

## Preparation, spectra, and fluxional behaviour of cyclopentadienylcobalt(III) complexes with dithiocarbamate and xanthate ligands. The crystal structure of $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\text{S}_2\text{CNEt}_2)]$

E. Patricia Cullen, John Doherty, A.R. Manning\*,

*Department of Chemistry, University College, Belfield, Dublin 4 (Ireland)*

Patrick McArdle\* and Desmond Cunningham

*Department of Chemistry, University College, Galway (Ireland)*

(Received December 14th, 1987)

### Abstract

The reactions of  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$  with thiuram disulphides,  $[(\text{R}_2\text{NCS}_2)_2]$ , give  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{CNR}_2)_2]$ , but it is better to use  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\eta^2\text{-S}_2\text{CNR}_2)]$  (I),  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\eta^2\text{-S}_2\text{COR})]$  (II), and their  $\text{C}_5\text{H}_4\text{Me}$  analogues, as precursors for  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\eta^1\text{-S}_2\text{CNR}_2)(\eta^2\text{-S}_2\text{CNR}_2)]$  (III),  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\eta^1\text{-S}_2\text{CNR}'_2)(\eta^2\text{-S}_2\text{CNR}'_2)]$  (IV),  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\eta^1\text{-S}_2\text{COR})(\eta^2\text{-S}_2\text{CNR}'_2)]$  (V), and  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\eta^1\text{-S}_2\text{COR})(\eta^2\text{-S}_2\text{COR}')]$  (VI) ( $\text{R}, \text{R}' = \text{Me}$  or  $\text{Et}$ ). The IR and  $^1\text{H}$  NMR spectra of I–VI are reported and assigned. They are consistent with structures that have pseudo-octahedral coordination about Co and planar  $\text{Co}(\eta^1\text{-S}\sim\text{S})$  and  $\text{Co}(\eta^2\text{-S}\sim\text{S})$  moieties where S–S are dithiocarbamate or xanthate ligands. The various fluxional processes undergone by these complexes have been investigated by dynamic  $^1\text{H}$  NMR spectroscopy. There is rotation about C– $\text{NEt}_2$  in  $\eta^2\text{-S}_2\text{CNEt}_2$  ligands and C– $\text{NR}_2$  in  $\eta^1$ -dithiocarbamate ligands which can be slowed at low temperatures for I, III, IV and V, but rotation about C–OEt is always fast for  $\eta^2\text{-S}_2\text{COEt}$  ligands in II and VI. Both III and IV undergo  $\eta^1\text{-}\eta^2$  ligand exchange but V and VI do not. In solution IV exists as a mixture of the two possible isomers with  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\eta^1\text{-S}_2\text{CNMe}_2)(\eta^2\text{-S}_2\text{CNEt}_2)]$  favoured at higher temperatures. An X-ray diffraction study confirms the pseudo-octahedral structure of  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\eta^2\text{-S}_2\text{CNEt}_2)]$  with its planar diethyldithiocarbamate ligand.

### Introduction

During investigations into the chemistry of complexes of the general type  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{L})(\text{S}\sim\text{S})]$  ( $\text{S}\sim\text{S}^- = 1,1\text{-dithiolate anion}$ ) it was found that  $[\text{Co}(\eta\text{-}$

$C_5H_5)(CO)_2]$  reacts with thiuram disulphides to give  $[Co(\eta-C_5H_5)(S_2CNR_2)_2]$  derivatives (R = Me or Et) which proved to be fluxional. We describe here this and a more rational route to these complexes involving reaction of  $[Co(\eta-C_5H_5)(I)(\eta^2-S_2CNR_2)]$  with  $Na[S_2CNR_2]$ , and extension of it to the preparation of other  $[Co(\eta-C_5H_5)(\eta^1-S\sim S)(\eta^2-S\sim S)']$  where  $S\sim S$ ,  $S\sim S' = S_2CNR_2$  or  $S_2COR$ . The infrared and  $^1H$  NMR spectra of these compounds and their  $[Co(\eta-C_5H_5)(I)(\eta^2-S\sim S)]$  precursors are reported, and assigned, and their fluxional behaviour discussed in detail. The structure of  $[Co(\eta-C_5H_5)(I)(S_2CNEt_2)]$  has been determined by an X-ray diffraction study.

Stephenson et al. used this route to prepare  $[Ru(\eta-C_6H_6)(\eta^1-S_2PR_2)(\eta^2-S_2CNR_2)]$ , a wide range of  $[Rh(\eta-C_5Me_5)(\eta^1-S\sim S)(\eta^2-S\sim S)']$  derivatives where  $(S\sim S)(S\sim S)' = (S_2CNR_2)_2$ ,  $(S_2COR)_2$ ,  $(S_2PR_2)_2$ ,  $(S_2CNMe_2)(S_2COMe)$ , and  $(S_2CNMe_2)(S_2PR_2)$  (R = Me, Et, or Ph), and  $[Ir(\eta-C_5Me_5)(S_2CNMe_2)_2]$ . They also investigated the  $^1H$  NMR spectra and fluxional behaviour of these complexes [1].

## Experimental

Previously published methods were used to prepare  $[Co(\eta-C_5H_5)(I)(S_2CNR_2)]$  [2] and  $Na[S_2COR]$  [3] (R = Me or Et). Other chemicals were purchased and used as received.

Unless otherwise stated, all reactions were carried out at room temperature under nitrogen. Ethanol was distilled under nitrogen before use; other solvents were dried by refluxing over calcium hydride and distilled before use. Tetrahydrofuran was further purified by distillation from sodium and benzophenone.

The  $^1H$  NMR spectra were run on a JEOL PFT 100 and JNM-GX 270 spectrometers.  $CDCl_3$ ,  $CD_2Cl_2$ ,  $CD_3C_6D_5$ , and  $CS_2/CD_2Cl_2$  were used as solvents with  $SiMe_4$  as the internal standard.

Infrared spectra were run on a Perkin-Elmer 283B spectrometer and calibrated with polystyrene [4].

Analyses were carried out in the Analytical Laboratory of University College, Dublin.

### *Preparation of $[Co(\eta-C_5H_5)(S_2CNR_2)_2]$*

A mixture of  $[Co(\eta-C_5H_5)(CO)_2]$  (4 mmol) and  $[(Me_2NCS_2)_2]$  (4mmol) in dichloromethane (50  $cm^3$ ) was stirred for 30 min. The dark solution was filtered, the solvent removed at reduced pressure, and the residues redissolved in dichloromethane (10  $cm^3$ ) and chromatographed on alumina. Dichloromethane eluted  $[Co(S_2CNMe_2)_3]$ , which was isolated by removal of the solvent at reduced pressure. Dichloromethane/ethanol (80/20) eluted a dark green compound, which was isolated by removal of the solvent at reduced pressure. Recrystallization of the residues from toluene gave  $[Co(\eta-C_5H_5)(S_2CNMe_2)_2]$  as deep purple crystals in 10% yield. This method was also used to prepare  $[Co(\eta-C_5H_4Me)(S_2CNMe_2)_2]$ .

