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PERFLUOROALKYL DERIVATIVES OF CHROMIUM AND COBALT CONTAINING SULPHUR DONOR LIGANDS

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Summary

Perfluoroalkyl derivatives of chromium(III) have been prepared containing dithiocarbamate ligands, e.g. $R_fCr(DTC)_2py$. The complexes have a *cis* arrangement of pyridine and R_f groups as determined by the X-ray crystal structure determination of $C_3F_7Cr(Me_2NCS_2)_2py$. An analogous cobalt(III) complex $C_3F_7Co(Et_2NCS_2)_2py$ has also been prepared in small yield and ^{19}F NMR measurements indicate a similar structure.

Introduction

Organometallic compounds of cobalt(III) have received much attention in recent years, particularly those compounds containing various coordinating chelate ligands in addition to the organo group [1]. Chelate ligands providing N_4 (dioximines, porphyrins) and O_2N_2 (salicylaldimines, betaketodiimines, etc.) donor groupings have predominated. The synthesis of a variety of such molecules containing S atoms as part of the donor grouping has not yet been readily achieved although a perfluoroalkylcobalt(III) [2] derivative of *N,N'*-ethylenebis(thioacetylacetonediimine) has been prepared in relatively low yield by one of the conventional routes.

The observation that sulphur coordination appears to weaken the Co—C bond in compounds of the Vitamin B_{12} class [3,4] indicates that there would be considerable interest in the properties of a wider variety of organometallic compounds containing sulphur donor ligands.

The preparation of perfluoroalkylchromium(III) [5] derivatives containing a variety of chelating groups has provided a suitable route for achieving the synthesis of derivatives of that metal with the sulphur bonding dithiocarbamate ligands. A related CoR_f derivative has also been obtained by a similar reaction.

Results

Perfluoroalkylchromium derivatives

$CrCl_2(CH_3CN)_2$ reacts readily with R_fI to form a mixture of acetonitrile solvated $CrCl_2R_f$ and $CrCl_xI_{3-x}$ species [5]. Reaction of this mixture with suitable dithiocarbamate ligands (as sodium salts) in the presence of pyridine brought about the rapid formation of a mixture of $R_fCr(DTC)_2py$ and $Cr(DTC)_3$ which were separated by fractional crystallisation.

The complexes (Table 1) are all dark-brown crystalline compounds, the colour lightening somewhat as the alkyl group on the dithiocarbamate increases in size. They are reasonably soluble in a variety of solvents giving air stable solutions but slow decomposition occurs when the solutions are exposed to direct sunlight. Decomposition has also been observed when solutions of the compounds are passed through columns of various chromatographic materials such as alumina, florisil or silica.

The IR spectra of the compounds all show the expected strong C—F absorptions in the 1400—1000 cm^{-1} region together with the characteristic 'thioureide' band in the region 1480—1590 cm^{-1}. Each compound also showed two characteristic bands in the regions of 570 nm and 450 nm with extinction coefficients comparable to those of the 645 nm and 490 nm bands of tris(diethyldithiocarbamate)chromium(III) [6,7] which were assigned to the *d—d* transitions $^4A_{2g} \rightarrow {}^4T_{2g}$ (570 nm) and $^4A_{2g} \rightarrow {}^4T_{1g}$ (450 nm).

NMR measurements

The ^1H NMR spectrum of $C_3F_7Cr(Et_2NCS_2)_2py$ shows very wide bands but data were obtainable for the *N*-CH_2 protons which exhibited very large chemical shifts and for CH_3 protons. Comparable spectra have been reported [8] for $Cr(Et_2NCS_2)_3$. The spectrum of the organometallic compound shows a doublet

