

Table 1 SI
 Frequency data and assignment of the vibrational modes of [Cp₂Co][EL₆] complexes, according to Ref. 11

		(1) [Cp ₂ Co][PF ₆]		(2) [Cp ₂ Co][AsF ₆]		(3) [Cp ₂ Co][SbF ₆]		(6) [Cp ₂ Co] ₃ [Co(CN) ₆] ^b	
		Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman
A _{1g}	v(CH)		3135 m		3131 m		3129m		3135 m
A _{2u}	v(CH)	3129 m		3127 m		3124 m		3132 m	
E _{1u}	v(CH)	3129 m		3119 mw		3124 m		3122 m	
E _{1g}	v(CH)		3119 mw		3116 mw		3113 mw		3115 mw
E _{2g}									3121 w
E _{1g}	v(CC)		1421 m		1425, 1421 m		1424 sh, 1422m		1419 m
E _{1u}	v(CC)	1418 s		1417ms		1417 s		1417 m	
E _{2g}	v(CC)		1362 w		1368 w		1369 w		
A _{2u}	v(CC)	1116 vw		1115 vw		1115 w			
A _{1g}	v(CC)		1113 vs		1112 s	1111 w	1111s		1112 s
E _{2g}	δ(CH)		1077 wsh, 1070 m	1072 vw	1078 mw	1072 mw	1074 mw		1061 m
E _{2u}	δ(CH)	1062 mw		1059 vw		1059 w			
E _{1u}	δ(CH)	1012 m		1014 mw		1014 ms		1008 m	
E _{1g}	δ(CH)		1010 w		1018 w, 1013 w		1017w , 1012w		1008 w
E _{2g}	γ(CH)		947 vw	945 vw	946 vw	945 w	947 vw		

E_{1u}	$\gamma(\text{CH})$	909 m, 900 m		902 vw, 893 vw		903 sh, 895 mw		897 mw	
A_{2u}	$\gamma(\text{CH})$	870 ms		869 ms		869 s		863 s	
E_{1g}	$\gamma(\text{CH})$		857 w, 854 w		858 w		861sh, 857w		
A_{1g}	$\gamma(\text{CH})$		851 w		849w		849 w		854 w
E_{1u}	tilt (CpCoCp)	505 w		507 mw		507 ms			
A_{2u}	ν (CpCoCp)	457 m		464 ms		460 s			
E_{1g}	tilt (CpCoCp)		393 m, 387 m		393 m,		391m, 382mw		388 ms
A_{1g}	ν (CpCoCp)		317 s	323	321 vs		319vs		317 s
A_{1g}	$\nu(\text{E-F})$		741 m		681 mw		645mw		
T_{1u}	$\nu(\text{E-F})$	833 vs vbr		700 s, 691 s		659, 653 vs			
E_g	$\nu(\text{E-F})$		573, 570 vw		580 mw		579vw, br		
T_{1u}	$\delta(\text{E-F})$	557 s		397 vs		176 sh 172 (ATR)			
T_{2g}	$\delta(\text{E-F})$		470 w		382 m	276	278mw		
?	?	375							
?	?		288 vw			290w			
E_{1u}	bend (CpCoCp)	179ms, 172 sh (ATR)		179, 175 (ATR)					155
?	?	68 (ATR)							
?	?	57 (ATR)		57 (ATR)					
?	?				97				
?	?				61				

?	?			78, 66 (ATR)					
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b) 2185 s R 2165 m R 2158 m ir (v(CN)) 566 m ir 501 m ir 456 m ir 433 s br ir 444 vw R ((v(Co-CN) e def. (Co-C-N))

Table 2SI

Frequency data and assignment of the vibrational modes of other [Cp₂Co][X] complexes, according to Ref. 11

