Chem. Pharm. Bull.
17(4) 653—660 (1969)

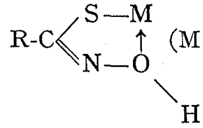
UDC 547.298.71-174 : 547.582.5-174

Studies on Thiohydroxamic Acids and Their Metal Chelates. VI.[1] Some Reactions of Metal Complexes of Thiohydroxamic Acids

Kōichi Nagata

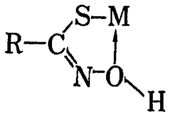
Shionogi Research Laboratory, Shionogi & Co., Ltd.[2]

(Received December 25, 1967)

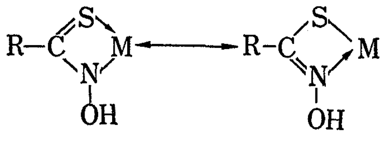
Chemical reactivities of the metal complexes of thiohydroxamic acids was investigated. By alkylation or acylation, all the metal complexes except the nickel complex was dissociated to the corresponding metal ions and derivatives of thiohydroxamic acid. The nickel complex was benzoylated without undergoing the dissociation in chilled sodium hydroxide. Sodium or zinc salts or some derivatives of benzothiohydroxamic acid underwent the Lossen rearrangement, and the rearrangement products were isolated. However, the nickel complex did not give the rearrangement products in alkaline solution because of the stability of the chelated structure. From those results, it was confirmed that the hydroxyimino group of thiohydroxamic acid is in the syn configuration to the sulfur atom and that the transition metal complexes possess the five-membered chelate structure as shown in formular  (M=metal ion) in the solid state.

In the preceding paper[1] it was shown by the infrared spectral studies that metal complexes of thiohydroxamic acid (I) possess hydroxyimino group in the solid state, and therefore the chelate structure of Ic, which resembles to those of metal complexes of hydroxamic acids, is least conceivable, and that it may be assignable to either Ia or Ib which is coordinated with both mercapto and hydroxyimino groups simultaneously. At the same time, X-ray crystallographic studies[3] revealed that bis(acetothiohydroxamato) nickel has really S-O coordinated square-planar structure as shown in formula Ia ($R=CH_3$, M=Ni), in which the C-N bond has a double bond character.

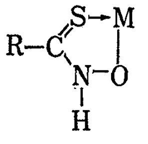
This study was attempted to confirm the chelate structures from some chemical reactions of thiohydroxamic acids and their metal complexes.



Ia



Ib₁ **Ib₂**



Ic

Results and Discussion

(A) Alkylation and Acylation of Metal Complexes of Thiohydroxamic Acids

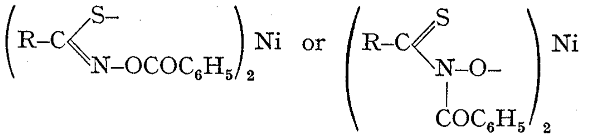
Methylation[4] of bis(dimethylglyoximato) nickel and benzylation[4,5] or acetylation[6] of bis(2-pyridinealdehyde oximato) palladium or platinum have been reported. Therefore, metal complexes of thiohydroxamic acids may also be expected to undergo such reactions, as far as their structures are formulated in Ia, Ib and Ic.

---

[1] Part V: K. Nagata, *Chem. Pharm. Bull.* (Tokyo), **15**, 70 (1967).
[2] Location: *Sagisukami, Fukushima-ku, Osaka.*
[3] T. Sato, K. Nagata, M. Shiro, and H. Koyama, *Chem. Commun.*, **1966**, 192; *ibid.*, **1967**, 215.
[4] D.H. Busch, *Advan. Chem. Ser.*, **37**, 15 (1963).
[5] W.R. Findley, *Dissertation Abstr.*, **24**, 962 (1963).
[6] R.A. Krause, D.C. Jicha, and D.H. Busch, *J. Am. Chem. Soc.*, **83**, 528 (1961).

By benzoylation in ice-cooled sodium hydroxide solution, nickel benzothiohydroxamate gives orange or brown colored complexes which possess such characteristic properties of metal chelates as relatively low melting point and dissolution into chloroform, benzene or ethyl acetate. The analytical data of the benzoylated nickel complexes (II) are summarized in Table I.