Solutions of  $Na[S_2CNR_2] \cdot nH_2O$  (R = Me,  $n = 2$ ; or R = Et,  $n = 3$ ) (4 mmol) in ethanol (10  $cm^3$ ) were added dropwise to those of  $[Co(\eta-C_5H_5)(I)(S_2CNR_2)]$  (4 mmol) in dichloromethane (50  $cm^3$ ). The mixtures were stirred for 1 h. After removal of the solvents, the dark residues were dissolved in dichloromethane (10  $cm^3$ ) and the solutions filtered. The filtrates were then chromatographed on alumina and worked-up as above to give green  $[Co(S_2CNR_2)_3]$  and  $[Co(\eta-C_5H_5)(S_2CNR_2)_2]$

as deep purple crystals in yields of 40–60%. This method was also used to prepare  $[\text{Co}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{S}_2\text{CNR}_2)_2]$  and  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{CNMe}_2)(\text{S}_2\text{CNEt}_2)]$ . This last was obtained by both routes.

*Preparation of  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\text{S}_2\text{COR})]$*

Solutions of  $\text{Na}[\text{S}_2\text{COR}]$  ( $\text{R} = \text{Me}$  or  $\text{Et}$ ) (4 mmol) in ROH (10 cm<sup>3</sup>) were prepared in situ from NaOR and CS<sub>2</sub> [3] and added slowly to solutions of  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{I}_2]$  (4 mmol) in dichloromethane (40 cm<sup>3</sup>). After 1 h the solvents were removed from the dark green reaction mixtures to give brown oils. These decomposed during column chromatography, so they were dissolved in benzene and the sodium iodide was removed by filtration. Removal of the benzene and recrystallization of the residues from dichloromethane/pentane mixtures gave the  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\text{S}_2\text{COR})]$  as dark brown powders in yields of ca. 70%.

$[\text{Co}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{I})(\text{S}_2\text{COR})]$  ( $\text{R} = \text{Me}, \text{Et}$ ) were prepared similarly.

*Preparation of  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{CNR}_2)(\text{S}_2\text{COR}')$*

Solutions of  $\text{Na}[\text{S}_2\text{COR}']$  (4 mmol) in ROH (10 cm<sup>3</sup>;  $\text{R}' = \text{Me}$  or  $\text{Et}$ ; see above) were added slowly to solutions of  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\text{S}_2\text{CNR}_2)]$  (4 mmol;  $\text{R} = \text{Me}$  or  $\text{Et}$ ) in dichloromethane (40 cm<sup>3</sup>). After 30 min the dark brown solutions were filtered, the solvents removed at reduced pressures, and the residues extracted with benzene. The filtered extracts were evaporated to dryness at reduced pressures, and the residues crystallized from dichloromethane/pentane mixtures to give  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{CNR}_2)(\text{S}_2\text{COR}')] as brown powders in ca. 60% yield.$

The same compounds were obtained in similar yields from  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\text{S}_2\text{COR})]$  and  $\text{Na}[\text{S}_2\text{CNR}_2] \cdot n\text{H}_2\text{O}$

*Preparation of  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{COR})_2]$*

Solutions of  $\text{Na}[\text{S}_2\text{COR}]$  (4mmol) in ROH (10 cm<sup>3</sup>) were prepared in situ (see above) and added slowly to solutions of  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\text{S}_2\text{COR})]$  (4 mmol) in dichloromethane (10 cm<sup>3</sup>). After 10 min the reaction became dark brown. The solvents were removed at reduced pressure and the resultant tars dissolved in toluene (20 cm<sup>3</sup>). The filtered solutions were cooled to give  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{COR})_2]$  as dark brown powders in ca. 40% yields.

The compounds prepared are listed in Table 1, along with their melting points and analyses. Their infrared spectra are given in Table 2, and their <sup>1</sup>H NMR spectra in Table 3.

*X-ray crystal structure determination of  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\text{S}_2\text{CNEt}_2)]$*

$\text{C}_{10}\text{H}_{15}\text{NS}_2\text{CoI}$ ,  $M = 399.18$ , monoclinic,  $a$  9.892(2),  $b$  10.616(3),  $c$  13.163(3) Å,  $\beta$  97.41(2)°,  $U$  1370.75 Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calcd}}$  1.932 Mg m<sup>-3</sup>,  $F(000)$  780,  $\lambda(\text{Mo-K}\alpha)$  0.71069 Å, space group  $P2_1/c$ .

All intensity data were obtained as described by Ferguson et al. [5] on a Hilger and Watts Y290 diffractometer using a crystal with dimensions 0.25 × 0.25 × 0.40 mm. The data were collected by the  $\theta$ – $2\theta$  method within the range  $2 < \theta < 24^\circ$ , and were corrected for Lorentz and polarisation effects but not for absorption. A total of 1744 reflections with  $I > 3\sigma I$  were obtained. Unit cell parameters were determined by a least squares fit of  $\theta$  values between 12 and 20° measured on the diffractometer.

Table 1

Melting points and analyses of the compounds described in the text.

Compound <sup>a</sup>	M.p. (°C)	Analyses (Found (calcd.) (%))			
		C	H	N	S
Co(Cp)(I)(S <sub>2</sub> CNMe <sub>2</sub> )	dec.236	25.6 (25.8)	3.2 (2.9)	3.7 (3.7)	17.7 (17.2)
Co(Cp)(I)(S <sub>2</sub> CNEt <sub>2</sub> )	177–179	30.0 (30.0)	3.8 (3.7)	3.2 (3.5)	15.7 (16.0)
Co(Cp')(I)(S <sub>2</sub> CNMe <sub>2</sub> )	dec.172	27.7 (27.9)	3.6 (3.6)	3.3 (3.6)	16.4 (16.5)
Co(Cp')(I)(S <sub>2</sub> CNEt <sub>2</sub> )	dec.125	31.8 (31.8)	4.1 (4.3)	3.4 (3.3)	15.7 (15.4)
Co(Cp)(I)(S <sub>2</sub> COMe)	> 230	33.2 (23.4)	2.6 (2.2)		17.4 (17.8)
Co(Cp)(I)(S <sub>2</sub> COEt)	113–114	25.9 (25.8)	2.6 (2.2)		18.0 (17.2)
Co(Cp')(I)(S <sub>2</sub> COMe)	84–85	26.5 (25.8)	2.6 (2.6)		16.8 (17.2)
Co(Cp')(I)(S <sub>2</sub> COEt) <sup>b</sup>	66–68	27.3 (27.3)	2.8 (3.0)		15.1 (15.7)
Co(Cp)(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub>	> 230	35.8 (36.2)	4.6 (4.6)	7.4 (7.6)	34.8 (35.1)
Co(Cp)(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub>	> 230	42.9 (42.8)	6.1 (5.9)	6.5 (6.6)	30.0 (30.0)
Co(Cp')(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub>	102–106	38.1 (37.9)	5.0 (5.2)	7.3 (7.3)	33.5 (33.7)
Co(Cp')(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub>	74–76	43.6 (44.1)	6.1 (6.4)	6.3 (6.4)	29.7 (29.0)
Co(Cp)(S <sub>2</sub> CNMe <sub>2</sub> )(S <sub>2</sub> CNEt <sub>2</sub> )	dec.90	39.4 (39.7)	5.0 (5.3)	6.9 (7.1)	32.1 (32.6)
Co(Cp)(S <sub>2</sub> COMe)(S <sub>2</sub> CNMe <sub>2</sub> )	114–115	33.9 (34.2)	3.7 (3.9)	4.1 (3.9)	36.3 (36.4)
Co(Cp)(S <sub>2</sub> COEt)(S <sub>2</sub> CNMe <sub>2</sub> )	144–146	35.7 (36.1)	4.5 (4.3)	3.8 (3.8)	34.5 (35.0)
Co(Cp)(S <sub>2</sub> COMe)(S <sub>2</sub> CNEt <sub>2</sub> ) <sup>c</sup>	228–230	36.6 (37.1)	4.7 (4.8)	3.5 (3.6)	33.4 (33.0)
Co(Cp)(S <sub>2</sub> COEt)(S <sub>2</sub> CNEt <sub>2</sub> )	112–114	39.6 (39.7)	4.7 (5.0)	3.3 (3.5)	32.4 (32.5)
Co(Cp)(S <sub>2</sub> COMe) <sub>2</sub>	> 230	31.5 (31.9)	3.4 (3.2)		37.4 (37.8)
Co(Cp)(S <sub>2</sub> COEt) <sub>2</sub>	> 230	36.0 (36.0)	4.0 (4.0)		35.8 (35.0)

