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Studies on Cobaloxime Compounds. I. Synthesis of Various Cobaloximes and Investigation on Their Infrared and Far-Infrared Spectra

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Cobaloximes with the general formula: $[CoX(DH)_2B]$ or $[RCo(DH)_2B]$ (X: Cl, CN. R: Alkyl groups such as methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, benzyl, or hydroxypropyl. DH: Dimethylglyoximato monoanion. B: Bases such as water, nicotinamide, *p*-toluidine, pyridine, γ-picoline, imidazole, or 4-vinylpyridine), and polymeric cobaloximes with the general formula: $[Co(OH)(DH)_2$(Copoly–AM-VPy)] (Copoly–AM-VPy: a low molecular weight copolymer of acrylamide and 4-vinylpyridine), were synthesized and their infrared and far-infrared spectra were examined. The frequency shifts by changing the axial ligands were discussed.

The resemblance of cobaloxime compounds, including alkylcobaloximes, to cobalamin compounds in their chemical behavior has been clarified to a great extent by Schrauzer and Kohnle.[1,2] Compounds other than alkylcobaloximes, *e. g.*, the reduced states of cobaloximes, have been reported to serve as catalysts in some reduction reactions.[3,4]

In this paper we wish to report the synthesis of various cobaloximes including polymeric cobaloximes by improved methods and an investigation on their infrared spectra.

Results and Discussion

Synthesis of Cobaloximes. Some chlorocobaloximes were prepared by the general method similar to Tschugaeff's synthesis of $CoX(DH)_2B$:[5]

$$CoCl_2\cdot(6H_2O) + 2DH_2 + 2B + 1/4\,O_2 \rightarrow CoCl(DH)_2B + B\cdot HCl + 1/2\,H_2O\ (+6H_2O).$$

In these reactions, one equivalent amount of base is consumed to neutralize HCl produced in the reactions. Thus, instead of such organic bases, we could employ one equivalent of NaOH as follows:

$$CoCl_2\cdot(6H_2O) + 2DH_2 + B + NaOH + 1/4\,O_2 \rightarrow CoCl(DH)_2B + NaCl + 3/2\,H_2O\ (+6H_2O).$$

The results are summarized in Table 1. The product is essentially the same as those obtained by the former method. The latter method is preferable when the organic base is too invaluable to be used in such a side reaction, or when it is desirable for all basic residues such as polymeric ligands to form cobaloximes:

$$n\mathrm{CoCl_2}\cdot(6\mathrm{H_2O}) + 2n\mathrm{DH_2} + \text{(B)}_n + n\mathrm{NaOH} + n/4\cdot\mathrm{O_2} \longrightarrow \mathrm{CoCl(DH)_2}\text{(B)}_n + n\mathrm{NaCl} + 3n/2\cdot\mathrm{H_2O}\ (+6\mathrm{H_2O}).$$

When two equivalent NaOH are used in the reaction in the absence of the organic base, hydroxoaquocobaloxime is produced:

$$CoCl_2\cdot(6H_2O) + 2DH_2 + 2NaOH + 1/4\,O_2 \rightarrow Co(OH)(DH)_2(H_2O) + 2NaCl + 1/2\,H_2O\ (+6H_2O).$$

As an extension of this idea, all pyridine residues in a low molecular weight copolymer of acrylamide-(AM) and 4-vinylpyridine(VPy) were completely complexed with cobaloxime, which was confirmed by Co analysis. The molecular weights and AM/VPy molar ratios of polymeric ligands are shown in Table 2.

Cyanocobaloximes were prepared by the general method:

$$Co(CH_3COO)_2\cdot(4H_2O) + 2DH_2 + NaCN + 2B + 1/4O_2 \rightarrow Co(CN)(DH)_2B + B\cdot HOOCCH_3 + CH_3COONa + 1/2H_2O\ (+4H_2O).$$

1) G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, **97**, 3056 (1964).
2) G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968); and the references cited therein.
3) T. Mizuta and T. Kwan, *Nippon Kagaku Zasshi*, **88**, 471 (1967).
4) E. N. Sal'nikova and M. L. Khidekel, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 223 (1967); *Chem. Abstr.*, **66**, 104996*h* (1967).
5) L. Tschugaeff, *Ber*, **39**, 2694 (1906); *ibid.*, **40**, 3498 (1907).

