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Synthesis of Vitamin B_{12} Model Compounds

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Bis(dimethylglyoximato)cobalt(III) complexes with the general formula: $[CoX(DH)_2B_A]$ (X: CN^-, NO_2^-, $SeCN^-$, SCN^-, Br^-. D: dianion of dimethylglyoxime. B_A: such biologically interesting bases as imidazole, benzimidazole, 5,6-dimethylbenzimidazole, pyridine, γ-picoline, 4-vinylpyridine, nicotinic acid, isoquinoline, 5-amino-4-imidazolecarboxamide, and 6-aminopurine) were prepared from dimethylglyoxime, the base, and an adequate cobalt(III) salt. The treatment of $[CoCN(DH)_2Imd]$ (Imd: imidazole) with boron trifluoride etherate afforded $[Co(CNBF_3)(DBF_2)_2Imd]$ in an 86% yield. The reduction of $[CoCl(DH_2)Imd]$ with sodium borohydride gave a labile $[Co(I)H(DH)_2Imd]$, which was directly converted with phenylacetylene into a stable $[Co(III)(C_6H_5CH{=}CH)(DH_2)Imd]$ in a 60% yield and into $[Co(DH)_2Imd]\cdot H_2O$ in a 30% yield. These products were structurally elucidated on the basis of their spectral data.

It is known that bis(dimethylglyoximato)cobalt(III) complexes uniquely reproduce the fundamental reactions of cobalamins and are thus excellently suited for the study of the mechanisms of vitamin B_{12}-catalyzed biochemical processes.[1,2] Whereas simple alkylcobaloximes are found to be unusually stable, a surprising variation in the reactivity of the cobalt-carbon bond results from the introduction of the substituents into the cobalt-bound alkyl group.[3]

In this paper we wish to describe the preparation of new bis(dimethylglyoximato)cobalt(III) complexes containing such biologically interesting bases as imidazole, benzimidazole, 5,6-dimethylbenzimidazole, nicotinic acid, 5-amino-4-imidazolecarboxamide, and 6-aminopurine. The reactivities of some cobaloximes and the structures of these products are also discussed.

Results and Discussion

Preparation of Cobaloximes. $[CoCN(DH)_2B_A]$-*type Complexes.* Ablov[4] reported the preparation of $[CoCN(DH)_2Pyr]\cdot\frac{1}{2}H_2O$ (Pyr: pyridine) by a sequence of ligand substitution reactions:

$$[CoH_2O(DH)_2NCS] \rightarrow K[CoCN(DH)_2NCS] \rightarrow [CoCN(DH)_2Pyr]\cdot\tfrac{1}{2}H_2O.$$

On the other hand, our present preparative method is shown by:

$$4DH_2 + 2Co(OCOCH_3)_2 + 2KCN + 4B_A + \tfrac{1}{2}O_2 \rightarrow 2[CoCN(DH)_2B_A] + 2B_A\cdot CH_3COOH + 2CH_3COOK + H_2O.$$

A similar procedure has recently been reported by Varhelelyi[5] using several aromatic amines as the basic component. This report prompted us to publish this paper. The yields, compositions, colors, and results of analyses of the products using various bases are summarized in Table 1.

The yields of the products were generally lower than those of the $[CoCl(DH)_2B_A]$-type complexes described in the next paragraph. When 5-amino-4-imidazolecarboxamide or 6-aminopurine was used, the base did not coordinate to the cobalt atom, and the product was $H[Co(CN)_2(DH)_2]\cdot 2H_2O$, which was presumably formed by:

$$4DH_2 + 2Co(OCOCH_3)_2 + 2KCN + \tfrac{1}{2}O_2 \rightarrow 2H[Co(CN)_2(DH)_2] + 2CH_3COOK + H_2O.$$

$[CoCl(DH)_2B_A]$-*type Complexes.* It is well known that stable $[Co(III)Cl(DH)_2NH_3]$ can be prepared readily from DH_2, ammonia, and cobalt(II) chloride.[6] Similarly, several complexes with various bases were prepared by:

$$4DH_2 + 2CoCl_2\cdot 6H_2O + 4B_A + \tfrac{1}{2}O_2 \rightarrow 2[CoCl(DH)_2B_A] + 2B_A\cdot HCl + H_2O.$$

These results are summarized in Table 2.

$[CoX(DH)_2Imd]$-*type Complexes.* This type of

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[1] G. N. Schrauzer and G. Klatel, *Angew. Chem.*, **77**, 130 (1965).

[2] G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, **88**, 3738 (1966).

[3] G. N. Schrauzer and R. J. Windgassen, *bid.*, **89**, 1999 (1967), and the references cited therein.

[4] A. B. Ablov and G. K. Syrtsova, *Zhur. neorg. Khim.*, **10**, 1980 (1965).

[5] Cs. Varhelelyi and S. Kovendi, *J. prakt. Chem.*, **306**, 209, 341 (1967).

[6] L. Tschugaeff, *Ber.*, **39**, 2694 (1906); *ibid.*, **40**, 3498 (1907).

TABLE 1. PREPARATION OF $[CoCN(DH)_2B_A]$

B_A	Yield %	Composition	Found (Calcd) C%	H%	N%	Color
Imidazole	48.5	$[CoCN(DH)_2C_3H_4N_2]\cdot\frac{1}{2}H_2O$	37.43 (37.80	5.01 4.88	24.79 25.00)	orange yellow
Benzimidazole	10.1	$[CoCN(DH)_2C_7H_6N_2]\cdot H_2O$	42.57 (42.58	4.77 4.91	21.65 21.73)	yellow
5,6-Dimethyl-benzimidazole	8.5	$[CoCN(DH)_2C_9H_{10}N_2]\cdot 3/2H_2O$	44.47 (44.27	5.56 5.57	20.18 20.08)	yellow
Pyridine	25.0	$[CoCN(DH)_2C_5H_5N]\cdot\frac{1}{2}H_2O$	41.69 (41.56	5.02 5.00	20.38 20.84)	yellow
4-Vinyl pyridine	31.2	$[CoCN(DH)_2C_7H_7N]$	45.69 (45.72	5.21 5.04	19.84 19.99)	brown
Nicotinic acid	8.5	$[CoCN(DH)_2C_6H_5HNO_2]$	41.57 (41.44	4.87 4.37	16.34 15.98)	red brown
Isoquinoline	27.9	$[CoCN(DH)_2C_9H_7N]\cdot 2/3H_2O$	46.98 (47.38	4.95 4.79	19.12 18.84)	yellow
Ammonia	79.5	$[CoCN(DH)_2NH_3]\cdot 3/2H_2O$	41.57 (41.44	4.87 4.37	16.34 15.98)	orange yellow
Triphenyl-phosphine	24.5	$[CoCN(DH_2)(C_6H_5)_3P]\cdot 3/2H_2O$	54.16 (54.45	5.31 5.25	11.92 11.76)	brown
γ-Picoline	32.7	$[CoCN(DH)_2C_6H_7N]\cdot\frac{1}{2}H_2O$	43.14 (43.17	5.28 5.31	20.21 20.14)	brown yellow

