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8. Kōichi Nagata and Satoshi Mizukami: Studies on Thiohydroxamic Acids and Their Metal Chelates. Ⅳ.*1 Reaction of Thiohydroxamic Acids with Metal Ions.

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Reactivities of thiohydroxamic acids (I) and O-methylthiohydroxamic acids (II) with metal ions are studied. It was found that the behaviors of I resemble those of hydroxamic acids rather than II or other reagents including mercapto group. Namely, I react with Fe (III), Ti (IV), UO_2(II), VO (II) which show the characteristic color reaction with hydroxamic acid, and furthermore I gave the Fe (III) and Cu (II) salts without any changes of the valencies, differing from II. Some properties of the isolated transition metal salts indicated that these salts have probably the chelate structures.

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It has been well known that hydroxamic acids show characteristic color reactions with a few kinds of metal ions such as Fe(III), UO_2(II), VO(II), Ti(IV) and their reaction is available for the colorimetric determinations of these ions or many kinds of organic compounds.

Cambi[1] has isolated some metal salts of thiohydroxamic acids and determined their magnetic susceptibility, but any other studies, especially from the standpoint of analytical application, have not been mentioned. In the preceding papers*1,*3 we reported the preparation of sodium thiohydroxamate, sodium O-methylthiohydroxamate and their derivatives. In this paper their specificities and selectivities with various metal ions were studied and compared with those of hydroxamic acids, and the effect of sulfur as ligand atom was examined.

(A) Reactivities of Thiohydroxamic Acids with Metal Ions

Color reactions of metal ions were tested with thiohydroxamic acids, O-methylthiohydroxamic acids and their derivatives. The colored precipitates were obtained only by the compounds including mercapto group, and the compounds including oxime group only, such as the S-alkyl derivatives or the disulfides, did not show any reactions. The results are presented in Table I, as compared with those of hydroxamic acids.

Thiohydroxamic acids gave the colored water-insoluble precipitates with ions such as Mn, Co, Ni, Pd which did not show any reaction with hydroxamic acids. Especially, it is to be noted that a few kinds of metal ions, such as Fe(III), Ti(IV), UO_2(II), VO(II), which develop the characteristic color with hydroxamic acids also react very sensitively with thiohydroxamic acids, and the colors of metal salts of thiohydroxamic acids are more bathochromic than those of hydroxamic acids, but their limit concentrations are almost the same in the both cases.

O-methylthiohydroxamic acids also gave the water-insoluble precipitates with some transition metal ions, but they did not show any color reaction with UO_2, VO, and Ti, and were oxidized to the disulfides by Fe(III) with the development of transient blue color. Analogous oxidations were found for Cu(II), yielding the disulfides and Cu(I) salts of O-methylthiohydroxamic acids. These behaviors of

*1 Part III: This Bulletin, **14**, 1263 (1966).

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*3 Part I: This Bulletin, **14**, 1249 (1966).

1) L. Cambi, T. Bacchetti, E. Paglia: Rend. Ist. Lombardo Sci. Lettere B., **90**, 577 (1956).

Table I. Comparison of Reactivities with Metal Ions

Metal ion	Thiohydroxamic acid			O-Methylthiohydroxamic acid			Hydroxamic acid		
	Appearance	pH[a]	Limit conc.[b] (γ/0.05 ml.)	Appearance	pH[a]	Limit conc.[b] (γ/0.05 ml.)	Appearance	pH[a]	Limit conc.[b] (γ/0.05 ml.)
Ag (I)	white ppt. (blackened)			white ppt.			—		
Mn (II)	g. brown ~y. brown ppt.	1~8	1~10	—			—		
Fe (II)	orange ppt. (blackened)			—			—		
Co (II)	g. brown ~y. brown ppt.	3~10	0.5~1.5	p. blue ppt.	2~10	0.5~3	—		
Ni (II)	orange ~red ppt.	3~10	1~5	r. brown ppt.	2~9	2~4	—		
Pd (II)	brown ppt.	1~6	2~15	o. brown ppt.	1~10	0.3	—		
Cu (II)	green ppt.	1~10	1~4	g. yellow ppt.	3~10	1~5	green sol. ~green ppt.	2~10	50
Zn (II)	white ppt.	1~8		white ppt.			—		
Cd (II)	〃			〃			—		
Hg (II)	〃	1~8		〃	1~10		—		
Sn (II)	〃	1~4		〃			white ppt.	2~4	
Pb (II)	white ~yellow ppt.	1~6		yellow ppt.	1~10		〃	6	
UO_2(II)	red sol. ~red ppt.	1~8	2~15	—			orange sol.	1~8	4
VO (II)	green ~violet ppt.	1~8	0.2~10	—			y. green ~r. violet sol.	1~8	10
Al (III)	white ppt.	1~6		—			—		
As (III)	〃	1~4		—			—		
Cr (III)	bl. green ppt.	1~7		green ppt.	1~7		bl. green sol.	1~3	
Fe (III)	blue sol. ~d. violet ppt.	1~10	0.05~0.3	green sol. (transience)			red ~orange sol.	1~10	0.5
Au(III)	white ppt.	1~6		white ppt.			—		
Ti (IV)	orange ppt.	1~8	2~40	—			yellow sol.	1~8	15
Pt (IV)	yellow ppt.			white ppt.			—		

