the stabilization of the protonated configuration of the cyanide ligand in the transition state. Although the initial protonation of the cyanide ligand is thought to occur on the nitrogen atom,[20] it is possible that the proton is transferred to the carbon atom in the activated complex and that in this configuration the proton is stabilized by an adjacent water molecule.

The activation parameters for k_1 are subject to rather large uncertainties and it is difficult to draw definite conclusions from them. If it is assumed that the trends in Table III are valid, then it is seen that $\Delta H^{\ddagger}$ is approximately constant for this series of complexes and $\Delta S^{\ddagger}$ becomes more negative in going from the monocyano to the tricyano complex. Since the Cr–C bond strength should increase with the increase in positive charge in going from the tricyano to the monocyano complex, a compensating factor must be involved which keeps the $\Delta H^{\ddagger}$ values for these complexes constant. This factor may be the involvement of coordinated water molecules in stabilizing the protonated cyanide ligand in its transition state, referred to above. This process should be more favorable for the monocyano complex than for the others and should act to decrease the activation energy.

Because of its greater positive charge, the solvent water molecules should be drawn closest and should be most highly ordered in the case of the monocyano complex, and the least amount of additional ordering would be needed to bring an incoming (substituting) water molecule into its transition-state position (whatever that may be). The value of $\Delta S^{\ddagger}$ for the aquation of the monocyano complex should therefore be less negative than for the dicyano complex and, similarly, the value of $\Delta S^{\ddagger}$ for the dicyano aquation reaction should be less negative than the value for the tricyano reaction, in agreement with experiment.

Acknowledgment.—We are indebted to Dr. R. Krishnamurthy, who first isolated the 1,2,3-tricyanotriaquochromium(III) complex.

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Hydrogen and Metal Complexes of Some 3-Cyanoformazans

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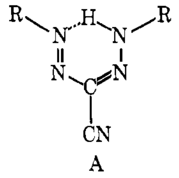
1,5-Bis(2-hydroxyphenyl) (I), 1,5-bis(2-hydroxy-4-nitrophenyl) (II), 1,5-bis(2-hydroxy-5-sulfophenyl) (III), 1,5-bis(2-carboxyphenyl) (IV), 1,5-bis(2-arsonophenyl) (V), 1,5-bis(8-quinolyl) (VI), 1,5-bis(8-quinaldyl) (VII), and 1,5-bis(4-antipyrinyl) (VIII) derivatives of 3-cyanoformazan were prepared and their hydrogen and metal complexes were investigated. The investigation involved the following metals: calcium, scandium, lanthanum, thorium, vanadium(V), molybdenum(VI), manganese(II), iron(II), iron(III), cobalt(II), nickel, copper(II), palladium(II), zinc, cadmium, mercury(II), lead(II), and bismuth. Complex ZnH_2L of compound VI and complexes CuL and PdL of compound VIII are of unusual stability. The values of logarithmic overall stability constants are 32.4, 28.2, and 28.1, respectively.

Introduction

The formazan skeleton is a good carrier of π-bonding and chelating properties. Wizinger with coworkers[1,2] prepared several derivatives of 1,5-bis(2-hydroxyphenyl)formazan and 1,5-bis(2-carboxyphenyl)formazan and investigated the composition of the solid chromium(III), copper(II), and nickel complexes. Hunter and Roberts[3] pointed out the symmetry of the formazan molecule as a basic requirement for its good chelating and chromogenic properties. Recently, Dziomko and his coworkers[4,5] investigated 1,5-bis(2-hydroxyphenyl)formazan and some of its derivatives as extractants for metals.

The interesting metallochromic properties and ease of preparation were why we investigated the complexation of some 3-cyanoformazans; see formula A.



A

I, R = 2-hydroxyphenyl
II, R = 2-hydroxy-4-nitrophenyl
III, R = 2-hydroxy-5-sulfophenyl
IV, R = 2-carboxyphenyl
V, R = 2-arsonophenyl
VI, R = 8-quinolyl
VII, R = 8-quinaldyl
VIII, R = 4-antipyrinyl

Experimental Section

Apparatus.—All photometric measurements were made with a double-beam Unicam 800B recording spectrophotometer. Quartz cells (1 cm) were used throughout. An Orion Model 801 pH

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(4) V. M. Dziomko and V. M. Ostrovskaya, *Tr. Vses. Nauch.-Issled. Inst. Khim. Reaktivov Osobo Chist. Khim. Veshchestv*, **28**, 201 (1966).