TABLE 1

ANALYTICAL DATA FOR PERFLUOROALKYLCHROMIUM(III)DITHIOCARBAMATE COMPOUNDS

Complex	Stoichiometry	Analysis found (calc.)				
		C	H	N	S	F
$C_2F_5Cr(Et_2NCS_2)_2py$	$C_{17}H_{25}CrF_5N_3S_4$	37.3 (37.4)	4.4 (4.6)	7.5 (7.7)		17.7 (17.4)
$C_3F_7Cr(Me_2NCS_2)_2py$	$C_{14}H_{17}CrF_7N_3S_4$	31.2 (31.1)	3.2 (3.2)	7.5 (7.8)	23.9 (23.7)	
$C_3F_7Cr(Et_2NCS_2)_2py$	$C_{18}H_{25}CrF_7N_3S_4$	36.2 (36.2)	4.4 (4.2)	7.0 (7.0)	21.6 (21.5)	
$C_3F_7Cr(i\text{-}Pr_2NCS_2)_2py$	$C_{22}H_{33}CrF_7N_3S_4$	40.4 (40.6)	5.2 (5.1)	6.1 (6.4)		20.2 (20.4)
$C_3F_7Cr(Bz_2NCS_2)_2py$	$C_{38}H_{33}CrF_7N_3S_4$	54.8 53.3 (54.0)	4.1 3.9 (3.9)	5.1 (5.0)		15.7 (15.5)
$C_4F_9Cr(Et_2NCS_2)_2py$	$C_{19}H_{25}CrF_9N_3S_4$	35.2 (35.3)	3.8 (3.9)	6.2 (6.5)		26.5 (26.4)
$C_3F_7Cr(Et_2NCS_2)_2$-cyclohexylamine	$C_{19}H_{33}CrF_7N_3S_4$	37.0 (37.1)	5.4 (5.3)	6.8 (6.9)		

TABLE 2

MAGNETIC MOMENT VALUES FOR SEVERAL OF THE COMPOUNDS

	μ_{eff} (BM) (293 K)
$C_3F_7Cr(Et_2NCS_2)_2py$	4.02
$C_4F_9Cr(Et_2NCS_2)_2py$	4.12
$C_3F_7Cr(Me_2NCS_2)_2py$	4.3

for the CH_2 protons as appears in the spectrum of the tris complex as distinct from the iron(III) and manganese(III) tris(diethyldithiocarbamates) where only one peak is observed [8]. Golding et al. [8] has offered an explanation for this effect in the CrS_6 compounds in terms of the existence of enantiomers having high energy barriers to interconversion so that differences between the environments of the CH_2 protons exist due to the asymmetry of the complex. It has been established by an X-ray diffraction study (see below) that $C_3F_7Cr(Et_2NCS_2)_2py$ has a *cis*-type arrangement of the C_3F_7 and py groups so that the non-equivalence of CH_2's may be explained in an alternative fashion in the present case.

The spectrum of the complex when run at 347 K displays a general upfield shift and sharpening of the peaks. The shift is believed to result from an increase in electron spin relaxation.

The ^{19}F NMR of $C_4F_9Cr(Et_2NCS_2)_2py$ shows only two distinguishable peaks at −83 and −128 ppm (from $CFCl_3$). They have been tentatively assigned to the δ-CF_3 and γ-CF_2 groups respectively assuming that paramagnetic broadening should be least for these two further groups. The ^{19}F spectra of R_f—Co—Schiff base derivatives [9] would indicate that the allocation of bands would be as above.

Magnetic moments

The values for several of the compounds are shown in Table 2. In each case the moment is greater than the spin only value for a d^3 ion. This increase in moment has been observed in perfluoroalkylchromium(III)salicylaldimine [5] complexes, $(Cr(salen)L_2)^+$ derivatives [10], and for a number of other organometallic chromium(III) compounds [11,12]. An explanation for the observations has been suggested [5].

The structure of $C_3F_7Cr(Me_2NCS_2)_2py$

The structure of $C_3F_7Cr(Me_2NCS_2)_2py$ has been established by a single crystal X-ray diffraction study *. The heptafluoropropyl and pyridine groups are arranged *cis* to each other in the molecule and there is a significant elongation of the Cr—S bond in the position *trans* to the C_3F_7 group (Cr—S, 2.457 Å) compared to the other three Cr—S linkages (av. Cr—S, 2.392 Å). This "*trans* influence" has been noted in the structures of other Cr organometallic compounds viz. dichloro-*p*-tolyl-tris(tetrahydrofuran)chromium(III) [13] and the

* The structural investigation has been carried out by Dr. Marcia Scudder. Full details will be published in a subsequent paper.

bis(phenyl) and bis(2-methoxyphenyl)-bis(2,2'-bipyridyl)chromium(III) iodide [14]. The latter compound also has a *cis* arrangement of the organo groups which it is believed is encouraged by the considerable steric interference that might otherwise exist between the 6 and 6' hydrogens of neighbouring planarly coordinated bipyridyl molecules which would exist if the methoxyphenyl groups were in a *trans* configuration.

