

# Vibrational Analysis of Metal Complexes of 1,3-Dithiomalonamide & 2,4-Dithiobiuret

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Received 20 October 1976; accepted 9 February 1977

The infrared spectra of Ni(II), Cd(II) and Hg(II) complexes of 1,3-dithiobiuret and Ni(II) and Pd(II) complexes of 2,4-dithiomalonamide have been assigned on the basis of a normal coordinate treatment for the in-plane vibrations of the nickel(II) complexes. The assignment of frequencies of the metal complexes are discussed by referring to the assignments in related molecules. The Raman spectrum of dithiomalonamide is also reported.

THE compounds 1,3-dithiomalonamide (DTM) and 2,4-dithiobiuret (DTB) are structurally analogous to  $\beta$ -dithioketones which have been studied extensively<sup>1-3</sup>. But only recently the coordination behaviour of DTM and DTB has received some attention<sup>4-8</sup>. In general the infrared studies on dithionamides are meagre compared to those on monothionamides<sup>9-12</sup>. Coupled vibrations are expected for thioamides making empirical assignments difficult. In view of the fact that except a few cases majority of reports available on metal-sulphur vibrations are a result of empirical studies<sup>13</sup>, we thought it worthwhile to study the IR spectra of some complexes of DTM and DTB. The infrared frequencies have been assigned with the help of normal vibrational analysis made for the nickel(II) complexes using Wilson's *GF* matrix method and Urey-Bradley force function. The Raman spectrum of DTM is also reported.

## Materials and Methods

DTB was prepared according to a known procedure<sup>14</sup> by passing  $H_2S$  to an aqueous solution of dicyandiamide. It was recrystallized from water, m.p. 181°. DTM was prepared by passing  $H_2S$  to a mixture of triethanolamine and malononitrile in ethanol (95%) at room temperature<sup>15</sup>. It was recrystallized from ethanol, m.p. 213°.

*Preparation of complexes: Dichlorobis(2,4-dithiobiuret)nickel(II)*—This was prepared by a known method<sup>5</sup> [Found: Ni, 14.82; C, 12.60; H, 2.60; N, 21.23. Calc. for  $NiCl_2 \cdot 2DTB$ : Ni, 14.68; C, 12.01; H, 2.50; N, 21.01%].

*Dichlorobis(2,4-dithiobiuret)cadmium(II)*—An ethanolic solution of DTB was added to an aq. ethanolic solution of  $CdCl_2$  with constant stirring. The resulting pale yellow precipitate of the cadmium complex was filtered, washed several times with aq. ethanol and dried over concentrated  $H_2SO_4$  [Found: Cd, 23.92; C, 10.23; H, 1.82; N, 18.14. Calc. for  $CdCl_2 \cdot 2DTB$ : Cd, 24.79; C, 10.49; H, 2.20; N, 18.52%].

*Dichloro(dithiobiuret)mercury(II)*—An ethanolic solution of DTB was added to a solution of  $HgCl_2$  in ethanol with constant stirring. The resulting

white precipitate was filtered, washed with ethanol and dried over concentrated  $H_2SO_4$  [Found: Hg, 48.5; C, 5.97; H, 1.47; N, 9.77. Calc. for  $HgCl_2 \cdot DTB$ : Hg, 49.33; C, 5.90; H, 1.73; N, 10.33%].

*Dichlorobis(dithiomalonamide)nickel(II)*—This was prepared following a known procedure<sup>5</sup> [Found: Ni, 14.56; S, 31.73. Calc. for  $NiCl_2 \cdot 2DTM$ : Ni, 14.76; S, 32.19%].

*Dichlorobis(dithiomalonamide)palladium(II)*—A method similar to that used for Ni(II) complex was followed. The yellow complex formed was washed with ethanol and then with acetone and dried over conc.  $H_2SO_4$  [Found: Pd, 23.55; S, 28.13; N, 12.64; C, 16.41. Calc. for  $PdCl_2 \cdot 2DTM$ : Pd, 23.88; S, 28.93; N, 12.57; C, 16.20%].