(5) V. M. Dziomko, V. M. Ostrovskaya, and M. Z. Partashnikova, *ibid.*, **26**, 79 (1964).

TABLE I

PROPERTIES OF PREPARED COMPOUNDS

Compd	Yield, %	Mp, °C	Mol wt	R_f[a]	Anal, % C Calcd	C Found	H Calcd	H Found	N Calcd	N Found	X Calcd	X Found
I	31	209	281.3	0.98(r)	59.8	59.6	3.9	3.9	24.9	24.8	...	...
II	10	147	371.3	0.96(g)	45.3	45.4	2.4	2.5	26.4	26.3	...	...
III	42	>300	439.4	0.15(r)	38.3	38.4	2.1	2.1	15.9	16.0	4.6[b]	4.5[b]
IV	35	225	337.3	0.90(o)	57.0	56.9	3.3	3.4	20.8	20.9	...	...
V	64	>300	497.1	0.62(y)	33.8	33.9	2.6	2.6	14.1	14.0	30.1[c]	29.9[c]
VI	41	150	351.4	0.93(v)	68.4	68.1	3.4	3.5	27.9	27.8	...	...
VII	43	>300	379.4	0.89(v)	69.6	69.5	4.5	4.5	25.8	25.9	...	...
VIII	43	143	469.5	0.94(y)	61.4	61.3	4.9	5.0	26.8	27.0	...	...

[a] The values of R_f were obtained with Whatman paper no. 1, at 25°, in 1-butanol–water–acetic acid (5:2:1). The color of individual spots was (g) green, (o) orange, (e) red, (v) violet, and (y) yellow. All compounds were chromatographically pure. [b] Sulfur. [c] Arsenic.

TABLE II

STABILITY CONSTANTS,[a] MOLAR ABSORPTIVITIES, AND ISOSBESTIC POINTS OF HYDROGEN COMPLEXES

Compd		Complex L		HL		H_2L		H_3L		H_4L
I	Log K_i			12.5 ± 0.1		10.4 ± 0.0		7.2 ± 0.2		...
	λ_{max}, nm	535		570		490		475		...
	$\epsilon_{\lambda(max)} \times 10^{-4}$	2.6		2.37		3.27		2.05		...
	λ_{isos}, nm		415, 550		410, 670		405, 528			
II	Log K_i			13.2 ± 0.2		10.3 ± 0.1		8.0 ± 0.3		5.1 ± 0.1
	λ_{max}, nm	655		460		454		575		395
	$\epsilon_{\lambda(max)} \times 10^{-4}$	2.50		2.00		1.95		2.05		2.80
	λ_{isos}, nm		380, 550		400, 485		505, 610		350, 435	
III	Log K_i			14.6 ± 0.1		12.4 ± 0.1		7.3 ± 0.3		...
	λ_{max}, nm	530		525		565		465		...
	$\epsilon_{\lambda(max)} \times 10^{-4}$	3.10		2.93		2.25		1.67		
	λ_{isos}, nm		435, 636		560		410, 530			
IV	Log K_i			11.3 ± 0.1		4.8 ± 0.1		2.7 ± 0.3		...
	λ_{max}, nm	463		435		442		434		...
	$\epsilon_{\lambda(max)} \times 10^{-4}$	3.20		1.95		1.83		1.63		...
	λ_{isos}, nm		424, 531		400, 470		423, 486			
V	Log K_i			13.9 ± 0.3		11.7 ± 0.1		9.3 ± 0.1		7.2 ± 0.0
	λ_{max}, nm	470		466		470		480		465
	$\epsilon_{\lambda(max)} \times 10^{-4}$	4.20		3.80		3.90		3.80		2.20
	λ_{isos}, nm		420, 528		...		517		455	
VI	Log K_i			14.0 ± 0.1		8.4 ± 0.1		6.5 ± 0.2		...
	λ_{max}, nm	510		505		500		470		...
	$\epsilon_{\lambda(max)} \times 10^{-4}$	4.55		3.90		2.05		2.00		...
	λ_{isos}, nm		335, 680		440, 600		440, 568			
VII	Log K_i			14.6 ± 0.1		8.8 ± 0.1		6.6 ± 0.2		3.4 ± 0.1
	λ_{max}, nm	510		505		500		490		...
	$\epsilon_{\lambda(max)} \times 10^{-4}$	3.20		3.10		2.05		2.00		...
	λ_{isos}, nm		450, 680		440, 600		440, 510			
VIII	Log K_i			14.7 ± 0.1		9.8 ± 0.1		0.8 ± 0.1		...
	λ_{max}, nm	480		527		300		400		...
	$\epsilon_{\lambda(max)} \times 10^{-4}$	2.50		1.47		2.55		0.95		...
	λ_{isos}, nm		425, 530		415, 470		330, 370			