TABLE I. Benzoylated Nickel Thiohydroxamate (II)



R	Appearance	mp (°C)	Yield (%)	Formula	Analysis (%)										$\nu_{C=O}$ (cm^{-1}) in CCl_4
					Calcd.					Found					
					C	H	N	Ni	Mol. wt.	C	H	N	Ni	Mol. wt.	
CH_3	r. orange powder	150—151	15	$C_{18}H_{16}O_4$-N_2S_2Ni	48.35	3.61	6.26	13.13	448	48.40	3.75	6.62	13.24	429	1722
C_2H_5	r. brown scale	107—108	10	$C_{20}H_{20}O_4$-N_2S_2Ni	50.65	4.24	5.90	12.35		50.56	4.36	5.66	12.04		1734
n-C_3H_7	v. brown prism	122—123	10	$C_{22}H_{24}O_4$-N_2S_2Ni	52.50	4.81	5.57	11.67		52.65	4.65	5.40	12.15		1730
iso-C_3H_7	o. brown powder	115—116	6	$C_{22}H_{24}O_4$-N_2S_2Ni	52.50	4.81	5.57	11.67		52.85	4.86	5.37	11.45		1731
C_6H_5[a]	o. brown powder	138	20	$C_{28}H_{20}O_4$-N_2S_2Ni	58.87	3.53	4.90	10.28	571	58.89	3.72	5.07	10.21	600	1741
p-CH_3-C_6H_4	o. brown powder	136	25	$C_{30}H_{24}O_4$-N_2S_2Ni	60.11	4.04	4.67	9.80	599	59.83	4.16	4.53	10.03	602	1741
m-CH_3-C_6H_4	r. orange needle	129—130	25	$C_{30}H_{24}O_4$-N_2S_2Ni	60.11	4.04	4.67	9.80		59.97	4.19	4.85	9.54		1742
p-Cl-C_6H_4	o. brown powder	136	15	$C_{28}H_{18}O_4$-$N_2S_2Cl_2Ni$	52.53	2.83	4.38	9.17		52.22	3.10	4.40	9.38		1740
p-C_6H_5COO-C_6H_4	o. brown powder	137	6	$C_{42}H_{28}O_8$-N_2S_2Ni	62.16	3.48	3.45	9.23		61.95	3.44	3.32	7.25		1743[b]
m-C_6H_5COO-C_6H_4	o. brown powder	126—128	6	$C_{42}H_{28}O_8$-N_2S_2Ni	62.16	3.48	3.45	9.23		61.67	3.56	3.46	7.29		1745[b]
p-CH_3O-C_6H_4[c]	orange powder	120—121	20	$C_{30}H_{24}O_6$-N_2S_2Ni	57.07	3.83	4.44	9.30		56.74	4.05	4.55	9.11		1738
β-$C_{10}H_7$	r. orange powder	147	12	$C_{36}H_{24}O_4$-N_2S_2Ni	64.40	3.60	4.17	8.74		64.26	3.58	4.05	8.96		1742
α-C_4H_3O	r. orange powder	145—146	15	$C_{24}H_{16}O_6$-N_2S_2Ni	52.29	2.93	5.08	10.65		51.81	3.12	5.06	10.82		1738

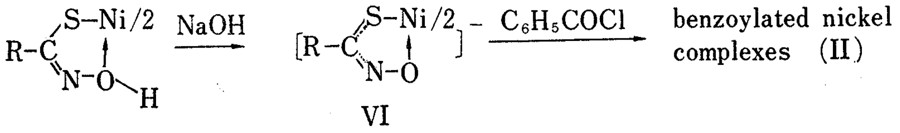
r.: red, v.: violet, o.: orange

[a] [c] Their molar magnetic susceptibilities (e.m.u.) are -88×10^{-6} and -220×10^{-6}, respectively.

[b] These bands are mixed with $\nu_{C=O}$ in substituted group.

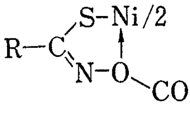
Benzoylation of the other metal complexes are unsuccessful. Cadmium and zinc complexes produce S,O-dibenzoylthiohydroxamic acid [$C_6H_5C\Big\langle{}^{SCOC_6H_5}_{NOCOC_6H_5}$, (III)] almost quantitatively, while cobalt and copper complexes are decomposed to the corresponding ligands. In the case of palladium complexes, brown powders having the same properties as II are obtained, but the pure complexes cannot be isolated because of their gradual decomposition during repeated purification.

