SYNTHESIS AND CHARACTERIZATION OF MIXED CYANOTHIOCYANATE AND CYANOSELENOCYANATE COMPLEXES OF BIS(CYCLOPENTADIENYL)-TITANIUM, -VANADIUM AND -CHROMIUM

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Summary

The complexes $(\eta\text{-}C_5H_5)_2Ti(CO)_2$ and $(\eta\text{-}C_5H_5)_2M$, (M = V, Cr) react with $(SeCN)_2$ to give the isoselenocyanide complexes $(\eta\text{-}C_5H_5)_2M(NCSe)_2$, (M = Ti, V, Cr), but with $X(CN)_2$, (X = Se, S) they give the mixed complexes $(\eta\text{-}C_5H_5)_2$-$M(CN)(NCX)$, (M = Ti, V, Cr; X = S, Se). All the compounds have been characterized by elemental analyses, magnetic moments, and IR and EPR spectra.

Introduction

Because of their particular electronic properties (low oxidation level in the metal and less than 18 e^- in its environment), the title cyclopentadienyls react very readily with pseudohalogens, and oxidation at the metal takes place. Thus, oxidative addition of $(SCN)_2$ to $(\eta\text{-}C_5H_5)_2M$, (M = V, Cr) forms $(\eta\text{-}C_5H_5)_2V(NCS)_2$ and $(\eta\text{-}C_5H_5)_2Cr(NCS)(SCN)$, respectively [1]. Again, cyanogen halides XCN (X = Br, I), readily replace the carbonyl ligands of $(\eta\text{-}C_5H_5)_2Ti(CO)_2$ to give the mixed halocyanide complexes $(\eta\text{-}C_5H_5)_2TiX(CN)$, (X = Br, I) [2]. Furthermore, oxidative addition of $S(CN)_2$ to complexes of d^8 electronic configuration, gives mixed cyanothiocyanate complexes [3].

Results and discussion

Addition of ethereal solutions of $(SeCN)_2$ and $X(CN)_2$ (X = Se, S) to solutions of $(\eta\text{-}C_5H_5)_2Ti(CO)_2$ under N_2 causes loss of carbon monoxide and formation, in quantitative yield, of solids, which were shown to be $(\eta\text{-}C_5H_5)_2Ti(NCSe)_2$ (already known [4]), and $(\eta\text{-}C_5H_5)_2Ti(CN)(NCX)$ (X = Se, S).

Similarly, addition of ethereal solutions of the same pseudohalogens, to ethereal solutions of $(\eta\text{-}C_5H_5)_2M$ (M = V, Cr) causes precipitation of solids,

which have been shown to be $(\eta\text{-}C_5H_5)_2V(NCSe)_2$ (previously prepared by another method [5]), $(\eta\text{-}C_5H_5)_2Cr(NCSe)(SeCN)$, and $(\eta\text{-}C_5H_5)_2M(CN)(NCX)$ (X = Se, S).

In Tables 1 and 2 we list some IR data for the synthesized compounds, with corresponding assignments, based on the assumption of a distorted tetrahedral symmetry of the ligands, C_{2v} or C_s depending on the case. The spectra show the characteristic bands of the cyclopentadienyl ligands at 3100, 1400, 1100, 1000 and 800 cm^{-1}; some of them (especially those corresponding to ωCC, δCH and γCH) appear as doublets, owing to a decrease in the symmetry with respect to the corresponding bis(cyclopentadienyl) belonging to the D_{5d} group. This decrease in symmetry implies the change of degenerate species (E) into non-degenerate species (A, B and A', A''). The presence and frequencies of these bands indicate that the cyclopentadienyl rings are π-bonded [6]. Furthermore, the presence of the band at 1100 cm^{-1}, corresponding to γCH, indicates that no substitution has taken place in the cyclopentadienyl rings.

