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# Polymeric transition metal complexes of 1,4-bis-(4pyridylsulfenylmethyl)benzene and of its 2-pyridyl analogue

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#### Abstract

The preparations are reported of a range of complexes of  $Mn^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$  and  $Cu^{II}$  with 1,4-bis-(4-pyridylsulfenylmethyl)benzene (B4PSB) and of complexes of  $Co^{II}$ ,  $Ni^{II}$  and  $Cu^{II}$  with the 2-pyridyl analogue (B2PSB), together with relevant spectroscopic data. X-Ray crystallographic studies on  $Co(B2PSB)(NO_3)_2$  show the presence of a chain structure in which five-coordinate cobalt centers are linked by bridging (B2PSB) ligands, with the remaining coordination sites about each metal atom being occupied by one very asymmetrically chelating nitrate group and an oxygen atom of a unidentate nitrate. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: X-ray structure; Polymeric complexes; Bis(pyridine) ligands

#### 1. Introduction

There is currently appreciable interest in the types of polymeric arrays which can be prepared by the interaction of metal salts with extended-reach ligands of type I, in which pairs of 4-pyridyl units are linked by an appropriate spacer group, and it has been shown that variations in the linking unit influence the types of structure formed [1-8]. With a related aim, we have been exploring the network-forming ability of linked pyrrolidin-2-thione (e.g. II) [9] and pyridin-2-thione (e.g. III) [10,11] ligands, which can be obtained by the action of Lawesson's reagent on their bis(pyrrolidin-2-one) and bis(pyridin-2-one) analogues. Parallel studies, using the direct reaction between  $\alpha, \alpha'-1, 4$ -dibromoxylene and the sodium salts of 2- or 4-mercaptopyridine have afforded the complementary types of ligand, IV (B2PSB) and V (B4PSB) respectively, in which the sulfur atoms are incorporated into the spacer group connecting pairs of 2or 4-pyridyl donor groups. We report here some metal complexes of IV and V and the results of an X-ray study on Co(B2PSB)(NO<sub>3</sub>)<sub>2</sub>.



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# 2. Experimental

#### 2.1. Preparation of compounds

# 2.1.1. 1,4-Bis-(2-pyridylsulfenylmethyl) benzene

Sodium (1.70 g, 74 mmol) was dissolved in butan-1-ol (150 cm<sup>3</sup>) in a flask fitted with a reflux condenser and a CaCl<sub>2</sub> drying tube. Pyridin-2-thione (5.0 g, 45 mmol) and  $\alpha, \alpha'$ -1,4-dibromoxylene (5.93 g, 22.5 mmol) were added and the mixture was refluxed (graphite bath, 120°C) for 5 h. Upon cooling, golden needle-like crystals separated. The butan-1-ol was removed and then diethylether (200 cm<sup>3</sup>) was added to the slightly damp solid, and the mixture stirred thoroughly. The product was extracted into dichloromethane, dried over anhydrous magnesium sulfate and crystallized by slow evaporation. The tancolored crystals were dried in vacuo over P2O5 (yield 85%, mp 75-76°C). Found: C, 66.6: H, 5.0; N, 8.6. Calc. for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub>: C, 66.6; H, 5.0; N, 8.6%. MS(EI) 324 (M<sup>+</sup>). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  4.42 (4H, s), 7.00 (2H, m), 7.16 (2H, m), 7.34 (4H, s), 7.47 (2H, m), 8.45 (2H, d). The constitution of the ligand is also confirmed by the structure of the complex  $Co(B2PSB)(NO_3)_2$ .

#### 2.1.2. 1,4-Bis-(4-pyridylsulfenylmethyl)benzene

This was obtained by essentially the same procedure and on the same scale, but using pyridin-4-thione and extracting the product into chloroform instead of dichloromethane (yield 76%, mp 187–190°C). Found: C, 66.6: H, 4.9; N, 8.6. Calc. for  $C_{18}H_{16}N_2S_2$ : C, 66.6; H, 5.0; N, 8.6%. MS(EI) 324 (M<sup>+</sup>). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  4.19 (4H, s), 7.10 (4H, d), 7.36 (4H, s), 8.38 (4H, d).