<sup>a</sup> Cp =  $\eta$ -C<sub>5</sub>H<sub>5</sub> and Cp' =  $\eta$ -C<sub>5</sub>H<sub>4</sub>Me. <sup>b</sup> +0.25 CH<sub>2</sub>Cl<sub>2</sub> confirmed by <sup>1</sup>H NMR spectroscopy. <sup>c</sup> +0.5 H<sub>2</sub>O.

The structure was solved by a combination of Patterson search and direct methods (SHELX86) [6] and refined by full matrix least squares procedures (SHELX76) [7]. All calculations were carried out on a VAX 11/785 computer using atomic scattering factors for hydrogen and non-hydrogen atoms and anomalous dispersion correction factors for non-hydrogen atoms taken from the literature [8,9,10]. All non-hydrogen atoms were refined anisotropically. The final *R* value was 0.0392 and *R<sub>w</sub>* was 0.0436. The final difference map showed a maximum electron density of 0.32 e/Å<sup>3</sup> and a minimum of -0.51 e/Å<sup>3</sup>.

Table 2  
Infrared spectra of the compounds (in KBr) described in the text

Compound <sup>a</sup>	Absorption bands <sup>b</sup> and assignments <sup>c</sup>				$\nu(\text{C-N})$
	$\nu(\text{Co-S})_s$	$\nu(\text{Co-S})_a$	$\nu(\text{C-S})_a$	$\nu(\text{C-S})_s$	
Co(Cp)(IX) <sub>2</sub> CNMe <sub>2</sub>	343	440	583	1055(m)	1532(s)
Co(Cp)(IX) <sub>2</sub> CNEt <sub>2</sub>	340	440	578	1055(m), 1062(m)	1512(s)
Co(Cp')X(S <sub>2</sub> CNMe <sub>2</sub> )	346	441	595	1050(m)	1538(s)
Co(Cp')X(S <sub>2</sub> CNEt <sub>2</sub> )	342	440	580	1060(m)	1501(s)
Co(Cp)(IX) <sub>2</sub> COMe				1029(m), 1111(m)	1246(s)
Co(Cp)(IX) <sub>2</sub> COEt	322	456	578	1032(m), 1120(m)	1242(s)
Co(Cp')X(S <sub>2</sub> COEt)				1025(m), 1119(m)	1241(s)
Co(Cp')X(S <sub>2</sub> COMe)				1036(m), 1109(m)	1248(s)
Co(Cp')X(S <sub>2</sub> COEt)				1048(m), 1120(m)*	1475(m)*1531(s)
Co(Cp)(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub>	342	441, 450*	560*575	1055(m), 1062(m), 1122(m)*	1508(m)*1518(s)
Co(Cp)(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub>			567*584	1046(m), 1122(m)*	1475(m)*1530(s)
Co(Cp')X(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub>	348	445, 455*	580(br)	1128(m)	1480(sh)*1510(s)
Co(Cp')X(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub>	352		560*578	1073(m), 1116(m)	1460(m)*1522(s)
Co(Cp)(S <sub>2</sub> CNMe <sub>2</sub> )X(S <sub>2</sub> CNEt <sub>2</sub> )	352	440, 450*	580(br)	1056(m), 1070(v), 1132(m), 1185(m)	1538(s)
Co(Cp)(S <sub>2</sub> COMe)(S <sub>2</sub> CNMe <sub>2</sub> )	353	443, 470*	568*, 583	1031(m), 1055(m), 1119(m)*1190(m)	1522(s)
Co(Cp)(S <sub>2</sub> COEt)(S <sub>2</sub> CNMe <sub>2</sub> )	342	440	582(br)	1043(br,m)1148(m), 1203(m)	1520(s)
Co(Cp)(S <sub>2</sub> COMe)(S <sub>2</sub> CNEt <sub>2</sub> )	345	420, 460*	568*585	1034(m), 1150(m), 1182(m)	
Co(Cp)(S <sub>2</sub> COEt)(S <sub>2</sub> CNEt <sub>2</sub> )				1034(m), 1109(m), 1122(sh), 1196(m)	
Co(Cp)(S <sub>2</sub> COMe) <sub>2</sub>				1030(m,br), 1090(m,br), 1112(m)	
Co(Cp)(S <sub>2</sub> COEt) <sub>2</sub>	322	410, 442	564, 588		1243(s)

<sup>a</sup> Cp =  $\eta^5\text{-C}_5\text{H}_5$  and Cp =  $\eta^5\text{-C}_5\text{H}_4\text{Me}$ . <sup>b</sup> Peak positions in  $\text{cm}^{-1}$  with relative peak heights in parentheses, m, medium; s, strong; br, broad; and all others weak. The asterisks indicate vibrations due to  $\eta^1$  ligands where these can be identified. <sup>c</sup> s symmetric vibration and a, antisymmetric vibration.