TABLE 2. PREPARATION OF $[CoCl(DH)_2B_A]$

B_A	Yield %	Composition	Found (Calcd) Co%	N%	Cl%	Color
Imidazole	75.6	$[CoCl(DH)_2C_3H_4N_2]\cdot H_2O$	15.0 (14.4	20.60 20.46	8.43 8.63)	yellow brown
AICA*	46.7	$[CoCl(DH)_2C_4H_6N_4O]\cdot 3/2H_2O$	12.85 (12.43	23.30 23.45	7.42 7.43)	yellow brown
Adenine	8.5	$[ClCl(DH)_2C_5H_5N_5]\cdot 4H_2O$		23.27 (23.71	7.20 6.67)	red brown
Pyridine	60.5	$[CoCl(DH)_2C_5H_5N]$	14.48 (14.58	17.19 17.34	9.14 8.78)	brown
4-Vinyl pyridine	74.5	$[CoCl(DH)_2C_7H_7N]\cdot H_2O$	14.0 (13.2	15.91 15.64	7.91 7.92)	brown
Nicotinic acid	65.5	$[CoCl(DH)_2C_6H_5NO_2]\cdot H_2O$	12.96 (12.65	15.31 15.38	7.53 7.61)	brown
Triphenyl-phosphine	57.8	$[CoCl(DH)_2(C_6H_5)_3P]$**		9.51 (9.55)		red brown

* AICA: 5-Amino-4-imidazolecarobxamide

** Found: P, 5.30%. Calcd: 5.28%.

TABLE 3. PREPARATION OF $[CoX(DH)_2Imd]$ (Imd: Imidazole)

X	Yield %	Composition	Found (Calcd) C%	H%	N%	Color
NO_2	11.2	$[CoNO_2(DH)_2Imd]$	32.79 (32.60	4.62 4.48	23.80 24.20)	red brown
SeCN	8.5	$[CoSeCN(DH)_2Imd]\cdot\frac{1}{2}Imd$	32.94 (32.67	4.35 4.06	22.58 22.41)	brown
SCN	8.5	$[CoSCN(DH)_2Imd]\cdot\frac{1}{2}(Imd\cdot H_2O)$	35.93 (35.41	4.77 4.62	23.92 24.47)	red brown
NCO	8.5	$[CoNCO(DH)_2Imd]$	36.32 (36.10	5.08 4.54	24.92 24.56)	yellow
Br	32.6	$[CoBr(DH)_2Imd]$			19.40 (19.32)	yellow

complex was prepared by:

$$4DH_2+2Co(OCOCH_3)_2\cdot 4H_2O+2KX+4Imd+\tfrac{1}{2}O_2 \rightarrow 2[CoX(DH)_2Imd]+2Imd\cdot CH_3COOH + 2CH_3COOK + H_2O.$$

Likewise, the preparation of $[CoBr(DH)_2Imd]$ was followed by:

$$4DH_2 + 2CoBr_2 + 2Imd + \tfrac{1}{2}O_2 \rightarrow 2[CoBr(DH)_2Imd] + 2Imd\cdot HBr + H_2O.$$

The products are summarized in Table 3.

Some Reactions of Cobaloximes. The treatment of $[CoCN(DH)_2Imd].\tfrac{1}{2}H_2O$ with boron trifluoride etherate afforded $[Co(CNBF_3)(DBF_2)_2\text{-}Imd]$ in an 86% yield. Since it is known[7] that vitamin B_{12S}, a two-electron reductant of vitamin B_{12}, shows specific reactivity with electrophilic reagents, giving complexes which are sensitive to light and air, $[CoCl(DH)_2Imd]$ was treated with sodium borohydride in a methanol-water mixture to afford a brownish-green colored, two-electron reductant. This was also unstable in air, so it was confirmed by conversion with phenylacetylene into $[Co(III)(C_6H_5CH{=}CH)(DH)_2Imd]$:

$$4[Co(III)Cl(DH)_2Imd] + NaBH_4 \rightarrow 4[Co(I)H(DH)_2Imd] + NaBCl_4.$$

$$[Co(I)H(DH)_2Imd] + C_6H_5C{\equiv}CH \rightarrow [Co(III)(C_6H_5CH{=}CH)(DH)_2Imd].$$

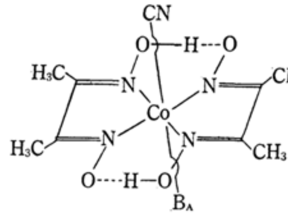
The side-formation of $[Co(II)(DH)_2Imd]$ in this reaction might be explained by:[2]

$$[Co(III)(C_6H_5CH{=}CH)(DH)_2Imd] + [CoCl(DH)_2Imd] \rightarrow [Co(II)(DH)_2Imd] + C_6H_5CH{=}CHCl.$$

$$[Co(I)H(DH)_2Imd] + [Co(III)(C_6H_5CH{=}CH)\text{-}(DH)_2Imd] \rightarrow [Co(II)(DH)_2Imd] + C_6H_5CH{=}CH_2.$$

These reactivities are similar to those of vitamin B_{12S}.