#### 2.2. Metal complexes

Analytical data (Microanalytical Laboratory, Imperial College), colors and yields of the complexes are given in Table 1. Preparative details are summarized below. The cobalt(II) and nickel(II) iodide and thiocyanate starting reagents were prepared metathetically by mixing concentrated methanol solutions of the corresponding metal nitrates and sodium iodide or potassium thiocyanate respectively and removal of the precipitated alkali metal nitrates. Unless stated otherwise, the metal complexes were collected by filtration, washed with a small amount of the solvent used for the preparation and then dried *in vacuo* over  $P_2O_5$ .

*Caution*! Although we did not observe any explosive behavior with the copper(II) perchlorate compounds described below, all metal perchlorates must be regarded as potentially explosive and appropriate safety measures taken.

# 2.2.1. $CoX_2(B2PSB)$ (X=Cl, Br)

These compounds precipitated on mixing a solution of cobalt(II) chloride hexahydrate (0.074 g, 0.31 mmol) or

cobalt(II) bromide hexahydrate (0.101 g, 0.31 mmol) respectively in ethanol (2 cm<sup>3</sup>) with a solution of B2PSB (0.097 g, 0.30 mmol) also in ethanol (5 cm<sup>3</sup>). IR: chloride v(Co-Cl) 300, 326 cm<sup>-1</sup>; bromide v(Co-Br) 230, 260 cm<sup>-1</sup>.

#### 2.2.2. $CoI_2(B2PSB)$

This was prepared as for the previous complexes, and on the same scale, but with the cobalt(II) iodide in a mixture of ethanol  $(2 \text{ cm}^3)$  and methanol  $(0.4 \text{ cm}^3)$ .

# 2.2.3. $M(NO_3)_2(B2PSB)$ (M = Co, Ni)

A solution of the respective, hydrated metal nitrate (0.044 g, 0.15 mmol) in ethanol  $(2 \text{ cm}^3)$  was added to one of B2PSB (0.049 g, 0.15 mmol) also in ethanol  $(5 \text{ cm}^3)$ . In the case of the cobalt complex the clear, purple solution was left to crystallize slowly, until crystals of suitable quality for X-ray study had formed. After removal of some of the crystals the remainder of the solution was concentrated to *ca*  $1 \text{ cm}^3$ , treated with nitromethane  $(5 \text{ cm}^3)$  and then refluxed, and a good yield of the purple complex separated. A similar procedure was used to obtain the nickel complex, but in that case crystals were not grown.

# 2.2.4. $Cu(B2PSB)_2(ClO_4)_2$

This green complex precipitated on mixing ethanolic solutions of hydrated copper(II) perchlorate (0.056 g, 0.15 mmol in 2 cm<sup>3</sup>) and B2PSB (0.097 g, 0.30 mmol in 5 cm<sup>3</sup>). IR:  $v_4$ (ClO<sup>-</sup><sub>4</sub>) 623 cm<sup>-1</sup>.

# 2.2.5. $MnCl_2(B4PSB) \cdot H_2O$

This complex precipitated on addition of a solution of B4PSB (0.049 g, 0.15 mmol) in nitromethane (5 cm<sup>3</sup>) to one of  $MnCl_2$ ·4H<sub>2</sub>O (0.030 g, 0.15 mmol) in ethanol (2 cm<sup>3</sup>).

#### 2.2.6. $CoBr_2(B4PSB)$

Addition of a solution of  $CoBr_2 \cdot 6H_2O$  (0.049 g, 0.15 mmol) in a mixture of ethanol (0.5 cm<sup>3</sup>) and nitromethane (1 cm<sup>3</sup>) to one of B4PSB (0.049 g, 0.15 mmol) in hot (80°C) nitromethane (5 cm<sup>3</sup>) gave the complex as a fine blue powder.

#### 2.2.7. $CoI_2(B4PSB)$

This was obtained as for the previous complex, and on the same scale, but using a solution of cobalt(II) iodide in a mixture of methanol  $(0.2 \text{ cm}^3)$  and nitromethane  $(1 \text{ cm}^3)$ .

#### 2.2.8. $Co(NCS)_2(B4PSB)_2 \cdot 2H_2O$

This pink complex precipitated on the addition of a solution of cobalt(II) thiocyanate (0.15 mmol) in a mixture of methanol (0.2 cm<sup>3</sup>) and nitromethane (1 cm<sup>3</sup>) to a solution of B4PSB (0.097 g, 0.3 mmol) in nitromethane (7 cm<sup>3</sup>). IR: v(CN) 2053 cm<sup>-1</sup>.