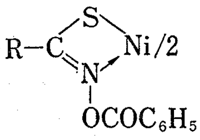
When nickel benzothiohydroxamate is treated with methyl iodide or dimethyl sulfate in sodium hydroxide solution, it dissociates nickel ion and gives S-methylbenzothiohydroxamic acid [$C_6H_5C\Big\langle{}^{SCH_3}_{NOH}$ (IV)] and S,O-dimethylbenzothiohydroxamic acid [$C_6H_5C\Big\langle{}^{SCH_3}_{NOCH_3}$ (V)] as main products. Similar results are obtained in the other transition metal complexes. The results seem to indicate that the alkylation and the acylation are principally affected by the stabilities of the metal complexes in alkaline solution. In the case of alkylation, warming of the reaction mixture is likely to facilitate the dissociation of the metal complexes. It is no doubt that II are produced by the direct benzoylation of the anionic nickel chelates (VI) which are stable in alkaline solution, because the benzoylation of thiohydroxamic acids gives unstable S-benzoylated or S,O-dibenzoylated derivatives which have no ability to form metal complexes.[7]

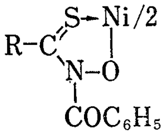


The benzoylated nickel complexes (II) are diamagnetic in the solid state, and they take monomeric form in solution as shown in Table I. In addition, the absorption spectra of II (Fig. 1) are similar to those of the corresponding nickel thiohydroxamate,[8] and the absorption maxima (λ_{max}) and the molar absorptivities (ε) are very different from those of octahedral nickel chelates.[9]

Therefore, three types of square-planar structure, IIa, IIb, and IIc, are possibly considered.


IIa


IIb


IIc

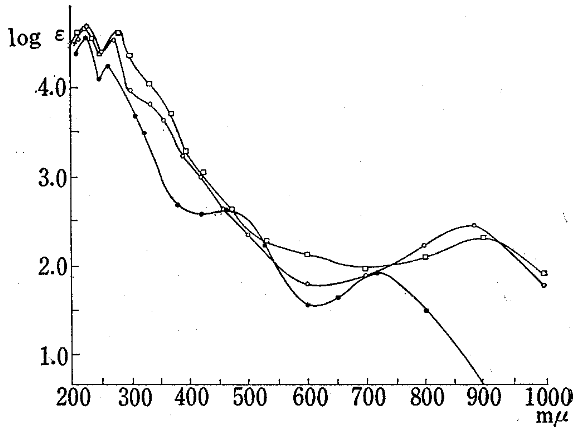


Fig. 1. Absorption Spectra of Benzoylated Nickel Thiohydroxamate (II) (in EtOH)

●—●—● R=CH$_3$
○—○—○ R=C$_6$H$_5$, p-CH$_3$-C$_6$H$_4$
□—□—□ R=p-CH$_3$O-C$_6$H$_4$

The infrared spectra of II show the C=O stretching band ($\nu_{C=O}$) at 1720—1730 cm^{-1} (for R=alkyl) or at 1740 cm^{-1} (for R=aryl) in carbon tetrachloride solution. Since neither O-benzoyl- nor N-benzoylthiohydroxamic acid, the respective ligands for the complexes IIa and IIc, cannot be synthesized,[7] direct comparisons of $\nu_{C=O}$ of II with those of the ligands are impossible. It has been found, however, that O-benzoyl derivatives of thiohydroxamic acid, such as $\mathrm{R{-}C}\langle{}^{SCOC_6H_5}_{NOCOC_6H_5}$ and $(\mathrm{R{-}C}\langle{}^{S-}_{NOCOC_6H_5})_2$, give the $\rangle$NOC=O stretching band at 1770± 2 cm^{-1} in carbon tetrachloride[7] and tribenzoylhydroxylamine shows it at 1773 cm^{-1} in dioxane.[10] It has also been reported that $\nu_{C=O}$ of O-benzoylfluorenone oxime and its oxide

---

[7] K. Nagata and S. Mizukami, *Chem. Pharm. Bull.* (Tokyo), **14**, 1263 (1966).

[8] K. Nagata and S. Mizukami, *Chem. Pharm. Bull.* (Tokyo), **15**, 61 (1967).