The characteristic bands of the NCX (X = Se, S) ligands are listed in Table 3. The frequencies of these bands indicates [7,8] that in most cases the pseudohalide ligand is coordinated by the N atom. This is confirmed by measurement

TABLE 1

IR SPECTRA OF BIS(SELENOCYANATE) COMPLEXES [a]

Abbreviations: R = η-C$_5$H$_5$; vs = very strong; s = strong; m = medium; w = weak; o.p. = out-of-phase; i.p. = in-phase.

R$_2$Ti(NCSe)$_2$ (C_{2v})		R$_2$V(NCSe)$_2$ (C_{2v})		R$_2$Cr(NCSe)(SeCN) (C_s)		Assignment
3100m	A$_1$	3090m	A$_1$	3090m	A'	νCH
2050vs	B$_1$	2083vs	B$_1$	2120s	A'	νCN o.p. or νCN of MSCN
2015vs	A$_1$	2065vs A	A$_1$	2042vs		νCN i.p. or νCN of MNCN
1440m		1440m		1438m		
	B$_2$ + A$_1$		B$_2$ + A$_1$		A' + A'	ωCC
1435m		1420m		1423m		
1125w	A$_1$	1120w	A$_1$	1150w	A'	γCH
1071w	B$_2$	1070w	B$_2$			γCH
1022m		1020m		1015m		
	B$_2$ + A$_1$		B$_2$ + A$_1$		A' + A''	δCH
1010m		1002m		1003m		
838vs		834vs		839vs		
820s	B$_1$ + A$_1$	827s	B$_1$ + A$_1$	819vs	A' + A''	γCH
700w						
620w	B$_1$	620w	B$_1$	590w		
593w	A$_1$	596w	A$_1$			νCSe
				540w		νCSe of MSeCN
457w	B$_1$	472w	B$_1$	440w		δNCSe
448w	A$_1$	450w	A$_1$			
420m	B$_2$	425w	B$_2$	420w	A'	π_{as}R
397m	B$_2$	395m	B$_2$	392w	A''	ν_{as}MR
352m	B$_1$	360w	B$_1$	350w	A'	νMN
252w	A$_1$	262w	A$_1$	306w	A'	ν_sMR
230w	A$_1$	240m	A$_1$	240m	A'	π_sR
178m	B$_1$	167m	B$_1$	180w	A'	δMNCSe

[a] Data in cm^{-1}.

TABLE 2

IR SPECTRA OF MIXED COMPLEXES [a]

Abbreviations: R = η-C_5H_5; X = S, Se; vs = very strong; s = strong; m = medium; w = weak; sh = shoulder.

R₂Ti(CN)(NCSe)	R₂V(CN)(NCSe)	R₂Cr(CN)(NCS)	R₂Ti(CN)(NCS)	R₂V(CN)(NCS)	R₂Cr(CN)(NCS)	Assignment	C_s
3110m	3100m	3092m	3100m	3100m	3090m	νCH	A'
2080m	2120m	2118m	2082m	2122m	2121m	νCN	A'
2035vs	2060vs	2040vs	2020vs	2057vs	2040vs	νCN(XCN)	A'
1440m	1445m	1440m	1438m	1442m	1440m ⎫	ωCC	A' + A''
1430m	1435m	1432m	1430m	1431m	1434m ⎭		
1140w	1120w	1140w	1135w	1120w	1160w	γCH	A'
1070w	1070w	1050w	1070w	1068w	1070w	γCH	A'
1014(sh)	1018m	1005m	1015(sh)	1020m	1015m ⎫		
1008m	1003m		1010m	1008m	1005m ⎭		
820vs	838vs	850(sh)	820vs	840vs	835(sh) ⎫	δCH	A' + A''
740s		832(sh)			820vs ⎭	γCH	A' + A''
		820vs					
593w	620w	560w				νCSe	A'
450w	458w	460w	484w	472w	480w	δNCX	A'
420w	425w	440w		428w	435w	π_{as}R	A''
392m	395m	415w	400m	397m	415m	ν_{as}MR	A''
370w	356w	400w	372m	367w	400w	νMCN	A'
350m	330m	348w	350w	320w	362w	νMNCX	A'
282w	290w	306w	290w	282(sh)	302(sh)	ν_sMR	A'
218w		240w	260w	250w		π_sR	A'
170w	170w	178w	180w	186w	176w	δMNCX	A'

[a] Data in cm^{-1}.