Complex	Color	Analysis (%) <sup>a</sup>			Yield(%)
		С	Н	Ν	
Ligand IV $(=L)$					
CoCl <sub>2</sub> L	blue	47.8 (47.6)	3.5 (3.6)	6.2 (6.2)	61
CoBr <sub>2</sub> L	blue	39.9 (39.8)	2.9 (3.0)	5.1 (5.2)	56
CoI <sub>2</sub> L	green	34.5 (33.9)	2.5 (2.5)	4.4 (4.4)	60
$Co(NO_3)_2L$	purple	42.7 (42.6)	3.0 (3.2)	11.0 (11.0)	81
Ni(NO <sub>3</sub> ) <sub>2</sub> L	green	42.6 (42.6)	3.0 (3.2)	10.9 (11.1)	79
$[CuL_2](ClO_4)_2$	green	47.6 (47.5)	3.8 (3.5)	5.8 (6.2)	66
Ligand V $(=L')$					
MnCl <sub>2</sub> L'·H <sub>2</sub> O	cream	46.5 (46.2)	3.5 (3.9)	5.9 (6.0)	64
CoBr <sub>2</sub> L'	blue	39.8 (39.8)	3.1 (3.0)	5.1 (5.2)	50
CoI <sub>2</sub> L′	green	34.2 (33.9)	2.6 (2.5)	4.7 (4.4)	73
$Co(NCS)_2L_2' \cdot 2H_2O$	pink	53.1 (53.1)	3.7 (4.2)	10.0 (9.8)	66
NiCl <sub>2</sub> L'·H <sub>2</sub> O	yellow	46.1 (45.8)	3.6 (3.8)	6.0 (5.9)	56
NiBr <sub>2</sub> L'	tan	39.4 (39.8)	3.1 (3.0)	5.1 (5.2)	58
NiI <sub>2</sub> L′	orange-brown	34.6 (33.9)	2.7 (2.5)	4.71 (4.4)	69
NiI <sub>2</sub> L <sub>2</sub> '	green	45.1 (45.0)	3.5 (3.4)	5.9 (5.8)	65
Ni(NO <sub>3</sub> ) <sub>2</sub> L'·H <sub>2</sub> O	green	41.3 (41.2)	3.1 (3.5)	10.6 (10.7)	53
Ni(NCS) <sub>2</sub> L'	green	47.9 (48.1)	3.3 (3.2)	11.0 (11.2)	79
CuCl <sub>2</sub> L'	turquoise	47.2 (47.1)	3.5 (3.5)	5.9 (6.1)	41
CuBr <sub>2</sub> L'	green	39.7 (39.5)	3.0 (2.9)	5.1 (5.1)	40
CuL' <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	purple	45.5 (45.6)	3.7 (3.8)	6.0 (5.9)	55

Table 1 Analytical data, colors and yields of the complexes formed by ligands  $\mathbf{IV}$  and  $\mathbf{V}$ 

<sup>a</sup> Calculated values are given in parentheses.

#### 2.2.9. $NiCl_2(B4PSB) \cdot H_2O$ and $NiBr_2(B4PSB)$

These compounds precipitated when solutions of nickel(II) chloride hexahydrate (0.036 g, 0.015 mmol), or nickel(II) bromide hexahydrate (0.036 g, 0.015 mmol) respectively, in a mixture of ethanol ( $0.5 \text{ cm}^3$ ) and nitromethane ( $1 \text{ cm}^3$ ) were added to a hot solution of B4PSB (0.049 g, 0.15 mmol) in nitromethane ( $5 \text{ cm}^3$ ).

# 2.2.10. $Ni(NO_3)_2(B4PSB) \cdot H_2O$

This was prepared as for the previous complexes, and on the same scale, but the solution of B4PSB was added to the nickel nitrate solution.