[a] $K_i = [H_iL][H]^{-1}[H_{i-1}L]^{-1}$.

meter, with a glass and calomel electrode pair, was used for pH measurements.

General Preparation of Compounds I–VIII.—A 0.02-mmol amount of the corresponding amine (Aldrich Chemical Co.) was dissolved in 20 ml of water and 5 ml of 12 *M* hydrochloric acid. [In the case of product III, the 2-aminophenol-4-sulfonic acid and sodium nitrite were dissolved in 20 ml of 1 *M* sodium hydroxide and the solution was dropped into 10 ml of 6 *M* hydrochloric acid within the same conditions as previously given.] The solution was cooled to −3° and stirred mechanically. A solution of 1.40 g of sodium nitrite in 10 ml of water was added, keeping the temperature in the range 0 to −5°. The solution of the diazonium salt was transferred to a funnel and was added dropwise to a well-stirred solution of 20 ml of 5 *M* sodium hydroxide and 0.85 g of cyanoacetic acid, keeping the temperature in the range 0° to −5°. The solution was allowed to stand for 30 min and was then acidified with 10 ml of 12 *M* hydrochloric acid. [The acidification with hydrochloric acid was necessary to produce the decarboxylation of cyanoacetic acid. However, in the case of compounds VI–VIII after standing for 1 hr, a solution containing 16 g of sodium acetate (trihydrate) in 40 ml of water was added to assist precipitation.] After standing overnight, the mixture was filtered with suction through a glass sinter of medium porosity and recrystallized twice from ethanol. [Compound III was recrystallized from water.] The products form dark brick red needles; their properties are listed in Table I.

Reagents and Measurements.—Ethanolic solutions (2.00 × 10^{-4} *M*) of individual compounds were used. Compound III was used in aqueous solution. The solutions were quite stable within the usual storage conditions of 2 weeks. The stock solu-

