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Synthesis and Characterization of Trans-[Co^{III}(acacen)L_2].NCS, Trans-[Co^{III}(acacen)L_2]ClO_4 and Trans-[Co^{III}(acacen)(NCS)L] (L = Piperidine, Benzylamine, Morpholine, Pyrrolidine). X-ray Structure Determination of Trans-[Co(acacen)(pprdn)$_2$].NCS Containing N-H...NCS Hydrogen Bond

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A series of complexes of the type trans-[Co(acacen)L_2].NCS, 1a-4a; trans-[Co(acacen)L_2]ClO_4, 1b-4b; and trans-[Co(acacen)(NCS)L], 1c-4c (where acacen is N,N′-ethylenebis(acetylacetoneiminato) dianion; L= piperidine (pprdn), 1; benzylamine (bzlan), 2; morpholine (mrpln), 3, and pyrrolidine(prldn), 4,) have been synthesized and characterized by elemental analysis and spectroscopic methods. The crystal and molecular structure of the complex trans-[Co(acacen)(pprdn)$_2$].NCS, 1a, was determined by X-ray crystallography. The compound crystallizes in the monoclinic space group $P2_1/n$, a = 9.643(3)Å, b = 9.042(3)Å, c = 28.800(6)Å, β = 96.96(2)Å, V = 2443(1) Å^3, Z = 4 and R = 4.05% and R_w = 4.57% for 4574 reflections (F_o > 4σ (F)). The $(NCS)^-$ group is neither coordinated to the cobalt(III) center nor acting merely as a counter ion, but it is hydrogen bonded to one of the coordinated amines (i.e. Co-N-H....NCS). The observed ν(CN) for the thiocyanate ion and ν(N-H) for the amine ligands are also consistent with such an interaction. The ^{1}H NMR, IR and the electronic spectra are also reported and discussed.

INTRODUCTION

Thiocyanate occupies a special place among small anionic ligands. It has been extensively used in the synthesis of linkage isomers (see [1] and references cited therein) and in the study of electron transfer reactions [2,3]. The bonding modes of this ligand have been shown to be subject to a variety of directive influences [4,5] among them being the nature of the coordinated metal atom, the electronic and steric requirement of other ligands in the coordination sphere, the kinetics of the reaction involved in the course of synthesis and the nature of the solvent interaction in solutions. The fact that thiocyanate has the potential of forming (NCS)...H-N-M and intermolecular hydrogen bonds of the type M-SCN...H-X-M (X = O or N) in the solid state or M-SCN...HOR in hydroxylic solvents has previously been established [6-10]. In the course of attempting to synthesize trans-[Co(acacen)(NCS)(amine)], several new complexes of the type trans-[Co(acacen)(amine)$_2$].NCS were prepared and the existence of the Co-N-H...NCS hydrogen bond between NCS and the coordinated amine in these complexes was noticed. The results of the structural and spectroscopic studies on this mode of interaction of thiocyanate in crystals are presented here.

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EXPERIMENTAL SECTION

Reagents

N, N′-ethylenebis(acetylacetoneiminato) dianion = (acacen) was prepared as described in the literature [11]. $Co(OH)_2$ was freshly prepared prior to each synthesis by adding an aqueous solution of NaOH to a solution of $Co(NO_3)_2.6H_2O$ in water (with a molar ratio of 2:1), filtering the precipitate immediately and washing it with acetone. Piperidine (pprdn) (Aldrich), benzylamine (bzlan), morpholine (mrpln), pyrrolidine (prldn) (Merck) were distilled under reduced pressure. All other chemicals were commercial reagent grade and used as received from Aldrich and Merck.

Physical Measurements

UV-visible absorption spectra in solutions were measured by a Shimadzu UV-240 spectrophotometer. Infrared spectra were recorded as KBr pellets on a Shimadzu 435 IR spectrophotometer.

^1H NMR spectra were obtained on a Varian EM-390 90MHz and a General Electric QE-300 FT NMR spectrometer. Proton chemical shifts were referenced to residual protons in solvent ($CDCl_3$, 7.24 ppm vs $(CH_3)_4Si$). Elemental analyses were performed by using a Heraeus CHN-O-RAPID elemental analyzer.

Synthesis

Trans-[Co(acacen)(pprdn)$_2$].NCS (1a)

A solution of acacenH_2 (2.24 g, 10 mmol) in acetone (50 ml) was added to a stirred suspension of freshly prepared $Co(OH)_2$ (0.93 g, 10 mmol) in acetone (100 ml). The reaction mixture was refluxed for 2 hrs under an atmosphere of purified nitrogen [12]. The resulting red-brown solution was cooled to room temperature (25°C) and the small solid residue was filtered out. 2.0 ml (20 mmol) of piperidine was added to the filtrate (containing trans-[Co(acacen)$_2$(OH_2)$_2$]) followed by 1.94 g (20 mmol) of KSCN. Hydrogen peroxide (3.0 ml) was then added dropwise with stirring during a period of 1 hr and the reaction mixture was left overnight. The solid residue was filtered out and the resulting solution was then allowed to stand undisturbed for 48 hrs. Dark brown crystals were obtained and recrystallized from methanol-acetone-water (10:5:1 v/v) mixture. The crystals were isolated by filtration, washed with a 30 ml mixture of ethanol-ether (1:9 v/v) and dried in vacuo. Yield 3.20 g (63%). Anal. Calcd. for $C_{23}H_{40}N_5O_2SCo$: C, 54.22; H, 7.86; N, 13.75. Found: C, 53.50; H, 7.70; N, 13.50%.

Trans-[Co(acacen)(bzlan)$_2$].NCS (2a)

This complex was prepared by a procedure similar to that for compound 1a, except that benzylamine (2.1 ml, 20 mmol) was used as the amine ligand and 10 ml of water was added to the final solution for crystallization. Brown crystals were obtained and recrystallized from ethanol-water (9:1 v/v) mixture. The crystals were isolated by filtration, washed with 30 ml mixture of ethanol-ether (1:9 v/v) and dried in vacuo. Yield 3.42 g (62%). Anal. Calcd. for $C_{27}H_{36}N_5O_2SCo$: C, 58.59; H, 6.51; N, 12.66. Found: C, 58.60; H, 6.50; N, 12.45%.

