Dinuclear copper(I) complexes of 24-membered bibracchial tetraimine Schiff base macrocycles derived from 2,5-diformylthiophene [1]

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Abstract

The synthesis of dinuclear copper(I) complexes of bibracchial tetraimine Schiff base macrocycles derived from the cyclocondensation of 2,5-diformylthiophene and the amines N,N-bis-(2-aminoethyl)-2-phenylethylamine, N,N-bis-(2-aminoethyl)-n-butylamine and N,N-bis-(2-aminoethyl)-t-butylamine is described. The structures of three such complexes are reported. The complex $[Cu_2L^3(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$ crystallises in the monoclinic space group $P2_1/c$ and has unit-cell dimensions $a = 15.897(4)$, $b = 13.329(4)$, $c = 21.999(5)$ Å, $\beta = 90.85(2)°$, $Z = 4$; the Cu–Cu separation is 5.201 Å. The complex $[Cu_2L^4(CH_3CN)_2](PF_6)_2 \cdot 0.64CH_3CN$ crystallises in the monoclinic space group $P2_1/n$ and has unit-cell dimensions $a = 17.243(5)$, $b = 11.451(6)$, $c = 26.534(8)$ Å, $\beta = 100.08(2)°$, $Z = 4$; the Cu–Cu separation is 5.386 Å. The complex $[Cu_2L^6(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$ crystallises in the triclinic space group $P\bar{1}$ and has unit-cell dimensions $a = 13.122(3)$, $b = 13.2116(3)$, $c = 13.718(3)$ Å, $\alpha = 104.92(3)°$, $\beta = 91.96(3)°$, $\gamma = 96.19(3)°$, $Z = 2$; the Cu–Cu separation is 5.215 Å. In each complex there is a strongly bonded acetonitrile molecule coordinated to each copper atom. The reaction of $[Cu_2L^3(CH_3CN)_2](PF_6)_2$ with carbon monoxide is discussed. © 1998 Elsevier Science S.A.

Keywords: Copper(I); Bibracchial Schiff base macrocycle; Thiophene; X-ray crystal structure

1. Introduction

The cyclocondensation of tris(2-aminoethyl)amine (tren) with 2,6-diacetylpyridine or 2,5-diformylfuran, in the presence of appropriate metal templates, readily yields mono- or homodi-nuclear metal-containing molecular clefts [1–10] L^1 and L^2 are representative of the 24-membered bibracchial tetraimine Schiff base macrocycles which provide the clefts and they have been used to complex barium, copper(I) and copper(II), silver(I) and manganese(II). The incorporation of a range of functionalised triamines into the macrocyclic frameworks has provided the conformational flexibility to vary the homodinuclear intermetallic separation from ca. 3.0 Å to in excess of 6 Å [2,5,7], and also to incorporate anions as intermetallic spacers [6,9,10].

L¹   L²
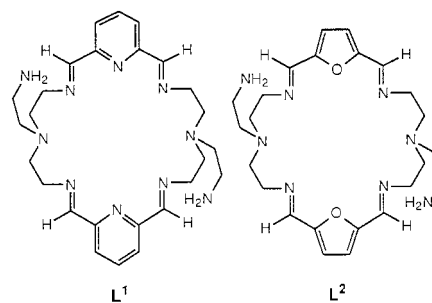
We have recently extended our study of such macrocycles to include species derived from the reactions of 2,5-diformylthiophene and the amines N,N-bis-(2-aminoethyl)-2-phenylethylamine, N,N-bis-(2-aminoethyl)-n-butylamine and N,N-bis-(2-aminoethyl)-t-butylamine in the presence of silver(I) salts in order to determine whether the macrocycles could be formed in the presence of non-coordinating pendant arms [11]. Herein we report the synthesis of the corresponding

homodinuclear copper(I) complexes together with the crystal structures of two such complexes and comment on the reactivity of the complexes.

2. Experimental

Elemental analyses were carried out by the University of Sheffield Microanalytical service. I.r. spectra were recorded as KBr discs or as liquid films between NaCl plates, using a Perkin Elmer 297 (4000 to $600 \, cm^{-1}$) or a Perkin Elmer 1600 (4000 to $400 \, cm^{-1}$) infrared spectrophotometer. ^1H and ^{13}C NMR spectra were recorded using a Bruker ACF-250 (250 MHz), a Bruker AM-250 (250 MHz) or a Bruker WH-400 (400 MHz) spectrometer. Electron impact (e.i.) and chemical impact (c.i., ammonia) mass spectra were recorded on a Kratos MS25 spectrometer; positive ion fast atom bombardment (fab) mass spectra were recorded using a Kratos MS80 or a VG PROSPEC spectrometer (the matrix used was 4-nitrobenzyl alcohol).

2.1. Ligand synthesis

2,5-Diformylthiophene was prepared by the method of Chadwick and Wilbe [12]. N,N-Bis-(2-aminoethyl)-2-phenylethylamine (L^4) was prepared by the method of Ref. [4]; N,N-bis-(2-aminoethyl)-t-butylamine (L^3), N,N-bis-(2-aminoethyl)-n-butylamine (L^6) and N,N-bis-(2-aminoethyl)-2-methylthioethylamine (L^5) were prepared by the method of Ref. [11].

Macrocycle	Pendant arm
L^3	$(CH_3)_3C$
L^4	$C_6H_5(CH_2)_2$
L^5	$CH_3S(CH_2)_2$
L^6	$CH_3(CH_2)_3$
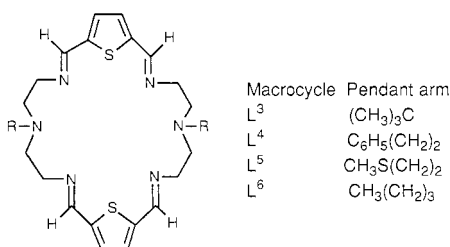
2.2. Macrocycle L^3

N,N-Bis-(2-aminoethyl)-t-butylamine (0.159 g, 1 mmol) was dissolved in methanol ($5 \, cm^3$) and added dropwise to a solution of 2,5-diformylthiophene (0.140 g, 1 mmol) in methanol ($5 \, cm^3$). The resulting solution was stirred at room temperature for 3 h before the solvent was removed under reduced pressure to yield an orange solid. L^3 was recrystallised from acetonitrile to produce a cream coloured microcrystalline solid. Yield = 0.126 g, 48%; m.p. = −204 °C; i.r. (KBr disc) $\vartheta_{C=N} = 1628 \, cm^{-1}$; m.s. (e.i.) $[L^1]^+$ 526 a.m.u.; microanalysis (%) found (required for $C_{28}H_{42}N_6S_2$) C 63.75(63.84), H 7.99(8.04), N 16.12(15.96), S 12.23(12.15).

2.3. Metal complexation reactions

All solvents were distilled and degassed prior to use and all manipulations were performed under a nitrogen atmosphere. Tetrakis(acetonitrile) copper(I) hexafluorophosphate was synthesised by the method of Kubas [13].

2.4. $[Cu_2L^3(CH_3CN)_2](PF_6)_2$

Macrocycle L^3 (100 mg, 0.19 mmol) was dissolved in distilled acetonitrile ($15 \, cm^3$) in a Schlenk tube before tetrakis(acetonitrile) copper(I) hexafluorophosphate (156 mg, 0.42 mmol) was added to produce a red solution. The reaction mixture was then warmed at 50 °C for 15 min to complete the reaction, after which it was filtered. The volume of the solvent was then reduced to ca. $5 \, cm^3$, and an equal volume of distilled diethyl ether was added. After cooling at 0 °C for several hours the product precipitated from solution as a red solid, which was recrystallised from an acetonitrile and diethyl ether mixture. Yield = 0.152 g, 78%; m.p. = 215 °C (decomposition); i.r. (KBr disc) $\vartheta_{C=N} = 1622 \, cm^{-1}$, $\vartheta_{PF_6} = 841$ and $558 \, cm^{-1}$; m.s. (+ve fab) $[Cu_2L^3PF_6]^+$ 799 a.m.u.; microanalysis [bulk sample] (%) found (required for $C_{32}H_{48}Cu_2F_{12}N_8P_2S_2$) C 37.77 (37.46), H 4.78 (4.72), N 11.38 (10.92).

2.5. The cyclo-condensation of N,N-bis-(2-aminoethyl)alkylamines with 2,5-diformylthiophene in the presence of lead(II) ions

The appropriate N,N-bis-(2-aminoethyl)alkylamine (5 mmol) in methanol ($100 \, cm^3$) was added dropwise to a solution at reflux temperature of 2,5-diformylthiophene (0.7 g, 5 mmol) and the appropriate lead(II) salt—lead nitrate, lead thiocyanate or bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)lead(II)— 5 mmol) in methanol ($200 \, cm^3$). The reaction was then heated at reflux temperature for 1 h. The cream precipitate produced was collected by filtration; where possible the product was then recrystallised from methanol.