#### 2.2.11. NiI<sub>2</sub>(B4PSB)

A solution of nickel(II) iodide (0.15 mmol) in a mixture of methanol (1 cm<sup>3</sup>) and nitromethane (1 cm<sup>3</sup>) was added dropwise over a period of 2 min to a refluxing solution of B4PSB (0.049 g, 0.15 mmol) in nitromethane (5 cm<sup>3</sup>). The solution was momentarily brown in color, but the first few drops of the nickel iodide solution caused the formation of a green solid. As more nickel iodide was added the brown color was maintained for longer periods between the additions and the green solid finally became orange–brown.

#### 2.2.12. $NiI_2(B4PSB)_2$

This was prepared by a similar method but using 0.3 mmol of B4PSB and 0.1 mmol of nickel(II) iodide, when the formation of the green complex was sustained.

#### 2.2.13. Ni(NCS)<sub>2</sub>(B4PSB)

The same procedure was employed as for NiI<sub>2</sub>(B4PSB), and on the same scale, but using nickel(II) thiocyanate instead of nickel(II) iodide. IR: v(CN) 2112 cm<sup>-1</sup>.

#### 2.2.14. $CuX_2(B4PSB)$ (X=Cl, Br)

These compounds were obtained as for their nickel(II) analogues, and on the same scale, but they separated as very fine powders and were collected by centrifuging.

## 2.2.15. $Cu(B4PSB)_2(ClO_4)_2 \cdot 2H_2O$

Addition of a solution of hydrated copper(II) perchlorate (0.026 g, 0.07 mmol) in a mixture of ethanol (1 cm<sup>3</sup>) and nitromethane (1 cm<sup>3</sup>) to a solution of B4PSB (0.049 g, 0.15 mmol) in nitromethane (5 cm<sup>3</sup>) gave a cloudy purple solution, from which a purple microcrystalline powder separated within 24 h. IR:  $v_4$ (ClO<sup>-</sup><sub>4</sub>) 623 cm<sup>-1</sup>.

#### 2.3. Spectroscopy

The EPR spectra were measured at room temperature on a Varian E12 X-band (*ca* 9.5 GHz) spectrometer using powdered samples. Mass spectra (EI) were obtained on a Varian Autospec Q mass spectrometer. The other spectroscopic measurements were carried out as described previously [11].

# 2.4. Crystallography

#### 2.4.1. Crystal data

For Co(B2PSB)(NO<sub>3</sub>)<sub>2</sub>, 1: C<sub>18</sub>H<sub>16</sub>CoN<sub>4</sub>O<sub>6</sub>S<sub>2</sub>, M=507.4, triclinic, space group PĪ, a=7.522(2)Å, b=8.563(2)Å, c=17.534(2)Å,  $\alpha$ =89.99(2)°,  $\beta$ =86.81 (2)°,  $\gamma$ =68.73(2)°, U=1050.7(2)Å<sup>3</sup>, Z=2,  $D_c$ =1.604 g cm<sup>-3</sup>,  $\mu$ (Mo K<sub> $\alpha$ </sub>)=1.059 mm<sup>-1</sup>,  $\lambda$ =0.71073Å, F(000) =518. A dark red block of dimensions 0.40×0.33× 0.27 mm was used.

#### 2.5. Data collection and processing

Data were collected on a Siemens P4/PC diffractometer with graphite monochromated Mo K<sub>a</sub> radiation using  $\omega$ scans; 3677 independent reflections were measured ( $7 < 2\theta < 45^{\circ}$ ) of which 3175 were considered observed ( $|F_o| > 4\sigma(|F_o|)$ ). The data were corrected for Lorentz and polarization factors; no absorption correction was applied.

#### 2.6. Structure analysis and refinement

The structure was solved by direct methods. The nonhydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealized, C– H=0.96 Å, assigned isotropic thermal parameters,  $U(H) = 1.2U_{eq}(C)$ , and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least-squares, based on *F*, to give R=0.0325 and  $R_w=0.0374$ (w<sup>-1</sup> =  $\sigma^2(F) + 0.0007F^2$ ). The mean and maximum shift/error in the final refinement were 0.000 and 0.001 respectively and the maximum and minimum residual electron densities in the final  $\Delta F$  map were 0.25 and  $-0.23 \text{ e Å}^{-3}$ , respectively. Computations were carried out using the SHELXTL PLUS PC system [12]. Selected bond lengths and angles are listed in Table 2.

