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Synthesis and characterization of *trans*-[Co(III)(bpb)(amine)₂]X (X = NCS, ClO₄). X-ray crystal structure of *trans*-[Co(III)(bpb)(pyrrolidine)₂]NCS \cdot 0.5H₂O containing intermolecular N-H $\cdot \cdot \cdot$ O=C hydrogen-bonding

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Abstract

A series of complexes of the type *trans*-[Co(III)(bpb)(amine)₂]X (X = NCS, amine = pyrrolidine (prldn) (1), benzylamine (bzlan) (2), and X = ClO₄, amine = pyrrolidine (prldn) (3), benzylamine (bzlan) (4), piperidine (pprdn) (5), morpholine (mrpln) (6), and bpb = N,N'-bis(2-pyridinecarboxamide)-1,2-benzene dianion) have been synthesized and characterized by elemental analyses, IR, UV–Vis, and ¹H NMR spectroscopy. The crystal and molecular structure of 1.0.5H₂O was determined by X-ray crystallography. The compound crystallizes in the triclinic space group $P\overline{1}$, a = 9.4059(8) Å, b = 11.3047(10) Å, c = 12.8451(11) Å, $\alpha = 81.984(2)^{\circ}$, $\beta = 83.761(2)^{\circ}$, $\gamma = 85.456(2)^{\circ}$, V = 1341.6(2) Å³, Z = 2 and final $R_1 = 0.039$ ($wR_2 = 0.0625$) for 5723 independent reflections with $I > 2\sigma(I)$ and 368 parameters. The structure consists of chains of complexes linked by moderately strong N–H···O=C hydrogenbonds zig-zagging along the **c** lattice translation. The IR, UV–Vis, and ¹H NMR spectra of the complexes are also discussed. \mathbb{C} 2002 Elsevier Science B.V. All rights reserved.

Keywords: N4-amido complexes of Co(III); Axial amines; IR, UV-Vis, ¹H NMR; Crystal structure of trans-[Co(bpb)(pyrrolidine)2]NCS·0.5H₂O

1. Introduction

There is a large volume of literature on coordination compounds containing the thiocyanate ligand [1-7]. The diversity of the role played by thiocynate in the structural chemistry and the kinetics of the reactions [8,9] of this class of complexes is still attracting interest to their synthesis and characterization. We have recently synthesized a series of *trans*-[Co(acacen)(amine)₂]NCS complexes [10] and studied their solid state deamination–anation reactions [11]. As an extension of this work, we have turned our attention to the synthesis and characterization of *trans*-[Co(III)(bpb)(a-

mine)₂]X (X = NCS, ClO₄) complexes, to further investigate the role played by the equatorial ligand in the chemistry of these complexes.

While in *trans*-[Co(acacen)(amine)₂]NCS complexes a $N-H\cdots NCS$ intramolecular hydrogen-bonding exists between the aminic hydrogen of one of the axial amines and the thiocyanate anion [10], a moderately strong intermolecular hydrogen-bonding of the type $N-H\cdots O=C$, between the aminic hydrogen of one molecule and the C=O group of the equatorial amide ligand of another is observed in *trans*-[Co(bpb)(pyrrolidine)₂]-NCS $\cdot 0.5H_2O$ ($1 \cdot 0.5H_2O$), showing a stacked structure, Fig. 2. This hydrogen-bonding has an interesting influence on the decarbonylation of one of the amide C=O groups following the deamination–anation reaction in the solid state at high temperatures [12].

We report herein the synthesis and characterization of trans-[Co(bpb)(amine)₂]X complexes (Scheme 1). The X-ray crystal structure of trans-[Co(bpb)(prldn)₂]NCS·

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 $0.5H_2O$ is also reported. The details of thermal deamination-anation, and decarbonylation of these complexes have been published in a separate report [12].

2. Experimental

2.1. Chemicals

1,2-Phenylenediamine was recrystallized from hot ethanol before use. Piperidine (pprdn) (Aldrich), benzylamine (bzlan), morpholine (mrpln), pyrrolidine (prldn) (Merck) were distilled under reduced pressure. All other chemicals were of commercial reagent grade and used as received from Aldrich and Merck.