ppt.: precipitation, sol.: solution, g.: greenish, y.: yellowy, bl.: blue, r.: red, o.: orange, p.: pale.
—: Apparent change was not observed.
a) "pH" indicates that the precipitation or the colored solution summarized in the item of "Appearence" were obtained in this pH range.
b) Limit concentrations which are ranged in this item indicates the obtained values for the series of the ligand compounds, such as aliphatic, aromatic compounds listed in Part I.[*3]

O-methylthiohydroxamic acids with the metal ions are rather commonly found for reagents including mercapto group.

From these results it is apparent that the behaviors of thiohydroxamic acids with metal ions closely resemble those of hydroxamic acids rather than reagents including mercapto group although thiohydroxamic acids are more apt to give the water-insoluble salts than hydroxamic acids because they have sulfur as ligand atom.

The effects of substituents on the limit concentration of some metal ions were examined with a series of thiohydroxamic and O-methylthiohydroxamic acids, but any systematic results could not be obtained. Although we especially expected the effect of *o*-hydroxyphenyl group with Fe(III), any availability was not found. Additions of thiohydroxamic acids on the mixed aqueous solution of bivalent metal ions gave the precipitates in the order Pd(II), Cu(II), Pb(II), Co(II) Zn(II) and Cd(II), and Mn(II), in

TABLE II. Metal Complexes of Thiohydroxamic Acids; $\left(R-C\begin{matrix}S-\\ \diagdown\\ N-OH\end{matrix}\right)_n M$ (M=Metal ion)

No.	R	M	n	Appearance (recrystn. solvent)	m.p. (decomp.) (℃)	Formula	Analysis (%) Calcd. C	H	N	M	Found C	H	N	M
Ia	CH_3	Ni (II)	2	r. brown prism (MeOH)	>280	$C_4H_8O_2N_2S_2Ni$	20.10	3.37	11.73	24.56	20.34	3.48	11.60	24.52
Ib	C_2H_5	〃	〃	r. brown needle (MeOH)	〃	$C_6H_{12}O_2N_2S_2Ni$	27.00	4.53	10.49	21.99	27.52	4.71	10.36	21.93
Ic	n-C_3H_7	〃	〃	〃	〃	$C_8H_{16}O_2N_2S_2Ni$	32.56	5.47	9.49	19.90	32.61	5.51	9.55	20.26
Id	C_6H_5	〃	〃	r. brown prism (MeOH)	〃	$C_{14}H_{12}O_2N_2S_2Ni$	46.31	3.33	7.72	16.16	46.42	3.47	7.93	16.22
Ie	p-CH_3-C_6H_4	〃	〃	r. brown amorph. (EtOH)	〃	$C_{16}H_{16}O_2N_2S_2Ni$	49.12	4.12	7.16	15.01	49.53	4.24	7.20	15.51
If	m-CH_3-C_6H_4	〃	〃	r. brown scale (EtOH)	〃	〃	49.12	4.12	7.16	15.01	49.50	4.22	6.96	14.64
Ig	p-Cl-C_6H_4	〃	〃	y. green amorph. (EtOH)	〃	$C_{14}H_{10}O_2N_2S_2Cl_2Ni$	38.92	2.33	6.48	13.59	39.28	2.51	6.40	13.46
Ih	m-Cl-C_6H_4	〃	〃	y. green amorph. (Me_2CO-EtOH)	228～230	$C_{14}H_{10}O_2N_2S_2Cl_2Ni$	38.92	2.33	6.48	13.59	39.27	2.46	6.77	13.30
Ii	p-CH_3O-C_6H_4	〃	〃	d. green scale (Me_2CO-EtOH)	216	$C_{16}H_{16}O_4N_2S_2Ni$	45.42	3.81	—	13.87	45.35	3.90	—	13.93
Ij	m-NO_2-C_6H_4	〃	〃	r. brown scale (EtOH)	>280	$C_{14}H_{10}O_6N_4S_2Ni$	37.11	2.22	12.37	12.95	37.40	2.42	12.37	13.20
Ik	β-$C_{10}H_7$	〃	〃	y. green amorph. (EtOH)	〃	$C_{22}H_{16}O_2N_2S_2Ni$	57.04	3.48	6.05	12.67	56.86	3.57	6.17	12.29
Il	α-C_4H_3O	〃	〃	r. brown scale (EtOH)	〃	$C_{10}H_8O_4N_2S_2Ni$	35.01	2.35	8.17	17.12	35.23	2.40	8.51	16.74
Im	α-C_4H_3S	〃	〃	y. green scale (EtOH)	〃	$C_{10}H_8O_2N_2S_4Ni$	32.02	2.15	7.47	15.65	32.10	2.31	7.23	15.57
IIa	CH_3	Pd (II)	〃	brown amorph. (MeOH)	〃	$C_4H_8O_2N_2S_2Pd$	16.76	2.81	9.77	37.12	16.75	3.01	9.39	37.05
IIb	C_6H_5	〃	〃	r. brown needle (MeOH)	176～177	$C_{14}H_{12}O_2N_2S_2Pd$	40.93	2.94	6.82	25.90	41.09	3.14	6.76	25.75
IIc	〃	〃	〃	grey powder (insol.)	184～187	〃	40.93	2.94	6.82	25.90	41.09	3.06	6.80	26.34