In the case of the present molecule there would not appear to be any steric reason why two dithiocarbamate anions should not adopt a planar arrangement about chromium(III) thus allowing a possible *trans* positioning of pyridine and C_3F_7. Indeed such a planar arrangement is known to exist in bis(diisopropyldithiocarbamate)nickel(II) [15]. There has however so far been no evidence from TLC examination of samples of the Cr compound or of other related compounds prepared in this work that two forms of the complexes exist. A *trans* type arrangement of the organo group and a pyridine molecule does occur in C_3F_7Cr(salen)py * where the tetradentate salen ligand clearly favours coordition in a plane [16].

The remaining structural parameters are very similar to those reported for other metal dithiocarbamates eq. the average C—S bond length of 1.72 Å in this complex is similar to that in $(n\text{-}Pr_2NCS_2)_2Ni$ [17], $(Me_2NCS_2)_2Zn \cdot py$ [18] and $(Et_2NCS_2)Na \cdot 3H_2O$ [19], and only slightly greater than those in $(n\text{-}Bu_2NCS_2)_3Fe$ [20] or $(Et_2NCS_2)_3Co$ [21,22]. The average N—C(S_2) length 1.38 Å is indicative of considerable double bond character and this too is a common feature with other dithiocarbamates.

Chemical properties

The general chemical behaviour of this group of compounds has been examined using $C_3F_7Cr(Et_2NCS_2)_2py$ as a test compound.

Refluxing the complex in aqueous ethanol for 24 h causes decomposition yielding the $C_3F_7Cr(H_2O)_5)^{2+}$ cation which becomes visible by formation of a pink solution showing the characteristic absorptions of perfluoroalkylpentaquochromium(III) cations at 523 and 390 mm [30].

The coordinated pyridine molecule is not lost on warming the complex in vacuo to 110°C while general decomposition begins at about 130—140°C.

The ligand was slowly replaced by the stronger base cyclohexylamine in benzene solution to yield $C_3F_7Cr(Et_2NCS_2)_2 \cdot C_6H_{11}NH_2$. The reaction of triethylamine however did not lead to isolation of the corresponding NEt_3 complex. Indeed the cyclohexylamine-containing complex can be readily synthesised by using the amine in place of pyridine in the preparation whereas the addition of NEt_3 at that stage caused loss of the organometallic intermediate and only $Cr(Et_2NCS)_3$ was isolated.

The C_3F_7 group could also be displaced by reaction of the complex with further $NaEt_2DTC$ when $Cr(Et_2NCS_2)_3$ was obtained in high yield.

Carbon monoxide did not react with $C_3F_7Cr(Et_2NCS_2)_2py$ in benzene solution at room temperature whereas sulphur dioxide brought about decomposition and partial conversion to the tris complex $Cr(Et_2NCS_2)_3$.

* Salen = anion of *N,N'*-ethylenebis(salicylaldimine)

Alkylchromium derivatives

A number of unsuccessful attempts have been made to prepare alkylchromium dithiocarbamate complexes. Direct reaction of alkyl halides with $CrCl_2(CH_3CN)_2$ to yield alkylchromium(III) halide species does not occur so that the analogous route to that used to prepare the perfluoroalkyl compounds was not open.

Acetylchloride or trifluoroacetylchloride does react with $CrCl_2(CH_3CN)_2$, however the products further reacted with $Na(Et_2NCS_2)$ to give $Cr(Et_2NCS_2)_3$ together with a compound whose analysis corresponds to $CrCl_2py_2(Et_2NCS_2)$ and an acylchromium(III) compound was not detected. The complex [23] believed to be chromium(II) $(Et_2NCS_2)_2$ was allowed to react with $CH_3Co(salen)H_2O$ in an attempt to obtain a methyl group transfer, as occurs between many cobalt(II)/cobalt(III) compounds [24] and between chromium(II)/cobalt(III) systems [25]. The products $Cr(Et_2NCS_2)_3$ and $Co(Et_2NCS_2)_3$ were detected but no evidence for $CH_3Cr(Et_2NCS_2)_2H_2O$ was found. Similar results attended the reaction of $CH_3Co(dmg)_2H_2O$ * with the chromium(II) complex. Espenson and Shveima [25] have shown that essentially quantitative transfer of an alkyl group occurs between $RCo(dmg)_2H_2O$ and chromium(II) in aqueous solution so that the observations of formation of the tris(dithiocarbamate)- chromium-(III) and cobalt(III) is unexpected.