Trans-[Co(acacen)(mrpln)$_2$].NCS (3a)

This complex was prepared by a procedure similar to that for compound 1a, except that morpholine (1.80 ml, 20 mmol) was used as the amine ligand. Dark brown crystals were obtained and recrystallized from dichloromethane-ethanol (1:1 v/v) mixture. The crystals were isolated by filtration, washed with ethanol and dried in vacuo. Yield 3.49 g (68%). Anal. Calcd. for $C_{27}H_{36}N_5O_4SCo$: C, 49.12; H, 7.00; N, 13.65. Found: C, 49.10; H, 6.80; N, 13.70%.

Trans-[Co(acacen)(prldn)$_2$].NCS (4a)

This complex was prepared by a procedure similar to that for compound 1a, except that pyrrolidine (1.70 ml, 20 mmol) was used as the amine ligand. Dark brown crystals were obtained and recrystallized from dichloromethane-acetone-cyclohexane (1:1:1 v/v) mixture. The crystals were isolated by filtration, washed with propane-2-ol and dried in vacuo. Yield 2.84 g (59%). Anal. Calcd. for $C_{21}H_{36}N_5O_2SCo$: C, 52.39; H, 7.48; N, 14.56. Found: C, 52.20; H, 7.40; N, 14.30%. Caution! Transition-metal complex perchlorates are known to be hazardous and must be treated with care, especially in the presence of organic solvents.

Trans-[Co(acacen)(pprdn)$_2$](ClO_4) (1b)

A solution of acacenH_2 (1.12 g, 5 mmol) in ethanol (30 ml) was added to a stirred suspension of freshly prepared $Co(OH)_2$ (0.465 g, 5 mmol) in ethanol (70 ml). The reaction mixture was refluxed for 2 hrs under an atmosphere of purified nitrogen. The resulting red-brown solution was cooled to room temperature (25°C) and the small solid residue was filtered out. 1.50 ml (15 mmol) of piperidine was added to the filtrate (containing trans-[Co(acacen)$_2$(OH_2)$_2$]) and air was bubbled through the solution for 3 hrs, and then was filtered off. A solution of $NaClO_4$ (2.45 g, 20 mmol) in ethanol (30 ml) was then added to the final filtrate. Dark brown crystals were obtained after 48 hrs. and recrystallized from ethanol. The crystals were isolated by filtration, washed with a 30 ml mixture of ethanol-ether (1:9 v/v) and dried in vacuo. Yield 2.20g (80%). Anal. Calcd. for $C_{22}H_{40}N_4O_6ClCo$: C, 47.96; H, 7.27; N, 10.17. Found: C, 48.50; H, 7.10; N, 9.90%.

Trans-[Co(acacen)(bzlan)$_2$]ClO_4 (2b)

The procedure was the same as for 1b, except that benzylamine (1.57 ml, 15 mmol) was used as the amine ligand. Yield 2.23 g (75%). Anal. Calcd. for

$C_{26}H_{36}N_4O_6ClCo$: C, 52.48; H, 6.06; N, 9.42. Found: C, 52.30; H, 6.00; N, 9.15%.

Trans-[Co(acacen)(mrpln)$_2$]ClO$_4$ (3b)

The procedure was the same as for 1b, except that morpholine (1.35 ml, 15 mmol) was used as the amine ligand and the product was recrystallized from dichloromethane-acetone-ethanol (1:1:1 v/v). Yield 2.11 g (76%). Anal. Calcd. for $C_{20}H_{36}N_4O_8ClCo$: C, 43.28; H, 6.49; N, 10.10. Found: C, 44.50; H, 6.40; N, 10.00%.

Trans-[Co(acacen)(prldn)$_2$]ClO$_4$ (4b)

The procedure was the same as for 3b, except that pyrrolidine (1.25 ml, 15 mmol) was used as the amine ligand. Yield 1.91 g (73%). Anal. Calcd. for $C_{20}H_{36}N_4O_6ClCo$: C, 45.93; H, 6.89; N, 10.72. Found: C, 46.50; H, 7.00; N, 11.00%.

Trans-[Co(acacen)(NCS)(pprdn)] (1c)

This complex was prepared in acetone by a procedure similar to that for 1a, except that piperidine (1 ml, 10 mmol) was added to the filtrate containing trans-[Co(acacen)$(OH_2)_2$], followed by a solution of KSCN (0.97 g, 10 mmol) in water (5 ml) and then hydrogen peroxide (3 ml). After removal of the solvent on a rotary evaporator (45°C), the product was initially purified by chromatography using a column (15cm × 2.5cm) of acid- washed alumina followed by recrystallization from chloroform ethanol. Dark brown crystals were obtained and isolated by filtration, washed with a 30 ml mixture of ethanol-ether (1:9 v/v) and dried in vacuo. Yield 2.97 g (70%). Anal. Calcd. for $C_{18}H_{29}N_4O_2SCo$: C, 50.94; H, 6.84; N, 13.20. Found: C, 50.50; H, 6.90; N, 13.50%.

Trans-[Co(acacen)(NCS)(bzlan)] (2c)

This complex was prepared by a procedure similar to that for 1c, except that benzylamine (1.05 ml, 10 mmol) was used as the amine ligand. The product was recrystallized from dichloromethane-acetone-cyclohexane (6:1:6 v/v). Dark brown crystals were obtained and isolated by filtration, washed with a 30 ml mixture of ethanol-ether(1:9 v/v) and dried in vacuo. Yield 2.37 g (53%). Anal. Calcd. for $C_{20}H_{27}N_4O_2SCo$: C, 53.81; H, 6.05; N, 12.56. Found: C, 53.80; H, 6.20; N, 12.70%.

Trans-[Co(acacen)(NCS)(mrpln)] (3c)

This complex was prepared in acetone by a procedure similar to that for 1c, except that morpholine (0.90 ml, 10 mmol) was used as the amine ligand and the product was recrystallized from dichloromethane-acetone-ethanol (1:3:1 v/v) mixture. The crystals were isolated by filtration, washed with 2-propanol -acetone (1:1 v/v) and dried in vacuo. Yield 3.15 g (74%). Anal. Calcd. for $C_{17}H_{27}N_4O_3SCo$: C, 47.89; H, 6.33; N, 13.15. Found: C, 47.80; H, 6.30; N, 13.10%.

Trans-[Co(acacen)(NCS)(prldn)] (4c)

This complex was prepared in acetone by a procedure similar to that for 1c, except that pyrrolidine (0.85 ml, 10 mmol) was used as the amine ligand and the product was recrystallized from dichloromethane-acetone-cyclohexane (1:1:1 v/v) mixture. The crystals were isolated by filtration, washed with propane-2-ol and dried in vacuo. Yield 2.77 g (68%). Anal. Calcd. for $C_{17}H_{27}N_4O_2SCo$: C, 49.76; H, 6.59; N, 13.66. Found: C, 49.80; H, 6.40; N, 13.70%.