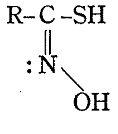
[9] S. Bffagni, L.M. Vallarino, and J.V. Quagliano, *Inorg. Chem.*, **3**, 480 (1964); A.B.P. Lever, J. Lewis, and R.S. Nyholm, *J. Chem. Soc.*, **1963**, 5042; L. Sacconi, "Essays in Co-ordination Chemistry," ed. by W. Schneide, G. Anderegg, and R. Gut, Birkhäuser Verlag, Basel, 1964, p. 148; L.M. Venanzi, *J. Chem. Soc.*, **1958**, 719; L.M.L. Goodgame, M. Goodgame, and F.A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).

[10] O. Exner, *Collection Czech. Chem. Commun.*, **27**, 2285 (1962).

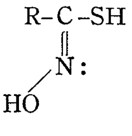
occur respectively at 1747 cm^{-1} and 1763 cm^{-1} in chloroform.[11] Furthermore, according to our observations, $\nu_{\mathrm{C=O}}$ of O-acetyl-2-pyridinealdehyde oxime appears at 1779 cm^{-1} in solid, but its palladium chelates in which palladium ion is coordinated with hydroxyimino nitrogen[6] show $\nu_{\mathrm{C=O}}$ at 1788 cm^{-1} in solid. These results indicate that the decrease of the electron-density at the nitrogen atom of oxime esters results in a shift of $\nu_{\mathrm{C=O}}$ to higher wave-numbers. If the structures of II are represented in formula IIb, $\nu_{\mathrm{C=O}}$ should be found at higher frequencies than 1770 cm^{-1}, at which the $\rangle$N–OC=O bands of tribenzoylhydroxylamine or O-benzoyl derivatives of thiohydroxamic acids occur. Therefore, the structure IIb is less probable because $\nu_{\mathrm{C=O}}$ of II is in 1720—1740 cm^{-1} region as mentioned above. On the one hand, if II has the structure IIa, such a somewhat larger shifts to lower frequencies of $\nu_{\mathrm{C=O}}$ of II may be explained by the similar reasons as that $\nu_{\mathrm{C=O}}$ of amide is smaller than that of ester of carboxylic acid, because the electronic state of the coordinated oxygen atom resembles that of the normal nitrogen atom. The fact that II is hydrolyzed easily to produce nickel complex of thiohydroxamic acid, when kept standing for a long period of time at room temperature, is also considered to support the structure IIa, because IIc may be regarded as nickel complex of N-thioacyl derivative of benzohydroxamic acid so that such an easy hydrolysis of benzoyl group may not be taken place. On the other hand, it is possible to consider that the nucleophilic attack may occur to form IIc at the nitrogen atom of the ligand, owing to the spreading of the electric charge by the formation of anionic chelate ring VI. In fact, $\nu_{\mathrm{C=O}}$ of II resembles considerably to the $\rangle$N–C=O frequencies of tribenzoylhydroxylamine at 1715 cm^{-1} (in dioxane),[10] so that evidences are insufficient at present to conclude about the alternative of the structure, IIa or IIc.

(B) Rearrangement of Some Derivatives and Metal Complexes of Thiohydroxamic Acids

Although Benn[12] had postulated that the hydroxyimino group of S-alkylthiohydroxamate is likely to have syn configuration to sulfur atom, no systematic studies have been made on the steric configurations of the thiohydroxamic acid derivatives. If the hydroxyimino group of thiohydroxamic acid is assigned to be in the syn configuration to the sulfur atom, the structures of the metal chelates should have formula Ia, and, if assigned to anti configuration, formula Ib is probable.



(syn-form)



(anti-form)

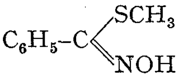
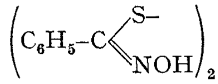
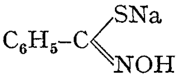
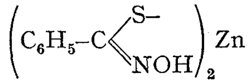
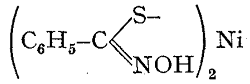
From this point of view, the rearrangement reactions of some derivatives or the sodium, zinc and nickel complexes of benzothiohydroxamic acid were examined under various conditions with which the Lossen rearrangements were carried out. The results are summarized in Table II.

