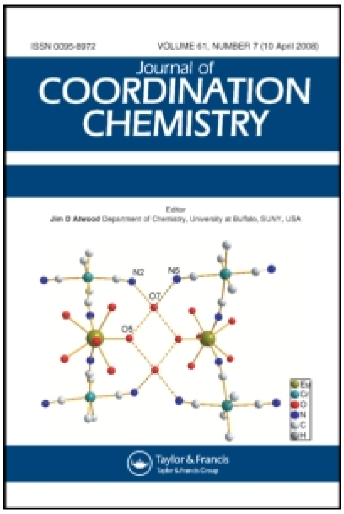

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Studies on the Metal Amide Bond 21. Metal Complexes of Chiral Phenyl-Substituted Bis-Picolinamide Tetradentates

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STUDIES ON THE METAL AMIDE BOND 21.* METAL COMPLEXES OF CHIRAL PHENYL-SUBSTITUTED BIS-PICOLINAMIDE TETRADENTATES.

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Two new *C*-phenyl bis-picolinamide tetradentates, *N,N'*-bis(2-pyridinecarboxamide)-1,2-diphenylethane (bpstienH_2) and *N,N'*-bis(2-pyridinecarboxamide)phenylethane (bpstyenH_2) together with their deprotonated complexes of bivalent Cu, Ni and Pd have been prepared and characterised. A crystallographic analysis of the two copper(II) complexes is reported, with the *S*-bpstyenH_2 ligand found to be susceptible to racemisation under the warm basic conditions used in the syntheses.

{[*N,N'*-Bis(2-pyridinecarboxamido)-*S,S*-1,2-diphenylethane]copper(II)}, $C_{26}H_{20}N_4O_2Cu$ is monoclinic, spacegroup $P2_1$ (No. 4), with a = 11.170(3), b = 10.853(4), c = 18.570(7) Å, β = 103.74(3)°, *Z* = 4, with two molecules in the asymmetric unit. The structure was refined to *R* = 0.039 for 2519 reflexions. Each molecule is five coordinate with the fifth position occupied by an amide oxygen atom of a neighbouring molecule. These Cu–O(amide) distances are 2.554(7) and 2.757(6) Å. The stereochemistry of molecule 1 closely resembles a square-based pyramid, whereas that for molecule 2 approximates a distorted trigonal bipyramid. In each case the central five-membered chelate ring has a λ conformation with the two phenyl substituents occupying the axial positions in a rare configuration.

{Aqua[*N,N'*-bis(2-pyridinecarboxamido)phenylethane]-copper(II)}-sesquihydrate, $C_{20}H_{21}N_4O_{4.5}Cu$, is monoclinic, space group $P2_1/c$ (No. 14), with a = 12.122(4), b = 10.691(2), c = 15.952(4) Å, β = 110.76(2)°, *Z* = 4. The structure was refined to *R* = 0.046 for 1939 reflexions. The stereochemistry of the five-coordinate copper atom approximates a square pyramid with the copper atom displaced 0.26 Å towards the apical water molecule (Cu–O 2.251(5) Å). In the enantiomer containing S-bpstyen the central five-membered chelate ring has a δ conformation with the phenyl substituent occupying an equatorial position.

In solution the palladium(II) and nickel(II) deprotonated metal complexes of the *S,S*- and *S*- ligand forms are shown by ^1H NMR analysis, in conjunction with their chiroptical properties, to each have a λ *gauche* central chelate ring conformation with the phenyl substituent(s) occupying axial positions.

Keywords: Amides, tetradentates, copper complexes, optical activity, X-ray structures

INTRODUCTION

The conformations adopted by *C*-substituted optically active 1,2-diamines on coordination to a variety of first-row transition metals have been exhaustively investigated,

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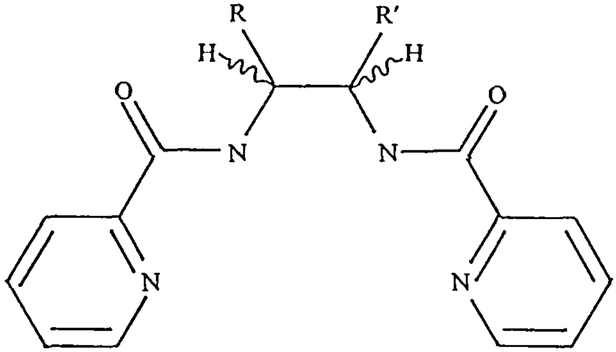
both in the solid state[1–3] and in solution.[4–8] Without exception it has been found that any substituent on the chelate ring occupies the energetically more favourable equatorial position.[9,10] Any substituents on the nitrogen atoms are also observed to adopt equatorial positions on coordination by these bidentates.[11–13] Similar conformations are observed on octahedral coordination for optically active *C*- and N-substituted flexible N_4 tetradentates based on picen‡.[14–16]



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A reduction in the inherent flexibility of these tetradentates would be achieved by the conversion of the secondary amine groups to planar amides.[17–18] We have previously reported details of the synthesis and characterisation of a number of metal complexes of *trans*-bpchxn (1, R,R′ = ($-CH_2\,CH_2\,CH_2CH_2-$), in which the conformation of the central chelate ring is determined by the hand of the relatively inflexible diamine. As an extension of this study we have synthesised and characterised the ligands, *S*,*S*-bpstienH_2 (1, R = R′ F3= C_6H_5) and *S*-bpstyenH_2 (1, R = C_6H_5, R′ = H), and representative metal complexes in order to determine the effect of incorporating a *C*-substituted central diamine bridge with higher rotational flexibility.

EXPERIMENTAL

Microanalyses were carried out by AMDEL Laboratories, Melbourne. NMR spectra were recorded on a Varian XL-200 spectrometer and are reported in ppm relative to DSS, TMS or known solvent resonances used as internal calibrants. Circular dichroism (CD) spectra were recorded on a JASCO SP-500C spectropolarimeter at ambient temperatures with 10^{-3} M solutions or as 0.5% *w*/*w* KBr discs. Optical rotations were measured at 589 nm on an Optical Activity AA-10 automatic polarimeter. Electronic spectra were recorded using a Shimadzu UV-160 recording spectrophotometer.

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‡ Picen is 2,5-diaza-1,6-di(2′-pyridyl)hexane,
bpchxnH_2 is *N*,*N*′-bis(2′-pyridinecarboxamide)-1,2-cyclohexane,
bpstienH_2 is *N*,*N*′-bis(2′-pyridinecarboxamide)-1,2-diphenylethane,
bpstyenH_2 is *N*,*N*′-bis(2′-pyridinecarboxamide)phenylethane.

,S-*BpstienH*$_2$.*H*$_2$*O*

he ligand was prepared as a cognate synthesis of a previously published method.[19] ,*S*-Stilbenediamine[20] (2.0 g, 9.42 mmol) dissolved in pyridine (5 cm^3) was added to a ot solution of picolinic acid (2.3 g, 18.84 mmol) and triphenyl phosphite (5.85 g, 8.84 mmol) in pyridine (25 cm^3). The mixture was heated on a steam bath (*ca* 3 h) ntil crystals commenced to form in the hot solution. Upon cooling to room emperature the resultant solid was triturated with diethyl ether (5 cm^3), collected at he pump, then washed with 3 × 10 cm^3 portions of acetone and air dried.

Yield: 2.91 g (73%) *Anal.* Calc. for $C_{26}H_{24}N_4O_3$: C, 70.89; H, 5.49; N, 12.72. ound: C, 71.83; H, 4.73; N, 12.60%. Mp. 215–216°C uncorr. NMR, solvent, D_2Cl_2, ppm; 5.62 (q, 4H);* 7.28 (br m, 10H); 7.42 (q, 2H); 7.82 (t, 2H); 8.10 (d, H); 8.56 (d, 2H); 8.9 (br d, 2H); {1.66 (s, $2H(H_2O)$}. $[\alpha]_D = +30.0 \pm 0.5°$ ($c = 1$, HCl_3).

-*BpstyenH*$_2$

tyrenediamine was synthesised and resolved according to published procedures,[21] vith the more soluble diastereomer isolated from the resolution being the 1 : 1 [*S*-tyenH$_2$] [*R*,*R*-(+) tart] salt ($[\alpha]_D = +4.6°$ $c = 1$, H_2O). A sample of this salt (3.0 g, 0.5 mmol) was dissolved in cold water (10 cm^3), hydrated lithium hydroxide 0.879 g, 21 mmol) was slowly added followed by pyridine (50 cm^3), and the mixture hen was cooled in an ice-bath. The relatively insoluble lithium tartrate which formed vas filtered off and any water present was removed on a rotary evaporator at 50°C. The product mixture was again filtered and this pyridine solution containing the free liamine was added to a hot solution of picolinic acid (2.59 g) and triphenyl phosphite 6.52 g) in pyridine (25 cm^3). The mixture was heated on a steam bath for 4 h before he remaining pyridine was removed at reduced pressure to leave a dark orange-rown oil. This was dissolved in chloroform (100 cm^3), washed with saturated odium carbonate solution (2 × 50 cm^3) followed by water (50 cm^3) then dried over nhydrous sodium sulphate. The dried chloroform extract was reduced in volume, pplied to a column of neutral activated alumina (30 × 3 cm) and eluted with hloroform. The yellow elutant was heated with activated charcoal (2 g), filtered nder suction through a small pad of celite and the remaining solvent removed at educed pressure. The resultant off-white solid was recrystallised from methanol to give colourless needles up to 1 cm in length.