IId	C_6H_5	Pd(II)	2 (+1 mol. dioxane)	r. brown needle (dioxane)	176～177	$C_{18}H_{20}O_4N_2S_2Pd$	43.34	4.04	5.61	21.33	43.55	4.11	5.78	21.45
IIe	*p*-CH_3O-C_6H_4	〃	2	o. brown needle (pyridine–ether)	201～203	$C_{16}H_{16}O_4N_2S_2Pd$	40.82	3.43	5.95	22.60	40.87	3.66	5.90	22.64
IIIa	CH_3	Fe (III)	3	d. violet powder (insol.)	—	$C_6H_{12}O_3N_3S_3Fe$	22.09	3.71	12.88	17.12	22.45	3.98	12.49	17.13
IIIb	C_6H_5	〃	〃	d. violet powder (EtOH)	—	$C_{21}H_{18}O_3N_3S_3Fe$	49.22	3.54	8.20	10.90	48.86	3.64	7.93	11.24
IIIc	*p*-CH_3-C_6H_4	〃	3 (+1H_2O)	d. violet powder (ether–petr. ether)	155～160	$C_{24}H_{24}O_3N_3S_3Fe\cdot H_2O$	50.35	4.58	7.34	9.75	50.27	4.60	7.19	10.08
IIId	*m*-Cl-C_6H_4	〃	3	d. violet powder (insol.)	125～130	$C_{21}H_{15}O_3N_3S_3Cl_3Fe$	40.96	2.46	6.82	10.00	40.46	2.77	6.51	11.47
IIIe	*p*-CH_3O-C_6H_4	〃	〃	d. violet powder (EtOH–petr. ether)	132～136	$C_{24}H_{24}O_6N_3S_3Fe$	47.84	4.02	6.97	9.27	47.48	3.99	7.03	9.77
IVa	CH_3	Cu (II)	2	g. violet powder (insol.)	>280	$C_4H_8O_2N_2S_2Cu$	19.71	3.31	11.49	26.06	19.98	3.54	11.47	26.56
IVb	C_6H_5	〃	〃	green powder (insol.)	〃	$C_{14}H_{12}O_2N_2S_2Cu$	45.70	3.29	7.61	17.27	46.09	3.38	7.27	17.08
IVc	*p*-CH_3O-C_6H_4	〃	〃	〃	212	$C_{16}H_{16}O_4N_2S_2Cu$	44.90	3.77	6.55	14.85	45.12	3.87	6.62	15.01
V	C_6H_5	Co (II)	〃	d. violet amorph. (MeOH)	—	$C_{16}H_{16}O_4N_2S_2Co$	46.28	3.33	7.71	—	46.02	3.52	7.99	—
VI	〃	Mn (II)	2 ($\frac{1}{2}H_2O$)	d. green powder (MeOH) (hygroscopic)	—	$C_{16}H_{16}O_4N_2S_2Mn\cdot\frac{1}{2}H_2O$	45.65	3.56	7.80	—	45.69	3.61	7.61	—
VII	〃	Pt (IV)	4	y. green powder (EtOH)	—	$C_{28}H_{24}O_4N_4S_4Pt$	41.82	3.01	6.97	24.28	41.82	3.24	6.86	23.87
VIII	CH_3	Pb (II)	1	yellow powder (insol.)	>280	C_2H_3ONSPb	8.08	1.36	4.71	69.69	8.27	1.16	4.71	69.27
IXa	〃	Zn (II)	2	white amorph. (Me_2CO)	*	$C_4H_8O_2N_2S_2Zn$	19.56	3.28	11.41	26.62	19.87	3.53	11.24	26.32
IXb	C_6H_5	〃	〃	white needle (Me_2CO)	*	$C_{14}H_{12}O_2N_2S_2Zn$	45.48	3.27	7.58	17.68	45.63	3.37	7.46	17.51
IXc	*p*-CH_3O-C_6H_4	〃	〃	white needle (pyridine–ether)	*	$C_{16}H_{16}O_4N_2S_2Zn$	44.71	3.75	6.52	15.21	45.08	3.89	6.72	15.47
Xa	CH_3	Cd (II)	〃	white powder (insol.)	*	$C_4H_8O_2N_2S_2Cd$	16.41	2.76	9.57	—	16.45	2.99	9.35	—
Xb	C_6H_5	〃	〃	〃	*	$C_{14}H_{12}O_2N_2S_2Cd$	40.34	2.90	6.72	—	40.38	3.06	7.26	—

