blocks, $M = 1\,418.1$, monoclinic, $a = 11.719(8)$, $b = 33.37(3)$, $c = 14.961(12)$ Å, $\beta = 104.0(1)°$, $U = 5\,677.3$ Å^3, $F(000) =$

Table 3. Fractional atomic co-ordinates (10^4) for (**2**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu(1)	1 436(2)	858(1)	1 676(2)
Cu(2)	1 095(2)	1 764(1)	3 298(2)
N(01)	2 657(12)	751(5)	820(11)
C(02)	3 672(20)	566(7)	974(18)
C(03)	4 436(17)	553(6)	553(14)
C(04)	4 216(18)	795(7)	−188(16)
C(05)	3 226(16)	1 006(6)	−464(14)
C(06)	2 417(19)	966(7)	15(16)
N(11)	666(15)	1 098(5)	478(13)
C(12)	1 207(15)	1 180(5)	−62(13)
C(13)	787(15)	1 291(6)	−1 005(13)
C(14)	−378(23)	1 486(8)	−1 075(20)
C(15)	−975(19)	1 477(7)	−382(16)
C(16)	−419(15)	1 264(6)	399(13)
N(21)	−285(11)	1 075(4)	2 036(9)
C(22)	−977(16)	1 213(6)	1 186(14)
C(23)	−2 179(19)	1 243(8)	1 098(17)
C(24)	−2 711(19)	1 166(7)	1 702(16)
C(25)	−2 119(14)	1 043(5)	2 579(13)
C(26)	−748(14)	1 023(5)	2 737(13)
N(31)	1 012(14)	1 179(5)	3 891(12)
C(32)	85(11)	957(4)	3 599(10)
C(33)	−78(13)	654(5)	4 063(11)
C(34)	614(13)	540(5)	4 872(12)
C(35)	1 563(14)	772(5)	5 107(13)
C(36)	1 838(16)	1 133(6)	4 653(14)
N(41)	2 579(11)	1 751(4)	4 349(10)
C(42)	2 716(13)	1 429(5)	4 872(12)
C(43)	3 712(12)	1 338(5)	5 543(11)
C(44)	4 459(20)	1 638(7)	5 801(17)
C(45)	4 501(15)	1 970(6)	5 312(13)
C(46)	3 499(15)	2 035(7)	4 657(14)
N(51)	414(14)	306(6)	1 534(13)
C(52)	873(18)	72(7)	2 359(16)
C(53)	141(18)	−267(7)	2 457(16)
C(54)	−848(21)	−362(8)	1 879(18)
C(55)	−1 332(21)	−166(8)	1 079(18)
C(56)	−705(22)	213(8)	911(19)
N(61)	2 363(13)	557(5)	2 737(11)
C(62)	3 314(14)	730(6)	3 248(13)
C(63)	3 817(21)	491(8)	4 137(18)
C(64)	3 557(20)	160(8)	4 283(17)
C(65)	2 479(18)	−64(7)	3 736(15)
C(66)	1 895(17)	140(7)	2 926(15)
N(71)	2 784(15)	1 312(6)	2 484(13)
C(72)	3 082(20)	1 665(8)	2 249(17)
C(73)	4 253(20)	1 809(8)	2 472(16)
C(74)	5 035(33)	1 575(12)	2 964(25)
C(75)	4 755(24)	1 235(9)	3 251(20)
C(76)	3 550(14)	1 064(6)	3 080(13)
N(81)	1 249(16)	1 882(6)	1 954(13)
C(82)	259(24)	2 132(9)	1 523(22)
C(83)	53(20)	2 314(8)	761(17)
C(84)	1 056(20)	2 297(8)	413(18)
C(85)	2 143(20)	2 087(7)	682(17)
C(86)	2 164(23)	1 880(8)	1 574(19)
N(91)	−484(13)	2 031(5)	2 891(12)
C(92)	−1 310(18)	2 070(7)	3 488(16)
C(93)	−2 334(21)	2 268(8)	3 160(19)
C(94)	−2 628(24)	2 468(9)	2 291(20)
C(95)	−1 784(20)	2 426(8)	1 806(19)
C(96)	−691(15)	2 245(6)	2 098(14)
P(1)	8 144(9)	3 608(3)	685(8)
F(11)	7 391(22)	3 272(9)	159(22)
F(12)	8 118(49)	3 740(9)	−251(25)
F(13)	6 873(21)	3 855(9)	567(14)
F(14)	7 796(39)	3 467(9)	1 504(20)
F(15)	8 697(22)	3 991(8)	970(23)
F(16)	9 186(25)	3 340(13)	600(36)
P(2)	3 680(7)	4 900(2)	2 132(5)
F(21)	4 109(14)	4 709(6)	1 391(14)
F(22)	5 064(22)	4 889(5)	2 713(18)
F(23)	3 313(16)	5 119(7)	2 898(14)
F(24)	3 333(21)	4 485(6)	2 454(14)
F(25)	3 986(23)	5 317(6)	1 926(19)
F(26)	2 350(20)	4 986(5)	1 564(17)
P(3)	5 251(8)	3 053(3)	3 880(7)
F(31)	4 331(14)	2 989(6)	4 366(16)
F(32)	6 206(23)	2 840(7)	4 772(15)
F(33)	5 684(22)	3 369(9)	4 447(18)
F(34)	6 233(18)	3 110(6)	3 288(16)
F(35)	5 019(29)	2 681(8)	3 428(28)
F(36)	4 566(15)	3 354(6)	3 282(15)
N(200)	1 658(21)	2 831(8)	3 109(19)
C(201)	1 604(10)	2 953(4)	2 480(10)
C(202)	1 888(24)	3 231(9)	1 970(20)
C(101)	7 384(18)	4 514(7)	4 055(17)
C(103)	7 261(28)	4 327(11)	3 572(25)
C(102)	6 531(35)	4 088(13)	2 537(28)