TABLE III

EFFECTIVE AND OVERALL STABILITY CONSTANTS OF METAL COMPLEXES

Compd	Complex	pH	$\Delta A_1/\Delta A_2$	Log K_n	Log $\alpha_{L(H)}$	Log β_{jn}
I	BiH_4L_2	4.05	2.57	10.7	18.0	62.9
		4.45	2.33	11.3	16.8	62.8
		4.77	2.22	11.9	15.9	62.8
	CuH_4L_2	4.05	2.20	11.8	18.0	64.0
		4.45	2.10	12.6	16.8	64.1
		4.77	2.06	13.2	15.9	64.1
	ScH_4L_2	5.27	3.30	9.9	14.3	59.6
		5.51	2.69	10.5	13.6	59.7
		6.20	2.24	11.6	11.6	59.6
	ZnH_4L_2	5.80	2.27	11.5	12.7	60.2
		6.20	2.19	11.9	11.6	59.8
		6.45	2.12	12.4	10.8	59.9
		6.94	2.06	13.2	9.5	60.0
II	BiH_4L_2	5.80	3.86	8.9	10.5	53.2
		6.20	3.61	9.1	9.7	53.2
		6.45	3.26	9.3	9.1	53.4
		6.94	3.42	9.2	8.1	53.2
	$CuHL_2$	5.02	6.20	7.8	12.4	37.6
		5.27	4.17	8.7	11.8	37.6
		5.51	3.10	9.5	11.2	37.5
	LaH_3L_2	6.20	5.12	8.3	9.7	46.2
		6.45	3.79	8.9	9.1	46.6
		6.94	3.27	9.3	8.1	46.4
	ZnH_4L_2	5.80	3.53	9.1	10.6	53.5
		6.20	3.39	9.2	9.7	53.3
		6.45	3.10	9.5	9.1	53.6
		6.94	3.14	9.4	8.1	53.4
III	ZnH_4L_2	5.27	2.64	10.0	23.7	78.4
		5.51	2.27	10.9	22.7	78.4
		5.80	2.17	11.2	21.6	78.4
IV	CuH_2L_2	5.80	2.48	10.3	5.5	33.0
		6.20	2.46	10.3	5.1	32.9
		6.45	2.45	10.3	4.9	33.0
	NiL_2	6.94	7.96	5.8	4.4	14.5
		7.89	6.55	7.6	3.4	14.5
		8.23	4.58	8.6	3.1	14.8
IV	ThH_2L_2	4.05	3.22	9.4	8.1	33.7
		4.45	2.65	10.0	7.4	33.8
		4.77	2.29	10.8	6.9	33.4
V	PbH_xL	6.94	2.16	5.8	...	...
VI	$CdHL_2$	7.89	2.10	12.1	6.6	33.3
		8.09	2.09	12.3	6.4	33.1
		8.23	2.07	12.5	6.2	33.1
		8.44	2.05	13.0	5.8	33.1
	CuH_2L	1.25	2.67	4.9	25.1	32.5
		1.54	2.37	5.4	24.2	32.7
		1.82	2.26	5.7	23.4	32.7
		2.18	2.24	5.7	22.4	32.5
	$HgHL_2$	8.09	2.22	11.1	6.4	32.0
		8.23	2.16	11.5	6.2	32.0
		8.44	2.11	11.9	5.8	32.0
		8.61	2.03	12.2	5.6	32.0
	ZnH_2L	1.10	2.83	4.7	25.5	32.4
		1.54	2.73	4.8	24.2	32.2
		1.82	2.36	5.5	23.4	32.5
		2.18	2.27	5.7	22.4	32.4
VII	$CdHL_2$	8.61	2.29	10.8	6.5	32.4
		9.01	2.12	11.9	5.8	32.6
		9.26	2.11	12.0	5.5	32.5
VIII	BiH_2L_2	1.10	3.42	9.2	22.5	56.4
		1.25	3.00	9.5	22.1	56.3
		1.54	2.38	10.5	21.5	56.6
		1.82	2.15	11.6	20.9	57.0
	CuL	0.82	2.53	5.2	23.8	28.3
		1.10	2.27	5.7	22.5	28.2
		1.25	2.16	6.0	22.1	28.2
	PdL	1.10	2.33	5.5	22.5	28.0
		1.25	2.16	6.1	22.1	28.2
		1.54	2.10	6.5	21.5	28.0
		1.82	2.05	7.2	20.9	28.1
	ScH_2L_2	4.05	2.17	11.4	16.4	52.2
		4.45	2.09	12.2	15.5	52.3
		4.77	2.06	12.8	14.9	52.3

tions of metal salts (usually nitrates or perchlorates) were 1.00×10^{-4} *M*. The pH was adjusted by means of perchloric acid and hexamine (pH 1.10–6.90), perchloric acid and borax (pH 7.58–9.01), borax and sodium hydroxide (pH 9.26–10.82), and sodium hydroxide (pH 10.93–15.80). The ionic strength between pH 1.10 and 12.95 was kept constant (0.10 *N*) by means of sodium perchlorate.[6] The sequence of buffer, reagent, and metal ion was adhered to during the preparation of all measured solutions; the temperature was kept at 25 ± 1°. The absorbance of the solutions was measured against a water blank.

Results

Hydrogen Complexes.—The stability constants of hydrogen complexes of the individual compounds were determined photometrically by a method described earlier.[6] The results are collected in Table II.