Yield: 1.40 g (39%) *Anal.* Calc. for $C_{20}H_{18}N_4O_2$: C, 69.35; H, 5.24; N, 16.17. Found: C, 69.40; H, 5.50; N, 16.30%. Mp. 168°C uncorr. NMR, solvent, $CDCl_3$, ppm; 4.20 (t, 2H); 5.47 (q, 1H); 7.40 (m, 7H); 7.83 (t, 2H); 8.18 (t, 2H); 8.42 (br t, 1H); 8.57 (q, 2H); 8.84 (br d, 1H). $[\alpha]_D = +47.0 \pm 0.5°$ ($c = 1$, $CHCl_3$).

[*Pd*(S,S-*bpstien*)]

A suspension of the ligand, *S*,*S*-bpstienH$_2$.H$_2$O (0.20 g, 0.454 mmol) in water (20 cm^3) was heated slowly, with acetone being added dropwise until complete dissolution was obtained. To this solution was slowly added a solution of K_2PdCl_4 (0.1413 g, 0.433 mmol) in water (5 cm^3). After filtration the reaction solution was heated gently until all the acetone had evaporated and then was left to stand for 2 days. The well-formed yellow crystals which resulted were collected at the pump, washed with a minimum amount of ice-cold water and air dried.

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* br = broad, d = doublet, s = singlet, t = triplet, m = multiplet, q = quartet.

Yield: 0.203 g (85%), *Anal.* Calc. for $C_{26}H_{20}N_4O_2Pd$: C, 59.27; H, 3.82; N, 10.6 Found: C, 59.43; H, 3.66; N, 10.71%.

[Ni(S,S-bpstien)]

S,S-BpstienH_2.H_2O (0.25 g, 0.57 mmol) was dissolved in a warm acetone/wat mixture as described above and a solution of $NiCl_2.6H_2O$ (0.1349 g, 0.57 mmol) water (5 cm^3) was added. The mixture was then cooled and the pH carefully adjust to 8.0 by dropwise addition of 2 M NaOH. The deep-orange coloured soluti resulting was filtered and left to stand for 4 days and the dark-orange crystals whi had formed were collected at the pump, washed with a minimum amount of ice-co water and air dried.

Yield: 0.224 g (82%), *Anal.* Calc. for $C_{26}H_{20}N_4O_2Ni$: C, 65.17; H, 4.21; N, 11. Found: C, 65.20; H, 4.10; N, 11.80%.

[Cu(S,S-bpstien)]

A sample of the ligand, *S,S*-bpstienH_2.H_2O (0.25 g, 0.57 mmol), was dissolved in warm acetone water mixture as described above and a solution of copper(II) aceta (0.104 g, 0.57 mmol) dissolved in a minimum amount of water was added, imme ately producing a deep-purple solution. The solution was filtered and left to sta overnight and the resultant deep-purple needles were collected at the pump, wash with a minimum amount of ice-cold water and air dried.

Yield: 0.246 g (96%), *Anal.* Calc. for $C_{26}H_{20}N_4O_2Cu$: C, 64.52; H, 4.17; N, 11. Found: C, 64.50; H, 4.10; N, 11.50%. This product was used for the X-r crystallographic analysis reported below.

[Pd(S-bpstyen)] and [Ni(S-bpstyen)]

The synthetic procedures for these complexes were similar to those of the analogo bpstien complexes reported above, substituting *S*-bpstyenH_2 ligand (0.150 g, 0. mmol) and a stoichiometric quantity of either K_2PdCl_4 or $NiCl_2.6H_2O$.

Yield: 0.185 g (95%) and 0.141 g (78%) respectively, *Anal.* Calc. for $C_{20}H$ N_4O_2Pd: C, 53.29; H, 3.58; N, 12.43. Found: C, 53.60; H, 3.50; N, 12.20. Calc. $C_{20}H_{16}N_4O_2Ni$: C, 59.60; H, 4.00; N, 13.90. Found: C, 59.60; H, 3.90; N, 12.20

[Cu(bpstyen)(H_2O)].1.5H_2O

The optically active ligand, *S*-bpstyenH_2 (0.14 g, 0.4 mmol), was dissolved in a wa acetone/water mixture as described above and copper(II) acetate (0.08 g) dissolved a minimum volume of water was added. The resultant blue solution was heated remove the acetone and the pH of the hot solution was adjusted to 8.0 by dropw addition of 2 M NaOH, causing the expected colour change to deep purple. T mixture was left to stand for 5 days and the deep-purple crystalline product collected at the pump, washed with a minimum amount of ice-cold water and dried.

Yield: 0.150 g (83%), *Anal.* Calc. for $C_{20}H_{21}N_4O_{4.5}$ Cu: C, 53.03; H, 4.67; 12.37. Found: C, 53.10; H, 4.50; N, 12.40%. This product was used for the X- crystallographic analysis reported below.

[Cu(S-bpstyen)].4H$_2$O

The synthetic procedure used for the racemic sesquihydrate form reported above was repeated using *S*-bpstyenH$_2$ (0.20 g, 0.58 mmol) and a stoichiometric amount of copper(II) acetate. However, the resultant blue reaction solution was cooled to 0°C before adjusting the pH to 7.5, after which fine grey-blue needles began to form immediately. These were collected after 2 h, washed with ice-cold water and air dried.

Yield: 0.246 g (88%), *Anal.* Calc. for $C_{20}H_{24}N_4O_6Cu$: C, 50.05; H, 5.04; N, 11.67. Found: C, 49.90; H, 4.80; N, 11.60%.

TABLE I

Summary of crystal data, data collection and refinement details.

	[Cu(*S*,*S*-bpstien)]	[Cu(*rac*-bpstyen)(H$_2$O)].1.5H$_2$O
Colour	purple	purple
Crystal data		
Formula	$C_{26}H_{20}N_4O_2Cu$	$C_{20}H_{21}N_4O_{4.5}Cu$
M_r	484.0	453.0
Crystal system	monoclinic	monoclinic
Space group	$P2_1$ (No. 4)	$P2_1/c$ (No. 14)
a (Å)	11.170(3)	12.122(4)
b (Å)	10.853(4)	10.691(2)
c (Å)	18.570(7)	15.952(4)
β (°)	103.74(3)	110.76(2)
U (Å)^3	2189.3	1933.0
D_m (by flotation)	1.45	1.52
Z	4	4
D_c (g cm^{-3})	1.468	1.556
μ(Mo-Kα) (cm^{-1})	10.7	12.2
F(000)	996	936
Intensity Data		
Crystal habit	plates lying on (001) 0.4 × 0.2 × 0.04 mm	plates lying on (001) 0.74 × 0.50 × 0.15 mm
Instrument	Nicolet XRD-P3 four-circle diffractometer [22]	
Radiation	Mo-Kα	Mo-Kα
Temperature °C	−135	−130
2θ range (°)	4.0–45.0	4.0–50.0
Absorption corr.	empirical [22]	
Transmission (max, min)	0.755, 0.820	0.763, 0.976
No. of reflexions: total	3203	3117
$I > 3\sigma(I)$	2519	1939
Refinement		
Computer	FACOM 340S	
Programs	written by F.S.S.	
Scattering factors	neutral atom [23]	
Anomalous disp.	yes [23]	no
Least squares matrices	block (3)	full
Anisotropic	all non-hydrogen	
H atoms	not refined	
Weighting scheme		
w =	$(2.0 + 0.01\lvert F_o\rvert + 0.03\lvert F_o\rvert^2)^{-1}$	$(3.0 + 0.01\lvert F_o\rvert + 0.0005\lvert F_o\rvert^2)^{-1}$
R	0.039	0.046
$R' (= \{\Sigma w\Delta^2/\Sigma w\lvert F_o\rvert^2\}^{\frac{1}{2}}$	0.048	0.059
Final Δ map (e Å^{-3})	$<\lvert 0.5\rvert$	$<\lvert 0.6\rvert$

Structure Determination

Unit cell data for both compounds were initially determined from precession photographs using Mo-K_α radiation. Accurate cell parameters were obtained from a least-squares fit to diffractometer data. These, together with data collection, structure determination and refinement details, are summarised in Table I. The two structures, each solved by the heavy atom method, were refined by least-squares calculations in which $\Sigma w\Delta^2$ was minimised. Difference maps were used to locate the approximate positions of the hydrogen atoms, which were optimised assuming N–H, C–H and O–H to be 1.0 Å.