1 420, space group $P2_1/c$ (no. 14), $Z = 2$, $D_m = 1.68$, $D_c = 1.70$ g cm^{-3}, Mo-K_α radiation ($\lambda = 0.710\,7$ Å), μ(Mo-K_α) = 10.1 cm^{-1}.

Data collection and processing. 7 173 [for (**1**)] and 7 711 [for (**2**)] independent reflections with 2θ(max.) of 50° were measured on a Stoe Stadi 2 diffractometer, of which 3 543 with $I > 2\sigma(I)$ in (**1**) and 2 256 with $I > 2\sigma(I)$ in (**2**) were used in subsequent calculations.

Structure analysis and refinement. In both structures, the positions of the metal atoms were determined from the Patterson function. Remaining atoms were determined from Fourier maps. In (**1**) a solvent water molecule was located and in (**2**) two molecules of acetonitrile. In (**1**) the structure was refined [Cu, P, F, O, N, and C anisotropic, H isotropic in calculated positions] to $R = 0.072$ ($R' = 0.075$). In (**2**) the structure was refined [Cu, P, and F anisotropic, C and N isotropic, H isotropic in calculated positions] to $R = 0.087$ ($R^1 = 0.090$). Calculations were performed using full-matrix least-squares methods with a weighting scheme $w = (\sigma^2(|F|) + 0.03\,|F|^2]^{-1}$. Scattering factors were taken from ref. 9. Calculations were performed using SHELX 76 on the Amdahl V7 Computer at the University of Reading.[10] Positional co-ordinates are given in Tables 2 and 3 and molecular dimensions in the metal co-ordination spheres are compared in Table 4. Least-squares planes information is provided in Table 5.

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

2,2′:6′,2″:6″,2‴:6‴,2⁗-Quinquepyridine was prepared by the method of Kröhnke[6] as a pale grey powder. Crude yields of the ligand from the one-pot reaction of 2,6-bis(3′-dimethylammonio-1′-oxopropyl)pyridine dichloride with two equivalents of [2′-oxo-2′-(2″-pyridyl)ethyl]pyridinium iodide in the presence of an excess of ammonium acetate were of the order of 50%. The structure of the ligand was confirmed by electron impact (M^+, m/z 387) or f.a.b. ($M + H^+$, m/z 388) mass

Table 4. Selected bond lengths (Å) and interbond angles (°) for (**1**) and (**2**)