X-RAY CRYSTALLOGRAPHY

Crystals of trans-[Co(acacen)$(pprdn)_2$].NCS, 1a, were removed from their mother liquor and immediately coated with a protective hydrocarbon oil. The crystal selected for data collection was mounted in a cold stream of a Siemens R3m/V diffractometer equipped with a locally-modified Enraf-Nonius low temperature apparatus. Only random fluctuations of less than 1% in the intensities of the two standard reflections were observed during the course of data collection. The space group was uniquely determined to be $P2_1/n$ by the observation of systematic absences. The structure was solved by direct methods. Computer programs were from SHELXTL PLUS [13] installed on a MicroVAX 3200 computer. Neutral atom scattering factors and corrections for anomalous dispersion were from the International Tables [14]. An absorption correction was applied using program XABS [15]. One reflection (0,0,2) appeared to suffer extinction and was omitted from the later stages of refinement. Hydrogen atoms were located in a difference map and refined using a riding model, with N-H and C-H bonds fixed at 0.96 Å, and isotropic U of 0.03 $Å^2$. Final refinement (based on F) was carried out with anisotropic thermal parameters for all non-hydrogen atoms using 289 parameters and 4574 reflections with $F > 4\sigma(F)$. The largest feature on a final difference map was 0.40 e $Å^{-3}$ in height. The crystallographic data for 1a are summarized in Table 1 and final positional parameters are presented in Tables 2A and 2B.

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization

The Schiff base acacenH_2 reacts with $Co(OH)_2$ in an inert atmosphere to give N, N′-ethylenebis (acetylacetoniminato) cobalt(II) hydrate [12]. This complex has been used under oxidizing conditions to prepare many complexes of the type trans-[Co(acacen)XY] [12,16]. In an attempt to synthesize trans-[Co(acacen)(NCS)L], 1c-4c, (L = pprdn, bzlan, mrpln and prldn) a new

Table 1. Crystallographic data for complex 1a.

Chemical Formula	**$C_{23}H_{40}CoN_5O_2S$**	**Space Group**	**$P2_1/n$**
fw	509.6	T, °C	-143
a,Å	9.643 (3)	λ, Å	0.71073
b,Å	9.042 (3)	ρ_{calc}, g cm^{-3}	1.36
c,Å	28.800 (6)	μ,mm^{-1}	0.80
β, deg	96.96 (2)	Transmission Coeff	0.746-0.946
V,Å^3	2493 (1)	R(F$_o$)^1	4.05
Z	4	R$_w$(F$_o$)^1	4.57

1) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| R_w = \Sigma||F_o| - |F_c||w^{1/2}/\Sigma|F_o w^{1/2}|$.

Table 2A. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å^2 × 10^3).

	x	y	z	U(eq)
Co	3913(1)	3282(1)	1131(1)	15(1)
O(1)	3981(2)	2344(2)	544(1)	19(1)
O(2)	5696(2)	4027(2)	1039(1)	19(1)
N(1)	2151(2)	2448(2)	1220(1)	18(1)
N(2)	3811(2)	4304(2)	1702(1)	19(1)
N(3)	4867(2)	1488(2)	1455(1)	18(1)
N(4)	3069(2)	5129(2)	794(1)	18(1)
C(1)	2958(3)	1634(3)	313(1)	18(1)
C(2)	1712(3)	1290(3)	473(1)	22(1)
C(3)	1362(2)	1619(3)	925(1)	20(1)
C(4)	3213(3)	1182(3)	-172(1)	28(1)
C(5)	7(3)	998(3)	1052(1)	27(1)
C(6)	6412(3)	4949(3)	1315(1)	20(1)
C(7)	5995(3)	5570(3)	1712(1)	25(1)
C(8)	4721(3)	5264(3)	1893(1)	20(1)
C(9)	7807(3)	5338(3)	1160(1)	31(1)
C(10)	4452(3)	6073(3)	2332(1)	28(1)
C(11)	2500(3)	4056(3)	1905(1)	25(1)
C(12)	1817(3)	2655(3)	1701(1)	26(1)
C(13)	6069(3)	935(3)	1225(1)	26(1)
C(14)	6659(3)	-523(3)	1432(1)	27(1)
C(15)	7126(3)	-354(3)	1955(1)	30(1)
C(16)	5907(3)	219(3)	2194(1)	30(1)
C(17)	5321(3)	1647(3)	1967(1)	24(1)
C(18)	3664(3)	5462(3)	352(1)	27(1)
C(19)	3213(3)	6973(3)	151(1)	30(1)
C(20)	1635(3)	7065(3)	53(1)	25(1)
C(21)	987(3)	6702(3)	495(1)	26(1)
C(22)	1508(2)	5235(3)	709(1)	22(1)
S	675(1)	-2278(1)	1862(1)	31(1)
N(5)	3010(3)	-1297(3)	1456(1)	49(1)
C(23)	2050(3)	-1702(3)	1628(1)	28(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

series of trans[Co(acacen)L$_2$].NCS complexes, 1a-4a, were successfully prepared, in which the NCS group forms hydrogen bond to one of the coordinated amines. The preparation was carried out using Co, L, NCS in a 1:2:2 molar ratio and H_2O_2 as the oxidizing agent. Recrystallization of these complexes, 1a-4a, in the presence of perchlorate anion yields trans-[(acacen)L$_2$]ClO$_4$ 1b′−4b′ with spectroscopic properties identical to those for the trans-[(acacen)L$_2$]ClO$_4$, 1b-4b, produced by direct synthesis. In the preparation of 1b-4b, it was desired to carry out the reaction in the absence of water and reduce the possibility of the coordinated amine hydrolysis. This was accomplished by using absolute ethanol as the reaction solvent and air oxidation of the reaction mixture in the oxidation step. In contrast, an aqueous solution of KSCN was used (in order to have a high enough concentration of NCS$^-$ ion) in the synthesis of trans-[Co(acacen)(NCS)L], 1c-4c, complexes, which were prepared by using Co, L, NCS in a 1:1:1 molar ratio and H_2O_2 as the oxidizing agent.

Table 3 summarizes the visible spectral data of the trans-[Co(acacen)L$_2$]$^+$ and trans-[Co(acacen)(NCS)L] complexes studied in this work along with some other related complexes. In terms of the similarities in ligation, spectral features are best compared with those of other [Co(acacen)XL] complexes [16], which exhibit a broad band for the first ligand field transition. The visible absorption spectra of the complexes are presented in Figure 1. As expected, almost identical absorption spectra were observed for a, b and b′ complexes of each amine, i.e. 1a, 1b and 1b′, etc. (Figure 1A). As mentioned previously, the 1b-4b perchlorate complexes were prepared by direct synthesis , whereas the 1b′-4b′ were produced from the ethanolic solutions of 1a-4a upon recrystallization in the presence of NaClO$_4$.

