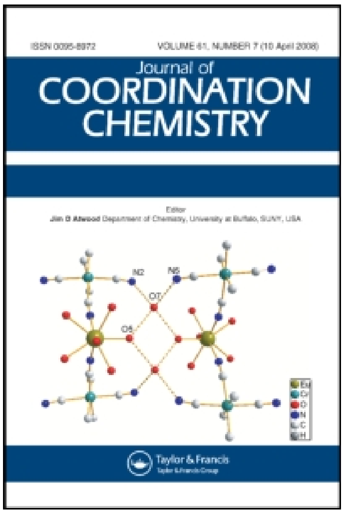

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THE COORDINATION CHEMISTRY OF CIS- AND TRANS-1,2-BIS(2-PYRIDYL)ETHYLENE. FOUR-, FIVE-, AND SIX-COORDINATE COMPLEXES OF NICKEL(II) AND ZINC(II)

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THE COORDINATION CHEMISTRY OF CIS- AND TRANS-1,2-BIS(2-PYRIDYL)ETHYLENE. FOUR-, FIVE-, AND SIX-COORDINATE COMPLEXES OF NICKEL(II) AND ZINC(II)

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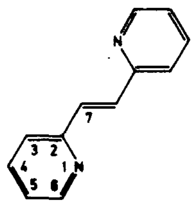
The preparation of cis- and trans-1,2-bis(2-pyridyl)-ethylene (BPE) is described and the different coordination behavior of the two isomers on the basis of their complexes with nickel(II) and zinc(II) are discussed. Fourteen new complexes have been prepared and characterized utilizing electronic spectra, vibrational spectra (conventional and far-infrared), magnetism, electrolytic conductance, and thermal analysis. Eleven further complexes could be detected by thermal analysis. Whereas zinc complexes of both ligands are tetrahedral, the nickel complexes of trans-BPE are planar and octahedral, those of cis-BPE tetrahedral, square-planar and five-coordinate. In chloroform solution the dissociation equilibrium $Ni(cis\text{-}BPE)_2Cl_2$ (five-coordinate) $\rightleftharpoons$ $Ni(cis\text{-}BPE)Cl_2$ (tetrahedral) + cis-BPE was studied spectrophotometrically. By the addition of methanol to cis-BPE complexes under mild conditions, tetragonal 1,2-bis(2-pyridyl)ethyl-methylether complexes are obtained.

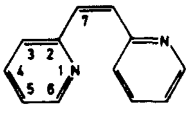
INTRODUCTION

The coordination chemistry of ligands containing two 2-pyridyl groups linked by a diatomic bridge such as $-CH_2-CH_2-$, $-CH{=}CH-$ (trans), $-CO-CO-$, $-N{=}N-$, $-S-S-$, has been previously studied.[1] Complexes of trans-1, 2-bis (2–pyridyl)ethylene (trans-BPE) with cobalt(II), nickel(II) and copper(II) salts were described by Brierley and Geary.[2] From the nickel(II) halides, these authors isolated two complexes: yellow $Ni(trans\text{-}BPE)_{1/2}Cl_2$ with unknown structure, and blue $Ni(trans\text{-}BPE)Br_2$ to which they ascribe a tetrahedral stereochemistry. The preparation of an iron(II) complex with the composition $[Fe(BPE)_3]\,[Fe_4(CO)_{13}]$ was reported by Hieber and Kahlen.[3]

To date no reports are available on the coordination behaviour of cis-1,2-bis(2-pyridyl)ethylene (cis-BPE). Our interest in this ligand arose from the expectation that as a potential chelating agent, it could form seven-membered chelate rings, which can be visualized as vinylogues of the very stable 1,2-diimine chelates.[4–7] This paper describes the preparation and characterization of nickel(II) halide and perchlorate complexes and zinc(II) chloride complexes of cis-BPE. For purposes of comparison, the corresponding complexes of trans-BPE were also prepared and studied, in the course of which large discrepancies were found when compared with Ref. 2.



trans-BPE



cis-BPE

EXPERIMENTAL

Physical Measurements

Thermal analysis were carried out with Netsch Thermo-analyser Model 429 which records TG, DTG and DTA simultaneously. The sample, approximately 100 mg, was heated in vacuo (5.10^{-5} mm Hg) at a rate of 2°/min from room temperature to 500°C. Alumina was used as reference sample. Magnetic measurements were obtained by the Gouy method. The molar susceptibilities are corrected for diamagnetism. Electrolytic conductances were measured at 25 °C using a Wayne Kerr B 221 universal bridge. A Knauer vapor-pressure osmometer was employed for the molecular weight determination. Nmr spectra of the ligands were obtained with a Varian A 60-A and a Bruker HFX 90 spectrometer. Perkin–Elmer Model 21 and 221 spectrophotometers were employed to record infrared spectra as KBr pellets, Beckman IR 12 spectrometer was used to run far infrared spectra on nujol mulls. Visible and ultraviolet spectra of chloroform solutions were taken on a Zeiss DMR 21 spectrophotometer equipped with a constant-temperature compartment and the reflectance spectra on a Zeiss ZR 21 attachment with the DMR 21 spectrophotometer.

Analyses

Elemental analyses for carbon, hydrogen, and nitrogen were carried out at the Institute of Physiological Chemistry, halogen analyses at the Institute of Chemistry, University of Tübingen. Metal analyses were performed by Dr. F. Pascher, Microanalytical Laboratory, Bonn.

Preparation of Ligands

trans-1,2-bis(2-pyridyl)ethylene. Following the method of Marvel, Tweedie and Economy[12] for the preparation of trans-BPE, we obtained 1,2-bis(2-pyridyl) ethanol as the main product (65% yield). 1,2-bis (2-pyridyl)ethanol (40 g, 0.2 mol) was refluxed for two hours with acetic anhydride (200 g, 2 mol). The reaction mixture was evaporated to dryness and the residue distilled in a sabre flask. Crystallization from benzene gave white crystalline trans-BPE (m.p. 118°C) in 75% yield.

cis-1,2-bis(2-pyridyl)ethylene. A solution of trans-BPE (2.2 g, 12 mmol) and benzil (0.27 g, 1.3 mmol) in benzene (850 ml) was irradiated for 1 hr with a 450 Watt Hanovia 679 A/36 mercury lamp, using a solidex glass immersions well. The solvent was evaporated and the residues of 10 batches combined and chromatographed on Al_2O_3 with chloroform as eluent. By concentrating the eluent solution and cooling to 0°C, a part of trans-BPE crystallized out and could be removed by filtration. The filtrate was chromatographed several times on silica gel/acetone, and fractions with R_f value 0.24 were subsequently fractionally crystallized from n-pentane/ether (7:1). cis-BPE was obtained as a white crystalline product melting at 39.0–39.5°C. Yield 80%. *Anal.* Calcd. for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53; N, 15.37. Found: C, 78.79; H, 5.59; N, 15.78.