*Analysis*—The complexes were analysed for the metal contents by standard methods. The C, H and N analysis were obtained by micro-analysis carried out at the Bhabha Atomic Research Centre, Bombay.

*Infrared and Raman spectra*—The infrared spectra of the solid samples in the range 4000-400  $cm^{-1}$  were recorded on a Carl-Zeiss UR10 spectrophotometer while for the IR spectra in the range 250-400  $cm^{-1}$  were recorded on a Perkin-Elmer 521 spectrophotometer in nujol mull and KBr. The laser Raman spectrum of the solid sample of DTM was taken on a Cary 81 spectrophotometer using argon ion laser, through the courtesy of Prof. J. R. Scherer, US Department of Agriculture, Albany, to whom our grateful thanks are due. The spectra of DTB and  $NiCl_2 \cdot DTB$  were also obtained from 400 to 40  $cm^{-1}$  on a Beckman RIIC interferometer, through the courtesy of Prof. R. T. Bailey, the University of Strathclyde, Scotland, UK, whom we gratefully thank.

*Normal coordinate treatment*—In order to simplify the calculations, 1:1 models of these complexes were considered. Such an assumption does not introduce any serious difference in the application of the results to the 1:2 complexes<sup>13</sup>.

The 1:1 molecular models of both types of complexes belong to the point group  $C_{2v}$  and only the in-plane type of vibrations are calculated. The frequencies of interest belong to this category.

There are 33 normal vibrations for the 1:1 molecular model of Ni-DTB of which the in-plane modes are  $12A_1+11B_2$ . The Ni-DTM complex has 36 normal vibrations, and the in-plane modes are  $13A_1+11B_2$  modes.

The symmetry coordinates were constructed as usual. The structure parameters (Fig. 1) for  $NiCl_2 \cdot 2DTB$  were taken from the palladium complex. The structure parameters (Fig. 1) used for Ni-DTM were based on those of thioacetamide<sup>16</sup> and nickel(II) dithioacetylacetonate<sup>2</sup>. The initial Urey-Bradley force constants for Ni-DTB were transferred from DTB<sup>17</sup> and for Ni-DTM mostly from cyanothioacetamide<sup>18</sup> (CTAM). The force constants connected with the coordinate bonds were taken from nickel(II) dithioacetylacetonate<sup>2</sup>. The initial force constants were modified progressively to obtain a good agreement between the observed and calculated frequencies. The final set of force constants for both the complexes are shown in Table 1. The force constants were found to be satisfactorily transferable. Notably, the force constants are similar for both the systems.

## Results and Discussion

### Dithiobiuret

In the complexes of DTB with chlorides of nickel, cadmium and mercury, metal ions are expected to coordinate readily through the thiocarbonyl sulphur atoms. The observed and calculated frequencies for  $NiCl_2 \cdot 2DTB$  along with their assignment from the potential energy distributions (PED) are given in Table 2. The infrared frequencies of DTB and its metal complexes are listed in Table 3 and the assignment of the bands based on those of  $NiCl_2 \cdot 2DTB$  is also indicated.

The intensities of some of the infrared bands are weaker in complexes as compared to those in the ligand and the bands in the complexes tend to be broad. It is likely that in all the three complexes DTB is acting as a bidentate ligand coordinating through both the sulphur atoms as in the palladium (II) complex, whose structure has been determined by X-ray diffraction method<sup>7</sup>. The spectral features

