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# ELECTRONIC SPECTRA OF PSEUDO- -TETRAHEDRAL Co (II) COMPLEXES WITH THE ORGANOMETALLIC LIGANDS

$[M(\eta^5-C_5H_5)_2(SR)_2]$   
( $M = Mo, W$ )

*The synthesis and electronic spectra and magnetic properties of some binuclear complexes of the general formula  $[(\eta^5-C_5H_5)_2M-(SR)_2Co X_2]$  and trinuclear complexes of the general formula  $[(\eta^5-C_5H_5)_2M-(SR)_2Co-(SR)_2M(\eta^5-C_5H_5)_2] X_2$  ( $M = Mo, W$ ;  $R = \text{alkyl or aryl}$  and  $X = \text{halogen}$ ). It is shown that the nature of the substituent  $R$  does not appreciably affect the electronic spectra of the Co(II) central atom.*

## 1 — INTRODUCTION

The synthesis and electronic spectra of some binuclear complexes of the general type  $[(\eta^5-C_5H_5)_2M-(SR)_2Co X_2]$  (I) ( $M = Mo, W$ ;  $R = \text{alkyl or aryl}$ ,  $X = \text{halogen or pseudo-halogen}$ ) were reported by DIAS and GREEN [1]. These authors attribute some differences in the electronic spectra of the Co(II) central atom to the influence of the substituent  $R$  and suggest that that influence operates mainly through a lowering of symmetry around the cobalt atom; however the evidence available at that time was scarce. Recent work by WEILB and RICHARDS [2] has shown that in cobalt complexes with substituted amino-imine ligands the substituent  $R$  does not appreciably affect the spectral parameters.

We set out to re-examine this problem; in order to do so, we prepared a new range of organometallic ligands  $[M(\eta^5-C_5H_5)_2(SR)_2]$  (II) ( $M = W$ ,  $R = n-C_3H_7$ ,  $s-C_3H_7$ ,  $t-C_4H_9$ ,  $n-C_5H_{11}$ ,  $n-C_6H_{13}$ ,  $n-C_7H_{15}$ ,  $n-C_{14}H_{29}$ ;  $M = Mo$ ,  $R = n-C_3H_7$ ,  $s-C_3H_7$ ,  $t-C_4H_9$ ,  $n-C_7H_{15}$ ,  $n-C_{14}H_{29}$ ). Using these ligands we synthesised some new binuclear complexes of type (I) as well as the new trinuclear complexes  $[(\eta^5-C_5H_5)_2M-(SR)_2Co-(SR)_2M(\eta^5-C_5H_5)_2] X_2$  (III) ( $M = W$ ,  $R = CH_3$ ,  $X = Cl, Br, I$ ;  $R = s-C_3H_7$ ,  $X = Br, I, PF_6$ ) and studied their electronic spectra. The results of the present work agree with those reported by WEILB and RICHARDS [2].

## 2 — CHEMICAL STUDIES

Organometallic ligands (II) were prepared from  $[M(\eta^5-C_5H_5)_2 X_2]$  ( $X = \text{halogen}$  and the respective thiol in the presence of a base using the methods described in the literature for analogous compounds [3,4]. The new compounds are crystalline solids of different shades of brown, very soluble in dichloromethane, in acetone and in ethanol although in the latter the solubility decreases with the increasing number of carbon atoms in the alkyl substituent. They are moderately stable in air in the solid state, the thermal stability decreasing as the substituent becomes larger. The analytical data for these compounds is given in Table I.

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Table 1  
Analytical data on compounds  $[M(\eta^5-C_5H_5)_2(SR)_2]$

Compound	Colour	M.P. (°C)	Analysis % req. (found)			
			C	H	S	M
$[W Cp_2(S n-C_3H_7)_2]$	reddish-brown	d 180	41.4(41.3)	5.2(4.8)	—	—
$[W Cp_2(S s-C_3H_7)_2]$	»	d 180	41.4(41.3)	5.2(4.9)	—	39.6(39.2)
$[W Cp_2(S t-C_4H_9)_2]$	»	d 170	44.0(43.2)	5.7(5.0)	—	37.3(37.2)
$[W Cp_2(S n-C_5H_{11})_2]$	golden-brown	d 150	46.15(45.6)	6.2(6.2)	—	35.3(34.7)
$[W Cp_2(S n-C_6H_{13})_2]$	»	d 130	48.2(48.0)	6.6(6.5)	11.7(11.0)	—
$[W Cp_2(S n-C_7H_{15})_2]$	reddish-brown	160	50.0(50.5)	7.0(6.9)	11.1(10.7)	—
$[W Cp_2(S n-C_{14}H_{29})_2]$	golden-brown	130	59.0(59.3)	8.9(8.9)	8.3(8.4)	—
$[Mo Cp_2(S n-C_3H_7)_2]$	»	d 170	51.0(50.9)	6.4(6.4)	—	—
$[Mo Cp_2(S s-C_3H_7)_2]$	»	d 160	51.0(50.8)	6.4(6.3)	—	—
$[Mo Cp_2(S t-C_4H_9)_2]$	reddish-brown	d 170	53.4(53.0)	7.0(7.0)	—	—
$[Mo Cp_2(S n-C_7H_{15})_2]$	golden-brown	d 140	59.0(58.9)	8.3(8.3)	13.1(12.8)	19.6(19.5)
$[Mo Cp_2(S n-C_{14}H_{29})_2]$	»	130	66.6(67.1)	10.0(10.1)	9.4(9.1)	14.0(13.5)