TABLE II

Final atomic coordinates (fractional × 10^4) for non-hydrogen atoms with estimated standard deviations in parentheses for [Cu(*S*,*S*-bpstien)].

	n = 1			n = 2		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Cu(n)	1233.9(9)	424.9	810.4(6)	3950.8(10)	4714.0(12)	4288.8(6)
N(n11)	1868(6)	1955(7)	1425(4)	3461(6)	2995(7)	3906(4)
N(n21)	−523(6)	−72(6)	821(4)	5644(7)	5196(7)	4197(4)
N(n1)	2947(6)	333(7)	770(4)	2382(6)	4683(7)	4510(4)
N(n2)	1165(6)	−1118(7)	294(4)	3767(6)	6466(7)	4382(4)
C(n11)	3038(8)	2214(8)	1404(5)	2286(8)	2753(8)	3955(5)
C(n12)	3610(9)	3261(10)	1688(6)	1739(10)	1626(9)	3749(6)
C(n13)	2995(10)	4122(10)	2029(6)	2401(10)	701(9)	3500(6)
C(n14)	1804(10)	3859(11)	2079(7)	3602(9)	973(9)	3459(6)
C(n15)	1263(9)	2781(9)	1763(6)	4061(8)	2092(10)	3666(5)
C(nO1)	3699(8)	1243(9)	1044(5)	1631(9)	3770(8)	4276(5)
O(n1)	4808(6)	1351(6)	1063(4)	548(6)	3640(7)	4297(5)
C(n1)	3345(8)	−791(9)	481(5)	1959(7)	5830(7)	4795(5)
C(n2)	2211(7)	−1402(8)	−16(5)	2598(8)	6930(8)	4488(5)
C(n111)	4013(8)	−1685(8)	1099(5)	2222(7)	5867(8)	5633(5)
C(n112)	4557(8)	−2740(10)	895(5)	3206(8)	5237(8)	6099(5)
C(n113)	5182(10)	−3539(10)	1430(6)	3428(7)	5391(10)	6857(5)
C(n114)	5252(9)	−3335(10)	2165(6)	2700(9)	6147(10)	7174(5)
C(n115)	4688(10)	−2308(10)	2386(5)	1722(9)	6776(9)	6720(5)
C(n116)	4054(8)	−1501(8)	1845(5)	1496(8)	6607(9)	5963(5)
C(n211)	2035(8)	−939(8)	−800(5)	1757(7)	7466(8)	3808(5)
C(n212)	1185(8)	−27(9)	−1097(5)	1949(8)	7347(9)	3104(5)
C(n213)	1098(9)	413(12)	−1811(5)	1129(10)	7870(10)	2489(5)
C(n214)	1814(10)	−39(10)	−2247(6)	77(9)	8435(10)	2574(5)
C(n215)	2665(10)	−962(9)	−1981(5)	−130(9)	8604(9)	3276(6)
C(n216)	2757(8)	−1419(8)	−1249(5)	709(8)	8086(8)	3895(5)
O(n2)	58(6)	−2914(6)	−10(4)	4844(5)	8318(6)	4518(4)
C(nO2)	233(8)	−1859(9)	237(4)	4745(7)	7164(9)	4420(5)
C(n21)	−766(7)	−1211(8)	543(5)	5867(8)	6416(8)	4305(5)
C(n22)	−1935(9)	−1753(9)	467(5)	6959(8)	6953(8)	4308(5)
C(n23)	−2847(9)	−1059(11)	657(6)	7927(8)	6242(9)	4234(6)
C(n24)	−2609(8)	117(8)	935(5)	7768(8)	4961(8)	4146(5)
C(n25)	−1411(8)	548(9)	1004(4)	6605(8)	4496(8)	4120(5)

For the hydrated complex these maps showed a peak attributable to a second lattice water molecule, the height of which was consistent with half occupancy and therefore in accord with the elemental analyses obtained for the complex. The positional disorder for this molecule is manifest in its close proximity (1.78 Å) to the site occupied by the symmetry related molecule at 1–x, 1–y, 1–z. Final non-hydrogen atomic parameters for both structures are given in Tables II and III.

TABLE III
Final atomic coordinates (fractional × 10^4) for non-hydrogen atoms with estimated standard deviations in parentheses for $[Cu(bpstyen)H_2O].1{\cdot}5H_2O$.

	x/a	*y/b*	*z/c*
Cu	561.8(7)	1426.7(7)	1418.9(5)
O(w1)	1475(5)	1526(6)	2916(3)
N(11)	946(5)	−370(4)	1234(3)
N(21)	−1073(4)	1529(5)	1530(3)
N(1)	1851(4)	1751(4)	994(3)
N(2)	264(4)	3166(4)	1167(3)
C(11)	1816(6)	−443(5)	896(4)
C(12)	2255(5)	−1569(6)	729(4)
C(13)	1776(6)	−2678(6)	893(4)
C(14)	863(7)	−2619(6)	1230(4)
C(15)	473(6)	−1459(6)	1384(4)
C(O1)	2291(6)	813(6)	703(4)
O(1)	2977(4)	802(4)	274(3)
C(1)	2018(5)	3029(5)	736(4)
C(111)	3244(5)	3562(6)	1169(4)
C(112)	3664(6)	4453(6)	713(5)
C(113)	4721(7)	5076(7)	1155(6)
C(114)	5357(7)	4823(8)	2035(6)
C(115)	4978(7)	3921(9)	2496(6)
C(116)	3919(6)	3299(7)	2055(4)
C(2)	1163(5)	3913(6)	996(4)
(O2)	−1031(4)	4783(4)	1051(3)
C(O2)	−708(5)	3651(6)	1193(4)
C(21)	−1506(5)	2705(6)	1375(4)
C(22)	−2613(6)	3014(6)	1374(4)
C(23)	−3322(6)	2082(8)	1528(5)
C(24)	−2868(7)	883(7)	1703(5)
C(25)	−1752(7)	634(6)	1707(5)
O(w2)	3470(5)	2737(5)	4067(4)
O(w3)	5140(13)	4375(14)	4682(10)

RESULTS AND DISCUSSION

The optically active diamine precursors were synthesised using published procedures. The 1:1 tartrate salt of styrenediamine was isolated by the method of Bernth and Larsen.[21] Resolution was effected by the removal of the less soluble *R*-styen tartrate salt by the method of Reihlen *et al.*[24] and the more soluble diastereomer, containing *S*-styen, successively precipitated on addition of diethyl ether to the methanolic reaction solution. These product crops were combined and fractionally recrystallised until a constant rotation of +4.6° was achieved. The ratio of diamine to tartrate was confirmed by ^{1}H NMR measurements. This may be compared with results published for the 1:2 tartrate salt of Reihlen *et al.* ($[\alpha]_D = 6.5°$) and the salt of Gullotti *et al.* (+14.0°; no ratio given).[25]

TABLE IV

Selected molecular dimensions for the complex molecules with estimated standard deviations in parentheses.

(a) Distances (Å)

	[Cu(*SS*-bpstien)]				[Cu(bpstyen)H_2O]	
	Molecule 1		Molecule 2			
	x = 1	x = 2	x = 1	x = 2	x = 1	x = 2
Cu–O*	2.544(7)		2.757(6)		2.251(5)	
Cu–N(x1)	2.044(8)	2.040(7)	2.025(7)	2.008(7)	2.023(5)	2.054(5)
Cu–N(x)	1.935(7)	1.921(7)	1.892(7)	1.925(7)	1.942(5)	1.910(5)
N(x1)–C(x1)	1.346(11)	1.342(11)	1.362(11)	1.353(11)	1.345(8)	1.352(8)
N(x1)–C(x5)	1.362(12)	1.308(11)	1.322(12)	1.351(11)	1.357(8)	1.356(8)
C(x1)–C(Ox)	1.529(13)	1.537(12)	1.522(13)	1.550(12)	1.536(8)	1.498(8)
C(Ox)–O(x)	1.236(11)	1.232(11)	1.228(11)	1.267(11)	1.250(7)	1.267(8)
C(Ox)–N(x)	1.317(11)	1.300(11)	1.305(12)	1.317(11)	1.297(8)	1.301(8)
N(x)–C(x)	1.445(11)	1.453(11)	1.473(11)	1.456(12)	1.462(7)	1.454(8)
C(1)–C(2)	1.530(12)		1.566(12)		1.562(8)	
C(x)–C(x11)	1.553(13)	1.510(13)	1.513(12)	1.501(13)	1.511(8)	

(b) Angles (°)