2.5.1. $Pb_2L^4(SCN)_4$

Yield = 2.760 g, 87%; m.p. ≈ 195 °C (decomposition); i.r. (KBr disc) $\vartheta_{SCN} = 2020 \, cm^{-1}$; $\vartheta_{C=N}$ $1622 \, cm^{-1}$; m.s. (fab$^+$) $[HL^4]^+$ 622 a.m.u.; microanalysis (%) found (required for $C_{40}H_{42}N_{10}Pb_2S_6$) C 37.15(37.84), H 2.96(3.33), N 11.84(11.03), S 15.78(15.15).

2.5.2. $Pb_2L^4(NO_3)_4$

Yield = 1.992 g, 62%; m.p. $\approx 225\,°C$ (decomposition); i.r. (KBr disc) $\vartheta_{C=N}$ 1624 cm^{-1}; ϑ_{NO_3} = 1384 cm^{-1}; m.s. (fab$^+$) [PbL^4(NO$_3$)]$^+$ 892 a.m.u.; microanalysis (%) found (required for C$_{36}$H$_{42}$N$_{10}$O$_{12}$Pb$_2$S$_2$ · H$_2$O) C 33.20(33.18), H 3.37(3.40), N 10.19(10.75), S 4.16(4.92).

2.5.3. $Pb_2L^4(hfac)_4$

Yield = 0.707 g, 20%; m.p. $\approx 206\,°C$ (decomposition); i.r.(KBr disc) $\vartheta_{C=N}$ 1626 cm^{-1}; ϑ_{hfac} = 1664, 1646, 1196, 1138 cm^{-1}; m.s. (fab$^+$) [PbL^4(hfac)]$^+$ 1037 a.m.u.; microanalysis (%) found (required for C$_{56}$H$_{50}$F$_{24}$N$_6$O$_8$Pb$_2$S$_2$ · CH$_3$CN) C 36.03(36.46), H 2.69(2.80), N 5.19(5.13), S 3.21(3.36).

2.5.4. $Pb_2L^5(SCN)_4$

Yield = 1.830 g, 67%; m.p. $\approx 210\,°C$(decomposition); i.r. (Kbr disc) ϑ_{SCN} = 2050 cm^{-1}; $\vartheta_{C=N}$ 1622 cm^{-1}; m.s. (fab$^+$) insoluble in matrix, microanalysis (%) found (required for C$_{28}$H$_{38}$N$_8$Pb$_2$S$_6$ · 2H$_2$O) C 28.77(28.93), H 2.91(3.40), N 10.85(11.24).

2.5.5. $Pb_2L^5(hfac)_4$

Yield = 2.263 g, 50%; m.p. $\approx 218\,°C$(decomposition), i.r. (Kbr disc) $\vartheta_{C=N}$ 1632 cm^{-1}; ϑ_{hfac} = 1650, 1202, 1136 cm^{-1}; m.s. (fab$^+$) [PbL^5(hfac)]$^+$ 977 a.m.u., microanalysis (%) found (required for C$_{46}$H$_{46}$F$_{24}$N$_6$O$_8$Pb$_2$S$_4$ · H$_2$O) C 29.85(30.23), H 2.49(2.65), N 5.05(4.60), S 6.70(7.02).

2.5.6. $Pb_2L^6(NO_3)_4$

Yield = 1.902 g, 64%; m.p. $\approx 244\,°C$(decomposition); i.r. (KBr disc) $\vartheta_{C=N}$ = 1621 cm^{-1} and ϑ_{NO_3} = 1384 cm^{-1}; m.s. (fab$^+$) [Pb$_2$L^6(NO$_3$)$_3$]$^+$ 1127 a.m.u.; microanalysis (%) found (required for C$_{28}$H$_{42}$N$_{10}$O$_{12}$Pb$_2$S$_2$) C 28.61(28.52), H 3.81(3.80), N 11.77(11.47), S 5.02(5.25).

2.6. Transmetallation reactions of the dilead complexes of macrocycles L^4, L^5, L^6 with tetrakis(acetonitrile) copper(I) hexafluorophosphate

All solvents were distilled and degassed prior to use and all manipulations were performed under a nitrogen atmosphere. To a suspension of the appropriate di-lead macrocycle (0.5 mmol) in distilled acetonitrile (80 cm^3) was added tetrakis(acetonitrile) copper(I) hexafluorophosphate (1.1 mmol) as a solid. The resulting solution was then heated at reflux temperature overnight. After the solution had cooled to room temperature the insoluble lead salts were removed by filtration under nitrogen. The volume of solvent was then reduced to ca. 5 cm^3 and an equal volume of distilled diethyl ether added. After cooling at 0 °C for several hours the product precipitated as a red powder, which was purified by recrystallisation from a mixture of acetonitrile and diethyl ether.

2.6.1. $Cu_2L^4(SCN)(PF_6)$ (from $[Pb_2L^4](SCN)_4$)

Yield = 0.114 g, 24%; m.p. $\approx 105\,°C$ (decomposition); i.r. (KBr disc) ϑ_{SCN} = 2119 cm^{-1}, $\vartheta_{C=N}$ = 1619 cm^{-1}; ϑ_{PF_6} = 841, 558 cm^{-1}; δH (CD$_3$CN): 8.58 (4H, s, imine), 7.57 (4H, s, thiophene), 7.25 (10H, m, phenyl), 3.74 (8H, br, CH$_2$), 2.75 (16H, br, CH$_2$); m.s. (fab$^+$) [Cu$_2$L^4(SCN)]$^+$ = 808 a.m.u.; microanalysis (%) found (required for C$_{37}$H$_{42}$Cu$_2$F$_6$N$_7$P$_1$S$_3$) C 45.99(46.63), H 4.44(4.44), N 9.99(10.29).

2.6.2. $[Cu_2L^4(CH_3CN)_2](PF_6)_2$ (from $[Pb_2L^4](NO_3)_4$)

Yield = 0.207 g, 37%; m.p. $\approx 208\,°C$ (decomposition); i.r. (KBr disc) $\vartheta_{C=N}$ = 1618 cm^{-1}, ϑ_{PF_6} = 839, 557 cm^{-1}; m.s. (fab$^+$) [Cu$_2$L^4(PF$_6$)]$^+$ 894 a.m.u.; bulk sample microanalysis (%) found (required for C$_{36}$H$_{42}$Cu$_2$F$_{12}$N$_6$P$_2$S$_2$ · CH$_3$CN · H$_2$O) C 42.04(42.14), H 3.97(4.42), N 9.13(9.83).

2.6.3. $Cu_2L^5(PF_6)_2$ (from $[Pb2L^5](SCN)_4$)

Yield = 0.201 g, 41%; m.p. $\approx 240\,°C$ (decomposition); i.r. (KBr disc) $\vartheta_{C=N}$ = 1623 cm^{-1}, ϑ_{PF_6} = 840, 558 cm^{-1}; δH (CD$_3$CN): 8.65 (4H, s, imine), 7.63 (4H, s, thiophene), 3.81 (8H, m, CH$_2$), 2.97 (16H, m, CH$_2$), 1.95 (6H, s, CH$_3$); δC (CD$_3$CN): 160.0, 144.0, 137.04, 62.73, 54.40, 49.58, 38.03, 17.72; m.s. (fab$^+$) [Cu$_2$L^5(PF$_6$)]$^+$ 833 a.m.u.; microanalysis (%) found (required for C$_{26}$H$_{38}$Cu$_2$F$_{12}$N$_6$P$_2$S$_4$) C 31.86(31.87), H 3.99(3.91), N 8.53(8.58).

2.6.4. $[Cu_2L^6(CH_3CN)_2](PF_6)_2$ (from $[Pb_2L^6](NO_3)_4$)

Yield 0.077 g, 15%, m.p. $\approx 240\,°C$ (decomposition), i.r. (KBr disc) $\vartheta_{C=N}$ = 1622 cm^{-1}, ϑ_{PF_6} = 840, 558 cm, m.s. (fab$^+$) [Cu$_2$L^6(PF$_6$)]$^+$ 799 a.m.u.

2.7. The reaction of $[Cu_2L^3(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$ with carbon monoxide

Macrocycle L^3 (180 mg, 0.34 mmol) was dissolved in distilled methanol (60 cm^3) and tetrakis(acetonitrile) copper(I) hexafluorophosphate (254 mg, 0.68 mmol) was added to produce a red solution. The solution was then stirred for 15 min before it was evacuated and then purged with carbon monoxide four times. The colour of the solution lightened significantly after approximately 5 min. The reaction was then stirred overnight before a pale orange solid was filtered off; the volume of the solution was then reduced to 30 cm^3) to produce a second crop of product. Yield $\approx 70\%$; i.r. ϑ_{CO} = 2091 cm^{-1}, $\vartheta_{C=N}$ = 1625 cm^{-1}, ϑ_{PF_6} = 841, 558 cm^{-1}; δC [(CD$_3$)$_2$CO]: 162.9, 159.2, 143.9, 141.6, 137.8, 136.2, 64.4, 64.2, 59.8, 58.5, 53.4, 52.7, 27.3, 26.8; m.s. (+ve fab) [Cu$_2$L^{3}PF$_6$]$^+$ 799 a.m.u.