2.2. Physical measurements

¹H NMR spectra were obtained on a BRUKER AC-200 MHz and a BRUKER AVANCE DRX500 (500 MHz) spectrometer. Proton chemical shifts are reported in parts per-million (ppm) relative to an internal standard of Me₄Si. IR spectra were recorded as KBr pellets on a Shimadzu 435 instrument. UV–Vis spectra were obtained on a Shimadzu UV-240 spectrophotometer. Elemental analyses were performed by using a Heraeus CHNO-RAPID elemental analyzer.

2.3. Synthesis

2.3.1. H₂bpb ligand and [Co(II)(bpb)]·H₂O Complex N,N'-bis[(2'-pyridinecarboxamide)-1,2-benzene] =

H₂bpb and [Co(II)(bpb)]·H₂O were prepared as described in the literature [13]. The assignment of the ¹H NMR spectrum of H₂bpb is quite straightforward; ¹H NMR (200 MHz, CD₃CN, assignments as in Scheme 1): [$\delta = 7.33$ (2H, AA'XX', $J_m = 3.5$, $J_o = 6.1$, H_f), 7.57

(2H, m, H_b), 7.84 (2H, AA'XX', $J_m = 3.5$, $J_o = 6.0$, H_e), 7.98 (2H, m, H_c), 8.22 (2H, brd, $J_{cd} = 7.9$, H_d), 8.56 (2H, brd, $J_{a,b} = 5.0$, H_a), 10.20 (2H, br s, H_{amidic}). The chemical shifts match those reported in the literature [13].

2.3.2. $trans - [Co(bpb)(prldn)_2]NCS \cdot 0.5H_2O$ (1.0.5H₂O)

To a solution of 786 mg (2 mmol) of [Co(II)(bpb)]. H₂O complex in 50 ml methanol was added dropwise 0.67 ml (8 mmol) of pyrrolidine and air was bubbled through the solution for 3 h. Small portions of methanol were added during this period to compensate for evaporation. The final reaction mixture was filtered off and a solution of 194 mg (2 mmol) potassium thiocyanate in methanol was added to the filtrate followed by 25 ml of toluene. Dark green crystals were obtained after 48 h. These crystals were isolated by filtration and washed with a mixture of ethanol-ether (1:9 v/v), and dried in vacuo. Yield 85%. Anal. Calc. for C₂₇H₃₀N₇O₂SCo·0.5 H₂O (584.58): C, 55.47; H, 5.34; N, 16.72. Found: C, 55.53; H, 5.28; N, 16.84%. IR: v_{max} cm^{-1} (KBr): 3165(m, N-H), 2045(s, NC_{NCS}), 1628(s, C=O), 1596(s, C=C), 1566(s, C-N). ¹H NMR (200 MHz, CD₃CN): pyrrolidine, $[\delta = 1.27 (8H, m, C^{3}H_{2}C^{4}H_{2}), 1.52 (4H, m, NC^{2,5}H), 2.05 (4H, m, m, NC^{2,5}H), 2.05 (4H, m, m, MC^{2,5}H), 2.05 (4H, m, M, M)$ $NC^{2,5}H$), 3.33 (2H, br s, NH)], bpb, [$\delta = 7.10$ (2H, AA'XX, $J_{\rm m} = 3.4$, $J_{\rm o} = 6.1$, $H_{\rm f}$), 8.00 (2H, m, $H_{\rm b}$), 8.28 $(2H, dd, J_m = 1.7, J_o = 7.6, H_d), 8.39 (2H, m, H_c), 8.88$ (2H, AA'XX', $J_{\rm m} = 3.5$, $J_{\rm o} = 6.1$, $H_{\rm e}$), 9.48 (2H, br d, $J = 5.7, H_a$].