		(4) [Cp ₂ Co][I]		(5) [Cp ₂ Co][I ₃]		(7) [Cp ₂ Co][Co(CO) ₄] ^a		(8) [Cp ₂ Co][Br ₃] ^b		(9) [Cp ₂ Co][FeI ₄] ^c		(10) [Cp ₂ Co][HCl ₂]	
		Ir ^a	Raman	Ir ^a	Raman	Ir ^a	Raman	Ir ^a	Raman	Ir	Raman	Ir	Raman
A _{1g}	ν(CH)		3096 mw		3102 w		3129 mw		3109mw		3107 mw		3113 mw
A _{2u}	ν(CH)	3083 sh		3092 s		3128 w		3097w		3095 mw		3095 s	
E _{1g}	ν(CH)		3060 mw		3085 vw		3112 w		3091 mw		3090 w		3087 vw sh
E _{1u}	ν(CH)	3054 s		3092		3120 mw		3097 w		3095 mw		3095 s	
E _{2g}	ν(CH)						3120 w				3097 w		3092 vw sh
E _{1g}	ν(CC)		1419 w		1416 vw		1422 m		1416 m		1413 vw		1420 w
E _{1u}	ν(CC)	1410 s		1408 s		1417 s		1410 s		1408 vs		1413 vs	
E _{2g}	ν(CC)		1362 vw	1353 mw br	1362 vw	1348 w	ca 1358 w br		1353 w		1364 vw		1365 vw
A _{2u}	ν(CC)	1114 s		1113 mw		1115 w		1111 w		1111 w		1113 m	
A _{1g}	ν(CC)		1109 s		1108 w		1111 s		1108 s		1111 m		1110 s
E _{2g}	δ(CH)		1052 w		1063 vw		1065 m		1069 m		1061 m		1077 w 1070 w
E _{2u}	δ(CH)	1062 m		1056 w		1062 mw		1054 w		1059 w 1046 w			
E _{1u}	δ(CH)	1002 s		1005 s		1014 m 1010 m		1007 ms		1004 vs		1008 w	
E _{1g}	δ(CH)		1004 mw		1006 vw		1015 mw 1010 mw		1008 w		1006 vw		1007 vw
E _{2g}	γ(CH)		953 vw		939 vw			945 w	947 w		938 vw		

E_{1u}	$\gamma(\text{CH})$	855 s		858 m		896 w		893 m		884 m		899 vw	
A_{2u}	$\gamma(\text{CH})$	818 ms		823 mw		861 s		862 s		853 w 845 w		863 s 853 s	
E_{1g}	$\gamma(\text{CH})$		872 w		864 vw				854 w		888 m		
A_{1g}	$\gamma(\text{CH})$		852 w		849 vw	834 m ?	849 w		849 w		862 m 848 m		854 vw 849 vw
E_{1u}	tilt (CpCoCp)	499 s		502 mw				503 ms		502 mw		501 m 497 sh	
A_{2u}	$\nu(\text{CpCoCp})$	458 vs		461 vs				464 ms		467 vs		465 s 461 s	
E_{1g}	tilt (CpCoCp)		394 m		396 w				401 m		391 sh 382 m		392 mw 384 mw
A_{1g}	$\nu(\text{CpCoCp})$		326 vs		325 s		320 vs		329 vs		327 vs		319 vs

a) 2002 mw, 1898 vs br, 1879 vs br, 1863 vs br, 1846 m (Ir); 2000 ms, 1914 s, 1878 s, 1870 s (Raman) $\nu(\text{C-O})$; 557 s sh, 554 s, 502 m, 455 ms (Ir); 522 mw, 436 s, 398 m, 386 s (Raman): $\nu(\text{Co-CO})$; def. (Co-C-O)

b) 203 m, 159 vs (Raman): $\nu(\text{Br-Br})$

c) 158 vs (Raman), $\nu(\text{Fe-I})$; 107 vs (Raman), def. (I-Fe-I)

Table 3 SI

Frequency data and assignment of the vibrational modes of the octahedral $[\text{EF}_6]^-$ anions.