TABLE 3

IR BANDS OF XCN LIGANDS [a]

Compounds	νCX	δNCX	νCN	CN of XCN	
				Nujol [b]	CH$_2$Cl$_2$ solution
R$_2$Ti(NCSe)$_2$	600	457		2050(2.4)	2050
	593	448		2015(2.3)	2015
R$_2$Ti(CN)(NCSe)	593	450	2080	2035(2.4)	2030
R$_2$Ti(CN)(NCS)	c	428	2082	2020(2.4)	2018
R$_2$V(NCSe)$_2$	620	472		2083(1.8)	2080
	596	450		2065(1.9)	2063
R$_2$V(CN)(NCSe)	620	458	2120	2060(1.7)	2060
R$_2$V(CN)(NCS)	c	472	2122	2057(1.7)	2057
R$_2$Cr(NCSe)(SeCN)	590	435		2120(0.4)	2122
	540	425		2042(1.8)	2038
R$_2$Cr(CN)(NCSe)	590	460	2118	2040(1.8)	2038
R$_2$Cr(CN)(NCS)	c	473	2121	2040(1.7)	2040

[a] Data in cm^{-1}; R = η-C$_5$H$_5$. [b] In parenthesis the internal standard ratio determined by Bayley method [9].
[c] νCS obscured by cyclopentadienyl absorption.

of the internal standard ratio of the band corresponding to νCN of XCN in the solid state, using salicylic acid as standard [9].

The IR spectra of (η-C$_5$H$_5$)$_2$Ti(NCSe)$_2$ and (η-C$_5$H$_5$)$_2$V(NCSe)$_2$ are identical to the ones described by other authors [4,5]. Each of the compounds contains two NCSe ligands, giving rise to identical vibrational modes. These modes may be in phase or out of phase, thus explaining the presence of separated bands corresponding to νCN and νCSe (see Table 3). In the complexes with thiocyanate ligands the bands corresponding to νCS are masked by the strong absorption corresponding to γCH in the 800 cm^{-1} region.

In contrast to the Ti and V derivatives, (η-C$_5$H$_5$)$_2$Cr(NCSe)(SeCN) shows in the range 2000—2200 cm^{-1} (Fig. 1) a sharp band with medium intensity at 2120 cm^{-1}, and another one broad and very strong band at 2042 cm^{-1}. The internal standard ratios of these bands are given in Table 3. This result can be explained by assuming that one of the selenocyanate ligands is coordinated through the Se atom and the other through the N atom. Thus the bands which appear at 2120 cm^{-1} (νCN) and 540 cm^{-1} (νCSe) correspond to the M—SeCN group and those which appear at 2042 cm^{-1} (νCN) and 590 cm^{-1} (νCSe) to M—NCSe. Similar effects are found in (η-C$_5$H$_5$)$_2$Cr(NCS)(SCN), which was synthesized from bis(cyclopentadienyl)chromium(II) and (SCN)$_2$ [1].

The stretching and bonding vibrations of the metal—ligand bonds are expected to lie in the range 500—20 cm^{-1}. In the compounds we have made the bands corresponding to ν_{as} MR appear between 415—390 cm^{-1}. That is, they are at higher frequencies than in the corresponding original bis(cyclopentadienyl) compounds owing to the increase of the oxidation level of the metal and to the higher number of electrons surrounding it.