2.8. Crystal structure data and determination

Crystal data and experimental conditions for complexes $[Cu_2L^3(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$, $[Cu_2L^4(CH_3CN)_2](PF_6)_2 \cdot 0.64CH_3CN$, and $[Cu_2L^6(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$, are listed in Table 1. The molecular structures are illustrated in Figs. 1, 4 and 5 respectively. Selected bond lengths and bond angles with standard deviations in parentheses are presented in Tables 3, 6 and 7.

For all structures, complex scattering factors were taken from the program package SHELXL93 [14] as implemented on the Viglen 486dx computer.

2.8.1. $[Cu_2L^3(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Siemens P4 diffractometer by the omega scan method. Of the 4219 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 2293 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0593$ ($wR_2 = 0.1731$, for all 2989 data, 540 parameters, mean and maximum and δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.312 and $0.374 e^- Å^{-3}$. Unit weights were used in the latter stages of refinement.

2.8.2. $[Cu_2L^4(CH_3CN)_2](PF_6)_2 \cdot 0.64CH_3CN$

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Siemens P4 diffractometer by the omega scan method. Of the 8710 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 1326 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0611$ ($wR_2 = 0.2243$, for all 6732 data, 560 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.280 and $0.369 e^- Å^{-3}$. Unit weights were used in the latter stages of refinement.

Table 1
Crystal data and structure refinement for $[Cu_2L^3(CH_3CN)_2(PF_6)_2 \cdot CH_3CN$, $[Cu_2L^4(CH_3CN)_2](PF_6)_2 \cdot 0.64CH_3CN$, and $[Cu_2L^6(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$

Empirical formula	$C_{34}H_{51}Cu_2F_{12}N_9P_2S_2$	$C_{41.28}H_{49.92}Cu_2F_{12}N_{8.64}P_2S_2$	$C_{34}H_{51}Cu_2F_{12}N_9P_2S_2$
Formula weight	1066.98	1148.28	1066.98
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	15.897(4)	17.243(5)	13.122(3)
b (Å)	13.329(4)	11.451(6)	13.211(3)
c (Å)	21.999(5)	26.534(8)	13.718(3)
α (deg)	90	90	104.92(3)
β (deg)	90.85(2)	100.08(2)	91.96(3)
γ (deg)	90	90	96.19(3)
Volume (Å³)	4661(2)	5158(4)	2279.8(9)
Z	4	4	2
Density (calc.) (Mg m^{-3})	1.521	1.479	1.554
Absorption coefficient (mm^{-1})	1.155	1.050	1.181
$F(000)$	2184	2344	1092
Crystal size (mm³)	$0.60 \times 0.40 \times 0.22$	$0.65 \times 0.43 \times 0.28$	$0.6 \times 0.3 \times 0.3$
θ range for data collection (deg)	1.79 to 22.50	1.94 to 22.50	1.91 to 25.00
Index ranges	$-1 \leq h \geq 6, -1 \leq k \geq 14,$ $-23 \leq l \geq 23$	$-1 \leq h \geq 18, -1 \leq k \geq 12,$ $-28 \leq l \geq 28$	$-14 \leq h \geq 14, -15 \leq k \geq 15,$ $-14 \leq l \geq -15,$
Reflections collected	4219	8710	9715
Independent reflections	2989 ($R_{int} = 0.0726$)	6732 ($R_{int} = 0.0425$)	6265 ($R_{int} = 0.0495$)
Refinement method		Full matrix least squares on F²	
Data/restraints/parameters	2989/0/540	6732/5/560	6265/1/556
Goodness of fit on F^2	1.046	0.653	0.969
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0593, wR2 = 0.1602$	$R1 = 0.0611, wR2 = 0.1397$	$R1 = 0.0537, wR2 = 0.1300$
R indices (all data)	$R1 = 0.0743, wR2 = 0.1731$	$R1 = 0.3110, wR2 = 0.2243$	$R1 = 0.0765, wR2 = 0.1355$
Largest diff. peak and hole (e$^-$ Å^{-3})	0.374 and -0.312	0.369 and -0.280	1.535 and -0.877

2.8.3. $[Cu_2L^6(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on an Enraf-Nonius FAST area detector. Of the 9715 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 4144 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0537$ ($wR_2 = 0.1355$ for all 6265 unique data, 556 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.877 and $1.535\,e^-\,\text{Å}^{-3}$. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0613P)^2 + 0.00P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement.

2.8.4. Supplementary material

Atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic thermal vibrational parameters, hydrogen atom position parameters and observed structure amplitudes and calculated structure factors have been deposited with the Editor.

## 3. Results and discussion

3.1. Synthesis of a metal-free macrocycle (L^3) bearing t-butyl pendant arms

Schiff base macrocycles derived from the direct cyclocondensation of α,ω-diamines with 2,5-diformylthiophene have previously been reported [15,16]. The analogous reactions between the N,N-bis-(2-aminoethyl)alkylamines, N,N-bis-(2-aminoethyl)-2-phenylethylamine, N,N-bis-(2-aminoethyl)-t-butylamine, and N,N-bis-(2-aminoethyl)-2-methylthioethylamine, and 2,5-diformylthiophene resulted in the isolation of amorphous orange solids. In the corresponding reaction involving N,N-bis-(2-aminoethyl)-t-butylamine, however, recrystallisation of the orange solid from either acetonitrile or acetone resulted in the isolation of a cream coloured compound in a yield of 48%. This product, L^3, was assigned as a macrocycle on the basis that the i.r. spectrum had no peaks corresponding to unreacted amine or carbonyl groups but had a

Table 2
^{1}H nmr and ^{13}C nmr assignments for macrocycle L^3 and complex $[Cu_2L^3CH_3CN)_2](PF_6)_2$
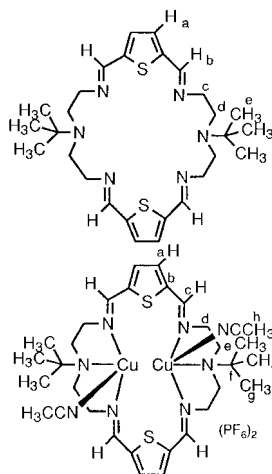
Macrocycle L^3			Complex $Cu_2L^3CH_3CN)_2](PF_6)_2$				
	δH (CDCl$_3$)	Coupling (Hz)		δH (CD$_3$CN)	Coupling (Hz)	δC (CD$_3$)$_2$CO	δC (CD$_3$CN)
a	7.15 (4H,s)		a	7.56 (4H,s)		7.71 (4H,s)	135.5
b	8.18 (4H,d)	$^4J_{bc} = 1$	b	—			143.0
c	3.64 (8H,td)	$^3J_{cd} = 7$	c	8.55 (4H,t)	$^4J_{cd} = 1.2$	8.80 (4H,s)	159.1
d	2.93 (8H,t)		d	3.67 (4H,br)	$^2J_{ee'}, {}^3J_{de'}, {}^3J_{d'e'} = 4$ or 7.5 or 14.5	3.80 (8H,m)	64.3
e	1.10 (18H,s)		d'	3.58 (4H,m)			—
			e	3.21 (4H,br)		3.37 (4H,m)	58.7
			e'	2.47 (4H,ddd)		2.62 (4H,m)	—
			f	—			53.0
			g	1.26 (18H,s)		1.30 (18H,s)	26.7
			h	obscured			2.32 (6H,s)

strong absorption at $1628 \, \text{cm}^{-1}$ corresponding to an imine bond and that the highest peak in the FAB mass spectrum at 526 a.m.u. corresponded to a '2 + 2' cyclocondensation product. A satisfactory elemental analysis was also obtained.

Although the macrocycle L^3 was only slightly soluble in most organic solvents at room temperature, it was possible to record a ^{1}H nmr spectrum in $CDCl_3$ (Table 2). Interestingly, four bond coupling is observed between the imine protons and the protons H_c, allowing their assignment as the protons adjacent to the imine nitrogen. No geminal coupling is observed between the protons in the environments H_c or in H_d. This suggests that the macrocycle is conformationally flexible in solution, so that averaged chemical environments are seen for both protons in these two environments.

The formation of L^3 is attributed to a combination of factors. Firstly the bulky t-butyl pendant group restricts rotation about the tertiary amine limiting intermolecular polymerisation [17]. Secondly, due to the restricted rotation about the tertiary amine, the loss of internal entropy upon cyclisation is small, favouring the occurrence of cyclisation [18]. Condensation of N,N-bis-(2-aminoethyl)-t-butylamine with 2,5-diformylfuran or 2,6-diformylpyridine, however, resulted in only polymeric products, suggesting that another significant factor is the ability of 2,5-diformylthiophene to adopt a conformation in solution favourable for macrocycle formation thus effecting conformational control of the reaction [19]. It has been shown, by dipole moment studies in solution and nmr studies on the liquid crystalline phase, that 2,5-diformylthiophene adopts a predominantly cis–cis conformation, whilst 2,5-diformylfuran and 2,6-diformylpyridine are in predominantly cis–trans and trans–trans conformations respectively [20–24]. The cis–cis conformer could lead directly to cyclocondensation whereas for the cis–trans and trans–trans conformers a modified reaction, using a template, would be required.