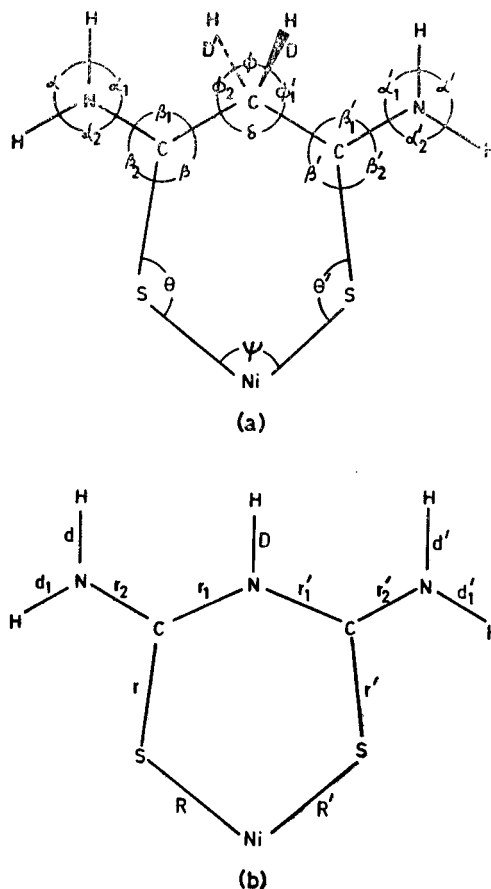


Fig. 1 — Structure and internal coordinates of (a) Ni-DTM and (b) Ni-DTB complexes

of the metal complexes can be explained on this basis.

The X-ray structure analysis has revealed that DTB has *trans-cis* CS-NH-CS group<sup>19</sup>. On bidentate coordination of DTB through sulphur atoms, the spectrum gets somewhat simplified probably because of the apparent  $C_{2v}$  symmetry for the coordinated ligand.

TABLE 1 — UREY-BRADLEY FORCE CONSTANTS (mdyn/Å) OF (a) DTB AND (b) DTM COMPLEXES OF NICKEL(II)

	a	b		a	b	a	b	
$K_{NH}$	5.52	5.02	$H_{HNH}$	0.39	0.42	$F_{HNH}$	0.00	0.000
$K_{NH}$	5.56		$H_{HNC}$	0.33	0.325	$F_{HNC}$	0.72	0.485
$K_{CH}$	—	4.25						
$K_{CN}$	6.60	6.55	$H_{NCN}$	0.13		$F_{NCN}$	1.05	
$K_{CN}$	3.45		$H_{NCS}$	0.10	0.10	$F_{NCS}$	1.15	1.06
$K_{CS}$	2.80	3.25	$H_{N'CS}$	0.22		$F_{N'CS}$	0.78	
$K_{NIS}$	1.80	1.88	$H_{HN'C}$	0.34		$F_{CN'H}$	0.40	
$K_{CC}$	—	2.85	$H_{CNC}$	0.32		$F_{CNC}$	0.14	
$f_{NH,NH}^*$	-0.22	-0.20	$H_{CSNi}$	0.25	0.24	$F_{SNIS}$	0.40	0.46
$k^\dagger$		-0.0495	$H_{SNIS}$	0.12	0.45	$F_{CSNi}$	0.05	0.05
			$H_{NCC}$		0.20	$F_{NCC}$		0.87
			$H_{CCS}$		0.28	$F_{CCS}$		0.37
			$H_{CSC}$		0.40	$F_{CSC}$		0.28
			$H_{HCC}$		0.33	$F_{HCC}$		0.45
			$H_{HCH}$		0.364	$F_{HCH}$		0.12

\*Non-Urey-Bradley constant.

†Intramolecular tension in mdyn/Å.