		KPF₆		KAsF₆		NaSbF₆	
		ATR	Raman	ATR	Raman	ATR	Raman
A_{1g}	νE-F		752		691		673
T_{1u}	νE-F	801 835 (nj)		707 (KBr) 680 (ATR)		665 (KBr) 666 (ATR) 674 (nj)	
E_g	νE-F		580		579		581
T_{2g}	δE-F		478	389 (KBr) 372	375	281	283
T_{1u}	δE-F	550 555 (ATR) 560 (nj)		414 (KBr) 422		160	
T_{2g}	δE-F						

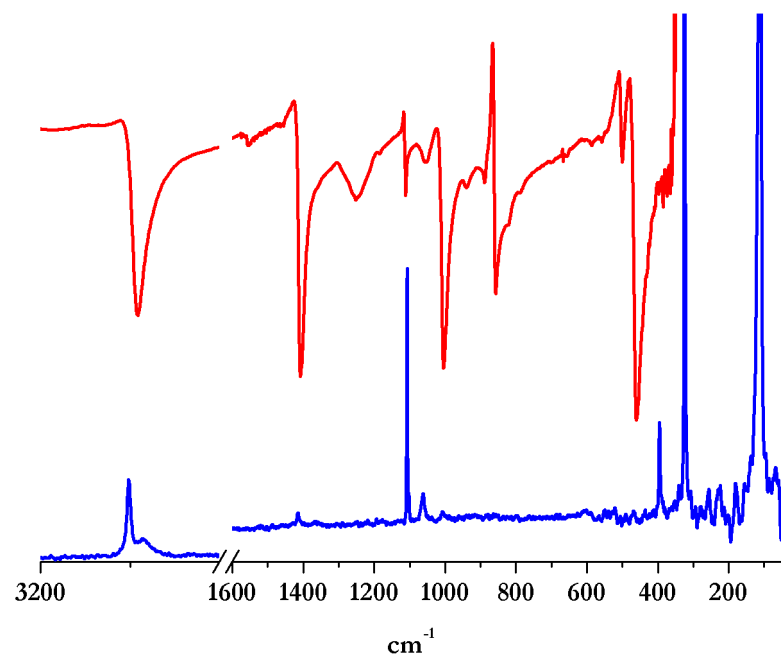


Figure 1 SI. Infrared (ATR, top) and Raman (crystal, bottom) spectra of the complex **5**.

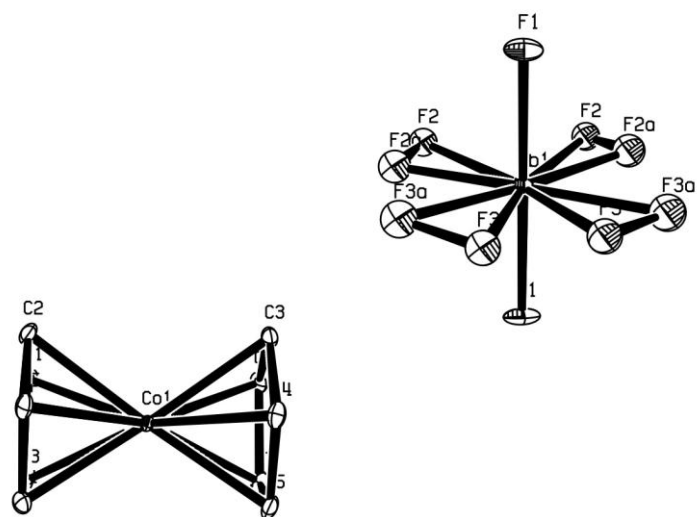


Figure 2 SI. Arrangement of ions in complex 3. Disordered fluorine atoms are highlighted.

