methylsilane as internal standard showed single peaks at δ 2.66 p.p.m. $[(\underline{\mathrm{CH_3}})_2\mathrm{N}\text{-}]$, 3.20 p.p.m. $(\underline{\mathrm{CH_3}}\text{-}\overset{\mathrm{N}}{\mathrm{N}}\text{-C=})$, and 7.12 p.p.m. $(\underline{\mathrm{H}}\text{-}\overset{\mathrm{N}}{\mathrm{C}}\text{=})$ in the ratio of 6:3:1 in accord with the proposed structure, and the infrared spectrum was also consistent.

Isolation of 1,1-Dimethyl-2-β-carboethoxy-β-cyanovinyl-2-methylhydrazine (VIII). The ethanol mother liquor from the preparation of V, *h*, was worked up as in the previous experiment. From the chloroform extract was obtained a semisolid which was crystallized from benzene-hexane to give approximately 200 mg. of the title compound, m.p. 77–79° C. Anal. Calcd. for $C_9H_{15}N_3O_2$: N, 21.3. Found: N, 20.8.

The PMR spectrum in deuteriochloroform with tetramethylsilane as internal standard showed single peaks at δ 2.60 p.p.m. $[(\underline{\mathrm{CH_3}})_2\mathrm{N}\text{-}]$, 3.15 p.p.m. $(\underline{\mathrm{CH_3}}\text{-}\overset{\mathrm{N}}{\mathrm{N}}\text{-C=})$, and 7.55 p.p.m. $(\underline{\mathrm{H}}\text{-}\overset{\mathrm{N}}{\mathrm{C}}\text{=})$ and a triplet at 1.3 p.p.m. $(\underline{\mathrm{CH_3}}\text{-}\mathrm{CH_2}\text{-O})$ and a quartet at 4.22 p.p.m. $(\mathrm{CH_3}\underline{\mathrm{CH_2}}\text{-O})$ in the ratio of 6:2:1:3:2 in accord with the proposed structure, and the infrared spectrum was also consistent.

Quaternary Hydrazines IV, *g* and *h*. The aminimide V, *g*, 5 grams in 20 ml. of 2-propanol was treated with 3 ml. of 50% hydriodic acid. Ether was added to the cloud point, and the solution was cooled to give IV, *g*, which could be recrystallized from 2-propanol. A similar procedure using methanol in place of 2-propanol gave the iodide IV, *h*. All attempts to prepare an acid salt of V, *i*, using hydriodic, hydrochloric, or perchloric acid in alcohols or water resulted in recovery of the crystalline imide.

ACKNOWLEDGMENT

The author is indebted to N. Burlingame for excellant technical assistance and to P.S. Magee and G.K. Kohn for stimulating discussions during the course of this work. L. M. Moore performed the microanalyses.

LITERATURE CITED

(1) Gibson, M.S., Murray, A.W., *J. Chem. Soc.* **1965**, p. 880.
(2) Hinman, R.L., *J. Am. Chem. Soc.* **78**, 1645 (1956).
(3) Hinman, R.L., Flores, M., *J. Org. Chem.* **24**, 660 (1959).
(4) Johnson, A.W., "Ylide Chemistry," p. 266, Academic Press, New York and London, 1966.
(5) Renouf, E., *Chem. Ber.* **13**, 2169 (1880).
(6) "Varian NMR Spectra Catalog," Varian Associates, 1962.
(7) Wawzonek, S., Chua, J., Yeakey, E.L., McKillip, W., *J. Org. Chem.* **28**, 2376 (1963).
(8) Wawzonek, S., Gueldner, R.C., *Ibid.*, **30**, 3031 (1965).
(9) Wawzonek, S., Meyer, D., *J. Am. Chem. Soc.* **76**, 2918 (1954).
(10) Wawzonek, S., Yeakey, E., *Ibid.*, **82**, 5718 (1960).

RECEIVED for review March 13, 1967. Accepted July 17, 1967.