Bands corresponding to ν_sMR [10] appear in the range 300—250 cm^{-1}; those corresponding to νMCN and νMNCX (X = Se, S) are found in the range 320—400 cm^{-1} [11]. In the complexes of general formula (η-C$_5$H$_5$)$_2$M(NCX)$_2$, νMNCX a band of medium intensity appears in the range 300—350 cm^{-1}. But in the spec-
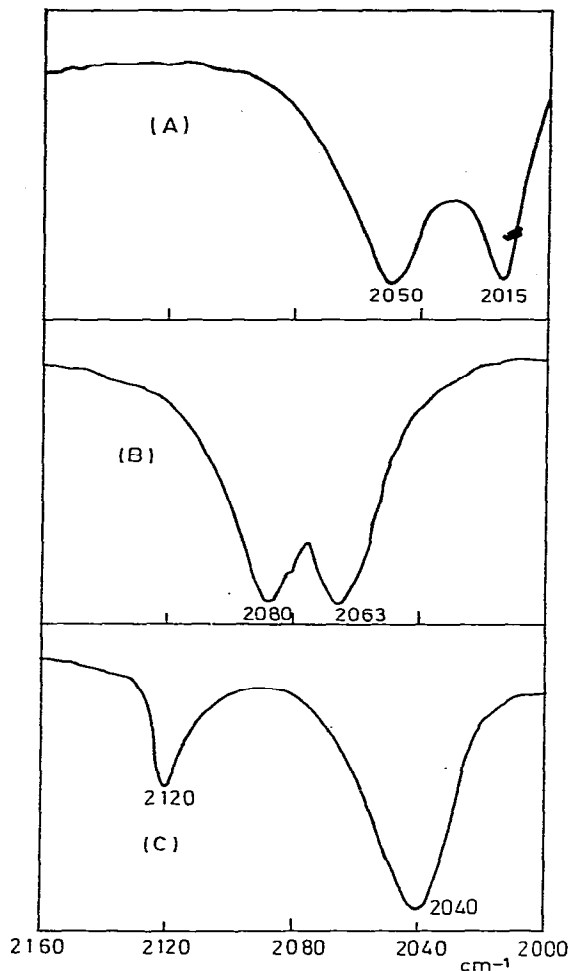
Fig. 1. νCN bands of (A) (η-C$_5$H$_5$)$_2$Ti(NCSe). (B) (η-C$_5$H$_5$)$_2$V(NCSe)$_2$. (C) (η-C$_5$H$_5$)$_2$Cr(NCSe)(SeCN).

tra of the mixed (η-C$_5$H$_5$)$_2$M(CN)(NCX) complexes two bands appear in the range 320—400 cm^{-1}, and these must arise from νMCN and νMNCX.

In other mixed complexes of this type [12—14], the sequence of frequencies is: νMCN > νMNCS > νMNCSe; we have therefore assigned the highest frequency in this range to νMCN and the lowest to νMNCX.

A band with medium intensity appears in the range 180—170 cm^{-1} and we assign it to δMNCX following the same kind of reasoning previously reported [1]. This assignment is only tentative because of the limited available data for this range of the spectra.

The magnetic moments (see Experimental) of the complexes we have synthesized, as well as the EPR spectra show that the metal is in a formal tetravalent positive oxidation state. The EPR spectra of the vanadium(IV) complexes in chloroform solution, at room temperature show eight lines, due to the coupling of the non-paired electron with the ^{51}V (I = 7/2) nucleus. These spectra can be

explained using the spin Hamiltonian:

$$\hat{H} = g\beta H \cdot \hat{S}_z + AI_z\hat{S}_z \tag{1}$$

for systems with $S = \frac{1}{2}$, and applying the 2nd order correction [15]. The spectra of these complexes in mixtures of CHCl$_3$/EtOH at $-160°$C are shown in Fig. 2, and can be interpreted by use of the equation obtained by Stewart and Porte [16]. The parameters of the spin Hamiltonian (1) are shown in Table 4. The value of $g_z \approx 2000$ indicates that the molecule essentially has a fundamental state d_z2. The hyperfine coupling constant A values can be used as a measurement of the metal—ligand bond covalency [17], because A decreases when covalency increases; this means that when we replace a NCX ligand in $(\eta\text{-}C_5H_5)_2$-V(NCX)$_2$ (X = Se, S) by a CN ligand, the covalent character of the bond increases, because A decreases (see Table 4). Similar behaviour was noted previously for complexes of the type $(\eta\text{-}C_5H_5)_2$VX(CN) (X = CN, Cl, Br, I) [1].