	[Cu(*SS*-bpstien)]				[Cu(bpstyen)H_2O]	
	Molecule 1		Molecule 2			
	x = 1	x = 2	x = 1	x = 2	x = 1	x = 2
N(11)–Cu–N(2)	162.5(3)		156.3(3)		158.4(2)	
N(21)–Cu–N(1)	161.6(3)		164.2(3)		160.2(2)	
N(11)–Cu–N(21)	114.6(3)		113.1(3)		110.0(2)	
N(1)–Cu–N(2)	81.9(3)		82.7(3)		82.4(2)	
N(x1)–Cu–N(x)	81.3(3)	81.3(3)	82.7(3)	82.7(3)	82.1(3)	81.4(2)
N(x1)–Cu–O*	79.9(2)	77.3(2)	79.4(2)	85.5(2)	98.5(2)	91.9(2)
N(x)–Cu–O*	116.2(3)	112.0(3)	96.7(3)	120.8(3)	102.0(2)	99.3(2)
Cu–N(x1)–C(x1)	111.3(6)	110.3(5)	109.8(6)	112.8(6)	111.6(4)	111.0(4)
Cu–N(x1)–C(x5)	130.4(6)	131.0(6)	133.2(6)	130.6(6)	131.0(4)	131.0(4)
C(x1)–N(x1)–C(x5)	117.8(8)	118.5(8)	116.9(8)	116.3(8)	117.4(5)	117.9(5)
N(x1)–C(x1)–C(Ox)	121.2(8)	117.8(7)	116.5(8)	113.9(7)	115.6(5)	115.3(5)
C(x1)–C(Ox)–O(x)	120.4(9)	119.9(8)	119.9(8)	119.4(7)	118.1(5)	120.0(5)
C(x1)–C(Ox)–N(x)	110.8(7)	108.9(8)	110.5(8)	112.3(8)	111.9(5)	113.1(6)
O(x)–C(Ox)–N(x)	128.7(7)	131.2(8)	129.6(9)	128.3(8)	130.0(6)	126.9(6)
Cu–N(x)–C(Ox)	119.5(6)	121.1(6)	119.8(6)	117.9(6)	118.1(4)	119.1(4)
Cu–N(x)–C(x)	116.9(5)	116.2(5)	117.1(5)	118.2(6)	118.3(4)	118.4(4)
C(Ox)–N(x)–C(x)	123.5(7)	122.7(7)	121.7(7)	123.6(7)	120.4(5)	122.3(5)
N(x)–C(x)–C(x11)	112.9(7)	112.3(7)	113.1(7)	114.9(8)	115.8(5)	
N(x)–C(x)–C(x ± 1)	107.9(7)	107.3(7)	107.4(6)	106.7(7)	108.6(4)	109.2(5)
C(x11)–C(x)–C(x ± 1)	111.0(7)	109.7(7)	111.1(7)	110.7(7)	106.7(5)	

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* For [Cu(*SS*-bpstien)]: Molecule 1 O is O(12) at $-x, \frac{1}{2}+y, -z$. Molecule 2 O is O(22) at $1-x, y-\frac{1}{2}, 1-z$. For [Cu(bpstyen)H_2O] O is O(w1).

BpstyenH_2 was found to be susceptible to racemisation under warm basic conditions; similar behaviour has been reported previously for styrenediamine.[26] Nevertheless under controlled conditions it was possible to synthesise the optically active complexes reported above. Reaction of the ligands with nickel(II) and palladium(II) produced characteristic diamagnetic square-planar complexes,[27–29] whereas with copper(II) the familiar deep-blue/purple five-coordinate complexes are formed. With the [Cu(*S*-bpstyen)] complex, epimerisation of the ligand was found to occur if the reaction conditions were not strictly controlled. Table IV gives selected molecular dimensions and Table V summarises data for structural distortions present in the molecules for both copper(II) compounds.

TABLE V

Data for the analysis of distortions in the complex molecules with angles in (°) and distances in (Å). Detailed definitions of distortions and torsion angles are given in ref. 34.

	[Cu(*SS*-bpstein)]		
	Molecule 1	Molecule 2	[Cu(bpstyen)H_2O]
Cu environment			
Tetrahedral twist[a]	2.5	22.5	2.9
Angle Cu–O[b]/N_4-plane	28.0	27.6	5.0
ΔCu above N_4-plane	0.12	0.12	0.26
Torsion angle			
N(1)C(1)C(2)N(2)	−32.7	−28.7	−16.0
Pyramidal distortions			
C(On)	3.2, 0.4	1.3, 1.8	3.1, 2.7
N(n)	4.2, 0.6	13.6, 6.9	20.4, 3.1
Pyridyl ring distortions			
γ	2.5, 0.9	0.3, 2.0	1.4, 2.8
δ	1.4, 0.3	0.2, 1.1	0.8, 1.7
Torsion angles and specific distortions about the 'peptide unit'			
$\Delta\psi_{CC}$	3.4, −7.6	−7.7, −1.2	6.8, 4.1
$\Delta\omega$	8.1, 6.6	−4.7, 1.5	11.2, −0.3
θ_N	−4.4, 0.6	14.0, 7.1	−20.5, −3.1
θ_C	3.2, 0.4	1.3, 1.8	3.2, −2.7
$\Delta\Phi_{NC}$	19.4, 30.9	40.9, 28.1	−13.0, 16.2
Pyridyl-pyridyl contacts			
C(15)...C(25)	3.84(1)	3.80(1)	3.68(1)
H(15)...H(25)	2.27	2.23	2.08

[a] Taken as the average dihedral angle between N_3 planes.

[b] See Table IV for definition of the O atoms.

The molecular diagrams[30] of the two [Cu(*S*,*S*-bpstien)] complexes in the asymmetric unit, together with the atomic labelling scheme, are shown in Figure 1. If the two phenyl rings are ignored each molecule is related by an approximate *n*-glide operation perpendicular to *b*. Each molecule increases its coordination number to five by bonding of the amide oxygen O(n2) from an adjacent molecule related to each

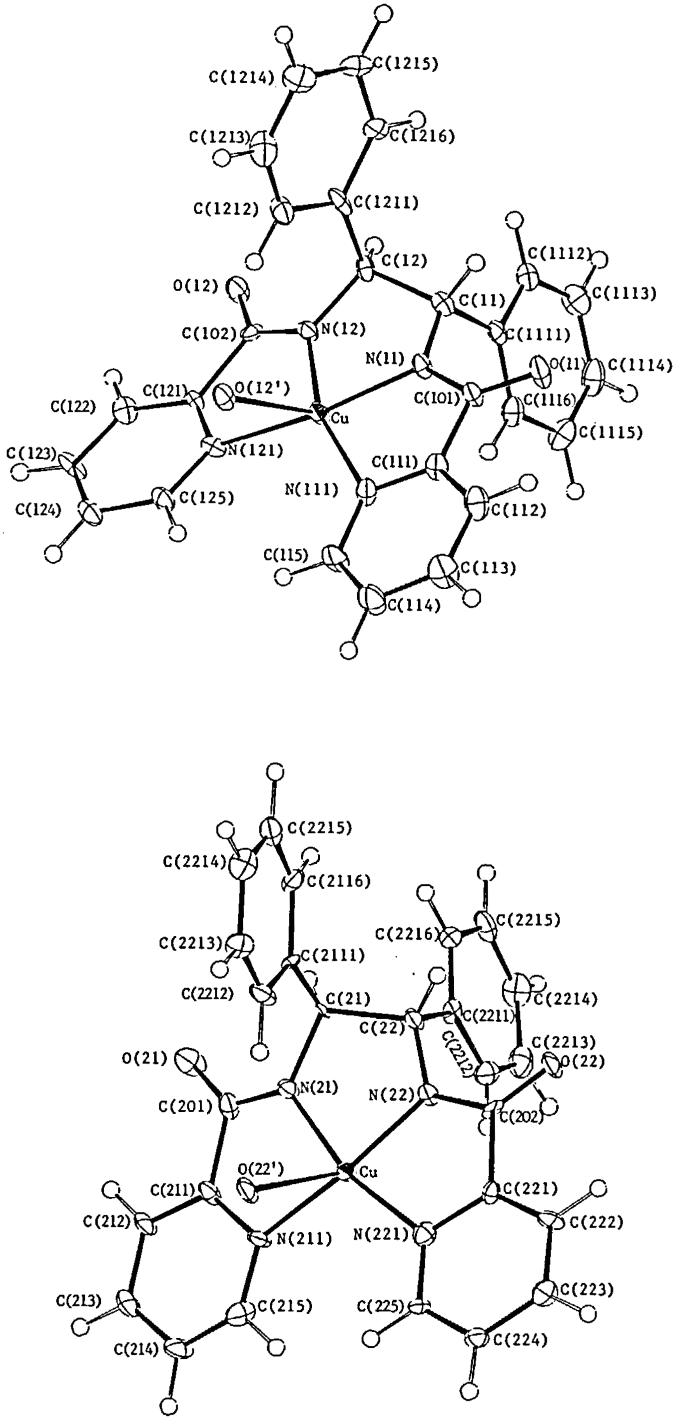

FIGURE 1 Perspective drawings of the two crystallographically independent molecules of [Cu(*S*,*S*-bpstien)] showing the atom labelling scheme for the complex; thermal ellipsoids are drawn to include 35% probability.

by screw axis symmetry. This produces helical chains of molecules (Figure 2) along *b* linked by Cu–O (*amide*) bridges. The apical Cu–O distances are relatively long, being 2.554(7) and 2.757(6) Å respectively. The stereochemistry of molecule 1 closely resembles a square-based pyramid whereas that for molecule 2 is more clearly distorted towards trigonal-bipyramidal geometry. In both molecules the ligand acts as an N_4 tetradentate with average Cu–N(py) distances of 2.03(1) Å and Cu–N-(amide) 1.92(1) Å. Molecule 2 exhibits a considerable tetrahedral twist in the N_4 coordination plane (Table V) but in both structures the copper atom lies 0.12 Å out from this plane towards the apical oxygen atom. For molecule 1 there is little distortion in the amide groups (Table V). Conversely, in molecule 2 both amide nitrogens exhibit a significant degree of pyramidal distortion (N(21) *ca* 23%, N(22) *ca* 11%).