Table 3

<sup>1</sup>H NMR spectra of some of the complexes described in the text

Compound <sup>a</sup>	T (°C)	Resonance <sup>b,c</sup>				Cp
		$\eta^2$ -CH <sub>3</sub>	$\eta^1$ -CH <sub>3</sub>	$\eta^2$ -CH <sub>2</sub>	$\eta^1$ -CH <sub>2</sub>	
Co(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>3</sub>	21	3.26				
Co(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>3</sub>	21	1.25(t, J 7.2)		3.61(m), 3.82(m)		5.11
Co(Cp)(I)(S <sub>2</sub> CNMe <sub>2</sub> )	21	3.08				4.68
Co(Cp)(I)(S <sub>2</sub> CNEt <sub>2</sub> ) <sup>d</sup>	81	0.80(t, J 7.0)		3.17(q)		4.60
Co(Cp)(I)(S <sub>2</sub> CNEt <sub>2</sub> ) <sup>d</sup>	21	0.72(t, J 7.2)		2.98(m), 3.07(m) /		5.40
Co(Cp)(I)(S <sub>2</sub> COMe)	21	4.13		4.6(q)		5.48
Co(Cp)(I)(S <sub>2</sub> COEt)	21	1.5(t, J 7.4)				5.31
Co(Cp)(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub>	55	3.36				5.07
Co(Cp)(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub>	21	3.19	3.45			5.17
Co(Cp)(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub> <sup>e</sup>	-76	3.13	3.42, 3.48			5.30
Co(Cp)(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub>	60	1.30(t, br)			3.85(br)	5.31
Co(Cp)(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub>	21	1.20(t, J = 7.0)	1.27(t, J 7.1), 1.30(t, J 7.1)	3.52(m), 3.69(m) <sup>g</sup>	4.11(q), 4.14(q)	5.05
Co(Cp)(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> <sup>d</sup>	21	0.77(br)	1.22(br)	2.93(br), 3.11(br)	4.05(br)	5.05
Co(Cp)(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> <sup>d</sup>	0	0.72(t, J 6.7)	1.12(t, J 6.7)	2.86(m), 3.09(m) <sup>h</sup>	3.98(br), 4.09(br)	4.96
Co(Cp)(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> <sup>d</sup>	-50	0.63(t, J 6.7)	1.18(br), 1.20(br)	2.65(m), 2.95(m) <sup>h</sup>	3.88(q, J 6.7), 4.00(q, J 6.7)	5.30
Co(Cp)(S <sub>2</sub> CNMe <sub>2</sub> )(S <sub>2</sub> CNEt <sub>2</sub> )	55	1.22(br)		3.53(br)	Hidden	5.70
Co(Cp)(S <sub>2</sub> CNMe <sub>2</sub> )(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> A <sup>e,k</sup>	21	1.20(t, J 7.1)	3.49(br)		3.98(br)	5.20
Co(Cp)(S <sub>2</sub> CNMe <sub>2</sub> )(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> B <sup>e,k</sup>	21	3.12(br)	1.24(t, J 7.1)			5.20
Co(Cp)(S <sub>2</sub> CNMe <sub>2</sub> )(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> A <sup>e,k</sup>	-76	1.19(t, J 6.8)	3.45, 3.41			5.20
Co(Cp)(S <sub>2</sub> CNMe <sub>2</sub> )(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub> B <sup>e,k</sup>	-76	3.14	1.24(t), 1.2.6(6)		3.89(q, J 7.0)(3.96(q, J 7.0)	5.20
Co(Cp)(S <sub>2</sub> COMe)(S <sub>2</sub> CNMe <sub>2</sub> )	20	3.12	4.13			5.31
Co(Cp)(S <sub>2</sub> COEt)(S <sub>2</sub> CNMe <sub>2</sub> )	20	3.12	1.44(t, J 6.9)		4.60(q)	5.23
Co(Cp)(S <sub>2</sub> COMe)(S <sub>2</sub> CNEt <sub>2</sub> )	20	1.21(t, J 7.0)	4.11	3.55(m), 3.70(m)		5.23
Co(Cp)(S <sub>2</sub> COEt)(S <sub>2</sub> CNEt <sub>2</sub> )	20	1.19(t, J 7.1)	1.45(t, J 7.1)	3.48(m), 3.62(m) /	4.61(q)	5.22
Co(Cp)(S <sub>2</sub> COMe) <sub>2</sub>	20	4.38	1.38			5.26
Co(Cp)(S <sub>2</sub> COEt) <sub>2</sub>	20	1.34(t, J 7.1)	1.44(t, J 7.1)	4.47(q)	4.59(q)	5.34

<sup>a</sup> Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>. <sup>b</sup> Chemical shifts in ppm downfield from Me<sub>4</sub>Si as internal standard. All resonances are singlets unless stated otherwise; br, broad; t, triplet; q, quartet; and m, multiplet. J is CH<sub>2</sub>/CH<sub>3</sub> coupling constant in Hz. <sup>c</sup> Spectra measured in chloroform solution unless it is stated otherwise. <sup>d</sup> Spectra measured in CD<sub>3</sub>C<sub>6</sub>D<sub>5</sub> solution. <sup>e</sup> Spectra measured in CD<sub>2</sub>Cl<sub>2</sub>/CS<sub>2</sub> solution. / J<sub>AB</sub> 15.0 Hz. <sup>g</sup> J<sub>AB</sub> 14.1 Hz. <sup>h</sup> J<sub>AB</sub> 14.5 Hz. <sup>i</sup> J<sub>AB</sub> 12.9 Hz. <sup>j</sup> J<sub>AB</sub> 13.9 Hz. <sup>k</sup> A = [Co(Cp)( $\eta^1$ -S<sub>2</sub>CNMe<sub>2</sub>)( $\eta^2$ -S<sub>2</sub>CNEt<sub>2</sub>)]; B = [Co(Cp)( $\eta^1$ -S<sub>2</sub>CNEt<sub>2</sub>)( $\eta^2$ -S<sub>2</sub>CNMe<sub>2</sub>)].

Table 4

Fractional atom coordinates and thermal parameters for [Co( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(I)(S<sub>2</sub>CNEt<sub>2</sub>)]

Atom	x	y	z	U <sub>eq</sub>
I	0.19433(4)	0.17533(3)	0.19102(3)	0.0553(3)
Co	0.33473(6)	0.37110(7)	0.25987(5)	0.0419(4)
S(1)	0.16118(13)	0.50865(13)	0.23027(9)	0.0485(7)
S(2)	0.35556(14)	0.44707(12)	0.10268(10)	0.0504(7)
N(1)	0.1479(5)	0.6082(4)	0.0424(3)	0.054(3)
C(1)	0.2144(5)	0.5346(4)	0.1130(4)	0.044(3)
C(2)	0.1875(9)	0.6145(7)	-0.0619(5)	0.077(4)
C(3)	0.2792(9)	0.7168(9)	-0.0773(7)	0.099(6)
C(4)	0.0293(7)	0.6839(6)	0.0622(5)	0.064(4)
C(5)	0.0613(8)	0.8136(7)	0.0951(8)	0.092(6)
C(6)	0.3968(11)	0.2773(10)	0.3923(7)	0.118(7)
C(7)	0.5043(9)	0.2793(7)	0.3280(7)	0.082(5)
C(8)	0.5380(7)	0.3992(7)	0.3162(5)	0.071(4)
C(9)	0.4583(7)	0.4765(7)	0.3666(5)	0.073(4)
C(10)	0.3725(8)	0.4039(12)	0.4156(5)	0.097(6)

Table 5

Some bond lengths and angles for [Co( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(I)(S<sub>2</sub>CNEt<sub>2</sub>)]

Bond lengths ( $\text{\AA}$ )			
Co-I	2.597(1)	Co-S(1)	2.249(1)
Co-S(2)	2.255(1)	Co-C(6)	2.032(6)
Co-C(7)	2.044(7)	Co-C(8)	2.073(6)
Co-C(9)	2.068(6)	Co-C(10)	2.066(7)
S(1)-C(1)	1.716(5)	S(2)-C(1)	1.697(5)
N(1)-C(1)	1.323(7)	N(1)-C(2)	1.477(9)
N(1)-C(4)	1.473(8)	C(2)-C(3)	1.446(12)
C(4)-C(5)	1.466(9)	C(6)-C(7)	1.442(15)
C(6)-C(10)	1.406(16)	C(7)-C(8)	1.330(12)
C(8)-C(9)	1.367(10)	C(9)-C(10)	1.368(11)
Bond angles ( $^\circ$ )			
S(1)-Co-I	95.6(1)	S(2)-Co-I	94.2(1)
S(2)-Co-S(1)	76.5(1)	C(1)-S(1)-Co	86.8(2)
C(2)-N-C(1)	120.9(5)	C(1)-S(2)-Co	87.0(2)
C(4)-N-C(2)	116.9(5)	C(4)-N-C(1)	122.2(5)
N-C(1)-S(1)	123.0(4)	S(2)-C(1)-S(2)	109.6(3)
C(3)-C(2)-N	114.2(6)	N-C(1)-S(2)	127.3(4)
C(10)-C(6)-C(7)	105.9(7)	C(5)-C(4)-N	114.7(6)

Table 6

Coalescence temperatures  $T_c$ (K) and  $\Delta G_{T_c}^*$  (kcal mol<sup>-1</sup>) for the described fluxional processes