The EPR spectra of the chromium(IV) complexes, in chloroform solution at $-170°$C show an intense signal at about 3300 G, corresponding to the $\Delta m = 1$ transition, and a very weak signal at lower values of the magnetic field (1600 G) corresponding to the forbidden transition $\Delta m = 2$. The g values and the line widths are given in Table 5. These spectra are similar to those observed for chromium(IV) complexes [19,20]. In general, the EPR spectra for these d^2 ions can be interpreted using the spin Hamiltonian:

$$H = \beta H g \cdot S + D(S_z2 - 2/3) + E(S_x2 - S_y2)$$

where D and E are the zero field splitting parameters.

In our complexes a single very narrow (≈ 20 G) signal appears at 3300 G, and that indicates that D and E values must be very small.
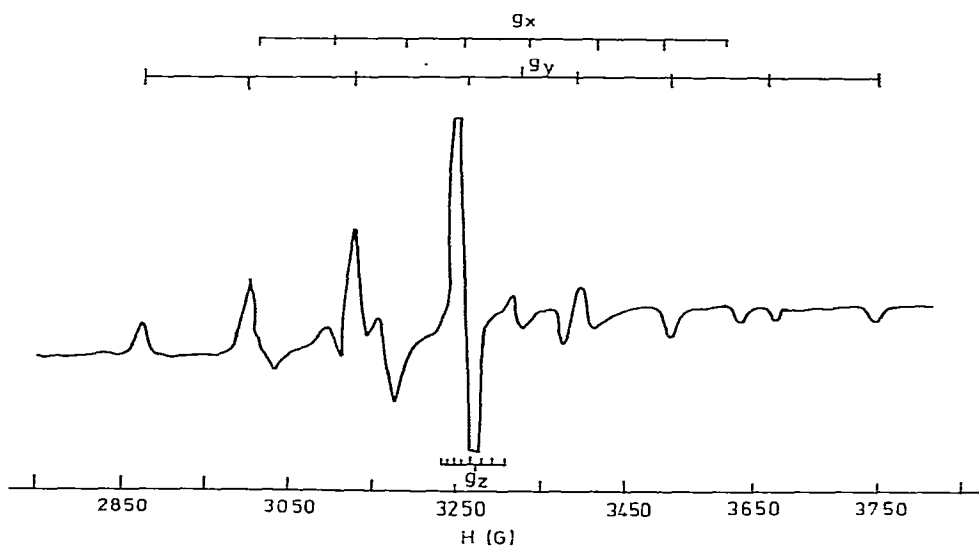

Fig. 2. EPR spectra of a solution of $(\eta\text{-}C_5H_5)_2$V(NCSe)$_2$, in CHCl$_3$/EtOH glass (9/1) at $-160°$C.

TABLE 4

EPR SPECTRA OF VANADIUM(IV) COMPLEXES ı

	g_{iso}	A_{iso}[b]	A_x[b]	A_y[b]	A_z[b]	g_x	g_y	g_z
$(\eta\text{-}C_5H_5)_2V(NCSe)_2$	1.981	68.35	69.5	107.8	31.7	1.985	1.957	2.000
$(\eta\text{-}C_5H_5)_2V(CN)(NCSe)$	1.983	53.69	60.1	103.0	11.2	1.982	1.970	2.000
$(\eta\text{-}C_5H_5)_2V(CN)(NCS)$	1.981	55.49	58.3	95.8	12.1	1.985	1.956	2.000
$(\eta\text{-}C_5H_5)_2V(NCS)_2$ [a]	1.982	68.6	71.2	115.3	19.2	1.988	1.958	2.000

[a] Data from Stewart and Porte [18]. [b] $\times 10^{-4}$ cm^{-1}.

TABLE 5

EPR SPECTRA OF CHROMIUM(IV) COMPLEXES AT $-160°C$

	$\Delta m = 1$			$\Delta m = 2$		
	g_{iso}	H	line width [a]	g	H	line width [a]
$(\eta\text{-}C_5H_5)_2Cr(NCSe)(SeCN)$	1.996	3275	20	3.922	1667	15
$(\eta\text{-}C_5H_5)Cr(CN)(NCSe)$	1.991	3272	23	3.939	1660	12
$(\eta\text{-}C_5H_5)Cr(CN)(NCS)$	1.996	3275	20	3.915	1670	10

[a] In gauss.