S-Methylbenzothiohydroxamic acid (IV) gives only S-methylphenylthiocarbamate (1 in Table II) by the treatment with phosphorous pentachloride in ether or with benzenesulfonyl chloride in sodium hydroxide solution, but in pyridine some of the by-products, phenylisothiocyanate and benzonitrile, are also obtained. These results indicated that the hydroxyimino group is in the syn configuration to the sulfur atom and then the phenyl group migrates into the nitrogen atom from the carbon. In acetic acid, IV gives a large amount of benzonitrile and a little amount of aniline, that is the rearrangement product. This may be resulted from the fact that the addition of proton to the nitrogen atom facilitates the cleavage of the N–O and C–S linkages.

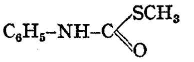
---

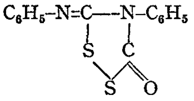
[11] J.P. Freeman, *J. Am. Chem. Soc.*, **80**, 5954 (1958).
[12] M.H. Benn, *Can. J. Chem.*, **42**, 2393 (1964).

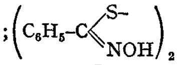
TABLE II. Rearrangement Products of Salts and Derivatives of Benzothiohydroxamic Acid

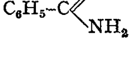
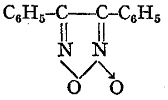
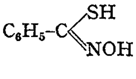
No.	Reagents compds.	PCl_5 in ether Rearranged compd.	Unrearranged compd.	$C_6H_5SO_2Cl$ in NaOH Rearranged compd.	Unrearranged compd.
1	 $C_6H_5{-}C\begin{array}{l}\diagup SCH_3\\ \diagdown NOH\end{array}$ (IV)	(1) 100%	0%	(1) 75% (3) 20% 95%	0%
2	 $\left(C_6H_5{-}C\begin{array}{l}\diagup S-\\ \diagdown NOH\end{array}\right)_2$ (VII)	(2) 40% (5) 32% (4) 14% 86%	0%	(2) 36% (4) 5% (3) 7% 48%	(7) 43%
3	 $C_6H_5{-}C\begin{array}{l}\diagup SNa\\ \diagdown NOH\end{array}$	(2) 34%	(7) 46%	(4) 66% (6) 8% 74%	(7) 11%
4	 $\left(C_6H_5{-}C\begin{array}{l}\diagup S-\\ \diagdown NOH\end{array}\right)_2Zn$	(2) 20% (4) 8% 28%	(7) 55% (11) 13% 68%	(2) 36% (4) 47% 83%	(7) 6% (12) 10% 16%
5	 $\left(C_6H_5{-}C\begin{array}{l}\diagup S-\\ \diagdown NOH\end{array}\right)_2Ni$	(2) 25% (2) 22%	(7) 63% (7) 44% (11) 17% 61%	(2) 3%	(7) 43% (12) 33% 76%

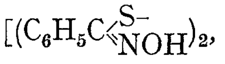
No.	$C_6H_5SO_2Cl$ in C_5H_5N Rearranged compd.	Unrearranged compd.	HCl in AcOH Rearranged compd.	Unrearranged compd.
1	(1) 52% (2) 4% 56%	(7) 18% (12) 17% 35%	(3) 25%	(7) 50% (8) 15% 65%
2	(2) 60%	(7) 25%	(2) 3%	(7) 41% (8) 16% (10) 8% 65%
3	(4) 36% (6) 4% 40% (4) 47% (6) 6% (2) 2% 55%	(7) 20% VII 35% 55% (7) 14% VII 27% 41%	0%	(7) 30% (8) 22% (9) 5% 57%
4	(4) 52% (2) 5% (6) 2% 59%	(7) 18% VII 19% 37%	0%	(7) 52% (8) 18% (9) 10% 80%
5	(2) 9% (4) 10%	VII 80% (7) 10% 90% VII 40% (7) 45% 85%	0%	(7) 37% (8) 3% (9) 8% (12) 23% 71%

rearranged compounds: (1);  $C_6H_5{-}NH{-}C\begin{array}{l}\diagup SCH_3\\ \diagdown O\end{array}$ (2); $C_6H_5{-}NCS$ (3); $C_6H_5{-}NH_2$

(4); $C_6H_5{-}NHCSNH{-}C_6H_5$ (5);  (6); $C_{14}H_{10}N_2OS$

unrearranged compounds: (VII);  $\left(C_6H_5{-}C\begin{array}{l}\diagup S-\\ \diagdown NOH\end{array}\right)_2$ (7); $C_6H_5{-}CN$ (8); $C_6H_5{-}CONH_2$

(9);  $C_6H_5{-}C\begin{array}{l}\diagup S\\ \diagdown NH_2\end{array}$ (10);  (11);  $C_6H_5{-}C\begin{array}{l}\diagup SH\\ \diagdown NOH\end{array}$ (12); starting material

In the rearrangement of the disulfide of thiobenzohydroxamic acid [ $(C_6H_5C\begin{array}{l}\diagup S-\\ \diagdown NOH\end{array})_2$, (VII)], phenylisothiocyanate and its derivatives are main products in both cases using phosphorous pentachloride and benzenesulfonyl chloride. Then, the syn configuration is also supposed for VII.