TABLE 1. SYNTHESIS OF CHLOROCOBALOXIMES

Composition	Yield (%)	Formula (M. W.)	Found (Calcd) (%) C	H	N	Cl	Color
$CoCl(DH)_2(H_2O)$	34	$C_8H_{16}N_4O_5CoCl$ (342.63)	28.00 (28.04)	4.65 (4.71)	16.25 (16.35)	11.56 (10.35)	pale brown
$CoCl(DH)_2$(nico)[a]	58	$C_{14}H_{20}N_6O_5CoCl$ (446.74)	38.00 (37.64)	4.91 (4.51)	17.82 (18.81)	8.99 (7.94)	ocher
$CoCl(DH)_2$(tolu)[a]	95	$C_{15}H_{23}N_5O_4CoCl$ (431.77)	41.80 (41.73)	5.43 (5.37)	16.01 (16.22)	7.67 (8.21)	light brown
$CoCl(DH)_2$(py)[a]	63	$C_{13}H_{19}N_5O_4CoCl$ (403.71)	38.22 (38.68)	4.57 (4.74)	16.93 (17.35)	8.86 (8.78)	ocher
$CoCl(DH)_2$(pico)[a]	86	$C_{14}H_{21}N_5O_4CoCl$ (417.74)	40.20 (40.25)	5.28 (5.07)	16.56 (16.77)	8.21 (8.50)	light brown
$[CoCl(DH)_2(VPy)]\cdot H_2O$[a]	87	$C_{15}H_{23}N_5O_5CoCl$ (447.75)	40.60 (40.23)	5.16 (5.18)	15.86 (15.65)	8.18 (7.92)	ocher
$CoCl(DH)_2$(imd)[a]	68	$C_{11}H_{18}N_6O_4CoCl$ (392.69)	33.16 (33.65)	4.67 (4.62)	21.52 (21.40)	10.89 (9.03)	ocher

a) nico: nicotinamide, tolu: *p*-toluidine, py: pyridine, pico: *γ*-picoline, VPy: 4-vinylpyridine, imd: imidazole

TABLE 2. POLYMERIC COBALOXIMES [Co(OH)-(DH)$_2$(Copoly-AM-VPy)]

No.	Copoly-AM-VPy (Ligand) $\bar{M}_n \times 10^{-2}$ [a]	AM/VPy ratio[b]	Co(OH)(DH)$_2$ (Copoly-AM-VPy) $\bar{M}_n \times 10^{-2}$ [c]	Numbers of cobaloxime-unit/a polymer chain[d]
HC025	30	11.9	40	3.2
HC029	24	12.8	31	2.4
HC027	14	13.7	18	1.3
HC030	8.3	17.5	10	0.62

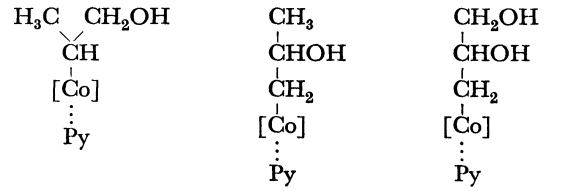
a) Determined by cryoscopic method.
b) Calculated by using the absorbance at 257 mμ due to the pyridine residue.
c), d) Estimated by using $\bar{M}_n$ and AM/VPy ratio of polymeric ligand.

In these reactions, one equivalent base is again consumed to neutralize acetic acid formed in the reaction. We found that without neutralizing acetic acid the cobaloximes are formed with one equivalent base to Co-$(CH_3COO)_2$:

$$Co(CH_3COO)_2\cdot(4H_2O) + 2DH_2 + NaCN + B + 1/4O_2 \rightarrow Co(CN)(DH)_2B + CH_3COOH + CH_3COONa + 1/2H_2O\ (+\ 4H_2O).$$

The results of syntheses obtained by one of the two procedures are summarized in Table 3.

Various alkylcobaloximes were synthesized by the general methods according to Schrauzer and Windgassen,[6] from $CoCl_2\cdot 6H_2O$, DH_2, NaOH, and alkyl halide with or without $NaBH_4$ in an anaerobic condition. Some hydroxypropylcobaloximes, *i. e.*, *β*-hydroxy-isopropyl-, *β*-hydroxy-*n*-propyl-, and *β*,*γ*-dihydroxy-*n*-propyl-(pyridine)cobaloximes, were also synthesized with 2-bromo-1-propanol, 1-bromo-2-propanol, or glycerol *α*-monochlorohydrin, respectively, as the alkylating agents which are schematically described as:



These cobaloximes might be considered as model compounds for possible intermediates in an enzymatic reaction, *i. e.*, in propanediol dehydratase system.