r.: red, y.: yellowy, o.: orange, g.: greenish, d.: dark
*: These compounds were colored slowly over 200°.
insol.: These compounds were insoluble in all solvents, then precipitated salts were washed with water, EtOH and ether.

Table III. Metal Complexes of O-Methylthiohydroxamic Acid; $\left(R\text{-}C\langle^{S-}_{NOCH_3}\right)_n M$ (M=Metal ion)

No.	R	M	n	Appearance (recrystn. solvent)	m.p. (decomp.) (°C)	Formula	Analysis (%) Calcd. C	H	N	M	Found C	H	N	M
XIa	CH_3	Ni (II)	2	g. yellow powder ($CHCl_3$-ether)	156～157	$C_6H_{12}O_2N_2S_2Ni$	26.99	4.53	10.49	21.99	26.88	4.53	10.36	21.77
XIb	C_6H_5	〃	〃	o. brown powder ($CHCl_3$-ether)	191～192	$C_{16}H_{16}O_2N_2S_2Ni$	49.13	4.12	7.16	15.01	49.02	4.32	7.40	15.52
XIc	p-CH_3-C_6H_4	〃	〃	o. brown powder (EtOH-petr. ether)	>280	$C_{18}H_{20}O_2N_2S_2Ni$	51.57	4.81	6.68	14.00	51.43	4.89	6.72	14.23
XId	p-Cl-C_6H_4	〃	〃	o. brown powder (insol.)	>280	$C_{16}H_{14}O_2N_2S_2Cl_2Ni$	41.77	3.07	6.09	12.76	42.00	3.18	6.27	12.67
XIIIa	CH_3	Pd (II)	〃	o. brown powder ($CHCl_3$-ether)	210～213	$C_6H_{12}O_2N_2S_2Pd$	22.90	3.84	8.90	33.81	22.74	3.84	8.80	33.49
XIIIb	C_6H_5	〃	〃	r. orange powder (insol.)	231～233	$C_{16}H_{16}O_2N_2S_2Pd$	43.76	3.67	6.38	24.30	43.94	3.86	6.03	23.65
XIV	〃	Co (II)	〃	p. blue powder (AcOEt-petr. ether)	160	$C_{16}H_{16}O_2N_2S_2Co$	49.10	4.12	7.16	—	48.59	4.38	7.36	—
XV	〃	Cu (I)	1 ($+\frac{1}{2}H_2O$)	yellow powder ($CHCl_3$-petr. ether)	205	$C_8H_8ONSCu\cdot\frac{1}{2}H_2O$	40.24	3.80	5.87	26.61	40.66	3.55	5.95	25.39
XVIa	CH_3	Zn (II)	2 ($+H_2O$)	white powder (AcOEt)	163	$C_6H_{12}O_2N_2S_2Zn\cdot H_2O$	24.71	4.84	9.60	22.41	25.21	5.02	9.81	22.33
XVIb	C_6H_5	〃	2	〃	172～173	$C_{16}H_{16}O_2N_2S_2Zn$	48.31	4.05	7.04	16.43	47.71	4.34	6.93	17.96
XVII	〃	Cd (II)	〃	white powder (insol.)	>280	$C_{16}H_{16}O_2N_2S_2Cd$	43.20	3.63	6.30	—	42.76	3.72	6.37	—

g.: greenish, o.: orange, r.: red, p.: pale
insol.: As these compounds were insoluble in all solvents, they were washed with water, EtOH and ether.