The direct reaction of $Na(Et_2NCS_2)$ with $C_6H_5CH_2CrCl_2(THF)_3$ [11] was also attempted but the major yield was of $Cr(Et_2NCS_2)_3$ suggesting that the benzyl group can be readily removed by a strong coordinating group such as a dithiocarbamate.

Effort is still being directed towards finding a satisfactory synthetic route for the synthesis of alkylchromium derivatives containing chelating ligands.

Perfluoroalkylcobalt(III)dithiocarbamates

A number of cobalt(II) complexes have been found to react with organic halides to form organometallic cobalt(III) derivatives [26]. In view of the pronounced ease of oxidation of cobalt(II) → cobalt(III) in the presence of dithiocarbamate ligands attemps have been made to prepare cobalt(III) organometallics by reaction of organic halides with cobalt(II) species in the presence of two equivalents of a dithiocarbamate ligand. Only in the case of the reactions of perfluoroalkyl iodides have organometallic compounds been formed in detectable yields in addition to the tris(dithiocarbamate)cobalt(III) complex which is the major reaction product under most reaction conditions examined.

Well authenticated cobalt(II) dithiocarbamate complexes do not appear to exist, with the possible exception of bis(diethyldithiocarbamate)*o*-phenanthrolinecobalt(II) reported by Holah and Murphy [27]. This complex is either unreactive towards alkyl- or perfluoroalkyl- iodides or is converted to the cobalt-(III)tris(dithiocarbamate) complex. The species described recently as a cobalt-(II)piperidinedithiocarbamate [28] derivative has been shown to be a mixture of the tris-cobalt(III) derivative and either cobalt(II) acetate or a hydroxyacetate, the latter component being responsible for the reported paramagnetism.

The mechanism of oxidation of cobalt(II) in the presence of dithiocarbamate

* dmg = anion of dimethylglyoxime

ligands has not been examined but the present results suggest that one possible route may involve a disproportionation reaction of the form

$$2Co^{II}(DTC)_2 \rightarrow [Co^{III}(DTC)_2]^+ + [Co^{I}(DTC)_2]^-$$

The cobalt(III) species could attach a third dithiocarbamate ligand to give $Co(DTC)_3$ while the cobalt(I) species could react with an organic halide as do many other cobalt(I) species to give either an $RCo(DTC)_2$ product or to reform cobalt(II) $(DTC)_2$. Cobalt(II) products have been observed in unsuccessful attempts to prepare organocobalt(III) derivatives from the reaction * of [cobalt(I)mben]$^-$ [22] or [cobalt(I)amben]$^-$ [29] with alkyl or perfluoroalkyl halides. [cobalt(I)sacacen]$^-$ does yield a small amount of a perfluoroalkylcobalt(III) complex [2] together with a major yield of the original cobalt(II) complex.

The compound $C_3F_7Co(Et_2NCS_2)_2py$ has been obtained in low yield from the reaction of C_3F_7I with $CoCl_2py_2$ in the presence of $(Et_2NCS_2)^-$. It is reasonably stable to light in the solid state as are other perfluoroalkylcobalt(III) derivatives but shows loss of the R_f group on continued refluxing in 50% aqueous alcohol for some hours. $Co(Et_2NCS_2)_3$ is formed in the reaction.

The ^{19}F NMR spectrum of the complex shows a triplet at δ 79.34 ppm (J = 12.8 Hz) which is due to the γ-CF_3 group. A further group of resonances centred at δ 120.8 is poorly resolved but could be a doublet from an AB pattern due to splitting of the β-CF_2 group by the α-CF_2. The ABX_3 pattern centred at δ 94.8 ($^2J_{FF}$ = 260 Hz) is considered to arise because of non-equivalence of two α fluorines which can each cause splitting of the peaks due to each other, giving rise to two sets of doublets. The separation between the two "inner" peaks of the doublet is 238 Hz.

The values for these assignments are essentially similar to those found in other C_3F_7cobalt(III) derivatives [9].

The non-equivalence of two fluorines is evidence in favour of a *cis* type arrangement of C_3F_7 and pyridine. If the arrangement were *trans* with the dithiocarbamate groups occupying equatorial co-ordinating sites then the fluorine atoms should be in equivalent environments. The arrangement of groups is thus analogous to that determined for the Cr complex by direct structural analysis.