Metal Complexes of Cyanoformamidines, Oxamidines, and Oxalimidates

H. M. WOODBURN, R. H. SALVESEN, J. R. FISHER, W. E. HOFFMAN, E. L. GRAMINSKI, and R. L. VAN DEUSEN
Department of Chemistry, State University of New York at Buffalo, Buffalo, N. Y. 14214

The preparation and physical characteristics of copper and nickel complexes of a number of cyanoformamidines, oxamidines, and oxalimidates are described. Cyanoformimidates failed to produce complexes under the conditions used.

IN THE investigation of the reactions of cyanogen with organic compounds (*5–11*), it was often found useful or necessary to convert the product into a derivative which could be stored for long periods of time without deterioration. Recently, references have been made to the utilization of oxamidines and oxalimidates in syntheses or analytical processes (*1–4*). Since many of these compounds are unstable, a number of metal complexes are reported which have been accumulated over the years, whose stability and solubility might make them of interest in the research areas indicated.

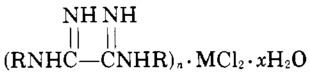
The molecular formulas, physical appearance, and melting points for all complexes are given in Tables I, II, and III. No attempt was made to determine the actual structure of any complex. However, details characteristic of the preparation of each class are given in the Experimental section. The procedure given leads to the complex described and does not preclude the possibility that a change in method might yield a complex of different metal to substrate ratio

Table I. Metal Complexes of Cyanoformamidines

R	x	Appearance	M.P., ° C.
		$(R_2NC_2N_2)_2Cu \cdot xH_2O$	
Ethyl	2	Light red powder	203–4 dec.
n-Propyl	2	Light red powder	207–8 dec.
n-Butyl	2	Red needles	184–5 dec.
n-Amyl	2	Red needles	185–6 dec.
Allyl	2	Red crystals	201–3 dec.
		$(R_2NC_2N_2)Ni \cdot xH_2O$	
Ethyl	1	Bright yellow powder	314–7 dec.
n-Butyl	1	Bright yellow powder	245–8 dec.
n-Butyl	2	Orange yellow powder	243–5 dec.[a]
n-Amyl	1	Bright yellow powder	227–30 dec.
n-Amyl	2	Orange yellow powder	185–8 dec.

[a] Color change, orange to yellow at 170° to 80° C.

Table II. Metal Complexes of Aliphatic Oxamidines

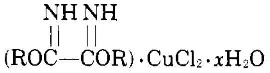


$(RNH\overset{\overset{NH}{\|}}{C}-\overset{\overset{NH}{\|}}{C}NHR)_n\cdot MCl_2\cdot xH_2O$

R	*n*	M	*x*	Appearance	M.P., ° C.
Ethyl	2	Cu	2	Light red crystals	214–5 dec.[a]
n-Butyl	2	Cu	2	Red crystals	221–3 dec.[a]
Ethyl	2	Ni	2	Yellow crystals	318–20 dec.
n-Butyl	2	Ni	2	Orange yellow crystals	299 dec.
Ethyl	1	Mn	4	Bronze-red powder	212–4 dec.
2-Hydroxyethyl	1	Cu	0	Bright blue crystals	178–9 dec.
2-Hydroxyethyl	2	Ni	7	Yellow orange powder	224–5 dec.

[a] Color change, red to blue at about 80° C.

Table III. Copper Complexes of Oxalimidates



$(RO\overset{\overset{NH}{\|}}{C}-\overset{\overset{NH}{\|}}{C}OR)\cdot CuCl_2\cdot xH_2O$

R	*x*	Appearance	M.P., ° C.
Ethyl	0	Bright blue powder	98–100 dec.
n-Butyl	0	Green crystals	182–3 dec.
Benzyl	0.5	Light green powder	149 dec.
β-Phenylethyl	0.5	Bright green crystals	162 dec.
Cinnamyl	1	Bluish green powder	130 dec.

or different degree of hydration. No complex is included for which the analytical results were not within acceptable limits. (The quantity of diallylcyanoformamidine copper complex available permitted qualitative analysis only.)

The following observations supplement the information in the tables.

CYANOFORMAMIDINES

Yields of copper complexes ranged from 65 to 83% of theoretical. Nickel complexes were slow to form and for that reason may have escaped detection under reaction conditions identical to those which produced copper complexes. From a different set of conditions, the yields of nickel complexes were only 13 to 15%. Both types of complexes were insoluble in water, aqueous NaOH, ether, ligroin, and petroleum ether. Solubility in the following increased as the organic part of the complex became heavier: aqueous acids, ethanol, acetone, ethyl acetate, dioxane, benzene, toluene, aniline, and nitrobenzene.