Table 2  
Analytical data on compounds  $[(\eta^5-C_5H_5)_2M-(SR)_2-Co Cl_2]$

Compound	Colour	M.P. (°C)	C	Analysis (%) req. (found)				Co	Cl
				H	S	M			
$[Cp_2 W-(S n-C_3H_7)_2-Co Cl_2]$	dark green	d 200	32.3(32.3)	4.1(4.2)	—	—	—	—	—
$[Cp_2 W-(S s-C_3H_7)_2-Co Cl_2]$	»	d 190	32.3(32.1)	4.1(4.3)	—	—	—	—	—
$[Cp_2 W-(S t-C_4H_9)_2-Co Cl_2]$	»	d 180	34.7(34.8)	4.5(4.5)	—	—	—	—	—
$[Cp_2 W-(S n-C_5H_{11})_2-Co Cl_2]$	green	d 160	36.9(36.4)	5.0(5.4)	—	28.3(28.6)	9.1(8.6)	—	—
$[Cp_2 W-(S n-C_6H_{13})_2-Co Cl_2]$	dark green	110	38.95(39.2)	5.4(5.2)	—	27.1(27.7)	—	10.45(10.9)	—
$[Cp_2 W-(S n-C_7H_{15})_2-Co Cl_2]$	green	100	40.8(41.0)	5.7(5.7)	9.1(8.5)	26.0(26.4)	—	—	—
$[Cp_2 W-(S n-C_{14}H_{29})_2-Co Cl_2]$	dark green	90	50.65(50.67)	7.6(7.7)	7.1(7.0)	—	6.5(6.1)	14.0(14.3)	—
$[Cp_2 Mo-(S n-C_3H_7)_2-Co Cl_2]$	bright green	d 170	37.95(38.4)	4.8(5.1)	—	—	—	—	—
$[Cp_2 Mo-(S s-C_3H_7)_2-Co Cl_2]$	»	d 160	37.95(37.27)	4.8(4.8)	—	18.95(18.55)	—	—	—
$[Cp_2 Mo-(S t-C_4H_9)_2-Co Cl_2]$	dark green	d 130	40.5(40.1)	5.3(5.2)	—	—	—	—	—
$[Cp_2 Mo-(S n-C_7H_{15})_2-Co Cl_2]$	bright green	130	46.6(46.6)	6.5(6.7)	—	—	—	—	—
$[Cp_2 Mo-(S n-C_{14}H_{29})_2-Co Cl_2]$	»	100	56.0(56.0)	8.4(8.4)	—	—	—	—	—

Table 3  
Analytical and Conductimetric data on Compounds  $[[(\eta^5-C_5H_5)_2 M(SR)_2]_2 Co | X_2]$

Compound	Colour	M.P. (°C)	Analysis req. (found)		Conductivity (ohm <sup>-1</sup> cm <sup>2</sup> )
			C	H	
$[[(\eta^5-C_5H_5)_2 W-(S CH_3)_2]_2-Co   Cl_2]$	brown	d 230	30.5 (30.2)	3.4 (3.4)	230 (a)
$[[(\eta^5-C_5H_5)_2 W-(S CH_3)_2]_2-Co   Br_2]$	brown	d 165	27.85(28.1)	3.1 (3.3)	180 (a)
$[[(\eta^5-C_5H_5)_2 W-(S CH_3)_2]_2-Co   I_2]$	dark brown	d 270	25.5 (25.2)	2.9 (3.0)	200 (b)
$[[(\eta^5-C_5H_5)_2 W-(S s-C_3H_7)_2]_2-Co   Br_2]$	greenish-brown	d 190	35.5 (35.7)	4.5 (4.3)	185 (a)
$[[(\eta^5-C_5H_5)_2 W-(S s-C_3H_7)_2]_2-Co   I_2]$	brown	d 240	32.65(33.1)	4.1 (4.3)	180 (b)
$[[(\eta^5-C_5H_5)_2 Mo(S CH_3)_2]_2Co   I_2]$	dark brown	d 200	30.2 (30.5)	3.4 (3.6)	170 (b)

(a) Acetonitrile; (b) Nitrometano.

Binuclear complexes (I) were prepared from anhydrous  $\text{CoCl}_2$  and ligands (II) in dry ethanol or dichloromethane/ethanol. The complexes are green crystalline solids, moderately stable in air. They are insoluble in most of the common solvents but are soluble in hydrochloric acid, nitromethane and dichloromethane. The solubility in  $\text{CH}_2\text{Cl}_2$  is strongly dependent on the nature of R, following the order  $n\text{-C}_3\text{H}_7 \sim s\text{-C}_3\text{H}_7 < t\text{-C}_4\text{H}_9 < n\text{-C}_5\text{H}_{11} < n\text{-C}_6\text{H}_{13} < n\text{-C}_7\text{H}_{15} < n\text{-C}_{14}\text{H}_{29}$ . The more soluble complexes could be recrystallised; the less soluble ones were washed prior to drying. Analytical data are given in Table 2. Conductivity measurements have shown the complexes to be neutral; the complexes are paramagnetic and the values of magnetic moments are included in Table 4.