Base Substitution Reaction of Alkylaquocobaloximes. The water molecule coordinating to Co atom in alkylaquocobaloximes is readily displaced by another organic base:

TABLE 3. SYNTHESIS OF CYANOCOBALOXIMES

Composition	Yield (%)	Formula (M. W.)	Found (Calcd) (%) C	H	N	Color
$Co(CN)(DH)_2(H_2O)$	70	$C_9H_{16}N_5O_5Co$ (333.20)	31.39 (32.44)	4.23 (4.84)	20.48 (21.02)	brown
$Co(CN)(DH)_2$(py)[a]	26	$C_{14}H_{19}N_6O_4Co$ (394.28)	42.74 (42.65)	4.77 (4.86)	21.29 (21.32)	ocher
$Co(CN)(DH)_2$(tolu)[a]	94	$C_{16}H_{23}N_6O_4Co$ (422.33)	45.31 (45.50)	5.60 (5.49)	20.17 (19.90)	ocher
$Co(CN)(DH)_2$(pico)[a]	56	$C_{15}H_{21}N_6O_4Co$ (408.30)	42.91 (44.13)	5.15 (5.18)	20.48 (20.58)	yellow

a) py: pyridine, tolu: *p*-toluidine, pico: *γ*-picoline

6) G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, **88**, 3738 (1966).

Table 4. Synthesis of alkylcobaloximes

$RCo(DH)_2B$ R	B[a]	Formula (M. W.)	Found (Calcd) (%) C	H	N	Color
CH_3	H_2O	$C_9H_{19}N_4O_5Co$ (322.21)	33.89 (33.55)	5.87 (5.94)	17.43 (17.39)	reddish orange
CH_3	nico	$C_{15}H_{23}N_6O_5Co$ (426.32)	42.01 (42.26)	5.46 (5.44)	19.73 (19.71)	orange
CH_3	tolu[b]	$C_{16}H_{28}N_5O_5Co$ (429.37)	44.73 (44.76)	6.52 (6.57)	16.34 (16.31)	orange
CH_3	py	$C_{14}H_{22}N_5O_4Co$ (383.30)	43.63 (43.87)	5.74 (5.79)	18.51 (18.27)	orange
CH_3	pico	$C_{15}H_{24}N_5O_4Co$ (397.32)	45.52 (45.35)	6.11 (6.09)	17.52 (17.63)	yellow
CH_3	imd	$C_{12}H_{21}N_6O_4Co$ (372.27)	38.70 (38.72)	5.67 (5.69)	22.72 (22.57)	yellow
CH_3CH_2	H_2O	$C_{10}H_{21}N_4O_5Co$ (336.24)	35.82 (35.72)	6.28 (6.30)	16.29 (16.66)	orange
CH_3CH_2	py	$C_{15}H_{24}N_5O_4Co$ (397.32)	44.95 (45.35)	6.17 (6.09)	17.50 (17.63)	orange
$CH_3CH_2CH_2$	H_2O	$C_{11}H_{23}N_4O_5Co$ (350.26)	37.19 (37.72)	6.48 (6.62)	16.26 (16.00)	reddish orange
$CH_3CH_2CH_2$	py	$C_{16}H_{26}N_5O_4Co$ (411.35)	47.06 (46.72)	6.42 (6.37)	17.06 (17.03)	orange yelllow
$CH_3CH_2CH_2$	pico	$C_{17}H_{28}N_5O_4Co$ (425.38)	48.21 (48.00)	6.37 (6.64)	16.56 (16.46)	yellow
$CH_3CH_2CH_2$	imd	$C_{14}H_{25}N_6O_4Co$ (400.33)	42.65 (42.00)	6.68 (6.29)	20.52 (20.99)	yellow
$CH_3CH_2CH_2CH_2$	H_2O	$C_{12}H_{25}N_4O_5Co$ (364.29)	39.58 (39.57)	7.08 (6.92)	15.61 (15.38)	reddish orange
$CH_3CH_2CH_2CH_2$	py	$C_{17}H_{28}N_5O_4Co$ (425.38)	48.53 (48.00)	6.61 (6.64)	15.99 (16.46)	orange yellow
$CH_3CH_2CH_2CH_2$	pico	$C_{18}H_{30}N_5O_4Co$ (439.40)	48.83 (49.20)	6.98 (6.88)	16.03 (15.94)	yellow
$CH_3CH(CH_3)$	H_2O	$C_{11}H_{23}N_4O_5Co$ (350.26)	37.43 (37.72)	6.66 (6.62)	16.37 (16.00)	reddish brown
$CH_3CH(CH_3)$	py	$C_{16}H_{26}N_5O_4Co$ (411.35)	46.82 (46.72)	6.50 (6.37)	17.24 (17.03)	orange
$C_6H_5CH_2$	py	$C_{20}H_{26}N_5O_4Co$ (459.39)	51.56 (52.29)	5.55 (5.71)	15.37 (15.25)	orange
$CH_3CH(OH)CH_2$	py	$C_{16}H_{26}N_5O_5Co$ (427.35)	44.36 (44.97)	6.22 (6.13)	17.24 (16.39)	yellow
$HOCH_2CH(CH_3)$	py	$C_{16}H_{26}N_5O_5Co$ (427.35)	44.46 (44.97)	6.18 (6.13)	15.85 (16.39)	dark ocher
$HOCH_2CH(OH)CH_2$	py	$C_{16}H_{26}N_5O_6Co$ (443.35)	43.11 (43.35)	5.87 (5.91)	15.34 (15.80)	orange yellow