Longer λ_{max}(LF) were observed in the electronic spectra of 1c-4c (Figure 1B) relative to those for the corresponding a and b, bis(amine), complexes. The shift, which is due to replacing one of the axial amines by a weaker NCS ligand, is more noticeable for bzlan (24 nm) and prldn (21 nm) than for pprdn (5 nm) and mrpln (5 nm) compounds.

The ^{1}H NMR spectral data of trans-[Co(acacen)L$_2$].NCS and trans-[Co(acacen)L$_2$](ClO$_4$) complexes are given in Table 4. A source of reference, R = trans-[Co(acacen)(py)(N$_3$)], is also included for

Table 2B. H-Atom coordinates ($\times 10^4$) and isotropic displacement coefficients ($Å^2 \times 10^3$).

	x	y	z	U
H(3A)	4184	710	1425	30
H(4D)	3356	5938	999	30
H(2A)	1023	788	262	30
H(4A)	3986	506	-146	30
H(4B)	3478	2040	-337	30
H(4C)	2428	723	-354	30
H(5A)	-632	1786	1095	30
H(5B)	172	447	1338	30
H(5C)	-382	364	802	30
H(7A)	6621	6265	1880	30
H(9A)	7679	5687	843	30
H(9B)	8394	4477	1175	30
H(9C)	8240	6093	1363	30
H(10A)	3585	6604	2282	30
H(10B)	5191	6765	2422	30
H(10C)	4417	5336	2570	30
H(11A)	1877	4872	1830	30
H(11B)	2685	3983	2239	30
H(12A)	2166	1830	1890	30
H(12B)	823	2702	1703	30
H(13A)	6796	1666	1259	30
H(13B)	5777	806	897	30
H(14A)	5949	-1270	1385	30
H(14B)	7433	-832	1275	30
H(15A)	7889	332	2005	30
H(15B)	7435	-1290	2087	30
H(16A)	6200	386	2521	30
H(16B)	5182	-514	2186	30
H(17A)	4543	1974	2119	30
H(17B)	6031	2394	2012	30
H(18A)	3353	4720	124	30
H(18B)	4665	5416	407	30
H(19A)	3541	7722	374	30
H(19B)	3626	7150	-131	30
H(20A)	1308	6374	-189	30
H(20B)	1359	8041	-53	30
H(21A)	-12	6671	427	30
H(21B)	1220	7473	720	30
H(22A)	1132	5092	1000	30
H(22B)	1166	4451	501	30

Table 3. Visible spectral data for 1a-4a, 1b-4b and 1c-4c complexes in ethanol, and some related compounds.

Complex	λ_{max}/nm*
trans-[Co(acacen)(pprdn)$_2$].NCS (1a)	437(1.12)
trans-[Co(acacen)(pprdn)$_2$]ClO$_4$ (1b)	437(1.12)
trans-[Co(acacen)(pprdn)(NCS)] (1c)	442(1.37)
trans-[Co(acacen)(bzlan)$_2$].NCS (2a)	406(1.25)
trans-[Co(acacen)(bzlan)$_2$]ClO$_4$ (2b)	406(1.25)
trans-[Co(acacen)(bzlan)(NCS)] (2c)	430(1.53)
trans-[Co(acacen)(mrpln)$_2$].NCS (3a)	444(0.98)
trans-[Co(acacen)(mrpln)$_2$]ClO$_4$ (3b)	444(0.97)
trans-[Co(acacen)(mrpln)(NCS)] (3c)	449(1.26)
trans-[Co(acacen)(prldn)$_2$].NCS (4a)	417(0.97)
trans-[Co(acacen)(prldn)$_2$]ClO$_4$ (4b)	417(0.97)
trans-[Co(acacen)(prldn)(NCS)] (4c)	438(1.19)
trans-[Co(acacen)(N$_3$)(Py)]	452(1.91)†
trans-[Co(F$_6$acacen)(N$_3$)(Py)]	435(2.57)†

* $\epsilon \times 10^{-3}$/mol^{-1}L cm^{-1} (in parentheses).

† [16].

comparison [16]. The overall pattern of resonances of trans-[Co(acacen)(amine)$_2$].NCS, 1a-4a, and trans-[Co(acacen)(amine)$_2$](ClO$_4$), 1b-4b are comparable (in the acacen region) to that of R. The singlet at about 5.00-5.10 ppm corresponds to the = CH- protons of acacen; the four ethylenediamine protons give a singlet at about 3.80-4.10 ppm. The signals at about 2.20 and 2.35 ppm are assigned to the two sets of CH$_3$ protons.

In the ^{1}H NMR spectra of compounds 1a and 1b, the piperidine protons appear as multiplets at 1.40 to 2.00 ppm and the N-H proton appears as a shoulder, to the left of CH$_3$(N) signal, at about 2.40 ppm. In the case of compounds 2a and 2b (Figure 2), the phenyl protons of benzylamine appear as a multiplet centered at about 7.30 ppm and the multiplet centered at 3.18 ppm is assigned to the four benzylic protons. The four amine protons appear as a multiplet centered at 2.87 ppm for 2a and at 2.43 ppm for 2b. It appears that the Co-N-H...(NCS) hydrogen bonding in 2a is strong enough to retain its existence in solution to some extent and cause the amine protons of 2a to appear at a lower field relative to 2b (i.e. 2.87 ppm vs 2.43 ppm). These two multiplets disappear when D$_2$O is added to the NMR samples of 2a and 2b and the four benzylic protons appear as a singlet centered at 3.18 ppm in the NMR spectra of both complexes, which confirms the spectral assignment. The proton resonances of the coordinated morpholine in 3a and 3b appear at 3.55 (m) and 2.00-2.20 (m) ppm for CH$_2$-O-CH$_2$ and CH$_2$-N-CH$_2$ protons respectively and at about 2.20 ppm (as a shoulder) for the N-H protons. In pyrrolidine complexes, 4a and 4b, the CH$_2$ protons of the coordinated amine appear as multiplets at about 1.60 to 2.00 ppm and the N-H protons at about 2.40 ppm. In all cases the chemical shifts along with the integration data are consistant with the coordination of two amine ligands in 1a-4a and 1b-4b complexes.