Although trinuclear complexes of the type  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{SR})_2\text{-M}'(\text{SR})_2\text{-M}(\eta^5\text{-C}_5\text{H}_5)_2]^{2+}$  have been reported namely for  $\text{M}=\text{Nb}$ ,  $\text{R}=\text{CH}_3$ ,  $\text{M}'=\text{Ni}$ ,  $\text{Pd}$ ,  $\text{Pt}$  [5];  $\text{M}=\text{Mo}$ ,  $\text{W}$ ,  $\text{R}=\text{CH}_3$ ,  $\text{M}'=\text{Pt}$

[7], no similar compounds were known for  $\text{M}'=\text{Co}$ . Reaction of ligands (II) with tetrahalocobaltato salts in dichloromethane, in the presence of  $\text{PF}_6$ , gave brown crystalline compounds identified as the hexafluorophosphate salts of trinuclear complexes (III). The analytical and conductimetric data for these compounds are given in Table 3. These compounds are fairly stable in air being moderately soluble in nitromethane and acetonitrile and insoluble in the other common organic solvents. The complexes are paramagnetic and the values of magnetic moments are given in Table 5.

### 3 — SPECTROSCOPIC STUDIES

Electronic spectra of complexes (I) and (III) were recorded both in solution and in the solid state (diffuse reflectance). The spectra are described in Tables 4 and 5 and some representative examples are shown in figs. 1-3.

Table 4  
Electronic spectra and magnetic moments of Complexes  $[\text{Cp}_2\text{M}(\text{SR})_2\text{CoCl}_2]$

Complex	Band position (molar extinction coefficient)					$\mu_{eff}$ (B.M.)
	$\nu_3(^4T_1(P) \rightarrow ^4A_2)$	$f(\nu_3) \times 10^3$	$\nu_2(^4T_1(F) \leftarrow ^4A_2(F))$		$\nu_1(^4T_2(F) \leftarrow ^4A_2(F))$	
			Solution	Diffuse Reflectance		
[Cp <sub>2</sub> W—(S <i>n</i> —C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> Co Cl <sub>2</sub> ]	17.38 (282); 15.63 (285); 13.60 (429)	5.0	7.41 (88); 6.14 (18)	7.4; 5.8*; 4.4*		4.8
[Cp <sub>2</sub> W—(S <i>s</i> —C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> —Co Cl <sub>2</sub> ]	17.45 (269); 15.63 (273); 13.71 (433)	3.5	7.53 (94); 5.74 (35)	7.4; 6.03*; 4.05*		4.8
[Cp <sub>2</sub> W—(S <i>t</i> —C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> —Co Cl <sub>2</sub> ]	17.67 (285); 15.60 (237); 13.82 (411)	3.9	7.76 (105); 6.17 (44)	7.6; 6.06*		4.6
[Cp <sub>2</sub> W—(S <i>n</i> —C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> —Co Cl <sub>2</sub> ]	17.50 (304); 15.61 (309); 13.73 (443)	5.4	7.46 (101); 5.74 (48)	7.3; 5.8	4.40 (43); 3.96 (75)	4.5
[Cp <sub>2</sub> W—(S C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> —Co Cl <sub>2</sub> ]	17.50; 16.667; 15.61; 13.291	—	8.72; 7.36	8.5; 7.4*; 6.0*; 5.3*; 4.9*		4.4
[Cp <sub>2</sub> W—(S <i>n</i> —C <sub>6</sub> H <sub>13</sub> ) <sub>2</sub> —Co Cl <sub>2</sub> ]	17.32 (288); 15.88 (296); 13.64 (421)	5.0	7.46 (97); 5.70 (41)	7.3; 5.8*; 4.6*	4.36 (62); 3.94 (86)	
[Cp <sub>2</sub> W—(S <i>n</i> —C <sub>7</sub> H <sub>15</sub> ) <sub>2</sub> —Co Cl <sub>2</sub> ]	17.35 (296); 15.57 (313); 13.67 (436)	5.2	7.44 (92); 5.65 (42)	7.4; 6.1; 4.3*		4.2
[Cp <sub>2</sub> W—(S <i>n</i> —C <sub>14</sub> H <sub>29</sub> ) <sub>2</sub> —Co Cl <sub>2</sub> ]	17.40 (528); 15.68 (476); 13.64 (471)	7.7	7.50 (78); 5.74 (35)	7.4; 5.9	4.23 (43); 3.94 (55)	4.8
[Cp <sub>2</sub> W—(S <i>n</i> —C <sub>14</sub> H <sub>29</sub> ) <sub>2</sub> —Co Cl <sub>2</sub> ] (a)	16.77; 15.267; 13.70	—		—		
[Cp <sub>2</sub> Mo—(S <i>n</i> —C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> —Co Cl <sub>2</sub> ]	17.38 (240); 15.63 (264); 13.68 (424)	4.0	7.49 (94); 5.70 (32)	7.4; 5.9; 4.4*		4.7
[Cp <sub>2</sub> Mo—(S <i>s</i> —C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> —Co Cl <sub>2</sub> ]	17.17 (235); 15.68 (257); 13.69 (436)	4.5	7.48 (103); 6.54 (39)	7.3; 6.0*; 4.4		4.2
[Cp <sub>2</sub> Mo—(S <i>t</i> —C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> —Co Cl <sub>2</sub> ]	17.54 (421); 15.63 (341); 13.83 (539)	3.8	—	—		4.5
[Cp <sub>2</sub> Mo—(S <i>n</i> —C <sub>7</sub> H <sub>15</sub> ) <sub>2</sub> —Co Cl <sub>2</sub> ]	17.43 (259); 15.56 (277); 13.68 (450)	3.7	7.51 (99); 6.782 (45)	7.4; 6.0*; 4.4*	4.44 (35); 3.97 (67)	4.7
[Cp <sub>2</sub> Mo—(S <i>n</i> —C <sub>14</sub> H <sub>29</sub> ) <sub>2</sub> —Co Cl <sub>2</sub> ]	17.45 (368); 15.68 (337); 13.69 (418)	5.7			4.37 (89); 4.00 (129)	4.7