2.3.3. $trans-[Co(bpb)(bzlan)_2]NCS(2)$

This complex was synthesized as described for 1 except that 0.8 ml (8 mmol) benzylamine was added as the amine, and 25 ml ethanol instead of toluene was added to the final solution for crystallization. The resulting dark green crystals were isolated and washed with a mixture of ethanol-ether (1:5 v/v) and dried in vacuo. Yield 90%. Anal. Calc. for C33H30N7O2sco (647.64): C, 61.20; H, 4.67, N, 15.14. Found: C, 61.30; H, 4.60; N, 15.60%. IR: $v_{\text{max}} \text{ cm}^{-1}$ (KBr): 3198, 3105(m, N-H), 2055(s, NC_{NCS}), 1628(s, C=O), 1601(s, C=C), 1563(s, C-N). ¹H NMR (200 MHz, CD₃CN): benzylamine, $[\delta = 2.70 (4H, m, C'H_2), 2.89 (4H, br s, NH_2),$ 6.69 (4H, m, ArH), 7.08 (6H, m, ArH)], bpb, [$\delta = 7.04$ $(2H, AA'XX', J_m = 3.4, J_o = 5.60, H_f), 7.91 (2H, m, H_b),$ 8.18 (2H, dd, $J_{\rm m} = 1.7$, $J_{\rm o} = 7.6$, $H_{\rm d}$), 8.32 (2H, m, $H_{\rm c}$), 8.87 (2H, AA'XX', $J_{\rm m} = 3.5$, $J_{\rm o} = 6.2$, $H_{\rm e}$), 9.38 (2H, br d, J = 5.2, H_a)].

2.3.4. trans- $[Co(bpb)(prldn)_2]ClO_4(3)$

To a solution of 786 mg (2 mmol) of $[Co(bpb)] \cdot H_2O$ in 50 ml methanol was added dropwise 0.54 ml (6 mmol) of pyrrolidine and air was bubbled through the solution for 3 h. Several portions of methanol were added during this period to compensate for evaporation. The final reaction mixture was filtered off and a solution of 280 mg (2 mmol) of NaClO₄·H₂O in methanol was added to the filtrate. Dark green crystals were obtained after 48 h. The product was isolated by filtration and washed with cold ethanol and ether and finally recrystallized from acetonitrile-ethanol (1:2 v/v). The resulting dark green crystals were collected, washed with cold ethanol and ether and dried in vacuo. Yield 74%. Anal. Calc. for C₂₆H₃₀ClN₆O₆Co (616.94): C, 50.62; H, 4.90, N, 13.62. Found: C, 50.30; H, 4.80; N, 13.50%. IR: v_{max} cm⁻¹ (KBr): 3164(m, N-H), 1628(s, C=O), 1595 (s, C=C), 1566(s, C–N). ¹H NMR (500 MHz, CD₃CN): pyrrolidine, $[\delta = 1.28 \ (8H, m, C^3H_2C^4H_2), 1.53 \ (4H, m, m)$ NC^{2,5}H), 2.10 (4H, m, NC^{2,5}H), 3.23 (2H, br s, NH)], bpb, $[\delta = 7.11 (2H, AA'XX', J_m = 3.4, J_o = 6.1, H_f), 7.99$ $(2H, m, H_b)$, 8.28 $(2H, dd, J_m = 1.7, J_o = 7.6, H_d)$, 8.40 $(2H, m, H_c)$, 8.89 $(2H, AA'XX', J_m = 3.5, J_o = 6.1, H_e)$, 9.45 (2H, br d, J = 5.7, H_a)].

2.3.5. $trans - [Co(bpb)(bzlan)_2]ClO_4(4)$

This complex was prepared by a procedure similar to that for **3**, except that benzylamine (0.63 ml, 6 mmol) was used as the amine ligand. Yield 85%. *Anal*. Calc. for $C_{32}H_{30}CIN_6O_6Co$ (689.00): C, 55.78; H, 4.39, N, 12.20. Found: C, 55.60; H, 4.40; N, 12.20%. IR: v_{max} cm⁻¹ (KBr): 3200, 3105 (m, N–H),1628 (s, C=O), 1602 (s, C=C), 1560 (s, C–N). ¹H NMR (200 MHz, CD₃CN): benzylamine, [$\delta = 2.72$ (4H, m, C⁷H₂), 2.89 (4H, br s, NH₂), 6.71 (4H, m, ar H), 7.14 (6H, m, ar H)], bpb, [$\delta = 7.07$ (2H, AA'XX', $J_m = 3.3$, $J_o = 6.0$, H_f), 7.94 (2H, m, H_b), 8.20 (2H, dd, $J_m = 1.7$, $J_o = 7.8$, H_d), 8.34 (2H, m, H_c), 8.88 (2H, AA'XX', $J_m = 3.3$, $J_o = 6.1$, H_e), 9.40 (2H, br d, J = 5.7, H_a)].