The ^{1}H NMR spectral data of trans-[Co(acacen)(NCS)L], 1c-4c, are also given in Table 4. The most significant feature of the NMR spectra of group 3 complexes is that, as in complex R, the four CH$_2$ protons of the acacen ligand appear as an AA'BB' multiplet centered at about 3.70 ppm, which

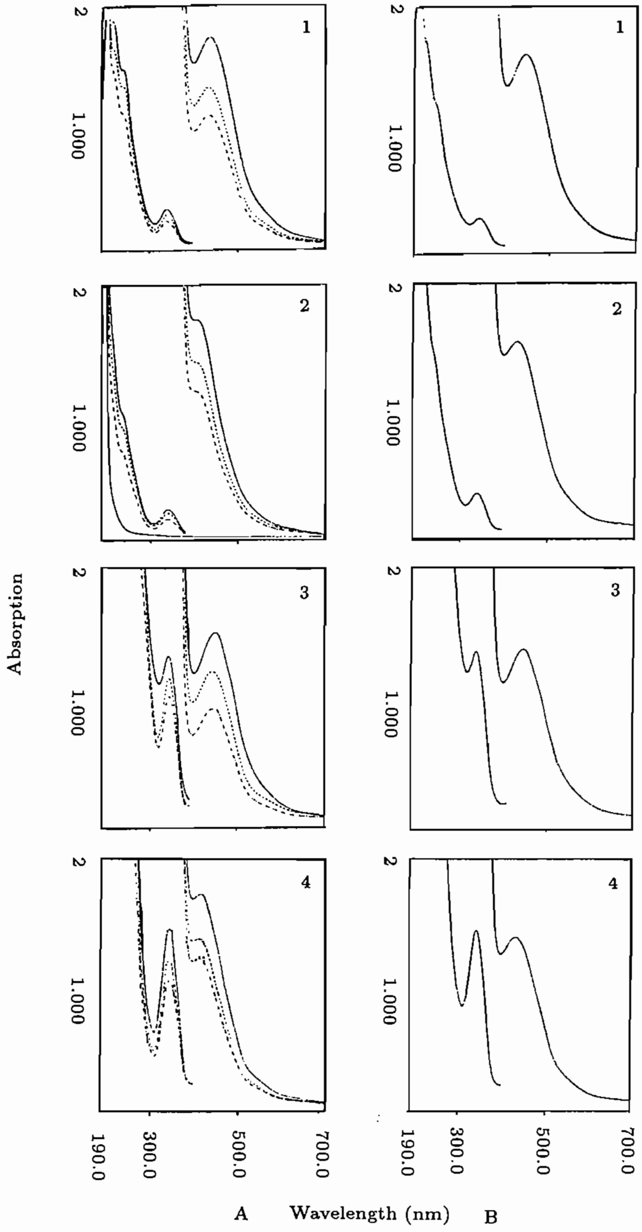

Figure 1. (A) Visible absorption spectra of 1a-4a (—), 1b-4b (- - -) and 1b-4b (- - -), in EtOH at 1b′-4b′ 25°C. (B) Visible absorption spectra of 1c-4c in EtOH, at 25°C.

is consistent with the coordination of one amine and one NCS^- ligand in trans axial positions.

It is evident from the NMR data, taken together with the microanalytical results and the electronic and IR spectra (vide infra) that the 1a-4a, 1b-4b and 1c-4c complexes have distorted octahedral structures with the tetradentate ligand occupying equatorial sites and can be presented as trans-[Co(acacen)(amine)$_2$].NCS, trans-[Co (acacen) (amine)$_2$]ClO_4 and trans-[Co(acacen)(amine)(NCS)] respectively.

The important features of the infrared spectra

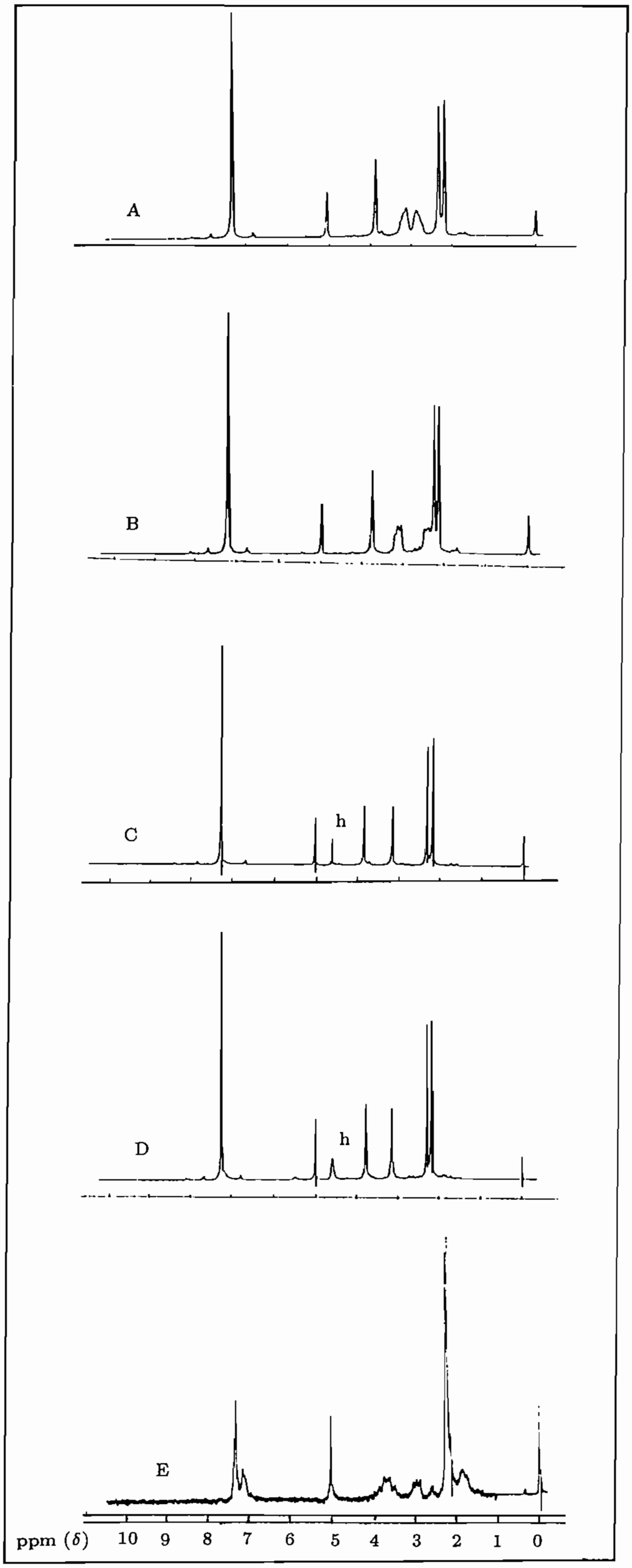

Figure 2. The ^1H NMR spectra of 2a-2c complexes in $CDCl_3$. A) Trans-[Co(acacen)(bzlan)$_2$].NCS (2a); B) Trans-[Co(acacen)(bzlan)$_2$]ClO_4 (2b); C) 2a + D_2O; D) 2b + D_2O; E) Trans-[Co(acacen)(bzlan)(NCS)] (2c). h = H_2O.