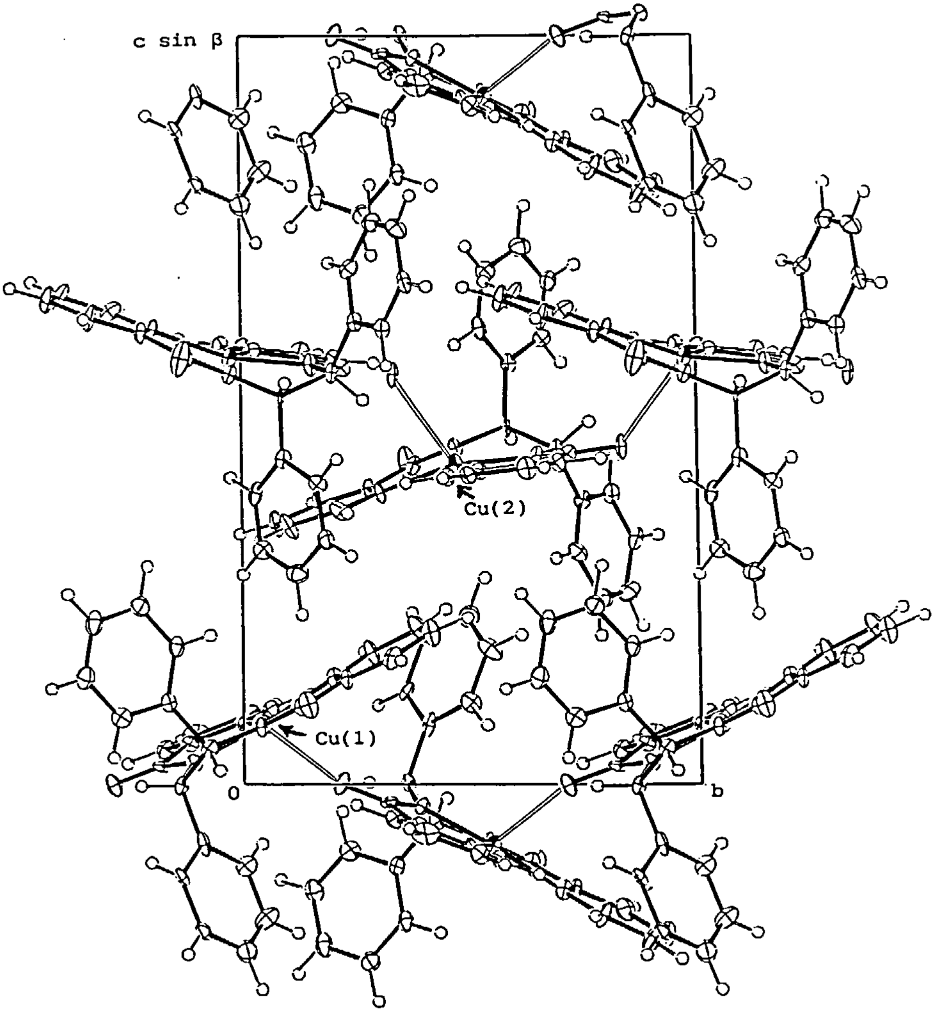

FIGURE 2 A packing diagram of the [Cu(*S*,*S*-bpstien)] molecules in the unit cell.

The central five-membered chelate rings in both molecules have a λ conformation, with the two phenyl groups occupying *trans* axial positions; the central N–C–C–N torsion angles are 32.6° and 28.7° respectively with corresponding Ph–C–C–Ph angles of 142.4 and 138.9°.

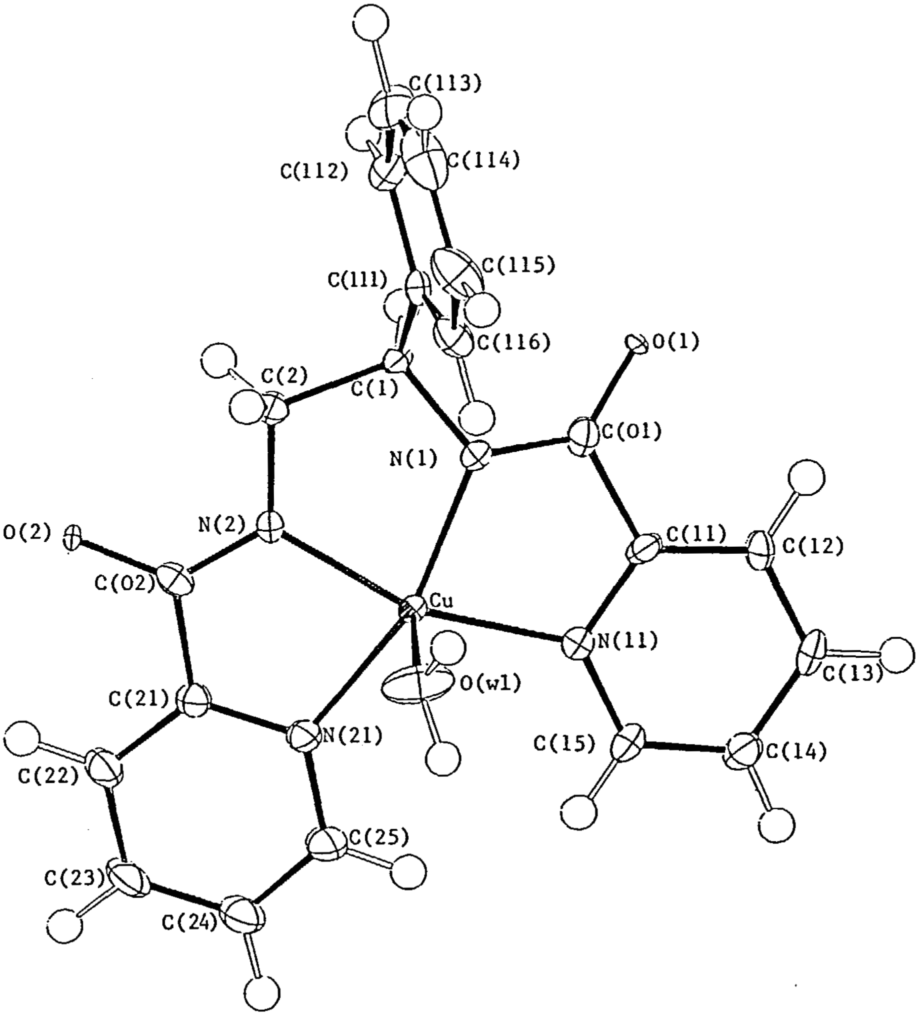

FIGURE 3 Perspective drawing of [Cu(bpstyen) (H_2O)] showing the atom labelling scheme; thermal ellipsoids are drawn to include 35% probability. In this particular case, only one hand of the racemate is shown.

The perspective drawing[30] depicted in Figure 3 shows the [Cu(bpstyen)(H_2O)] complex molecule which has *R* absolute configuration at the asymmetric carbon atom. The central five-membered chelate ring of this enantiomer has λ conformation with the phenyl substituent disposed in a *quasi* equatorial orientation, which is in contrast with that observed in the diphenyl-substituted analogue (*loc. cit.*). The N–C–C–N torsion angle of 16.0° reflects a more closely planar arrangement than that observed in the bpstien complex. The stereochemistry of the copper atom is close to a square-based pyramid with the copper atom lying 0.26 Å above the N_4 plane towards the apical water molecule (Cu...O 2.251 Å). This arrangement is consistent with several analogous copper bis-picolinamide structures,[17,18,31–34] as are the copper nitrogen distances. One of the amide nitrogen atoms exhibits a marked pyramidal distortion (N(1) ≈ 33%). A lattice hydrogen bonding network is obvious, involving the water molecules and the amide oxygen atoms, details of which are given in Table VI.