Metal Complexes.—The dependence of complex formation on pH was investigated photometrically. The molar metal:ligand ratio of the complex in the pH range of maximum absorbance was determined by the method of continuous variation.[7] The effective stability constants K_n of complexes were determined by the proportional-absorbances method.[8] From a set of effective stability constant values, the composition of the complex MH_jL_n and its overall stability constant β_{jn} were determined by means of the equation (for its development see ref 9)

$$\log K_n\alpha_{L(H)}{}^n = -j(\text{pH}) + \log \beta_{jn} \qquad (1)$$

where $\alpha_{L(H)}$ designates the coefficient of side reactions of the ligand with hydrogen ions.[10] We have

$$\alpha_{L(H)} = \sum_0^I [\text{H}]^i K_0 K_1 K_2 \ldots K_i \qquad K_0 = 1 \qquad (2)$$

Obtained values are listed in Table III.

The effective stability constant K_n may be expressed in the form of the parameter equation

$$(x - y)(1 - ny)^n = yR_n \qquad (3)$$

where

$$[\text{MH}_j\text{L}_n]/c_L = y \qquad (4a)$$

$$c_M/c_L = x \qquad (4b)$$

and

$$R_n = K_n{}^{-1}c_L{}^{-n} \qquad (5)$$

$[\text{MH}_j\text{L}_n]$ is the actual concentration of the complex,

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(6) B. Budesinsky, *Talanta*, **16**, 1277 (1969).

(7) B. Budesinsky, *Collect. Czech. Chem. Commun.*, **32**, 235 (1967).

(8) B. Budesinsky, *J. Inorg. Nucl. Chem.*, **31**, 1345 (1969).

(9) B. Budesinsky and K. Haas, *Acta Chim.* (*Budapest*), **39**, 7 (1963).

(10) A. Ringbom, "Complexation in Analytical Chemistry," Interscience, New York, N. Y., 1963, p 38.

and c_M and c_L are the total concentrations of the metal and the ligand, respectively.

Differentiation of eq 3 gives

$$y' = \frac{(1 - ny)^n}{R_n + (1 - ny)^n - n^2(x - y)(1 - ny)^{n-1}} \qquad (6)$$

The slope of the curve $y = f(x)$ in the point $x = y = 0$ is given by

$$y_0' = 1/(R_n + 1) \qquad (7)$$

The absorbance of a solution of the chromogenic compound alone is

$$A_L = \sum_0^I \epsilon_i[H_iL] = \bar{\epsilon}_i c_L \qquad (8)$$

If the metal is present, we have

$$A_T = \epsilon_{jn}[MH_jL_n] + \bar{\epsilon}_i(c_L - n[MH_jL_n]) \qquad (9)$$

Performing the measurement of A_L and A_T at the same pH, the distribution of complexes H_iL should be the same and therefore the value of $\bar{\epsilon}_i$ should be the same in both eq 8 and 9. The combination of (8) and (9) gives

$$\Delta A = A_T - A_L = [MH_jL_n](\epsilon_{jn} - n\bar{\epsilon}_i) \qquad (10)$$

Introducing the effective molar absorptivity

$$\Delta\epsilon = (\Delta A/c_M)_0 \qquad (11)$$

for the point $\Delta A = c_M = 0$, we obtain after the combination of (4), (7), (10), and (11)

$$\Delta\epsilon = (\epsilon_{jn} - n\bar{\epsilon}_i)/(R_n + 1) \qquad (12)$$

Assuming the error of photometric measurement ±1%, eq 12 shows that $\Delta\epsilon$ is independent of concentration c_L only if we have

$$R_n \leq 10^{-2} \qquad (13)$$

The values of R_n, ϵ_{jn}, and $\Delta\epsilon$ together with average values of the logarithmic overall stability constants are presented in Table IV.

