

Vibrational Spectra & Normal Coordinates for Semicarbazide & Semicarbazide Hydrochloride

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The infrared spectra of semicarbazide, semicarbazide hydrochloride and its N-deuterated derivative have been measured in the solid state. The normal coordinate analysis has been made for semicarbazide and its hydrochloride- d_0 and $-d_6$. A Urey-Bradley force function supplemented with a valence force field for the out-of-plane vibrations of the planar skeleton has been employed. The calculated frequencies fit the observed frequencies for all the three molecules satisfactorily. The assignments of the fundamental frequencies have been discussed by referring to the isotopic frequency shift, group frequencies in related molecules and the theoretical band assignments derived from force constant calculations. The potential barriers to the internal rotation for the $-NH_2$, $-NH_3$ and $-CN$ groups are estimated from the force constants for semicarbazide hydrochloride.

MANY metal complexes of semicarbazide (SC) have been investigated¹⁻⁴ using various physicochemical methods. However, only one infrared study has been made on semicarbazide, by Mashima⁵, who assigned tentatively some characteristic bands. Semicarbazide is isoelectronic with N-methylurea(NMU) for which the vibrational spectra and normal coordinate analysis have recently been reported⁶. Further, the normal coordinate calculations of the thio and seleno analogues of semicarbazide have been carried out by one of us⁷. Thus, reliable force constants from related molecules are available for transference to SC. Infrared assignments for hydrazine derivatives, the chemistry of which is rich and diverse⁸, are scanty. It was felt that it would be of interest to make a detailed vibrational assignments for semicarbazide and its hydrochloride with the aid of normal coordinate analysis. The normal coordinate treatment of semicarbazide hydrochloride (SCHCl) and its deuterated species would provide further support for the IR band assignments in case of SC also.

Materials and Methods

Semicarbazide was obtained using Campbell's procedure² and was recrystallized from absolute ethanol. SCHCl was a BDH reagent and it was purified by recrystallization from alcohol. The deuterated SCHCl was obtained by repeated exchange reactions with D_2O . SC could not be deuterated since it is affected by water. The infrared spectra of the solid samples were recorded on a Perkin-Elmer spectrophotometer model 580 in the region 4000-200 cm^{-1} in nujol mull and polyethylene pellet. The instrument was calibrated using the standard

frequencies of polystyrene. The spectra of SCHCl between 200 and 70 cm^{-1} were measured on a Grubb Parsons spectrophotometer in polyethylene pellet.

Normal coordinate analysis — Both SC and SCHCl possess the molecular point group symmetry C_s . There are 24 normal vibrations for SC classified as 16 a' (in-plane) and 8 a'' (out-of-plane) modes and the 27 fundamentals of SCHCl are divided into 18 a' and 9 a'' modes. Both a' and a'' modes are infrared and Raman active. The structural parameters employed for SC and SCHCl are given in Table 1. The bond lengths and bond angles of SC are based on the X-ray structure data⁹ of thiosemicarbazide (TSC) and the C=O distance was taken from SCHCl. The parameters of SCHCl were transferred from the known X-ray crystal structure data¹⁰ with minor adjustments.

TABLE 1 — STRUCTURAL PARAMETERS OF SC AND SCHCl

	Bond length (Å)		Bond angle		
	SC	SCHCl	SC	SCHCl	
NH	1.020	1.020	OCN	120°	123°
NN	1.399	1.420	CCN'	120°	120°
CN'	1.337	1.370	NCN	120°	114°
CN	1.337	1.350	CN'H	120°	123°
CO	1.220	1.220	NN'H	120°	123°
			CNN	120°	114°
			CNH	120°	120°
			HNH	120°	120°
			HN ₁ N	109°28'	109°28'
			HN ₁ H	109°28'	109°28'

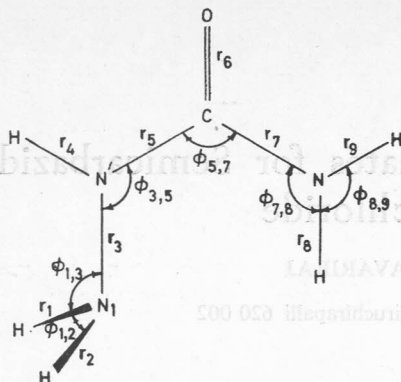


Fig. 1 — Structure and internal coordinates of semicarbazide.