TABLE 2 — INFRARED FREQUENCIES (cm<sup>-1</sup>) OF  
 DICHLOROBIS(DITHIOBIURET)NICKEL(II) AND  
 THEIR ASSIGNMENT

Mode	Obs.	Calc.	p.d.*	Assignment† (PED, %) <dd>‡</dd>
A <sub>2</sub>	3390	3394	0.1	ν <sub>s</sub> NH <sub>2</sub> (99)
	3300	3292	0.2	νNH (99)
	3170	3176	0.2	ν <sub>s</sub> NH <sub>2</sub> (99)
	1665	1664	0.1	δNH <sub>2</sub> (84), ν <sub>s</sub> CN (13)
	1490	1502	0.8	ν <sub>s</sub> CN (69)
	1320	1324	0.3	rNH <sub>2</sub> (80)
	1550	1048	2.2	ν <sub>s</sub> CN' (41), ν <sub>s</sub> CS (21),
	1000			δNCS (15)
	720	684	4.3	ν <sub>s</sub> CS (61), δring (23)
	710			
	630	619	1.0	δring (50), ν <sub>s</sub> CN' (26)
	620			
	420	418	0.5	ν <sub>s</sub> MS (54), ν <sub>s</sub> CN' (18),
				δNCS (17)
B <sub>2</sub>	296	298	0.7	δNCS (55), ν <sub>s</sub> MS (23)
	275	277	0.7	δring (75), ν <sub>s</sub> MS (16)
	3390	3389	0.0	ν <sub>a</sub> NH <sub>2</sub> (100)
	3170	3176	0.2	ν <sub>a</sub> NH <sub>2</sub> (99)
	1665	1664	0.1	δNH <sub>2</sub> (79), ν <sub>a</sub> CN (15)
	1625	1626	0.1	δNH (70)
	1430	1429	0.1	ν <sub>a</sub> CN (71), δNH (15)
	1360	1352	0.6	rNH <sub>2</sub> (60), ν <sub>a</sub> CN' (22)
	1126	1118	0.7	ν <sub>a</sub> CN' (65), rNH <sub>2</sub> (24)
	744	753	1.2	ν <sub>a</sub> CS (74)
	505	511	1.2	δNCS (58), ν <sub>a</sub> MS (21),
				δring (15)
				δring (69), δNCS (20)
		350	359	2.6
	304	300	1.3	ν <sub>a</sub> MS (70)

\*p.d. = percentage deviation =  $(|v_{\text{obs}} - v_{\text{calc}}| \times 100) / v_{\text{obs}}$ .

†ν = stretching, δ = bending, r = rocking, a = asymmetric, and s = symmetric.

‡Contributions from δring are combined.

 TABLE 3 — INFRARED FREQUENCIES (cm<sup>-1</sup>) OF  
 2,4-DITHIOBIURET AND ITS COMPLEXES AND,  
 THEIR ASSIGNMENT

DTB	NiCl <sub>2</sub> .2DTB	CdCl <sub>2</sub> .2DTB	HgCl <sub>2</sub> .DTB	Main assignment*
3360 s	3390 m	3360 m	3350 sh	νNH <sub>2</sub> , νNH
3280 s	3300 mb	3270 m	3280 mb	
3185 mb	3170 w	3185 w	3185 m	
3115 w				
3040 wb				
1645 s	1665 s	1640 sh	1620 sh	δNH <sub>2</sub>
1626 ms				
1575 ms	1625 vs	1618 vs	1582 m	δNH
1495 mw	1490 vs	1512 s	1515 s	ν <sub>a</sub> CN
1410 m	1430m	1440 s	1470 s	ν <sub>s</sub> CN
		1420 s		
1350 m	1360 s	1382 m	1385 s	rNH <sub>2</sub>
1285 w	1320 msh	1315 w	1330 s	rNH <sub>2</sub>
1240 mw		1265 s		
1120 s	1126 mb	1120 vw	1115 mw	ν <sub>a</sub> CN'
1010 m	1050 mw	1040 vw	1040 wb	ν <sub>s</sub> CN'
	1000 m	985 ms	975 mw	
955 sh				πNH
844 vs	744 ssh	720 m	720 m	νCS
838 vs				
780 s	720 m	690 m	660 vw	νCS
	710 wsh			
735 s	860 vw	808 ms	790 mw	τNH <sub>2</sub>
710 m				
640 s				πSk
	630 w	610 s	615 w	δring
	620 m			
599 sb	555 w	545 sh	540 w	wNH <sub>2</sub>
550 s				
515 sb				πSk
470 s	505 mw	505 sb	470 w	δNCS
	420 w	425 m	400 m	νMS
				+δNCS
396 s	350 ms	†	†	δSk (ring)
	275 w			
	304 w	†	†	νMS
297 m	296 w	†	†	δNCS
	330 m			
258 vs	240 w	†	†	πSk
240 s	200 sh			

\*τ = torsion, w = wagging, π = out-of-plane bending, Sk = skeletal.