There were three further small unresolved peaks observed in the ^{19}F spectrum (80.8, 88.0, 125.5 ppm) which might indicate the presence of the '*trans*' isomer. Heating a sample dissolved in d^5-pyridine at 70°C failed to bring about any shift in the relative intensities of the '*cis*' and possible '*trans*' peaks.

Experimental

Preparation of $R_fCr(DTC)_2py$ compounds

In a typical experiment $CrCl_2(CH_3CN)_2$ (2.04 g, 0.01 mol) was suspended in a mixture of acetonitrile (80 ml) and ethanol (15 ml) through which nitrogen was passed to remove oxygen. Excess perfluoralkyl iodide (2 ml) was then added and the mixture rapidly changed colour to brown-green as the solid dissolv-

* mben = dianion of *N,N'*-ethylenebis(*o*-mercaptobenzaldimine); amben = dianion of *N,N'*-ethylenebis(*o*-aminobenzaldimine); sacacen = dianion of *N,N'*-ethylene bis(thioacetylacetonimine).

ed. The solution was stirred for 30 min and then was introduced the appropriate sodium dithiocarbamate (0.025 mol) dissolved in deaerated ethanol. After stirring for a further 30 min the solvent was removed and the residue redissolved in the minimum amount of warm 10% pyridine-ethanol and the solution filtered. The filtrate was allowed to evaporate slowly and the blue tris(dithiocarbamate)chromium(III) which precipitated, removed. The perfluoro-organometallic eventually crystallized after the major part of the tris complex had been recovered. The product was recrystallized from ethanol containing a small amount of pyridine to yield brown crystals of the organometallic compound. Yields ranged from 10—30%.

A cyclohexylamine derivative

(1) An excess of cyclohexylamine (2 ml) was added to a benzene solution of $C_3F_7Cr(Et_2NCS_2)_2py$. The solution was stirred for 12 h then evaporated to dryness. The residue was washed with ethanol to remove unreacted pyridinate then recrystallized from a 50% ethanol/benzene solution as red needles. (2) The compound was most easily prepared by addition of cyclohexylamine instead of pyridine in the normal preparation.

Light sensitivity

$C_3F_7Cr(Et_2NCS_2)_2py$ was dissolved in ethanol (8×10^{-3} *M*) and the solution placed in a quartz vessel exposed to direct sunlight. The visible spectrum of the sample was compared at intervals with that of a freshly prepared solution. Complete decomposition had occurred after about 10 h exposure.

Chemical reactions of $C_3F_7Cr(Et_2NCS)_2py$

Water: A solution of the complex (8×10^{-3} *M*) in a 1 : 1 ethanol/water mixture was refluxed. The colour of the solution slowly became bright pink over 24 h and the spectrum of the resulting solution showed the peaks at 523 and 390 nm which are typical [30] for perfluoroalkylchromium pentaquo complexes.

Excess dithiocarbamate: To a solution of complex (0.33×10^{-3} *M*) in ethanol was added excess $Na(Et_2NCS_2)$ (1×10^{-3} *M*) and the mixture stirred for 12 h. The product was $Cr(Et_2NCS_2)_3$. Yield 100%.

SO_2: The solid complex was allowed to stand for 48 h in contact with liquid SO_2 at 20°C in a sealed reaction vessel. Eventually the SO_2 was removed and the residue extracted with pyridine containing 10% ethanol. $Cr(Et_2NCS_2)_3$ was the major product detected. No evidence for unreacted $C_3F_7Cr(Et_2NCS_2)_2py$ was found.

CO: The organometallic was recovered unchanged after CO was bubbled through a solution of the complex in benzene for 48 h at 20°C.

Attempted syntheses of alkyl and aryl derivatives

(1) Alkyl transfer: $Cr(Et_2NCS_2)_2$ prepared by the method of Fackler and Holah [23] was suspended in deaerated ethanol and to this was added an equivalent amount of either $MeCo(dmg)_2H_2O$, $MeCo(salen)H_2O$ or $C_3F_7Co(salen)$-H_2O dissolved in ethanol. The mixture was examined by TLC for evidence of a new organometallic species. In each case both $Co(Et_2NCS_2)_3$ and $Cr(Et_2$-