Compound <sup>a</sup>	Process <sup>b</sup>	$T_c$ (K) <sup>c</sup>	Solvent	$\Delta G_{T_c}^*$
Co(Cp)(I)(S <sub>2</sub> CNEt <sub>2</sub> )	C	344 <sup>d</sup>	CD <sub>3</sub> C <sub>6</sub> D <sub>5</sub>	17.8
Co(Cp)(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub>	A	268	CS <sub>2</sub> /CD <sub>2</sub> Cl <sub>2</sub>	14.4
	B	324	CDCl <sub>3</sub>	16.3
Co(Cp)(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub>	A	288 <sup>d</sup>	CD <sub>3</sub> C <sub>6</sub> D <sub>5</sub>	14.6
	B	325	CS <sub>2</sub> /CD <sub>2</sub> Cl <sub>2</sub>	16.3
	B	331	CDCl <sub>3</sub>	16.6
Co(Cp)(S <sub>2</sub> CNMe <sub>2</sub> )(S <sub>2</sub> CNEt <sub>2</sub> )	A <sup>e</sup>	258	CS <sub>2</sub> /CD <sub>2</sub> Cl <sub>2</sub>	13.9
	A <sup>f</sup>	258	CS <sub>2</sub> /CD <sub>2</sub> Cl <sub>2</sub>	13.9

<sup>a</sup> Cp =  $\eta$ -C<sub>5</sub>H<sub>5</sub>. <sup>b</sup> A = rotation of  $\eta^1$ -S<sub>2</sub>CNR<sub>2</sub> ligand. B =  $\eta^1$ - $\eta^2$  ligand exchange. C = rotation of  $\eta^2$ -S<sub>2</sub>CNEt<sub>2</sub> ligand. <sup>c</sup> Determined with 100 MHz field strength with errors of  $\pm 2$  kcal mol<sup>-1</sup> for  $\Delta G^*$ .

<sup>d</sup> Determined with 270 MHz field strength with errors of  $\pm 1$  kcal mol<sup>-1</sup> for  $\Delta G$ . <sup>e</sup> For rotation of the  $\eta^1$ -S<sub>2</sub>CNMe<sub>2</sub> ligand. <sup>f</sup> For rotation of the  $\eta^1$ -S<sub>2</sub>CNEt<sub>2</sub> ligand.

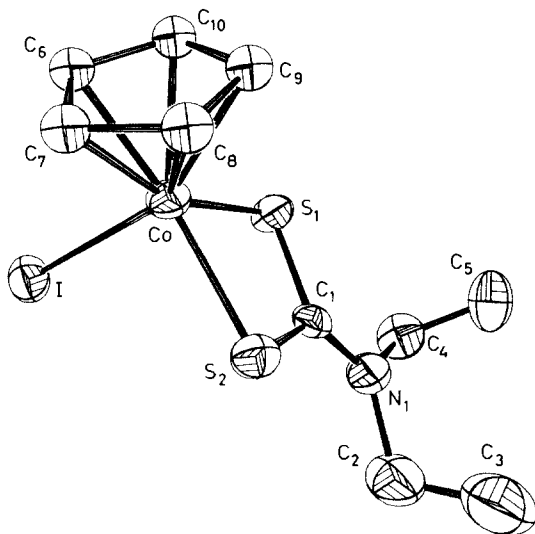
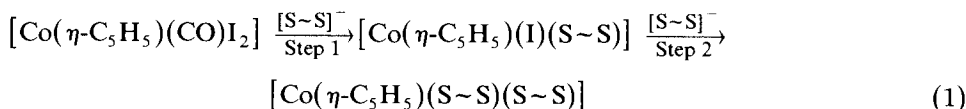


Fig. 1. The structure of  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\text{S}_2\text{CNEt}_2)]$ .

The structure of the molecule is shown in Fig. 1 [11]. Final atom coordinates are listed in Table 4. Selected bond lengths and angles are shown in Table 5. Tables of anisotropic thermal parameters, hydrogen atom coordinates, and lists of observed and calculated structure factors may be obtained from the authors.

## Results and discussion

Although  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{CNR}_2)_2]$  may be obtained by the thermal reaction of  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$  with thiuram disulphides,  $[(\text{R}_2\text{NCS}_2)_2]$ , a wide variety of related mixed ligand  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{S}\sim\text{S})(\text{S}\sim\text{S})]$  complexes,  $[\text{S}\sim\text{S}]^-$  = dithiolate anion, are better prepared by the reactions as shown in eq. 1 using a dichloromethane/alcohol mixture as the reaction solvent. The route is similar to that used by Stephenson et al. to prepare related  $\text{Rh}(\eta\text{-C}_5\text{Me}_5)$  derivatives [1].



Previously step 1 was used to prepare the dark green  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\text{S}_2\text{CNR}_2)]$  (I) [2]. It has now been extended to the brown  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\text{S}_2\text{COR})]$  (II) where (a)  $\text{R} = \text{Me}$  or (b)  $\text{R} = \text{Et}$ , and some  $\eta\text{-C}_5\text{H}_4\text{Me}$  analogues of these. Previous attempts to prepare xanthate complexes of the type  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{L})(\text{S}_2\text{COR})]\text{I}$  ( $\text{L} =$  tertiary phosphine) by a modification of step 1 starting from  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{L})\text{I}_2]$  always gave  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{L})(\text{S}_2\text{CO})]$  [12].

Step 2 has been used to convert I into the green  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{CNR}_2)_2]$  (III),  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{CNMe}_2)(\text{S}_2\text{CNEt}_2)]$  (IV), and the brown  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{CNR}_2)(\text{S}_2\text{COR})]$  (V) ((a)  $\text{R}, \text{R}' = \text{Me}, \text{Me}$ ; (b)  $\text{R}, \text{R}' = \text{Me}, \text{Et}$ ; (c)  $\text{R}, \text{R}' = \text{Et}, \text{Me}$ ; and (d)  $\text{R}, \text{R}' = \text{Et}, \text{Et}$ ) II have also been used as precursors for V as well as for the brown  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{COR})_2]$  (VI) ((a)  $\text{R} = \text{Me}$  and (b)  $\text{R} = \text{Et}$ ).



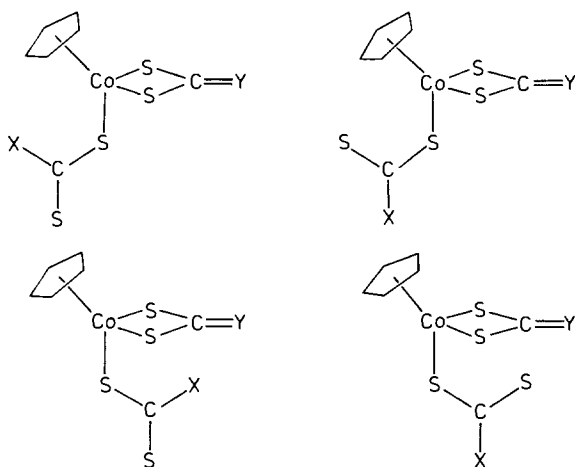


Fig. 2. The proposed structures and isomers of  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-S}_2\text{CX})(\eta^2\text{-S}_2\text{CY})]$  complexes.

The various complexes are solids, soluble in most organic solvents. Those containing xanthate ligands decompose more readily than those that do not. All decompose in solution at higher temperatures even in the absence of air.