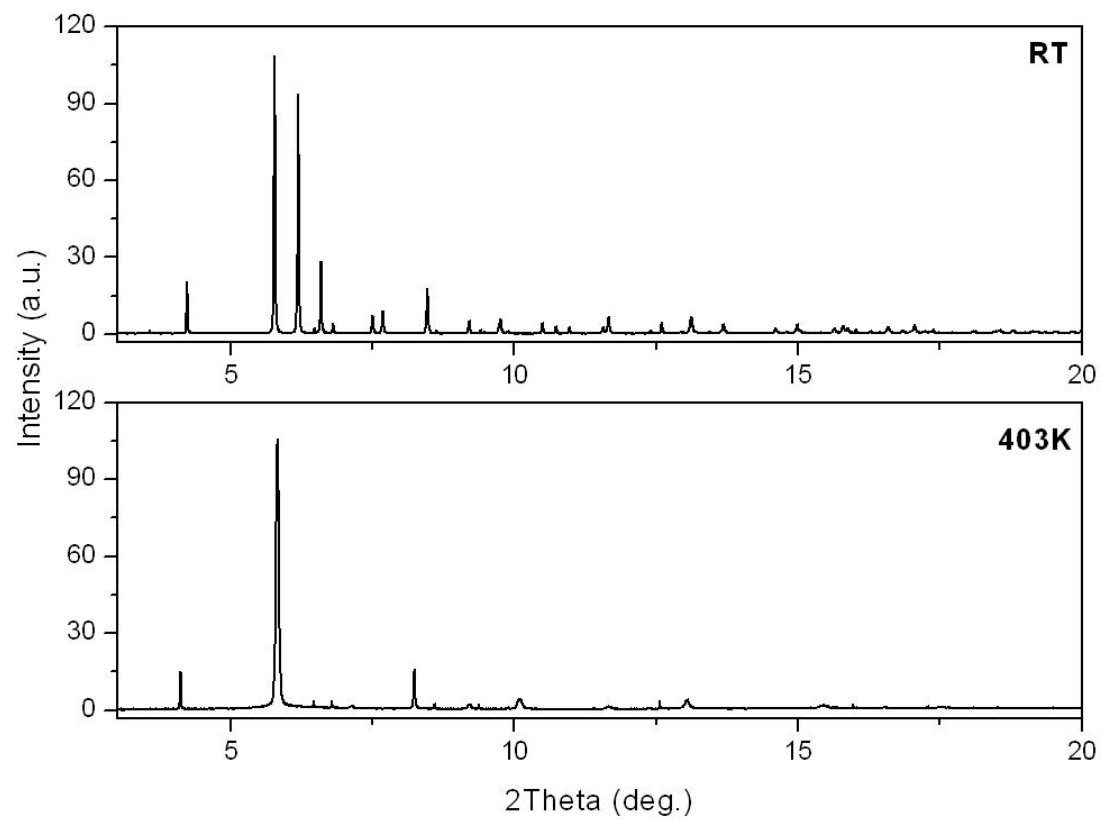
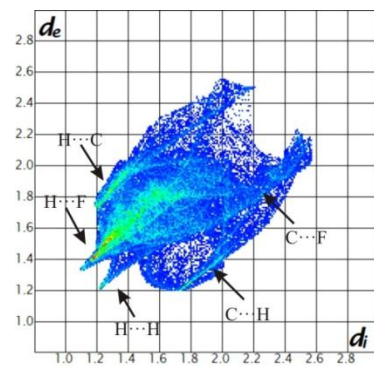
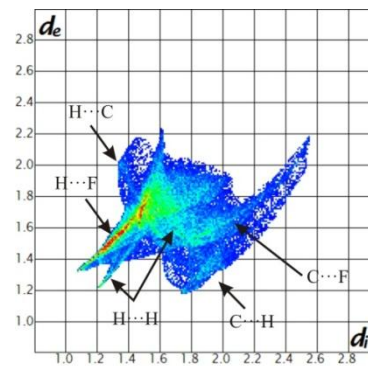


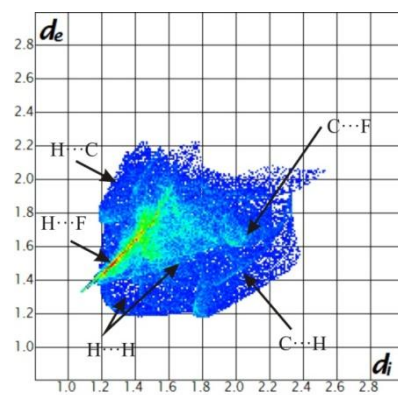
Figure 3 SI. XRPD patterns of the complex **3** at RT and 403K