Structural Elucidation. The ultraviolet and visible spectra of $[CoCN(DH)_2B_A]$-type complexes showed similar absorption patterns regardless of the kind of base, except for triphenylphosphine; the absorption maxima ranged from 240 to 245 mμ ($\log \varepsilon = 4.4$), from 280 to 290 (shoulder, 3.7—3.8) and from 330 to 340 (shoulder, 3.1—3.4), as is shown in Figs. 1 and 2 and in Table 4; the strongest absorption due to a coordinated dimethylglyoximate ion[8] was too strong for the other two absorptions to be obvious. Considering their similarity in the spectra of $[Co(DH)_2(NH_3)_2]Cl$, $[CoCl(DH)_2NH_3]$, $H[CoCl(DH)_2]$,[9,10] and $[Co(DH)_2A_2]Cl$[11] (A: butylamine, ammonia, pyridine), we concluded that our $[CoCN(DH)_2B_A]$-type complexes have similar structures, in which two dimethylglyoximate ions are coordinated and are coplanar with the cobalt, taking a cyano group and the base in a *trans*-configuration as is illustrated in Scheme 1. When triphenylphosphine was used, the UV pattern was quite different from those of the above compounds, as is shown in Fig. 3; it manifested an absorption at 374 mμ which rather resembled that of $[Co\text{-}(DH)_2A']Cl$ (A′: aniline and its derivatives),[11] where an absorption at 340—380 mμ is interpreted as a charge-transfer spectrum from aniline to the cobalt atom. Therefore, we interpreted the absorption at 374 mμ as being due to a charge-transfer from triphenylphosphine to the cobalt atom. Furthermore, based on Nakahara's UV spectral data about other bis(dimethylglyoximato)cobalt-(III) complexes,[9] we concluded that the cobalt-



Scheme 1

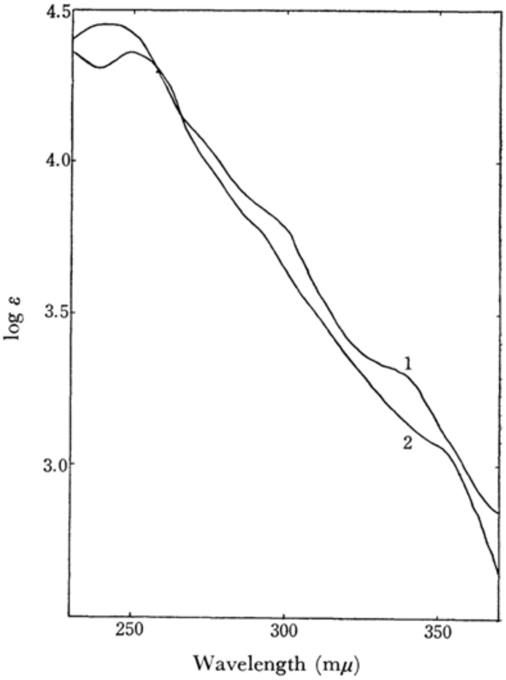


Fig. 1. UV Spectra of $[CoX(DH)_2Pyr]$ (X=CN, Cl).

Solvent: MeOH

1, $[CoCN(DH)_2Pyr]$ 2, $[CoCl(DH)_2Pyr]$

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[7] R. Bonnet, *Chem. Revs.*, **63**, 573 (1963).

[8] A. Nakahara, This Bulletin, **27**, 560 (1954).

[9] A. Nakahara, *ibid.*, **28**, 207 (1955).

[10] H. Kuroya, *J. Inst. Polytechnics, Osaka City Univ.*, **1**, No. 2, Ser. C, 11 (1950).

[11] C. Matsumoto, T. Kato and K. Shinra, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **86**, 1266 (1965).

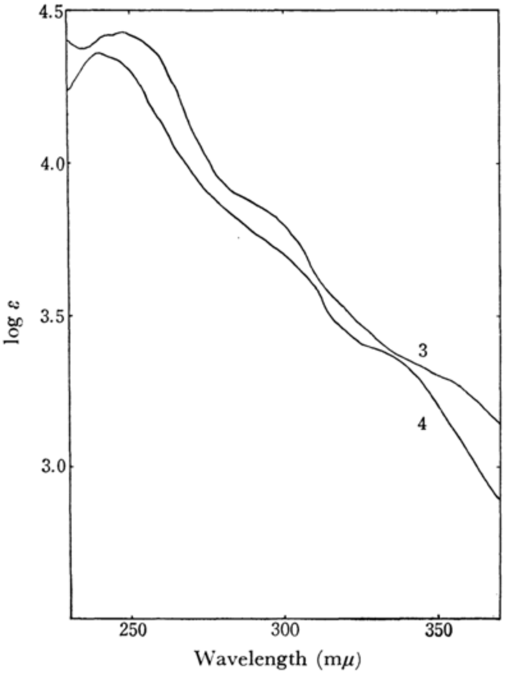

Fig. 2. UV Spectra of [CoX $(DH)_2$ Imd] (X=CN, Cl).
Solvent: MeOH
3, [CoCl$(DH)_2$Imd] 4, [CoCN$(DH)_2$Imd]

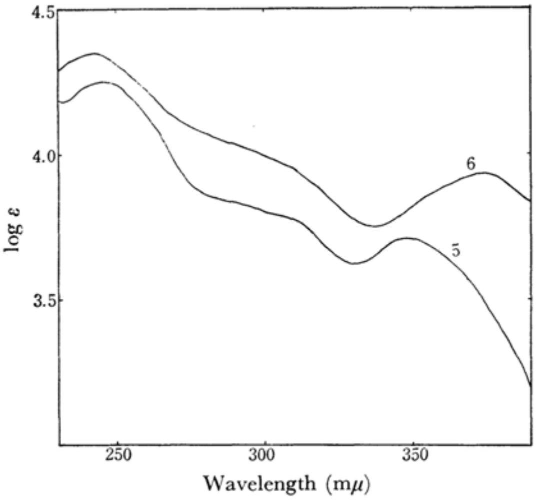

Fig. 3 UV Spectra of [CoSeCN$(DH)_2$Imd] and [CoCN$(DH)_2$P$(Ph)_3$].
Solvent: MeOH
5, [CoSeCN(DH_2)Imd] 6, [CoCN$(DH)_2$P$(Ph)_3$]

(III) formed an ionic bonding with the phosphorus atom in [CoCN$(DH)_2$P$(Ph)_3$].