accordance with the stability order[2] of bivalent metal ions. The same results have been reported with S-O coordinating reagents by Tanaka.[3]

(B) Isolations and Properties of the Metal Salts

The isolated salts of thiohydroxamic and O-methylthiohydroxamic acids and their analytical data with some of their properties are summarized in Table II and III. Among these salts, Ni(II), Pd(II) and Zn(II) salts were most stable and could be obtained as crystals from hot solvents, but the salts of Fe(III), Co(II), Mn(II) which are apt to change the valency were instable on heating.

In the series of salts of thiohydroxamic acids the ratio of the ligand to metal corresponded to valencies of the ions with some exception. The composition of Pb(II) salts was abnormal in which the ratio of ligands to metal was one to one, the analogous results have been reported for Pb(II) dimethylglyoximate.[4] Attempts to isolate Bi(III), UO_2(II), VO(II) salts failed because of the difficulties of recrystallization. The isolated salts had generally high decomposition points but most of them did not show any constant values with gradual decomposition on heating. The salts were very soluble in alkaline solution, but sparingly soluble or insoluble in organic solvents. The solubilities are presented in Table IV. On the other hand, most of the salts of O-methylthiohydroxamic acids are soluble in organic solvents such as ethyl acetate and chloroform, and show constant decomposition points around 200°. Their compositions corresponded to those of thiohydroxamic acids.

Table IV. Solubility of Metal Salts of Thiohydroxamic Acid

Metal salt	Solubility								Addition of EDTA to alkaline solution
	dil. NH_4OH	0.1*N* NaOH	C_5H_5N	MeOH	Me_2CO	AcOEt	$CHCl_3$	C_6H_6	
Zn (II)	±	*	##	+	+	−	−	−	
Cd (II)	±	*	#	−	−	−	−	−	
Cu (II)	+	##	−	−	−	−	−	−	decolored
Pd (II)	+	##	##	±	#	−	−	−	not decolored
Ni (II)	+	##	##	#	#	−	−	−	decolored in NH_4OH, not decolored in 0.1*N* NaOH
Co (II)	±	#	##	#	#	#	+	+	not decolored
Mn (II)	±	#	##	#	##	#	#	#	〃
Fe (III)	+	#	##	#	#	#	#	+	decolored in NH_4OH, not decolored in 0.1*N* NaOH
Pt (IV)	±	#	##	#	#	+	+	±	
Pb (II)	−	−	−	−	−	−	−	−	

* These salts were hydrolyzed in NaOH.
− : practically insoluble, ± : very slightly soluble, + : slightly soluble,
: sparingly soluble, ## : soluble

The typical ultraviolet and visible absorption spectra of some metal salts of thiohydroxamic acids are shown in Fig. 1, 2 and 3. All the transition metal salts show remarkably strong bands (log ε : 3~4) between the near ultraviolet and visible region, and some of them, such as Ni(II) salts give one more weak band at longer wave lengths. The intensities of the bands indicate the former bands are probably due to the ligand field absorption and the latter to the electron transfer absorption. These bands are also found in sodium hydroxide solution with some shifts of the absorption maxima. Furthermore, it is to be mentioned that the salts did not give the hydroxide

2) H. Irving, R. J. P. Williams : Nature, **162**, 746 (1948).
3) H. Tanaka : This Bulletin, **10**, 1129 (1962).
4) M. Ishibashi, H. Funahashi : Nippon Kagaku Zasshi, **59**, 503 (1938).

precipitates in alkaline solution and most of them were not decolored by the addition of ethylenediaminetetraacetic acid as shown in Table V.