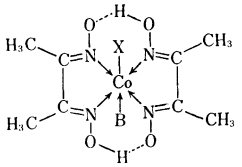
a) nico: nicotinamide, tolu: *p*-toluidine, py: pyridine, pico: *γ*-picoline, imd: imidazole
b) This complex has a water of crystallization: $[CH_3Co(DH)_2(tolu)]\cdot H_2O$.

$$RCo(DH)_2(H_2O) + B \rightarrow RCo(DH)_2B + H_2O.$$

Thus, the addition of equimolar amount of imidazole to methylaquocobaloxime in methanol causes immediate color change in the solution from reddish orange to yellow. This indicates the immediate formation of methyl(imidazole)cobaloxime, which was actually isolated in quantitative yield. The alkylcobaloximes synthesized are summarized in Table 4.

Investigation on the Infrared and Far-Infrared Spectra. All the cobaloximes were identified by elemental analysis and infrared spectra. Characteristic absorption bands of chlorocobaloximes, methylcobaloximes, and (pyridine)cobaloximes are tabulated in Tables 5, 6, and 7, respectively.

The Band between 1700 and 1900 cm^{-1}: All the spectra of the complexes investigated contain a weak broad band between 1700 and 1900 cm^{-1}. It has been proved that this absorption is attributable to intramolecular hydrogen bridges[7] which are schematically shown below.



This conclusion has been supported by NMR spectra.[8] The hydrogen bonded OH frequencies indicated in

7) A. Nakahara, J. Fujita, and R. Tsuchida, This Bulletin, **29**, 296 (1956).
8) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, **1963**, 6041.

TABLE 5. CHARACTERISTIC IR ABSORPTION BANDS OF CHLOROCOBALOXIMES (cm^{-1})

$CoCl(DH)_2B$: B	$\nu_{O-H\cdots O}$	$\nu_{C=N}$	ν_{N-O}	ν_{N-O}	$\nu_{Co-N(DH)}$
H_2O	1790	1570	1232	1080	508
p-Toludine	1760—50	1570—64	1229 or 1245	1092	513
Nicotinamide	—[a]	1570,[b] 1565—60, or 1550	1236	1090	513
Pyridine	1740	1563—53	1242	1091	512
Imidazole	1730—20	1561—51	1236	1087	511
γ-Picoline	1710	1562—53	1240	1092	513
4-Vinylpyridine	1700	1549—8	1241	1091	515

a) This band is obscure owing to the overlapping with strong $\nu_{C=O}$ band of nicotinamide at 1691 cm^{-1}.
b) It is not known which band is attributable to $\nu_{C=N}$. Others are characteristic bands of amide group.

TABLE 6. CHARACTERISTIC IR ABSORPTION BANDS OF CO-METHYL COBALOXIMES (cm^{-1})

$CH_3Co(DH)_2B$: B	$\nu_{O-H\cdots O}$	$\nu_{C=N}$	ν_{N-O}	ν_{N-O}	$\nu_{Co-N(DH)}$
H_2O	1780	1570	1230	1083	512
Nicotinamide	—[a]	1563	1233	1087	515
p-Toluidine	1770	1564	1234	1088	518
Pyridine	1760—50	1561	1239	1090	516
Imidazole	1760	1562—52	1234	1087	516
γ-Picoline	1760	1562	1238	1090	517

a) This band is obscure owing to the overlapping with strong $\nu_{C=O}$ band of nicotinamide at 1692 cm^{-1}.