Neither a copper nor a nickel complex of *N*-dimethylcyanoformamidine could be isolated, and a variety of conditions failed to yield complexes of cobalt.

OXAMIDINES

The complexes described were soluble in water, insoluble in ethanol and ether. Color changes, following the addition of oxamidines to solutions of cobalt, chromium, and iron salts in both states of oxidation, hinted at complex formation but conditions could not be found which would cause them to precipitate out.

OXALIMIDATES

Complexes of low molecular weight (diethyl and dibutyl) were soluble in water and ethanol. However, as the molecular weight increased solubility decreased, and from di-*N*-octyl on, the complexes were practically insoluble in water, ethanol, and ether. This change probably had considerable effect on the yields of products, which ranged from 6% for diethyl- to 82% for bis-(β-phenylethyl)-oxalimidate.

No complexes could be isolated from a number of additional oxalimidates which were available [*sec*-butyl, bis-(α-phenylethyl), dicyclohexyl, and difurfuryl]. Furthermore, all attempts to produce complexes of cyanoformimidates [the product of the addition of one molecule of alcohol to cyanogen, ROC(=NH)CN] were unsuccessful.

EXPERIMENTAL

N-Diethylcyanoformamidine Copper Complex. Addition of 6.75 grams (0.04 mole) of $CuCl_2\cdot 2H_2O$ in the form of a molar aqueous solution, to 5 grams (0.04 mole) of *N*-diethylcyanoformamidine, produced a light green precipitate. The mixture was boiled for a few minutes, after which 6*N* NH_4OH was added until the precipitate had completely dissolved. On cooling in an ice bath, light red crystals began to form and after 30 minutes, 5.76 grams (83% yield) were recovered.

Before analysis the solid was dissolved in 6*N* HCl, filtered, and reprecipitated by 10% NaOH. It was then recrystallized four times by dissolving in ethanol and adding water until solid began to deposit. M.p. 203–4° C. decomposed.

Anal. Calcd. for $C_{12}H_{20}N_6Cu\cdot 2H_2O$: C, 41.5; H, 6.9; N, 24.2; Cu, 18.2. Found: C, 41.4; H, 7.3; N, 24.0; Cu, 18.3.

The complex was also obtained by treating aqueous or ethanolic solutions of *N*-diethylcyanoformamidine (6-gram samples) with 20 ml. of 6*N* NH_4OH and then adding 1*M* aqueous $CuCl_2$ until a light green precipitate just began to form. After the solution cooled for 30 minutes, precipitation of the copper complex was complete.

The same complex was produced by the substitution of $Cu(NO_3)_2\cdot 3H_2O$ for cupric chloride. In this case the solid precipitated after the solution cooled for 1 hour without the addition of NH_4OH.

N-Di-*n*-butylcyanoformamidine Nickel Complex. To a boiling solution of 5.4 grams (0.03 mole) of *N*-di-*n*-butylcyanoformamidine in 15 ml. of ethanol, was added 40 ml. of 1*M* alcoholic $NiCl_2\cdot 6H_2O$. A light blue-green precipitate appeared. The solution was cooled and 6*N* NH_4OH added until the precipitate dissolved. After 2 days, a bright yellow precipitate had formed and 1.1 grams (14%) were recovered.

The crystals were dissolved in 6*N* HCl; the solution was filtered and 10% NaOH added until the solution was alkaline to brilliant yellow paper, and precipitation was complete. This procedure was repeated twice more after which the solid was recrystallized three times from ethanol. M.p. 245–8° C. decomposed.

Anal. Calcd. for $C_{10}H_{19}N_3Ni\cdot H_2O$: C, 46.6; H, 8.2; N, 16.3; Ni, 22.7. Found: C, 46.5; H, 7.9; N, 16.3; Ni, 22.8.

When a solution of the complex in commercial alcohol (approx. 93% ethanol) was very slowly evaporated, the resulting solid was more orange in color than before, had a melting point of 243–5° C. decomposed, and gave the analysis of a dihydrate.