3.2. Complexation of macrocycle L^3 with tetrakis(acetonitrile) copper(I) hexafluorophosphate

Addition of tetrakis(acetonitrile) copper(I) hexafluorophosphate to a suspension of macrocycle L^3 in either acetonitrile or methanol produced an immediate red coloration, indicating complexation, the product was then precipitated from solution, as a red powder, by the addition of diethyl ether.

Changes in the i.r. spectrum of the red product, when compared to that of the free macrocycle, confirmed that complexation had occurred. A lowering of the imine band from $1628 \, \text{cm}^{-1}$ to $1622 \, \text{cm}^{-1}$ was observed together with the appearance of bands at 841 and $558 \, \text{cm}^{-1}$ attributable to the hexafluorophosphate anions. The dinuclear nature of the product was confirmed by the highest peak in the FAB$^+$ mass spectrum at 799 a.m.u. corresponding to $[Cu_2L^3PF_6]^+$ and the formulation of the complex as $[Cu_2L^3(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$ was confirmed by elemental analysis.

Although a direct comparison is not possible due to solubility differences necessitating the use of different nmr solvents, the ^{1}H nmr spectrum of the dicopper(I) complex of L^3 nevertheless differs significantly from the spectrum of the free macrocycle (Table 2). It can be seen though that in the complex the pairs of ring protons at positions d and e are no longer equivalent, resulting in four distinct environments. The appearance of one signal of each pair as a broad signal and one as a more resolved signal suggests that the broadening originates from quadrupolar effects associated with the amine and imine nitrogen atoms, rather than from environmental exchange processes. The precise assignment of the coupling constants is prevented since only one signal $H_{e'}$ was completely resolved. The coupling relationships between the four ring protons can be clearly shown in a COSY spectrum of the complex. The spectrum when recorded in acetone allows the assignment of the signal at ca. 2.32 corresponding to the coordinated acetonitrile molecules (this signal is obscured by the water signal when the nmr is recorded in acetonitrile).

Recrystallisation of the complex $[Cu_2L^3(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$ from acetonitrile and diethyl ether at room temperature gave red crystalline blocks suitable for study by X-ray crystallography. The molecular structure is illustrated in Fig. 1. It can be seen that each copper(I) ion is in an approximately tetrahedral environment being coordinating to one tertiary amino- and two imino-nitrogen atoms originating from the macrocyclic ring with the fourth coordination site occupied by the nitrogen of an acetonitrile molecule. The bond distances and bond angles for these interactions are shown in Table 3. There is a further acetonitrile of solvation present in the molecule.

It can be seen that the macrocycle, although reasonably twisted, has not folded to adopt a molecular cleft and consequently the copper–copper separation is quite

Table 3
Selected bond distances and bond angles in the complex $[Cu_2L^3(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$

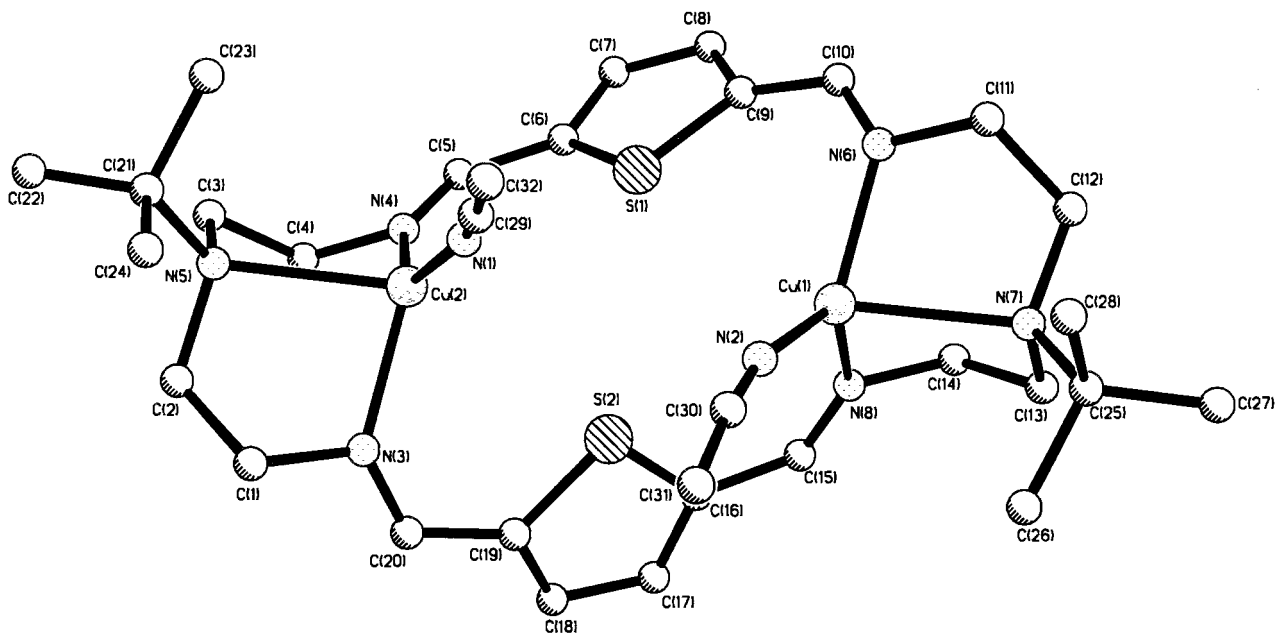| Bond lengths (Å)		N–Cu–N bond angles (deg)		
Cu(1)–N(2)	1.911(10)	123.8(3)	113.4(4)	125.6(3)
Cu(1)–N(6)	2.029(10)		80.5(4)	109.5(3)
Cu(1)–N(8)	2.024(6)			83.4(3)
Cu(1)–N(7)	2.322(9)			
		N(6)	N(7)	N(8)
Cu(2)–N(1)	1.921(10)	111.3(4)	137.4(3)	111.3(3)
Cu(2)–N(3)	2.054 8		110.4(3)	81.6(3)
Cu(2)–N(4)	1.984(11)			83.3(4)
		N(3)	N(4)	N(5)
Cu(1)…Cu(2)	5.201			

Fig. 1. Molecular structure of the dication $[Cu_2L^3(CH_3CN)_2]^{2+}$.

large. Steric repulsions cause the coordinated aceto-nitrile molecules to be oriented away from each other and contribute to the large copper–copper separation. Another contributing factor is demonstrated by comparison with disilver(I) complexes of bibracchial tetraimine Schiff base macrocycles containing pyridyl head units and bearing pendant arms capable of coordinating to the metal [2,25]. In these complexes it can be seen that when the silver ions share a bridging imino nitrogen the macrocycle adopts a molecular cleft. In contrast, in a related disilver macrocyclic complex with a non-coordinating pendant arm the absence of such a bridge leads to a more open conformation [3]. It is likely that in the complex $[Cu_2L^3(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$ the absence of a shared bridging group also contributes to the more open conformation observed.

3.3. Lead(II) templated reactions between the N,N-bis-(2-aminoethyl) alkylamines and 2,5-diformylthiophene

As a consequence of problems encountered in attempts to transmetallate disilver(I) complexes of macrocycles L^3-L^6 [11], it was decided that a templating ion electrochemically inert with respect to copper(I) ions should be used. Although barium(II) ions have previously been found to template the formation of 24-membered pendant arm macrocycles [1,2], they were found to be ineffective in the present reactions. This could be due to barium ions being 'hard' in character, whereas the 2,5-diformylthiophene is a fairly 'soft' ligand and consequently coordination between the two is disfavoured. Lead(II) ions have also previously been shown to template the formation of 24-membered macrocycles

[26]; furthermore, lead(II) ions are much 'softer' and therefore more amenable to coordination to 2,5-diformylthiophene.

The reactions with lead(II) salts were performed in a similar manner to the silver(I) templated reactions reported previously [11], but larger volumes of solvents were required due to solubility problems being encountered with the lead(II) salts. The products usually precipitated from the reaction mixture after between 1 and 2 h, and the more soluble products were collected after the reactions had been allowed to cool overnight. The compounds were characterised by the presence of strong imine and anion bands in their i.r. spectra. Unfortunately, when lead(II) thiocyanate was used the products were too insoluble to allow recrystallisation and so totally satisfactory elemental analyses were not obtained; similarly, the products were insufficiently soluble in the matrices used to perform fab$^+$ mass spectroscopy.

When oxyanions, such as nitrate or hexafluoroacetylacetonate, were employed then the lead(II) macrocyclic complexes formed were more soluble, allowing their recrystallisation and full characterisation. The fab$^+$ mass spectra were recorded and confirmed the '2 + 2' nature of the products [peaks corresponding to $[PbLX]^+$ were found at 892 (L^4; NO_3); 1037 (L^4; hfac); 977 (L^5; hfac); 796 (L^6; NO_3)].