The spectroscopic data, which will be discussed below, are consistent with I–VI the structures for I–VI shown in Fig. 2. There are similar to those found for  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{I})(\text{S}_2\text{CNET}_2)]$  (see below) and  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{CNBu}^t)(\text{CS}_3)]$  [12], with pseudo-octahedral coordination about Co complexes. I, III, IV and V all contain a bidentate dithiocarbamate ligand and a monodentate iodo, dithiocarbamate, dithiocarbamate, or xanthate ligand, respectively. Complexes II and VI contain bidentate xanthate and a monodentate iodo or xanthate ligand. In all of them there are two planes defined by  $\text{Co}(\eta^2\text{-S}_2\text{CNR}_2)$  or  $\text{Co}(\eta^2\text{-S}_2\text{COR})$  on the one hand and Co, X and the centroid of the cyclopentadienyl ring on the other. These are approximately perpendicular. X is either iodo or the coordinated S atom of the monodentate dithiocarbamate or xanthate ligand. The  $\eta^1$ -dithiolate ligands are assumed to be planar (cf. the structures of  $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\eta^1\text{-S}_2\text{COEt})]$  [13] and  $[\text{Pt}(\text{PPh}_3)(\eta^1\text{-S}_2\text{CNET}_2)(\eta^2\text{-S}_2\text{CNET}_2)]$  [14]) because of the trigonal hybridisation at C and N or O with multiple C–N or C–O bonding.

### *Infrared spectra*

The infrared spectra of dithiocarbamate complexes have received considerable attention [15]; those of xanthate derivatives are less well documented [16,17]. By comparison of the spectra of various compounds it has proved possible to identify many of the absorption bands due primarily to  $\nu(\text{Co-S})$ ,  $\nu(\text{C-S})$ ,  $\nu(\text{C-O})$  and  $\nu(\text{C-N})$  vibrations. These are listed and assigned where possible (Table 2), but some are weak, e.g.  $\nu(\text{Co-S})$ , or lie in crowded regions of the spectra, e.g.  $\nu(\text{C-S})$ , and have not been identified in every case. The assignments are based on the work of Glass et al. on dithiocarbamate complexes [15], which we have extended to xanthates by reference to ref. 16. The mixing between vibrations of different types of the same symmetry is likely to be extensive, and has to be accepted for any proposed assignment. It is probably particularly important for the xanthate complexes where

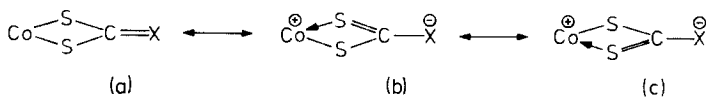


Fig. 3. Mesomeric forms of a  $\text{Co}(\eta^2\text{-S}_2\text{CX})$  moiety.

the  $\nu(\text{O-R})$ ,  $\nu(\text{C-O})$  and  $\nu(\text{C-S})$  vibrations lie between  $1000$  and  $1200\text{ cm}^{-1}$  for both mono- and bi-dentate ligands (cf. refs. 16 and 17). Consequently, for these compounds no attempt has been made to assign the relevant absorption bands other than to suggest that that at ca.  $1242\text{ cm}^{-1}$  is due to the vibration of  $\eta^2\text{-S}_2\text{COR}$  ligand which has primarily  $\nu(\text{CO})$  character.

We reported elsewhere [5] that the dithiocarbonate complex  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PMePh}_2)(\eta^2\text{-S}_2\text{CO})]$ , with  $\nu(\text{C-O})$   $1597, 1690\text{ cm}^{-1}$  [12], reacts with  $\text{MeSO}_3\text{F}$  to give a 1/1 adduct which was formulated as the xanthate complex  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PMePh}_2)(\eta^2\text{-S}_2\text{COMe})][\text{SO}_3\text{F}] \cdot 2.5\text{H}_2\text{O}$  ( $\nu(\text{CO})$   $1585, 1645\text{ cm}^{-1}$ ) with methylation at oxygen. This is different from the values reported here for IIa, IIb and VI of ca.  $1242\text{ cm}^{-1}$ , and the difference is too large to be ascribed to replacing the  $\text{PMePh}_2$  ligand by  $\text{I}^-$  (cf.  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PMePh}_2)(\eta^2\text{-S}_2\text{CNMe}_2)]\text{I}$  vs.  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\eta^2\text{-S}_2\text{CNMe}_2)]$  [2]). We thus conclude that alkylation of the dithiocarbonate derivative does not take place at oxygen, but elsewhere in the molecule, e.g. at the coordinated sulphur atom  $\text{S}_c$ .

The bonding in a  $\text{Co}(\eta^2\text{-S}_2\text{C=X})$  system may be described by a combination of the three resonance structures in Fig. 3. When the spectra of  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PMePh}_2)(\text{S}_2\text{CO})]$  and  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{I})(\text{S}_2\text{COR})]$  (Table 2) are compared, it can be seen that the frequencies of the  $\nu(\text{C-O})$  absorption bands have fallen from  $1597$  or  $1690$  to ca.  $1242\text{ cm}^{-1}$ , whereas those due to the  $\nu(\text{C-S})_{\text{as}}$  (as = asymmetric) modes have increased from  $845$  to  $1032$  or  $1120\text{ cm}^{-1}$ . These observations may be rationalized by assuming that on going from  $\text{X} = 0$  to  $\text{OR}^+$  the contribution of the resonance form (a) declines markedly while those of (b) and (c) increase. This suggests that the  $\text{C-OR}$  bonds in xanthates are little more than single bonds, whilst the  $\text{C-S}$  bonds have much double-bond character.

Four absorption bands were identified in the spectra of III and IV as due to the stretching vibrations of the  $\text{CoS}_c\text{C}(\text{S}_u)\text{NR}_2$  moiety with its monodentate dithiocarbamate ligand ( $\text{S}_c$  and  $\text{S}_u$  are the coordinated and uncoordinated S atoms, respectively). Two, at ca.  $450$  and  $1475\text{--}1508\text{ cm}^{-1}$ , have frequencies close to those for a  $\text{Co}(\eta^2\text{-S}_2\text{CNR}_2)$  species, and are assigned to vibrations largely of  $\nu(\text{Co-S}_c)$  and  $\nu(\text{C-N})$  character, respectively. The other two, at ca.  $560$  and  $1120\text{ cm}^{-1}$ , are probably due to vibrations largely of  $\nu(\text{C-S})$  character. We have shown that the basicity of the sulphur atom in a CS system increases as the  $\text{C-S}$  bond order decreases [18], and so it seems reasonable to suggest that the  $\text{C-S}_c$  bond would have the lower bond order, so that  $\nu(\text{C-S}_c)$  vibrations are responsible for the absorption bands at ca.  $560\text{ cm}^{-1}$ , whilst  $\nu(\text{C-S}_u)$  are responsible for those at  $1120\text{ cm}^{-1}$ . If this assignment is correct, the frequencies of the various absorption bands imply that when the dithiocarbamate ligands change from bidentate to monodentate coordination there is a decline in the  $\text{C-S}_c$  and  $\text{C=N}$  bond orders and an increase in the  $\text{C-S}_u$ . Furthermore as the bonding in  $\text{Co}\{\eta^1\text{-SC}(\text{S})\text{X}\}$  may be represented by a combination of three resonance forms (Fig. 4), it also implies that, when  $\text{X} = \text{NR}_2^+$  the contribution from (b) increases in importance while those of (a) and (c) decline

