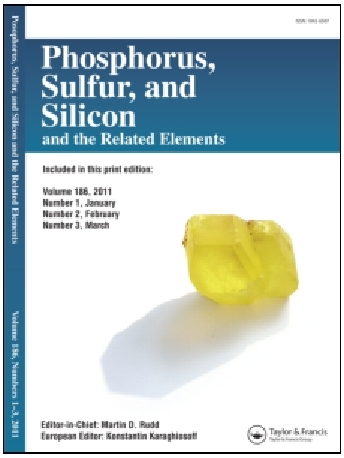

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SELENATION AS A TOOL TO IDENTIFY THE COBALT(II)-SULPHUR VIBRATIONS

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SELENATION AS A TOOL TO IDENTIFY THE COBALT(II)-SULPHUR VIBRATIONS

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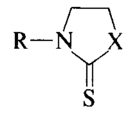
The F.I.R. spectra of CoL_2X_2 complexes ($X = Cl, Br, I$ and $L = \overline{RN \cdot CH_2 \cdot CH_2 \cdot NR' \cdot C}Y$, where for $R = H, R' = H$, Me, Et and $R = R' =$ Me, Et and $Y = S, Se$) have been investigated in order to locate the CoY vibrations by means of selenation. The mass effect of the halogens and selenium has enabled us to identify both νCoX and νCoY vibrations. The bending motions are strongly coupled.

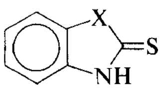
INTRODUCTION

In the last years we have been interested in assigning the vibrations arising from the thioamido group contained in several heterocyclic molecules. In particular we have considered the following pentaatomic rings[1–8]



R	*X*	*R*	*X*
H	CH_2	Me	O
H	O	Me	S
H	S.	Me	NMe
H	NH	Et	NEt
H	NMe		
H	NEt		

and similar heterocyclics condensed with a benzene ring:[9]

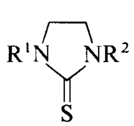


X = O, S, NH

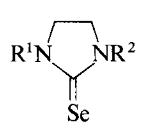
The main tool for the assignments has been "selenation," i.e. the substitution of the sulphur with selenium, first introduced by Jensen and Nielsen.[10] The assignments on some of these molecules have also been corroborated by a normal coordinate treatment.[6,7]

More recently,[11] we have tried the test selenation in order to identify the carbon-sulphur stretching vibrations in thioether-containing molecules; for this purpose, the i.r. spectra of thiazolidine-2-selone and its *N*-methyl derivative have been compared with those of selenazolidine-2-selone and *N*-methyl-selenazolidine-2-selone.

We now wish to report a far infrared investigation on the cobalt (II)-sulphur vibrations, based on selenation. For this aim, the complexes obtained between cobalt (II) halides and the following



R^1	R^2	
(1)	H	(2)
(3)	Me	(4)
(5)	Et	(6)
(7)	Me	(8)
(9)	Et	(10)



imidazolidines have been considered. Since the infrared spectra of these ligands have never been reported below 200 cm^{-1}, this study will be preceded by a short discussion on their spectra with regard to the bands falling in the 525–70 cm^{-1} range.

RESULTS AND DISCUSSION

As previously seen for the above imidazolidines.[2,3] the spectra of each sulphur compound and its

