

## Infrared Spectra of Dithiobenzoic Acid and its Metal Complexes

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### Results and Discussion

The present work deals with the preparation of metal complexes of dithiobenzoic acid and their IR spectra studies, specially in the low range where Metal-Ligand vibrations take place. The infrared spectra of DTB and its metal complexes between 1600-400  $\text{cm}^{-1}$  range is shown in Fig. A and the frequencies are listed in the Table 1. The peaks between 1600 and 1430  $\text{cm}^{-1}$  are characteristic of the aromatic ring itself, and normally three bands appear in this range. The infrared spectrum of DTB shows three bands at 1588, 1492 and 1473  $\text{cm}^{-1}$  which are well in the range of the (C=C) skeletal in-plane vibrations. The S-H stretching mode is assigned to the weak band appearing at 2550  $\text{cm}^{-1}$ . The C=S stretching frequency appears between 1250 and 1020  $\text{cm}^{-1}$  in most sulphur containing ligands and, therefore, the band at 1240  $\text{cm}^{-1}$  may be associated with the C=S vibration. The S-H deformation is assigned to the peak appearing at 930  $\text{cm}^{-1}$ . Two medium intensity bands are observed at 572 and 460  $\text{cm}^{-1}$  and may be attributed to the ring vibration in the infrared spectrum of DTB. The far infrared spectrum of the ligand has shown very poor absorption from which it is difficult to make precise assignments of the bands.

The infrared spectra of metal complexes are better defined than that of the acid. None of the complexes show (S-H) absorption. It is interesting to note that assuming the band at 1240  $\text{cm}^{-1}$  to be the (C-S) stretching mode in the ligand, this band shifts to a higher frequency in the case of  $\text{Pt}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  complexes (1280 and 1265  $\text{cm}^{-1}$ ), and to lower frequency in the case of  $\text{Cr}^{\text{III}}$  and  $\text{Co}^{\text{III}}$  complexes (1230 and 1225  $\text{cm}^{-1}$ ) respectively. An absorption which appears at 572  $\text{cm}^{-1}$  in the ligand has shown splitting at 570 and 576  $\text{cm}^{-1}$  in the  $\text{Pt}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  complexes. These bands may be associated with the ring deformation and (M-S) stretching vibrations. Similar assignments have been reported for dithiocarbamate complexes [3]. The  $\text{Cr}^{\text{III}}$  and  $\text{Co}^{\text{III}}$  complexes show a single relatively strong band in

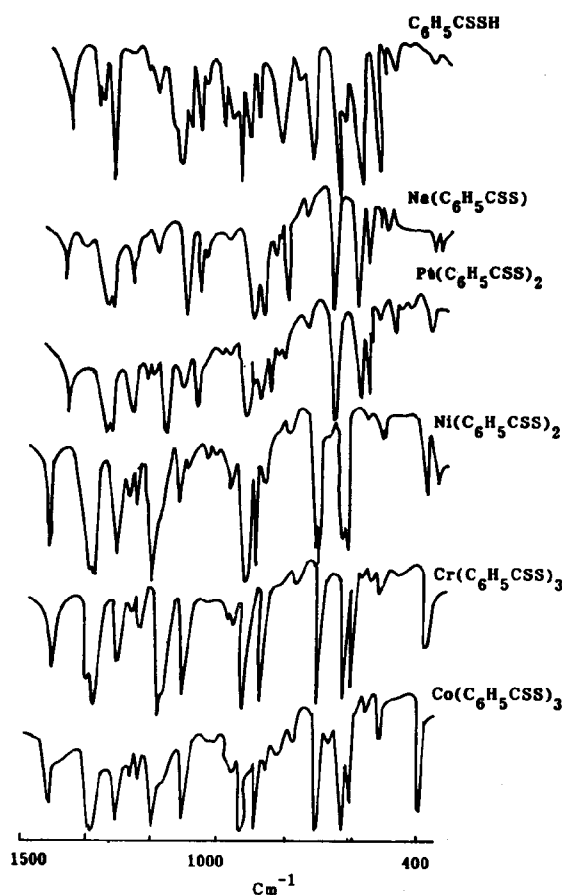


Fig. A: Wave numbers in  $\text{cm}^{-1}$

this range which may be due to an overlapping of the ring deformation and (M-S) stretching modes.

All these complexes show weak ill-defined bands in the low frequency show (400-100  $\text{cm}^{-1}$ ). The far infrared spectra of DTB and its complexes in the 400 - 100  $\text{cm}^{-1}$  is shown in Fig. B and the frequencies are listed in the Table 2. For infrared spectra of the complexes are of particular interest

because they may provide direct information concerning the metal-ligand co-ordinate bonds. The low frequency range between  $380\text{--}340\text{ cm}^{-1}$  is very similar in all the complexes and the same type of absorption is observed in the free ligand. Bands in this range may, therefore, be associated with the ligand vibrations.