(a) Acetonitrile solutions. — \*) Shoulder.

Table 5  
Electronic spectra and magnetic moments of Complexes [ $[\text{Cp}_2\text{M}(\text{SR})_2\text{Co} | \text{X}_2]$ ]

Complex	Band position (molar extinction coefficient)				$\mu_{\text{eff}}$
	$\nu_3 (^4T_1(P) \rightarrow ^4A_2)$	$F(\nu_3)$ $\times 10^3$	$\nu_2(^4T_1(F) \rightarrow ^4A_2(F))$		
			Solution	Diffuse reflectance	
$[   (\text{Cp}_2\text{W}-(\text{SCH}_3)_2)_2 \text{Co}   \text{Cl}_2 ]$	21.12; 18.68; 15.89	—	(b)	7.7; 6.1*; 5.4*; 4.6*	4.2
$[   (\text{Cp}_2\text{W}-(\text{SCH}_3)_2)_2 \text{Co}   \text{Cl}_2 ]^{(a)}$	18.2*; 16.97; 16.10*; 15.4*	—	7.14 (c)	—	—
$[   (\text{Cp}_2\text{W}-(\text{SCH}_3)_2)_2 \text{Co}   \text{Br}_2 ]$	16.76 (313); 15.40 (432); 13.54 (410)	5.9	7.25 (104)	—	4.3
$[   (\text{Cp}_2\text{W}-(\text{SCH}_3)_2)_2 \text{Co}   \text{Br}_2 ]$	18.1*; 16.42; 15.74	—	7.14 (c)	—	—
$[   (\text{Cp}_2\text{W}-(\text{SCH}_3)_2)_2 \text{Co}   \text{I}_2 ]$	17.00 (1000)	25.0	(b)	7.5; 5.9*; 5.4*; 4.6*	4.5
$[   (\text{Cp}_2\text{W}-(\text{SCH}_3)_2)_2 \text{Co}   \text{I}_2 ]^{(a)}$	16.47	—	7.00	—	—
$[   (\text{Cp}_2\text{W}-(\text{S}s-\text{C}_3\text{H}_7)_2)_2 \text{Co}   \text{I}_2 ]$	15.45 (733); 14.46 (899); 12.86 (1568)	11.0	7.05 (323); 5.51 (58)	7.3; 6.3*; 4.4	4.6
$[   (\text{Cp}_2\text{W}-(\text{S}s-\text{C}_3\text{H}_7)_2)_2 \text{Co}   \text{Br}_2 ]^{(a)}$	18*; 16.42; 15.74	—	7.14	—	4.7

(a) Acetonitrile solution; (b) Difficult to interpret; (c) Doubtful.

\* Shoulder.