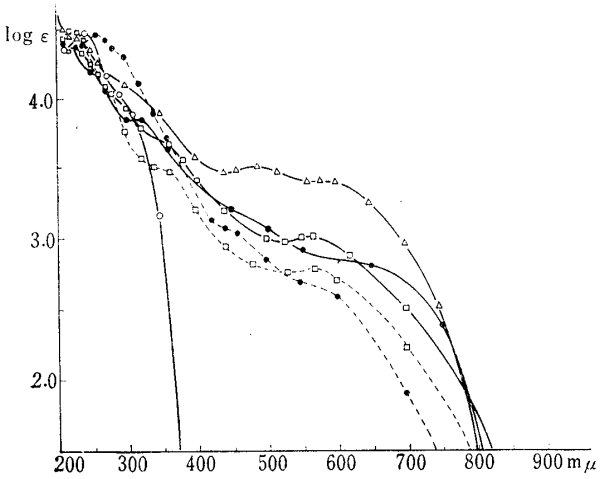

Fig. 1. Ultraviolet and Visible Spectra of $\left(C_6H_5C\begin{matrix}S-\\ \diagdown\!\!\diagup NOH\end{matrix}\right)_n M^{+n}$

○—○ M=Zn(II)
△—△ M=Fe(III)
□—□ M=Mn(II)
●—● M=Co(II)
} in EtOH

□·····□ M=Mn(II)
●·····● M=Co(II)
} in 0.1*N* NaOH

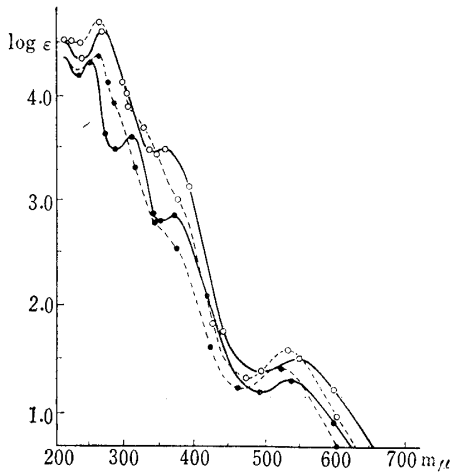

Fig. 2. Ultraviolet and Visible Spectra of $\left(R-C\begin{matrix}S-\\ \diagdown\!\!\diagup NOH\end{matrix}\right)_2 Pd$

●—● R=CH_3 (in EtOH)
●·····● R=CH_3 (in 0.1*N* NaOH)
○—○ R=C_6H_5 (in EtOH)
○·····○ R=C_6H_4 (in 0.1*N* NaOH)

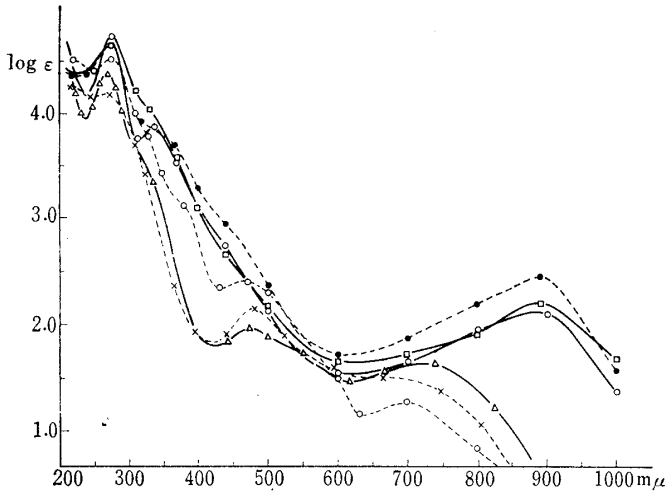

Fig. 3. Ultraviolet and Visible Spectra of $\left(R-C\begin{matrix}S-\\ \diagdown\!\!\diagup NOH\end{matrix}\right)_2 Ni$

△—△ R=CH_3
○—○ R=C_6H_5, *p*-CH_3-C_6H_4
●·····● R=*p*-Cl-C_6H_4
□—□ R=*p*-CH_3O-C_6H_4
} in EtOH

○·····○ R=C_6H_5, *p*-CH_3-C_6H_4, *p*-Cl-C_6H_4, *p*-CH_3O-C_6H_4
×·····× R=CH_3
} in 0.1*N* NaOH

From these observations about the solubilities in organic solvents, the characteristic absorption bands and the stabilities in alkaline solution, it seems to be likely that the transition metal salts of thiohydroxamic and O-methylthiohydroxamic acids, such as Ni(II), Pd(II), Fe(III), Mn(II), Co(II) salts, are not the ionic salts, but the chelate compounds.*4 This assumption is confirmed by the following facts.