The normal coordinate analysis was performed according to Wilson's GF matrix method¹¹. The structures and internal coordinates for SC and SCHCl are shown in Figs 1 and 2, respectively. The symmetry coordinates employed were similar to those of SC and NMU for SC and SCHCl, respectively. A simple Urey-Bradley force function with force constants transferred from TSC and NMU was employed. For the out of plane vibrations of the planar skeleton, a valence force field with the initial force constants taken from NMU and acetamide¹² was used.

The normal coordinate calculations were first carried out for SC. The force constants were afterwards transferred to SCHCl with minor modifications for the coordinate treatment. The initial calculated frequencies reproduced fairly well the observed frequencies of SC as well as SCHCl- d_0 and - d_8 lending confidence to the assignments obtained. Further, the potential energy distributions (PED) amongst the symmetry coordinates were fairly stable

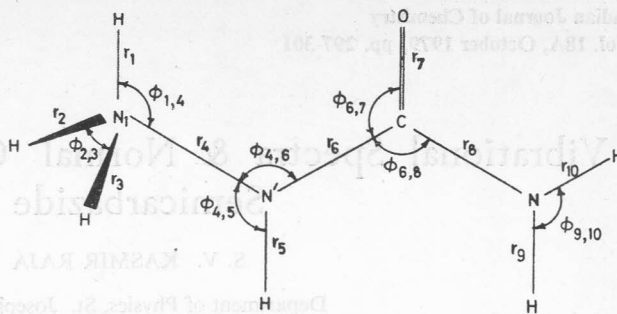


Fig. 2 — Structure and internal coordinates of monoprotonated semicarbazide cation.

during the course of iterations. An interaction constant P (NH, NH) for the amide NH_2 group has been introduced as done in the case of other amide and thioamide molecules^{13,14}. The force constants were refined as indicated in an earlier paper¹⁵.

The numerical computations were made on an IBM 360/44 digital computer at the Computer Centre of the Indian Institute of Science, Bangalore, with programs written in FORTRAN IV, which are similar to those of Schachtschneider¹⁶.

Results and Discussion

Force constants — The final force constants for SC and SCHCl are presented in Table 2. The values of these force constants seem to be reasonable and are close to the initial ones thus demonstrating the transferability of the Urey-Bradley force constants as in urea^{5,17,18} and amide derivatives^{19,20}. The force constants of SC, particularly the stretching and repulsion constants, are very similar to those of SCHCl, as expected. The agreement between the calculated and observed frequencies for SC, SCHCl- d_0

TABLE 2 — FORCE CONSTANTS OF SC AND SCHCl

Urey-Bradley constants (mdyn. \AA^{-1})		SC		SCHCl		SC		SCHCl		SC		SCHCl	
$K(\text{N}_1\text{H})$	4.75	4.35	$H(\text{HN}_1\text{H})$	0.59	0.49	$F(\text{HN}_1\text{H})$	0.10	0.09	$P(\text{NH}_2, \text{NH})$	-0.22	-0.18		
$K(\text{N}'\text{H})$	5.10	5.25	$H(\text{HN}'_1\text{N})$	0.15	0.25	$F(\text{HN}'_1\text{N})$	0.45	0.50	$k(\text{NH}_2)$				-0.012
$K(\text{NH})$	5.50	5.80	$H(\text{CN}'\text{N})$	0.27	0.14	$F(\text{C}'\text{NN})$	0.35	0.20					
$K(\text{NN})$	4.85	5.05	$H(\text{HN}'\text{N})$	0.12	0.18	$F(\text{HN}'\text{N})$	0.55	0.55					
$K(\text{CN}')$	5.70	4.85	$H(\text{HN}'\text{C})$	0.26	0.34	$F(\text{HN}'\text{C})$	0.48	0.50					
$K(\text{CN})$	5.95	5.50	$H(\text{NCN})$	0.27	0.88	$F(\text{NCN})$	0.55	0.55					
$K(\text{CO})$	8.05	6.80	$H(\text{OCN}')$	0.40	0.20	$F(\text{OCN}')$	1.50	1.25					
			$H(\text{OCN})$	0.34	0.11	$F(\text{OCN})$	1.60	1.40					
			$H(\text{HNC})$	0.28	0.35	$F(\text{HNC})$	0.46	0.52					
			$H(\text{HNH})$	0.43	0.34	$F(\text{HNH})$	0.00	0.00					