TABLE VI

A. Contact distances (Å) with estimated standard deviations in parentheses for $[Cu(bpstyen)H_2O].1{\cdot}5H_2O$.

(a) Proposed hydrogen bonding*			
O(w1)–H(w1a)...O(2^{I})	2.666(7)	O(w2)...O(w3)	2.592(16)
O(w1)–H(w1b)...O(w2)	2.783(8)	O(w3)...O(1^{III})	2.725(15)
O(w2)–H(w2a)...O(1^{II})	2.706(7)	O(w3)...O(1^{II})	3.092(14)
(b) Intermolecular distances <3.3 Å*			
C(13)...C(O2^{IV})	3.283(8)	C(24)...O(w3^{I})	3.279(17)
C(23)...C(w3^{V})	3.268(17)	C(24)...O(w3^{V})	3.283(18)

* Roman numeral superscripts refer to the following equivalent positions relative to x, y, z:
I $-x, y-\frac{1}{2}, \frac{1}{2}-z$ IV $-x, -y, -z$
II $x, \frac{1}{2}-y, \frac{1}{2}+z$ V $x-1, \frac{1}{2}-y, z-\frac{1}{2}$
III $1-x, \frac{1}{2}+y, \frac{1}{2}-z$

B. Intermolecular contacts < 3.3 Å with estimated standard deviations in parentheses* for [Cu(*S*,*S*-bpstien)].

N(121)...O(12^{I})	2.897(10)	O(12)...C(125^{IV})	3.130(11)
N(111)...O(12^{I})	2.977(9)	O(11)...C(124^{V})	3.241(11)
N(211)...O(22^{II})	3.105(10)	C(211)...C(222^{II})	3.252(13)
O(21)...C(2116^{III})	3.128(11)	N(221)...O(22^{II})	3.281(9)

* Superscript roman numerals refer to the following equivalent positions relative to x, y, z: I, $-x, \frac{1}{2}+y, -z$; II, $1-x, y-\frac{1}{2}, 1-z$; III, $-x, y-\frac{1}{2}, 1-z$; IV, $-x, y-\frac{1}{2}, -z$; V, $1+x, y, z$.

The proton NMR spectra of the palladium and nickel complexes are shown in Figure 4. All spectra are consistent with the molecules having C_2 or *pseudo* C_2 symmetry. The resonances for both the pyridyl and methine protons H(1) and H(2) appear at lower field for the palladium complexes compared with those for the nickel complexes; this is consistent with the differing deshielding abilities and ionic radii of the metals.[27] Again comparable results have been reported for analogous complexes.[27,34] The NMR spectra of the bpstyen complexes exhibit an ABC splitting pattern for the methine and methylene protons of the diamine bridge, as shown in Figure 5. For the *S* form of the diamine there are two conformations possible, which may be distinguished by NMR analysis. A δ conformation would result from the phenyl group being in the equatorial position, and a λ conformation from the phenyl group in the axial position. The δ *gauche* structure would give rise to three coupling

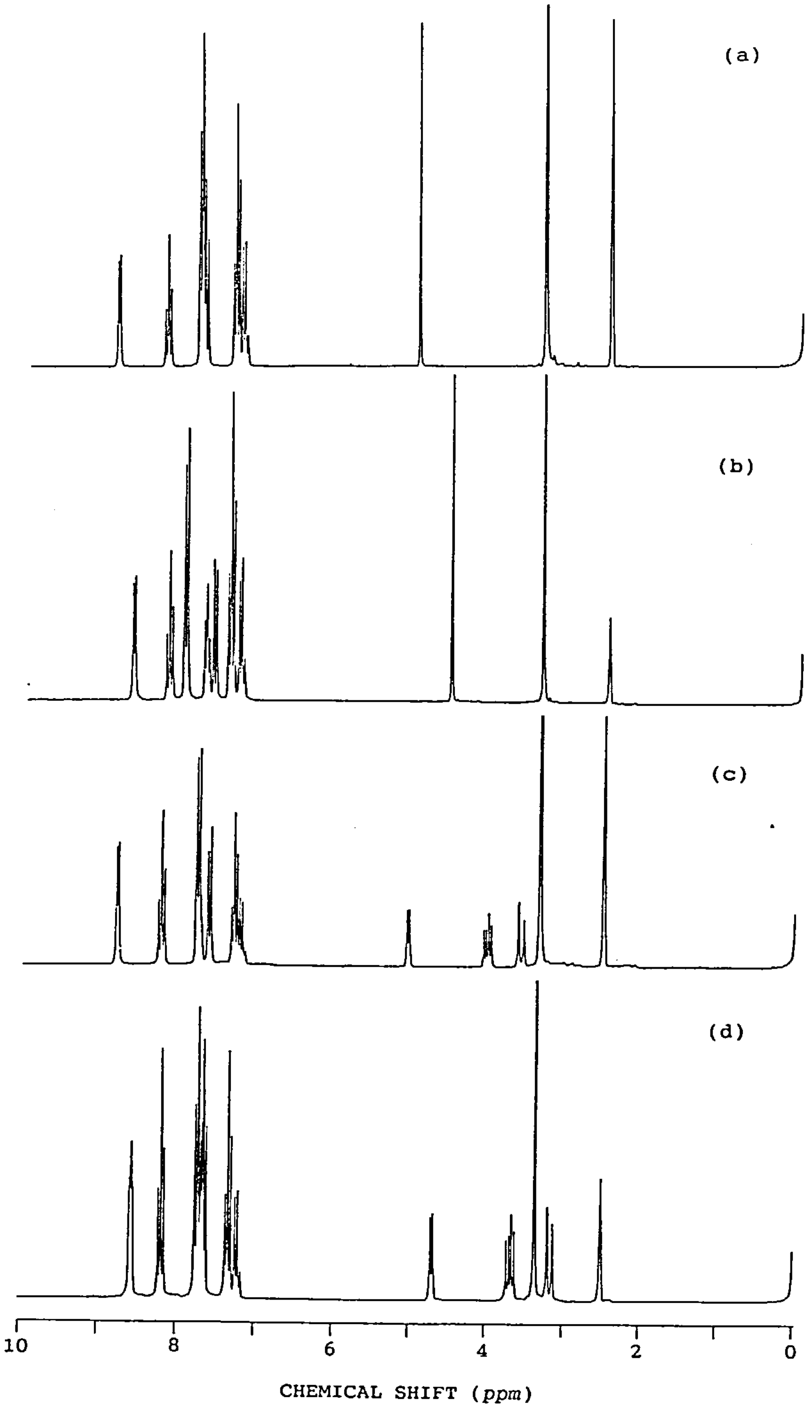

FIGURE 4 ^{1}H NMR spectra in DMSO-d_6 of a: [Pd(*S*,*S*-bpstien)]; b: [Ni(*S*,*S*-bpstien)]; c: [Pd(*S*-bpstyen)]; d: [Ni(*S*-bpstyen)].

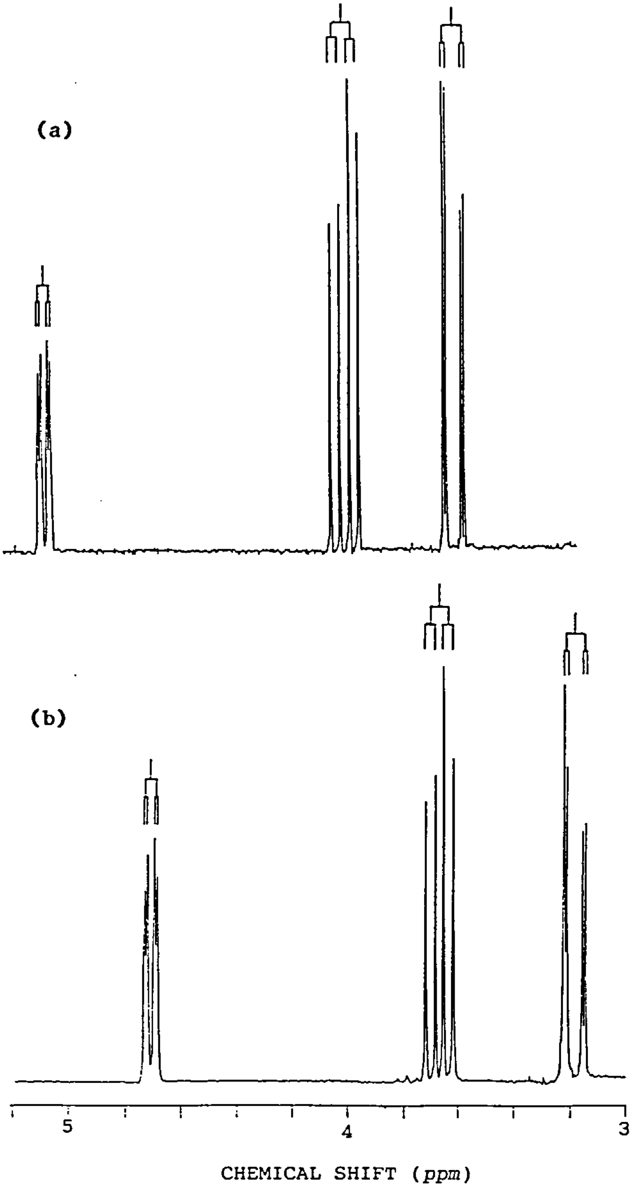

FIGURE 5 *ABX* regions of the ^{1}H NMR spectra in DMSO-d_6 of a: [Pd(*S*-bpstyen)]; b: [Ni(*S*-bpstyen)].

constants in its NMR spectrum, corresponding to *geminal*, *trans* and *gauche* proton dispositions, whereas the λ *gauche* structure would show coupling due to one *geminal* and two *gauche* dispositions.

