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9. **Kōichi Nagata**: Studies on Thiohydroxamic Acids and Their Metal Chelates. V. Infrared Spectra of Metal Chelates of Thiohydroxamic Acids.[*1]

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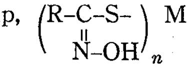
The infrared spectra of some metal salts of thiohydroxamic acids (I) and O-methylthiohydroxamic acids (II) were investigated, and it was decided that the salts have the structures including oxime group,  $\left(\begin{array}{l}\text{R-C-S-}\\ \quad\|\\ \ \ \text{N-OH}\end{array}\right)_n M^{+n}$ (M=Metal ion), by deuteration method. From the comparisons of the band frequencies which are attributed to the oxime group with those of the corresponding derivatives (S-methyl derivatives and disulfides of I or II) it was shown that some transition metal salts have the chelate structures. Although it was difficult to decide finally whether the chelate structures are the S-O coordinated or the S-N coordinated type, the former seemed to be more probable.

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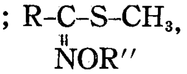
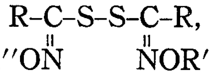
We have shown that some transition metal salts of thiohydroxamic acids must be chelates in the preceding paper,[*1] but their structures have been remained uncertain. In this paper we investigated the infrared spectra of the salts to determine their structures.

As pointed out in Part II,[*3] the ligands, thiohydroxamic acids, exist in thione form in the solid state but as thiol and thione tautomers in the liquid or in the solution. However, their metal salts undoubtedly exist in thiol form, including oxime groups, as described below. Therefore, since ordinary comparative study for the spectral feature of ligands with their salts was impossible, S-methyl derivatives (I;  $\begin{array}{l}\text{R-C-S-CH}_3\\ \quad\|\\ \ \ \text{NOR}''\end{array}$, R″=H (Ia) or CH_3 (Ib)) or disulfides (II;  $\begin{array}{l}\text{R-C-S-S-C-R}\\ \quad\ \|\qquad\quad\ \|\\ \text{R}''\text{ON}\quad\ \ \text{NOR}''\end{array}$, R″=H (IIa) or CH_3 (IIb)) of thiohydroxamic acids were used as reference compounds in place of ligands.

Infrared spectra of some metal complexes and their deuterated compounds are shown in Fig. 1 and 2. There seems no doubt that the complexes include oxime group in their molecules because the changes of the band frequencies after deuteration, as a whole, closely resemble that of compound Ia and IIa, the structures of which have been confirmed in Part III.[*4] That is, in Fig. 1 and 2 two bands at about 1600 cm^{-1} and 1430 cm^{-1} disappear on deuteration, and then new bands appear around 1550 cm^{-1} and 1020 cm^{-1}, accompanied by the slight shifts of the neighboring bands in their positions. These changes of band frequencies indicate that the OH deformation band shifted from 1430 cm^{-1} to 1020 cm^{-1} after deuteration so that C=N stretching band shifted from 1600 cm^{-1} to 1550 cm^{-1} by the extinguishment of the vibrational coupling between the OH deformation and C=N stretching band. In the high wavenumber region the broad OH stretching bands at about 3200 cm^{-1} remove to about 2300 cm^{-1} on deuteration, and the bands around 850 cm^{-1} which disappear after deuteration must be ascribed to the OH out-of-plane bending bands.

[*1] Part IV: This Bulletin, **15**, 61 (1967).

[*2] Sagisukami, Fukushima-ku, Osaka (永田耕一).

[*3] Part II: This Bulletin, **14**, 1255 (1966).

[*4] Part III: *Ibid.*, **14**, 1263 (1966). Infrared spectra of compound I and II have been presented.