Study of the complexes by nmr spectroscopy was hindered by the poor solubility of the compounds; consequently, the highly coordinating solvent deutero-dimethylsulphoxide had to be used. The ^{1}H nmr spectrum of the complex $Pb_2L^4(NO_3)_4$ (Table 4) is representative of the spectra of the lead complexes. The signals in the

Table 4
^{1}H((CD$_3$)$_2$SO) nmr assignments for Pb$_2$L^4(NO$_3$)$_4$
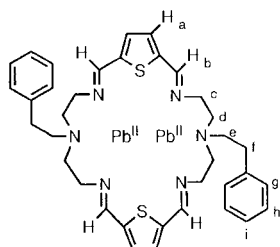
Proton	δ H (ppm)
a	8.24^a, 8.10^b, 8.12^b, 8.06^c (4H,s)
b	7.30^a, 7.28^b, 7.27^b, 7.26^c (4H,s)
c	3.52 (8H,br)
d	2.72 (16H,m)
e	
f	
g	7.16 (10H,m)
h	
i	

^{a} Pb$_2$L^4(NO$_3$)$_4$.
^{b} Pb$_1$L^4(NO$_3$)$_2$.
^{c} Free L^2.

aliphatic region are poorly resolved, while the phenyl, thiophene and imine protons are much better resolved. The imine proton gives rise to four separate signals, which have been shown by a COSY experiment not to arise from coupling with other protons. However, their appearance may be explained in terms of demetallation in the dimethylsulphoxide solvent. It has previously been reported that ^{1}H nmr spectra recorded in dimethylsulphoxide for certain metal complexes of macrocycles [27] and cryptands [28] showed signals attributable to both the metal complex and the free ligand; it appears that the dimethylsulphoxide coordinates more strongly to the metal than the macrocycle [28]. In the light of these observations it is proposed that of the four signals seen for the imine in Pb$_2$L^4(NO$_3$)$_4$ one arises from the dinuclear macrocyclic complex, two from the unsymmetrical mononuclear complex and one from the free macrocycle. From the integrations it can be estimated that the ratios in dimethylsulphoxide are approximately 2:1:1 (dinuclear complex:mononuclear complex:free macrocycle).

3.4. Transmetallation of the dilead pendant arm macrocycles with copper(I) hexafluorophosphate

The initial transmetallation reactions investigated involved the complexes Pb$_2$L^4(SCN)$_4$ and Pb$_2$L^5(SCN)$_4$ (Fig. 2). These reactions were performed, in a nitrogen

atmosphere, by suspending the appropriate lead macrocycle in either acetonitrile or methanol and then adding two equivalents of tetrakis(acetonitrile) copper(I) hexafluorophosphate.

The integrity of the macrocycles in the products was confirmed through the i.r. spectra and the presence of bands at ca. 1620 cm^{-1}, corresponding to an imine bond; no bands attributable to amine or carbonyl decomposition products were observed. Bands at ca. 840 and 560 cm^{-1} were assigned to the hexafluorophosphate anion and for the complex of macrocycle L^4 a band at 2119 cm^{-1}, corresponding to a thiocyanate anion, was also present. Nelson and Esho have reported a dicopper(I) complex, of macrocycle L^7, containing S-bridging thiocyanate [29]; comparison of the bands in the i.r. spectrum of Cu$_2$L^7(SCN)$_2$ (2105 cm^{-1}) and Cu$_2$L^4(SCN)(PF$_6$) (2119 cm^{-1}) suggests that a similar coordination mode is present in the latter.
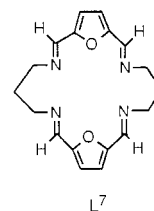
In Cu$_2$L^7(SCN)$_2$ two thiocyanate ions bridge the copper(I) ions to give tetrahedral geometry at each metal. Only one thiocyanate ion is present in the complex Cu$_2$L^4(SCN)(PF$_6$) and, by analogy with the crystal structure of [Cu$_2$L^3(CH$_3$CN)$_2$](PF$_6$)$_2 \cdot$CH$_3$CN, the ligand donors about the copper(I) ions are probably one tertiary amine nitrogen atom and two imine nitrogen atoms. The sulphur of a bridging thiocyanate anion can then occupy the remaining coordination sites on each metal. No thiocyanate anion is retained in the complex Cu$_2$L^5(PF$_6$)$_2$ and so it is likely in this complex that the sulphur donor atoms present in the pendant arms of the macrocycle occupy the fourth sites in the coordination
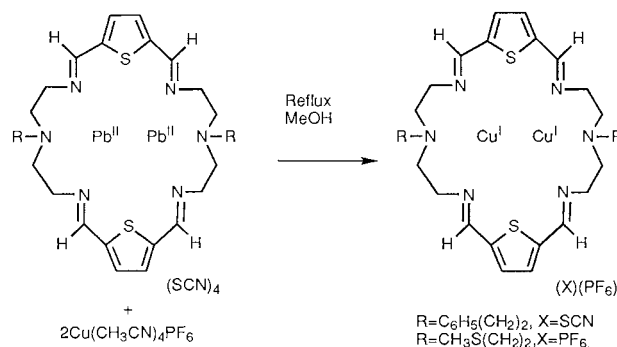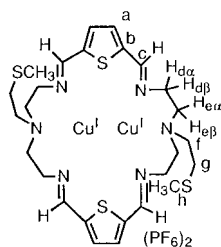

Fig. 2. Transmetallation reaction involving copper(I) hexafluorophosphate.

spheres of the copper(I) ions. Frustratingly, neither of the two complexes afforded crystals suitable for study by X-ray crystallography to support these proposals.

The mass spectra of the complexes confirmed that they were dinuclear copper(I) complexes and supported the presence of thiocyanate in the complex of macrocycle L^4. Finally, the complexes were characterised by satisfactory elemental analysis as $Cu_2L^4(SCN)(PF_6)$ and $Cu_2L^5(PF_6)_2$.

The ^1H nmr spectrum of $Cu_2L^4(SCN)(PF_6)$ is poorly resolved at room temperature, whereas the spectrum of $Cu_2L^5(PF_6)_2$ is clearly resolved, when recorded at 400 MHz. This suggests that the complex $Cu_2L^5(PF_6)_2$ maintains a high degree of rigidity in solution. Through the combination of COSY, C–H correlation and decoupling experiments the spectrum may be analysed (Table 5). The imine proton H_c exhibits four bond coupling to the protons at $H_{d\alpha}$ and $H_{d\beta}$ and consequently appears as an overlapping doublet of doublets. Decoupling at either $H_{d\alpha}$ or $H_{d\beta}$ causes the signal to collapse to a doublet with a coupling constant of 1.25 Hz. The methylene ring protons at $H_{d\alpha}$ and $H_{d\beta}$ are split into two separate signals showing them to be magnetically inequivalent; a similar situation arises for the protons $H_{e\alpha}$ and $H_{e\beta}$. If the imine proton H_c is decoupled then both $H_{d\alpha}$ and $H_{d\beta}$ clearly display a ddd splitting pattern of eight signals. The coordination of the sulphur pendant group is demonstrated by a downfield shift for the signal from the methyl of the thiomethyl group, when the signal for the complex is compared to the analogous signal in the free amine. For example $\delta H(CD_3CN) 2.05$ shifts to 2.35 ppm and $\delta C(CD_3CN) 15.69$ shifts to 17.72 ppm.
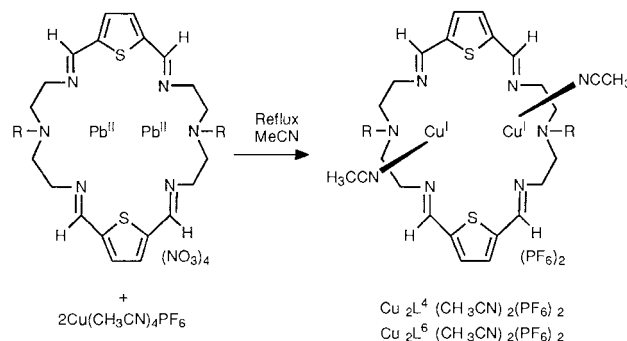

Fig. 3. Transmetallation reactions of $Pb_2L^4(NO_3)_4$ and $Pb_2L^6(NO_3)_4$.

Transmetallation of the complexes $Pb_2L^4(NO_3)_4$ and $Pb_2L^6(NO_3)_4$ with tetrakis(acetonitrile) copper(I) hexafluorophosphate was investigated with the aim of forming further dicopper(I) macrocycles without a coordinating anion or a donor atom present in the pendant arm. The reactions were performed in an analogous manner to the previous two transmetallation reactions and red-coloured complexes were formed (Fig. 3).

The integrity of the macrocycles was confirmed by the retention in the i.r. spectra of a peak corresponding to an imine bond; no bands attributable to either amine or carbonyl groups, were observed. The mass spectra of the complexes showed peaks at $[Cu_2LPF_6]^+$ (L^4; 899, L^6; 799).