Valence constants* (mydn. $\text{\AA}/\text{rad.}^2$)

	SC	SCHCl		SC	SCHCl
$f(\pi\text{NH})$	0.180	0.085	$f(\omega\text{NH}_2)$	0.045	0.090
$f(\pi\text{NH}, \tau\text{CN})$	0.035	—	$f(\tau\text{CN})$	0.065	0.075
$f(\pi\text{NH}, \tau\text{NH}_2)$	—	-0.022	$f(\tau\text{CN}, \tau\text{NH}_2)$	0.020	—
$f(\tau\text{CO})$	0.200	0.240	$f(\tau\text{N}_1\text{H}_2)$	0.034	—
$f(\tau\text{NH}_2)$	0.100	0.130	$f(\tau\text{NH}_2)$	—	0.033

1 mydn. $\text{\AA}^{-1} = 100 \text{ Nm}^{-1}$

* π , τ and ω have the same meaning as in Tables 3 and 4.

TABLE 3 — INFRARED FREQUENCIES (cm^{-1}) OF SC AND THEIR ASSIGNMENTS

Obs.	Calc.	Assignment*, (PED†, %)
<i>a'</i> mode		
3350	3343	$\nu_{as}\text{NH}_2(100)$
3210	3208	$\nu\text{NH}(100)$
3130	3124	$\nu_s\text{NH}_2(100)$
3020	3017	$\nu\text{N}_1\text{H}_2(100)$
1685	1678	$\nu\text{CO}(49), \nu\text{CN}(18)$
1640	1637	$\delta\text{NH}_2(53), \nu\text{CN}'(18)$
1595	1598	$\delta\text{N}_1\text{H}_2(84)$
1540	1550	$\nu\text{CN}'(34), \nu\text{CN}(25), \delta\text{NH}_2(23)$
1382	1384	$\delta\text{NH}(60), \nu\text{NN}(19)$
1195	1191	$\nu\text{NN}(53), \delta\text{NH}(31)$
1050	1087	$r\text{NH}_2(76)$
1008	991	$\nu\text{CN}'(29), \nu\text{CN}(27)$
775	775	$\omega\text{N}_1\text{H}_2(78)$
615	606	$\delta\text{CO}(77)$
560	564	$\delta\text{NNC}(45), \delta\text{NNC}(29)$
260	256	$\delta\text{NNC}(56), \delta\text{NNC}(38)$
<i>a''</i> mode		
3010	3015	$\nu\text{NH}_2(100)$
950	953	$t\text{NH}_2(93)$
665	678	$\tau\text{NH}_2(78)$
650	634	$\pi\text{NH}(55)$
520	527	$\omega\text{NH}_2(65)$
420	423	$\tau\text{N}_1\text{H}_2(45), \pi\text{CO}(36), \omega\text{NH}_2(18)$
340	328	$\pi\text{CO}(33), \tau\text{N}_1\text{H}_2(31), \tau\text{CN}(19)$
192	194	$\tau\text{CN}(71), \tau\text{N}_1\text{H}_2(21)$

*Description of the modes: ν —stretching, δ —bending, r —rocking, ω —wagging, t —twisting, τ —torsion and π —out-of-plane bending; *as*—antisymmetric and *s*—symmetric

†Potential energy distribution less than 15% is ignored.

and $-d_6$ is good indicating the applicability of the Urey-Bradley force field.

Band assignment

The frequency data along with their assignments for SC are presented in Table 3. Similar data for SCHCl and its deuterated species are shown in Table 4. A brief discussion of the assignments is given below. It is to be noted that the N-N bond is *trans* to the C=O group in SC, while in SCHCl it is *cis* with respect to the C=O bond, and that there is a change of conformation from SC to SCHCl.