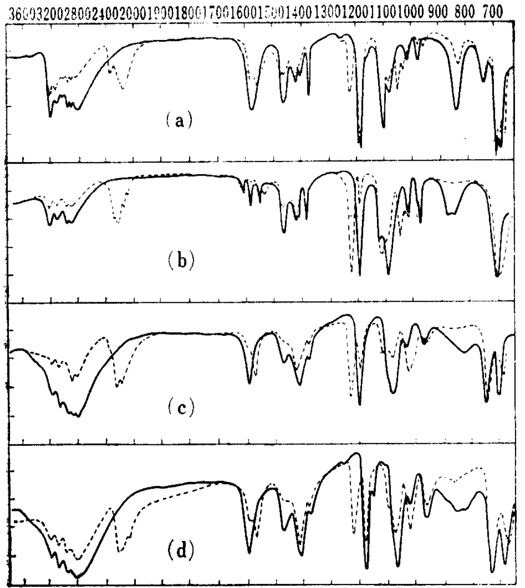


Fig. 1. Infrared Spectra of $\left(\mathrm{CH_3C}\genfrac{}{}{0pt}{}{\diagup \mathrm{S-}}{\diagdown \mathrm{NOH}}\right)_n \mathrm{M}^{+n}$ (KBr)

(a) M=Zn(II) (b) M=Fe(III)
(c) M=Ni(II) (d) M=Pd(II)

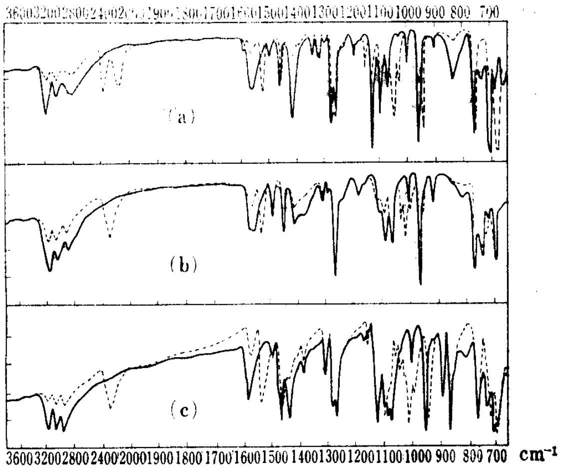
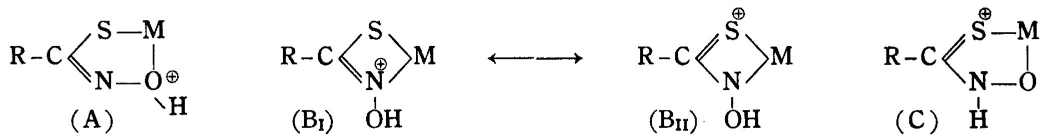


Fig. 2. Infrared Spectra of $\left(\mathrm{C_6H_5C}\genfrac{}{}{0pt}{}{\diagup \mathrm{S-}}{\diagdown \mathrm{NOH}}\right)_n \mathrm{M}^{+n}$ (KBr)

(a) M=Zn(II) (b) M=Ni(II)
(c) M=Pd(II)(+1 mol. dioxane)

——— original ------ deuterated

These investigations indicate that the structures of the metal chelates of thiohydroxamic acids are the formula (A) or (B). The formula (C) which corresponds to the structures of metal chelates of hydroxamic acids is not probable, because the formula (C) including -N-C=S group should show the characteristic "-N-C=S bands"[1] which undergo more complex changes in the region $1200\sim1600\ \mathrm{cm}^{-1}$ after deuteration as reported in Part II*[3] for thione-form of thiohydroxamic acids. The frequencies of



(M=Metal ion)

principal bands are tabulated in Table I∼IV for some metal salts of typical thiohydroxamic acids and O-methylbenzothiohydroxamic acid as compared with the corresponding S-methyl derivatives (compound I) and disulfides (compound II). Here, it is to be noted that the bands of the salts are in fair agreement with those of compound I and II in the $1200\sim1600\ \mathrm{cm}^{-1}$ region.