Observed coupling constants are summarised in Table VII, together with the corresponding torsion angles calculated by the Bothner-By[35] and Lemieux-Lown modified Karplus equations[36] for vicinal protons. Assignment of the resonances was assisted by spin-decoupling experiments. Observed doublet-pairs equivalent to one proton at lower field are attributable to the methine proton deshielded by the adjacent phenyl ring. The two doublet-pair signals observed at higher field display mutual coupling and are attributable to the *geminal* methylene protons. The *geminal* coupling constants ($J_{2,3}$) of 13.40 and 13.12 Hz for the Pd and Ni complexes respectively are consistent with reported values.[3-5,37] The other two coupling constants of ($J_{1,3}$) 2.17, 2.00 Hz and ($J_{1,2}$) 6.63, 7.21 Hz are consistent with those produced by *equatorial-axial* and *equatorial-equatorial* coupling,[38] respectively. Hence in each molecule the phenyl substituents are shown to be disposed in axial positions. In either analysis the sum of the calculated angles is close to 120°, confirming this structural analysis. The highest field signal in each case is attributable to the axial proton, consistent with the relative positioning of axial protons of cyclohexane rings.[38]

TABLE VII
NMR coupling constants and calculated H–C–C–H torsion angles.

		Calc. Angles (°)	
	Hz	Bothner-By [ref. 35]	Lemieux-Lown [ref. 36]
[Pd(*S*-bpstyen)]			
$J_{1,3}$	2.17	79.0	66.3
$J_{1,2}$	6.63	42.9	47.0
$J_{2,3}$	13.40	*geminal*	
[Ni(*S*-bpstyen)]			
$J_{1,3}$	2.00	84.0	67.2
$J_{1,2}$	7.21	39.3	44.8
$J_{2,3}$	13.12	*geminal*	

The coupling constants do not change significantly with increasing temperature (to 50°C), showing that in these square-planar nickel(II) and palladium(II) complexes the central chelate rings are fixed with the phenyl substituents in the axial positions. This is in stark contrast with the results of NMR conformational analyses of precursor 1,2-diamines (and others) on coordination to cobalt(III), palladium(II) and platinum(II).[3-5] These always have shown that the *R*- and *R*,*R*-isomers adopt a fixed λ conformation in solution with the substituent(s) occupying the equatorial position(s).

Electronic spectral results are presented in Figure 6 and Table VIII. The solution and solid state CD spectra of the optically active complexes are qualitatively the same, with the observed band shifts for the different metals corresponding to absorption band shifts (Table VIII). The CD solution spectra of the palladium and nickel complexes are found to be very similar to those of analogous *R*,*R*-bpchxn complexes.[39] For the copper(II) complexes the spectra recorded in both donor and non-donor solvents are qualitatively the same with respect to band height and sign. Although there are minor changes in band positions there is certainly no evidence for any change in configuration of complexes with changing solvent. Remarkably, this does not agree with the crystal structure of the *racemic* bpstyen copper complex (*vide*

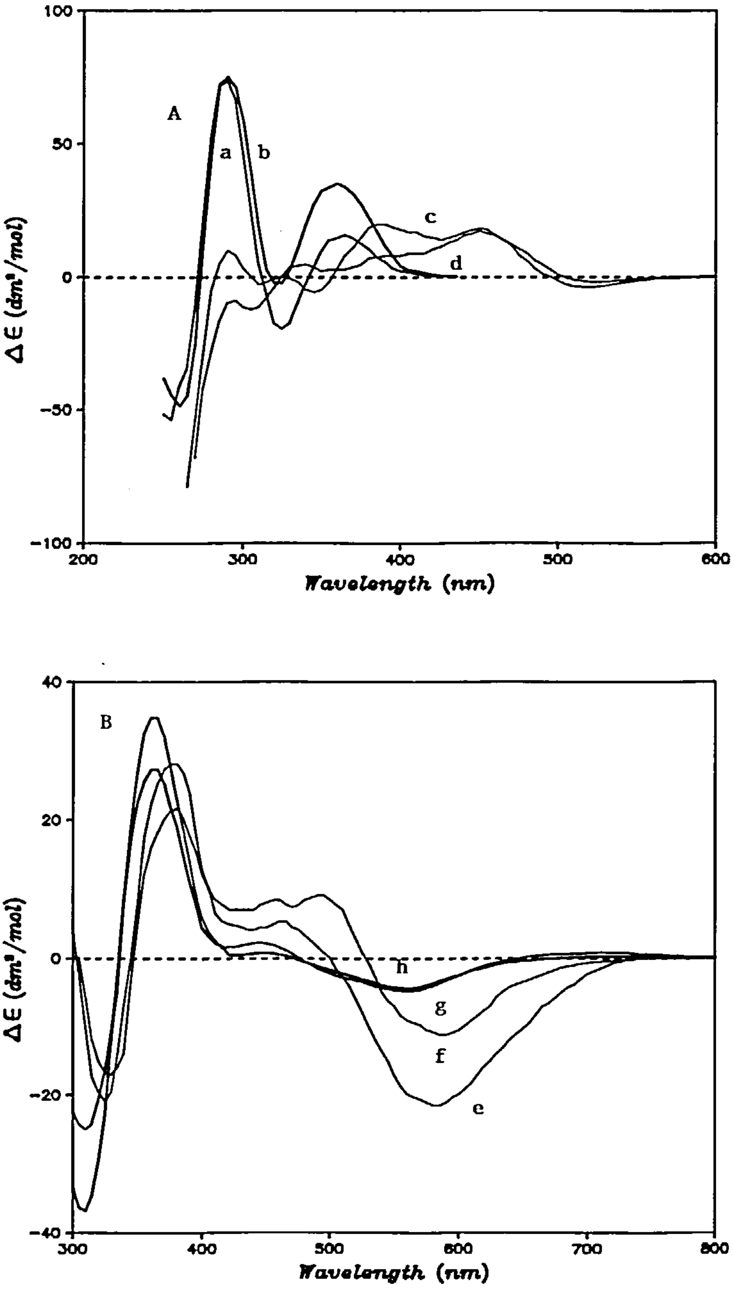

FIGURE 6 CD spectra of the complexes; A– a: [Pd(*S*-bpstyen)] in DMSO; b: [Pd(*S*,*S*-bpstien)] in DMSO; c: [Ni(*S*,*S*-bpstien)] in DMSO; d: [Ni(*S*-bpstyen)] in DMSO; B–e: [Cu(*S*-bpstyen)].4H_2O in KBr disc (arbitrary CD units); f: [Cu(*S*,*S*-bpstien)] in KBr disc (arbitrary CD units); g: [Cu(*S*-bpstyen)] in $CHCl_3$; h: [Cu(*S*,*S*-bpstien)] in $CHCl_3$.

TABLE VIII

Electronic spectral data for the bis-picolinamide metal complexes.

Complex	λ (nm)	$\varepsilon \times 10^{-3}$ (dm^2 mol^{-1})	$\Delta\varepsilon$ (dm^2 mol^{-1})
[Cu(*S*,*S*-bpstien)][a]	560		−4.58
	492	0.89	
	367		+28.49
	310		−36.62
	281	32.95	
[Pd(*S*,*S*-bpstien)][b]	357		+34.78
	345	69.63	
	322		−3.86
	290		+74.72
	274	91.12	
	260		−48.95
[Ni(*S*,*S*-bpstien)][b]	517		−3.93
	450		+18.65
	391	65.59	
	385		+20.12
	345		−5.89
	290		+9.82
	274	74.91	
[Cu(*S*-bpstyen)].4H_2O[a]	560		−4.85
	505	2.12	
	367		+35.08
	310		−25.44
	281	84.97	
[Cu(bpstyen)(H_2O)].1.5H_2O[a,c]	495	1.59	
	305(sh)	33.03	
	282	36.78	
[Pd(*S*-bpstyen)][b]	365		+15.53
	357	56.22	
	325		−20.71
	288		+74.55
	276	82.62	
	255		−53.84
[Ni(*S*-bpstyen)][b]	523		−2.12
	450		+16.97
	392	63.94	
	305		−12.74
	295		−9.34
	273	64.64	

[a] Solvent is chloroform. [b] Solvent is dimethylsulphoxide. [c] Racemic compound.

supra) in which the conformation of the central chelate ring is enantiomeric with its bpstien analogue, although with the phenyl group equatorial. This fact has interesting connotations for the mechanism of the observed base catalysed epimerisation.