TABLE 7. CHARACTERISTIC IR ABSORPTION BANDS OF (PYRIDINE)COBALOXIMES (cm^{-1})

$CoX(DH)_2$(pyridine): X	$\nu_{O-H\cdots O}$	$\nu_{C=N}$	ν_{N-O}	ν_{N-O}	$\nu_{Co-N(DH)}$
n-C_3H_7	1760	1563	1232	1088	515
$HOCH_2CH(OH)CH_2$	1760	1561	1233	1089	514
$CH_3CH(OH)CH_2$	1760	1562—55	1233	1088	515
C_2H_5	1760—50	1562—53	1235	1088	516
i-C_3H_7	1750—40	1561—52	1236	1081	515
CH_3	1760—50	1562	1239	1090	516
$C_6H_5CH_2$	1755	1560	1239	1090	516
n-C_4H_9	1750	1561—55	1232	1086	516
$HOCH_2(CH_3)CH$	1750—40	1563	1234	1089	515
Cl	1740	1563—53	1242	1092	512
CN	1730—20	1562—53	1244	1093	514

Tables 5, 6, and 7 are approximate values, nevertheless they showed the consecutive order of the strength of hydrogen bridges. These frequencies in chloro- or methyl-cobaloximes are shifted to lower wave numbers when the fifth ligand changes in the order H_2O> *p*-toluidine>pyridine>imidazole>*γ*-picoline. This is considered to be in the approximate order of the weakness of the electron donating power, whereas those in (pyridine)cobaloximes are shifted to lower wave numbers when the sixth ligand changes in the order alkyls>Cl>CN which is in the opposite direction from the donating power of the bases, *viz.*, the fifth ligands. This will be discussed later together with the shifts of other frequencies.

The Band at around 1560 cm^{-1}: The band at around 1560 cm^{-1} is attributed to C=N stretching frequency of dimethylglyoximato ligands.[7,9] The band is not affected by the change of the sixth ligand, *e. g.*, CN, Cl, alkyls. It is shifted to lower wave number when the fifth ligand changes in the order H_2O> *p*-toluidine>nicotinamide>pyridine>*γ*-picoline>imidazole>4-vinylpyridine, *i. e.*, with the increase of the interaction of the base with Co atom. Burger *et al.* reported on the basis of the frequency shift of the C=N vibration that the lower the C=N vibration frequency, the stronger the metal→N=C donor *π*-bond.[10] Our results suggest that the increase in electron density on the cobalt causes the increase of back donation from Co to nitrogen atoms of DH ligands, resulting in the increase in conjugation of the five membered chelate rings.

The Bands at around 1240 cm^{-1} and 1090 cm^{-1}: From the experiments by Blinc and Hadži,[9] we could assign the peaks of the spectra at around 1240 cm^{-1} and 1090 cm^{-1} to the N–O stretching vibrations. These two bands are shifted to lower wave numbers when the fifth ligand changes in the order 4-vinylpyridine> pyridine>*γ*-picoline>imidazole>*p*-toluidine>nicotinamide>H_2O, which is in the approximate order of the strength of electron donating power, as well as when the sixth ligand changes in the order CN>Cl> alkyls. Since the increase in the electron density in N–O bond is considered to cause the high frequency shift of the vibration, the high frequency shift caused by the change of the fifth ligand is explained by the electron donating power of the fifth ligands, *viz.*, the axial bases, while that caused by the change of the sixth ligand is unexpectedly in the opposite direction, which appears at first sight to be inconsistent with the effect of the fifth ligand, since cyanide is known as an electron withdrawing group stronger than others and hence it would cause the decrease in the electron density of N–O bond through the interaction with Co atom.

The Band at around 510 cm^{-1}: The band at around 510 cm^{-1} which is attributable to Co–N stretching frequency between Co and nitrogen atoms of dimethylglyoximato ligands is not affected by the change

9) R. Blinc and D. Hadži, *J. Chem. Soc.*, **1958**, 4536.
10) K. Burger, I. Ruff, and F. Ruff, *J. Inorg. Nucl. Chem.*, **27**, 179 (1965).

of the sixth ligand, *i. e.*, CN, Cl, alkyls similarly to the C=N vibration mentioned above, whereas it is shifted to higher wave number when the fifth ligand changes in the order H_2O<nicotinamide<pyridine, imidazole<*p*-toluidine, γ-picoline, which is not in an exact but approximate order of the strength of the interaction of the base with Co atom.