Preparation of Complexes

All aquated metal salts used were dehydrated with 2,2-dimethoxypropane by stirring the ethanolic solution for 3 hr at 40°C. All solvents were dried and distilled. The complexes were dried in vacuo at 60°C over P_2O_5. Thermogravimetric results refer to weight loss of each decomposition step (in %), which is characterized by the reaction interval (in °C). DTA peaks, which are all endothermic, are reported by t_{max} (in °C).

Ni(cis-BPE)$_2$Cl$_2$. $NiCl_2.6H_2O$ (0.59 g, 2.5 mmol) was dehydrated and dissolved in 10 ml ethanol. After adding cis-BPE (1.09 g, 6 mmol), ether was added until a cloudiness developed. Storage at −30°C for 24 hr gave dark green crystals which were collected and washed with ether/ethanol (6:1). Yield 94%. *Anal.* Calcd. for $C_{24}H_{20}N_4Cl_2Ni$: C, 58.34; H, 4.08; N, 11.34; Cl, 14.35; Ni, 11.88. Found: C, 58.19; H, 3.98; N, 11.34; Cl, 14.50; Ni, 12.26.
TG. Weight loss calcd. for 1 cis-BPE: 36.9. Found: 36.0 (118–182°C), 17.5 (208–237°C), 17.5 (312–410°C). *DTA.* 159, 230/233, 345/377/386°C.

Ni(cis-BPE)Cl$_2$. Ethanolic solutions of dehydrated $NiCl_2$ and cis-BPE were mixed in 1:1.1 mol ratio. After adding the same volume of chloroform, the solvent was cautiously evaporated in a stream of nitrogen at 35°C. The red-brown crystals which formed were collected and washed with chloroform. Yield 94%. *Anal.* Calcd. for $C_{12}H_{10}N_2Cl_2Ni$: C, 46.22; H, 3.23; N, 8.98; Cl, 22.74; Ni, 18.83. Found: C, 45.98; H, 3.19; N, 8.95; Cl, 23.03; Ni, 18.11.
TG. Weight loss calcd. for 1/2 cis-BPE: 29.2. Found: 27.9 (219–258°C), 27.9 (313–440°C). *DTA.* 251, 354/387°C.

This product was also prepared by heating $Ni(cis\text{-}BPE)_2Cl_2$ to constant weight in vacuo at 135°C. Weight loss calcd. for 1 cis-BPE: 36.9. Found: 36.9.

Ni(cis-BPE)$_2$Br$_2$.EtOH. To a solution of dehydrated $NiBr_2$ (0.55 g, 2.5 mmol) in 10 ml ethanol was added a solution of cis-BPE (1.09 g, 6 mmol) in 15 ml ethanol. The dark green crystals which separated on standing at −50°C were filtered off and washed with ethanol. Yield 83%. *Anal.* Calcd. for $C_{26}H_{26}N_4OBr_2Ni$: C, 49.64; H, 4.17; N, 8.91; Br, 25.41; Ni, 9.33. Found: C, 49.60; H, 4.05; N, 8.94; Br, 25.09; Ni, 9.21.
TG. Weight loss calcd. for 1 EtOH: 7.3, for 1 cis-BPE: 28.9. Found: 7.0 (110–136°C), 28.9 (171–201°C), 14.3 (236–263°C), 14.3 (283–354°C). *DTA.* 123, 189/194, 255, 310°C.

Ni(cis-BPE)$_2$Br$_2$. This complex was prepared from the preceding one by heating at 130°C in vacuo for 3 hr. *Anal.* Calcd. for $C_{24}H_{20}N_4Br_2Ni$: C, 49.45; H, 3.46; N, 9.61; Br, 27.42; Ni, 10.07. Found: C, 49.38; H, 3.64; N, 9.59; Br, 27.28; Ni, 9.78.

Ni(cis-BPE)Br_2. Ethanolic solutions of dehydrated $NiBr_2$ and cis-BPE were mixed in 1:1.1 mol ratio. Addition of chloroform gave the yellowish brown complex, which was filtered off and washed with chloroform. Yield 81%. *Anal.* Calcd. for $C_{12}H_{10}N_2Br_2Ni$: C, 35.96; H, 2.52; N, 6.99; Br, 39.88; Ni, 14.65. Found: C, 36.03; H, 2.48; N, 7.04; Br, 39.43; Ni, 13.60.
TG. Weight loss calcd. for 1/2 cis-BPE: 22.7. Found: 23.5 (232–275°C), 22.7 (285–349°C). *DTA.* 258, 322°C.

Ni(cis-BPE)$_2I_2\cdot 2CHCl_3$. This was prepared as for the preceding compound using dehydrated NiI_2. Yield 94%. *Anal.* Calcd. for $C_{26}H_{22}N_4Cl_6I_2Ni$: C, 34.10; H, 2.24; N, 6.12; Cl, 23.23; I, 27.71; Ni, 6.41. Found: C, 34.16; H, 2.37; N, 6.13; Cl, 22.89; I, 27.32; Ni, 6.24.
TG. Weight loss calcd. for 2 $CHCl_3$: 26.1, for 1 cis-BPE: 19.9. Found: 27.6 (108–157°C), 17.8 (157–216°C), 19.0 (223–250°C). *DTA.* 137, 200, 242°C.

Ni(cis-BPE)$_2(ClO_4)_2$. cis-BPE (1.09 g, 6 mmol) dissolved in 15 ml ethanol was added slowly to a stirred solution of dehydrated $Ni(ClO_4)_2$ (0.64 g, 2.5 mmol) in 20 ml ethanol. The yellow complex which precipitated immediately was collected and washed with ethanol. Yield 97%. *Anal.* Calcd. for $C_{24}H_{20}N_4O_8Cl_2Ni$: C, 46.34; H, 3.24; N, 9.01; Cl, 11.40; Ni, 9.44. Found: C, 46.45; H, 3.33; N, 8.90; Cl, 11:40; Ni, 9.37.
Decomposition at 282°C.