The rearrangements of sodium or zinc benzothiohydroxamate by benzenesulfonyl chloride seem to be essentially analogous to those of VII, because 1,3-diphenyl-2-thiourea, a main rearrangement product, is presumably obtained by the hydrolysis of phenylisothiocyanate, the main product in the case of VII. Since the S–S linkage of VII is apt to dissociate to thiohydroxamate anion[7] in alkaline solution, and sodium or zinc salts also easily dissociate, it is probable that the analogous results are obtained in both cases in sodium hydroxide solution. In pyridine, however, distinct difference has been found with regard to the occurrence of VII, but any further examination on the reaction mechanism did not made in this work. On the one hand, the treatment of the salts with phosphorous pentachloride in ether affords a large quantity of benzonitrile as well as phenylisothiocyanate. This may be resulted from the decomposition of thiohydroxamic acid, which is dissociated by hydrogen chloride generated from phosphorous pentachloride. Free thiohydroxamic acids are very unstable in acid or neutral solution.[13]

The reaction products of nickel benzothiohydroxamate with phosphorous pentachloride are nearly the same as those of the sodium or zinc salts, but in alkaline solution the rearrangement products are not obtained, and VII and benzonitrile are the main products. The rate-determining step in the Lossen rearrangement was reported to be preliminary ionization of the alkali salt of ester of hydroxamic acid, followed by the cleavage of the N–O linkage.[14] Therefore, the abnormal behaviour of the nickel complexes in sodium hydroxide or pyridine solution may be explained by assuming that the complex anion VI is stable in basic solution, that is the hydroxyimino group of the ligand are once esterified by benzenesulfonyl chloride and hydrolyzed again without successive ionization of the ester, and thus benzenesulfonyl chloride is consumed, while VI dissociates gradually to decompose without any rearrangements. Since the hydroxyimino group of VII obtained after the reaction is in the syn configuration, it is probable that nickel thiohydroxamate has also the hydroxyimino group of the syn configuration in the same manner observed in sodium or zinc salt.

Thus, since thiohydroxamic acids is revealed to have the hydroxyimino group in the syn configuration, the metal chelates probably form five-membered S–O coordinated structures Ia, which are supported in the solid state by X-ray crystallographic data. The structure Ib, proposed by Cambi[15] is not conceivable, even though every reagent possessing hydroxyimino group, such as dimethylglyoxime,[16] 2-hydroxybenzaldehyde oxime,[17] pyridine-2-aldehyde oxime,[6] forms metal chelate with the hydroxyimino nitrogen. Chelation like Ia was found in polynuclear complexes produced by the olation of metal ions or in cupric chelates with a series of ligand possessing hydroxy group.[18]

Experimental

Infrared spectra were taken with a Nippon Bunko double-beam model DS 201-B spectrometer. Ultraviolet and visible spectra were measured with a Hitachi model EPS-2U spectrometer. Molecular weight determination was carried out with a Mechrolab vapor pressure osmometer model 301-A in $CHCl_3$. Magnetic susceptibility was determined by the conventional Gouy's method.

Preparation of Thiohydroxamic Acid Derviatives and Their Metal Complexes——All the compounds used in the present work were prepared by the same procedures as shown previously.[7,8]

Reaction of Nickel Thiohydroxamate with Methylating Agent——Nickel benzothiohydroxamate (0.7 g) was treated with a little excess of $(CH_3)_2SO_4$ in 10% NaOH at 40—50° for 1 hr, and then the reaction mixtures were extracted with $CHCl_3$. By acidifying the aqueous layer, 0.3 g of the starting material was recovered.

---

[13] S. Mizukami and K. Nagata, *Chem. Pharm. Bull.* (Tokyo), **14**, 1249 (1966).