2.3.6. $trans - [Co(bpb)(pprdn)_2]ClO_4$ (5)

This complex was prepared by a procedure similar to that for **3**, except that piperidine (0.6 ml, 6 mmol) was used as the amine ligand and the product was recrystallized from methanol-acetone-ethanol (1:5:5 v/v). Yield 65%. *Anal*. Calc. for $C_{28}H_{34}ClN_6O_6Co$ (645.00): C, 52.14; H, 5.31, N, 13.03. Found: C, 51.00; H, 5.20; N, 13.00%. IR: v_{max} cm⁻¹ (KBr): 3150 (m, N–H), 1625 (s, C=O), 1600 (s, C=C), 1565 (s, C–N). ¹H NMR (200 MHz, CD₃CN): piperidine, [δ = 0.95 (2H, m, CH_{ax} of C₄), 1.05–1.20 (10H, m, CH₂CHCH₂), 1.80 (4H, br d, J = 11.8, NCH_{ax}), 1.93 (4H, br d, J = 12.1, NCH_{eq}), 2.29 (2H, br s, NH)], bpb, [δ = 7.11 (2H, AA'XX', J_m = 3.2, J_o = 6.0, H_d), 8.43 (2H, m, H_c), 8.89 (2H, AA'XX', J_m = 3.2, J_o = 6.0, H_e), 9.38 (2H, br d, J = 6.1, H_a)].

Compound 5 crystallizes in the triclinic space group $P\overline{1}$ with lattice constants 10.021(2), 11.330(2), 13.472(3) Å and 78.61(3), 83.46(3), 85.33(3)°. The structure consists of endless chains of complexes along [001]. These are connected by quite strong N-H···O=C

hydrogen-bonds (normalized lengths are 1.899 and 1.919 Å and angles 164 and 167°). There exists a void (channel) between four neighboring chains within which lie the disordered perchlorate anions. They hold the chains together by means of weak $C-H\cdots$ O hydrogen-bonds the lengths of which lie between 2.35 and 2.68 Å.

2.3.7. $trans - [Co(bpb)(mrpln)_2]ClO_4$ (6)

This complex was prepared by a procedure similar to that for **3**, except that morpholine (0.54 ml, 6 mmol) was used as the amine ligand and the product was recrystallized from acetonitrile–methanol–ethanol (4:8:1 v/v). Yield 70%. *Anal*. Calc. for $C_{26}H_{30}ClN_6O_8Co$ (648.94): C, 48.12; H, 4.66, N, 12.95. Found: C, 48.10; H, 4.60; N, 13.00%. IR: v_{max} cm⁻¹ (KBr): 3130(m, N–H), 1620(s, C=O), 1600 (s, C=C), 1560(s, C–N). ¹H NMR (200 MHz, CD₃CN): morpholine, [δ = 1.65 (4H, m, NCH_{ax}), 1.95 (4H, br d, NCH_{eq}), 2.98 (2H, br t, NH), 3.2 (8H, m, OCH₂], bpb, [δ = 7.13(2H, AA'XX', J_m = 3.6, J_o = 6.1, H_f), 8.05 (2H, m, H_b), 8.37 (2H, dd, J_m = 1.8, J_o = 7.1, H_d), 8.47 (2H, m, H_c), 8.92 (2H, AA'XX', J_m = 3.6, J_o = 6.2, H_e), 9.43 (2H, br d, J = 5.7, H_a)].

2.4. X-ray crystallography

Dark green crystals of $1.0.5H_2O$ were grown by slow evaporation of a methanolic solution mixed with toluene at room temperature (r.t.). A parallelepipede of approximate dimensions $0.30 \times 0.23 \times 0.17$ mm was mounted in the orifice of a glass capillary with the help of a high viscosity oil and cooled to 90 K with an Oxford Cryostream. Diffraction measurements were made on a Stoe IPDS using Mo K α radiation ($\lambda = 0.71073$ Å). The intensities were corrected for Lp effects and an absorption correction based on crystal habitus was carried out as well. The decay during the measurement was negligible.

The structure was easily solved with the help of DIRDIF-96 [14], and refined by means of SHELXTL5.5 [15]. All non-hydrogen atoms of $1 \cdot 0.5 H_2O$ were refined anisotropically, but the amine hydrogens and the water hydrogens were refined isotropically. The remaining hydrogens were made to ride on their associated carbon atoms. The water hydrogens were difficult to find in difference maps, but surprisingly easy to refine to very reasonable positions and IDPs (Table 3). Crystallographic data for the structure determination are listed in Table 1. Selected bond lengths and bond angles are presented in Table 2, and the hydrogen-bond lengths and angles are given in Table 3.