†Not investigated.

*NH frequencies* — Dithiobiuret exhibits five bands at 3360, 3280, 3185, 3115 and 3040 cm<sup>-1</sup> assignable to NH<sub>2</sub> and NH stretching modes, whereas in the metal complexes only three bands around 3390, 3300 and 3170 cm<sup>-1</sup> are observed. Similarly, instead of two NH<sub>2</sub> bending modes in DTB, at 1645 and 1626 cm<sup>-1</sup>, a single band around 1665 cm<sup>-1</sup> is observed in the nickel complex. These are in accordance with the change of structure of DTB from C<sub>s</sub> to C<sub>2v</sub> on bidentate coordination to the metal.

*CS and CN frequencies* — Coordination of thioamides through their thiocarbonyl sulphur atoms results in the decrease in C=S stretching frequency and an increase in the C-N stretching frequency<sup>10,12</sup>. The bands at 840 (doublet) and 780 cm<sup>-1</sup> in DTB can be assigned to C=S stretching<sup>17</sup>. The 840 cm<sup>-1</sup> band is lowered to 744, 720 and 720 cm<sup>-1</sup> in nickel, cadmium and mercury complexes respectively. Similarly, the 780 cm<sup>-1</sup> band shifts to 720, 690 and 660 cm<sup>-1</sup> respectively in the complexes of nickel, cadmium and mercury. The decrease in the 780 cm<sup>-1</sup> band is in the expected order of the tendency of the metals for sulphur coordination, Hg > Cd > Ni. The C=S frequency at 840 cm<sup>-1</sup> is not sensitive to the nature of the metal. This may be attributed to the fact this band is due to a mixed mode having lesser contribution from C=S stretching. On the other hand, the band at 780 cm<sup>-1</sup> is due to a nearly pure C=S stretching mode. The assignment of

the C=S stretching frequencies in the nickel complex around 744 and 720 cm<sup>-1</sup> is supported by the normal coordinate treatment, and in the spectrum of the nickel complex, there is no other band in the range 900-750 cm<sup>-1</sup>. The large shift in the 840 and 780 cm<sup>-1</sup> bands of DTB in the metal complexes should be attributed, in part, to the change in structure of the ligand from *trans-cis* to the *trans-trans* structure in the metal complexes and, in part, to the coordination of DTB to the metal.

The C-N stretching frequencies in DTB may be assigned at 1495 and 1410 cm<sup>-1</sup>. In the nickel complex, the C-N stretching modes occur at 1490 and 1430 cm<sup>-1</sup>, and thus they are not very sensitive to coordination possibly due to their highly coupled nature. However, the 1490 band of NiCl<sub>2</sub>.2DTB shifts to 1515 cm<sup>-1</sup> in cadmium and mercury complexes. Similarly, the 1430 cm<sup>-1</sup> band appears at 1440 (1420) and 1470 cm<sup>-1</sup> in cadmium and mercury complexes respectively.

*M-S frequencies* — The bands at 420 and 304 cm<sup>-1</sup> are due to symmetric and asymmetric νNi-S modes respectively. The 420 cm<sup>-1</sup> band is coupled with symmetric C-N stretching and NCS bending modes, while the 304 cm<sup>-1</sup> band is due to a nearly pure asymmetric Ni-S stretching. This is compatible with that in bis(dithioacetylacetonato)nickel(II), where from normal coordinate analysis<sup>2</sup>, the symmetric and asymmetric stretching modes have been assigned around 390 and 300 cm<sup>-1</sup>, respectively.