Anal. Calcd. for $C_{10}H_{19}N_3Ni \cdot 2H_2O$: C, 43.5; H, 8.4; N, 15.2; Ni, 21.3. Found: C, 43.1; H, 8.2; N, 15.0; Ni, 21.1.

If the dihydrate was put into solution with dilute HCl and reprecipitated with alkali, the monohydrate was obtained once more.

Sym-Diethyloxamidine Copper Complex. To a solution of 0.3 gram of *sym*-diethyloxamidine in 20 ml. of ethanol was added a solution containing 1 gram of anhydrous $CuCl_2$ in 20 ml. of ethanol. The mixture was thoroughly shaken, and a reddish solid settled out immediately leaving a blue-violet mother liquor. After standing for one-half hour, the red crystalline product was filtered off, washed several times with cold ethanol, and dried in vacuo. The yield was 0.38 gram (80%); m.p. 214° C. decomposed with a color change from red to blue at about 80° C.

Anal. Calcd. for $(C_6H_{14}N_4)_2 \cdot CuCl_2 \cdot 2H_2O$: C, 31.7; H, 7.1; N, 24.6; Cu, 14.0; Cl, 15.6. Molecular weight 455. Found: C, 31.8; H, 7.2; N, 24.5; Cu, 13.9; Cl, 15.7. Molecular weight (Rast method) 453.

Sym-Diethyloxamidine Nickel Complex. To a solution of 0.3 gram of diethyloxamidine in 20 ml. of ethanol was added with stirring a solution of 1 gram of $NiCl_2 \cdot 6H_2O$ in 20 ml. of ethanol. A yellow solid formed immediately. After several hours the mixture was filtered, and the yellow crystals were washed with ethanol and dried in vacuo. The m.p. was 318-20° C. decomposed, and there was no color change at lower temperatures. The yield was 0.33 gram (70%).

Anal. Calcd. for $(C_6H_{14}N_4)_2 \cdot NiCl_2 \cdot 2H_2O$: C, 32.0; H, 7.2; N, 24.9; Ni, 13.0; Cl, 15.8. Molecular weight 450. Found: C, 32.0; H, 7.4; N, 24.9; Ni, 12.9; Cl, 15.9. Molecular weight (Rast method) 453.

Sym-Diethyloxamidine Manganese Complex. To a solution of 0.3 gram of *sym*-diethyloxamidine in 20 ml. of ethanol was added with stirring a solution of 1 gram of $MnCl_2 \cdot 4H_2O$ in 20 ml. of water. The sludge which formed immediately was filtered off and the filtrate allowed to stand overnight. Dark red crystals separated out in clusters. They were filtered off, washed cautiously several times with ethanol, and dried in vacuo. The yield was 0.20 gram (53%); m.p. 212-4° C. decomposed.

Anal. Calcd. for $(C_6H_{14}N_4) \cdot MnCl_2 \cdot 4H_2O$: C, 21.2; H, 6.2; N, 16.5; Mn, 16.2; Cl, 20.9 Molecular weight 340. Found: C, 20.9; H, 6.1; N, 16.3; Mn, 16.3; Cl, 21.2. Molecular weight (Rast method) 345.

Bis-(2-Hydroxyethyl)-oxamidine Copper Complex. A solution of 1.74 grams (0.01 mole) of bis-(2-hydroxyethyl)-oxamidine in 35 ml. of hot ethanol was added to 3.4 grams (0.02 mole) of $CuCl_2 \cdot 2H_2O$ in 25 ml. of hot ethanol. The mixture turned dark green immediately. After about one-half hour, blue crystals began to appear on the walls of the reaction vessel. After 24 hours at room temperature, the solid was filtered off, washed with ethanol and dried in vacuo. M.p. 178-9° C. decomposed. The yield was good but was not determined exactly.

Anal. Calcd. for $(C_6H_{14}N_4O_2)CuCl_2$: C, 23.8; H, 4.5; N, 18.1; Cu, 20.5; Cl, 23.0. Found: C, 23.1; H, 4.9; N, 18.0; Cu, 20.0; Cl, 23.1.