Both [CoCl$(DH)_2$$B_A$]- and [CoX$(DH)_2$Imd]-type complexes showed patterns similar to [CoCN-$(DH)_2$B], as Tables 5 and 6 show. These similarities demonstrate that they have similar structures.

TABLE 4. UV ABSORPTION MAXIMA OF [CoCN$(DH)_2$$B_A$] (in MeOH)

B_A	Characteristic absorption band mμ	(log ε)	Other absorption band mμ	(log ε)
Imidazole	241	(4.46)	—	
Benzimidazole	242	(4.39)	—	
5,6-Dimethyl-benzimidazole	241	(4.40)	—	
Pyridine	241	(4.45)	—	
γ-Picoline	243	(4.42)	—	
4-Vinyl pyidine	246	(4.43)	—	
Nicotinic acid	245	(4.41)	—	
Isoquinoline	245	(4.46)	—	
Triphenyl-phosphine	241	(4.35)	374	(4.10)
Ammonia	242	(4.35)	—	
Dimethyl-glyoxime	226	(4.35)	—	

The fact that the characteristic band of a dimethylglyoximate ion in [CoCl$(DH)_2$$B_A$] showed somewhat bathochromic shifts compared with those of [CoCN-$(DH)_2$$B_A$] can be explained in terms of Tsuchida's spectrochemical series.[12] The same principle can be applied in explaining why the characteristic absorptions at around 250 mμ in [CoX$(DH)_2$Imd] were changed to some extent according to the species of the X ligand, as is shown in Table 6.

TABLE 5. UV ABSORPTION MAXIMA OF [CoCl$(DH)_2$$B_A$] (in MeOH)

B_A	Characteristic absorption band mμ	(log ε)	Other absorption band mμ	(log ε)
Imidazole	248	(4.43)	—	
AICA	258	(4.42)	—	
Adenine	264	(4.25)	—	
Pyridine	247	(4.38)	—	
4-Vinyl pyridine	248	(4.40)	—	
Nicotinic acid	250	(4.43)	—	
Triphenyl-phosphine	260	(4.45)	324	(4.17)
Ammonia	246	(4.38)	—	
Dimethyl-glyoxime	226	(4.35)	—	

TABLE 6. UV ABSORPTION MAXIMA OF [CoX$(DH)_2$Imd] (in MeOH)

X	Characteristic absorption band mμ	(log ε)	Other absorption band mμ	(log ε)
NO_2	245	(4.20)	—	
SeCN	242	(4.20)	348	(3.71)
NCO	244	(4.18)	—	
Br	250	(4.39)	—	

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[12] R. Tsuchida and M. Kobayashi, This Bulletin, **13**, 471 (1938); R. Tsuchida, *ibid.*, **13**, 388, 442 (1938).

The infrared spectra of the dimethylglyoximate moiety in [CoX(DH)$_2$B$_A$] are shown in Tables 7, 8, and 9. As may clearly seen from these tables, the weak absorption of ν_{OH} in [CoX(DH)$_2$B$_A$] at 1740—1770 cm^{-1} [13] demonstrate that these complexes take a *trans*-configuration between X and B$_A$; this further substantiates the conclusion from the UV data described above. This was also supported by the chemical behavior of these cobaloximes in readily forming an O–BF$_2$–O bonding by the interaction of two O–H–O bondings in cobaloximes with boron trifluoride etherate. The other assignments in these tables were made on the basis of Schrauzer's data.[3]

TABLE 7. IR SPECTRA OF [CoCN(DH)$_2$B$_A$] (cm^{-1})

B$_A$	$\nu_{C\equiv N}$	$\nu_{O-H\cdots O}$	$\nu_{C=N}$	ν_{NO}	δ_{NO}
Imidazole	2155	1750	1553	1240	1095
Benzimidazole	2160	1750	1569	1240	1095
5,6-Dimethylbenzimidazole	2155	1745	1565	1240	1097
Pyridine	2155	1745	1565	1243	1095
γ-Picoline	2160	1745	1560	1245	1094
4-Vinyl pyridine	2160	1750	1569	1240	1095
Nicotinic acid	2160	—	1568	1240	1098
Isoquinoline	2160	1750	1565	1242	1098
Triphenylphosphine	2155	1760	1560	1245	1090
Ammonia	2160	1760	1575	1242	1097
CN	2230	1740	1569	1248	1100

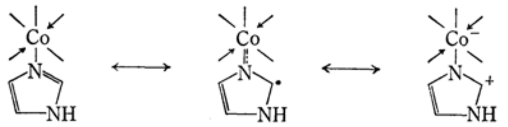
TABIE 8. IR SPECTRA OF [CoCl(DH)$_2$B$_A$] (cm^{-1})

B$_A$	$\nu_{O-H\cdots O}$	$\nu_{C=N}$	ν_{NO}	δ_{NO}
Imidazole	1740	1555	1239	1090
AICA	1760	1565	1243	1098
Adenine	1750	1570	1230	1095
Pyridine	1740	1560	1240	1090
4-Vinyl pyridine	1740	1560	1240	1090
Nicotinic acid	—	1570	1240	1098
Triphenylphsophine	1770	1560	1244	1090

TABLE 9. IR SPECTRA OF [CoX(DH$_2$)Imd]
(Imd: Imidazole) (cm^{-1})

X	$\nu_{O-H\cdots O}$	$\nu_{C=N}$	ν_{NO}	δ_{NO}
CN	1750	1533	1240	1095
NO$_2$	1755	1568	1243	1098
SeCN	1755	1565	1245	1098
SCN	1740	1567	1241	1093
NCO	1755	1565	1245	1098
Cl	1740	1555	1239	1090
Br	1750	1560	1239	1090

The multiple absorption bands due to ν_{NH} in imidazole at 2600—3110 cm^{-1} were changed into a single band at around 3150 cm^{-1} by the complex formation, as is shown in Table 10. This means that the formation of σ- or π-bonding between the nitrogen and the cobalt atom, as is shown in Scheme 2, causes any change in the electron density of an N–H bonding or the bond distance. The simplification of ν_{NH} absorption bands by the complex formation can be explained in terms of the prohibition of the tautomerism based on the prototropy of the imidazole ring proton. George[14] has pointed out that an acid dissociation constant of an imino group of a non-coordinated imidazole is less than that of a coordinated one to an iron atom, indicating the prohibition of the ionic structures by the complex formation.