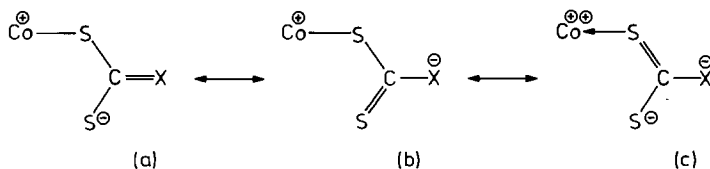


Fig. 4. Mesomeric forms of a  $\text{Co}(\eta^1\text{-S}_2\text{CX})$  moiety.

relative to the situation for  $\text{Co}(\eta^2\text{-S}_2\text{CX})^-$  (cf. above and Fig. 3). Similar arguments appear to apply to complexes of xanthate ligands ( $\text{X} = \text{OR}^+$ ) even though the absorption bands due to the  $\nu(\text{C}-\text{O})$  and  $\nu(\text{C}-\text{S}_u)$  vibrations of the  $\eta^1$ -ligands cannot be identified unambiguously. However the differences between  $\eta^1$ - and  $\eta^2$ -xanthates are less marked than for dithiocarbamates, a conclusion which may also be drawn from the  $^1\text{H}$  chemical shifts of the R groups (see below).

The frequencies of the absorption bands in the infrared spectra are consistent with the structures postulated in Fig. 1. Complex IV appears to be  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\eta^1\text{-S}_2\text{CNMe}_2)(\eta^2\text{-S}_2\text{CNEt}_2)]$  in the solid state, and this is the most important isomer in solution (see below). For V the dithiocarbamate ligand is always bidentate while the xanthate is always monodentate. These conclusions are also consistent with the  $^1\text{H}$  NMR spectra discussed below.

#### *$^1\text{H}$ NMR spectra and fluxionality*

The  $^1\text{H}$  NMR spectra are summarised in Table 3. The spectra of all complexes including IV always show a singlet resonance at  $\delta \sim 5$  ppm due to their  $\text{C}_5\text{H}_5$  protons whilst their  $\text{C}_5\text{H}_4\text{Me}$  counterparts give rise to two multiplets at  $\delta \sim 5$  ppm due to their ring protons and a singlet at  $\delta 1.7\text{--}2.0$  ppm due to the methyl group. However in all other respects the spectra of the two series of complexes are virtually identical. The integrated intensities of the various resonances exhibit the ratios anticipated on the basis of their molecular formulae.

The bidentate nature of the dithiocarbamate ligands in I is confirmed by the chemical shifts of their  $\text{R}_2\text{N}$  protons, which are comparable with those of  $[\text{Co}(\text{S}_2\text{CNR}_2)_3]$  complexes [19] (also see below and Table 3). For both Ia and Ic the  $\text{Me}_2\text{N}$  protons give rise to a singlet at all temperatures, but the spectra of Ib and Id are temperature-dependent. At lower temperatures the ethyl groups give rise to a well-defined triplet and a multiplet, due to their  $\text{CH}_3$  and  $\text{CH}_2$  protons, respectively. This indicates that whereas the two ethyl groups are equivalent, the two methylene protons within each are not because the two sides of the  $\text{Co}(\eta^2\text{-S}_2\text{CNEt}_2)$  plane are different and rotation about the  $\text{C}-\text{NEt}_2$  bond is slow on the NMR time-scale. Consequently the two methylene protons couple to each other as well as to the  $\text{CH}_3$  group. This has been confirmed by double resonance studies. At higher temperatures, rotation about the  $\text{C}-\text{N}$  bond becomes fast, exchange of the two Et groups takes place, and the four methylene protons of the  $\text{NEt}_2$  moiety become equivalent. The usual quartet-triplet pattern of the ethyl group resonance is then observed. Similar behaviour has been reported for  $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{X})(\eta^2\text{-S}_2\text{CNEt}_2)]$  complexes [1].

The  $^1\text{H}$  NMR spectra of II are independent of temperature between  $-50$  and  $+50^\circ\text{C}$ , with the  $\eta^2$ -xanthate ligands giving rise to singlet ( $\text{R} = \text{Me}$ ) or quartet-triplet ( $\text{R} = \text{Et}$ ) resonances. This indicates that rotation about the  $\text{C}-\text{OEt}$  bond is

always fast on the NMR time-scale, so that the CH<sub>2</sub> protons appear equivalent. It is consistent with the infrared spectroscopic data which imply low C–O bond orders.

The <sup>1</sup>H NMR spectra of III at room temperature show resonances due to the η<sup>1</sup>- and η<sup>2</sup>-dithiocarbamate ligands which can be distinguished clearly, the chemical shifts due to the former having the higher δ values. The spectra are temperature dependent and three fluxional processes have been identified. That of lowest energy is due to a slowing of the rotation about the C–NR<sub>2</sub> bond of the monodentate dithiocarbamate so that the two R differ and give rise to distinguishable signals at low temperatures. Double resonance studies show that the two methylene protons within each ethyl group are equivalent. This provides evidence that the planar η<sup>1</sup>-dithiocarbamate ligands lie perpendicular to the Co(η<sup>2</sup>-S<sub>2</sub>CNR<sub>2</sub>) plane in a plane defined by the Co atom, the centroid of the cyclopentadienyl group and the η<sup>1</sup>-S ligating atom, or oscillate rapidly back and forth through that plane. This process has been observed for other complexes containing η<sup>1</sup>-dithiocarbamate ligands, but it was not reported for [Rh(η-C<sub>5</sub>Me<sub>5</sub>)(η<sup>1</sup>-S<sub>2</sub>CNR<sub>2</sub>)(η<sup>2</sup>-S<sub>2</sub>CNR<sub>2</sub>)] derivatives (R = Me or Et) [1]. There are four different configurations of the Co(η<sup>1</sup>-S<sub>2</sub>CNR<sub>2</sub>)(η<sup>2</sup>-S<sub>2</sub>CNR<sub>2</sub>) moiety that are consistent with the above criteria (Fig. 2, X, Y = NR<sub>2</sub>). Although only one is present in solution, we are unable to say which. At lower temperatures the resonances due to the CH<sub>2</sub> group of the bidentate S<sub>2</sub>CNEt<sub>2</sub> ligands of IIIb and IIIc appear as a multiplet (cf. Ib and Id above), indicating slow rotation about the C–NEt<sub>2</sub> bonds. Line broadening clearly indicates that this becomes faster at higher temperatures, but it is masked because exchange of η<sup>1</sup>- and η<sup>2</sup>-dithiocarbamate ligands also becomes rapid for all III complexes. At these temperatures decomposition to [Co(S<sub>2</sub>CNR<sub>2</sub>)<sub>3</sub>] also becomes noticeable.

Interpretation of the <sup>1</sup>H NMR spectrum of IV is not straightforward because it exists in solution as a mixture of two isomers, [Co(η-C<sub>5</sub>H<sub>5</sub>)(η<sup>1</sup>-S<sub>2</sub>CNMe<sub>2</sub>)(η<sup>2</sup>-S<sub>2</sub>CNEt<sub>2</sub>)] and [Co(η-C<sub>5</sub>H<sub>5</sub>)(η<sup>1</sup>-S<sub>2</sub>CNEt<sub>2</sub>)(η<sup>2</sup>-S<sub>2</sub>CNMe<sub>2</sub>)], in a temperature-dependent equilibrium. Their ratio is ca. 2/1 below 0 °C, but shifts strongly in favour of the former isomer at higher temperatures. It is clear that the η<sup>1</sup> ligands of both isomers undergo a slowing of the rotation about their C–NR<sub>2</sub> bonds on cooling in the same way as III (see above) and coalescence temperatures have been obtained. Also there is a general broadening of resonances above ca. 40 °C which is consistent with the onset of η<sup>1</sup>–η<sup>2</sup> ligand exchange. Unfortunately thermal decomposition becomes extensive above ca. 50 °C, and so the high-temperature limiting spectrum could not be obtained.