	(**1**)	(**2**)		(**1**)	(**2**)
Cu(1)–N(01)	2.161(13)	2.167(17)	Cu(2)–N(31)	2.212(15)	2.159(18)
Cu(1)–N(11)	2.017(13)	1.971(18)	Cu(2)–N(41)	1.994(12)	2.044(12)
Cu(1)–N(21)	2.319(10)	2.327(14)	Cu(2)–N(81)	2.079(13)	2.099(21)
Cu(1)–N(51)	2.160(18)	2.180(18)	Cu(2)–N(91)	1.995(11)	2.011(15)
Cu(1)–N(61)	1.964(14)	1.968(15)	Cu(2)–O(100)	2.038(11)	—
Cu(1)–N(71)	2.378(15)	2.309(18)	Cu(2)–O(101)	2.683(16)	—
N(01)–Cu(1)–N(11)	77.2(5)	75.7(6)	N(31)–Cu(2)–N(41)	77.9(6)	77.2(5)
N(01)–Cu(1)–N(21)	151.3(5)	157.1(5)	N(31)–Cu(2)–N(81)	111.6(5)	125.9(7)
N(11)–Cu(1)–N(21)	75.4(6)	81.5(6)	N(41)–Cu(2)–N(81)	101.1(5)	119.1(6)
N(01)–Cu(1)–N(51)	106.4(6)	103.3(6)	N(31)–Cu(2)–N(91)	115.7(6)	113.4(6)
N(11)–Cu(1)–N(51)	95.1(6)	97.7(6)	N(41)–Cu(2)–N(91)	165.4(7)	142.4(6)
N(21)–Cu(1)–N(51)	84.5(5)	78.4(6)	N(81)–Cu(2)–N(91)	79.2(5)	85.0(7)
N(01)–Cu(1)–N(61)	102.4(7)	94.5(6)	N(31)–Cu(2)–O(100)	89.5(5)	—
N(11)–Cu(1)–N(61)	173.6(7)	169.3(7)	N(41)–Cu(2)–O(100)	86.1(4)	—
N(21)–Cu(1)–N(61)	105.7(5)	108.2(6)	N(81)–Cu(2)–O(100)	158.6(6)	—
N(51)–Cu(1)–N(61)	78.8(6)	80.2(6)	N(91)–Cu(2)–O(100)	88.8(5)	—
N(01)–Cu(1)–N(71)	83.7(5)	87.2(6)			
N(11)–Cu(1)–N(71)	110.8(6)	108.3(7)			
N(21)–Cu(1)–N(71)	98.1(5)	101.3(7)			
N(51)–Cu(1)–N(71)	153.8(5)	153.7(6)			
N(61)–Cu(1)–N(71)	75.4(6)	74.9(6)			

Table 5. Least-squares plane calculations for (**1**) and (**2**)[a]

Angles between planes (°)

Ligand A	(**1**)	(**2**)
0—1	9.1	11.3
1—2	20.9	17.4
2—3	51.2	48.3
3—4	6.0	12.0
Ligand B		
5—6	3.6	9.0
6—7	18.2	27.8
7—8	55.3	47.7
8—9	11.8	6.1

Stacking angles (°)	(**1**)	(**2**)
Angle between plane 012[b] and plane 89	4.5	4.7
Angle between plane 567[b] and plane 34	4.1	3.0

[a] Ligand A consists of rings 0, 1, 2, 3, and 4, ligand B consists of rings 5, 6, 7, 8, and 9 (see Figure 4 for labelling); atoms are numbered N(*n*1) or C(*nm*) (*n* = ring number, *m* = 2—6 inclusive); planes are all coplanar within experimental error. [b] Plane 012 contains the eighteen atoms of the three rings 0, 1, and 2; plane 89 contains the twelve atoms of the two rings 8 and 9; planes 34 and 567 are defined similarly.

spectroscopy, microanalysis (see Table 1), and ^{1}H n.m.r. spectroscopy. The ^{1}H n.m.r. spectrum was assigned on the basis of a double quantum filtered phase-sensitive COSY experiment. The lowest field protons (δ 8.65—8.8) are assigned to H^6, H^3, H$^{3'}$, and H$^{5'}$; the assignments of the remaining protons followed from the COSY experiment (H^5, δ 7.35; H^4, 7.88; H$^{4'}$, 8.01; H$^{3''}$, 8.48; H$^{4''}$, 8.04).

The metal complexes were prepared by the reaction of quinquepy with a solution of the metal(II) acetate in boiling methanol. The ligand is insoluble in methanol, but dissolves as the reaction proceeds. The dissolution of the ligand is associated with the formation of coloured solutions of the metal complexes. Treatment of the dark coloured solutions with ammonium hexafluorophosphate resulted in the deposition of the complexes $[M_2L_2][PF_6]_4$ (M = Co or Cu) or $[M_2L_2(O_2CMe)][PF_6]_3$ (M = Ni, Cu, or Zn). In addition to the two copper complexes described above, a third brown compound was also obtained from the reaction of copper(II) acetate with quinquepy, but this was obtained in better yield by the reaction of $[Cu(MeCN)_4][PF_6]$ with quinquepy under aerobic conditions.

The reaction of copper(II) acetate with quinquepy resulted in the formation of dark green solutions, from which a dark green-brown solid was obtained upon the addition of ammonium hexafluorophosphate. Recrystallisation of the solid from acetonitrile by diffusion of diethyl ether vapour into a solution led to the formation of a mixture of olive green and yellow-green crystals, and small amounts of a brown microcrystalline solid. The olive green and yellow-green crystalline products could be separated by hand from the mixture of crystals. Treatment of an acetonitrile solution of the yellow-green complex with an excess of sodium acetate resulted in the formation of blue-green solutions, from which olive green crystals identical to those previously described could be obtained.