[14] C.R. Hauser and S.W. Kantor, *J. Am. Chem. Soc.*, **72**, 4284 (1950); R.D. Bright and C.R. Hauser, *J. Am. Chem. Soc.*, **61**, 618 (1939).

[15] L. Cambi, T. Bacchetti and E. Paglia, *Rend. Ist. Lombardo Sci.*, *Lettere B*, **90**, 577 (1956).

[16] L.E. Godycki and R.E. Rundle, *Acta Cryst.*, **6**, 487 (1953); D.E. Williams, G. Wohlauer and R.E. Rundle, *J. Am. Chem. Soc.*, **81**, 755 (1959).

[17] L.L. Merritt, Jr., G. Gaure and A.E. Lessor, *Acta Cryst.*, **9**, 253 (1956); S.H. Simonen and C.E. Pfluger, *Acta Cryst.*, **10**, 471 (1957).

[18] A.E. Martell, S. Chaberek, Jr., *et al.*, *J. Am. Chem. Soc.*, **79**, 3036 (1957).

By adding ether to the concentrated $CHCl_3$ extracts, reddish orange powder (80 mg), presumably OH-bridged binuclear complex, was precipitated. S-Methylbenzothiohydroxamic acid (III) was yielded from the filtrate, and recrystallized from light petroleum (bp 30—50°). From the mother liquor of the recrystallization, were obtained benzonitrile and S,O-dimethylbenzothiohydroxamic acid (V), which were purified chromatographically on an alumina column. Benzonitrile was eluted from the column with light petroleum, and (V) with light petroleum–ether mixture (8:2). Treatment of nickel benzothiohydroxamate or *p*-methylbenzothiohydroxamate with CH_3I in 5% NaOH at room temperature gave a small amount of nickel hydroxide, and a large portion of the starting material was recovered.

Acylation of the Transition Metal Complexes of Thiohydroxamic Acid——a) Benzoylation of the Nickel Complex: A little excess of benzoyl chloride was added dropwise into an ice cold 10% NaOH (1.5 equivalents) solution of nickel thiohydroxamate (about 0.2 g), and the reaction mixtures were shaken vigorously. The precipitates deposited were collected by filtration, washed successively with 10% NaOH, water and EtOH, and then extracted with a minimum amount of $CHCl_3$. The benzoylated nickel thiohydroxamate (II), precipitated from the extracts by adding ether, was filtered and washed with a small amount of ether and dried at 40° *in vacuo* over P_2O_5. When a suspension of the benzoylated complex (0.21 g) in 10% Na_2CO_3 was heated on a steam bath for 2 hr, a trace of NiS was precipitated. 10 mg of 1,3-diphenyl urea was extracted from the filtrate with ether. By acidifying the aqueous layer, brown powder (105 mg), which was identified with an authentic sample of nickel benzothiohydroxamate, was precipitated. (II) was also hydrolyzed on standing the aqueous solution for a long period of time at room temperature.

b) Benzoylation of Palladium Complex: The palladium complex did not benzoylated by the same procedure shown above. Then, a mixture of palladium benzothiohydroxamate (0.43 g) and a little excess of benzoyl chloride in pyridine (2 ml) was allowed to stand for 3 hr at room temperature, and the solution was chilled and acidified with dilute HCl to afford yellow precipitates (0.43 g). Addition of large amount of ether into $CHCl_3$ solution of the precipitates gave brown powder showing characteristic C=O stretching band at 1735 cm^{-1}; mp 130—131° (decomp.). Repeated precipitation of this powder, using $CHCl_3$–ether or $CHCl_3$–AcOEt system, resulted in the decrease of the intensity of $\nu_{C=O}$, and the content of palladium increased.