In-plane vibrations—In the infrared spectra*, SC and SCHCl show bands at 3350 and 3130, and at 3430 and 3240, respectively, arising from the asymmetric and symmetric amide NH_2 stretching vibrations. The corresponding bands in NMU occur at 3460 and 3243. The NH stretching band may be assigned at 3210 and 3270 for SC and SCHCl, respectively, which is compatible with the NH stretching frequency of NMU at 3243. The symmetric (N) NH_2 stretching of SC may be assigned at 3020 which is lower than the corresponding band of TSC⁷ at 3180. The asymmetric and symmetric stretching modes of the NH_3 group may be attributed to bands at 2930 and 2890 in analogy with those present in hydrazinium hydrochloride²¹.

*The IR band positions are given in cm^{-1} throughout the paper.

 TABLE 4 — INFRARED FREQUENCIES (cm^{-1})* AND THEIR ASSIGNMENTS FOR SCHCl AND SCHCl- d_6

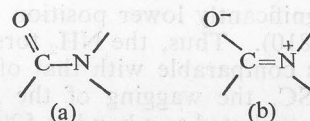
SCHCl- d_6		SCHCl		Assignment, (PED, %) [†]
Obsc.	Calc.	Obs.	Calc.	
<i>a'</i> mode				
2580	2539	3430	3425	$\nu_{as}\text{NH}_2(100)$
2410	2383	3270	3262	$\nu\text{NH}(100)$
2340	2330	3240	3226	$\nu_s\text{NH}_2(100)$
2160	2156	2930	2924	$\nu_{as}\text{NH}_3(100)$
2055	2071	2890	2889	$\nu_s\text{NH}_3(100)$
1665	1640	1682	1678	$\nu\text{CO}(14), \nu\text{CN}(18), \delta\text{NNC}(15)$
1172	1184	1585	1585	$\delta\text{NH}_2(83)$
1125	1126	1568	1569	$\delta\text{NH}_2(85)$
1475	1478	1530	1535	$\delta\text{NH}(36), \nu\text{CN}'(30)$
1095	1098	1480	1479	$\delta_s\text{NH}_3(88)$
930	944	1380	1371	$\nu\text{CN}(45), \delta\text{NH}(26)$
1320	1319	1220	1215	$\nu(\text{NN}(62)$
901	900	1182	1145	$r\text{NH}_2(61)$
760	757	1145	1088	$r\text{NH}_2(53), \nu\text{CO}(20)$
1015	1001	938	940	$r\text{NH}_3(37), \nu\text{CN}'(30)$
560	551	585	581	$\delta\text{OCN}(76)$
445	455	512	512	$\delta\text{NNC}(67)$
ni	205	225	224	$\delta\text{NNC}(81)$
<i>a''</i> mode				
2125	2160	3080	2928	$\nu\text{NH}_2(100)$
1055				
1020	1109	1580	1548	$\delta\text{NH}_2(92)$
802	817	1090	1054	$r\text{NH}_2(92)$
525	551	772	769	$\tau\text{NH}_2(95)$
640	602	722	724	$\omega\text{NH}_2(89)$
430	432	600	598	$\tau\text{NH}_3(34), \tau\text{CN}(34), \pi\text{NH}(30)$
430	428	465	469	$\pi\text{CO}(73)$
ni	235	315	315	$\tau\text{NH}_3(57), \pi\text{CO}(25)$
ni	129	155	143	$\tau\text{CN}(33), \pi\text{NH}(50)$

*The frequencies of SCHCl- d_6 are so matched as to approximately have the assignments shown for SCHCl.

†Symbols have the same meaning as in Table 3; ni—not investigated.

The C=O stretching coordinate contributes predominantly to a band near 1680 in both SC and its hydrochloride. The contribution from CN stretching is considerable for these bands, thus closely resembling the amide I band as in acetamide²² and N-methylacetamide^{23,24}. In NMU the carbonyl stretching band is found at a considerably lower frequency (1646).

The asymmetric and symmetric C-N stretching frequencies may be assigned at 1540 and 1008 for SC whereas in SCHCl, the C-N stretching modes are more coupled and contribute to the bands at 1534, 1380 and 940. The CN stretching frequencies indicate a fair amount of double bond character and favour considerable contribution from the canonical form (b) to the total structure of SC and SCHCl. The symmetric CN stretching band of NMU is exhibited at 918, which is about 100 cm^{-1} lower than that in urea¹⁸. As in SC, the CN asymmetric stretching of NMU mixed with NH_2 bending is found at 1577.