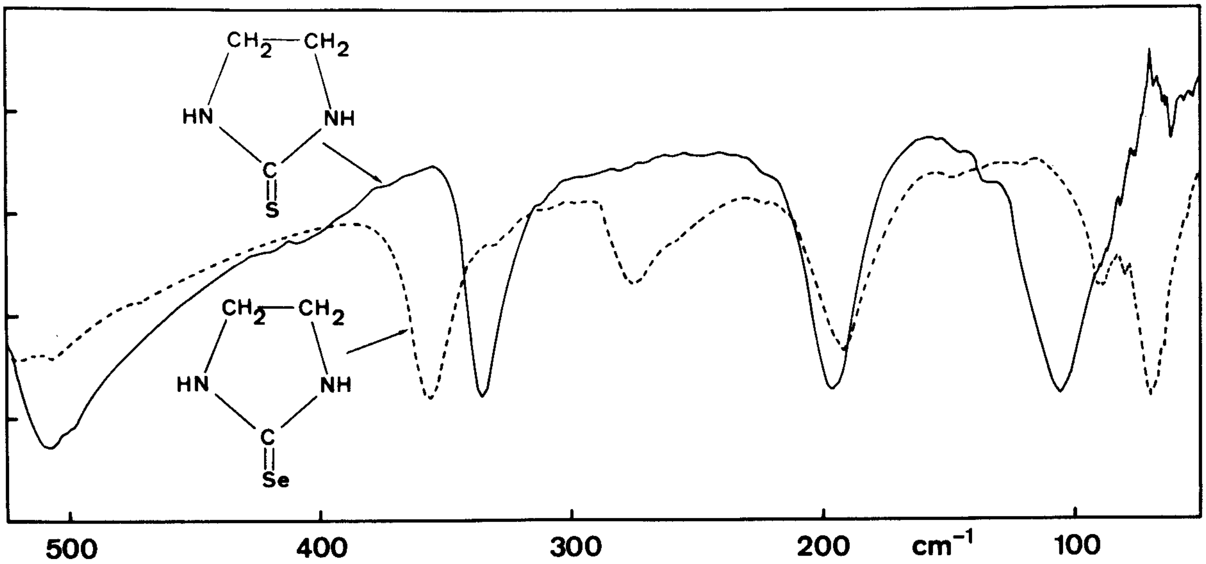


FIGURE 1 Superimposed spectra of imidazolidine-2-thione (full line) and -2-selone (dotted lines).

selenium isologue are practically identical in the fingerprint region, while they show significant changes only below 650 cm^{-1}. Then, νCS and νCSe stretching vibrations contribute chiefly to bands falling in the low frequency region, in accordance with the low π-bond order of the C $\overset{...}{=}$ S and C $\overset{...}{=}$ Se bonds.

In order to complete the investigation on the vibrational properties of the above molecules, the i.r. spectra of (1)–(10) have been recorded down to 70 cm^{-1}. Selenation works very well enhancing the bands due to the

$$>C=S$$

vibrations, as shown by the superimposed spectra of (**1**) and (**2**) reported in Figure 1. Three bands of (**1**) (i.e. 507, 337 and 106 cm^{-1}) move by selenation towards lower frequencies and occur in (**2**) at 357, 276 and 70 cm^{-1}. This indicates that these bands are chiefly produced by stretching and bending modes of CS and CSe, respectively.

The band at 196 cm^{-1} in (**1**) is also present in (**2**) at 192 cm^{-1}; a similar band is common to all the compounds here considered, thus proving that this band is originated from the imidazolidine ring. Analogous shifts are observed in all the other couples of isologue compounds, although some difficulties are found in examining the spectra of disubstituted derivatives.

All the spectra of the thionic and selonic imidazolidine are reported in Figures 2 and 3, respectively. The bands due to the C=S and C=Se modes, having probably the same vibrational nature, are joined with vertical lines.

All the complexes, here considered, have general formula CoL_2X_2 (X = Cl, Br, I) with a *pseudo*-tetrahedral environment around the Co(II).[12–16]

The infrared spectra of the complexes showed that in all cases the ligands bind the cobalt (II) through the sulphur or selenium atom. Then, in the far infrared spectra the vibrations arising from cobalt-sulphur/selenium and cobalt-halide bonds should be found. If only these vibrations are considered, neglecting the remaining part of the ligands, the F.I.R.'s should exhibit nine fundamentals ($4A_1 + A_2 + 2B_1 + 2B_2$) all i.r. active, with the exception of A_2. In addition to these vibrations, both the ligands' own bands and the lattice motions fall in the low frequency region to complicate the spectra. However, on the basis of selenation and the mass effect of the halogen, it is possible to identify the bands which retain relevant contributions of νCoS/Se and νCoX vibrations.

In order to establish the effect of selenation on the vibrational properties of the complexes with the sulphur ligands, their spectra have been superimposed on those of the selenium isologues. Two of these spectra are reported in Figure 4, as an example.