Recrystallisation of the complex $[Cu_2L^4CH_3-CN)_2](PF_6)_2$ from acetonitrile and diethyl ether with cooling at 0 °C produced crystals suitable for study by X-ray crystallography. The structure is illustrated in Fig. 4 with selected bond lengths and angles given in Table 6. It is similar to that of $[Cu_2L^3(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$ with each copper(I) ion in a distorted tetrahedral environment composed of one two imine nitrogen nitrogen atoms and one tertiary amine nitrogen atom from the ligand and a nitrogen atom from a molecule of acetonitrile. The copper–copper separation is again relatively large, 5.386 Å. The phenyl ethyl pendant arms are oriented upon the same side of the macrocycle and the macrocycle again is not folded. There is an acetonitrile molecule with a partial occupancy of 64% present in the complex.

The recrystallisation of $[Cu_2L^6(CH_3CN)_2](PF6)_2$ resulted in the deposition of a very small quantity of crystals. The crystal structure was obtained, by collecting the data at low temperature; unfortunately, too little pure compound then remained for an elemental analysis to be performed. The structure of $[Cu_2L^6(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$ (Fig. 5) reveals that the two copper(I) ions are again in distorted tetrahedral environments composed of two imine nitrogen atoms, one tertiary amine nitrogen atom and one acetonitrile nitrogen atom (Table 7). The copper–copper separation
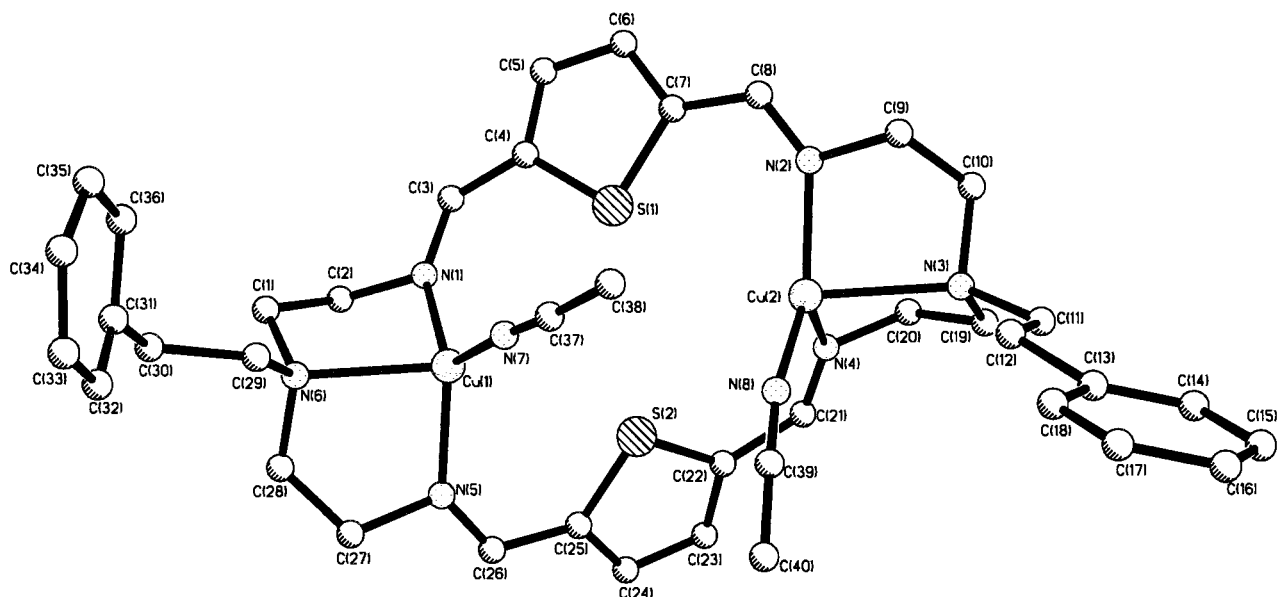
Table 5
^1H (CD_3CN) and ^{13}C (CD_3CN) assignments for $Cu_2L^5(PF_6)_2$

Atom	δC	δH	Coupling constant (Hz)
a	144.0	8.91 (4H,dd)	
b	137.0	—	
c	160.0	7.81 (4H,s)	$^4J H_c - H_{d\alpha} \vee H_{d\beta} = 1.25$
dα	62.7	4.12 (4H,m)	$^2J H_{d\alpha} - H_{d\beta} \approx 13.5$
dβ		3.93 (4H,m)	$^3J H_{d\alpha} - H_{e\alpha} = 7$
eα	54.4	3.26 (4R,ddd)	$^3J H_{d\alpha} - H_{e\beta} = 4$
eβ		3.10 (4H,ddd)	$^3J H_{d\beta} - H_{e\alpha} = 4.5$
f	49.6	3.17 (4H,dd)	$^3J H_{d\beta} - H_{e\beta} \approx 7.5$
g	38.0	3.04 (4H,dd)	$^2J H_{e\alpha} - H_{e\beta} = 13.5$
h	17.7	2.35 (6H,s)	

Fig. 4. Molecular structure of the dication $[Cu_2L^4CH_3CN)_2]^{2+}$.

is 5.215 Å and the two acetonitrile molecules are again oriented away from each other. The *n*-butyl pendant arm groups are oriented on the same side of the macro-cyclic ring. The conformation of the macrocycle, although possibly more twisted than $[Cu_2L^3(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$, is still not folded
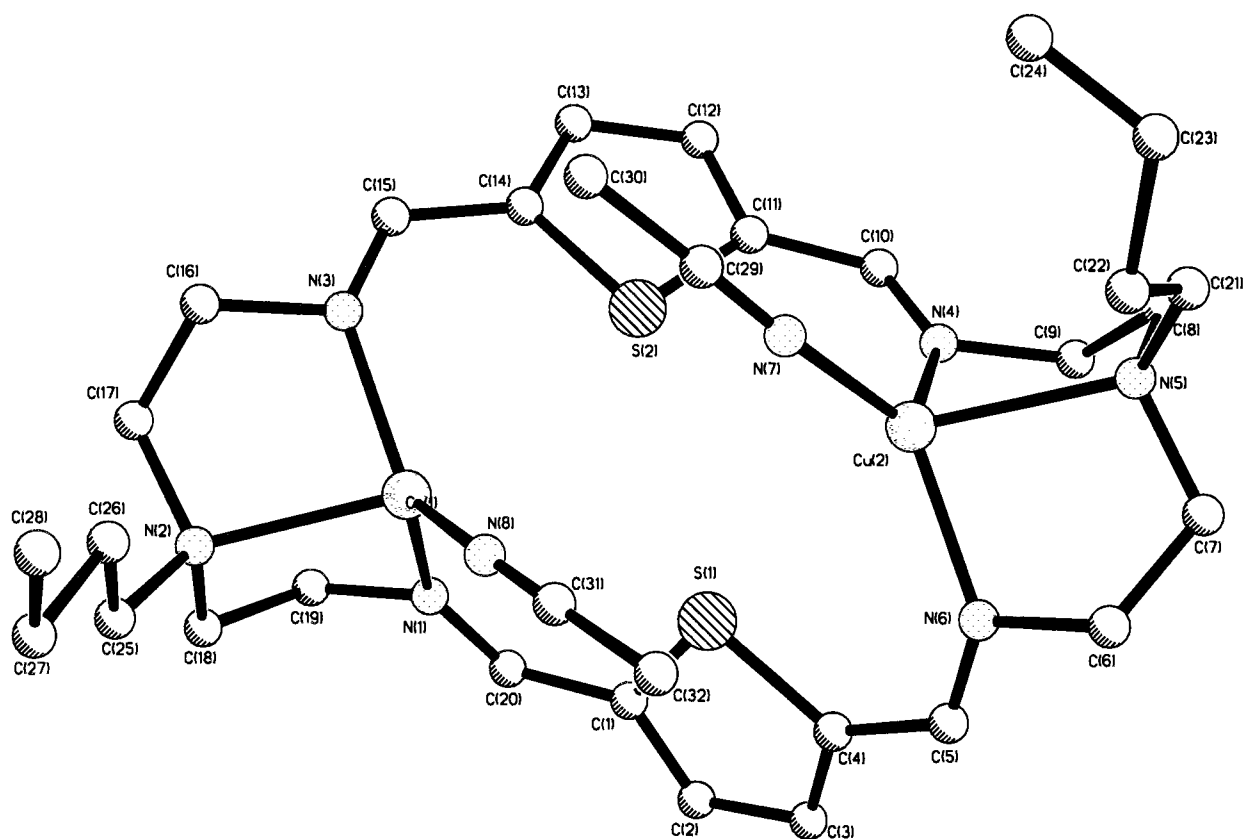
Fig. 5. Molecular structure of the dication $[Cu_2L^6(CH_3CN)_2]^{2+}$.