The hydrazinic NH_2 bending of SC is assigned at a lower frequency, 1595, than the amide NH_2 bending, 1640, which has a small contribution from the CN stretching coordinate. In SCHCl however the amide NH_2 bending mode is pure and is found at 1585. From the potential energy distributions, the nature of the rocking vibration of the amide NH_2 group is found to be nearly pure in both SC and its hydrochloride but the band occurs at a position more than 100 cm^{-1} lower in SC (1045) compared to that in SCHCl (1182). This assignment may be compared with the corresponding one in acetamide²² at 1152 and in NMU⁶ at 1170. According to the normal coordinate calculations, a band at 775 in the infrared spectrum of SC may be attributed to hydrazinic NH_2 wagging. The corresponding band in TSC⁷ and sulphonamide²⁵ occurs near 730.

A band of interest in the infrared spectra of hydrazo derivatives is that due to NN stretching vibration. The normal coordinate treatments suggest that a band at 1190 in SC and at 1220 in SCHCl may be assigned to the NN stretching band. Thus the NN stretching frequency in these two hydrazo compounds is somewhat higher than that in TSC (1160), and substantially higher than that in hydrazine²⁶ (1090). The increase in the NN stretching frequencies of SC and SCHCl may be said to be similar to the increase in the NN stretching frequency of hydrazine occurring on coordination to metal ions. In the metal complexes of hydrazine, the NN stretching frequency is assigned²⁶ near 1150.

The NH bending frequency of SC may be assigned at 1382, whereas in SCHCl, the NH bending mode is coupled and contributes principally to the bands at 1530 and 1380. The assignment of NH bending of SC is comparable to that of NMU at 1354 while that of SCHCl may be compared with that of TSC, where the bands at 1530 and 1380 have respectively 36 and 26 per cent contribution from NH bending.

The asymmetric and symmetric bending and the rocking vibrations of the NH_3 group of SCHCl may easily be identified with bands at 1568, 1480 and 1145 respectively, in agreement with bands assigned in glycine²⁷ at 1585, 1500 and 1130.

The C=O bending frequency of SC and SCHCl may be assigned to bands at 605 and 580, respectively. The position is compatible with those of acetamide²² and N-methylacetamide^{23,24} which show this frequency around 585 and that of urea¹⁸ at 575, but is lower than that of NMU⁶ assigned at 660. The NCN and CNN bending vibrations couple in SC and occur at 560 and 260, respectively, and in SCHCl they are nearly pure and are assigned respectively at 512 and 225.

Out-of-plane vibrations — There are five out-of-plane bending modes for the planar skeleton of SC and SCHCl. The torsional vibration of the amide NH_2 group for SC and SCHCl may be assigned respectively at 665 and 772. For SC, this mode occurs at, nearly the same position as in NMU (710), but is at a significantly lower position than that in acetamide¹² (810). Thus, the NH_2 torsional mode of SCHCl is comparable with that of acetamide. Similarly, in SC, the wagging of the planar NH_2 group may be attributed to a band at 520 in analogy

with the 531 band of NMU but the corresponding band in acetamide¹² is assigned at a much higher frequency, 700. The coordinate calculations for SCHCl indicated that a band near 720 may be assigned to NH_2 wagging which is in agreement with assignments in acetamide and thioacetamide²⁰ (~ 700). The out-of-plane deformations of the planar NH_2 group thus appear to be rather sensitive to the molecular environment. In a like manner, the out-of-plane C=O bending mode has been assigned differently. For example, for NMU⁶, it is assigned at 780, whereas for acetamide¹² it is assigned at 582 and in N-methylacetamide^{23,24} at 627. The bands at 420 and 465 in the infrared spectrum of SC and SCHCl, respectively, may be assigned to the C=O out-of-plane bending.

A band at 650 in the infrared spectrum of SC may be assigned to NH bending. This is comparable with the 590 band of NMU. Similarly, the assignment of 192 band in SC to C-N torsion is compatible with the similar assignment of a band at 183 in NMU. In SCHCl however the NH bending and CN torsion are highly coupled and occur at 600 and 155 respectively.