Table 1 Crystallographic data for trans-[Co(bpb)(prldn)₂]NCS $\cdot 0.5H_2O$ (1 $\cdot 0.5H_2O$)

Formula	$C_{27}H_{30}N_7O_2SCo \cdot 0.5H_2O$
Formula weight	584.58
Crystal system	Triclinic
Space group	<i>P</i> 1
Crystal size (mm)	$0.30 \times 0.23 \times 0.17$
Morphology	$\{100\}, \{0.10\}, \{00.1\}$ pinacoids
a (Å)	9.4059(8)
b (Å)	11.3047(10)
<i>c</i> (Å)	12.8451(11)
α (°)	81.984 (2)
β (°)	83.761 (2)
γ (°)	85.456 (2)
V (Å ³)	1341.6(2)
Z	2
$D_{\rm c} ({\rm mg}{\rm m}^{-3})$	1.469
Radiation (λ, \mathbf{A})	Μο Κα, 0.71073
$2\Theta_{\max}$ (°)	55.72
Temperature (K)	90 (1)
$\mu (mm^{-1})$	0.761
F(000)	620
Index ranges	$-12 \le h \le 12, -14 \le k \le 14,$
	$-16 \le l \le 16$
Reflections collected	12 399
Independent reflections	5723 $[R_{int} = 0.0398]$
Absorption correction	Integration
Max. and min. transmission	0.9737 and 0.9579
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5694/0/368
Goodness-of-fit on F^2	4.505
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0390, wR_2 = 0.0625$
R indices (all data)	$R_1 = 0.0504, wR_2 = 0.1605$
Weights	$[\sigma^2(F_0^2)]^{-1}$
Largest difference peak and	0.802 and $-0.465 \text{ e} \text{ Å}^{-3}$
hole	

Table 2

Selected bond lengths (Å) and angles (°) for $1 \cdot 0.5 H_2 O$

Bond lengths	
Co-N(1)	1.885(2)
Co-N(11)	1.8910(13)
Co-N(2)	2.0039(13)
Co-N(12)	1.981(2)
Co-N(5)	1.987(2)
Co-N(6)	2.008(2)
Bond angles	
N(1)-Co-N(11)	83.82(6)
N(1)-Co-N(12)	166.93(6)
N(11)-Co-N(12)	83.13(6)
N(1)-Co-N(5)	92.07(6)
N(11)-Co-N(5)	89.48(6)
N(12)-Co-N(5)	88.58(6)
N(1)-Co-N(2)	82.61(6)
N(11)-Co-N(2)	166.42(7)
N(12)-Co-N(2)	110.44(6)
N(5)-Co-N(2)	90.50(6)
N(1)-Co-N(6)	89.73(7)
N(11)-Co-N(6)	90.85(6)
N(12)-Co-N(6)	89.69(7)
N(5)-Co-N(6)	178.19(7)
N(2)-Co-N(6)	89.60(6)

3. Results and discussion

3.1. Synthetic study

Six new complexes (1-6) were prepared through the oxidation of $[Co(II)(bpb)] \cdot H_2O$ in the presence of the appropriate amine in methanol. A vigorous stream of air was passed through a solution of [Co(II)(bpb)]·H₂O in methanol to which was gradually added excess amine. The air oxidation was continued for a period of 3 h during which the color changed from red-brown to green. Dark green crystals of these complexes were obtained in good yield (65-90%). The presence of excess amine is especially important in the synthesis of 1 and 2 having NCS⁻ as the counterion. This is due to the fact that thiocyanate, as a strong nucleophile, can compete with the amine ligand and result in the formation of trans-[Co(bpb)(amine)(NCS)] complex as a byproduct. In fact, preparation of the diamine complexes of piperidine, and morpholine with NCS⁻ counterion was encountered with the formation of a mixture of the diamine and amineisothiocyanato complexes. This critical dependence of the composition of compounds in the cobalt thiocyanate systems on reaction conditions has been noted before [16].