**Dithiomalonamide**

The observed and calculated frequencies for NiCl<sub>2</sub>·2DTM along with their assignments from the potential energy distributions are given in Table 4. The Raman and infrared frequencies of DTM, together with the infrared frequencies of the complexes are shown in Table 5, where the assignment for the frequencies of the ligand molecule is indicated by comparison with those of the complexes.

*C-N and C=S stretching vibrations* — A comparison of the C-N and C=S stretching frequencies of DTM and its complexes for checking for the expected decrease in the C=S frequency and increase in the C-N frequency on coordination is not valid. There is great difference in the geometry of the ligand when free and complexed. The structure of DTM has not been established by X-ray method. From a comparison with its oxygen analogue<sup>20</sup>, malonamide, it is inferred that the two H<sub>2</sub>N-C=S groups of DTM are not coplanar, which gives DTM a low symmetry, C<sub>1</sub>. On bidentate coordination of DTM through

sulphur atoms, the effective symmetry of the ligand is expected to change to C<sub>2v</sub>. Apart from coordination, the change in the symmetry of the ligand consequent upon coordination of DTM may effect additional changes in the band positions of the ligand in the complexes, as in DTB.

In Ni(II) and Pd(II) complexes, the symmetric C-N stretching mode around 1470 cm<sup>-1</sup> is weakly coupled to NH<sub>2</sub> bending, while the asymmetric C-N stretching around 1520 cm<sup>-1</sup> is coupled with C-C stretching and CH<sub>2</sub> wagging modes. A strong band at 1460 cm<sup>-1</sup> in DTM can be attributed to C-N stretching in agreement with an earlier assignment<sup>10</sup>.

A sharp intense band around 810 cm<sup>-1</sup> in the ligand was assigned by Jensen and Nielsen<sup>10</sup> to C=S stretching. Unambiguous assignment of the infrared bands in the region 850-650 cm<sup>-1</sup> in the complexes of DTM appears to be difficult despite the normal coordinate calculations. The bands around 820 and 690 cm<sup>-1</sup> in the nickel complex, and around 840 and 720 cm<sup>-1</sup> in the palladium complex have similar shape and intensity. The bands around 800 and 700 cm<sup>-1</sup> in the complexes have been favoured by normal coordinate treatment to be predominantly asymmetric and symmetric C=S stretching modes respectively.

TABLE 4 — INFRARED FREQUENCIES (cm<sup>-1</sup>) OF NiCl<sub>2</sub>·2DTM AND THEIR ASSIGNMENT

Mode	Obs.	Calc.	p.d.	Assignment (PED, %)*	
A <sub>1</sub>	3200	3204	0.1	ν <sub>s</sub> NH <sub>2</sub> (100)	
	3000	2998	0.1	νNH <sub>2</sub> (100)	
	2930	2930	0.0	νCH <sub>2</sub> (100)	
	1665	1668	0.2	δNH <sub>2</sub> (77), ν <sub>s</sub> CN (20)	
	1475	1479	0.3	ν <sub>s</sub> CN (64), δNH <sub>2</sub> (13)	
	1410	1401	0.6	δCH <sub>2</sub> (95)	
	1340	1321	1.4	rNH <sub>2</sub> (42), ν <sub>s</sub> CC (25), ν <sub>s</sub> CS (12)	
	1010	1030	2.1	rNH <sub>2</sub> (39), ν <sub>s</sub> CC (32)	
	690	703	1.9	νCS (62), ν <sub>s</sub> CC (14)	
	608	600	1.3	δring (73)	
	427	418	2.1	ν <sub>s</sub> MS (52), δNCS (24)	
	360	346	3.9	δring (88)	
	308	307	0.3	δNCS (55), ν <sub>s</sub> MS (36)	
	B <sub>2</sub>	3200	3204	0.1	ν <sub>a</sub> NH <sub>2</sub> (100)
		3000	2998	0.1	ν <sub>a</sub> NH <sub>2</sub> (99)
1665		1665	0.0	δNH <sub>2</sub> (80), ν <sub>a</sub> CN (17)	
1520		1472	3.2	ν <sub>a</sub> CN (55), ν <sub>a</sub> CC (13), wCH <sub>2</sub> (13)	
1325		1318	0.5	wCH <sub>2</sub> (59), rNH <sub>2</sub> (20)	
1285		1290	0.4	rNH <sub>2</sub> (30), ν <sub>a</sub> CC (29), wCH <sub>2</sub> (19)	
1042		1051	0.9	ν <sub>a</sub> CC (47), rNH <sub>2</sub> (37)	
820		782	3.5	ν <sub>a</sub> CS (64), δNCS (11)	
800					
510		511	0.2	δNCS (59), ν <sub>a</sub> MS (23)	
332		337	1.5	δring (70)	
292		293	0.3	ν <sub>a</sub> MS (69), δNCS (15)	