Bis-(2-Hydroxyethyl)-oxamidine Nickel Complex. To a solution of 1.74 grams (0.01 mole) of bis-(2-hydroxyethyl)-oxamidine in 35 ml. of hot ethanol was added 4.8 grams (0.02 mole) of $NiCl_2 \cdot 6H_2O$ in 25 ml. of hot ethanol. The solution immediately turned brown and after about one-half hour a yellow solid began to precipitate. After 24 hours at room temperature, the yellow-orange solid was filtered off, washed with ethanol, and dried in vacuo. M.p. 224-5° C. decomposed. The yield was good but was not determined exactly.

Anal. Calcd. for $(C_6H_{14}N_4O_2)_2 \cdot NiCl_2 \cdot 2H_2O$: C, 28.1; H, 6.2; N, 21.8; Ni, 11.4; Cl, 13.8. Found: C, 27.8; H, 6.8; N, 22.2; Ni, 10.8; Cl,13.5.

Di-*n*-butyloxalimidate Copper Complex. A solution, 51.2 grams (0.3 mole), of $CuCl_2 \cdot 2H_2O$ in 250 ml. of absolute ethanol was slowly mixed with a solution of 60.3 grams (0.3 mole) of di-*n*-butyloxalimidate in 100 ml. of the same solvent. The mixture was cooled for 8 hours. Filtration and washing of the precipitate with cold absolute alcohol gave 61.4 grams (55%) of green crystals. These were recrystallized from absolute alcohol; m.p. 182–3° C. decomposed.

Anal. Calcd. for $(C_{10}H_{20}N_2O_2) \cdot CuCl_2$: C, 35.9; H, 6.0; N, 8.4. Found: C, 35.6; H, 6.3; N, 8.3.

Bis-(β-phenylethyl)oxalimidate Copper Complex. When saturated solutions of $CuCl_2 \cdot 2H_2O$ (1.7 grams; 0.01 mole) and bis-(β-phenylethyl)oxalimidate (2.9 grams; 0.01 mole) in absolute ethanol were mixed, there was an immediate precipitation of bright green crystalline material. This was thoroughly triturated in absolute alcohol. The weight of dry material was 3.6 grams (82%); m.p. 162° C. decomposed. The complex was insoluble in water, ethanol, and ether.

Anal. Calcd. for $(C_{18}H_{20}N_2O_2) \cdot CuCl_2 \cdot \frac{1}{2}H_2O$: C, 49.2; H, 4.8; N, 6.4; Cu, 14.5; Cl, 16.1. Found: C, 48.7; H, 5.2; N, 6.6; Cu, 14.8; Cl, 16.2.

LITERATURE CITED

(1) Behun, J.D. (to Wyandotte Chemicals Corp.), U. S. Patent **3,112,334** (Nov. 26, 1963); *CA* **60**, 5342c (1964).

(2) Papafil, M., Furnica, D., Hurduc, N., *Analele Stiint. Univ. "A.I. Cuza," Iasi. Sect. I* **5**, 135 (1959); *CA* **57**, 6600*i* (1962).

(3) Papafil, E., Papafil, M., Macovei, V., *Ibid.*, **2**, 251 (1956); *CA* **54**, 4483*g* (1960).

(4) Weidinger, H., Kranz, J., *Ber.* **97**, 1599 (1964).

(5) Woodburn, H.M., Lathroum, L.B., *J. Org. Chem.* **19**, 285-93 (1954).

(6) Woodburn, H.M., Moorehead, B.A., Bonner, W.H., *Ibid.*, **14**, 555-8 (1949).

(7) Woodburn, H.M., Moorehead, B.A., Chen, M.C., *Ibid.*, **15**, 535-40, 541-7 (1950).

(8) Woodburn, H.M., O'Gee, R.C., *Ibid.*, **17**, 1235-44 (1952).

(9) Woodburn, H.M., Pautler, B.G., *Ibid.*, **19**, 863-7 (1954).

(10) Woodburn, H.M., Pino, L.N., *Ibid.*, **16**, 1389-94 (1951).

(11) Woodburn, H.M., Sroog, C.E., *Ibid.*, **17**, 371-8 (1952).

RECEIVED for review March 29, 1967. Accepted May 20, 1967.