3.2. Description of structure of trans-[Co(bpb)(prldn)₂]NCS Hemihydrate (1.0.5H₂O)

Only a few cobalt(III) amide complexes have been reported in the literature [17–19]. To our knowledge, this is the first reported structure of a Co(III)(bpb)(N)₂ complex containing neutral N-donor axial ligands. Fig. 1 shows an ORTEP drawing of 1.0.5H₂O together with the atomic numbering scheme. The structure exhibits a distorted octahedral environment around cobalt, with the bpb ligand occupying the four equatorial positions. The four N-donor atoms define an almost perfect plane, with an average deviation from the least-square plane of 0.056 Å, the most offending atom being O(1) with a deviation of -0.102 Å. The two axial positions are occupied by two pyrrolidine ligands, adopting a puckered geometry in the envelope conformation. Despite some rotational dispersion in diffraction figure (indicating some minor degree of intergrowth) most of the structural parameters are well within literature values [20]. The internal coordinates of thiocyanate anion are 1.657(5), 1.148(4) Å, and $178.52(3)^{\circ}$ as compared with 1.630(14), 1.155(12) Å. Even the water molecule internal coordinates (0.92(4) Å, 0.86(3) Å and $117(4)^{\circ}$) lie delectably close to the values from neutron data (0.957 Å and 104.5°) [21].

Of the four Co-N bonds in the equatorial plane, the Co-N_{amide} bond distances to N(1) [1.885(2) Å] and N(11) [1.8910(13) Å], being comparable to the Co-N_{amine} values, are indicative of strong bonds of the

Table 3 Hydrogen-bond lengths (Å) and angles (°) for $1.0.5H_2O$

AcceptorH-Donor		or	Hydrogen-bond length (Å)	Hydrogen-bond angle (°)	H distance (Å)	
N	H_1	0	2.139	158	0.918	
N^{i}	H_2	0	2.136	164	0.863	
O_1	H_6^{ii}	N_6^{ii}	2.155	162	0.841	
O_1	H ⁱⁱ _{62a}	C_{62}^{ii}	2.573	124	0.960	
O ₁₁	H_5^{iii}	N_5^{iii}	1.891	157	1.005	
O ₁₁	H_{54b}^{iii}	C_{54}^{iii}	2.869	105	0.960	
O ₁₁	H ⁱⁱⁱ _{52b}	C_{52}^{iii}	2.797	121	0.960	
O ₁₁	H ^{iv} _{53a}	C_{53}^{iv}	2.831	140	0.960	
S	H_5^v	C_5^v	2.877	157	0.930	
S	H_{51a}	C ₅₁	2.948	132	0.960	
S	H_{64a}^{vi}	C_{64}^{vi}	2.980	126	0.960	
0	H _{62b}	C_{62}^{vii}	2.66	135	0.960	

Symmetry transformations used to generate equivalent atoms: (i) 1-x, 2-y, 1-z; (ii) -x, 1-y, -z; (iii) -x, 1-y, 1-z; (iv) 1+x, y, z; (v) 1-x, 1-y, -z; (vi) x, 1+y, z; (vi) -x, -y, 1-z.



Fig. 1. ORTEP plot of *trans*-[Co(bpb)(pyrrolidine)₂]NCS Hemihydrate $(1.0.5H_2O)$ with displacement ellipsoids drawn at the 50% level and a partial labelling scheme for the sake of clarity.

deprotonated amide nitrogens to cobalt. This is in agreement with the fact that the deprotonated amide nitrogen is a very strong s-donor. The deprotonated mode of coordination of the amide nitrogens is also evident from the absence of the amidic proton signal from the ¹H NMR spectrum of complex 1 (vide infra). The bond lengths to the pyridine nitrogens N(2)[2.0039(13) Å] and N(12) [1.981(2) Å] are relatively longer than those to Co-N(1) and Co-N(11), which is in accord with the lower donorability of the pyridine nitrogens. The nitrogen-cobalt-nitrogen bond angles in the equatorial plane comprise one angle which is larger than 90° (N(2)–Co–N(12)=110.44°) and three smaller than 90° (N(1)-Co-N(2) = 82.61°, N(1)-Co-N(11) = 83.82° , and N(11)-Co-N(12) = 83.13°). This indicates that there might be some strain in the coordination