Discussion

It may be seen from Table II that the values of logarithmic stability constants of complexes HL are influenced, first of all, by the field effect of the substituent R (see formula A). The sequence of substituents according to the increasing stability may be set up as

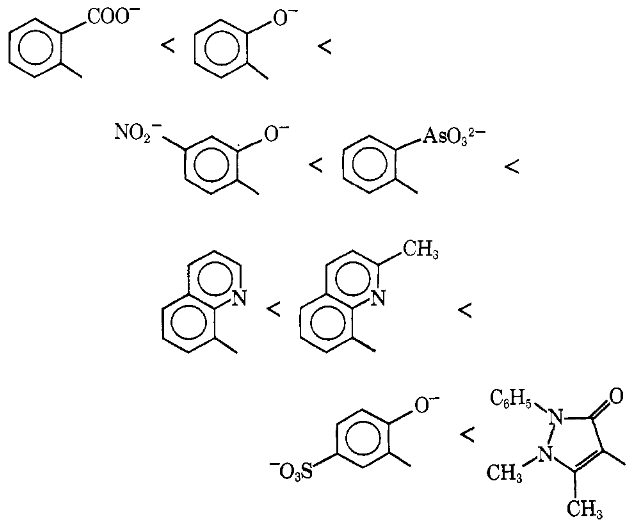
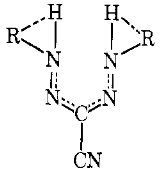


TABLE IV
AVERAGE LOGARITHMIC OVERALL STABILITY CONSTANTS AND MOLAR ABSORPTIVITIES OF COMPLEXES AND EFFECTIVE MOLAR ABSORPTIVITIES

Compd	Complex	Log β_{jn}	λ, nm	$10^{-4}\epsilon_{jn}$	−Log R_n	pH	$10^{-4}\Delta\epsilon$
I	BiH_4L_2	62.83	490	2.25	1.90	4.05	−1.75[a]
	CuH_4L_2	64.07	590	2.55	3.00	4.05	2.05
	ScH_4L_2	59.63	480	1.93	1.71	5.51	−2.15
	ZnH_4L_2	59.97	620	2.58	4.40	6.94	2.08
II	BiH_4L_2	53.25	570	1.28	0.53	6.45	−2.18
	$CuHL_2$	37.57	570	0.00	0.66	5.51	−2.31
	LaH_3L_2	46.40	570	0.34	0.52	6.94	−2.81
	ZnH_4L_2	53.45	570	0.90	0.66	6.45	−2.62
III	ZnH_4L_2	78.40	610	3.88	3.19	5.80	3.00
IV	CuH_2L_2	32.97	430	1.06	1.53	6.45	−2.76
	NiL_2	14.60	430	0.00	−0.24	8.23	−1.75
	ThH_2L_2	33.63	430	2.01	2.02	4.77	−1.75
V	PbH_xL	. . .	470	1.07	1.08	6.94	−1.25
VI	$CdHL_2$	33.15	590	3.89	4.20	8.44	3.00
	CuH_2L	32.60	490	0.24	1.04	2.18	−1.50
	$HgHL_2$	32.00	600	3.30	3.40	8.61	2.75
	ZnH_2L	32.37	590	2.88	0.96	2.18	2.25
VII	$CdHL_2$	32.50	500	1.35	2.02	8.61	−0.80
VIII	BiH_2L_2	56.58	620	2.50	1.79	1.82	2.50
	CuL	28.23	540	1.31	1.34	1.25	1.25
	PdL	28.08	560	1.29	2.50	1.82	1.25
	ScH_2L_2	52.27	530	5.85	4.00	4.77	5.65

[a] The negative sign indicates that $n\bar{\epsilon}_i > \epsilon_{jn}$.

The highest chromogenic effect is connected with the appearance of completely deprotonized particle L which is in agreement with its resonance possibilities. A smaller chromogenic effect is connected with formation of particle H_2L which may be explained by the formation of the symmetric structure B.



B

From the viewpoint of metal complex formation, all compounds have a tendency to form metal–hydrogen complexes according to the corresponding pH. This tendency is particularly obvious in derivatives of *o*-aminophenol because of the relatively high stability of the complex H_2L. Complexes of IV and V are weak due to the steric hindrance of groups $-COO^-$ and $-AsO_3^{2-}$. Similarly steric hindrance of both methyl groups is responsible for the poor complexation of VII. There is a remarkable difference in comparison with VI. Since we selected complexes with maximum absorptivity, many complexes we found have the metal:ligand molar ratio of 1:2. However, the course of pH–absorbance curves shows that the complexes with molar ratio of 1:1 are also formed.