Fast-atom bombardment mass spectroscopy of the complexes provided a valuable structural probe. The f.a.b. mass spectrum of the olive green and yellow-green complexes exhibited peaks centred at *m/z* 900, 1 045, and 1 190 (based on Cu = 63) which may be assigned to $[Cu_2L_2]^+$, $[Cu_2L_2(PF_6)]^+$, and $[Cu_2L_2(PF_6)_2]^+$ respectively. In addition, the olive green complex also exhibits peaks at *m/z* 959 and 1 104 which may be assigned to the species $[Cu_2L_2(O_2CMe)]^+$ and $[Cu_2L_2(PF_6)(O_2CMe)]^+$ respectively. These peaks are absent from the mass spectrum of the yellow-green complex. These observations are in accord with a formulation $[Cu_2L_2][PF_6]_4$ for the yellow-green complex, and $[Cu_2L_2(O_2CMe)][PF_6]_3$ for the olive green. The isotopic patterns of the peaks in the mass spectra fitted well with those predicted by simulation for the proposed structures; significantly, the patterns were only consistent with a Cu_2 formulation. In some spectra peaks were observed at *m/z* 1 108 and 1 253, which may be assigned to $[Cu_3L_2(PF_6)_n]^+$ (*n* = 1 or 2) respectively. The mass distributions support this assignment. These peaks were not observed consistently, even when running samples from the same batch of crystalline material under 'identical' conditions, and we believe them to be associated with some reaction occurring at the probe tip.

The brown copper complex may be isolated in low yield from the reaction of copper(II) acetate with quinquepy. However, the yields from this route were very variable, and the complex was difficult to separate from the dicopper(II) complexes discussed

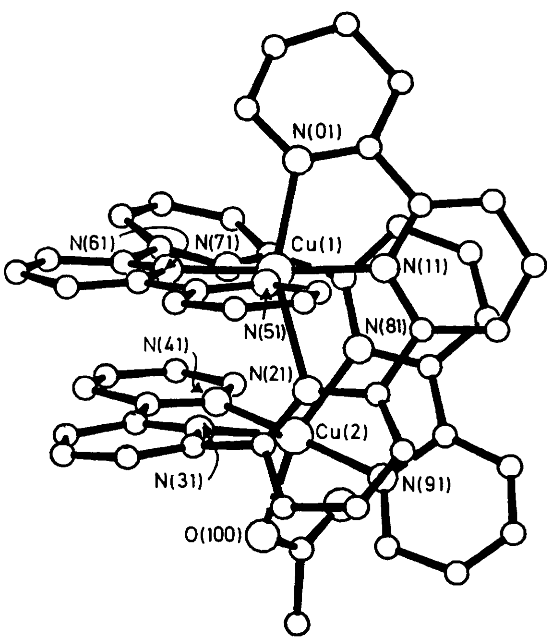

Figure 1. The crystal and molecular structure of one of the two enantiomeric cations $[Cu_2L_2(O_2CMe)]^{3+}$ in (**1**) showing the atomic numbering scheme adopted. Hydrogen atoms are omitted for clarity

above. It was noticed that solutions of either of the two dicopper(II) complexes in methanol or water darkened on standing in air, to give solutions from which the brown complex could be obtained. Brown solutions were also obtained upon treating solutions of the dicopper(II) complexes with reducing agents. The complex is best obtained by the reaction of copper(I) chloride or $[Cu(MeCN)_4][PF_6]$ with quinquepy in methanol or acetonitrile in air. The f.a.b. mass spectrum of the complex exhibits peaks centred at *m/z* 900, 1 045, and 1 190, assigned to $[Cu_2L_2]^+$, $[Cu_2L_2(PF_6)]^+$, and $[Cu_2L_2(PF_6)_2]^+$ respectively. The isotopic mass distribution corresponded exactly with that calculated for $C_{50}H_{34}Cu_2N_{10}$ (P and F are monotopic). Fragmentation peaks are observed centred at *m/z* 835 ($[CuL_2]^+$), 665, and 450 ($[CuL]^+$). These observations are consistent with a formulation $[Cu_2L_2][PF_6]_3$, *i.e.* a mixed-valence compound of copper(I) and copper(II).

All of the copper complexes described above are paramagnetic and give broad, featureless ^1H n.m.r. spectra in $(CD_3)_2SO$ solution. The magnetic moments of the dicopper(II) complexes are in the range $\mu_{eff.}$ = 2.0—2.2 B.M., whereas that of the mixed oxidation state complex $[Cu_2L_2][PF_6]_3$ is 2.1 B.M. [*per* copper(II) atom]. The magnetic moment of $[Cu_2L_2][PF_6]_3$ was investigated over the temperature range 95—273 K, and shown to obey normal Curie–Weiss behaviour. There was no indication of any electronic interactions between the two metal centres.

The crystal and molecular structures of complexes (**1**) and (**2**) have been determined, and the molecular structures of the cations are compared in Figures 1 and 2. In each of the Figures one of the two enantiomers present in the lattice is shown. Selected bond lengths and bond angles are listed in Table 4. The structural determinations confirm the binuclear formulation, and reveal that in both structures the two quinquepy ligands have adopted a double helical configuration about the two copper atoms. The double helical arrangement is emphasised in the space-filling diagram for (**2**) presented in Figure 3.