Now, formula (A) which has S-O coordinated five-membered chelate ring is more reasonable, because the strain of the chelate ring is smallest and the coordination with lone pair of electrons of the oxygen such as in formula (A) is reported for the polynuclear compounds produced by olation of metal ions. But formula (B) which has S-N coordinated four-membered chelate ring is not unlikely under the following considerations; larger bond radius and a smaller bond angle of sulfur atom than those of nitrogen or oxygen may be relieve the strain of the four-membered chelate ring to some extent. In fact, the S-S coordinated four-membered chelates have been reported

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1) C.N.R. Rao, R. Venkataraghavan: Spectrochim. Acta, 18, 541 (1962).

Table I. Comparison of Frequencies (cm^{-1}) for Salts and Derivatives of Acetothiohydroxamic Acid ($R=CH_3$)

Salts							(I)	(II)	
Na	Zn	Cd	Fe	Cu	Ni	Pd	$\text{R-C}\begin{smallmatrix}\diagup\text{SCH}_3\\ \diagdown\text{NOH}\end{smallmatrix}$	$\left(\text{R-C}\begin{smallmatrix}\diagup\text{S-}\\ \diagdown\text{NOH}\end{smallmatrix}\right)_2$	
3236 br, m 3135 sp, w	3215 sp, m 3122 w	3135 br	3212 sp, w 3077 br, m	3185 sp, w 3085 sp, m	3240 sp, w 3160 br, m	3200 sp, w 3100 br, m	3225 3081	3156 3025	ν_{OH}
1558	1584	1562	1578 1547	1589	1593	1595	1630	1629	$\nu_{C=N}$
1446	1468	1461	1459	1476	1468	1473	1493	1464	δ_{OH}
1433	1428 1419	1437 1407	1423 1407	1446 1419	1418 1404	1417	1420	1429	
1385 1368	1380	1380	1378	1385 1375	1388	1376	1374	1378	
1298 w	1262 v. w	1247 w					1325 w 1265 w 1248 w		
							1223 w	1218 w	
1176	1203 1194	1197	1196	1195	1199 1191	1182	1175	1159	
1095 w	1100 m 1089 w	1102 s	1122 sh 1099 s	1095 s	1103 s 1087 s	1072 s			*
1025 m	1021 w	1013 w	1020 m	1025 m	1025 m 997 w	1024 m 1022 w	1014 s	1024 s	*
	982 w	978 m	985 sh 977 m	977 m	975 m	964 m	982 m 974 m		*
926 s							918 s		*
821	842	830	869	910	818	830	738	797	γ_{OH}
	750 w	746 m			740 s 723 s	735 s			*
	699 s 687 s		709 s	710 s	702 s	685 s			*

* Marked difference in the frequency was observed between salt and derivatives of thiohydroxamic acid.
br: broad sp: sharp w: weak s: strong m: medium sh: shoulder

Table II. Comparison of Frequencies (cm^{-1}) for Salts and Derivatives of Benzothiohydroxamic Acid ($R=C_6H_5$)

Salts						(I)	(II)	
Na	Zn	Fe	Cu	Ni	Pd	$\text{R-C}\begin{smallmatrix}\diagup\text{SCH}_3\\ \diagdown\text{NOH}\end{smallmatrix}$	$\left(\text{R-C}\begin{smallmatrix}\diagup\text{S-}\\ \diagdown\text{NOH}\end{smallmatrix}\right)_2$	
3150 m 3050 w	3200 m 3070 w	3230 m	3230 m 3122 m	3190 m 3080 m	3180 m 3065 m	3235	3140	ν_{OH}
1600	1587	1580	1588	1596	1584	1608	1613 1600	
1569	1555	1557	1575	1577	1574	1576	1589	$\nu_{C=N}$
1483	1494	1496	1493	1491	1493	1492 1472	1495	
1453	1455	1466 1456	1454	1455	1448	1448	1449	
1410 1399	1407	1416 1406	1405	1414	1411	1426	1431	δ_{OH}
1339 w	1339 w	1342 w	1331 w	1348 w	1338 w			*
1282	1293	1292	1292	1292	1289	1288	1287	