Table 1: IR absorptions between  $1600\text{--}400\text{ cm}^{-1}$ 

(L)	NaL	PtL <sub>2</sub>	NiL <sub>2</sub>	CoL <sub>3</sub>	CrL <sub>3</sub>
3080vw	-	3080w	3080w	3080w	-
3060m	3070vw	3050m	3050w	3060w	3060w
3030w	3050	23020w	-	3020vw	-
2960w	2960vw	2950w	2950w	2960w	2960w
2920w	2920w	2920m	2920m	2920m	2920m
2550m	-	-	-	-	-
1588vs	1580ms	1585s	1587vs	1585s	1585s
1492s	-	-	-	-	-
1475s	-	1480w	1480w	1485	-
1445vs	1445s	1442s	1445s	1445s	1445s
1380vw	1370m	1370w	1380w	-	-
1330vw	1330vw	1335m	1330m	1330m	1335w
1310m	1292w	1310m	1310m	1310m	1310m
1260s	-	1280s	1265vs	1265s	1260vs
1240s	-	-	-	1225w	1230m
1210m	1210vs	1210m	-	-	-
1180s	1165s	1180s	1180s	1170s	1172vs
115w	1150s	1150w	1150w	1150w	1150w
1104m	-	1100vw	1095w	1100w	1100w
1080m	1070m	1080w	1060w	1075w	-
1052vs	-	-	-	1040sh	1040w
1025s	1005s	1025s	1025s	1020m	1025m
995ms	975s	990s	975s	990vs	985vs
-	-	-	950m	845vs	950vs-
930s	932m	-	-	-	932vs
-	-	920w	825w	920m	-
870w	-	-	875vw	880w	890w
832vs	832m	835w	845m	830w	830w
760vs	775vs	760vs	765vs	755vs	760vs
680vs	680vs	680vs	680vs	675vs	675vs
645vs	645vs	665vs	662vs	660vs	662vs
-	-	-	650s-	650w	630w
612m	610m	615w	610w	610m	610w
572m	585m	570w	570w	565m	580m
460m	440m	460m	430s	440vs	435s
-	422m	-	-	-	-

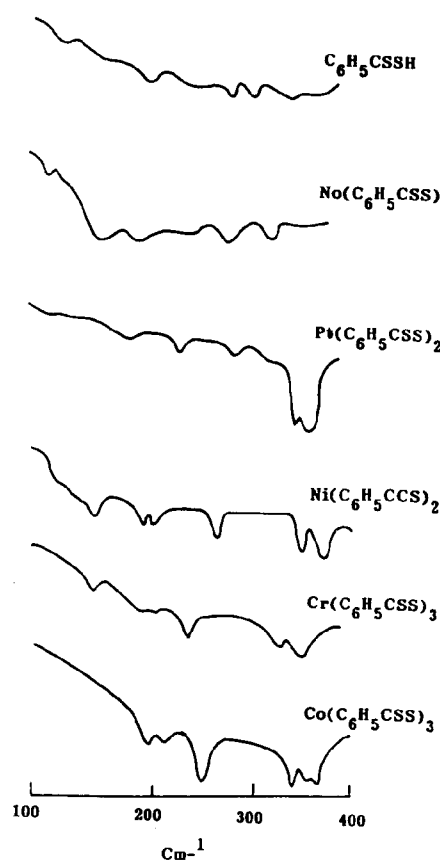
(W = weak S = Strong VS = very strong), (m = medium, VW = very weak ms = medium strong)

However, a band at  $258\text{ cm}^{-1}$  and  $235\text{ cm}^{-1}$  may be assigned to the (Ni-S) and (Pt-S) stretching modes respectively and they do not appear in the ligand spectrum. The absorption peaks at 248 and  $245\text{ cm}^{-1}$  are similarly attributed to the (Co-S) and (Cr-S) stretching vibrations respectively. The (M-S) assignments are constant with the previously published work [3].

Table 2: Low frequency IR absorptions between  $400\text{--}100\text{ cm}^{-1}$ 

(L)	NaL	PtL <sub>2</sub>	NiL <sub>2</sub>	CoL <sub>3</sub>	CrL <sub>3</sub>
380w	-	370m	395m	370m	365m
350w	-	355m	365s	357m	360m
-	-	-	-	3545m	340m
-	-	332m	330w	-	-
310m	-	-	-	-	-
285vw	285vw	285w	-	-	-
-	-	-	258m	-	-
-	-	-	-	248s	245s
-	-	235m	-	-	-
195vw	200vw	-	190w	205w	205w
-	-	180w	180w	192w	190w
-	-	-	130w	-	-

(L = C<sub>6</sub>H<sub>5</sub>CSS = DTB)

Fig. B: Wave numbers in  $\text{cm}^{-1}$ 

Since, the infrared spectra of the Pt<sup>II</sup> and Ni<sup>II</sup> complexes are very similar, the common planar structure already suggested is given further support.

In a like manner the spectral data for the Cr<sup>III</sup> and Co<sup>III</sup> complexes are entirely consistent with their proposed iso-structural octahedral configurations.

### Experimental

Dithiobenzoic acid was prepared as described by J. Houben [4] and its complexes with Pt<sup>II</sup>, Ni<sup>II</sup>, Cr<sup>III</sup> and Co<sup>III</sup> were prepared as described by Furlani and Luciani [1]. The elemental analysis are given below.

Complexes	C%		H	
	cal.	found	cal	found
Ni(DTB) <sub>2</sub>	46.02	45.89	2.74	2.96
Pt(DTB) <sub>2</sub>	33.52	32.7	2.00	2.12
Cr(DTB) <sub>3</sub>	49.29	48.97	2.95	3.34
Co(DTB) <sub>3</sub>	48.62	48.45	2.91	3.25

Low frequency infrared spectra were obtained as mulls-in liquid paraffin on a RIIC 720 spectrophotometer and spectra between 4000-400 cm<sup>-1</sup> on a Perkin-Elmer 125 spectrophotometer.

### References

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2. M. Bonamico and G. Dessy, *Chem. Commun.*, 483 (1968).
3. J. Chatt, L. A. Duncanson and L. M. Venanzi, *Nature*, **177**, 1402 (1956).
4. J. Houben, *Ber.*, **39**, 3219 (1906).