#### 3. Results and discussion

Both B2PSB (IV) and B4PSB (V) gave solid complexes with a range of first row transition metal ions Table 1. The complexes were generally rather insoluble and, as a result, crystals of suitable quality for single crystal Xray diffraction analysis were obtained in only one case,  $Co(B2PSB)(NO_3)_2$ . We shall discuss that X-ray result first as it provides a basis for inferring the structures of the other complexes from the spectroscopic studies.

#### 3.1. Structure of $Co(B2PSB)(NO_3)_2$

The X-ray study of the complex  $Co(B2PSB)(NO_3)_2$ shows the compound to be polymeric, the B2PSB ligand adopting a bridging role between the cobalt centers, bonding to them via the nitrogen atoms (Fig. 1). Each cobalt atom also has bonded to it one unidentate nitrate and one asymmetric bidentate nitrate ion (Fig. 2). The coordination geometry at Co is very distorted. It can probably be best described as distorted tetrahedral (involving N(1), N(22), O(103) and O(112)) but with a more loosely coordinated oxygen atom, O(113), occupying a fifth, more distant (2.333(2) Å) coordination site, without major perturbation of the tetrahedron. The Co-N(pyridyl) distances are asymmetric, with that to N(1), in a pseudo-trans position to the loosely linked O(113), being slightly longer (2.081(2) Å) than that to N(22) (2.037(2) Å). The solid state electronic spectrum of the compound (Table 3) shows strong d-d bands as expected from the non-centrosymmetric coordination geometry.

The B2PSB ligand has  $C_i$  symmetry about the center of the benzene ring, thus producing an *anti* geometry for the two terminal 2-mercaptopyridyl groups. The pyridyl and benzyl ring systems are steeply inclined to each other (58°) but with the C(6)–S(7)–C(8)–C(9) linkage being essentially planar, the principal torsional twist being about the C(8)–C(9) bond (68°). Despite the potential for

Co(1)-N(1)	2.081(2)	Co(1)–N(22)	2.062(2)		
Co(1)-O(103)	2.026(2)	Co(1)–O(112)	2.037(2)		
Co(1)-O(113)	2.333(2)				
N(1)-Co(1)-N(22)	106.2(1)	N(1)-Co(1)-O(103)	112.8(1)		
N(1)-Co(1)-O(112)	98.0(1)	N(1)-Co(1)-O(113)	155.3(1)		
N(22)-Co(1)-O(103)	96.3(1)	N(22)-Co(1)-O(112)	126.1(1)		
N(22)-Co(1)-O(113)	86.8(1)	O(103)-Co(1)-O(112)	117.4(1)		
O(103)-Co(1)-O(113)	85.7(1)	O(112)-Co(1)-O(113)	57.9(1)		
Co(1)-N(1)-C(2)	116.9(1)	Co(1)–N(1)–C(6)	125.2(1)		
Co(1)-N(22)-C(17)	118.9(1)	Co(1)-N(22)-C(21)	123.3(2)		
Co(1)-O(103)-N(100)	108.5(2)	Co(1)-O(112)-N(110)	100.2(1)		
Co(1)-O(113)-N(110)	86.8(1)				

Table 2 Selected bond lengths (Å) and angles (°) for Co(NO<sub>3</sub>)<sub>2</sub>(B2PSB)



Fig. 1. Part of the polymeric chain structure of Co(NO<sub>3</sub>)<sub>2</sub>(B2PSB).



Fig. 2. The coordination geometry about Co in the structure of  $Co(NO_3)_2(B2PSB)$ . The dashed line indicates the more loosely coordinated oxygen atom, O(113).

interchain  $\pi$ - $\pi$  interactions, a study of the packing of the chains reveals a marked absence of either face-to-face or edge-to-face interactions.

# 3.2. Other complexes of B2PSB (IV)

Nickel nitrate also forms a complex of stoichiometry  $Ni(B2PSB)(NO_3)_2$  analogous to the cobalt complex described above. Its solid state electronic spectrum Table 3 is typical of nickel(II) in an essentially octahedral coor-

dination geometry, both with respect to the band energies and lower band intensities, so it is probable that this compound resembles its cobalt(II) analogue in having a similar chain structure, but in this case with six-coordination at each nickel center by use of two bidentate nitrates.