\*For symbols see Table 2.

TABLE 5 — VIBRATIONAL FREQUENCIES (cm<sup>-1</sup>) OF DTM AND ITS COMPLEXES AND THEIR ASSIGNMENT

	DTM		NiCl <sub>2</sub> ·2DTM	PdCl <sub>2</sub> ·DTM	Main assignment
	Raman	Infrared			
		1636 vsb	1655 s	1660 s	δNH <sub>2</sub>
		1542 w		1547 w	
1480 w		1460 vsb	1520 msh	1515 mw	νCN
			1475 s	1470 ms	
			1410 m	1418 m	δCH <sub>2</sub>
1318 m		1382 m	1340 s	1325 s	rNH <sub>2</sub> +νCC
		1345 sh	1285 m	1285 s	
		1245 s			
		1218 s			
		1305 ms	1325 ms	1325 s	wCH <sub>2</sub>
		1160 sh	1185 vw	1182 w	
			1165 vw	1150 w	
1116 w		1080 sh	1080 w	1080 w	
		990 vs	1042 m	1040 sh	νCC+rNH <sub>2</sub>
980 m		975 vs	1010 s	1010 ms	
			930 w	970 w	rCH <sub>2</sub>
			820 s	840 s	νCS
801 ms		810 vs	800 msh	810 w	
			800 vs	780 m	τNH <sub>2</sub>
			752 mb	750 mw	wNH <sub>2</sub>
		750 vs	720 mw	750 mw	
		730 vs	690 s	716 s	νCS
			608 s	622 s	δSk
624 s		628 s			
		612 vsb			
		532 s	510 m	515 ms	δNCS
470 mw		468 s	470 vw	465 ms	πSk
433 w		426 m	427 m	420 m	νMS*+δSk
426 m					
			380 w	388 w	πSk
			360 w	360 m	δring
			332 w	340 w	
299 m	306 s		308 s	280 vw	δNCS
			292 shw	268 vw	νMS
185 m					
109 vs					

τ = torsion, w = wagging, π = out-of-plane bending, Sk = skeletal.

\*Not applicable to DTM.

*Metal-sulphur vibrations* — In the nickel complex, the bands at 427 and 293 (calc.)  $\text{cm}^{-1}$  are predominantly due to symmetric and asymmetric Ni-S stretching modes respectively. These are compatible with Ni-S stretching vibrations around 390 and 295  $\text{cm}^{-1}$  reported in the case of nickel(II) dithioacetylacetonate<sup>2</sup>. The symmetric Pd-S stretching mode is coupled with NCS bending and has contributions in the 420 and 280  $\text{cm}^{-1}$  bands, larger contribution being in the latter band. The asymmetric Pd-S stretching occurs around 265  $\text{cm}^{-1}$ . This assignment compares favourably with Pd-S asymmetric and symmetric stretching modes assigned around 285 and 380  $\text{cm}^{-1}$  respectively in palladium(II) dithioacetylacetonate<sup>2</sup>.

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