Besides the ligand absorption (L), the spectra differ for the two bands at 231 and 160 cm^{-1} for (**1**) and (**2**) respectively; these bands must be attributed to the prevailing νCoS and νCoSe

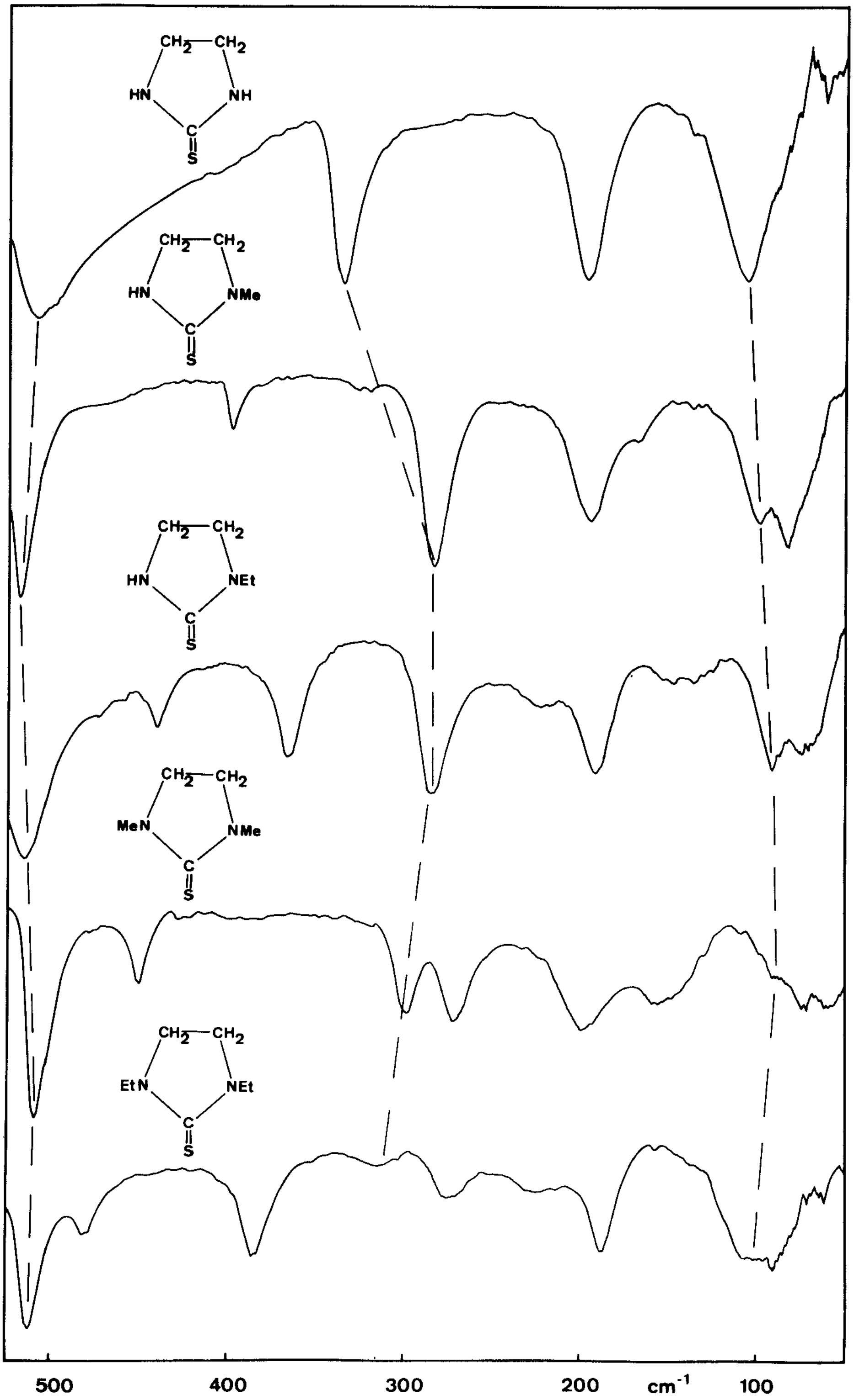


FIGURE 2 Spectra of the imidazolidine-2-thione compounds. The vertical lines connect bands originating from CS modes.