The solid state electronic spectra of the cobalt(II) halide complexes  $Co(B2PSB)X_2$  (X = Cl, Br, I) are, however Table 3, characteristic of essentially tetrahedral coordination geometry about the Co center [13], as they show

CoCl <sub>2</sub> (B2PSB)	6500 sh, 7200, 8700 sh, 16,700 <sup>b</sup>
CoBr <sub>2</sub> (B2PSB)	6200 sh, 7000, 8200 sh, 16,500 <sup>b</sup>
CoI <sub>2</sub> (B2PSB)	6900 <sup>b</sup> , 15,900 <sup>b</sup>
$Co(NO_3)_2(B2PSB)$	8700, 13,800 sh, 19,300
Ni(NO <sub>3</sub> ) <sub>2</sub> (B2PSB)	8700, 15,400, 24,100
$Cu(B2PSB)_2(ClO_4)_2$	17,700, 25,400
CoBr <sub>2</sub> (B4PSB)	6700, 9100, 16,500 <sup>b</sup>
CoI <sub>2</sub> (B4PSB)	5900 sh, 6500, 9100, 15,700 <sup>b</sup>
$Co(NCS)_2(B4PSB)_2 \cdot 2H_2O$	9400, 17,500 sh, 20,000
NiCl <sub>2</sub> (B4PSB)·H <sub>2</sub> O	6100, 8500, ca 12,000 sh, 13,900, ca 23,000 br
NiBr <sub>2</sub> (B4PSB)	6000, 8000, 13,700, <i>ca</i> 23,000 br
NiI <sub>2</sub> (B4PSB)	5900, 8000, 13,400°
NiI <sub>2</sub> (B4PSB) <sub>2</sub>	7400 br, 12,000 sh, 16,000°
CuCl <sub>2</sub> (B4PSB)	14,400 br
CuBr <sub>2</sub> (B4PSB)	15,000 br
$Cu(B4PSB)_2(ClO_4)_2 \cdot 2H_2O$	17,700

Electronic spectra<sup>a</sup> (cm<sup>-1</sup>) of some complexes formed by ligands IV and V

<sup>a</sup> By reflectance method.

<sup>b</sup> Center of strong multicomponent band.

<sup>c</sup>d-d bands at higher energy obscured by strong electron transfer absorption.

strong, overlapping bands in the range 6000–9000 cm<sup>-1</sup> (transitions to components of  ${}^{4}T_{1}(F)$ ) and a strong, multicomponent band in the visible region (transitions to components of  ${}^{4}T_{1}(P)$ ). Additional evidence [14, 15] for tetrahedral coordination geometry for Co(B2PSB)Cl<sub>2</sub> is provided by the v(Co–Cl) bands at 300 and 326 cm<sup>-1</sup>. These results are consistent with these cobalt(II) halide compounds also forming chains analogous to those in Co(B2PSB)(NO<sub>3</sub>)<sub>2</sub> but with the cobalt centers comprising tetrahedral [CoN<sub>2</sub>X<sub>2</sub>] units.

Table 3

Reaction of B2PSB with hydrated copper(II) perchlorate in ethanol gave a complex of stoichiometry  $Cu(B2PSB)_2(ClO_4)_2$ , the X-band powder EPR spectrum of which was of the axial type with  $g_{\perp} = 2.050$  and  $g_{\parallel} = 2.237$  and with Cu hyperfine splitting of 17.5 mT on  $g_{\parallel}$ . These results are consistent with a planar CuN<sub>4</sub> coordination geometry about each copper center and with negligible interaction between adjacent copper centers. The solid state electronic spectrum shows a broad d–d band at 17,700 cm<sup>-1</sup> and a strong band, probably of electron-transfer origin, at 25,400 cm<sup>-1</sup>. Taken in conjunction with the bridging capability of B2PSB demonstrated for Co(B2PSB)(NO\_3)\_2, these observations suggest that the cations in [Cu(B2PSB)\_2](ClO\_4)\_2 are linked by B2PSB bridges so as to form a sheet array.

#### 3.3. Complexes of B4PSB (V)

The products of the reaction of B4PSB with cobalt(II) bromide or iodide closely resemble those formed by the 2-pyridyl analogue as they have the stoichiometry  $Co(B4PSB)X_2$  (X=Br, I) and their electronic spectra Table 3 show the presence of tetrahedrally coordinated metal centers. There is, however a greater splitting of

the components of the  $v_2$  band system (transitions to components of  ${}^{4}T_1(F)$ ) in the near IR region, indicative of a greater distortion from strict  $T_d$  symmetry at the cobalt centers.