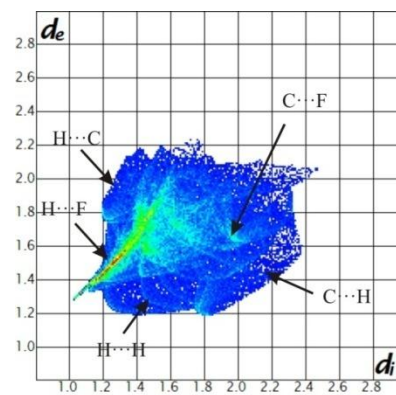
(1a)



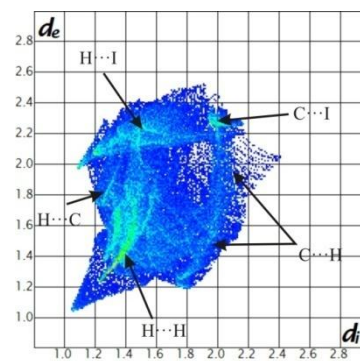
(1b)



(2)



(3)



(4)

Figure 4 SI. (HS fingerprint plots of the $[\text{Cp}_2\text{Co}^+]$ moiety in compounds **1**, **2**, **3** and **4**. Arrows indicate regions with a predominant contribution from atom pairs involved in intermolecular interactions since only pairs of (d_i , d_e) distances are reported irrespectively of type of atoms involved.)

Figure 4SI shows the HS fingerprint plots of the cobaltocenium ions in compounds **1**, **2**, **3** and **4** while the different contact percentages are reported in Table 4SI. The plots are built by considering the contacts formed by one Cp_2Co unit with the first shell atoms only.

Table 4SI. (Percentage values of contacts formed by the atoms of a $[\text{Cp}_2\text{Co}^+]$ moiety with surrounding atoms in compounds **1**, **2**, **3** and **4**.)

	1a	1b	2	3	4
C···H	10.2	8.2	8.2	7.9	11.8
H···H	25.2	37.8	35.6	34.6	64.9
H···C	13.1	0.7	5.1	4.7	5.5
H···X	48.7	48.9	46.2	47.4	15.7
C···X	2.8	4.5	4.9	5.4	2.1

As compound **1** has two independent cobaltocenium molecules (**1a** and **1b**) in the unit cell, two corresponding 2D histograms are reported. The fingerprint plot **1a** is rather symmetric along the diagonal (where $d_i=d_e$) indicating the same occurrence of (d_i , d_e) and (d_e , d_i) couples (in this case of H···H and C···H contacts, see table 4SI). This reveals the close packing of the molecules in the crystal.¹⁷ The spikes in the bottom-left part indicate that H···F and H···H are the shortest contacts. For the H···F contacts $d_e > d_i$ suggesting the donor nature of the C-H bond involved in HBs with the fluorine. The **1b** 2D plot shows an interesting difference with respect to **1a**: it is not symmetric and presents a predominance of H···H and H···F contacts. This difference indicates that **1b** molecules mainly interact with **1a**.

Compounds **2** and **3** show very similar 2D fingerprint plots which differ from that of **1**. It is relevant that both compounds have only one $[\text{Cp}_2\text{Co}^+]$ moiety in the unit cell and similar trigonal space group, whereas complex **1** has a monoclinic P21/c space group. As for **1a**, the lack of symmetry with respect the diagonal $d_i=d_e$ is due to the different number of C···H and H···C contacts.

The 2D fingerprint plot of complex **4** is clearly different: the histogram is largely dominated by H···H interactions, whereas the number of H···I contacts is one third of the number of H···F in complexes **1**, **2** and **3**.