In (**1**) the two copper atoms are non-equivalent: Cu(1) is six-co-ordinate and bonded to three consecutive nitrogen atoms from each quinquepy ligand, whilst Cu(2) is five-co-ordinate and bonded to the two remaining nitrogen atoms from each quinquepy, and an oxygen of a monodentate acetate. Complex (**2**) is remarkably similar. The principal differences are associated with the loss of the co-ordinated acetate group, to leave a six-co-ordinate copper(II) centre and a four-co-ordinate copper(I) centre. The gross geometry of the yellow-green complex of stoicheiometry $[Cu_2L_2]^{4+}$ is presumably closely related.

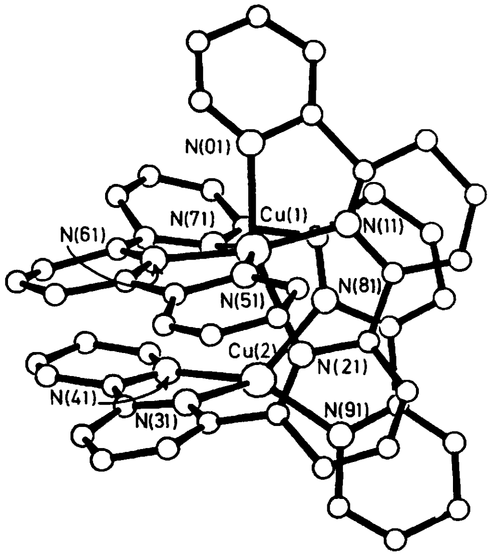

Figure 2. The crystal and molecular structure of one of the two enantiomeric cations $[Cu_2L_2]^{3+}$ in (**2**) showing the atomic numbering scheme adopted. Hydrogen atoms are omitted for clarity

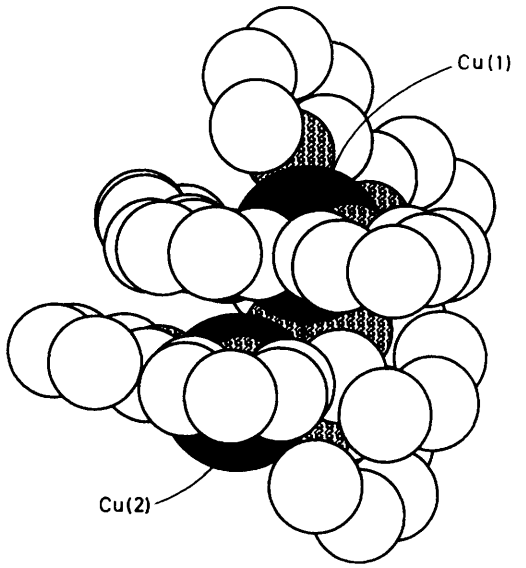

Figure 3. A space filling diagram of one of the enantiomeric cations $[Cu_2L_2]^{3+}$ in (**2**)

The six-co-ordinate copper atoms in (**1**) and (**2**) are in very similar distorted octahedral arrays, in which each ligand presents a *pseudo* terpyridyl donor set to the metal. The distortions are related to those observed in other copper(II) complexes of 2,2′:6′,2″-terpyridine.[11] The bond lengths to the two terminal pyridine rings [figures are given for (**1**) but those

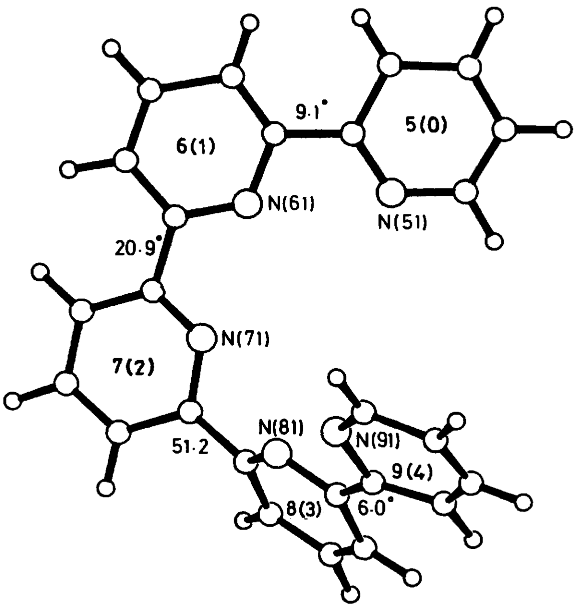

Figure 4. A view of one of the two independent ligands in the $[Cu_2L_2(O_2CMe)]^{3+}$ cation in (**1**), showing the twist angles about the C–C bonds and the numbering of rings 0—4 and 5—9. The other ligand in (**1**) and the two independent ligands in (**2**) are generally similar