The chemical shifts confirm unambiguously that IV are [Co(η-C<sub>5</sub>H<sub>5</sub>)(η<sup>1</sup>-S<sub>2</sub>COR')(η<sup>2</sup>-S<sub>2</sub>CNR<sub>2</sub>)] with bidentate dithiocarbamate ligands. This is consistent with their infrared spectra (see above). The <sup>1</sup>H NMR spectra are independent of temperature below 50 °C, and above this decomposition becomes rapid. The multiplet resonance due to the methylene protons of the η<sup>2</sup>-S<sub>2</sub>CNEt<sub>2</sub> shows that rotation about the C–NEt<sub>2</sub> bond is slow (see above), whilst the quartet-triplet resonances due to the η<sup>1</sup>-S<sub>2</sub>COEt show that rotation about the C–OEt bond is fast even at –50 °C.

The complexes [Co(η-C<sub>5</sub>H<sub>5</sub>)(η<sup>1</sup>-S<sub>2</sub>COR)(η<sup>2</sup>-S<sub>2</sub>COR)] (VI) also decompose rapidly in solution above ca. 50 °C. Their <sup>1</sup>H NMR spectra are independent of temperature between –50 and +50 °C. When R is Me only a singlet resonance due to the xanthate ligands is observed. However we feel that this is a consequence of accidental coincidence of chemical shifts rather than rapid η<sup>1</sup>–η<sup>2</sup> ligand exchange

because when R is Et two distinct quartets and triplets are observed. These are respectively due to CH<sub>2</sub> and CH<sub>3</sub> protons of the  $\eta^1$ - and  $\eta^2$ - ligands that are undergoing rapid rotation about their C–OEt bonds.

Although it proved more straight-forward to estimate coalescence temperatures,  $T_c$ , using the 270 MHz. as opposed to the 100 MHz. spectrometer, the value of  $\Delta G_{T_c}^\ddagger$  calculated from the different sets of  $T_c$  [19] were very similar (Table 4). The estimated barrier to rotation about the C–N bonds of the S<sub>2</sub>CNR<sub>2</sub> ligands is ca. 18 kcal mol<sup>-1</sup> when it is bidentate in IIb, but only ca. 14 kcal mol<sup>-1</sup> when it is monodentate in IIIa and IIIb. This is consistent with the lower C–N bond-order for the  $\eta^1$ -dithiocarbamate ligand suggested by infrared spectroscopy. These values are comparable with those of 17–20 kcal mol<sup>-1</sup> for  $\eta^2$ -C–N rotation in [M(S<sub>2</sub>CNR<sub>2</sub>)<sub>4</sub>] derivatives (M = Ti, Zr or Hf) [20], and of ca. 15 kcal mol<sup>-1</sup> found for  $\eta^1$ -rotation in [CH<sub>2</sub>(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>] (R = Me or Et) [21]. The  $\Delta G^\ddagger$  for the exchange of  $\eta^1$ - and  $\eta^2$ -dithiocarbamate ligands is ca. 16.5 kcal mol<sup>-1</sup> irrespective of R. These values are much lower than the corresponding values of  $\Delta G_{298}^\ddagger$  for the [M( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)(S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub>] complexes, which are 17.9 kcal mol<sup>-1</sup> for M = Rh and 20.2 kcal mol<sup>-1</sup> for M = Ir, but are higher than those of 10.5–12 kcal mol<sup>-1</sup> found for [Pt(S<sub>2</sub>CNR<sub>2</sub>)(PMe<sub>2</sub>Ph)] [21].

#### *Structure of [Co( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(I)(S<sub>2</sub>CNEt<sub>2</sub>)]*

Our efforts to grow suitable crystals of III were unsuccessful, but we obtained good crystals of Ib. An X-ray diffraction study has shown that this has the expected pseudo-octahedral structure, with piano-stool coordination about the cobalt atom. The dithiocarbamate ligand is bidentate and planar, as expected from the spectroscopic data discussed above. There are no unusual bond lengths or angles; the Co–S distances of 2.249(1) and 2.255(1) Å are very close to the values of 2.235(3) and 2.252(3) Å found in [Co( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(CNBu<sup>t</sup>)(S<sub>2</sub>CS)] [12]. The C–S lengths in these two species are also comparable.

#### References

- 1 D.R. Robertson and T.A. Stephenson, J. Chem. Soc. Dalton Trans., (1978) 486.
- 2 J. Doherty and A.R. Manning, J. Organomet. Chem., 253 (1983) 81.
- 3 A.I. Vogel, Practical Organic Chemistry, 3rd edit., Longmans-Green, New York 1956, p. 499.
- 4 Tables of Wavenumbers for the Calibration of Infrared Spectrometers, Butterworths, London, 1961.
- 5 E.C. Alyea, G. Ferguson, and R. Restivo, Inorg. Chem., 14 (1975) 2491.
- 6 G.M. Sheldrick, SHELX86, a computer program for crystal structure determination, University of Göttingen, 1986.
- 7 G.M. Sheldrick, SHELX76, a computer program for crystal structure determination, University of Cambridge, England, 1976.
- 8 D.T. Cromer, and J.B. Mann, Acta Crystallogr., A, 24 (1968) 321.
- 9 R.F. Stewart, E.R. Davidson, and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
- 10 D.T. Cromer, and D.J. Liberman, J. Chem. Phys., 53 (1970) 1891.
- 11 C.K. Johnson, ORTEP Oak Ridge Natl. Lab. (Rep) ORNL (U.S.), 1965, ORNL–3794, revised 1971.
- 12 J. Doherty, J. Fortune, A.R. Manning, and F.S. Stephens, J. Chem. Soc. Dalton Trans., (1984) 1111.
- 13 C. Tisipis, G. Manoussakis, D.P. Kessissoglou, J.C. Huffman, L.N. Lewis, M.A. Adams, and K.G. Caulton, Inorg. Chem., 19 (1980) 1459.
- 14 J.P. Fackler jr., L.D. Thompson, I.J.B. Lin, T.A. Stephenson, R.O. Gould, J.M.C. Alison, and A.J. Fraser, Inorg. Chem., 21 (1982) 2397.
- 15 D.A. Brown, W.K. Glass, and M.A. Burke, Spectrochim. Acta A, 32 (1976) 137.

- 16 G.W. Watt and B.J. McCormick, *Spectrochim. Acta*, 21 (1965) 753.
- 17 F. Sato, K. Nakamura, and M. Sato, *J. Organomet. Chem.*, 67 (1974) 141.
- 18 J. Fortune and A.R. Manning, *Organometallics*, 2 (1983) 1719.
- 19 T.R. Jack and J. Powell, *Canad. J. Chem.*, 53 (1975) 2558.
- 20 S.L. Hawthorne, A.H. Bruder, and R.C. Fay, *Inorg. Chem.*, 22 (1983) 3363.
- 21 J.M.C. Allison and T.A. Stephenson, *J. Chem. Soc. Dalton Trans.*, (1973) 254