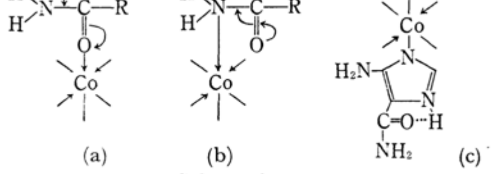
Scheme 2

TABLE 10. NH STRETCHING VIBRATION
OF IMIDAZOLE (cm^{-1})

Compound	ν_{NH}
[Imidazole]	3110—2600 (m*)
[CoCN(DH)$_2$Imd]	3150 (m)
[CoNO$_2$(DH)$_2$Imd]	3150 (m)
[CoSeCN(DH)$_2$Imd]	3150 (s*)
[CoSCN(DH)$_2$Imd]	3140 (s)
[CoCl(DH)$_2$Imd]	3150 (m)
[CoNCO(DH)$_2$Imd]	3150 (m)
[CoBr(DH)$_2$Imd]	3150 (m)

* Strength. m: medium and s: strong.

As for 5-amino-4-imidazolecarboxamide, a question arises regarding to which position the cobalt atom is bound. The infrared spectrum of [CoCl(DH)$_2$AICA] (AICA: 5-amino-4-imidazolecarboxamide) gives some information on this point; it is expected[15] that if the amidocarbonyl were coordinated to a cobalt atom, as is shown in (a) of Scheme 3, the ν_{NH} absorption of the amidocarbonyl



Seheme 3

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[13] A. Nakahara, This Bulletin, **29**, 296 (1956). He concluded that an absorption band at 1725 cm^{-1} of hydrogen dichloro-bis(dimethylglyoximato)cobalt(III) was attributable to an OH stretching frequency when intramolecular O–H···O hydrogen bonds were formed.

[14] P. George, I. H. Hanania and D. H. Irvine, *J. Chem. Soc.*, **1964**, 5689.

[15] N. Gerrad, *ibid.*, **1960**, 2144.

group would shift to a lower wave number. If it were coordinated to the nitrogen atom of the amide group (b), the ν_{NH} absorption would shift to a lower, but the ν_{CO} absorption of the amide would shift to a higher wave number. Table 11 indicates that the ν_{NH} absorption shifted up by about 10 cm^{-1} and that the ν_{CO} absorption shifted down by about 17 cm^{-1}, indicating that [CoCl(DH)$_2$AICA] has no such linkages as shown in (a) and (b). The slight shift of the ν_{CONH_2} absorption to a lower wave number can be explained in terms of the prohibition of the prototropy of an imidazole-ring proton by the complex formation, resulting in the easier formation of hydrogen bond than free AICA. This suggests that the cobalt atom is coordinated to the nitrogen atom of the imidazole ring, as is shown in (c) of Scheme 3.

TABLE 11. CHARACTERISTIC IR ABSORPTION BANDS OF AICA (cm^{-1})

Compound	ν_{CONH_2}	ν_{as-NH_2}	ν_{s-NH_2}	ν_{CONH_2}	δ_{NH_2}
AICA	3430	3300	3220	1680	1624
[CoCl(DH)$_2$-AICA]	3440	3300	3230	1663	1621

The same problem is encountered in 6-aminopurine. The basicity of adenine is not strong enough for the basic center to be the same as the coordination center; therefore, the basic center is not very important in this case. If the cobalt atom were coordinated to an amino group of adenine, the ν_{NH} absorption should shift to a wave number lower by 100—150 cm^{-1}, while the δ_{NH} absorption should not change at all or shift to a slightly higher wave number.[16] The fact that both the γ_{NH} and δ_{NH} absorptions shifted to lower wave numbers, as is shown in Table 12, indicates the absence of any coordination of the amino group to the cobalt atom. The 12 cm^{-1} shift of the $\nu_{C=C,C=N}$ of the purine ring to a higher wave number upon the complex formation may be explained in terms of the lowering of the resonance contribution of the purine ring. Considering that pseudo B_{12}, which is different from B_{12} in containing adenine instead of 5,6-dimethylbenzimidazole, has a coordinate bond between the nitrogen atom of the imidazole ring and the cobalt atom,[17] [CoCl(DH)$_2$Adenine] may be supposed to have the same type of coordinate bond.

TABLE 12. CHARACTERISTIC IR ABSORPTION BANDS OF ADENINE (cm^{-1})

	ν_{as-NH_2}	ν_{s-NH_2}	δ_{NH}	$\nu_{C=C,C=N}$
Adenine	3290	3110	1668	1605
[CoCl(DH)$_2$-$C_5H_5N_5$]	3310	3190	1655	1617

Table 13 shows the characteristic infrared absorption bands of the chelates involving benzimidazole ($C_7H_6N_2$) and 5,6-dimethylbenzimidazole ($C_9H_{10}N_2$). All had a common strong band at 3120 cm^{-1} upon the complex formation; this band perhaps originated from the prohibition of the tautomerism based on the prototropy of a benzimidazole-ring proton. The fact that the absorptions due to both the ν_{NH} of the imidazole ring and the $\nu_{C=C}$ of the phenyl part did shift to higher wave numbers may be caused by the decrease in the conjugation of the benzimidazole ring, as is shown in (c) of Scheme 3.

TABLE 13. CHARACTERISTIC IR ABSORPTION BANDS OF CHELATES INVOLVING BENZIMIDAZOLE AND 5,6-DIMETHYLBENZIMIDAZOLE (cm^{-1})

Compound	ν_{NH}	$\nu_{C=N}$	$\nu_{C=C}$
Benzimidazole	3120—2450	1621	1590
[CoCN(DH)$_2$C$_7$H$_6$N$_2$]	3130	1625	1598
[CoCN(DH)$_2$C$_9$H$_{10}$N$_2$]	3130	1630	1952

Table 14 shows the characteristic infrared absorption bands of the chelates involving pyridine derivatives in comparison with those of pyridine derivatives. If a nitrogen-cobalt linkage were formed of σ- and π-bonding, a decrease in the conjugation of the pyridine ring would be expected; such a decrease is, in fact, shown in this table by the 10—30 cm^{-1} shift to a higher wave number of the absorption due to the $\nu_{C=C}$ of the pyridine ring.