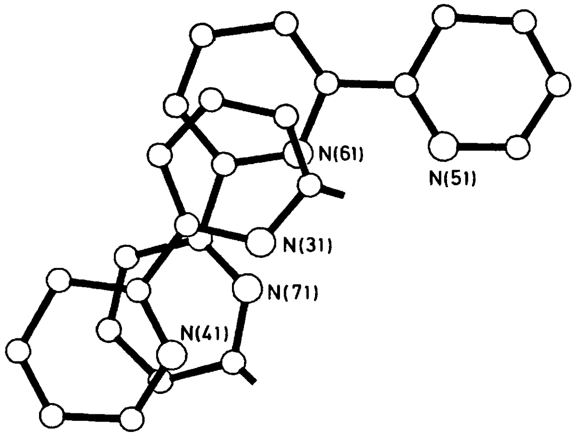

Figure 5. A view of the overlap of one of the 'terpyridyl' fragments in (**1**) with the 'bipyridyl' fragment it stacks with. The other independent stacking interaction in (**1**) and the two independent interactions in (**2**) are generally similar

for (**2**) are similar] of 2.161(13) and 2.160(18) Å are similar, as are those to the 'central' rings of the terpyridine moiety of 2.017(13) and 1.964(14) Å. The interactions with the remaining two pyridine ligands are weaker and rather less symmetrical. This reflects the helical twist of the ligand, which is most apparent at these rings, and results in considerable distortion of the 'axial' interactions [N(01)–Cu(1)–N(21) 151.3, N(61)–Cu(1)–N(11) 173.6°].

In (**1**) the five-co-ordinate copper atom is bonded to the two remaining pyridine rings of each ligand, and the oxygen atom of an acetate group. Once again, the interactions with the two terminal pyridine rings are similar [Cu(2)–N(91) 1.995(11) and Cu(2)–N(41) 1.994(12) Å]. The two remaining Cu–N interactions are dissimilar [Cu(2)–N(31) 2.212(15) and Cu(2)–N(81) 2.079(13) Å]. The geometry about the metal is not usefully categorised in terms of a regular geometry. The copper is bonded to one oxygen of the acetate group [Cu(2)–O(100) 2.038(11) Å] and exhibits a weak interaction with the other [Cu(2)–O(101) 2.683(16) Å]. A similar geometry is likely to exist in the cation $[Cu(bipy)(terpy)]^{2+}$ (bipy = 2,2′-bipyridine, terpy = 2,2′:6′,2″-terpyridine).[12]

In (**2**) the second copper atom is four-co-ordinate, with the Cu–N distances varying in the range 2.011(15)—2.159(18) Å. The geometry of Cu(2) may be regarded as being derived from tetrahedral, with the constraints of an intraligand bite angle of *ca.* 80° within the 'bipyridine'. The angles in the two structures are compared in Table 4. The major change has occurred in the position of N(41); in particular the N(41)–Cu(2)–N(91) angle is reduced to 142.4(6) from 165.4(7)°, no doubt because of the tetrahedral preferences of the copper(I) atom. Despite the differences in co-ordination number, the distances do not differ dramatically from those observed in (**1**) and serve to emphasise the structural rôle played by the stacked double helical array of ligands in dictating the geometry of the final complex.

The quinquepy ligands are principally twisted about the interannular bonds between the bidentate and terdentate portions of the molecules. The two quinquepy ligands are similar, but not identical. All bond lengths and bond angles within individual pyridine rings are unremarkable. The interannular distances vary considerably in the range 1.445(23)—1.527(20) Å, although this is not simply related to the metal–ligand or ligand–ligand interactions. The most significant and noticeable feature is the twisting of the ligands into non-planar configurations to form the helical arrangement. The interannular angles in the two ligands are illustrated in Figure 4; the angles refer to one of the two non-equivalent ligands in (**1**). In both structures the principal twist [51—55° in (**1**) and 47.7—48.3° in (**2**)] is about the bond between the 'terpyridine' and 'bipyridine' portions of the ligands (rings 2 and 3, and rings 7 and 8), although smaller twists of 18—20° between rings 1 and 2 and rings 6 and 7 are also apparent.