1250	1266 1253	1259	1266	1267	1262	1249	1242	
1187 1176	1188 1180	1195	1185	1184	1183	1178	1175 1158	
1107 s	1118 s	1113m	1110m	1104 w	1102 w			*
1099 sh	1094m	1094m	1093m	1087m	1082m	1078 w	1074 w	*
1070m	1070m	1075m	1072m	1068 s	1065 s			*
1034	1033	1033	1032	1025	1024	1033	1031	
1000	1000	1000	1000	1000	988	1005	1001	
950 s	958 s	958 s	958 s	959 s	948 s	993m 964m	974 s 938 s	*
916 w 908 w	923 w 920 w	923 w 920 w	915 w	913 w	911 w	922 s	928 s 915 s	*
842 822	842 837	842 837	835	840 808	839 808	739	740	γ_{OH}
787 752	762 742	760	783 757	760 740	756	771	761	
697 s 681m	708 s 686m	727 s 688 s	726 s 683m	718m 685 s	689 sh 682 s	702 s	694 s	*

* Marked difference in the frequency was observed between salt and derivatives of thiohydroxamic acid.
w: weak s: strong m: medium sh: shoulder

TABLE III. Comparison of Frequencies (cm^{-1}) for Salts and Derivatives of O-Methylbenzothiohydroxamic Acid ($R=C_6H_5$)

Salts							(I)	(II)	
Na	Zn	Cd	Cu(I)	Co	Ni	Pd	$R-C\begin{smallmatrix}\diagup SCH_3\\ \diagdown NOCH_3\end{smallmatrix}$	$\left(R-C\begin{smallmatrix}\diagup S-\\ \diagdown NOCH_3\end{smallmatrix}\right)_2$	
1600 1581	1581	1583	1603 1581	1581	1586	1584	1580		
1514	1517	1531	1550	1517	1534	1526	1554	1564 1549	$\nu_{C=N}$
1492	1495	1493	1489	1498	1294	1492	1491	1491	
1313	1315 1291	1312		1313 1291	1316	1311	1333 1322 1290	1319 1289	
1253	1265	1257	1221	1267	1257	1254	1268	1268 1250	
1187 1177	1194 1178	1178	1175	1195 1180	1188 1181	1180	1186	1184	
1154	1149	1160	1159		1160	1158	1178	1160	
1078	1077	1078	1072	1078	1081		1081	1076	
1044	1050	1046	1054	1048	1041	1050	1046	1046	
1023	1030	1028	1030	1030	1027	1029	1026	1025	
1002 w	1003 w	1003 w		1004 w	1005 w	1002 w	1000 s 983m	1003 w	*
970 br, s	978 s	972 s 966 s	989 s 962 w	973 s	958 s	977 s	958 s	955 s	*
929m	922m	918 w	919 w	922 w	929 w	916 w	933 s	918 s	*
839	870 862	870	860	867 859	856	879	877	870 856	
778	770	764	778	772	768	764	778	764	
	729	729	740	731	712	731	732		
704	694	703 691	698	695	699	690	715	706	

* Marked difference in the frequency was observed between salt and derivatives of O-methylthiohydroxamic acid.
br: broad w: weak s: strong m: medium

Table IV. Assigned Bands in Bis(thiohydroxamato)Ni (II), and Comparison of Their Frequencies with Those of Derivatives of Thiohydroxamic Acid