First, the molecular weight of the Ni(II) and Pd(II) salts of thiohydroxamic acids measured in ethanol and acetone are identical with the calculated values, and the fact that these salts include no crystal water or crystal solvents is evident from their analytical data in the solid. These results indicate that the salts are monomeric and

*4 No definite conclusion has been drawn about the nature of the ligand-metal bond in some white salts which are hydrolyzed in 0.1*N* NaOH, such as Zn (II), Cd (II) salt, but they seem to have a rather ionic bond, as mentioned in our following papers.

they are scarcely dissociated in solution, so that it is impossible to satisfy the requirements of coordination number four for these metal ions without assuming the chelate structures.

Next, sodium benzothiohydroxamate and Pd(II) yielded two forms of precipitates which give the same analytical data and the close similarity of infrared spectra as shown in Fig. 4, in spite of their remarkable differences of their colors and solubilities. The gray precipitate, (b), obtained from neutral solution was insoluble in all organic solvents, but the brown one, (a), obtained from acid solution was soluble in acetone or alcohol and recrystallized as red brown needles from methanol. These observations indicate that the two forms of Pd(II) salts must be *cis-trans* isomers due to the dsp^2 square-planar chelate structures. The brown one may be *trans*-isomer because the color was identical with those of (O-methylthiobenzohydroxamato)Pd(II) which cannot have the *cis*-form on account of a steric hindrance by the methyl groups.

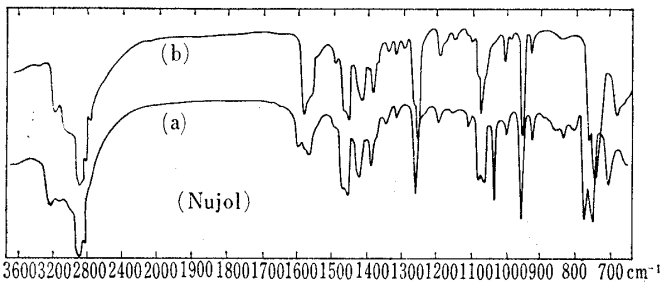

Fig. 4. Infrared Spectra of $\left(C_6H_5\text{-}C\begin{matrix}S\text{-}\\ NOH\end{matrix}\right)_2Pd$

(a) Red brown needles from MeOH (IIb).
(b) Grey powder which is insoluble in organic solvents (IIc).

Lastly, the Ni(II) salts of thiohydroxamic acids are diamagnetic as already pointed out by Cambi,[1] and our determined values were also identical with his results. Furthermore the colors of the salts also closely resemble those of some Ni(II) chelates, such as orange red bis(salicylaldiminato)Ni(II), red bis(dimethylglyoxamato)Ni(II)[5] and green bis(salicylaldoxamato)Ni(II),[6] of which the squar-planar structures have been confirmed by X-ray investigations. Therefore, it is probable to suppose that the Ni(II) salts of thiohydroxamic acids have also dsp^2 square-planar chelate structures. Although two types of the color red-brown and green, were found in these Ni(II) salts as shown in Table II, it is extremely unlikely to assume that such differences of the color are resulted from the geometric isomerism, because *cis-trans* isomerism of the Ni(II) chelates are very scarce in the literatures and the ultraviolet absorption spectra of the both types of the salts show close analogies with each other as shown in Fig. 3, except that the green type give the barely observable shoulder at near 440 mμ. In fact, the colors change very easily. For example, the addition of sodium *p*-methoxybenzothiohydroxamate to the Ni(II) acetate give red precipitates but the color turns to green by washing with ethanol. Hence the differences of the color must result from the slight differences of the crystal structures.

Experimental

Sodium thiohydroxamates and sodium O-methylthiohydroxamates used were prepared by previously reported methods in Part I,*3 and other derivatives of thiohydroxamic acids were presented in our previous paper.*1 Hydroxamic acids were obtained by conventional preparative procedure. Infrared spectra were recorded with a Nippon Bunkō double-beam spectrophotometer, model DS 201-B. Visible and ultraviolet spectra were obtained with a Hitachi spectrophotometer, model EPS-2U. All melting points were uncorrected.

Investigation of Reactivity with Metal Ions——The solutions (about 5 w/v %) of sodium thiohydroxamate, sodium O-methylthiohydroxamate, hydroxamic acids and other derivatives of thiohydroxamic acid in water or

5) L. E. Godycki, R. E. Rundle : J. Chem. Phys., **19**, 1205 (1951); Acta Cryst., **6**, 487 (1953).
6) L. L. Merritt, Jr., C. Guare, A. E. Lessor, Jr. : Acta Cryst., **7**, 650 (1954); **9**, 253 (1956); L. L. Merritt, Jr. : Anal. Chem., **25**, 718 (1953); E. A. Shugam : Trudy Vsesoyuz. Nauch. Issledovatel. Inst. Khim. Reaktivov, 53 (1958) (Chem. Abstr., **54**, 20401i (1960)).