Rearrangement of Metal Complexes or Some Derivatives of Benzothiohydroxamic Acid——a) Reaction with PCl_5 in Ether: A little excess of PCl_5 was added dropwise under vigorous agitation into a solution or suspension of the sample (about 1 g) in absolute ether in a ice bath. The mixtures were allowed to stand for another 3 hr at room temperature, and then poured into ice cold water.

i) S-Methylbenzothiohydroxamic Acid (IV): The separated ether layer, after washing successively with 10% Na_2CO_3 and water, was evaporated to almost dryness. The oily residues which contained chlorine were dissolved in 10 ml of H_2SO_4. When the solution was warmed, hydrogen chloride was evolved and was precipitated S-methylphenylthiocarbamate (1 in Table II), which was recrystallized from light petroleum, mp 81.5°.

ii) Disulfide of Benzothiohydroxamic Acid (VII): The chlorine containing residues were treated with 50% H_2SO_4. The separated oil was dissolved again in ether and chromatographed on an alumina column, and the elution was performed with light petroleum–ether mixtures. Phenylisothiocyanate (2 in Table II), benzonitrile (7 in Table II), 4-phenyl-1,5-phenylimino-1,2,4-dithiazolid-3-one (5 in Table II), mp 118°, and 1,3-diphenyl-2-thiourea (4 in Table II) were found in the eluates. The content of phenylisothiocyanate was determined spectrophotometrically with $E_{282}m\mu$.

iii) Sodium, Zinc or Nickel Salts of Benzothiohydroxamic Acid: From the reaction mixtures, unreacted salts were recovered by filtration. After filterating the metal salts, the reaction mixtures were extracted with ether, and the extracts were evaporated to dryness. The compounds (2) and (7) were extracted from the oily residues with light petroleum, and the content of (2) was determined spectrophotometrically. From the residue which was insoluble in light petroleum, (4) was yielded.

b) Reaction with $C_6H_5SO_2Cl$ in NaOH Solution: A little excess of $C_6H_5SO_2Cl$ and 5 ml of 1N NaOH were added into an acetone solution of the sample, 0.5—1.0 g in 10 ml. The mixtures, after refluxing for 3 hr, was concentrated to almost dryness. When small amount of water was added into the residues, the unreacted starting material or some water–insoluble products such as (1), was recovered. From the ether extract of the aqueous solution, aniline was afforded. When the ether extract was concentrated and light petroleum was added into this residue, (4) was precipitated. After filtration, the petroleum solution was applied to the chromatographic separation on an alumina column, and (2) and (7) were eluted with light petroleum–ether mixture (8:2). The elution of (4) was achieved with ether. In the case of (VII), $C_{14}H_{10}ON_2$, colorless plates (mp 106°) IR ν_{max} 1667 cm^{-1} (6 in Table II), was eluted with light petroleum–ether mixture from the column.

c) Reaction with $C_6H_5SO_2Cl$ in Pyridine: A pyridine solution of the sample, 0.5—1.0 g in 4 ml, was allowed to stand overnight in the presence of one equivalent $C_6H_5SO_2Cl$. In the case of nickel benzothiohydroxamate, blue crystals of $(C_6H_5SO_3)_2Ni\cdot 2C_5H_5N$ was precipitated. The reaction mixtures were then poured into chilled HCl, and extracted with ether. The extracts, being washed successively with dilute HCl and water, were dried and concentrated. Addition of light petroleum into the concentrated ether solution gave the precipitates of VII and (4). The content of VII was determined gravimetrically as zinc benzothiohydroxamate by treating it with zinc powder in AcOH at 50° for 1 hr. After filtering, the petroleum solution was chromatographed on an alumina column. (2), (7) and (4) were eluted with light petroleum–ether mixture (8:2), VII and (6) with the mixture (5:5) and (1) with the mixture (4:6). In the case of nickel benzothiohydroxamate, when treated with 2 equivalents $C_6H_5O_2SCl$, the same result was obtained.

d) Reaction with HCl in AcOH: HCl gas was bubbled into a AcOH solution of the sample, about 0.7 g in 6 ml, and the mixtures were stood overnight in an air tight flask at room temperature. Then, after being heated for 15 min on a steam bath, the mixtures were made alkaline with Na_2CO_3 and extracted with ether. The extracts were concentrated. Addition of light petroleum to the residue gave benzamide (8 in Table II). After filtering, the mother liquor was chromatographed on an alumina column, and (2) and (7) was eluted with light petroleum. Elution with light petroleum–ether (8:2) afforded (3) and $C_{14}H_{10}O_2N_2$ (colorless prisms, mp 117°), which was presumed as 3,4-diphenylfurazan-2-oxide (10 in Table II). Elution with the mixture (2:8) gave a small amount of benzothioamide (9 in Table II). Nickel benzothiohydroxamate was inert against this reaction.

Acknowledgement The author expresses his thanks to Prof. M. Kishita, University of Osaka, for the measurement of magnetic susceptibility.