Compounds	ν_{OH}	ν_{OD}	ν_{OH}/ν_{OD}	$\nu_{C=N(H)}$	$\nu_{C=N(D)}$	Shift	δ_{OH}	δ_{OD}	δ_{OH}/δ_{OD}	γ_{OH}
Aliphatic compound										
$\left(\mathrm{R{-}C}\begin{smallmatrix}\mathrm{S-}\\ \mathrm{NOH}\end{smallmatrix}\right)_2\mathrm{Ni}$										
$\mathrm{R=CH_3}$	3240sp, m 3160m	2280sp, m 2200br, w	1.42 1.44	1590	1566	−24	1472	1023	1.44	818br,w
$\mathrm{R=C_2H_5}$	3190m 3100m	2290	1.39 1.35	1582	1558	−24	1398	1003	1.39	815br,w
$\mathrm{R=}n\mathrm{{-}C_3H_7}$	3180w 3085m	2258	1.41 1.37	1581	1559	−22	1436	1020	1.41	808br,m
$\mathrm{R=iso{-}C_3H_7}$	3182sp, m 3070m	2225	1.43 1.38	1587	1557	−30	1448	1028	1.41	862br,m
$\mathrm{R{-}C}\begin{smallmatrix}\mathrm{S{-}CH_3}\\ \mathrm{NOH}\end{smallmatrix}$ a)	3220±5	2375±5	1.36±0.1	1628±2	1602±2	−26	1418±2	1102±7	1.29	740±2
$\left(\mathrm{R{-}C}\begin{smallmatrix}\mathrm{S-}\\ \mathrm{NOH}\end{smallmatrix}\right)_2$ a)	3160±60	2340±40	1.35±0.1	1632±3	1610	−22	1455±10	1100±10	1.32±0.2	760±40
Aromatic compound										
$\left(\mathrm{R{-}C}\begin{smallmatrix}\mathrm{S-}\\ \mathrm{NOH}\end{smallmatrix}\right)_2\mathrm{Ni}$										
$\mathrm{R=C_6H_5}$	3190sp, m 3080br, w	2320	1.38 1.33	1565	1539	−26	1398	1020	1.37	808br,w
$\mathrm{R=}p\mathrm{{-}CH_3{-}C_6H_4}$	3175m 3070m	2305	1.38 1.33	1574	1537	−37	1388	1029	1.35	750*
$\mathrm{R=}m\mathrm{{-}Cl{-}C_6H_4}$	3182m 3080m	2320	1.37 1.33	1574	1532	−42	1396	1030	1.36	735*
$\mathrm{R{-}C}\begin{smallmatrix}\mathrm{SCH_3}\\ \mathrm{NOH}\end{smallmatrix}$ a)	3220±20	2345±40	1.32±0.2	1600±10	1576±6	−24	1436±10	1090±3	1.32	744±30
$\left(\mathrm{R{-}C}\begin{smallmatrix}\mathrm{S-}\\ \mathrm{NOH}\end{smallmatrix}\right)_2$ a)	3190±50	2350±50	1.37±0.5	1610±2	1588±6	−22	1433±8	1083±3	1.32	720±15

a) These compounds have been investigated in Part III.*4

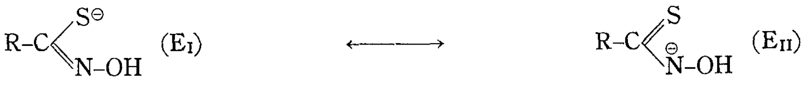
* Since these bands were mixed with another bands, their accurate frequencies could not be assigned.

sp: sharp br: broad w: weak m: medium

for the metal chelates of dithiocarbamic acids or dithioacids. In this case of thiohydroxamic acids the resonance effect between the formula (B_I) and (B_{II}) may contribute to the chelate stability. Furthermore, it is to be noted that metal ions are apt to coordinate with nitrogen atom in oxime group as reported for the chelates of some useful organic reagents, such as dimethylglyoxime, salicylaldoxime and pyridine-2-aldoxime.

Although the final decision is impossible, some informations about the question which the formula (A) or (B) is more probable are available from the infrared spectral data.

The C=N stretching bands of the salts are observed in some lower frequency region than those of compound I and II, as shown in Table I~IV. For the sodium or zinc salts it is apparent that such a shift is due to the contribution of the ionic formula (E_I) and (E_{II}). For the nickel or palladium salts in which the bonds between



$$\mathrm{R{-}C}\begin{smallmatrix}\mathrm{S^{\ominus}}\\ \mathrm{N{-}OH}\end{smallmatrix}\ (\mathrm{E_I}) \longleftrightarrow \mathrm{R{-}C}\begin{smallmatrix}\mathrm{S}\\ \ominus\ \mathrm{N{-}OH}\end{smallmatrix}\ (\mathrm{E_{II}})$$