TABLE 14. CHARACTERISTIC IR ABSORPTION BANDS OF PYRIDINE DERIVATIVES (cm^{-1})

Compound	$\nu_{C=C}$, ν_{CO}	$\nu_{C=C,C=N}$	$\Delta\nu_{C=C,C=N}$
4-Vinyl pyridine	1631	1598	—
[CoCl(DH)$_2$C$_7$H$_7$N]	—	1617*	$-\Delta 19$
[CoCN(DH)$_2$C$_7$H$_7$N]	—	1622*	$-\Delta 24$
Pyridine	—	1580	—
[CoCl(DH)$_2$C$_5$H$_5$N]	—	1609	$-\Delta 29$
[CoCN(DH)$_2$C$_5$H$_5$N]	—	1609	$-\Delta 29$
Nicotinic acid	1710	1600	—
[CoCl(DH)$_2$C$_6$H$_5$NO$_2$]	1720	1610	$-\Delta 10$
[CoCN(DH)$_2$C$_6$H$_5$NO$_2$]	1723	1607	$-\Delta\ 7$
γ-Picoline	—	1609	—
[CoCN(DH)$_2$C$_6$H$_7$N]	—	1622	$-\Delta 13$
Isoquinoline		1630	—
[CoCN(DH)$_2$C$_9$H$_7$N]		1638	$-\Delta\ 8$

Table 15 shows the characteristic infrared absorption bands of X in [CoX(DH)$_2$Imd] (X: NO$_2$, NCO). As for [CoNO$_2$(DH)$_2$Imd], there are possible two structures; it can be assigned either to a nitro or to a nitrito complex. Nakamoto[18] has

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16) J. Chatt, L. A. Duncanson and L. M. Venanzi, *ibid.*, **1955**, 4461.

17) E. A. Kaczka, D. E. Wolf, F. A. Kuehl and K. Folkers, *J. Am. Chem. Soc.*, **73**, 3569 (1951).

18) K. Nakamoto, J. Fujita and H. Haruta, *ibid.*, **80**, 4517 (1958).

provided a method of discrimination by means of infrared spectral comparison. As is shown in Table 14, the infrared spectrum of $[CoNO_2(DH)_2Imd]$ was compared with those of known nitro and nitrito complexes. From its similarity to the former, we concluded that $[CoNO_2(DH)_2Imd]$ was a nitro complex. Likewise, our $[CoNCO(DH)_2Imd]$ was concluded to be an isocyanato complex with a cobalt-nitrogen bonding.[19)]

TABLE 15. CHARACTERISTIC IR ABSORPTION BANDS OF $[CoX(DH)_2Imd]$ (cm^{-1})

X: NO_2

Compound	ν_{as-NO_2}	ν_{s-NO_2}	δ_{NO_2}
$[Co(NH_3)_5NO_2]Cl_2$	1428	1310	824
$[Co(NH_3)_5ONO]Cl_2$	1468	1065	825
$[CoNO_2(DH)_2Imd]$	1425	1323	822

X: NCO

Compound	$\nu_{N=C=O}$
$Et_4N[Co(NCO)_4]$	2217(shoulder), 2179(very strong)
$[CoNCO(DH)_2Imd]$	2200 (very strong)

As for thiocyanato- and selenocyanatocobaloxime, these complexes are shown by their microanalyses (Table 3) to consist of 1 mol of $[CoSCN(DH)_2Imd]$ or $[CoSeCN(DH)_2Imd]$ and ½mol of $Imd \cdot H_2O$. This means that the thiocyanate- and selenocyanate ions and imidazole have some specific characteristics as ligands in these complexes; concerning this subject many papers have been published.[20)] As is shown in Table 16, absorptions due to $\nu_{C=N}$ shifted to higher wave numbers in the following sequence:

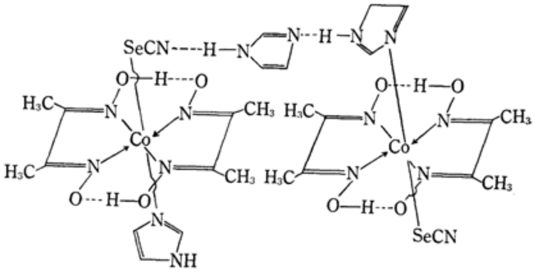
$$\text{M-CS(Se)} < \text{M-S(Se)CN} < \text{M-NCS(Se)-M,M-NCS(Se)-B}$$

where M is the metal and where B is a base such as $PyrH^-$, NH_4^-, or Et_4N^-.

From Table 16, it can be said that:

$$\text{M-NCS(Se)} < 2080\ cm^{-1} \text{ and M-S(Se)CN} > 2080\ cm^{-1}$$

It is generally believed that Co(III) forms a Co–S(Se) bonding in the thiocyanatocomplexes of B_{12}[21)] and in $(NH_4)[Co(SeCN)_2(DH)_2] \cdot 3H_2O$.[22)] The presence of an absorption due to ν_{CN} at 2135 cm^{-1} in $[CoSCN(DH)_2Imd]$. ½ $Imd \cdot H_2O$ and at 2120 cm^{-1} in $[CoSeCN(DH)_2Imd]$. ½Imd, both located in the >2080 cm^{-1} region, demonstrates that these two complexes have a bridged structure with a



Scheme 4

TABLE 16. $\nu_{C\equiv N}$ OF THIOCYANATO- AND SELENOCYANATOCOMPLEXES (cm^{-1})