From the collection of investigated metals, it may be seen that most stable complexes are formed with ions of configuration d^8, d^9, and d^{10}. This may be explained by the combined action of the following three effects: (1) The coordination ability of the individual metal ions, (2) the (M→L)π-bonding effect, and (3) the chelate cage effect.

Since we have tetradentate planar ligands (formula A), we can also expect the formation of the square-planar complexes. Copper(II) and palladium(II) prefer this type of coordination so that the stability of complexes CuL and PdL of VIII may be explained in that way.

The (M→L)π-bonding effect of all compounds is given by the extensive resonance within the π-electron system and by the strong electrophilic effect of the cyano group. From the viewpoint of the metal ion, the (M→L)π-bonding effect increases with the increasing number of d electrons. This may explain the stability of some d^{10} complexes.

The existing differences in the stability of zinc, cadmium, and mercury(II) complexes may be explained by the action of the chelate cage effect. The most stable complexes are formed by zinc (ionic radius 0.74 Å); see the complexes of VI, Table III. The appearence of the chelate cage effect is given by the rigid planar structure of all compounds (see formula A).

Cobalt(II) produces a rapid catalytic oxidation of IV at pH 8.1. This reaction is highly selective and sensitive and will be described separately.

Comparison with recently published 3-(4-antipyrinylazo)pentane-2,4-dione[11] shows that a similar compound, *i.e.*, 1,5-bis(4-antipyrinyl)-3-acetylformazan, may be formed too. However, the cleavage of pentane-2,4-dione occurs with much greater difficulty than that of cyanoacetic acid.

Conclusion

The investigated compounds form most stable complexes with zinc, copper(II), and palladium(II). Complex ZnH$_2$L of VI and complexes CuL and PdL of VIII show good prospects for use as a highly selective means for these metals.

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Conformational Analysis of Coordination Compounds. IV. Conformational Energies and Activation Energies for Ring Inversion of Ethylenediamine Complexes

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The free energy differences between the various configurations of M(en)$_3$ have been calculated for a number of M–N bond lengths. The marked preference for configurations of the types D(δδδ), L(λλλ), D(δδλ), and L(λλδ) which occurs for M–N = 2.0 Å was found largely to be removed for complexes with M–N = 2.3 Å. The calculations included for the first time an estimation of an entropy contribution to the conformational energies arising from differences in the vibrational freedom of the chelate rings in the various configurations. The calculations also included a study of the lowest energy transition state for ring inversion. This was found to be of the envelope type and to provide a barrier to inversion of about 5 kcal mol^{-1} for M–N = 2.0 Å increasing to about 7 kcal mol^{-1} for M–N = 2.3 Å. The results of the calculations were used as the basis for a rationalization of the observed nmr spectra of the tris-ethylenediamine complexes of a number of metal ions. It was concluded that the room-temperature spectra were the result of rapid ring inversion, the variation with the metal ion being due to a number of factors controlling the effective chemical shift difference between the axial and equatorial methylene protons.

The nmr spectra of diamagnetic complexes of the type M(en)$_3$ exhibit widely differing CH resonances depending on the central metal ion. For the N-deuterated ruthenium(II) complex, detailed fine structure has been observed and analyzed in terms of an AA′BB′ system.[1] For the equivalent cobalt(III) complex a broad unresolved band has been observed,[2] for rhodium(III) and iridium(III) a narrow band with definite fine structure, and for platinum(IV) a very sharp peak with ^{195}Pt satellites.[3] For the above complexes, even for the ruthenium(II) complex with the well-resolved fine structure, it has not been possible to determine from the published spectra the rate of ring inversion or whether one configuration is markedly preferred over the other possible structures.

The ethylenediamine chelate rings have puckered conformations with either δ or λ chirality. To date, no reliable estimate has been made of the activation energy for the inversion from one chirality to the other. However, experimental data are available for the relative free energies of the four configurations D(δδδ) {=L(λλλ)}, D(δδλ) {=L(λλδ)}, D(δλλ) {=L(λδδ)}, and D(λλλ) {=L(δδδ)} for cobalt complexes where the M–N bond length is 2.0 Å.[4–7] No information is

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