the metal ion and the ligand atom are more covalent the shifts must result from the spreading of the π-electrons on the C=N link over the chelate ring. If the structures of these salts are formula (B) the C=N stretching frequencies must show almost the same values as those of the sodium or zinc salts because the resonance effect between the formula (B_I) and (B_{II}) must be almost the same as the ionic effect between formula (E_I) and (E_{II}). But the obtained C=N frequencies of the nickel or palladium salts were higher than those of the sodium or zinc salts. This fact is likely to favor the formula (A) as the structure of the chelates.

Next, the OH stretching frequencies of the metal chelates were lower than those of Ia and IIa, while the OH out-of-plane frequencies of the metal chelates showed somewhat large shifts to higher wave numbers. Such a relation between the shift of the OH stretching and out-of-plane band is in agreement with that reported for a series of compounds including oxime group.[2)] In carbon tetrachloride solution the shift of the OH stretching band was more remarkably observed. As shown in Fig. 3b, compound Ia or IIa showed the non-associated and associated OH stretching bands at 3600 cm^{-1} and about 3250 cm^{-1}, respectively, and the latter band disappeared with dilution, but such a non-associated OH stretching bands could not be found for the metal chelates as shown in Fig. 3a and their spectral features were the same as in the solid state. Since the formation of the intramolecular hydrogen bonding, such as reported for the metal chelates of dimethylglyoxime or salicylaldoxime, is impossible in this case, whether the structures are the formula (A) or (B), such downward frequency shifts of the OH stretching bands must be due to the decrease of the force constant of the OH bonding and the resultant increase of the acidity of the oxime group with the chelation. The downward frequency shifts of the NH stretching bands with the formation of the metal complexes have been well known for the compounds including amino or imino group.[3~6)] Although it was very interesting for us to investigate the infrared spectra of the metal complexes of pyridine-2-aldoxime in

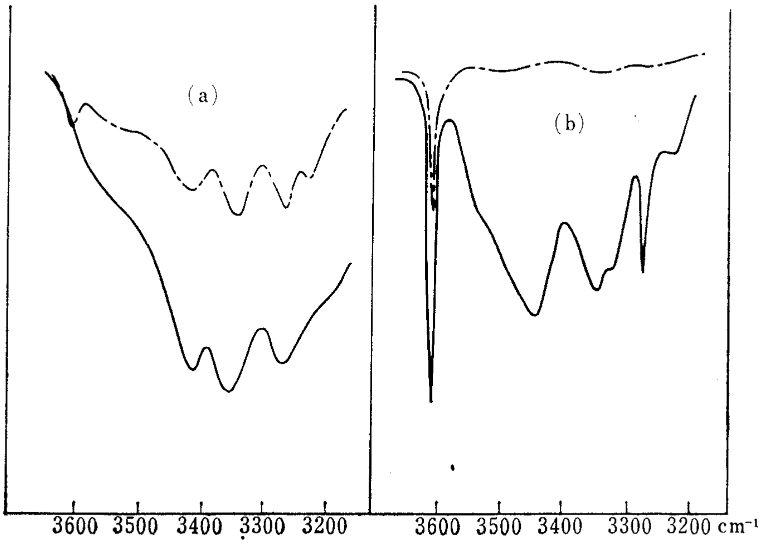


Fig. 3. OH Stretching Bands of Salts and Some Derivatives of Benzothiohydroxamic Acid (in CCl_4)

(a) ——— $\left(\mathrm{C_6H_5C}\begin{smallmatrix}\diagup S^-\\ \diagdown NOH\end{smallmatrix}\right)_2$ Co 0.003*M*

—·—·— $\left(\mathrm{C_6H_5C}\begin{smallmatrix}\diagup S^-\\ \diagdown NOH\end{smallmatrix}\right)_2$ Mn 0.002*M*

(b) ——— $\mathrm{C_6H_5C}\begin{smallmatrix}\diagup SCH_3\\ \diagdown NOH\end{smallmatrix}$ 0.005*M*