$NCS_2)_3$ were detected together with the unreacted organometallic starting compound but no new organometallic species. (2) A mixture of $C_6H_5CH_2Cl_2Cr$-(THF)3 [11] (20 mmol) and sodium diethyldithiocarbamate (9 g, 40 mmol) in tetrahydrofuran was stirred at room temperature for 3 h. $Cr(Et_2NCS_2)_3$ was precipitated in high yield. (3) $CrCl_2(CH_3CN)_3$ (3 g, 14.6 mmol) reacted with acetyl chloride (2 ml, 28 mmol) in acetonitrile. Over a period of 12 h the $CrCl_2$-$(CH_3CN)_3$ dissolved to give a light purple solution. Sodium diethyldithiocarbamate (8.2 g, 36.5 mmol) dissolved in ethanol was added and the mixture stirred for 1 h. The solvent was then removed and the residue extracted with ethanol leaving the bulk of the $Cr(Et_2NCS_2)_3$ undissolved. Pyridine was added to the filtrate until fumes were no longer evolved then the solution allowed to crystallize giving light green crystals. (Found: C, 42.0; H, 4.5; Cl, 16.9; S, 15.0. $C_{15}H_{20}N_3Cl_2S_2Cr$ calc.: C, 42.1; H, 4.7; Cl, 16.6; S, 14.9%) IR spectrum: 1606s, 1507vs, 1475m, 1442vs, 1379s, 1357m, 1301w, 1279s, 1217m, 1207m, 1151m, 1094w, 1076(sh), 1068s, 1047m, 1018m, 999w, 917w, 850w, 770vs, 723w, 698vs, 645s.

$C_3F_7Co(Et_2NCS_2)_2py$

Cobalt acetate $4H_2O$ (2.49 g, 10 mmol) was dissolved in methanol (50 ml) and pyridine (1.6 ml, 20 mmol). A slight excess of heptafluoro-n-propyliodide (1.5 ml, 12 mmol) was added followed as rapidly as possible by sodium diethyldithiocarbamate (4.53 g, 20 mmol) in methanol (50 ml). The whole operation was conducted with nitrogen passing through the solution.

The immediate precipitate of green $Co(Et_2NCS_2)_3$ (95% based on dithiocarbamate used) which appeared was filtered and water added dropwise with stirring to the filtrate (1 ml) to remove further tris derivative. The green-brown solution was allowed to evaporate to yield a mixture of the organometallic compound and tris(dithiocarbamate) complex. The complex was purified by repeated fractional crystallization from benzene. Yield circa 5% based on dithiocarbamate.

Thin layer chromatography was useful in testing for the presence of $Co(Et_2NCS_2)_3$ and $C_3F_7Co(Et_2NCS_2)_2py$. Using alumina as the absorbent and benzene as eluant green $(CoEt_2NCS_2)_3$ appeared just ahead of the brown organometallic spot as the solvent advanced. Found: C, 36.0; H, 4.23; F, 21.7; N, 7.03; S, 21.0. $C_{18}H_{25}F_7N_3S_4Co$ calc.: C, 35.8; H, 4.18; F, 22.0; N, 6.96; S, 21.3%) IR spectrum: 1613w, 1495s, 1318s, 1300m, 1270vs, 1223s, 1210vs, 1185s, 1150s, 1090m, 1072s, 1040m, 1012m, 1007m, 985s, 906m, 845m, 790s, 775w, 764sm, 698s, 673s. ^1H NMR spectrum: δ 1.3 (multiplet); 3.8 (multiplet); 7.0—7.6 ppm (multiplet). UV visible spectrum: Absorption bands appeared at 17.100 cm^{-1} (η = 360), 21.300 (η = 620), 28.600 (η = 14.500), 31250 (η = 28.300).

Constitution of "bis(piperidyldithiocarbamate)" [28]

Cobalt acetate $4H_2O$ (1.25 g, 5 mmol) was reacted with sodium piperidyldithiocarbamate dihydrate (2.19 g, 10 mmol) in ethanol. The immediate green precipitate was filtered, washed with water, dried and recrystallized from benzene. This procedure left a pink residue, insoluble in benzene. Crude product before recrystallization: Found: C, 34.2; H, 4.90; N, 5.85. $C_{12}H_{20}N_2S_4Co$ calc.:

C, 38.0; H, 5.31; N, 7.38% $C_{18}H_{30}N_3S_6Co$ calc.: C, 40.1; H, 5.60; N, 7.78%. After one recrystallization: Found: C, 39.9; H, 5.60; N, 7.10%. The magnetic moment of the crude complex was 2.8 BM calculated as $Co(pipNCS_2)_2$. After one recrystallization the moment was 0.6 BM calculated as $Co(pipNCS_2)_3$.

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