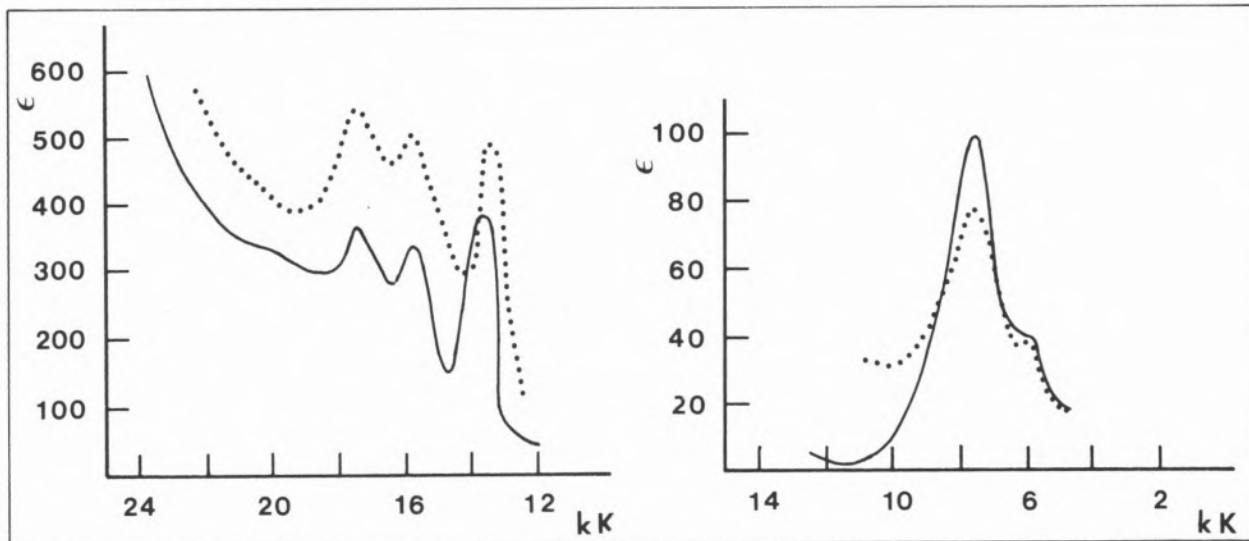


Fig. 1

— $[(\eta\text{-C}_5\text{H}_5)_2\text{Mo}-(\text{S}-\text{C}_{14}\text{H}_{29})_2\text{Co} | \text{Cl}_2]$  in dichloromethane  
... $[(\eta\text{-C}_5\text{H}_5)_2\text{W}-(\text{S}-\text{C}_{14}\text{H}_{29})_2\text{Co} | \text{Cl}_2]$  in dichloromethane

Above 23 kK the spectra of the polynuclear complexes are analogous to the spectra of the free organometallic ligands (II). An assignment of the spectra of latter type of compounds has already been discussed [8]. Below 23 kK the spectra are typical of pseudo-tetrahedral Co(II) complexes [9, 10], showing two fairly intense bands, one in the visible,  $\nu_3$  (23–12 kK), and another in the near infrared,  $\nu_2$  (9–5 kK). In some complexes a third band,  $\nu_1$ ,

less intense than the other two and at lower energies ( $\sim 4$  kK), is also present.

Bands  $\nu_2$  and  $\nu_3$  show a structure which is believed to be mainly due to splitting of d orbitals caused by a lowering of symmetry [11–14] although spin-orbit coupling, vibronic coupling, Jahn-Teller distortion and mixing of states  $^2\text{G}$  and  $^4\text{P}$  may also contribute [15]. The highest energy component of band  $\nu_2$ , the most sensitive to the distortion in relation to Td

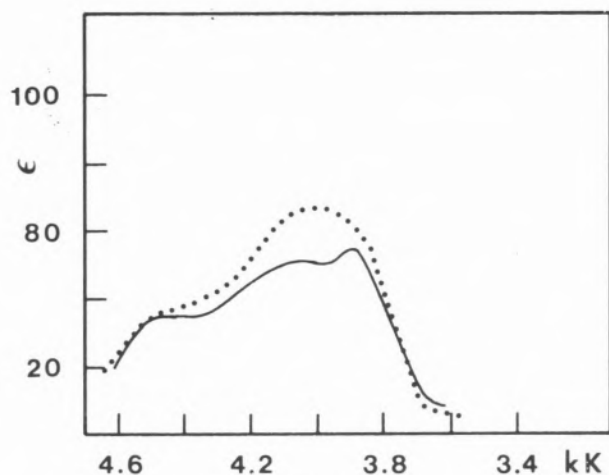


Fig. 2

...[( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> Mo-(S n-C<sub>14</sub>H<sub>29</sub>)<sub>2</sub>-Co Cl<sub>2</sub>] in dichloromethane  
 —[( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> W-(S n-C<sub>14</sub>H<sub>29</sub>)<sub>2</sub>-Co Cl<sub>2</sub>] in dichloromethane

symmetry [16] is not sensitive to the nature of substituent R in the spectra of complexes (I) and (III) even when R = *t*-C<sub>4</sub>H<sub>9</sub>.

Although the assignment of band  $\nu_1$  in Co(II) complexes has been disputed [17] there is ample evidence in the literature in favour of considering that band as arising from the d-d transition  ${}^4T_2(F) \leftarrow {}^4A_2$  which becomes allowed in symmetries lower than Td [18-22]. We base our assignment on the absence of such a band in the spectra of the free ligand [M( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(SR)<sub>2</sub>], on its low intensity and in the agreement between its energy and the value of

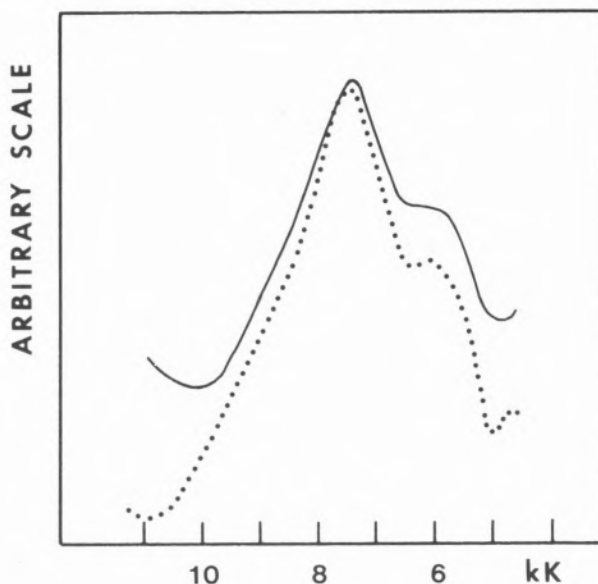


Fig. 3

Diffuse reflectance electronic spectra  
 —[( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> W-(S n-C<sub>14</sub>H<sub>29</sub>)<sub>2</sub>-Co Cl<sub>2</sub>]  
 ...[( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> Mo-(S n-C<sub>14</sub>H<sub>29</sub>)<sub>2</sub>-Co Cl<sub>2</sub>]

10 Dq calculated from  $\nu_2$  and  $\nu_3$ ; the agreement observed in this work being better than the one found by COFFEN and co-workers [19].