An apt comparison may be made with the coordination behaviour of the chiral *salen* Schiff base tetradentates, which is well documented.[40–45] For the *pseudo* square-planar Cu(II) and Co(II) complexes the 1,2-diaminopropane and 2,3-diaminobutane-based salen ligands the methyl substituent(s) on the central chelate ring have been observed to adopt the extremely rare axial disposition in the solid state, as demonstrated in the crystallographic analyses of both these complexes.[46,47] The cause of this unusual orientation has been attributed to a steric interaction which would result between the azomethine proton and any equatorial substituent.[43] The crystal structure of the equatorially-substituted mono-phenyl copper complex, shows this to be incorrect, since steric repulsion caused by the amide oxygen atom would be greater than that of the azomethine proton. For the *trans* cyclohexane analogues of these complexes[41–45] the cyclohexane fragment must adopt a skew-chair di-equatorial conformation. Hence, if this steric interaction is to be avoided, the absolute configuration of the central chelate ring in these complexes must be opposite to that for the *C*-substituted ligands of the same hand.

The inherent inflexibility of the bis-picolinamides caused by the desired planarity of the secondary amide groups, in conjunction with the bulky and rigid terminal pyridine rings, restrict the conformations possible on coordination. The crystallographic analyses of [Cu(*trans*-bpchxn)H_2O].H_2O,[18] [Cu(*trans*-bpchxn)H_2O].$2H_2O$[32] and [Ni(*trans*-bpchxn)][28] demonstrate the mode of coordination of this ligand, with the cyclohexane ring adopting a skew-chair conformation in which the methine protons are necessarily *trans* to each other. In each case the deprotonated amide nitrogen has a flattened pyrimidal geometry, and B-strain[48] imposed on the molecule by the steric interaction of protons on the terminal pyridyl rings is somewhat alleviated by rotational distortions within the non-planar amide chelate rings.

Analogous complexes with *C*-substituted diamine bridges such as the title bpstienH_2 and bpstyenH_2 ligands, which do not contain a ring component, would adopt the same overall topology with the outer chelate rings influencing the conformation adopted by the central chelate ring and the substituents on it. Any resulting steric strain within the molecule could be relieved in part by the rotational flexibility of the diamine bridge. It therefore would seem that the energetically preferred conformation of the bpstien central chelate ring has the two phenyl substituents *trans* to each other, *i.e.* in the axial positions. There is no indication of any other conformation, evidenced by the X-ray analyses of the [Cu(*S*,*S*-bpstien)] complex, and all NMR and chiroptical data.

The results obtained for the complexes of both ligands infer that on coordination to nickell(II), palladium(II) and copper(II) an axial orientation of the phenyl group(s) is enforced. However, under the more severe reaction conditions the [Cu(*S*-bpstyen)] complex was observed to epimerise at the asymmetric carbon. This is evidenced by the absorption spectra (Table VIII), which show differences between the optically active and epimerised species. The crystal structure of the racemic product suggests that when a fifth ligand coordinates in an apical position an equatorial conformation is more favoured. For the corresponding [Cu(*S*,*S*-bpstien)] complex it would seem that repulsion between the two vicinal phenyl substituents is a major determinant of the stereochemistry adopted.

SUPPLEMENTARY MATERIAL

Lists of anisotropic thermal parameters, complete Tables of bond lengths and angles and observed and calculated structure factors are available from F.S.S. on request.

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REFERENCES

1. Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Jpn.*, **35**, 1131 (1962).
2. Y. Saito, H. Iwasaki and H. Ota, *Bull. Chem. Soc. Jpn.*, **36**, 1543 (1963).
3. R. Kuroda and S.F. Mason, *J. Chem. Soc., Dalton Trans.*, 1016, (1977).
4. S. Yano, H. Ito, Y. Koike, J. Fujita and K. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 3184 (1969).
5. S. Yano, H. Ito, Y. Koike, J. Fujita and K. Saito, *J. Chem. Soc., Chem. Comm.*, 460, (1969).
6. S. Yano, M. Saburi, S. Yoshikawa and J. Fujita, *Bull. Chem. Soc. Jpn.*, **49**, 101 (1976).
7. E.A. Sullivan, *Can. J. Chem.*, **57**, 67 (1978).
8. S. Yano, T. Tukada, M. Saburi and S. Yoshikawa, *Inorg. Chem.*, **17**, 2520 (1978).
9. E.J. Corey and J.C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).
10. J.R. Gollogly and C.J. Hawkins, *Inorg. Chem.*, **8**, 1168 (1969).
11. D.A. Buckingham, L.G. Marzilli and A.M. Sargeson, *Inorg. Chem.*, **7**, 915 (1968).
12. M. Saburi, Y. Tsujito and S. Yoshikawa, *Inorg. Chem.*, **9**, 1476 (1970).
13. S. Yano, M. Saburi and S. Yoshikawa, *Bull. Chem. Soc., Jpn.*, **44**, 3486 (1971).
14. H.A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **82**, 5013 (1960).
15. M.W. Mulqi, F.S. Stephens, R.S. Vagg and P.A. Williams, *Inorg. Chim. Acta*, **88**, 183 (1984).
16. J.A. Chambers, T.J. Goodwin, F.S. Stephens, R.S. Vagg and P.A. Williams, *J. Coord. Chem.*, **17**, 277 (1988).
17. R.L. Chapman, F.S. Stephens and R.S. Vagg, *Acta Cryst.*, **B37**, 75 (1981).
18. M. Mulqi, F.S. Stephens and R.S. Vagg, *Inorg. Chim. Acta*, **51**, 9 (1981).
19. D.J. Barnes, R.L. Chapman, R.S. Vagg and E.C. Watton, *J. Chem. Eng. Data*, **23**, 349 (1978).
20. R.R. Fenton, R.S. Vagg and P.A. Williams, *Inorg. Chem. Acta*, **148**, 37 (1988) *and references therein.*
21. N. Bernth and E. Larsen, *Acta Chim. Scand.*, **A32**, 545 (1978).
22. G.M. Sheldrick, 'SHELXTL User Manual', Revision 3, Nicolet XRD Corporation, Cupertino, Calif., 1981.
23. 'International Tables for X-ray Crystallography', Vol. 4, (Kynoch Press, Birmingham, U.K., 1974), pp. 72–78 and 149.
24. H. Reihlen, E. Weinbrenner and G. v. Hessling, *Justus Liebigs Ann. Chem.*, **494**, 143 (1932).
25. M. Gullotti, A. Pasini, P. Fantucci, R. Ugo and R.D. Gillard, *Gazz. Chim. Ital.*, **102**, 855 (1972).
26. D.G. Neilson and D.F. Ewing, *J. Chem. Soc. (C)*, 393 (1966).
27. D.J. Barnes, R.L. Chapman, F.S. Stephens and R.S. Vagg, *Inorg. Chim. Acta*, **51**, 155 (1981).
28. M. Mulqi, F.S. Stephens and R.S. Vagg, *Inorg. Chim. Acta*, **52**, 73 (1981).
29. F.S. Stephens and R.S. Vagg, *Inorg. Chim. Acta*, **57**, 9 (1982).
30. C.K. Johnson, 'ORTEP', *Report ORNL*-3794, Oak Ridge National Laboratory, Tenn., U.S.A., 1965, revised 1971.
31. R.L. Chapman, F.S. Stephens and R.S. Vagg, *Inorg. Chim. Acta*, **43**, 29 (1980).
32. M. Mulqi, F.S. Stephens and R.S. Vagg, *Inorg. Chim. Acta*, **52**, 177 (1981).
33. F.S. Stephens and R.S. Vagg, *Inorg. Chim. Acta*, **57**, 43 (1982).
34. R.L. Chapman, F.S. Stephens and R.S. Vagg, *Inorg. Chim. Acta*, **52**, 161, 169 (1981).
35. A.A. Bothner-By, *Advn. Magn. Resonance*, **1**, 195 (1965).
36. R.U Lemieux and J.W. Lown, *Can. J. Chem.*, **42**, 893 (1964).
37. M. Barfield and D.M. Grant, *J. Chem. Phys.*, **36**, 2054 (1962).
38. V.M. Parikh, "Absorption Spectroscopy of Organic Molecules," (Addison-Wesley, Massachusetts, 1974), p. 123.

39. M.W. Mulqi, Ph.D. Thesis, Macquarie University (1981).
40. B. Bosnich, *J. Am. Chem. Soc.*, **90**, 627 (1968).
41. R.S. Downing and F.L. Urbach, *J. Am. Chem. Soc.*, **91**, 5977 (1969).
42. R.S. Downing and F.L. Urbach, *J. Am. Chem. Soc.*, **92**, 5861 (1970).
43. C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo and V. Valenti, *J. Chem. Soc., Dalton Trans.*, 754, (1973).
44. A. Pasini, M. Gullotti and R. Ugo, *J. Chem. Soc., Dalton Trans.*, 346 (1977).
45. E. Cesarotti, A. Pasini and R. Ugo, *J. Chem. Soc., Dalton Trans.*, 2147 (1980).
46. F.J. Llewellyn and T.N. Waters, *J. Chem. Soc.*, 2639 (1960).
47. M. Calligaris, G. Nardin and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 419 (1973).
48. J.G. Gibson and E.D. McKenzie, *J. Chem. Soc. (A)*, 1966 (1971).