Zn(cis-BPE)Cl_2. This complex precipitated as a white solid on mixing ethanolic solutions of $ZnCl_2$ and cis-BPE in 1:2.3 mol ratio. The product was collected and washed with ethanol. Yield 92%. *Anal.* Calcd. for $C_{12}H_{10}N_2Cl_2Zn$: C, 45.25; H, 3.16; N, 8.80; Cl, 22.26; Zn, 20.53. Found: C, 45.35; H, 3.23; N, 8.40; Cl, 22.04; Zn, 20.52.
TG. Weight loss calcd. for 1/2 cis-BPE: 28.7. Found: 29.0 (239–289°C). *DTA.* 281°C.

Ni(trans-BPE)Cl_2. trans-BPE (1.82 g, 10 mmol) in methanol (15 ml) was added to a stirred solution of dehydrated $NiCl_2$ (0.52 g, 4 mmol) in methanol (15 ml). The volume of the mixture was reduced to 20 ml and then ether (100 ml) was added. A pale yellow precipitate was obtained, which was filtered and washed with ether. Yield 94%. *Anal.* Calcd. for $C_{12}H_{10}N_2Cl_2Ni$: C, 46.22; H, 3.23; N, 8.98; Cl, 22.74; Ni, 18.83. Found: C, 46.59; H, 3.39; N, 8.79; Cl, 22.65; Ni, 18.60.
TG. Weight loss calcd. for 1/2 trans-BPE: 29.2. Found: 30.0 (181–207°C), 29.2 (296–430°C). *DTA.* 193°C.

Ni(trans-BPE)Br_2. This complex separated, when ethanolic solutions of trans-BPE and anhydrous $NiBr_2$ were mixed in 1:2.5 mol ratio. After heating the mixture at 80°C and stirring for 12 hr at room temperature, the pale brown precipitate was collected and washed with ethanol. Yield 77%. *Anal.* Calcd. for $C_{12}H_{10}N_2Br_2Ni$: C, 35.96; H, 2.52; N, 6.99; Br, 39.88; Ni, 14.65. Found: C, 36.14; H, 2.75; N, 6.91; Br, 39.24; Ni, 14.39.
TG. Weight loss calcd. for 1/2 trans-BPE: 22.7. Found: 23.2 (174–215°C), 23.0 (269–324°C). *DTA.* 187, 307°C.

Ni(trans-BPE)I_2. The preparation of this product was similar to that of the bromide. Using dehydrated NiI_2 (1.25 g, 4 mmol) and stirring the mixture for 3 hr at 70°C, a brown solid was obtained. Yield 94%. *Anal.* Calcd. for $C_{12}H_{10}N_2J_2Ni$: C, 29.13; H, 2.04; N, 5.66; I, 51.30; Ni, 11.87. Found: C, 29.63; H, 2.04; N, 5.67; I, 51.11; Ni, 11.05.
TG. Weight loss calcd. for 1/2 trans-BPE: 18.4. Found: 15.3 (211–275°C), 15.8 (275–371°C). *DTA.* 254, 323°C.

Zn(trans-BPE)$_{3/2}Cl_2$. trans-BPE (2.74 g, 15 mmol) in ethanol (30 ml) was added dropwise to a stirred solution of $ZnCl_2$ (0.84 g, 6 mmol) in ethanol (20 ml). The white solid was filtered off and washed with ethanol. Yield 93%. *Anal.* Calcd. for $C_{18}H_{15}N_3Cl_2Zn$: C, 52.78; H, 3.69; N, 10.26; Cl, 17. 31; Zn, 15.96. Found: C, 52.43; H, 3.63; N, 10.15; Cl, 17.36; Zn, 16.40.
TG. Weight loss calcd. for 1/2 trans-BPE: 22.2. Found: 22.2 (140–216°C), 23.0 (229–263°C). *DTA.* 202, 260, 310°C.

Ni(BPEtOMe)$_2I_2$. cis-BPE (1.11 g, 6 mmol) in ethanol (15 ml) was added to a stirred solution of dehydrated NiI_2 (0.78 g, 2.5 mmol) in ethanol (20 ml). After removing the solvent, the yellow precipitate was dissolved in methanol (30 ml) and the solution was allowed to stand for 2 days at room temperature. The light grey complex which separated from the blue solution by crystallization at –50°C and precipitation with ether was collected and washed with ethanol. Yield 93%. *Anal.* Calcd. for $C_{26}H_{28}N_4O_2I_2Ni$: C, 42.14; H, 3.81; N, 7.56; I, 34.25; Ni, 7.92. Found: C, 41.90; H, 3.79; N, 7.39; I, 34.06; Ni, 7.67.
TG. Found: 47.3 (177–237°C), 10.9 (299–310°C). *DTA.* 225, 305°C.

Ni(BPEtOME)$_2$(ClO$_4$)$_2$. Upon treating Ni(cis-BPE)$_2$(ClO$_4$)$_2$ with methanol at 60°C for 4 hr, the yellow complex turned to light violet without dissolving. The solid was filtered and washed with ethanol. Yield 95%. *Anal.* Calcd. for $C_{26}H_{28}N_4O_{10}Cl_2Ni$: C, 45.51; H, 4.11; N, 8.17; Cl, 10.33; Ni, 8.56. Found: C, 45.51; H, 3.98; N, 8.07; Cl, 10.40; Ni, 7.88.

Decomposition at 280°C.

Hydrolysis of this complex with aceton/water gave the free ligand, which was chromatographed on silica gel/aceton. *Anal.* Calcd. for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.39; H, 6.47; N, 13.15.

RESULTS AND DISCUSSION

Ligands

The preparation of trans-BPE has been described.[8-15] We prepared trans-BPE by the dehydration of 1,2-bis-(2-pyridyl)ethanol in boiling acetic anhydride. The reaction of 2-picolyllithium with pyridine-2-aldehyde yielded 1,2-bis(2-pyridyl)ethanol as the main product, and not trans-BPE as was reported by Marvel, Tweedy and Economy.[12]

cis-BPE was first prepared by Jerchel and Melloh[16] by the partial hydrogenation of bis(2-pyridyl)acetylene. The photochemical isomerization of 1,2-bis-(2-pyridyl)ethylenes has been investigated by several groups.[17-23] For the first time cis-BPE has now been prepared in crystalline form (m.p. 39.5°C) by sensitized photoisomerization followed by repeated chromatographic purification.