Experimental

All reactions were carried under oxygen-free N_2. The cyclopentadienyls $(\eta\text{-}C_5H_5)_2Ti(CO)_2$ [21] and $(\eta\text{-}C_5H_5)_2M$ (M = V, Cr) [22], and the pseudohalogens $(SeCN)_2$ [23], $Se(CN)_2$ [24] and $S(CN)_2$ [25] were made by the methods described in the references cited.

Ti and Se were determined gravimetrically and V and Cr spectrophotometrically.

The IR spectra were recorded at 4000—200 cm^{-1} on a Perkin—Elmer Model 225, using mulls of Nujol and Hostaflon between CsI windows. In the range of the stretching vibrations νCN, scale expansions of five and ten times were used. The internal standard ratio of the νCN band was determined by Bayley's method [9]. The spectra in the range 500—200 cm^{-1} were also recorded on a Beckman IR-720 interpherometer using polyethylene pellets.

Attempts were made to record Raman spectra using a He—Ne laser, but all samples were decomposed by the radiation even when a rotatory cell was used.

The EPR spectra were recorded at room temperature and at $-160°C$ using CHCl$_3$ or 9/1 CHCl$_3$/EtOH as solvents, on a Varian E-12 at a microwave frequency of 9 GHz (X band) with DPPH for calibration, the solution being placed in a quartz-glass sample tube of 4 mm diameter.

The magnetic moments were obtained by determination of the magnetic susceptibilities in a Gouy's magnetic balance, in the solid state at room temperature, [Ni(en)$_3$]S$_2$O$_3$ being used as standard. The diamagnetic corrections were taken from Selwood [26] and Earnshaw [27].

Preparation of (η-C₅H₅)₂Ti(NCSe)₂

In a 100 ml two-neck flask fitted with N_2 inlet, magnetic stirrer, and pressure-equalized dropping funnel, 1 g (4.2 mmol) of (η-C₅H₅)₂Ti(CO)₂ is dissolved in 50 ml of anhydrous diethyl ether saturated with N_2 free of oxygen and cooled at $-20°$C. A solution of 0.9 g (4.5 mmol) of (SeCN)₂ in 20 ml diethyl ether is slowly added dropwise. A dark green solid immediately appears, and evolution of CO is observed. The solid is filtered off on a cooled sintered glass disc ($-20°$C), washed several times with cooled diethyl ether, and dried in high vacuum. Anal.: Found: C, 36.50; H, 2.21; N, 6.82; Se, 39.87; Ti, 11.97. Calcd. for $C_{12}H_{10}N_2Se_2Ti$: C, 37.11; H, 2.57; N, 7.21; Se, 40.72; Ti, 12.37%.

Preparation of (η-C₅H₅)₂Ti(CN)(NCSe)

Following the procedure described above, 1 g (4.2 mmol) of (η-C₅H₅)₂Ti(CO)₂ is dissolved in 50 diethyl ether and a solution of 0.56 g (4.5 mmol) of Se(CN)₂ in 10 ml diethyl ether is added. A brown solid is obtained. Anal.: Found: C, 45.86; H, 3.12; N, 9.08; Se, 25.30; Ti, 14.97. Calcd. for $C_{12}H_{10}N_2SeTi$: C, 46.40; H, 3.23; N, 9.36; Se, 25.56; Ti, 15.53%.

Preparation of (η-C₅H₅)₂Ti(CN)(NCS)

The reaction is carried out as above with 1 g (4.2 mmol) of (η-C₅H₅)₂Ti(CO)₂ and 0.4 g (4.5 mmol) of S(CN)₂. A dark brown solid is obtained. Anal.: Found: C, 54.35; H, 3.24; N, 10.12; S, 11.96; Ti, 17.86. Calcd. for $C_{12}H_{10}N_2STi$: C, 54.96; H, 3.81; N, 10.68; S, 12.21; Ti, 18.34%.