It is also apparent from Figure 1 or 2 that the double helical geometry results in a stacking interaction between planar aromatic rings. Stacking interactions of this type are charge-transfer in origin and are known to be of importance in biological molecules and are thought to play a major rôle in drug-receptor interactions.[13] The importance of such interactions in dictating the configuration of co-ordination compounds has not been emphasised, although they have been invoked to rationalise kinetic phenomena.[14] The stacking interaction involves a 'terpyridine' fragment of one ligand with a bipyridine fragment of the other, and projections of the two non-equivalent interactions in the molecule are presented in Figure 5. Although the two interactions differ slightly in the precise alignment, the key features are similar. The average shortest distances between an atom in the bipyridine fragment from the plane of the approximately parallel terpyridine fragment of the other ligand is 3.25 and 3.35 Å for the two separate interactions. The typical interplanar distance in stacked systems is 3.4 Å.[13] In each complex the two stacked systems are approximately parallel, with least-squares planes calculations showing angles of intersection of 4—5°. It is apparent from Figure 3 that in (**2**) the plane of rings 3 and 4 is bent away from the position *trans* to N(91); as a consequence the plane of rings 5—7 (which stacks parallel to the plane of rings 3 and 4) is also shifted relative to the previous structure. These shifts allow a much closer approach of the two copper atoms [3.957(2) Å] in (**2**) than in (**1**) [4.503(2) Å]. In neither complex are there any intermolecular distances less than the sums of the van der Waals radii.

Although the crystal structure of the yellow-green complex has not been determined, the f.a.b. mass spectrum clearly indicates the presence of a $[Cu_2L_2]^{4+}$ core. Elemental analysis suggests a formulation $[Cu_2L_2][PF_6]_4{\cdot}MeCN$ to be appropriate, although it is uncertain whether the acetonitrile occupies a lattice site or replaces the acetato ligand in (**1**).

The electrochemical behaviour of these copper complexes has also been investigated. The cyclic voltammogram of an acetonitrile solution of (**2**) exhibits an oxidation wave centred at +0.15 V *vs.* $[Fe(\eta-C_5H_5)_2]-[Fe(\eta-C_5H_5)_2]^+$ and a reduction centred at —0.37 V *vs.* $[Fe(\eta-C_5H_5)_2]-[Fe(\eta-C_5H_5)_2]^+$. Both waves are near reversible with $E_c - E_a$ of 70—80 mV depending on the precise cell geometry. Both waves correspond to one-electron processes and we consider the oxidation leads to a Cu^{II},Cu^{II} species and the reduction to a Cu^{I},Cu^{I} complex. Support for this comes from the observations that (after the first scan) cyclic voltammograms of all three isolated copper complexes are identical.

Controlled potential oxidation of a solution of a known quantity of (**2**) in acetonitrile led to the formation of a pale green solution in a one-electron process (formula weight calculated for one electron, 1 362 ± 68, actual 1 415). The cyclic voltammogram of the green solution was identical in all respects to that of (**2**). The green complex was stable under the conditions of the experiment, and upon bulk reduction the same quantity of charge was passed. On this basis we regard the oxidation process as reversible. The electronic spectrum of the electrogenerated Cu^{II},Cu^{II} complex is identical to that of the isolated yellow-green compound, supporting the formulation of that complex as $[Cu_2L_2][PF_6]_4$ or $[Cu_2L_2(MeCN)][PF_6]_4$. An OTTLE experiment established the chemical reversibility of the reaction, and exhibited an isosbestic point at 692 nm. Exactly similar results were obtained from the cyclic voltammetry and bulk one-electron reduction of the yellow-green complex.

Bulk reduction of (**2**) is also a one-electron process (formula weight calculated 1 357 ± 68), although no changes in the colour of the solution were observed during the reduction or re-oxidation. A cyclic voltammogram of the reduced solution was very similar to that of (**2**). The e.s.r. spectrum of the yellow-green complex in an acetonitrile glass at 4 K revealed a broad poorly resolved apparently isotropic signal at $g = 2.054$. The broadening is consistent with hyperfine coupling to the copper, but at no temperature was this resolved (in either glassy or fluid solution). Compound (**1**) also exhibited a broad near-isotropic signal, centred at $g = 2.065$. Once again, no hyperfine coupling could be resolved. The e.s.r. spectrum of (**2**) exhibits an anisotropic signal centred at $g_{av} = 2.160$. The parallel and perpendicular components overlap and it is not possible to deconvolute the spectrum to obtain individual *g* values. The signal shows hyperfine coupling to the copper ($A_\perp$ = 215—240, $A_\parallel$ = 250—280 G). The detailed magnetic and e.s.r. spectroscopic properties of the copper complexes will be reported in a future paper.[15]

The reaction of nickel(II) acetate with quinquepy in methanol results in the formation of a pale green solution, from which a single pale green crystalline solid was obtained upon the addition of $[NH_4][PF_6]$. The f.a.b. mass spectrum of the complex exhibited peaks at *m/z* 1 035, 1 094, 1 180 and 1 239, which may be assigned to the species $[Ni_2L_2(PF_6)]^+$, $[Ni_2L_2(O_2CMe)(PF_6)]^+$, $[Ni_2L_2(PF_6)_2]^+$, and $[Ni_2L_2(O_2CMe)(PF_6)_2]^+$. Fragmentation peaks are observed at *m/z* 832 ($[NiL_2]^+$), 504 $\{[NiL(O_2CMe)]^+\}$, and 443 ($[NiL]^+$). This suggests that the compound is exactly analogous to the copper complex, and should be formulated $[Ni_2L_2(O_2CMe)][PF_6]_3$; microanalysis is in accord with this formulation. We have recently determined the crystal structure of this complex and shown it to be very similar to that of (**1**), differing only in the presence of a bidentate acetato group rather than a monodentate one.[15]