Other Bands Occurring in the Infrared Region: All the complexes show the weak broad bands between 2300 and 2400 cm^{-1}, which may be attributed to another hydrogen-bonded O–H frequency of bisdimethylglyoximato moiety according to Hadži.[9,11] The bands at around 1445 cm^{-1} and around 1375 cm^{-1} are due to asymmetric and symmetric deformation vibrations respectively, of methyl groups in dimethylglyoximes. The bands at around 980 cm^{-1} and 880 cm^{-1} may be attributed to deformation vibrations of OH in bisdimethylglyoximato moiety, and the band at around 740 cm^{-1} to C=N–O deformation vibration.

The characteristic absorption bands due to the axial ligands are also observed; pyridine derivatives show the weak bands at 3000—3150 cm^{-1} due to C–H stretching vibrations of pyridine ring, the band at 1600—1610 cm^{-1} to C=C and/or C=N stretching of pyridine ring, and the band at 750—780 cm^{-1} to C–H deformation of pyridine ring. The C–H stretchings of alkyl group linked to Co atom occurring at 2850—2960 cm^{-1} become distinct in intensity in the order CH_3<C_2H_5<C_3H_7<C_4H_9 as expected. In isopropyl(pyridine)cobaloxime, the characteristic absorption bands due to isopropyl group are clearly observed at 1375 and 1366 cm^{-1} which are symmetric deformation bands of CH_3 in isopropyl group, and 1187 and 1161 cm^{-1} which are skeleton vibrations of C–C–C in isopropyl group. In cyanocobaloximes, C≡N stretching vibration occurs at 2130—2200 cm^{-1}. Aquocobaloximes also show the characteristic bands due to H_2O molecule coordinating to Co atom; the ν_{O-H} at 2940—3110 cm^{-1}. δ_{O-H} at 830—838 cm^{-1}, and ν_{Co-O} at 357—378 cm^{-1}.

Other Bands Occurring in the Far-Infrared Region: The band at around 370 cm^{-1} in aquocobaloximes may be attributed to Co–O stretching vibration between Co atom and the coordinating water molecule. A few bands between 420—500 cm^{-1} other than that at around 510 cm^{-1} listed in Tables 5—7 may be attributable to Co–N stretching vibrations. All the alkylcobaloximes show an absorption band at around 325 cm^{-1}, which may be attributed to the Co–C stretching vibration, while methylcobalamin was reported to show the Co–C stretching band at 348 cm^{-1}.[12]

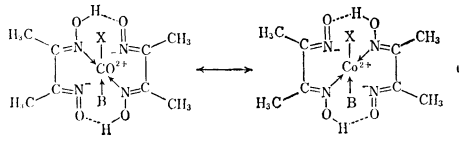
Polymeric Cobaloximes: Polymeric cobaloximes, *i. e.*, Co(OH)(DH)$_2$(Copoly–AM-VPy) showed characteristic absorption bands due to cobaloxime, other than due to the polymeric ligands; *e. g.*, ν_{N-O} at 1230 cm^{-1} and 1090 cm^{-1}, δ_{O-H} at 981 cm^{-1}, and ν_{Co-N} at 510—530 cm^{-1}.

Discussion on the Frequency Shift with Axial Ligands: The characteristic absorption bands mostly due to dimethylglyoximato ligands in these cobaloximes do not shift largely by the change of axial ligands. This suggests that the strength of the Co–N bonds in the equatorial position is not much affected by the change of the axial ligands because the Co–N(equatorial) bonds are very strong due to metal→N=C π-bond.

However, the definite relationship between the frequency shifts and the consecutive order of axial ligands was observed as mentioned above. In short, as the donating power of the base increases, $\nu_{O-H\cdots O}$ at around 1750 cm^{-1} and $\nu_{C=N}$ at around 1560 cm^{-1} shift to a lower wave number region, while ν_{N-O} at around 1240 cm^{-1} and 1090 cm^{-1}, and ν_{Co-N} at around 510 cm^{-1} to higher one. These results can be interpreted as follows. The coordination of more electron-donating base to Co atom causes the increase in electron density in Co atom. This facilitates the back donation from Co to the nitrogen atoms of dimethylglyoximato ligands, resulting in the increase in electron densities in C=N, and N–O bonds. The increase in electron density in N–O bonds causes the stronger hydrogen bridges of O–H···O and the higher frequency shifts of N–O stretching vibrations. The facilitated back donation from cobalt to nitrogen atoms of dimethylglyoxime means the increased metal-donor π-bond in the equatorial moiety of cobaloximes, which causes the stronger interaction of Co with equatorial N atoms, resulting in higher frequency shift of ν_{Co-N} vibration, and causes more conjugation in five membered chelate rings including Co atom, resulting in lower frequency shift of $\nu_{C=N}$ vibration.