EtOH were used as ligand solution. The aqueous solutions of various metal ions were prepared by using their commercially obtained acetate, chloride, sulfate, etc. Clark-Lubs's mixture was used as buffer solution.

a) Reactivities with metal ions were investigated as follows : After mixing 5 ml. of the buffer solution and few drops of the ligand and the metal solution, changes of the color of the metal solution and pH range in which the precipitation was occurred were recorded. If the precipitates could not be distinguished from the simple hydroxides, they were identified by proper methods, such as determination of the infrared spectra or ignition tests, and control tests were also carried out without the use of ligand solution.

b) Recognizable limit concentration was determined by addition of the ligand solution to the metal solution on a spot plate and by the following dilution of the metal solution until the color reaction could not be recognized.

c) The precipitating order of bivalent metal ions was determined as follows : An equivalent amount of the solutions of various bivalent metal ion were mixed each other, and an equivalent amount of ligand solution was added. The separated precipitate was collected by filtration, and identified qualitatively.

Preparation of Metal Salt——To a solution of sodium thiohydroxamate or sodium O-methylthiohydroxamate in pH 6 buffer was added a solution of metal ion. The precipitate was filtered, washed with water, and recrystallized from adequate solvents as shown in Table II and III. Since manganese, cobalt and iron salts of thiohydroxamic acid were unstable on heating, they were refined by dissolution in a large amount of EtOH at room temperature and concentration *in vacuo*, followed by addition of petroleum ether. The precipitate, such as cadmium or copper salts which was insoluble in various solvents was washed with water, EtOH and ether in this order, and dried.

Although the precipitate which was obtained by addition of water or ether to the solution of salts in pyridine was apt to be often contaminated by the addition of pyridine, a few salt such as bis(*p*-methoxybenzothiohydroxamato)Ni(II) was easily recrystallized by adding the solution in a minimal pyridine to a large amount of hot ethanol.

Bis(benzothiohydroxamato)Pd(II) which was prepared as the above mentioned manner was grey (IIc) and insoluble in various solvents. By contrast, the precipitate which was obtained by slow addition of aqueous solution of sodium thiohydroxamate to the solution of Na_2PdCl_4 in about 5*N* HCl was red and very soluble in Me_2CO. To the solution in Me_2CO was added the same amount of EtOH, concentrated on a steam bath, treated with charcoal, and filtered. On standing after addition of small amount of water, red brown crystals (IIa, b) was obtained. Further recrystallization of IIb from dioxane afforded the salts (IId) including a mole of dioxane.

Preparation of Copper Salt of O-Methylbenzothiohydroxamic Acid——To a hot aqueous solution of cupric acetate (0.67 m*M*) was slowly added an aqueous solution of sodium O-methyl-benzothiohydroxamate (1.3 m*M*) with stirring. After cooling, the separated resinous material was filtered and washed with water and EtOH. The residue was dissolved in $CHCl_3$, concentrated, followed by addition of EtOH. Recrystallization of the precipitate from $CHCl_3$-petroleum benzin gave cuprous O-methylbenzothiohydroxamate (XV). The above mentioned washings and the filtrate of the recrystallization solution were combined, and evaporated under reduced pressure to dryness, and the residue was extracted with ether. Evaporation of the solvent followed by recrystallization from dil. EtOH gave colorless needles, m.p. 62°, which did not depress the melting point of an authentic disulfide of O-methyl-benzothiohydroxamic acid.

Molecular Weight and Magnetic Susceptibility——Molecular weights were determined by using a Mechrolab vapor pressure osmometer, model 301-A and magnetic susceptibilities were determined by Gouy's method as conventional manner. Bis(acetothiohydroxamato)Ni(II) (Ia) : Mol. wt. Calcd. 239, Found 253 (in EtOH). Molar magnetic susceptibility (e.m.u.), -82×10^{-6}. Bis(*n*-butyrothiohydroxamato)Ni(II) (Ic) : 295, 294 (EtOH). Bis(benzothiohydroxamato)Ni(II) (Id) : 363, 360 (EtOH), -152×10^{-6}. Bis(benzothiohydroxamato) Pd(II) (IIb) : 411, 441 (Me_2CO). Bis(*p*-methoxybenzothiohydroxamato)Ni(II) (Ii) : -153×10^{-6}.

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