Solutions of the pale green complex in acetonitrile showed no oxidation waves in their cyclic voltammograms up to +1.5 V *vs.* $[Fe(\eta-C_5H_5)_2]-[Fe(\eta-C_5H_5)_2]^+$, but exhibited an irreversible reduction centred at −1.23 V *vs.* $[Fe(\eta-C_5H_5)_2]-[Fe(\eta-C_5H_5)_2]^+$. The reduction wave is dependent on the scan rate ($E_c - E_a$ = 190 mV at 20 mV s^{-1}, 240 mV at 200 mV s^{-1}). The relative intensities of the forward and reverse waves do not alter with scan rate, and we believe the large peak splitting is due to slow electron transfer to the complex. Bulk electrolysis of an acetonitrile solution (−1.4 V) resulted in a colour change to purple, followed by decomposition to a colourless solution containing a suspension of free quinquepy. We have been unable to prepare sufficiently long-lived samples of the reduced species to record the e.s.r. spectrum to determine whether the reduction has occurred at the metal or the ligand. However, analogy with the reduction of the nickel(II) complex of 4′,4‴-diphenyl-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine would suggest that a nickel(I) complex is formed.[16] The cyclic voltammogram also exhibits two further irreversible processes centred at −1.81 and −1.92 V *vs.* $[Fe(\eta-C_5H_5)_2]-[Fe(\eta-C_5H_5)_2]^+$.

The reaction of methanolic solutions of zinc acetate with quinquepy results in the formation of pale yellow solutions, from which $[NH_4][PF_6]$ precipitates a single pale yellow solid. The f.a.b. mass spectrum of the complex exhibited peaks centred at *m/z* 1 106 $\{[Zn_2L_2(O_2CMe)(PF_6)]^+\}$, 1 192 $\{[Zn_2L_2(PF_6)_2]^+\}$, 1 251 $\{[Zn_2L_2(O_2CMe)(PF_6)_2]^+\}$, and 1 337 $\{[Zn_2L_2(PF_6)_3]^+\}$. Fragmentation peaks are observed centred at *m/z* 451 ($[ZnL]^+$), 510 $\{[ZnL(O_2CMe)]^+\}$, 574 $\{[Zn_2L(O_2CMe)]^+\}$, and 836 ($[ZnL_2]^+$). These data together with elemental analysis suggest the complex should be formulated $[Zn_2L_2(O_2CMe)][PF_6]_3$. The cyclic voltammogram of the complex exhibits no oxidation waves up to +1.5 V *vs.* $[Fe(\eta-C_5H_5)_2]-[Fe(\eta-C_5H_5)_2]^+$, but shows three near reversible reduction waves between −1.4 and −1.9 V *vs.* $[Fe(\eta-C_5H_5)_2]-[Fe(\eta-C_5H_5)_2]^+$. The peak-to-peak splittings vary between 60 and 100 mV. Controlled potential electrolysis at 1.9 V of the pale yellow solution of the zinc complex in acetonitrile resulted in the formation of an intense purple solution, which decomposed very rapidly with the deposition of free quinquepy. The electrogenerated species are too short-lived for characterisation by e.s.r. spectroscopy, but we believe them to be ligand-centred ligand radical complexes.

The reaction of cobalt(II) acetate with quinquepy in methanol generates a pale pink solution, from which a pink crystalline solid may be obtained by the addition of $[NH_4][PF_6]$. The f.a.b. mass spectrum of the complex exhibits peaks centred at *m/z* 446 ($[CoL]^+$), 591 $\{[CoL(PF_6)]^+\}$, 892 ($[Co_2L_2]^+$, 1 037 $\{[Co_2L_2(PF_6)]^+\}$, 1 182 $\{[Co_2L_2(PF_6)_2]^+\}$, and 1 327 $\{[Co_2L_2(PF_6)_3]^+\}$. All attempts to obtain *X*-ray quality crystals of this Co^{II},Co^{II} complex have been unsuccessful to date, and its formulation must remain tentative. However, it is clear that a binuclear complex related to the others described in this paper is formed.

In conclusion, we have demonstrated the ability of quinquepy to form binuclear double helical complexes with first row transition-metal ions. The dicopper complexes show a range of stable oxidation states. However, none of the copper complexes described shows activity as a catalyst for the oxidation of phenol by dioxygen. We are currently investigating the potential of double helical complexes of sexipyridine and octapyridine as oxidation catalysts.

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