Compound	Frequency (cm^{-1})	Structure	Ref.**
KSCN	2053 s*		a
KSeCN	2070 s*		b
$K_2[Pt(SCN)_6]$	2125 s*	Pt–SCN	c
$K_2[Pt(SeCN)_6]$	2124 s*	Pt–SeCN	i
$((CH_3)_4N)_2[Co(NCS)_4]$	2075 s*		d
$((CH_3)_4N)_2[Co(NCSe)_4]$	2075 s*		d
$((C_2H_5)_4N)_2[Co(NCS)_4]$	2053 s*		i
$((C_2H_5)_4N)_2$-$[Co(NCSe)_4]$	2053 s*		i
$(NH_4)[Cr(NCS)_4$-$(NH_3)_2]$	2110	Cr–NCS	26
$[Co(Pyr)_2(NCS)_2]$	2088	Co–NCS–Co	e
$K_2[Co(NCS)_4]$	2058—2079	Co–NCS	f
$[(PyrH)_3Mo(NCS)_6]$	2037—2049		25
$[(PyrH)_4Mo_2O_3(NCS)_6]$	2066	Bridge suggested	25
$[Co(NH_3)_5(NCS)$-$(NO_3)_2]$	2114		g
$[Co(en)_2(NCS)_2]Cl \cdot H_2O$	2122		g
$[HgCo(NCS)_4]$	2137	Hg–SCN–Co	h
$[(CH_3)_4N]_3$-$[Cr(NCSe)_6]$	2067 s* 2041 sh*		26
$[Co(SCN(DH)_2Imd] \cdot$ ½$(Imd.H_2O)$	2135	Bridge suggested	
$[CoSeCN(DH)_2Imd] \cdot$ ½Imd	2120	Bridge suggested	

s*: strong. sh*: shoulder. **a) P. O. Kinell and B. Strandberg, *Acta Chem. Scand.*, **13**, 1067 (1959). b) H. W. Morgan, *J. Inorg. Nucl. Chem.*, **16**, 368 (1960). c) M. M. Chanberlain and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 6412 (1959). d) F.A. Cotton, D. M. L. Goodgame and T. E. Hass, *J. Inorg. Chem.*, **1**, 565(1962). e) P. Koshito, *Krystallografiya*, **4**, 239 (1959). f) Zhdanov, Tishchenko, and Zvanhova, *Zhur. Fis. Khim.*, **24**, (1950). g) J. Fujita, K. Nakamoto and M. Kobayashi, *J. Am. Chem. Soc.*, **78**, 3295 (1956). h) Tefferu, *Nature*, **159**, 610 (1947). i) A. Turco, C. Pecile and M. Nicolini, *J. Chem. Soc.*, **1962**, 3008.

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19) The complexes thus far reported in this field all have metal-nitrogen bonding. $K_2[Co(NCO)_4]$: C. M. Blomstrand, *J. prakt. Chem.*, **3**, (2), 221 (1871); $K[M(NCO)_3]$ (M: Cu, Cd), $M[(CH_2)_6N_4]_2[(H_2O)_4M(NCO)_4]$ (M: Co, Ni, Cu): R. Ripan, *Chem. Zentr.*, **12**, (i), 967 (1930). $(NEt_4)_2[M(NCO)_4]$ (M: Mn, Fe, Co, Ni, Cu, Zn, Cd) and $(NEt_4)_2[Fe(III)(NCO_4)]$: D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, **1964**, 2790; *ibid.*, **1965**, 266.

20) S. E. Livingstone, *Quart. Revs.*, **19**, 386 (1965) and the references cited therein.

21) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, **1960**, 1912.

22) A. V. Ablov and V. N. Safranski, *Zhur. neorg. Khim.*, **9**, 585 (1964).

Co–S(Se) bonding, while the imidazole intervenes, as is shown in Scheme 4. This is supported by the presence of a strong absorption due to the ν_{NH} of the imidazole ring; this absorption is clearly different from those of the other cobaloximes described above.

TABLE 17. IR ABSORPTION BANDS (cm^{-1})

Compound	$\nu_{C=N}$	ν_{B-O}	ν_{B-F}	δ_{B-O}
$[Ni(DBF_2)_2]$	1648	1193	1026	826
$[Co(CNBF_3)(DBF_2)_2Imd]$	1620	1203	1025	818

In Table 17 the infrared spectrum of $[Co(CNBF_3)(DBF_2)_2Imd]$ is compared with that of known $[Ni(DBF_2)_2]$, which possesses a bridged N–CN–BF_2 structure.[23] Their similar absorption patterns suggest that a bridged Co–CN–BF_2 bonding might also be involved in $[Co(CNBF_3)(DBF_2)_2Imd]$; this is further supported by the presence of an absorption due to ν_{CN} at 2240 cm^{-1}, located at a higher wave number than those of the general cobaloximes at 2155—2160 cm^{-1} described above.

TABLE 18. FAR-INFRARED SPECTRA OF $[CoX(DH)_2B]$-TYPE COMPLEXES (cm^{-1})

Compound	ν_{Co-N}
$[CoNO_2(DH)_2Imd]$	516
$[CoCN(DH)_2Imd]$	518, 519 sh*
$[CoCl(DH)_2Imd]$	518
$[CoCN(DH)_2Pyr]$	518, 529 sh*
$[CoCl(DH)_2Pyr]$	518

sh*: shoulder

Table 18 shows the far-infrared spectra due to ν_{Co-N} in $[CoX(DH)_2B_A]$-type complexes; the data are in good accordance with Schrauzer's data,[2] indicating no remarkable change upon a variation in the bases.

Experimental

Materials. Benzimidazole was prepared by the known method.[24] 5,6-Dimethylbenzimidazole was prepared from 4,5-diamino-1,2-dimethylbenzene[25] by the method of Takatori *et al.*[26] Potassium cyanate[27] and selenocyanate[28] were prepared by the usual methods. All the other reagents were commercially available and were used after purification if neccessary.

Preparation of Complexes. $[CoCN(DH)_2B_A]$, B_A: Imd. Into filtered solution[*1] of 2.8 g (0.024 mol) of DH_2 and 2.6 g (0.011 mol) of $Co(OCOCH_3)_2 \cdot 4H_2O$ in 100 m*l* of hot 80% ethanol, there was stirred 0.7 g (0.01 mol) of KCN[*2] at room temperature. To this stirred solution there was then added 1 g (0.015 mol) of imidazole, after which the reaction mixture was aerated for 1 hr. The precipitated yellow-purple powders were collected, washed thoroughly with water, ethanol, and finally with ether, and dried in air. The yield and the results of analysis are given in Table 1.