Table 6
Selected bond lengths and angles for $[Cu_2L^4(CH_3CN)_2](PF_6)_2 \cdot 0.64CH_3CN$

Bond lengths (Å)		Bond angles (deg)		
Cu(1)–N(1)	1.99(2)	119.9(6)	83.3(7)	121.5(7)
Cu(1)–N(5)	1.99(2)	84.1(7)		117.3(6)
Cu(1)–N(6)	2.25(2)			114.0(7)
Cu(1)–N(7)	1.895(14)			
		N(5)	N(6)	N(7)
Cu(2)–N(2)	1.98(2)	84.7(7)	117.8(7)	131.3(7)
Cu(2)–N(3)	2.277(12)		83.1(6)	105.2(6)
Cu(2)–N(4)	2.038(14)			110.8(6)
Cu(2)–N(8)	1.89(2)			
		N(3)	N(4)	N(8)
Cu(1)...Cu(2)	5.386			

into a deep molecular cleft. There is a further aceto-nitrile of solvation present in the molecule.

In each of the complexes the Cu–N$_{imine}$ bonds (ca. 2.0 Å) are shorter than the Cu–N$_{amine}$ bonds (ca. 2.3 Å). The Cu–N$_{acetonitrile}$ are the shortest interactions at ca. 1.9 Å, suggesting that the solvent is tightly bound.

The ^{1}H nmr spectra of the two complexes $[Cu_2L^4(CH_3CN)_2](PF_6)_2$ and $[Cu_2L^6(CH_3CN)_2](PF_6)_2$ showed resolved signals for the imine, thiophene and some of the protons of the pendant arm groups. However, as was seen for the corresponding disilver complexes, the methylene ring protons are broad in appearance. The signals of the protons at f and g overlap with the signals of the protons at e (Table 8). The broadening of the spectra arises due to the macrocycles having a reasonable degree of conformational flexibility in solution. Such flexibility probably occurs due to similar reasons as those discussed earlier for the complex $[Ag_2L^3(NO_3)](PF_6)$ [11].

3.5. The reactivity of the dicopper(I) macrocycles

Under a nitrogen atmosphere all the copper(I) macrocycles are relatively stable as solutions in acetone, acetonitrile or methanol. Kitajima et al. have characterised the complex $Cu[(CH_3)_2CO][HB(3,5-Ph_2pz)_3]$ $[HB(3,5-Ph_2pz)_3 =$ hydridotris(3,5-diphenyl-1-pyrazol-yl)borate] [30] which contains an acetone molecule coordinated to a copper(I) ion. However, no competitive coordination was observed with the acetonitrile molecules in the complexes $[Cu_2L^n(CH_3CN)_2](PF_6)_2$ ($n = 3,4,6$) during nmr experiments involving acetone as the solvent.
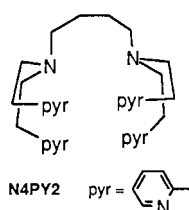
The exposure of samples of the complexes $[Cu_2L^{3-6}(CH_3CN)_2](PF_6)_2$ to dioxygen or the air at room temperature resulted in no reaction. Such inertness is in contrast to the findings of Karlin et al. for the complex $[Cu_2(N4PY2)(CH_3CN)_2](ClO_4)_2$ derived from an acyclic polypodal ligand, where the peroxide adduct was formed at $-85°C$ in dichloromethane [31]. The macrocyclic complex $[Cu_2L^7(MeCN)_2](BPh_4)_2$, prepared by Nelson et al. was also found to react with oxygen, in this case to form what was proposed as a μ-oxo dimer [32]. In the macrocyclic complex $[Cu_2L^7(MeCN)_2](BPh_4)_2$ the intermetallic separation is 3.35 Å and the copper(I) atoms are three-coordinate and so coordinatively unsaturated. In $[Cu_2(N4PY2)(CH_3CN)_2](ClO_4)_2$ the separation found in the solid state is 7.449(2) Å but the flexible nature of the ligand could allow a much shorter separation to be achieved in solution. The copper atoms are four coordinate but the open nature of the complex would allow easy access and removal of the coordinated solvent. The relatively large copper–copper separations in the complexes $[Cu_2L^n(CH_3CN)_2(PF_6)_2]$ ($n = 3,4,6$) of 5.201, 5.386 and 5.214 Å, together with the coordinative saturation of the metal ions, appear to confer stability with respect to oxidation on these complexes.
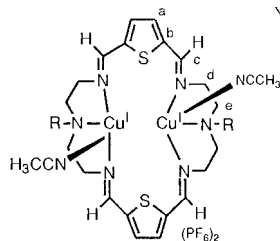
Attempts at performing the oxidations with hydrogen peroxide, resulted in oxidation of the copper(I) ions to copper(II), inferred by a colour change from red to green/brown. This was combined with decomposition of the macrocycles resulting in the isolation of uncharacterisable products. Difficulties encountered in attempting to form a copper(II) complex of L^4 via the transmetallation of Ag$_2$L^4(BF$_4)_2$ and Pb$_2$L^4(NO$_3)_4$ with copper(II) salts suggested that L^4 cannot adequately coordinate copper(II) ions and this would also contribute to the problems encountered when trying to oxidise the dicopper(I) macrocycles $[Cu_2L^{3-6}-(CH_3CN)_2](PF_6)_2$.
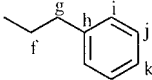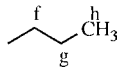
Karlin et al. have determined that the binding strengths of acetonitrile, carbon monoxide and triph-

N4PY2   pyr =

Table 7
Selected bond lengths and angles for $[Cu_2L^6(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$

Bond lengths (Å)		Bond angles (deg)		
Cu(1)–N(1)	2.051(5)	83.9(2)	113.0(2)	121.3(2)
Cu(1)–N(2)	2.246(5)		83.8(2)	114.2(2)
Cu(1)–N(3)	2.034(4)			123.8(2)
Cu(1)–N(8)	1.920(5)			
		N(2)	N(3)	N(8)
Cu(2)–N(4)	2.035(5)	83.3(2)	114.2(2)	118.2(2)
Cu(2)–N(5)	2.261(5)		82.7(2)	115.1(2)
Cu(2)–N(6)	2.024(5)			125.9(2)
Cu(2)–N(7)	1.940(5)			
		N(5)	N(6)	N(7)
Cu(1)...Cu(2)	5.215			

Table 8
^{1}H and ^{13}C nmr assignments for $[Cu_2L^4(CH_3CN)_2](PF_6)_2$ and $[Cu_2L^6(CH_3CN)_2](PF_6)_2$

|	$[Cu_2L^4(CH_3CN)_2](PF_6)_2$		$[Cu_2L^6(CH_3CN)_2](PF_6)_2$	
	δ H (CD$_3$CN)	δ C (CD$_3$CN)	δ H (CD$_3$CN)	δ C (CD$_3$CN)
a	8.61 (4H,s)	136.10	8.59 (4H,s)	135.95
b	—	143.23	—	143.18
c	7.11 (4H,s)	159.30	7.56 (4H,s)	159.09
d	3.73 (8H,mbr)	62.44	3.65 (8H,mbr)	62.37
e		59.17	2.85 (8H,mbr)	57.45
f	2.95 (16H,mbr)	55.19	2.73 (4H,mbr)	55.29
g		32.07	1.60 (4H,m)	27.89
h		143.23	1.31 (4H,m)	21.43
i		129.78	0.93 (6H,t)	14.27
j	7.27 (10H,m)	129.56		
k		127.21		

enylphosphine to the copper(I) ions in the complex $Cu_2(N4PY2)(ClO_4)_2$ lie in the order acetonitrile < carbon monoxide < triphenylphosphine [31]. In this work no reaction was found to occur between $[Cu_2L^3(CH_3CN)_2](PF_6)_2$ and triphenylphosphine, and the starting materials were recovered unchanged. This is attributed to steric interactions between the bulky triphenylphosphine, the macrocyclic ring and the pendant arms preventing coordination to the copper(I) ions. Carbon monoxide is much less sterically demanding than triphenyl phosphine and therefore its reactivity with $[Cu_2L^3(CH_3CN)_2](PF_6)_2$ was investigated. The macrocycle L^3 was suspended in methanol, to which was added tetrakis(acetonitrile) copper(I) hexafluorophosphate. After stirring for several minutes the solution had attained a deep red colour and no undissolved macrocycle remained, indicating the complex $[Cu_2L^3(CH_3CN)_2](PF_6)_2$ had been formed. The apparatus was then evacuated and filled with carbon monoxide several times. After stirring for a further 5 min, the solution changed from deep red to a very pale yellow colour, suggesting that a reaction such as exchange of the acetonitrile molecule at the copper atoms for carbon monoxide had taken place. Careful addition of diethyl ether (saturated prior to use with carbon monoxide) resulted in the precipitation of a cream powder, the i.r. spectrum of which showed bands corresponding to an imine (ca. 1625 cm^{-1}) and the hexafluorophosphate anion (at 841 and 558 cm^{-1}). A strong band at 2091 cm^{-1} corresponding to a coordinated carbon

monoxide was noted together with a very weak band at 2344 cm^{-1} attributed to a coordinated acetonitrile molecule. The mass spectrum of the product gave the same breakdown pattern as the starting complex and the elemental analysis was not satisfactory for $[Cu_2L^3(CO)_2](PF_6)_2$.