The gaussian decomposition of the bands was done by an approximate method; the areas were measured using a planimeter and the center of gravity of the bands was determined using a vectorial method.

Table 6

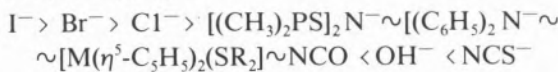
Ligand field parameters calculated from solution spectra for complexes [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>M-(SR)<sub>2</sub>-CoCl<sub>2</sub>] and [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>M-(SR)<sub>2</sub>-Co-(SR)<sub>2</sub>-M( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] X<sub>2</sub> and spin-orbit coupling constants ( $\lambda$ )

Complex	10 Dq (cm <sup>-1</sup> )	B (cm <sup>-1</sup> )	$\beta$	$\lambda$
[Cp <sub>2</sub> W-(S n-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> -Co Cl <sub>2</sub> ] <sub>2</sub>	4364	598	0,618	—
[Cp <sub>2</sub> W-(S s-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> -Co Cl <sub>2</sub> ]	4444	595	0,616	—
[Cp <sub>2</sub> W-(S t-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> -Co Cl <sub>2</sub> ]	4451	577	0,596	—
[Cp <sub>2</sub> W-(S n-C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> -Co Cl <sub>2</sub> ]	4071	629	0,650	166
[Cp <sub>2</sub> W-(S n-C <sub>6</sub> H <sub>13</sub> ) <sub>2</sub> -Co Cl <sub>2</sub> ]	4063	627	0,648	88
[Cp <sub>2</sub> W-(S n-C <sub>7</sub> H <sub>15</sub> ) <sub>2</sub> -Co Cl <sub>2</sub> ]	4092	629	0,650	—
[Cp <sub>2</sub> W-(S n-C <sub>14</sub> H <sub>29</sub> ) <sub>2</sub> -Co Cl <sub>2</sub> ]	4130	620	0,641	—
[Cp <sub>2</sub> Mo-(S n-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> -Co Cl <sub>2</sub> ]	4091	623	0,645	—
[Cp <sub>2</sub> No-(S s-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> -Co Cl <sub>2</sub> ]	4257	607	0,628	91
[Cp <sub>2</sub> Mo-(S n-C <sub>7</sub> H <sub>15</sub> ) <sub>2</sub> -Co Cl <sub>2</sub> ]	4064	605	0,626	—
[Cp <sub>2</sub> Mo-(S n-C <sub>14</sub> H <sub>29</sub> ) <sub>2</sub> -Cl <sub>2</sub> ]	4086	637	0,658	—
[ [Cp <sub>2</sub> W-(S CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> Co] Br <sub>2</sub> ]	4271	586	0,606	119
[ [Cp <sub>2</sub> W-(S CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> Co] I <sub>2</sub> ]	4045	757	0,781	165
[ [Cp <sub>2</sub> W-(S s-C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> ] <sub>2</sub> Co] I <sub>2</sub> ]	4041	550	0,568	—



The position of the center of gravity was found not to be sensitive to the solvent although the latter affects the resolution of the bands; a similar effect has been reported for cobalt complexes with substituted thioureas [23].

The spectral parameters were calculated using Tanabe-Sugano matrices [24, 25]. The values calculated are shown in Table 6. Although the values obtained for  $\lambda$  vary widely no conclusions can be drawn from this fact due to the approximate nature of 10Dq values and the considerable experimental error in the measurement of the magnetic susceptibilities both of which are used in the calculation of  $\lambda$ . However, the values obtained for  $\lambda$  are smaller than the value of the free ion ( $-178 \text{ cm}^{-1}$ ) as it was to be expected [10]. The parameters obtained for the trinuclear complexes (III) show that the «average field rule» used by DIAS [1a] is not in fact applicable here. On the basis of the 10Dq values calculated for the organometallic ligands  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SR})_2]$  we were able to place these ligands in the spectrochemical series:



The results described in Table 6 show that changing the substituent R ligands (II) does not change significantly the spectral parameters of the cobalt central atom.

A linear relationship for the values of  $(\nu_3 - \nu_2)$  in function of the values of B has been observed for cobalt complexes with thioureas and related ligands; although a simple explanation for this fact is not available, that relationship has been used to calculate approximate values of B, in a limited range of values of 10Dq [26]. Similar results were found for our compounds (figs. 4,5).

A more detailed treatment of the spectra now reported using the models of FLAMINI and co-workers [27] and of MENZEL and co-workers [28] for the calculation of parameters  $D_2$  and  $D_1$  is under way.