On the contrary, the effects caused by the change of the sixth ligand, *e. g.*, CN, Cl, alkyls, were observed to be inverse. As the donating power of the sixth ligand decreases, $\nu_{O-H\cdots O}$ shifts to lower wave number, while ν_{N-O} to higher. This opposite tendency in the *cis*-effect of two axial ligands might be interpreted as follows: Since the bonding orbitals of both the fifth and sixth ligands are considered to interact most strongly with the d_{z^2} orbital of the central metal than the second probable one, *i. e.*, $d_{x^2-y^2}$ and than other *d* orbitals, the effect of one of the axial ligands is considered to be larger on another axial ligand (*trans*-effect) than on the equatorial ligands (*cis*-effect). More electron-withdrawing ligand in the sixth position causes stronger interaction between the central metal and the fifth ligand in the *trans* position, which could be caused by decrease in the cobalt-base bond length. Donation of electron from the base to Co atom is thus facilitated, which results in stronger back donation from Co to the equatorial nitrogen atoms and hence in increase

11) In principle the appearance of two OH bands could be admitted and explained by the splitting of the vibrational levels due to proton tunnelling. The structure of cobaloxime, $CoX(DH)_2B$, may be schematically described in a resonance as follows:



The hydrogen atoms in the hydrogen bridges may not occupy a central position between the oxygen atoms, which would result in the appearance of two OH bands in 1700—1900 cm^{-1} and in 2300—2400 cm^{-1}.[9]

12) H. P. C. Hogenkamp, J. E. Rush, and C. A. Swenson, *J. Biol. Chem.*, **240**, 3641 (1965).

in electron density in the equatorial bisdimethylglyoximato moiety. More electron-donating ligand in the sixth position causes weaker interaction between Co and the fifth ligand, which results in an increase in the Co-base bond length, and hence in the decrease in electron density in the equatorial moiety.

Similar effects of the axial ligands which were observed in the electronic spectra are considered to be consistent with the results, *viz.*, the stronger the interaction between Co and the axial base, the higher the *d-d* transition energy, whereas the stronger the donating power of another axial ligand, the lower the *d-d* transition energy.

Experimental

Synthesis of Cobaloximes. Chlorocobaloximes: a) Chloro(nicotinamide)cobaloxime: A typical method for the synthesis of chloro(nicotinamide)cobaloxime is as follows. To a hot solution of 2.55 g (0.022 mol) of dimethylglyoxime (abbreviated as DH_2 hereinafter) in 80 m*l* of ethanol, was added 2.38 g (0.010 mol) of $CoCl_2 \cdot 6H_2O$ in 10 m*l* of ethanol with stirring. After a while, 2.68 g (0.022 mol) of nicotinamide in 20 m*l* of ethanol was added to the mixture, followed by stirring with aeration for a few hours at room temperature, resulting in precipitation of the product. The precipitated ocher powders were collected, washed with water, ethanol, and finally with ether, and dried *in vacuo*. The yield was 1.56 g (35%).

Another method in which NaOH is used instead of organic base to neutralize HCl produced is as follows. To a hot solution of 2.55 g (0.022 mol) of DH_2 in 80 m*l* of ethanol, was added 2.38 g (0.010 mol) of $CoCl_2 \cdot 6H_2O$ in 10 m*l* of ethanol with stirring. After a while, 1.34 g (0.011 mol) of nicotinamide in 10 m*l* of ethanol and 0.40 g (0.010 mol) of NaOH in 10 m*l* of H_2O were successively added. The mixture was worked up as above. The yield was 2.60 g (58%).

Other chlorocobaloximes with organic bases were prepared using organic bases instead of nicotinamide.

b) Chloroaquocobaloxime: To a hot solution of 12.8 g (0.11 mol) of DH_2 in 300 m*l* of methanol, 11.9 g (0.050 mol) of $CoCl_2 \cdot 6H_2O$ in 50 m*l* of H_2O was added with stirring at room temperature. Fifty milliliters of a saturated aqueous solution of KCl was added to the mixture which was stood overnight, resulting in crystallization of the product in pale brown fine needles. The yield was 5.8 g (34%).