I : $R_1=R_2=CH_3CN$
II : $R_1=CO$, $R_2=CH_3CN$
III: $R_1=R_2=CO$.
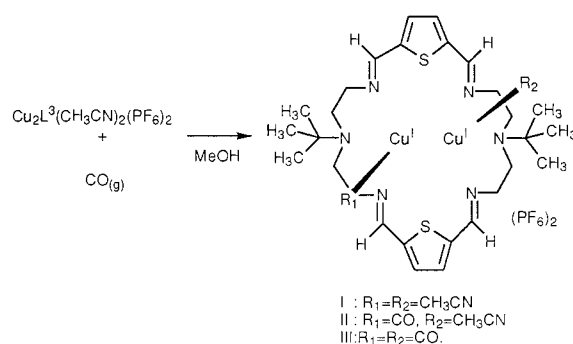
On dissolving the product in deuteroacetone under dinitrogen a pale red solution is obtained. The ^{1}H nmr spectra of this solution may be interpreted as arising from the presence of three species corresponding to $[Cu_2L^3(CH_3CN)_2](PF_6)_2$ (I), $[Cu_2L^3(CH_3CN)(CO)](PF_6)_2$ (II) and $[Cu_2L^3(CO)_2](PF_6)_2$ (III) (Table 9). In the imine region of the spectrum complexes I and III each give rise to one signal; complex II exhibits two signals corresponding to imines coordinated to two different types of copper(I) ion—one copper coordi-

Table 9
[1]H and ^{13}C assignments for the reaction of $[Cu_2L^3(CH_3CN)_2(PF_6)_2]$ with carbon monoxide
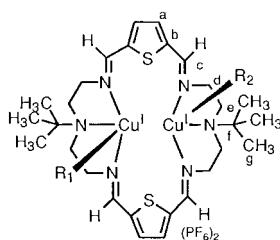
I : $R_1=R_2=CH_3CN$
II : $R_1=CO, R_2=CH_3CN$
III: $R_1=R_2=CO.$

	$\delta H[(CD_3)_2CO]$	$\delta C[(CD_3)_2CO]^{II}$
a	7.71^I, 7.78^{II}, 7.81^{II}, 7.87^{III}	136.2, 137.8
b	—	141.6, 143.9
c	8.80^I, 8.84^{II}, 8.99^{II}, 9.04^{III}	159.2, 162.9
d	3.41, 3.87	64.2, 64.4
e	2.69	58.5, 59.8
f	—	52.7, 53.4
g	$1.30^{I\&II}$, 1.38^{II}, 1.42^{III}	26.8, 27.3
CH_3CN	2.39	2.5, 118.7

nated to a carbon monoxide and one coordinated to an acetonitrile. In the thiophene region complexes I and III each give rise to one signal; complex II exhibits an AB system ($^3J_{AB} = 4 Hz$) indicating that the imines on either side of the thiophene ring are coordinated to copper(I) ions having different chemical environments. From the integrations of the imine and thiophene signals it can be estimated that the ratios of the complexes are approximately 1:1.75:5.2 (complex III:complex I:complex II).

The exchange of acetonitrile molecules for carbon monoxide at the copper(I) ions in the complex $[Cu_2L^3(CH_3CN)_2(PF_6)_2]$ is therefore possible. Unfortunately though, the exchange process appears to be an equilibrium which can easily revert back to the initial complex or to a mixed complex with one copper ion coordinated to an acetonitrile molecule and one coordinated to a carbon monoxide. Karlin et al. have reported similar difficulties during attempts to isolate $[Cu_2(XYL-O^-)(CO)_2(PF_6)_2$, where even under 1 atm of carbon monoxide the complex $Cu_2(XYL-O^-)(PF_6)_2$ was isolated [33].
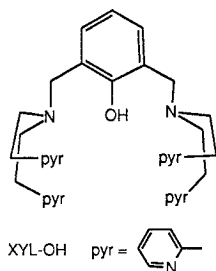
References

[1] D.E. Fenton, G. Rossi, Inorg. Chim. Acta 98 (1985) L29.
[2] H. Adams, N.A. Bailey, W.D. Carlisle, D.E. Fenton, G. Rossi, J. Chem. Soc. Dalton Trans., (1990) 1271.
[3] H. Adams, N.A. Bailey, D.E. Fenton, C. Fukuhara, P.C. Hellier, P.D. Hempstead, J. Chem. Soc. Dalton Trans., (1992) 729.
[4] D.E. Fenton, P.C. Hellier, Inorg. Chim Acta., 198–200 (1992) 577.
[5] N.A. Bailey, D.E. Fenton, P.C. Hellier, P.D. Hempstead, U. Casellato, P.A. Vigato, J. Chem. Soc. Dalton Trans., (1992) 2809.
[6] H. Adams, N.A. Bailey, M.J.S. Dwyer, D.E. Fenton, P.C. Hellier, P.D. Hempstead, J.-M. Latour, J. Chem. Soc. Dalton Trans., (1993) 1207.
[7] N.A. Bailey, C.O. Rodriguez de Barbarin, D.E. Fenton, P.C. Hellier, P.D. Hempstead, M. Kanesato, P.B. Leeson, J. Chem. Soc. Dalton Trans., (1995) 765.
[8] S.R. Collinson, D.E. Fenton, Coord. Chem. Rev. 48 (1996) 19.
[9] H. Adams, N.A. Bailey, N. Debaecker, D.E. Fenton, W. Kanda, J.-M. Latour, H. Okawa, H. Sakiyama, Angew. Chem. Int. Edn. Engl. 34 (1995) 2535.
[10] H. Adams, N.A. Bailey, S.R. Collinson, D.E. Fenton, C.J. Harding, S.J. Kitchen, Inorg. Chim. Acta 246 (1996) 81.
[11] H. Adams, N.A. Bailey, P. Bertrand, S.R. Collinson, D.E. Fenton, S.J. Kitchen, Inorg. Chim. Acta 250 (1996) 139.
[12] D.J. Chadwick, C. Wilbe, J. Chem. Soc. Perkin Trans. 1:, (1977) 887.
[13] G.J. Kubas, Inorg. Synth. 19 (1979) 90.
[14] G.M. Sheldrick, SHELXL 93, An Integrated System for Solving and Refining Crystal Structures from Diffraction Data, University of Göttingen, Germany, 1993.
[15] N.A. Bailey, M.M. Eddy, D.E. Fenton, G. Jones, S. Moss, A. Mukhapadhyay, J. Chem. Soc. Chem. Commun., (1981) 628.
[16] N.A. Bailey, M.M. Eddy, D.E. Fenton, S. Moss, A. Mukhopadhay, J. Chem. Soc. Dalton Trans., (1984) 2281.
[17] J.E. Richman, T.J. Atkins, J. Am. Chem. Soc. 96 (1974) 2268.
[18] B.L. Shaw, J. Am. Chem. Soc. 97 (1975) 3856.
[19] D.E. Fenton, R. Moody, J. Chem. Soc. Dalton Trans., (1987) 219.
[20] L. Lunazzi, G.F. Pedulli, M. Tiecco, C. Vincenzi, C.A. Veraani, J. Chem. Soc. Perkin Trans. 2:, (1972) 751.
[21] L. Lunazzi, G.F. Pedulli, M. Tiecco, C. Veracini, J. Chem. Soc. Perkin Trans. 2:, (1972) 755.
[22] T.N. Huckerby, Tetrahedron Lett., (1971) 3497.
[23] P. Bucci, C.A. Verancini, M. Longeri, Chem. Phys. Lett. 15 (1972) 396.
[24] P.L. Barli, M. Longeri, L.A. Veracini, Mol. Phys. 28 (1974) 1101.
[25] P.D. Hellier, Ph.D. Thesis, University of Sheffield, 1991.
[26] B.P. Murphy, J. Nelson, S.M. Nelson, M.G.B. Drew, P.C. Yates, J. Chem. Soc. Dalton Trans., (1987) 123.
[27] K.K. Abid, D.E. Fenton, Inorg. Chim. Acta 82 (1984) 223.

[28] T. Sato, K. Sakai, T. Tsubomura, Chem. Lett., (1993) 859.

[29] S.M. Nelson, F.S. Esho, J. Chem. Soc. Chem. Commun., (1981) 388.

[30] N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, Chem. Lett., (1989) 421.

[31] K.D. Karlin, M.S. Haka, R.W. Cruse, O.J. Meyer, A. Farooq, Y. Gultneh, J.C. Hayes, J. Zubieta, J. Am. Chem. Soc. 110 (1988) 1196.

[32] S.M. Nelson, F. Esho, A. Lavery, M.G.B. Drew, J. Am. Chem. Soc. 105 (1983) 5693.

[33] K.D. Karlin, R.W. Cruse, Y. Gultneh, A. Farooq, J.C. Hayes, J. Zubieta, J. Am. Chem. Soc. 109 (1987) 2668.