—·—·— $\left(\mathrm{C_6H_5C}\begin{smallmatrix}\diagup S\\ \diagdown NOH\end{smallmatrix}\right)_2$ 0.0005*M*

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2) Y. Matsui : Nippon Kagaku Zasshi, **83**, 985, 990 (1962).
3) G.F. Svatos, C. Curran, J.V. Quagliano : J. Am. Chem. Soc., **77**, 6159 (1955).
4) A. Rosenberg : Acta Chim. Scand., **10**, 840 (1956); **11**, 1390 (1957).
5) R.B. Penland, S. Mizushima, C. Curran, J.V. Quagliano : J. Am. Chem. Soc., **79**, 1575 (1957).
6) T.R. Harkins, J.L. Walter, O.E. Harsis, H. Freiser : *Ibid.*, **78**, 260 (1956).

solution because Hanania[7] reported the increase of the acidity of the oxime group with chelation, this attempt was impossible because of the insolubility of the complexes in non-polar solutions.

The difference of the structure between the formula (A) and (B) must affect the N–O and C–S stretching frequencies. In Table I∼III the followings are generally investigated; (i) one or two strong bands at 980∼1020 cm^{-1} of compound Ia and IIa disappear or decrease their strength remarkably and a new strong band appears at about 1100 cm^{-1} for metal complexes, (ii) the bands at about 1100 cm^{-1} of nickel or palladium complexes of thiohydroxamic acids are found in the lower frequency region compared with those of sodium or zinc salts, (iii) in O-methyl-thiohydroxamic acids the strong bands at 920 cm^{-1} of compound Ib and IIb decrease its strength remarkably for the metal complex, but new band at 1100 cm^{-1} is not observed, (iv) for the metal complexes a strong band which is absent for compound Ia and IIa presents at about 700 cm^{-1}, (v) the spectral features of all the metal salts resemble closely each other in 1000∼700 cm^{-1} region irrespective of the sort of the metal. Since the N–O stretching band of oxime group is in the range 900∼1000 cm^{-1},[2,8∼10] the above mentioned bands 1100 cm^{-1} for the metal salts of thiohydroxamic acids may result from the shifts of the N–O bands towards high frequencies because of the contributions of the formula (E) or (B). Similarly, the bands at 700 cm^{-1} which are found only for the metal salts may be ascribed to the shifts of the C–S bands. But the N–O and C–S bands are always coupled with other band, such as C–C stretching or other skeletal vibration bands, so that it is very difficult to determine the structures of the metal complexes from the investigations of these bands.

Another chemical evidences in support of the probable chelate structure will be reported in future.

Experimental

Infrared spectra were recorded with a Nippon Bunkō double-beam spectrometer, model DS 201-B, in potassium disks.

All metal salts and other derivatives of thiohydroxamic acid or O-methylthiohydroxamic acid were prepared by the methods in our previous papers.[*1,*3] To obtain deuterated samples, heavy water was added to the solution of relevant salts in anhydrous acetone or dioxane, and the mixture was concentrated slowly in a desiccator on P_2O_5. The resulting crystals were filtered, washed with anhydrous petroleum ether and dried. Bis(benzothiohydroxamato)Pd(II) contained one mole of dioxane. Original salts were recrystallized in the same manner as deuterated salts by using water in place of heavy water. Since sodium salts were very soluble in water and cadmium or copper salts were very sparlingly soluble in organic solvents, they could not be deuterated. Then, their infrared absorption bands were assigned by comparing with the similar bands of zinc, nickel and palladium salts.

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[7] G. H. I. Hanania, D. H. Irvine : J. Chem. Soc., **1962**, 2745.

[8] A. Palm, H. Werbin : Can. J. Chem., **32**, 858 (1954).

[9] D. Hadži : J. Chem. Soc., **1956**, 2725.

[10] J. Goubeau, I. Fromme : Z. Anorg. Chem., **258**, 18 (1949).