Table 4. ^{1}H NMR assignments⋆,†.

Complex	Acacen Protons			
	$CH_3(O)$	$CH_3(N)$	=C-H	$-(CH_2)_2-$
R*	2.20(s)	2.28(s)	5.08(s)	(3.23(m))
1a	2.20(s)	2.38(s)	5.07(s)	4.10(s)
1b	2.20(s)	2.38(s)	5.07(s)	4.10(s)
1c	2.20(s)	2.33(s)	5.00(s)	(3.65(m))
2a	2.20(s)	2.35(s)	5.05(s)	3.85(s)
2b	2.20(s)	2.35(s)	5.00(s)	3.82(s)
2c	2.30(s)	2.33(s)	5.15(s)	(3.75(m))
3a	2.18(s)	2.30(s)	5.05(s)	4.00(m)
3b	2.15(s)	2.33(s)	5.10(s)	4.00(s)
3c	2.10(s)	2.20(s)	5.00(s)	(3.20-3.90(m))
4a	2.13(s)	2.33(s)	5.05(s)	3.88(s)
4b	2.15(s)	2.32(s)	5.05(s)	3.85(s)
4c	2.20(s)	2.30(s)	5.10(s)	(3.70(m))

⋆ In ppm relative to TMS.

† s = singlet, t = triplet, m = multiplet.

* [12].

Table 5. Selected IR spectral data of cobalt complexes*.

Comp.	ν(N-H)^f (asym.)	ν(N-H)^h (asym.)	ν(N-H)^f (sym.)	ν(N-H)^h (sym.)	ν(N-H)^f	ν(N-H)^h	ν(NC) (NCS)
1a					3203	3142	2052
1b					3210		
1c					3145		2122
2a	3304	3284	3190	3082			2061
2b	3306		3250				
2c	3285		3200				2120
3a					3145	3115	2065
3b					3220		
3c					3175		2122
4a					3145	3130	2065
4b					3240		
4c					3180		2122

* KBr pellets.

f = free, h = hydrogen bonded.

for the complexes are summarized in Table 5. All compounds exhibit absorbances in the 1400-1600 cm^{-1} region associated with the coordinated acacen and the bands at 2800-3200 cm^{-1} assigned to C-H and N-H stretching features of the coordinated amines [12,17]. The single sharp band at 2052 cm^{-1} for 1a, 2061 cm^{-1} for 2a, 2065 cm^{-1} for 3a and 2065 cm^{-1} for 4a in the IR spectra of these complexes confirm the presence of the thiocyanate group in the complex lattice [18]. As it is clear from the X-ray structure of 1a (Figure 4), the thiocyanate anion is not coordinated to the metal center but it forms a Co-N-H...NCS hydrogen bond to one of the coordinated amines. It is this mode of interaction for NCS which brings up a remarkable change in the shape and ν(N-H) of the coordinated amine. While compound 1b, with two pprdn groups of identical environment, exhibits only one ν(N-H) at 3210 cm^{-1}, there are two distinct N-H bands in the infrared spectrum of compound 1a. One at 3203 cm^{-1} associated with the N-H group which is not involved in hydrogen bonding and the other at 3142 cm^{-1} assigned to the hydrogen bonded N-H. As it is expected the 3142 cm^{-1} and 2052 cm^{-1} bands disappear when compound 1a is recrystallized from absolute ethanol in the presence of $NaClO_4$ (Figure 3-1b′). In this process, compound 1a is converted into compound 1b′ and the thiocyanate group (and therefore the Co-N-H...NCS hydrogen bond) is removed from the crystal lattice.

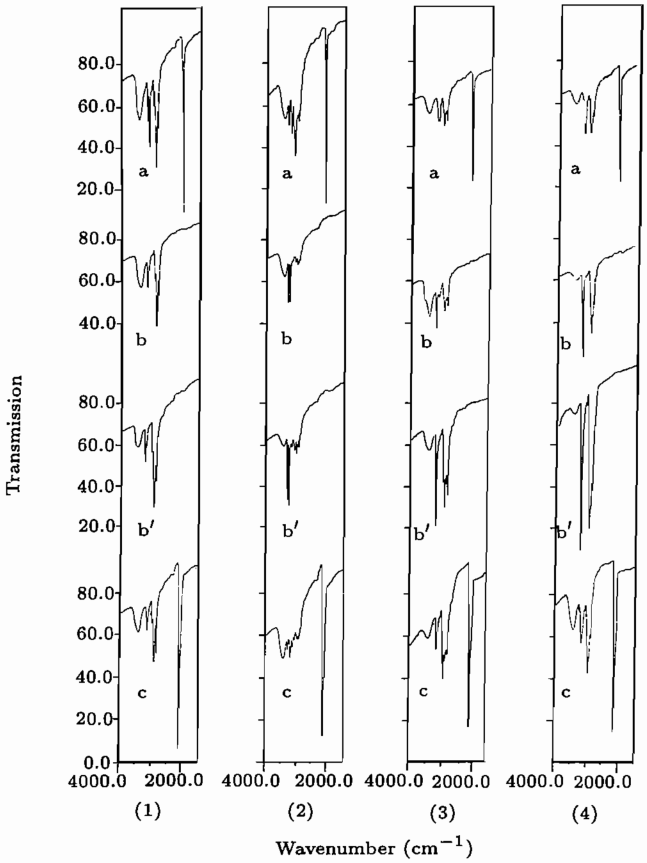

Figure 3. The 4000-1900 cm^{-1} region of the infrared spectra of 1a-4a, 1b-4b, 1b′-4b′, 1c-4c.