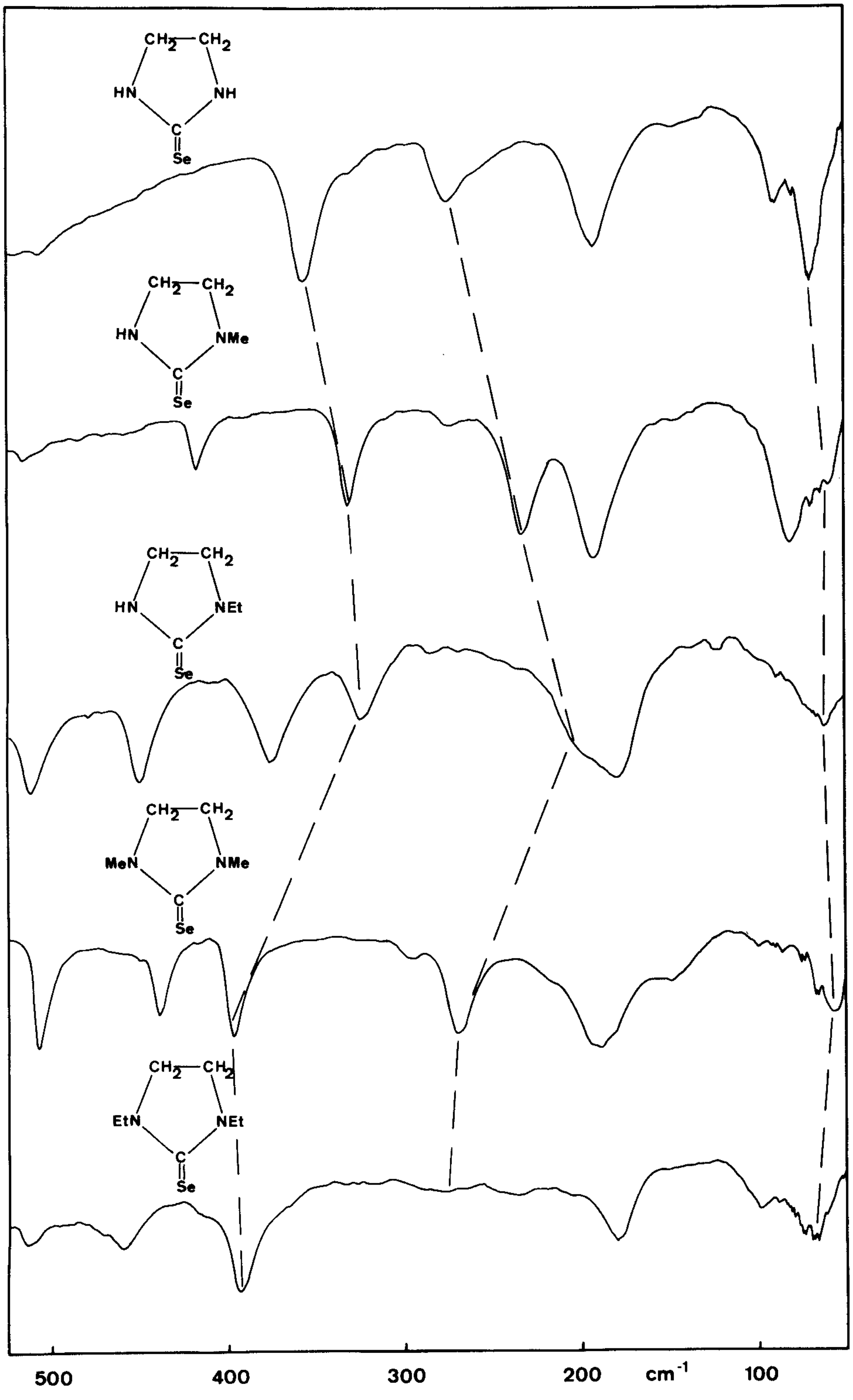


FIGURE 3 Spectra of the imidazolidine-2-selone compounds. The vertical lines connect bands originating from CSe modes.