The infrared spectrum of cis-BPE shows the expected band at 1638 cm^{-1} due to the C=C stretching vibration of the ethylenic group. The C–H rocking vibration of the ethylenic group appears at 1396 cm^{-1} for the cis-BPE, and at 1325 cm^{-1} for the trans-BPE.

The ^{1}H nmr spectra of both dipyridylethylenes consist of the expected ABCX system for the pyridine protons, together with a singlet arising from the ethylenic protons. The calculated chemical shifts and coupling constants are given in Table I.[24] A striking feature is the large shift (0.93 ppm) of the H_7 signal to higher field from trans to cis isomer. This effect, greater in magnitude than is the case with the stilbenes, supports the results of Coletta, Gambaro and Pasimeni,[25] who suggested, that the ethylenic protons of trans-BPE are much involved in the interaction with the lone pair electrons of the nitrogen atoms. The signals of the pyridine protons occur also at higher fields for the cis than for the trans isomer, but the differences are small in comparison to the shift of the olefinic protons.

TABLE I
^{1}H Chemical shifts δ (ppm) and coupling constants J (Hz) of cis- and trans-BPE in hexadeuteroacetone[a]

			δ		
Compound	H_3	H_4	H_5	H_6	H_7
trans-BPE	7.55	7.76	7.25	8.61	7.77
cis-BPE	7.42	7.60	7.18	8.53	6.84

Compound	$^3J_{34}$	$^4J_{35}$	$^5J_{36}$	$^3J_{45}$	$^4J_{46}$	$^3J_{56}$
trans-BPE	7.9	1.1	0.9	7.5	1.9	4.8
cis-BPE	8.0	1.2	0.9	7.6	1.8	4.8

[a] relative to ^{1}H resonance of Me_4Si.

By comparison of the ^{13}C nmr spectra of trans- and cis-BPE (Table II), a shift to higher field in the case of cis-BPE is encountered only for the carbon atom C_4, C_5 and C_6. The signals of C_2, C_3 and C_7 are shifted to lower field, presumably as a result of the steric influence of the configuration on these carbon atoms.

Complexes

The cis- and trans-BPE complexes were prepared either by reaction of the ligands with dehydrated metal salts, or by thermal decomposition. The BPEtOMe complexes were obtained by addition of methanol under mild conditions to the corresponding cis-BPE complexes. Some of the physical properties of the complexes are presented in Table III.

cis-BPE complexes. cis-BPE forms both 1:1 and 1:2 complexes with nickel(II) chloride and bromide. With nickel(II) iodide and perchlorate, 1:2 complexes are obtained, with zinc chloride a 1:1 complex is isolated.

TABLE II
^{13}C Chemical shifts δ (ppm) and one-bond ^{13}C–^{1}H coupling constants ^{1}J (Hz) in deuterochloroform[a]

				δ		
Compound	C_2	C_3	C_4	C_5	C_6	C_7
trans-BPE	154.5	122.8	136.2	122.1	149.3	131.3
cis-BPE	155.4	123.9	135.5	121.9	149.1	132.7

			$^1J_{CH}$		
Compound	C_3	C_4	C_5	C_6	C_7
trans-BPE	162	162	163	177	158
cis-BPE	164	162	162	177	158

[a] relative to ^{13}C resonance of Me_4Si

TABLE III
Colors, magnetic, conductance and electronic spectral data of complexes

Complex	Color	Magnetic moment[a] μcff B.M.	Molar conductance[b] ΛM S cm² mol⁻¹	Electronic reflectance spectra νmax kK
$Ni(cis\text{-}BPE)_2Cl_2$	green	3.25	10.8	5.7, 10.9, 15.8, 25.8
$Ni(cis\text{-}BPE)Cl_2$	red-brown	3.42	0.3	5.8, 9.0, 12.9, 19.5, 22.7
$Ni(cis\text{-}BPE)_2Br_2.EtOH$	green	3.21	22.4	5.6, 10.2, 15.9, 25.8
$Ni(cis\text{-}BPE)_2Br_2$	green	3.25	22.2	5.6, 10.2, 15.4, 24.9
$Ni(cis\text{-}BPE)Br_2$	yellowish brown	3.38	0.2	5.5, 8.9, 10.1, 13.0, 19.0, 22.3
$Ni(cis\text{-}BPE)_2I_2.2CHCl_3$	ochre	diamagnetic	27.1	11.1, 22.8
$Ni(cis\text{-}BPE)_2(ClO_4)_2$	yellow	diamagnetic	52.7	15.5, 23.8
$Zn(cis\text{-}BPE)Cl_2$	white			
$Ni(trans\text{-}BPE)Cl_2$	pale yellow	3.35		7.4, 11.9, 13.1, 22.7
$Ni(trans\text{-}BPE)Br_2$	pale brown	3.41		7.1, 11.3, 12.2, 18.5, 21.7
$Ni(trans\text{-}BPE)I_2$	dark brown	diamagnetic		10.7, 16.1, 21.3
$Zn(trans\text{-}BPE)_{3/2}Cl_2$	white			
$Ni(BPEtOMe)_2I_2$	light grey	3.18	56.5	9.1, 13.1, 15.3, 19.5, 27.6
$Ni(BPEtOMe)_2(ClO_4)_2$	light violet	3.22	59.9	8.9, 12.5, 14.7, 18.5

[a] at 23°C; all complexes obey the Curie–Weiss law in the range 77–310°K.
[b] in nitrobenzene at 25°C (10^{-3} M solutions).

In solid state, the green complexes $Ni(cis\text{-}BPE)_2Cl_2$, $Ni(cis\text{-}BPE)_2Br_2 \cdot EtOH$ and $Ni(cis\text{-}BPE)_2Br_2$ exhibit magnetic moments of ~3.2 B.M. corresponding to two unpaired electrons. The infrared spectra show the typical band of C=C stretching mode of the ethylenic group at about 1628 cm^{-1}, 10 cm^{-1} below the free ligand value. The frequency of the out-of-plane ring deformation vibration of the pyridine groups, which occurs in the spectrum of the free ligand at 406 cm^{-1}, is increased to ~430 cm^{-1} in the complexes, indicating that all pyridine groups are coordinated to the nickel ion.[26] The nickel–chloride stretching vibration of the chloride complex is observed at 275 cm^{-1}, indicating five-coordination.[27] A five-coordinate stereochemistry with the chromophore N_4X (X = halogen) is in accord with the electronic spectra of the three compounds, being similar to those of known high-spin five-coordinate (square-pyramidal) complexes.[28–30] The solid reflectance spectrum of $Ni(cis\text{-}BPE)_2Cl_2$ is recorded in Figure 1. According to Sacconi,[31] paramagnetism is to be expected for nickel(II) complexes with the donor set N_4X (X = Cl, Br).