The IR spectrum of the product, 1b′, is identical to that of the perchlorate salt, 1b, produced from direct synthesis. The same line of reasoning is valid for the benzylamine complexes 2a, 2b and 2b′. The two anti-symmetric and symmetric stretching modes of the coordinated NH_2 groups in complex 2b show bands at 3306 cm^{-1} and 3250 cm^{-1} respectively. However, in comparison, four N-H stretching bands, at 3304 cm^{-1}, 3284 cm^{-1}, 3190 cm^{-1} and 3082 cm^{-1} are observed in the IR spectrum of complex 2a (in which the NH_2 group is presumably involved in hydrogen bonding). In addition, a band at 2061 cm^{-1} features in the spectrum which is assigned to the NCS group forming hydrogen bond to the coordinated Ar-NH_2 (Figure 3-2a). When compounds 3a and 4a are converted into their perchlorate salts, 3b′ and 4b′, similar changes are observed in their IR spectra. The 2065 cm^{-1} band disappears and the N-H stretching bands, which are slightly split into doublets due to N-H....NCS hydrogen bonding in the parent complexes (peaks at 3115 and 3145 cm^{-1} for 3a, 3130 and 3145 cm^{-1} for 4a), appear as single bands at 3220 and 3240 cm^{-1} in the IR spectra of 3b′ and 4b′ respectively. The IR spectra of 3b′ and 4b′ are identical to those of the perchlorate salts, 3b and 4b, produced by direct synthesis. The above observations are in accord with several experimental [6,7,19–21] and theoretical reports [22,23] regarding the effect of hydrogen bonding on the shape and frequency of N-H stretching vibration involved in the N-H...X interactions.

The most significant feature of the IR spectra of trans-[Co(acacen)(amine)(NCS)], 1c-4c, complexes is the appearance of a single sharp band at about 2120 cm^{-1}, due to the CN stretching vibration of the coordinated thiocyanate ligand (Figure 3-3). As expected, only one ν(N-H) is observed in the N-H stretching region of the piperidine (3145 cm^{-1}), morpholine (3175 cm^{-1}) and pyrrolidine (3180 cm^{-1}) complexes. In the case of trans-[Co(acacen)(b zlan)(NCS)] 2c complex, although there is a considerable change in the N-H stretching region relative to 2a, its spectrum is somewhat different, in this region, from that of 2b (in which the hydrogen bonding is removed). This may be due to the existence of some intermolecular hydrogen bonding which has also been reported for other amineisothiocyanato complexes [10].

The observed changes in the IR spectra in going from 1a-4a to 1c-4c complexes are important in monitoring the "deamination-anation" kinetics of 1a-4a compounds [24].

Description of the Structure of Complex 1a

A diagram of the structure, together with the atom numbering scheme, is shown in Figure 4. All hydrogen atoms except the H_{3a}, involved in hydrogen bonding, have been omitted for clarity. The bond lengths are listed in Table 6 and the bond angles in Table 7. The coordination geometry around Co(III) is a distorted octahedral with the acacen ligand occupying the four equatorial positions. The acacen ring in

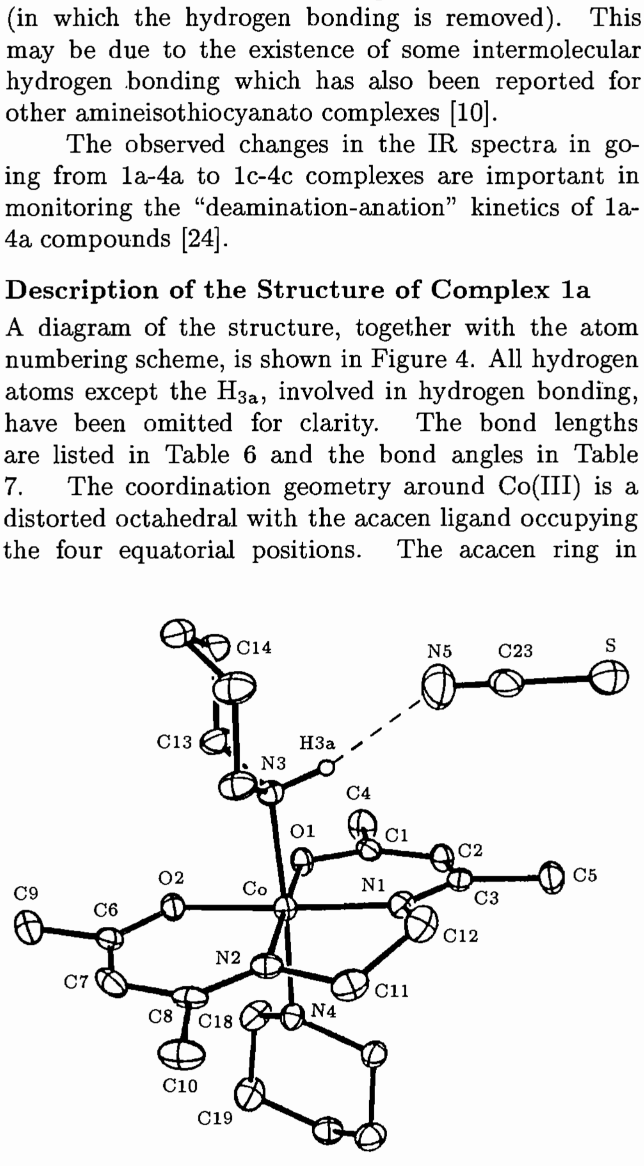

Figure 4. Perspective view of 1a showing the atom-labeling scheme and 50% thermal ellipsoids.

Table 6. Bond lengths (Å).

Co - O(1)	1.900(2)	Co - O(2)	1.894(2)
Co - N(1)	1.905(2)	Co - N(2)	1.899(2)
Co - N(3)	2.034(2)	Co - N(4)	2.050(2)
O(1) - C(1)	1.292(3)	O(2) - C(6)	1.293(3)
N(1) - C(3)	1.308(3)	N(1) - C(12)	1.471(3)
N(2) - C(8)	1.308(3)	N(2) - C(11)	1.473(3)
N(3) - C(13)	1.490(3)	N(3) - C(17)	1.493(3)
N(4) - C(18)	1.491(3)	N(4) - C(22)	1.498(3)
C(1) - C(2)	1.373(4)	C(1) - C(4)	1.504(4)
C(2) - C(3)	1.414(4)	C(3) - C(5)	1.507(4)
C(6) - C(7)	1.375(4)	C(6) - C(9)	1.509(4)
C(7) - C(8)	1.420(4)	C(8) - C(10)	1.509(4)
C(11) - C(12)	1.512(4)	C(13) - C(14)	1.528(4)
C(14) - C(15)	1.528(4)	C(15) - C(16)	1.523(4)
C(16) - C(17)	1.525(4)	C(18) - C(19)	1.525(4)
C(19) - C(20)	1.516(4)	C(20) - C(21)	1.521(4)
C(21) - C(22)	1.522(4)	S - C(23)	1.644(3)
N(5) - C(23)	1.161(4)		

terms of bond distances is symmetric within the limits of experimental error. The ligand-cobalt-ligand bond angles in the equatorial plane consists of two angles which are larger than 90° (N-Co-O) and two smaller than 90° (O-Co-O and N-Co-N). The five-membered chelation ring is twisted and all the six-membered chelation rings are folded along the O...N line, albeit to different extents, and the two N_2O_2 cores exhibit slight twisting. The two axial positions are occupied by two pprdn ligands having chair conformation.