Preparation of (η-C₅H₅)₂V(NCSe)₂

A similar procedure was used with 1 g (5.5 mmol) of (η-C₅H₅)₂V in 50 ml diethyl ether and 1.2 g (5.7 mmol) of (SeCN)₂ in 20 ml diethyl ether. The brown solid which immediately appears is filtered off on a cooled sintered glass disc ($-20°$C), washed several times with diethyl ether, and dried in high vacuum. Anal.: Found: C, 36.23; H, 2.16; N, 6.98; Se, 39.87; V, 12.62. Calcd. for $C_{12}H_{10}N_2Se_2V$: C, 36.82; H, 2.25; N, 7.16; Se, 40.40; V, 13.04%. $\mu_{eff.}$ = 1.67 BM (χ_{corr}^{mol} = 1.161).

Preparation of (η-C₅H₅)₂V(CN)(NCSe)

Similarly 1 g (5.5 mmol) of (η-C₅H₅)₂V reacts with 0.74 g (5.7 mmol) of Se(CN)₂ to give a dark brown solid. Anal.: Found: C, 45.89; H, 2.98; N, 8.62 Se, 24.78; V, 15.71. Calcd. for $C_{12}H_{10}N_2SeV$: C, 46.15; H, 3.20; N, 8.97; Se, 25.34; V, 16.36%. $\mu_{eff.}$ = 1.68 BM, (χ_{corr}^{mol} = 1.175).

Preparation of (η-C₅H₅)₂V(CN)(NCS)

Similarly 1 g (5.5 mmol) of (η-C₅H₅)₂V and 0.47 g (5.7 mmol) of S(CN)₂ give a green solid. Anal.: Found: C, 53.97; H, 3.12; N, 9.86; S, 11.92; V, 18.36. Calcd. for $C_{12}H_{10}N_2SV$: C, 54.33; H, 3.77; N, 10.56; S, 12.07; V, 19.24%. $\mu_{eff.}$ = 1.65 BM (χ_{corr}^{mol} = 1.133).·

Preparation of (η-C₅H₅)₂Cr(NCSe)(SeCN)

Similarly 1 g (5.4 mmol) of (η-C₅H₅)₂Cr and 1.21 g (5.8 mmol) of (SeCN)₂ give a red-brown solid. Anal.: Found: C, 36.12; H, 2.23; N, 6.98; Se, 39.72; Cr,

12.87. Calcd. for $C_{12}H_{10}N_2Se_2Cr$: C, 36.73; H, 2.55; N, 7.14; Se, 40.30; Cr, 13.26%. $\mu_{eff.}$ = 2.68 BM (χ_{corr}^{mol} = 2.988).

Preparation of (η-C_5H_5)$_2$Cr(CN)(NCSe)

Use of 1 g (5.4 mmol) of (η-C_5H_5)$_2$Cr and 0.75 g (5.8 mmol) of Se(CN)$_2$ gives a grey solid. Anal.: Found: C, 45.41; H, 3.02; Cr, 15.98; N, 8.61; Se, 24.89. Calcd. for $C_{12}H_{10}CRN_2Se$: C, 46.00; H, 3.19; Cr, 16.61; N, 8.94; Se, 25.23%. $\mu_{eff.}$ = 2.62 BM. (χ_{corr}^{mol} = 2.855).

Preparation of (η-C_5H_5)$_2$Cr(CN)(NCS)

Use of 1 g (5.4 mmol) of (η-C_5H_5)$_2$Cr and 0.48 (5.8 mmol) of S(CN)$_2$ gives a blue-green solid. Anal.: Found: C, 53.86; H, 3.27; Cr, 18.92; N, 10.12; S, 11.84. Calcd. for $C_{12}H_{10}CrN_2S$: C, 54.13; H, 3.75; Cr, 19.54; N, 10.52; S, 12.03%. $\mu_{eff.}$ = 2.66 BM (χ_{corr}^{mol} = 2.943).

All the compounds are aire stable.

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