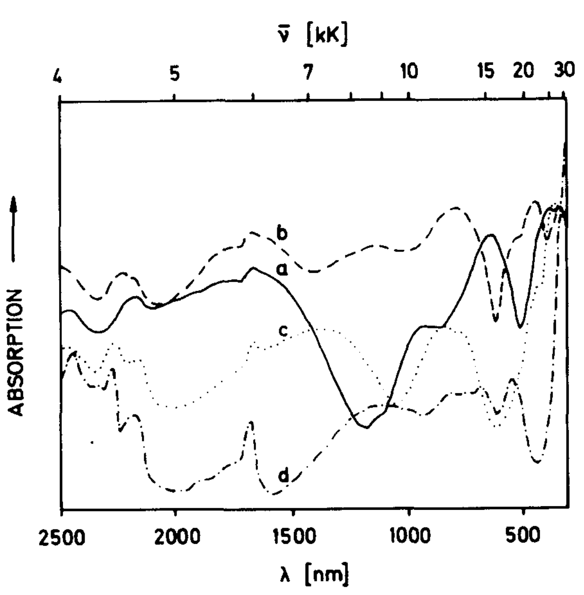


FIGURE 1 Reflectance spectra of (a) $Ni(cis\text{-}BPE)_2Cl_2$, (b) $Ni(cis\text{-}BPE)Cl_2$, (c) $Ni(trans\text{-}BPE)Cl_2$ and (d) $Ni(BPEtOMe)_2(ClO_4)_2$.

The thermal behaviour of the complexes in vacuo is illustrated by the thermoanalytical curves in Figures 2 and 3. Thus, decomposition occurs stepwise in the following way:

$$NiL_2X_2 \xrightarrow{-L} NiLX_2 \xrightarrow{-1/2L}$$

$$NiL_{1/2}X_2 \xrightarrow{-1/2L} NiX_2$$

(L = cis-BPE; X = Cl, Br)

In the case of $Ni(cis\text{-}BPE)_2Br_2 \cdot EtOH$, these endothermic decomposition steps are preceded by the cleavage of 1 mol ethanol. At the composition $Ni(cis\text{-}BPE)_{3/2}Br_2$, TG, DTG and DTA curves of this

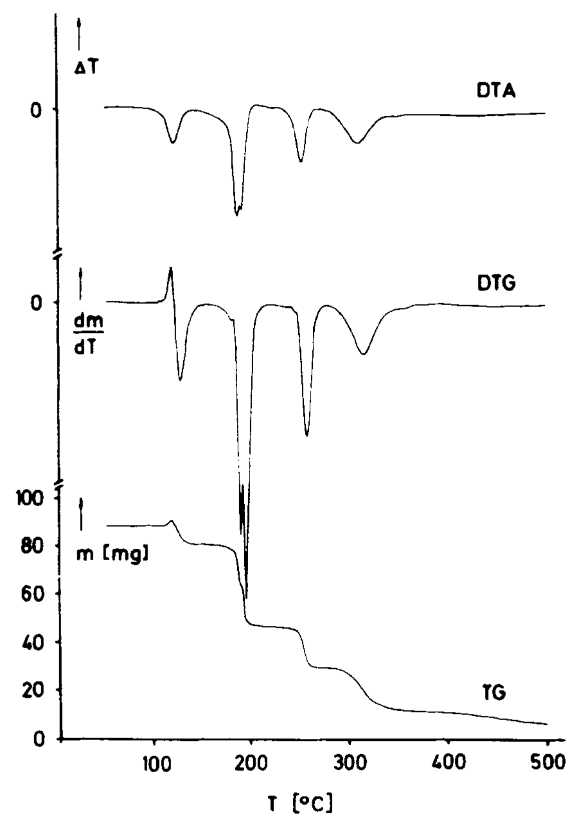


FIGURE 2 Thermoanalytical curves (TG, DTG and DTA) of Ni(cis-BPE)$_2$Br$_2$.EtOH.

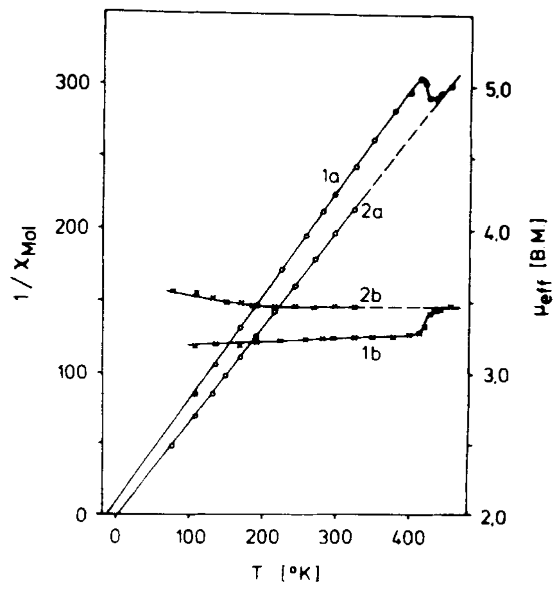


FIGURE 4 Reciprocal susceptibility (a) and magnetic moment (b) of Ni(cis-BPE)$_2$Cl$_2$ (1) and Ni(cis-BPE)Cl$_2$ (2) with temperature.