A band at 340 in the spectrum of SC may be attributed to the $-\text{NH}_2$ torsional mode of the $-\text{NHNH}_2$ group which is compatible with the assignment of similar modes in N-methylhydrazine²⁸ and N,N-dimethylhydrazine²⁹ respectively at 315 and 295. The NH_3 torsion of the SCHCl occurs as a mixed mode contributing to the bands at 600 and 315. In contrast, the corresponding band in glycine²⁷ (which has the zwitterion structure $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$) and $\text{NH}_2\text{NH}_3\text{Cl}$ ^{22,30} is assigned near 510. The other vibrations of the (N) NH_2 and NH_3 groups are easily assigned as shown in the Tables 3 and 4.

SCHCl- d_6 — There is good agreement between the observed and calculated frequencies for the deuterio isotopomer of SCHCl, as observed from Table 4, thus supporting the assignments derived for SCHCl itself. For brevity, the deuterium frequency shifts are not individually discussed. The deuterated SC could not be obtained, as already mentioned, by exchange reaction with D_2O , since SC is affected by water.

Internal rotation — The potential barriers for the internal rotation about the C-N and N-N bonds of the $-\text{CONH}_2$ and the $-\text{NHNH}_3$ groups respectively may be approximately calculated from the values of the respective torsional force constants. Employing the treatment used for NMU⁵ and acetamide¹², the barrier heights can be obtained from the relation,

$$V_{\text{NH}_2} = 2f(\tau\text{NH}_2) = 36.1 \text{ kcal/mol}$$

and

$$V_{\text{NH}_3} = 3/4(\tau\text{NH}_3) = 3.4 \text{ kcal/mol}$$

The value of V_{NH_3} lies in between those of NMU and N-methylthiourea³¹ (NMTU) (31.0 kcal/mol) and acetamide¹² (40.1 kcal/mol). The value of V_{NH_3} of SCHCl is higher than the corresponding V_{CH_3} in acetamide and NMU (1.3-1.7 kcal/mol).

Similarly, the barrier to internal rotation about the CN bond of the $-\text{CONH}-$ group is given by

$$V_{\text{CN}} = 2f(\tau\text{CN}) - \Delta V/4$$

where ΔV is the energy difference between the *cis* and *trans* isomers of SCHCl. The value for ΔV may be taken to be 2.0 kcal/mol as in the case in NMU. Then $V_{CN} = 21.1$ kcal/mol. The value obtained for V_{CN} of SCHCl is slightly lower than that for NMU and NMTU (~ 26.0 kcal/mol) and N-methyl thioformamide³² (28.0 kcal/mol).

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The characteristic bands of ETU, ETU- Δ and 2-methyl-ETU are listed along with their assignments. A brief discussion of the assignments is given below. The spectra of the metal complexes are separately discussed.

NH group vibrations—The symmetric and asymmetric NH modes (ν_1 and ν_2) are easily assigned to the broad bands centered at 3275 and 3250 and are found at 3293 and 3250 in the Raman. On deuteration, they are replaced in the IR spectrum by new bands at 2435 and 2400 respectively.

The symmetric NH bending mode occurs as a mixed vibration and contributes equally to the bands at 1528 and 1212. This assignment differs from the earlier assignment (~ 1200 exclusively) by Mecke et al. and Kishoo. In ETU- Δ bands at 800 and 802 may have contributions from ND bending. The asymmetric NH bending vibration in ETU is found as a pure vibration at 1376. On N-deuteration this band is shifted to 927 as is to be expected.

C-N and C-2 group vibrations—The symmetric ν_{CN} mixed mainly with NH bending is associated with the 1528 band as in secondary thioamides. The asymmetric ν_{CN} however, is pure and appears

investigation of the vibration spectra of analogous sulphur and selenium compounds is a subject of considerable current interest. A comparative study of the IR spectra of ETU and its selenium analogue, ethyleneselenouracil (ESU) is described in this paper. The IR spectra of 2-methyl and N,N'-dibenzyl-2-thiothiouracil and some transition metal complexes of ETU have also been investigated to further support the assignments for ETU.

Materials and Methods

ETU was synthesized and purified according to the method of Allen et al. N,N'-dibenzyl-2-thiothiouracil (ETU- Δ) was obtained by reported recrystallization of ETU from D₂O.

The 2-methyl derivative of ETU was prepared from ETU and methyl iodide according to Brand and Brand. The metal complex of the type MCl₂·2ETU [M=Co (II), Ni (II), Zn (II), Cd (II)] was prepared according to the method of Brand.

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