Graphical plot of  $(\nu_3 - \nu_2)$  vs B, for Co(II) complexes described in this work,  $\text{Co}(\text{L-L})\text{Cl}_2$

(L-L):

- 1,  $[\text{W Cp}_2(\text{Sn-C}_3\text{H}_7)_2]$ ; 2,  $[\text{Mo Cp}_2(\text{Sn-C}_3\text{H}_7)_2]$ ;
- 3,  $[\text{Mo Cp}_2(\text{Ss-C}_3\text{H}_7)_2]$ ; 4,  $[\text{W Cp}_2(\text{St-C}_4\text{H}_9)_2]$ ;
- 5,  $[\text{W Cp}_2(\text{Sn-C}_5\text{H}_{11})_2]$ ; 6,  $[\text{W Cp}_2(\text{Sn-C}_6\text{H}_{13})_2]$ ;
- 7,  $[\text{W Cp}_2(\text{Sn-C}_7\text{H}_{15})_2]$ ;
- 8,  $[\text{Mo Cp}_2(\text{Sn-C}_7\text{H}_{15})_2]$ ; 9,  $[\text{W Cp}_2(\text{Sn-C}_{14}\text{H}_{29})_2]$

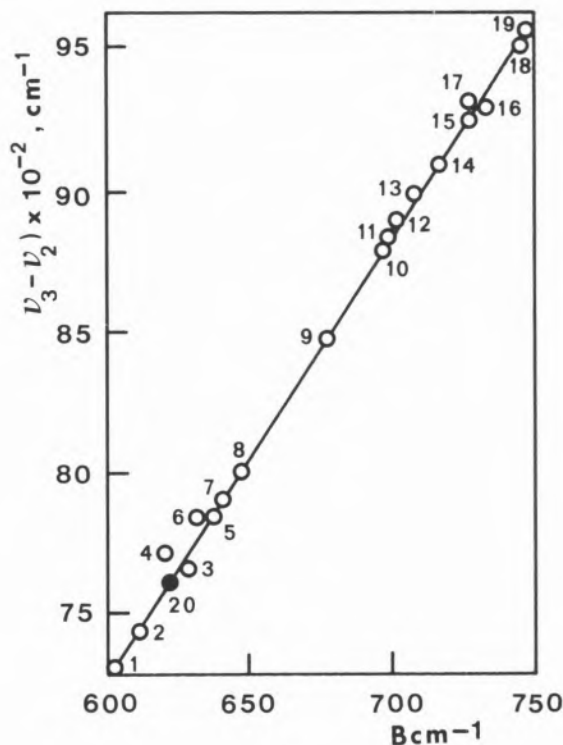


Fig. 4

Graphical plot of  $(\nu_3 - \nu_2)$  vs B' for tetrahedral Co(II) complexes of thiourea and related ligands [1,  $\text{Co}(\text{tu})_4(\text{ClO}_4)_2$ ; 2  $\text{Co}(\text{tac})_4(\text{ClO}_4)_2$ ; 3  $\text{Co}(\text{etu})_4(\text{ClO}_4)_2$ ; 4,  $\text{Co}(\text{tac})_2\text{I}_2$ ; 5,  $\text{Co}(\text{det})_4(\text{ClO}_4)_2$ ; 6,  $\text{Co}(\text{etu})_2\text{I}_2$ ; 7,  $\text{Co}(\text{dmt})_4(\text{ClO}_4)_2$ ; 8,  $\text{Co}(\text{tmt})_4(\text{ClO}_4)_2$ ; 9,  $\text{Co}(\text{etu})_2\text{Br}_2$ ; 10,  $\text{Co}(\text{tu})_2\text{Br}_2$ ; 11,  $\text{Co}(\text{dmt})_2\text{Br}_2$ ; 12,  $\text{Co}(\text{det})_2\text{Br}_2$ ; 13,  $\text{Co}(\text{tu})_2\text{Cl}_2$ ; 14,  $\text{Co}(\text{tac})_2\text{Br}_2$ ; 15,  $\text{Co}(\text{dmt})_2\text{Cl}_2$ ; 16,  $\text{Co}(\text{tac})_2\text{Cl}_2$ ; 17,  $\text{Co}(\text{tmt})_2\text{Br}_2$ ; 18,  $\text{Co}(\text{tmt})_2\text{Cl}_2$ ; 19,  $\text{Co}(\text{det})_2\text{Cl}_2$ ; 20,  $\text{Co}(\text{L-L})\text{Cl}_2$ ]

Abbreviations: tu = thiourea; tac = thioacetamide; dmt = N, N' — dimethylthiourea; det = N, N' — diethylthiourea; tmt = tetramethylthiourea; etu = ethylenethiourea and L — L =  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SR})_2]$ .