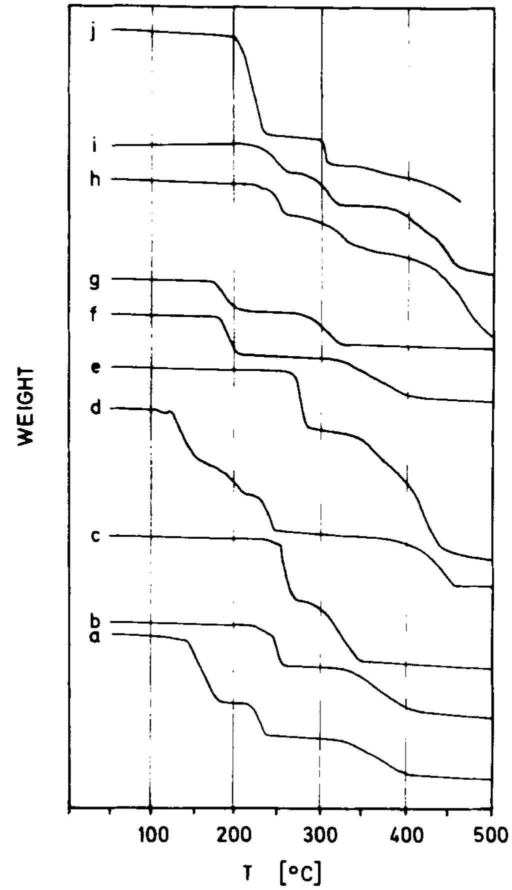


FIGURE 3 Thermogravimetric curves of (a) Ni(cis-BPE)$_2$Cl$_2$, (b) Ni(cis-BPE)Cl$_2$, (c) Ni(cis-BPE)Br$_2$, (d) Ni(cis-BPE)$_2$I$_2$.2CHCl$_3$ (e) Zn(cis-BPE)Cl$_2$, (f) Ni(trans-BPE)Cl$_2$, (g) Ni(trans-BPE)Br$_2$, (h) Ni(trans-BPE)I$_2$, (i) Zn(trans-BPE)$_{3/2}$Cl$_2$ and (j) Ni(BPEtOMe)$_2$I$_2$.

complex suggest a further intermediate compound.

Investigation of the first reaction step for Ni(cis-BPE)$_2$Cl$_2$ by magnetic measurement provides the temperature dependence of reciprocal molar susceptibility and magnetic moment shown in Figure 4. Below 135°C the susceptibility of the 1:2 complex follows the Curie–Weiss law. At 135°C the curve falls and finally changes to the straight line associated with the 1:1 complex. Accordingly, the magnetic moment increases during the reaction from 3.28 B.M., the moment of the 1:2 complex, to 3.45 B.M., the value for the 1:1 complex.

The dissociation of the complexes Ni(cis-BPE)$_2$X$_2$ occurs also in solution and leads to a temperature and concentration dependent equilibrium. Solutions of Ni(cis-BPE)$_2$Cl$_2$ in chloroform show a reversible color change from green to red upon increase in temperature

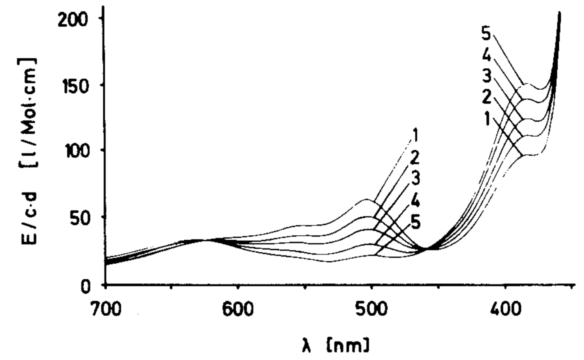


FIGURE 5 Electronic spectra of solutions of $Ni(cis\text{-}BPE)_2Cl_2$ in chloroform at 38.8°C on varying the concentration: (1) $1.7.10^{-3}$ M, (2) $2.8.10^{-3}$ M, (3) $4.7.10^{-3}$ M, (4) $1.0.10^{-2}$ M and (5) $2.0.10^{-2}$ M.

or decrease in concentration:

$$\underset{\text{green}}{Ni(cis\text{-}BPE)_2Cl_2} \rightleftharpoons \underset{\text{red}}{Ni(cis\text{-}BPE)Cl_2} + cis\text{-}BPE$$

The changes in visible absorption spectra of these solutions on varying the concentration at 38.8°C are illustrated in Figure 5. Using the absorbance at 390 and 500 nm, each of which is attributed solely to one of the complexes of equilibrium, the equilibrium quotient $K = [Ni(cis\text{-}BPE)Cl_2]\,[cis\text{-}BPE] / [Ni(cis\text{-}BPE)_2Cl_2]$ is determined from the spectra for three temperatures: $K = 8.8 \cdot 10^{-5}$ (19.2°C), $6.4 \cdot 10^{-4}$ (38.8°C), $2.6 \cdot 10^{-3}$ (56.6°C) mol l^{-1}. From the temperature dependence of K, a positive reaction entropy of ~170 J K^{-1} mol^{-1} and an endothermic enthalpy of ~70 kJ mol^{-1} is estimated. These values lie in the expected range for this type of dissociation reaction.[32–34]

The solution spectrum of $Ni(cis\text{-}BPE)_2Cl_2$ in chloroform is identical with the reflectance spectrum of the solid complex. The extinction coefficients (extrapolated by means of the equilibrium quotient) are consistent with the five-coordinate formulation: $\epsilon = 180$ (25.8 kK), 35 (15.8 kK) l mol^{-1} cm^{-1}. The osmometric molecular weight measurement of a $2.5 \cdot 10^{-2}$ molar solution in chloroform at 25°C indicates that this complex exists as monomer, i.e. both pyridine groups of the bidentate ligand are coordinated to the same nickel ion. The complex thus represents a chelate compound with a seven-membered chelate ring. The electronic solution spectrum of the $Ni(cis\text{-}BPE)Cl_2$ species is typical of pseudotetrahedral nickel complexes:[35] ν/kK (ϵ) = 6.8 (20), 10.7 (60), 12.0 (30), 18.2 sh, 19.9 (135). The low energy band at 6.8 kK is assigned to one of the components of the ν_1 $^3T_1(F) \rightarrow {}^3T_2(F)$ transition in tetrahedral symmetry. The bands at 10.7 kK and 19.9 kK are assigned to the transitions ν_2 $^3T_1(F) \rightarrow {}^3A_2(F)$ and ν_3 $^3T_1(F) \rightarrow {}^3T_1(P)$ respectively. The peak located at 12.0 kK is tentatively attributed to a spin-forbidden transition.

The molar conductances of the five-coordinate complexes in nitrobenzene lie, as expected, in the range of uni-univalent electrolytes. The lower value of the chloride (~11 S cm^2 mol^{-1}) compared with that of the bromides (~22 S cm^2 mol^{-1}) arises from the appreciable dissociation of the chloride complex to the non-conductive 1:1 complex at room temperature. The conductance of $Ni(cis\text{-}BPE)_2Br_2 \cdot EtOH$ indicates that the fifth coordination position is occupied by the bromide ion, but not by the alcohol. The ethanol molecule is probably linked to the free bromide ion by hydrogen bonding.