In contrast, the corresponding nickel(II) halide complexes Ni(B4PSB)X<sub>2</sub> (X = Br, I) have electronic spectra characteristic of halide bridged six-coordinate nickel(II), as in e.g. Ni(pyridine)<sub>2</sub>Br<sub>2</sub> [16], but in the present compounds with concomitant bridging by the B4PSB ligands. The electronic spectrum of the hydrated nickel chloride complex Ni(B4PSB)Cl<sub>2</sub>·H<sub>2</sub>O is also of the halide-bridged polymer type, and this compound probably also contains B4PSB cross-links, but, in the absence of direct X-ray confirmation, the possibility that the water molecule is coordinated cannot be ruled out. Similar comments apply to its manganese(II) analogue, Mn(B4PSB)Cl<sub>2</sub>·H<sub>2</sub>O, the X-band EPR spectrum of which shows the single broad g = 2 band characteristic [17] of polymeric halide-bridged [MnL<sub>2</sub>X<sub>2</sub>]<sub>n</sub> systems.

During the synthesis of the orange-brown compound Ni(B4PSB)I<sub>2</sub> it was noticed that a solid green product formed during the early stages of the addition of the nickel(II) iodide solution. Use of a 3:1 B4PSB:NiI<sub>2</sub> ratio of the reactants gave the green complex Ni(B4PSB)<sub>2</sub>I<sub>2</sub>, the solid state electronic spectrum of which is typical of six-coordinate NiL<sub>4</sub>X<sub>2</sub> compounds where L is a nitrogen donor heterocycle such as pyridine [18]. This implies the formation of a sheet structure for this complex via the bridging action of the B4PSB ligand and with a *trans*-NiN<sub>4</sub>I<sub>2</sub> coordination geometry at each nickel center.

The X-band powder EPR spectrum of CuCl<sub>2</sub>(B4PSB) is of the axial type with  $g_{\perp} = 2.065$  and  $g_{\parallel} = 2.229$ . This observation and the solid state electronic spectrum (broad, multicomponent band centered on 14,400 cm<sup>-1</sup>)

are consistent with *trans*-planar [CuN<sub>2</sub>Cl<sub>2</sub>] coordination geometry with the copper centers linked into chains by B4PSB bridges. From its electronic spectrum Table 3 the bromide analogue is also of this type.

The v(CN) band at 2053 cm<sup>-1</sup> in the IR spectrum of Co(NCS)<sub>2</sub>(B4PSB)<sub>2</sub>·2H<sub>2</sub>O shows that the anions are bonded via the nitrogen atom and the electronic spectrum of the solid complex Table 3 is typical of an octahedral [Co<sup>II</sup>N<sub>6</sub>] chromophore with an average ligand field strength parameter  $\Delta = 10,000 \text{ cm}^{-1}$  [19, 20]. This compound can, therefore, be assigned a structure in which the B4PSB ligands bridge the cobalt centers into sheets, and with the NCS groups bonded in *trans* positions via the N atoms. In contrast, the anions in the nickel(II) thiocyanate complex Ni(NCS)<sub>2</sub>(B4PSB) adopt a bridging role (v(CN) 2112 cm<sup>-1</sup>).

The EPR parameters  $(g_{\perp} = 2.052, g_{\parallel} = 2.247, \text{Cu hyperfine splitting of 17.5 mT on } g_{\parallel})$  and electronic spectrum (d–d band at 17,700 cm<sup>-1</sup>) observed for the purple complex Cu(B4PSB)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O are very similar to those of Cu(B2PSB)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> again indicating the formation of a sheet array in which planar [Cu<sup>II</sup>N<sub>4</sub>] centers are linked by bridging B4PSB ligands.

In summary, it is clear from the spectroscopic results that the bridging action of 1,4-bis-(2-pyridylsulfenylmethyl)benzene (B2PSB, IV) shown by the X-ray result for Co(B2PSB)(NO<sub>3</sub>)<sub>2</sub> is a general feature not only of the other complexes of that ligand but also of the complexes of its 4-pyridyl analogue. The differences are in the coordination geometries adopted by the various metal centers.

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