sphere due to the rigid geometry of the ligand. All cis- N_{eq} -Co- N_{ax} bond angles are within 2° of the idealized right angle. The trans-N(5)-Co-N(6) unit with a bond angle of $178.19(7)^{\circ}$ is almost linear. The distances between the cobalt atom and the two axial nitrogen donor atoms differ only slightly [Co-N(5) = 1.987(2)] Å and Co-N(6) = 2.008(2) Å] and compare well with the Co-N distances found in cobalt amine complexes [10,22,23] (e.g. $[Co(NH_3)_6]Cl_3$ (Co-N = 1.963 Å [23]). However, these two Co-Nax bond distances in 1. 0.5H₂O are slightly shorter than those observed for *trans*-[Co(acacen)(piperidine)₂]NCS (mean $Co-N_{ax} =$ 2.042(2) Å) [10]. Considering similar donor-abilities for pyrrolidine ($pK_a = 11.27$) and piperidine ($pK_a = 11.12$) [24], the shorter $Co-N_{ax}$ in 1.0.5H₂O is indicative of a stronger interaction between the cobalt atom and the axial amine ligands. In fact, it is expected that the weaker electron donating character of the equatorial bpb ligand (relative to acacen) in complexes 1-6 to be compensated for by the stronger axial amine interaction with cobalt atom. This also correlates well with the higher activation energies estimated for the dissociative deamination-anation process in 1, 2, and 5 complexes in the solid state relative to those for the corresponding acacen complexes [12].

An interesting feature of the structure of $1.0.5H_2O$ is the intermolecular hydrogen-bonding between adjacent molecules. The structure consists of chains of molecules linked by rather strong N-H···O=C hydrogen-bonds zig-zagging along the **c** lattice translation (Fig. 2). These main hydrogen-bonds are furthermore complicated by weak C-H···O=C hydrogen-bonds. There is a subtle, but interesting difference between the two carbonyl groups: While the secondary bond for O(1) is moderately strong, 2.57 Å (Table 3), there are three very weak bonds for O(11), with the additional feature that one of these reaches out to the chain in the next layer (Fig. 2). The chains are held together by weak C-H···S (parallel



Fig. 2. Hydrogen-bonding scheme in compound $(1 \cdot 0.5 H_2 O)$.

to (110)) and moderately strong $N \cdots H - O - H$ (perpendicular to (110)) hydrogen-bonds. The intermolecular $N-H \cdots O=C$ hydrogen-bonds play a significant role in controlling the solid state deamination-anation and decarbonylation processes of complex 1 at high temperatures [12].

3.3. Spectroscopic properties

Three main features are observed in the IR spectra of the new Co(III) complexes: (1) The vibrations due to the equatorial ligand including three main bands due to the C=O, C=C, and C-N stretching vibrations. These bands which appear at 1615, 1595, and 1560 cm^{-1} respectively, are common to all six complexes. (2) The bands corresponding to the amine N-H stretching vibrations, appearing in the 3105-3215 cm⁻¹ region. These vibrations are shifted by about $150-300 \text{ cm}^{-1}$ relative to the uncoordinated amines, which is in accord with expectation [25]. (3) The sharp stretching at 2045 cm^{-1} in 1 and 2055 cm^{-1} in 2, which clearly indicates that NCS⁻ acts as a counterion in 1 and 2 [25]. This is also evident from the X-ray crystal structure of complex $1.0.5H_2O$. The perchlorate stretching vibrations for the perchlorate salts 3-6 are observed in the corresponding region [25].

The electronic spectral properties of the complexes are listed in Table 4. There are several overlapping absorption bands in the spectrum of the Co(II)(bpb) complex including the two more distinct bands corresponding to the $d-\pi$ and intraligand (IL) transitions, which appear at 735 and 505 nm, respectively [13]. The electronic

Table 4 Spectral properties of cobalt(III) carboxamido complexes in acetonitrile solution

Complex	$\lambda_{\rm max}$, nm ($\varepsilon_{\rm max}$, M ⁻¹ cm ⁻¹	
	LF	ILCT
[Co(bpb)(prldn) ₂]NCS (1)	632 (160)	411 (5806)
[Co(bpb)(bzlan) ₂]NCS (2)	604 (200)	411 (6148)
$[Co(bpb)(prldn)_2]ClO_4$ (3)	630 (157)	412 (5816)
$[Co(bpb)(bzlan)_2]ClO_4$ (4)	600 (202)	410 (6241)
$[Co(bpb)(pprdn)_2]ClO_4$ (5)	675 (179)	410 (5856)
$[Co(bpb)(mrpln)_2]ClO_4$ (6)	699 (168)	409 (6208)
[Co(II)(bpb)·H ₂ O] ^a	735 (d-π*)	505 (IL)