Analogously to the 1:2 complexes, the complexes $Ni(cis\text{-}BPE)Cl_2$ and $Ni(cis\text{-}BPE)Br_2$ in solid state are high-spin five-coordinate. Their infrared spectra display the ν(C=C) band of the ethylenic group at 1630 cm^{-1} and at ca. 430 cm^{-1} the bands of the pyridine out-of-plane deformation vibrations. The absence of the corresponding band of the free ligand at 406 cm^{-1} indicates that both pyridine rings are coordinated. The intense ν(Ni–Cl) bands of the chloride complex at 293 and 271 cm^{-1} are located in a frequency range typical for five-coordination, and which excludes both tetrahedral and octahedral configurations. Also characteristic for a five-coordinate structure of the solid complexes are the electronic spectra which are similar to those of known trigonal-bipyramidal complexes[36–39] (Figure 1). In accordance with the five-coordination, the complexes are not monomeric, but associated in solid state, with the nickel ion being linked by bridging halide ions.

On the other hand, the complexes possess tetrahedral coordination sphere in solution, as is shown by electronic spectrum of the chloride complex (see above) and by conductances (Table III). In this case, the complexes with the donor group N_2X_2 (X = Cl, Br), in general not particularly stable, exist only in solution. In solid state they are stabilized by association, giving complexes with the donor group N_2X_3. Steric requirements of the ligand prevent the formation of octahedral coordination polymers. Apparently the energy difference between the monomer tetrahedral, and associated five-coordinate forms of these complexes is so small as a result of the compensation of steric and electronic effects, that even lattice and solvation effects are sufficient to influence the coordination in these complexes.

The thermal decomposition of $Ni(cis\text{-}BPE)Cl_2$ and

Ni(cis-BPE)Br_2 occurs stepwise according to the last two steps of the reaction scheme for the 1:2 complexes, as is seen from the TG curves (Figure 3).

In solid state, the yellow complexes Ni(cis-BPE)$_2I_2$ · 2 $CHCl_3$ and Ni(cis-BPE)$_2(ClO_4)_2$ have a square-planar structure based on their electronic spectra and their diamagnetism. Infrared spectra support the presence of bidentately coordinated cis-BPE ligand. The unsplit band at 622 cm^{-1} of perchlorate complex is indicative of non-bonded perchlorate groups. As in the case of the five-coordinate complexes, the ν(C=C) band of the ethylenic group is shifted slightly to lower frequency compared with that of the free ligand (iodide: 1634 cm^{-1}, perchlorate: 1631 cm^{-1}). In nitrobenzene solution, the perchlorate complex exhibit the expected molar conductance for a 1:2 electrolyte of 52 S cm^2 mol^{-1}.

Both complexes react with methanol which adds across the olefinic double bond of the ligand yielding tetragonal 1:2 complexes of 1,2-bis(2-pyridyl)ethylmethylether (see below). This reaction is an indication that the ligand molecules in the complexes Ni(cis-BPE)$_2I_2$ · 2$CHCl_3$ and Ni(cis-BPE)$_2(ClO_4)_2$ are arranged centrosymmetrically to the nickel ion, i.e. the ethylenic group of one ligand molecule lies above, the other below the NiN_4 plane.

The percholate complex is thermally very stable – no decomposition is observed at temperatures up to 280°C. In contrast, the iodide complex decomposes stepwise above 110°C according to the following scheme (Figure 3):

$$NiL_2I_2 \cdot 2CHCl_2 \xrightarrow{-2CHCl_3} NiL_2I_2 \xrightarrow{-L}$$

$$NiLI_2 \xrightarrow{-L} NiI_2$$

(L = trans-BPE)

With zinc chloride, cis-BPE forms a complex of the composition Zn(cis-BPE)Cl_2. The infrared spectrum implies a tetrahedral stereochemistry (Zn–Cl stretching mode at 308 and 327 cm^{-1}) and indicates that cis-BPE is coordinated as a bidentate ligand.

Heating in vacuo leads to decomposition via the intermediate compound Zn(cis-BPE)$_{1/2}Cl_2$, recognizable from the plateau in the thermogravimetric curve (Figure 3).

trans-BPE complexes. With nickel(II) halides, complexes of the composition Ni(trans-BPE)X_2 (X = Cl, Br, I) were isolated, with zinc chloride the complex Zn(trans-BPE)$_{3/2}Cl_2$. On the other hand, complexes of the form Ni(trans-BPE)$_2X_2$ and nickel(II) perchlorate complexes could not be synthesized.

In solid state, Ni(trans-BPE)Cl_2 and Ni(trans-BPE) Br_2 possess octahedral structure as is indicated by ir and uv spectra, and their magnetic moments. The band arising from the out-of-plane ring deformation vibration of the pyridine groups which occurs in the free ligand at 404 cm^{-1}, is shifted to 430–440 cm^{-1} in the complexes. This means both pyridine rings are coordinated. In the range 260–430 cm^{-1} no intensive absorption band is visible thus precluding the possibility of tetrahedral or five-coordinate stereochemistry. The reflectance spectra are characteristic for octahedral coordination, and are closely related to spectra of the corresponding anhydrous nickel halides[40] (Figure 1). The bands at ~7, ~11.5 and 22 kK are attributed to ν_1 $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ν_2 $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ν_3 $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions respectively for an octahedral ligand field about the nickel(II) ion, well in agreement with the Tanabe–Sugano diagram for octahedral d^8 complexes.[41] The shoulders at 13.1 kK (chloride) and 12.2 kK (bromide) may be assigned to the spin-forbidden transition to the E_{1g} level. The 10 Dq values (7400 cm^{-1} for X = Cl and 7100 cm^{-1} for X = Br, directly obtained from the position of the first transition band) are very low in comparison with other octahedral amine complexes of the composition Ni(amine)$_2X_2$[42] and lie in the range of the 10 Dq values of the uncomplexed nickel halides.[43] This may be a consequence of considerable steric hindrance in the trans-BPE nickel complexes. The nickel ion presumably achieves six coordination by polymerization by means of halide bridges and bidentately coordinated trans-BPE. The magnetic moments (Table III) fall in the range expected for nickel complexes with the donor group trans-N_2X_4 (3.3–3.5 B.M.).[44,45] Both complexes are insoluble in nitrobenzene.