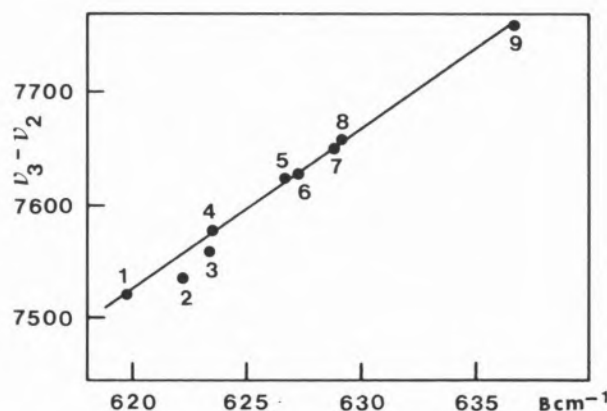


Fig. 5

## 4 — EXPERIMENTAL

All preparations and further manipulations were carried out under dinitrogen; tetrahydrofuran, toluene, petroleum ether, diethylether and dichloromethane were dried over sodium or calcium hydride and distilled just before use. The compounds  $[M(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_2]$  ( $M = \text{Mo}, \text{W}$ ) and  $[M(\eta^5\text{-C}_5\text{H}_5)_2\text{X}_2]$  ( $M = \text{Mo}, \text{W}$ ;  $\text{X} = \text{Cl}, \text{I}$ ) were prepared as described in the literature [29, 30].

$^1\text{H}$  n.m.r. spectra were determined on a JEOL JNM 100 PFT instrument. Infrared spectra were determined on a Perkin-Elmer 457 instrument in KBr pellets and were calibrated with polystyrene. Conductivity measurements were made at  $25^\circ\text{C}$  using a Radiometer CDM3 Conductivity Meter instrument calibrated with a standard KCl solution. Electronic spectra were measured in solution in a CARY 17 instrument; diffuse reflectance spectra were measured in a UNICAM SP 700 instrument. Magnetic susceptibility measurements were made by the Faraday method using a Gouy balance, type S.T.G.B., Newport Instruments, adapted with a D76762 accessory; calibration was done with purified Hg  $[\text{Co}(\text{NCS})_4]$ .

C, H, N and S analyses were carried out in this laboratory and at the Inorganic Chemistry Laboratory, Oxford. Metal analysis were carried out in this laboratory.

Typical preparations of the ligands  $[M(\eta^5\text{-C}_5\text{H}_5)_2(\text{SR})_2]$  and of the complexes  $[M(\eta^5\text{-C}_5\text{H}_5)_2(\text{SR})_2\text{-CoCl}]$  and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{SR})_2\text{-Co}(\text{SR})_2\text{-M}(\eta^5\text{-C}_5\text{H}_5)_2\text{X}_2]$  are described below:

a) *Preparation of  $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{S } n\text{-C}_3\text{H}_7)_2]$*

A suspension of  $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$  (0.8g) in ethanol ( $30\text{ cm}^3$ ) was added to an aqueous solution ( $10\text{ cm}^3$ ) of sodium hydroxide (2g) and was followed by the addition of *n*-propanethiol (0.32g). The mixture was stirred and refluxed for 30 m giving a red solution. The solvent was removed under vacuum, the brown residue was dissolved in the minimum amount of dichloromethane and chromatographed on an alumina column using dichloromethane/acetone (6:4) as the eluent; the main band (brown) was collected, filtered and the solvent was removed under vacuum giving a crystalline golden brown solid. This was re-

crystallised from dichloromethane/petrol ether, washed with ether and dried under vacuum. Yield *ca.* 70%.

b) *Preparation of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{S } n\text{-C}_3\text{H}_7)_2\text{-CoCl}]$*

A pre-filtered solution of  $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{S } n\text{-C}_3\text{H}_7)_2]$  (0.5 g;  $1.03 \times 10^{-3}$  mol) in absolute ethanol ( $30\text{ cm}^3$ ) was slowly added to a stirred solution of anhydrous cobalt chloride (0.14 g,  $1.03 \cdot 10^{-3}$  mol) in the same solvent ( $30\text{ cm}^3$ ) which had also been previously filtered.

During the addition dark green crystals precipitated; as there were too insoluble to be recrystallised they were rinsed with ethanol, dichloromethane and ether and were dried under vacuum. Yield *ca.* 70%.

c) *Preparation of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_3)_2\text{-Co}(\text{SCH}_3)_2\text{-W}(\eta^5\text{-C}_5\text{H}_5)_2]\text{Cl}_2$*

A pre-filtered solution of  $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SCH}_3)_2]$  (0.5 g  $1.2 \cdot 10^{-3}$  mol) in dichloromethane ( $15\text{ cm}^3$ ) was added to a stirred solution of  $[\text{N}(\text{C}_2\text{H}_5)_4]_2[\text{CoCl}_4]$  (0.18 g  $0.6 \times 10^{-3}$  mol) in the same solvent ( $10\text{ cm}^3$ ). During the addition brown crystals precipitated which were thoroughly washed with dichloromethane and ether and were dried under vacuum. Yield *ca.* 50%.

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## RESUMO

Descreve-se a síntese, espectros electrónicos e propriedades magnéticas de alguns complexos binucleares de fórmula geral  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{SR})_2\text{-Co X}_2]$  e dos complexos trinucleares de fórmula geral  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{SR})_2\text{-Co}(\text{SR})_2\text{-M}(\eta^5\text{-C}_5\text{H}_5)_2] \text{ X}_2$ . Conclui-se que a natureza do substituinte R não afecta aprecia-velmente os espectros electrónicos do átomo central de Co(II).