^a [13], Diffuse reflectance spectrum.

spectra of the new *trans*-[Co(III)(bpb)(amine)₂]X complexes show a low intensity (157 < ε < 202) ligand field band which, depending on the axial amine ligand field strength, appears in the region between 600 nm for benzylamine and 699 nm for morpholine. An intense intraligand charge-transfer band appears at around 410 nm in the spectra of all new Co(III) complexes. Similar spectral changes have been observed in the oxidative conversion of a planar Co(II)L complex (L = a tetradentate ligand with delocalized π system) to an octahedral complex with two amines in the axial positions [22,26].

The ¹H NMR spectral data for the free ligand H₂bpb and cobalt(III) complexes 1-6 are given in Section 2. There are three important features in the spectra of the complexes: (1) The absence of the amidic ($\delta = 10.2$) proton signal, which clearly indicates that the equatorial amide ligand is coordinated in a deprotonated form. (2) The expansion, toward downfield chemical shifts, of the aromatic proton signals range. These signals in the spectrum of the free H₂bpb ligand are located between 7.30 and 8.60 ($\Delta \delta = 1.30$ ppm), while in the spectra of the complexes they lie between 7.15 and 9.50 ppm ($\Delta \delta =$ 2.35 ppm), showing a common pattern in all complexes, Fig. 3. These signals have been assigned by comparison with the spectra of closely related complexes [27-29]and a number of rules by Kahl et al. [30]. (3) The appearance of the amine signals which indicate the coordination of two amine ligands in the axial positions. Aside from the aromatic protons of benzylamine which appear at about 6.7-7.0 ppm, other proton resonances of the axial amines appear between about 1.00 and 3.50 ppm. The downfield chemical shift of the amine N-H resonance appearing as a broad signal at lower fields (ca. 3.00-3.50 ppm) relative to the corresponding acacen complexes (ca. 2.40-2.80 ppm) indicates that the $Co-N-H \cdots O=C$ intermolecular hydrogen-bonding is probably strong enough to retain its character in solution.



Fig. 3. ¹H NMR spectrum (500 MHz) of *trans*- $[Co(bpb)(pyrrolidine)_2]ClO_4$ (3) in CD₃CN solution. The spectrum is labeled as to peak assignments discussed in the text.

4. Conclusion

We have reported the synthesis and characterization of several trans-[Co(bpb)(amine)₂]X complexes with bpb = N, N' - bis(2 - pyridinecarboxamide) - 1, 2 - benzenedianion as the equatorial ligand, and part of our characterization included the single-crystal X-ray structure analysis of *trans*-[Co(bpb)(pyrrolidine)₂]NCS. $0.5H_2O$ (1.0.5H₂O). The bpb ligand modifies the affinity of the cobalt metal center towards the axial ligands, therefore, a competition between the amines and NCS⁻ is observed for coordination to the axial positions. It seems that both the electronic and the steric effects contribute to this tendency. While all four trans-[Co(acacen)(amine)₂]NCS complexes have been prepared under common experimental conditions [10], the synthesis of bpb analogues proved to be successful only for pyrrolidine $(pK_a = 11.27)$ (1), and benzylamine $(pK_a = 9.33)$ (2). Mixtures of *trans*-[Co(bpb)(amine)2]NCS and trans-[Co(bpb)(amine)(NCS)] complexes obtained for piperidine $(pK_a = 11.12)$ and morpholine $(pK_a = 8.33)$ indicate that factors other than pure electronic effect, including the steric effect, might as well be operative. This remains to be tested by further theoretical studies on these complexes.

The crystal packing of $1.0.5H_2O$ is mainly determined by a moderately strong intermolecular N-H···O=C hydrogen-bond involving the axial amine nitrogen and the amido oxygen atom of two adjacent molecules. From the solid state kinetic data of complex 1 [12], it is evident that this intermolecular hydrogen-bonding is one of the major factors affecting the activation parameters of the deamination-anation and the decarbonylation of this complex at high temperatures.

5. Supplementary material

Full tables of bond lengths and angles and listing of atom coordinates, thermal parameters, and details of least-squares planes have been deposited with the Cambridge Crystallographic Data Center under no. CCDC-155326. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk.

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