Upon thermal decomposition in vacuo (Figure 3) the organic ligand is evolved in two steps, whereby an intermediate compound of the composition Ni(trans-BPE)$_{1/2}X_2$ is formed:

$$NiLX_2 \xrightarrow{-1/2L} NiL_{1/2}X_2 \xrightarrow{-1/2L} NiX_2$$

(L = trans-BPE; X = Cl, Br)

The complex Ni(trans-BPE)I_2 is diamagnetic. In the far-infrared spectrum, the band of the ring deformation vibration at 466 cm^{-1} indicate a stronger bonding of the bidentate ligand than is found for the bromide or chloride complex. The electronic reflectance spectrum is typical of a planar stereochemistry.[46,47] No d–d band is observed below 1000 cm^{-1}. Since the trans configuration of the ligand precludes the coordination of both pyridine rings on one nickel ion, the complex exists as a polymer bridged by the trans-BPE ligand. This accounts for the low solubility in nitrobenzene.

The thermal decomposition occurs in two steps, analogously to the reaction scheme of the corresponding chloride and bromide complexes (X = I) (Figure 3). It begins, however, at noticeable higher temperature (see Experimental).

The zinc chloride complex of trans-BPE, Zn(trans-BPE)$_{3/2}$Cl$_2$ seems to be dimeric with one bridging bidentate and two monodentate trans-BPE ligands. The very complex infrared spectrum of this complex displays bands typical for both coordinated and uncoordinated pyridine residues. The ν(Zn–Cl) bands appear at 316 cm^{-1} and 312 cm^{-1} and indicate a tetrahedral stereochemistry of the zinc ion.

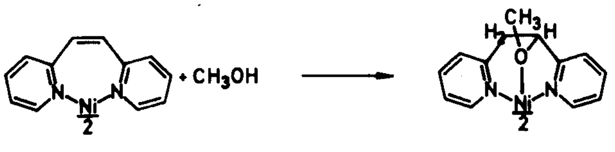
Zn(trans-BPE)$_{3/2}$Cl$_2$ undergoes thermal decomposition by successive loss of trans-BPE (Figure 3). The first two steps are:

$$ZnL_{3/2}Cl_2 \xrightarrow{-1/2L} ZnLCl_2 \xrightarrow{-1/2L} ZnL_{1/2}Cl_2$$

(L = trans-BPE)

As expected, the 1:1 complex formed in the first decomposition step has a simple ir spectrum, in which the free ligand bands are no longer present. The tetrahedral stereochemistry of the zinc ion however remains: ν(Zn–Cl) = 330 and 311 cm^{-1}. This complex may be polymeric through the organic ligand.

BPEtOMe complexes. The complexes of 1,2-bis(2-pyridyl)ethyl-methylether (BPEtOMe), Ni(BPEtOMe)$_2$I$_2$ and Ni(BPEtOMe)$_2$(ClO$_4$)$_2$ are formed by the addition of methanol across the ethylenic double bond of the cis-BPE complex of nickel iodide or perchlorate under mild conditions:



The complexes are paramagnetic (3.2 B.M.). Their infrared spectra reveal that BPEtOMe is coordinated as a tridentate ligand involving both pyridine residues and the ether oxygen atom. The ν(C–O–C) band of the free ligand obtained by hydrolysis of the complexes (at 1087 – 1107 cm^{-1}) is shifted by ca. 40 cm^{-1} to lower frequencies in the complexes, as is also observed with nickel(II) complexes of methanol.[48] The unsplit band at 621 cm^{-1} of perchlorate complex is indicative of non-coordinated perchlorate ion, in agreement with the results of conductance measurements which show for both complexes a 1:2 electrolyte behavior (Table III). The electronic reflectance spectra of BPEtOMe complexes, which are very similar to the absorption spectrum of the comparable complex [Ni(en)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$[49] suggest trans-octahedral configuration, with an NiN$_4$O$_2$ chromophore (Figure 1). As in the case of latter complex, the tetragonal distortion leads to appreciable splitting of the bands.

Ni(BPEtOMe)$_2$I$_2$ and Ni(BPEtOMe)$_2$(ClO$_4$)$_2$ are thermally quite stable. Decomposition of the iodide complex takes place at temperatures above 177°C, the perchlorate complex decomposes explosively at 280°C. Evolution of methanol is not observed. The decomposition of the iodide complex occurs in two well defined steps (Figure 3). The mass spectrum of this complex, and the elemental analysis of the first decomposition product support the postulate that during the first reaction step, the methyl group of the ligand reacts to at least some extent with the iodide ions of the complex in the sense of an ether cleavage.

CONCLUSION

The differing coordination behavior of the cis and trans isomers of 1,2-bis(2-pyridyl)ethylene can be summarized as follows:

trans-BPE, as a bidentate ligand, forms complexes in which one ligand molecule is coordinated to two metal ions, leading to polymeric structures with the ligand as bridging group. In the case of the complexes Ni(trans-BPE)X$_2$ (X = Cl, Br), because of the relatively low polarizability of these anions, the chains are also crosslinked by halogen bridging, whereby the coordination number of these complexes increases to six. In the case of the more polarizable anion X = I the four-coordinate structure is stable. The weak donor ClO_4^- is not capable of forming stable trans-BPE 1:1 complexes. The nonexistence of 1:2 complexes of trans-BPE must arise through the steric requirements of the bridging ligand.

cis-BPE differs from trans-BPE in coordination behavior in the following respects.

1) cis-BPE complexes are true chelate compounds – both pyridine nitrogen atoms are bound to

the same metal atom with the formation of a seven-membered ring.

2) 1:2 complexes can be obtained. The steric limitations of the trans-BPE are not existent in cis-BPE because of its chelating ability.

3) cis-BPE forms five-coordinate complexes with nickel(II) chloride and bromide. This fact is especially interesting considering the conformation of the seven-membered chelate ring in these complexes. Five-coordination is principally observed for divalent nickel with polydentate pyridine ligands, when steric requirements of the ligands precludes the formation of six-coordinate complexes.[30] Obviously, octahedral coordination of the complexes of cis-BPE is prevented by the fact that the π-electrons of the ethylenic group and the hydrogen atoms of carbon 6 block the sixth coordination position. This means that the seven-membered chelate ring deviates considerable from planarity, and that the pyridine rings are twisted substantially out of the plane of the ethylenic σ-bonds. A stabilization by cyclic delocalisation of the π-electrons as is observed with the 1,2-diimine five-membered ring chelates, is thus not to be expected in the case of the vinylogue seven-membered ring chelates.

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