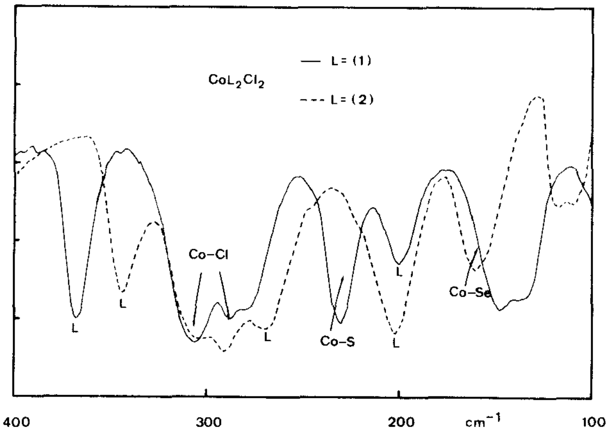


FIGURE 4 Superimposed spectra of cobalt(II) complexes of imidazolidine-2-thione (1) and -2-selone (2).

vibrations. The influence of selenation is also evidentiated by the two broad absorptions around 140 and 115 cm^{-1} in (**1**) and (**2**) complexes; their origin should be due to the deformations of *pesudo*-tetrahedral angles. The very strong absorbtions around 300 cm^{-1} are undoubtedly attributable to the νCoCl vibrations. It should be pointed out that, contrary to what the stereochemistry of the complexes predicts, only one band is evident in this case, clearly attributable to νCoS/Se; the fact that a second absorption is absent is not important, since it could be hidden by the other strong absorptions. The bands attributed to cobalt-sulphur and cobalt-selenium stretching vibrations on the basis of selenation are collected in Table I for the halide complexes of (1)–(10). As seen above for complexes of (**1**) and (**2**), most of the spectra exhibit only one νCoS/Se vibration.

We wish to point out that in the complexes of (1) νCoS occurs at wavenumbers significantly lower than in all the other ligands; this fact seems to be surprising since the negative charge on the sulphur atom is practically the same in the five compounds[3,17] and the CoS bonds should be expected to be of similar strength. On the other hand, the strong absorption around 300 cm^{-1} (Figure 4) present in the chloride complex of (**1**), cannot retain any νCS contribution, since no absorptions are observed for the corresponding bromide and iodide complexes in this range (see Figure 5).

The νCoSe vibrations fall in a narrower range of frequencies than the corresponding νCoS; even in these compounds only one νCoSe vibration is normally identified.

The mass effect of the halogen substitution is clearly shown in Figure 5. It should be pointed out that in the bromo derivative, the strong absorption due to νCoBr contains also the νCoS vibration. The overlapping of absorptions, due to cobalt-ligand and cobalt-halide vibrations, occurs frequently, especially in the cases of the cobalt surrounded by two chlorine and two sulphur atoms or by two selenium and two iodide atoms.

Table II summarizes the assignments of cobalt-halide stretching vibrations for all the complexes.

As can be seen in Table II, the νCoX's fall in narrow ranges in good agreement with complexes of the same symmetry.[18,19] An inspection of Figure 5 shows that the envelope of bands at about 140 cm^{-1}, sensitive to the substitution of sulphur with selenium (see Figure 4), is also sensi-

TABLE I

Cobalt-sulphur and cobalt-selenium stretching vibrations in *pseudo*-tetrahedral CoL_2X_2 complexes

Ligand	νCoS Cl	 Br	 I	νCoSe Cl	 Br	 I
(1)	231	240	233	–	–	–
(2)	–	–	–	160	198	200
(3)	330–321	328	328	–	–	–
(4)	–	–	–	214–184	232–200	181
(5)	337–320	333–322	336–323	–	–	–
(6)	–	–	–	211	210	226–205
(7)	309–274	297–280	287	–	–	–
(8)	–	–	–	186	184	178
(9)	275	278	276	–	–	–
(10)	–	–	–	174	174	186