$H[Co(CN)_2(DH)_2]$: When 5-amino-4-imidazolecarboxamide or 6-aminopurine was used as the base in the above experiments, fine, thin, yellow crystals (mp >300°C) were obtained in a yield of 31 or 43% respectively. They are quite soluble in ethanol.

Found: C, 31.38; H, 4.75; N, 22.23%. Calcd for $H[Co(CN)_2(DH)_2] \cdot 2H_2O$: C, 31.78; H, 5.07; N, 22.22%.

$[CoCl(DH)_2B_A]$: B_A: Imd. To a ho , filtered solution of 2.8 g (0.024 mol) of DH_2 and 2.5 g (0.011 mol) of $CoCl_2 \cdot 6H_2O$ in 100 m*l* of 95% ethanol,[*3] 1 g (0.015 mol) of imidazole was added; the reaction mixture was then kept standing overnight at room temperature. The resulting brown-yellow powder was filtered and worked up as above. The results are summarized in Table 2, together with those obtained using several other bases.[*4]

$[CoSeCN(DH)_2Imd] \cdot \frac{1}{2}Imd$: To a hot, filtered solution of 1.4 g (0.012 mol) of DH_2 and 1.3 g (0.006 mol) of $Co(OCOCH_3)_2 \cdot 4H_2O$ in 50 m*l* of hot ethanol, there was added 0.75 g (0.050 mol) of potassium selenocyanate. After it had been completely dissolved in the reaction mixture, 0.5 g (0.0075 mol) of imidazole was added. The resultant clear solution was aerated for 1 hr, after which the reaction mixture was kept standing overnight at room temperature. The crystalline precipitates were collected and worked up as above to afford a selenocyanatocomplex. Similarly, the corresponding isocyanato- and thiocyanatocomplex were prepared. These results are summarized in Table 3.

$[CoNO_2(DH)_2Imd]$: This was prepared similarly from 2.8 g (0.024 mol) of DH_2, 2.6 g (0.011 mol) of $Co(OCOCH_3)_2 \cdot 4H_2O$, 1 g (0.015 mol) of potassium nitrite, and 100 m*l* of hot 80% ethanol. The results are given in Table 3.

$[CoBr(DH)_2Imd]$: To a hot, filtered solution of 1.4 g (0.012 mol) of DH_2 and 1.7 g (0.006 mol) of $CoBr_2 \cdot 6H_2O$ in 50 m*l* of 95% ethanol, there was added 0.5 g (0.0075 mol) of imidazole; the reaction mixture was then kept standing overnight at room temperature, after which the precipitates were worked up as above. The results are given in Table 3.

$[Co(CNBF_2)(DBF_2)_2Imd]$: To 15 m*l* of boron trifluoride etherate there was added 0.5 g of $[CoCN(DH)_2Imd] \cdot \frac{1}{2}H_2O$, and the resulting red solution was kept standing overnight at room temperature. The precipitates were collected and worked up as above to give 0.8 g (86%) of fine, thin, yellow crystals, mp >300°C.

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23) G. N. Schrauzer, *Chem. Ber.*, **95**, 1438 (1962).

24) "Organic Syntheses," Coll. Vol. II, p. 65 (1943).

25) Noelting, Braun and Thesmar, *Ber.*, **34**, 2252 (1901).

26) K. Takatori, Y. Yamada and O. Kawasima, *J. Pharm. Soc. Japan*, **75**, 881 (1955).

27) "Inorganic Syntheses," **2**, 87 (1946).

28) "Inorganic Syntheses," **2**, 186, 188 (1946).

[*1] Without the filtering of the unidentified by-product, the crystallization of the produced complexes did not proceed smoothly.

[*2] A desired complex could not be isolated when the base was added to the reaction mixture before potassium cyanide was added.

[*3] When nicotinic acid, 5-amino-4-imidazolecarboxamide, or 6-aminopurine was used, a large amount of ethanol should be used for obtaining a clear solution because of the low solubility of these bases in ethanol.

[*4] The similar treatment of 2-vinylpyridine did not afford any complex.

Found: N, 17.90%. Calcd for $[Co(CNBF_3)(DBF_2)_2Imd]$: N, 17.93%.

$[Co(C_6H_5CH{=}CH)(DH)_2Imd]$ and $[Co(DH)_2Imd]\cdot H_2O$: Air in a suspension of 1.5 g (0.0037 mol) of $[CoCl(DH)_2Imd]$ in 10 m*l* of 80% methanol was completely removed at −70°C under a high vacuum. With strictly excluded air, a solution of 0.15 g (0.004 mol) of sodium tetrahydridoborate in a small amount of water was added to the reaction mixture. The mixture turned greenish-brown. Again, in the absence of air, 0.6 m*l* (0.0049 mol) of phenylacetylene was added to the reaction mixture and the mixture was kept standing overnight at room temperature. The resulting yellow crystals were collected and worked up as above to give 0.4 g (30%) of $[Co(DH)_2Imd]\cdot H_2O$, mp >300°C.

Found: C, 36.07; H, 5.23; N, 22.93%. Calcd for $[Co(DH)_2Imd]\cdot H_2O$: C, 35.93; H, 5.93; N, 22.53%.

The red filtrate was condensed to 30 m*l*, and the resulting orange needles were collected and recrystallized from chloroform to afford 1 g (60%) of $[Co(C_6H_5CH{=}CH)(DH)_2Imd]$, mp 232—233°C.

Found: C, 49.46; H, 5.68; N, 18.22%. Calcd for $[Co(C_6H_5CH{=}CH)(DH)_2Imd]$: C, 49.11; H, 5.52; N, 18.24%.

Measurements. The melting points were determined by a Yanagimoto micromelting-point apparatus and are uncorrected. The infrared spectra were measured in KBr pellets with a JASCO, Model IR-S infrared spectrometer, while the far-infrared were measured with a Perkin-Elmer grating infrared spectrometer, Model 337. All the ultraviolet and visible spectra were taken in methanol with a JASCO recording spectrometer, Model ORD/UV-5.

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