The most interesting structural feature is related to the hydrogen bond, formed between the thiocyanate group and a hydrogen atom from one of the coordinated pprdn ligands (Table 8). As in the typical hydrogen bonding situations, the H_{3a} atom is attached to N(3) by a short "normal" covalent bond (N(3)-H_{3a} 0.96 Å) and to N(5) by a longer, weaker "hydrogen bond" (H_{3a}...N(5), 2.15 Å). The N(3)...N(5) distance is calculated to be 3.09 Å. These values are within the observed range for typical N_a-H...N_b hydrogen bond distances (H...N_b, 2.20 Å and N_a...N_b, 3.10 Å) [25,26]. The H_{3a}...N(5) distance, 2.15 Å, is shorter by 0.60 Å than the sum of the van der Waals radii of hydrogen (1.20 Å) and nitrogen (1.55 Å). These results along with IR and ^{1}H NMR spectral data confirm the existence of

Table 7. Bond angles (°).

O(1) - Co - O(2)	84.6(1)	O(1) - Co - N(1)	94.1(1)
O(2) - Co - N(1)	177.5(1)	O(1) - Co - N(2)	177.2(1)
O(2) - Co - N(2)	95.2(1)	N(1) - Co - N(2)	86.2(1)
O(1) - Co - N(3)	89.4(1)	O(2) - Co - N(3)	88.9(1)
N(1) - Co - N(3)	89.0(1)	N(2) - Co - N(3)	93.4(1)
O(1) - Co - N(4)	89.8(1)	O(2) - Co - N(4)	87.7(1)
N(1) - Co - N(4)	94.4(1)	N(2) - Co - N(4)	87.3(1)
N(3) - Co - N(4)	176.5(1)	Co - O(1) - C(1)	125.1(2)
Co - O(2) - C(6)	124.8(2)	Co - N(1) - C(3)	126.6(2)
Co - N(1) - C(12)	112.2(1)	C(3) - N(1) - C(12)	120.6(2)
Co - N(2) - C(8)	125.8(2)	Co - N(2) - C(11)	114.0(1)
C(8) - N(2) - C(11)	119.9(2)	Co - N(3) - C(13)	113.3(2)
Co - N(3) - C(17)	116.0(2)	C(13) - N(3) - C(17)	108.7(2)
Co - N(4) - C(18)	113.4(2)	Co - N(4) - C(22)	117.6(2)
C(18) - N(4) - C(22)	109.3(2)	O(1) - C(1) - C(2)	125.6(2)
O(1) - C(1) - C(4)	114.4(2)	C(2) - C(1) - C(4)	120.0(2)
C(1) - C(2) - C(3)	125.3(2)	N(1) - C(3) - C(2)	122.3(2)
N(1) - C(3) - C(5)	120.6(2)	C(2) - C(3) - C(5)	117.1(2)
O(2) - C(6) - C(7)	125.8(2)	O(2) - C(6) - C(9)	113.4(2)
C(7) - C(6) - C(9)	120.7(2)	C(6) - C(7) - C(8)	125.4(2)
N(2) - C(8) - C(7)	122.7(2)	N(2) - C(8) - C(10)	120.0(2)
C(7) - C(8) - C(10)	117.3(2)	N(2) - C(11) - C(12)	109.1(2)
N(1) - C(12) - C(11)	109.7(2)	N(3) - C(13) - C(14)	112.9(2)
C(13) - C(14) - C(15)	110.5(2)	C(14) - C(15) - C(16)	109.2(2)
C(15) - C(16) - C(17)	111.1(2)	N(3) - C(17) - C(16)	113.1(2)
N(4) - C(18) - C(19)	112.5(2)	C(18) - C(19) - C(20)	110.7(2)
C(19) - C(20) - C(21)	109.7(2)	C(20) - C(21) - C(22)	112.2(2)
N(4) - C(22) - C(21)	113.5(2)	S - C(23) - N(5)	179.0(3)

Table 8. N-H...N bond lengths and angles.

Bond Lengths(Å)	
H(3A)-N(3)	0.960
H(3A)...N(5)	2.147
Bond Angle(o)	
N(3)-H(3A)...N(5)	167.1

Co-N-H...NCS interaction in 1a-4a complexes. The N-H...N bond is, like the X-H...Y hydrogen bonds (X= O, N, C and Y= O, N, S) [23, 25–27], a largely electrostatic, attractive interaction which affects the spectroscopic properties and crystal formation of the four complexes. In addition to its effect on the shape and the frequency of the IR bands (Table 5), it appears that this hydrogen bond interaction contributes to the easier crystal formation of 1a-4a complexes relative to 1b-4b and 1c-4c.

CONCLUSION

The results on the synthesis and characterization of trans-[Co(acacen)XY]$^{n+}$ indicate that the nature of the product depends on the nature of the amine ligand used, the solvent and the stoichiometry of the reaction.

The most novel structural feature of 1a-4a complexes is the existence of the N-H...NCS hydrogen bond between the coordinated amine and the uncoordinated NCS anion in the crystal lattice. The structural data along with the spectroscopic evidence support the existence of Co-N-H...NCS interaction in these complexes. To the best of our knowledge, these are the first piperidine, benzylamine, morpholine and pyrrolidine Co(III) complexes in which NCS appears with such a mode of interaction.

The deamination-anation reactions of 1a-4a complexes in solid state [24] as well as the existence of N-H....NCS hydrogen bonds in other related complexes with suitable amines along with the electrochemistry and photochemical behavior of 1c-4c complexes are currently being investigated, in an attempt to expand the exciting chemistry of thiocyanate.

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SUPPLEMENTARY MATERIAL AVAILABLE

Tables of all bond lengths, bond angles, anisotropic thermal parameters, hydrogen atom positions and data collection parameters for trans-[Co(acacen)(pipy)$_2$].NCS (10 pages) as well as listing of observed and calculated structure factors (21 pages) are available from M.A. on request.

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