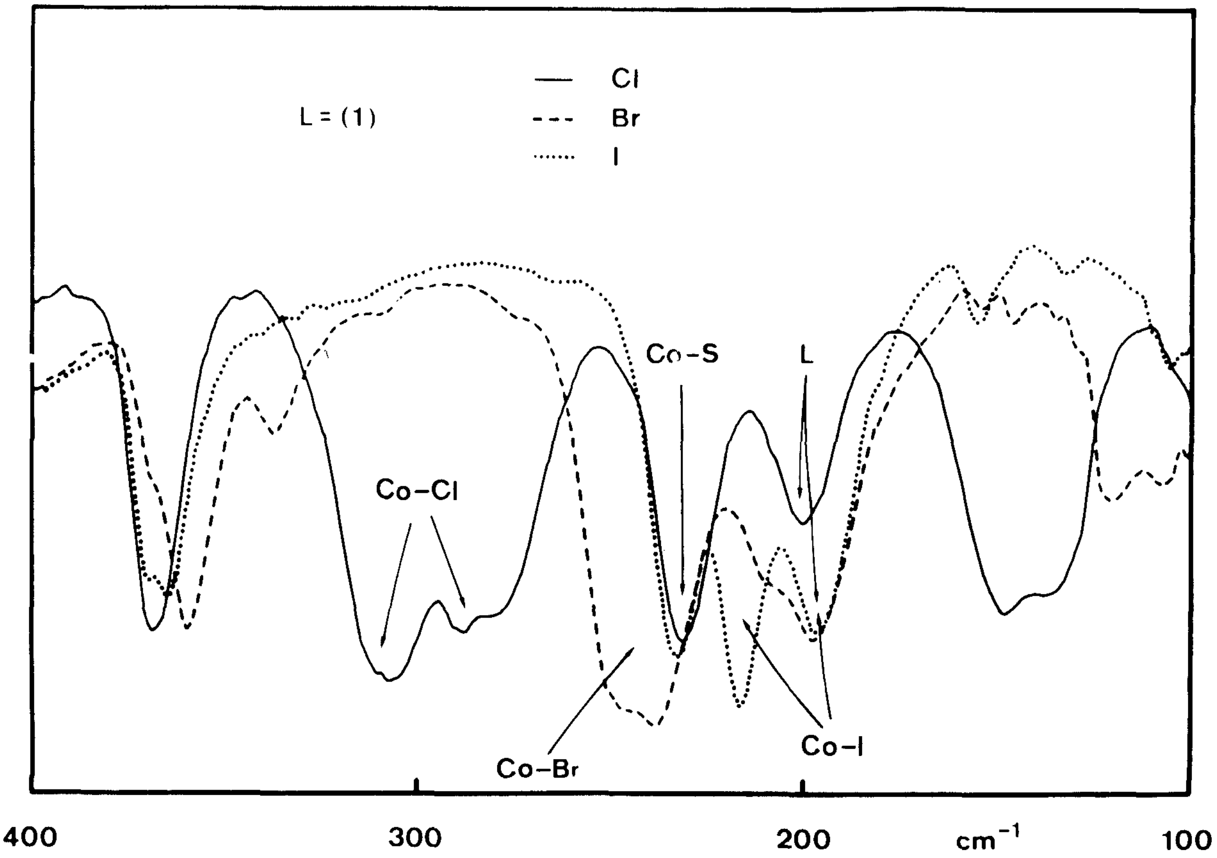


FIGURE 5 Superimposed spectra of the complexes obtained from (1) and cobalt(II) halides.

tive to the halide (Figure 5). This means that the bending modes of CoX_2 and CoS_2/Se_2 are strongly coupled and give rise to envelope of bands.

These vibrations generate broad absorptions falling into the region 148–103, 124–85 and 110–70 cm^{-1} for Cl, Br and I complexes, respectively.

TABLE II

Cobalt-halide stretching vibrations in *pseudo*-tetrahedral CoL_2X_2 complexes

Ligand	νCoCl	νCoBr	νCoI
(1)	306–288	240–208	216–197
(2)	304–292	230–212	200
(3)	321–293	237–205	220–200
(4)	318–304	232–200	210–201
(5)	320–302	252	212
(6)	316–304	242	226–205
(7)	323–309	241–208	208
(8)	312–304	245–224	200
(9)	320–298	245–204	196
(10)	310	245–234	204–186

EXPERIMENTAL

All the ligands and complexes have been prepared as previously described.[3,13–16]

The i.r. spectra were recorded as Nujol mulls with a Perkin-Elmer 325 and 180 instruments.

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