Cyanocobaloximes: A typical method for the preparation of cyano(pyridine)cobaloxime is as follows. To a hot solution of 6.40 g (0.055 mol) of DH_2 in 200 m*l* of methanol, 6.23 g (0.025 mol) of $Co(CH_3COO)_2 \cdot 4H_2O$ was added with stirring. After a while, 1.23 g (0.025 mol) of NaCN in 20 m*l* of H_2O, and 4.15 g (0.053 mol) of pyridine were added successively at room temperature, followed by stirring with aeration for a few hours, resulting in precipitation of the product. The yellow powders were collected, washed with water, methanol, and finally with ether and dried *in vacuo*. The yield was 1.80 g (18%).

Another method in which one equivalent base is enough to produce this complex instead of two is as follows: To a hot solution of 6.40 g (0.055 mol) of DH_2 in 150 m*l* of methanol, 6.23 g (0.025 mol) of $Co(CH_3COO)_2 \cdot 4H_2O$ was added with stirring. After a while, 2.08 g (0.026 mol) of pyridine and 1.23 g (0.025 mol) of NaCN in 20 m*l* of H_2O were added successively at room temperature, followed by stirring with aeration for a few hours, resulting in precipitation of the product. The product was worked up as above to give 2.55 g (26%) of yellow powders.

Other cyanocobaloximes with organic bases were prepared using organic bases, instead of pyridine.

Cyanoaquocobaloxime was prepared as above without adding any organic base but with additional 50 m*l* of H_2O.

Polymeric Cobaloximes——$Co(OH)(DH)_2$(Copoly-AM-VPy): Preparation of polymeric cobaloximes shown in Table 1 was reported.[13] A typical procedure is as follows: A hot solution of DH_2 in methanol was mixed with an aqueous solution of $CoCl_2 \cdot 6H_2O$ (DH_2: Co molar ratio 2) for an hour. An aqueous solution of the polymeric ligand (Copoly-AM-VPy) was then added to the reaction mixture (Co : VPy-residue ratio *ca.* 4), after the pH of the mixture was adjusted to 8.0—8.3. The reaction was complete within 3—4 hr. After concentration, the reaction mixture was applied to the Sephadex column (Sephadex LH-20 or G-25). From the first fraction, polymeric cobaloxime was recovered, followed by a by-product, *i. e.*, hydroxoaquocobaloxime. Alternatively the product was purified by repeated reprecipitation in water-acetone. The by-product was identified as $Co(OH)(DH)_2(H_2O)$ by elemental analysis and its infrared spectrum:

Found: C, 27.87; H, 5.25; N, 16.53%. Calcd for $C_8H_{17}N_4O_6Co$: C, 29.64; H, 5.29; N, 17.28%.

Hydroxoaquocobaloxime was also prepared as follows: To a hot solution of 12.8 g (0.11 mol) of DH_2 in 200 m*l* of methanol, was added 11.9 g (0.050 mol) of $CoCl_2 \cdot 6H_2O$ with stirring. After a while, 4.4 g (0.11 mol) of NaOH in 70 m*l* of H_2O was added to the mixture, followed by stirring with aeration for a few hours. The solution was evaporated to dryness and the residual product was applied to the Sephadex G-25 column to give dark brown hydroxoaquocobaloxime. The yield was 6.3 g (39%).

Found: C, 29.16; H, 3.95; N, 17.31%. Calcd for $C_8H_{17}N_4O_6Co$: C, 29.64; H, 5.29; N, 17.28%.

Alkylcobaloximes: Alkylcobaloximes were prepared according to two methods by Schrauzer and Windgassen;[6] by the reaction of alkyl halide with Co(I) species reduced by $NaBH_4$, and by that with Co(I) species formed by disproportionation of Co(II) species to Co(I) and Co(III) in alkaline media without any reducing agent. A typical method for the preparation of methylaquocobaloxime is as follows. To a stirred suspension of 29.0 g (0.250 mol) of DH_2 in 300 m*l* of methanol, 29.7 g (0.125 mol) of $CoCl_2 \cdot 6H_2O$ was added under nitrogen atmosphere. Methyl iodide, 25.4 g (0.180 mol), and 15.0 g (0.375 mol) of NaOH in 50 m*l* of H_2O were then successively added at $-20°C$, followed by stirring for an hour in a closed system. After evaporation of methanol under a reduced pressure, the remaining aqueous solution was stood overnight, resulting in the precipitation of dark red crystals. The yield was 15.8 g (80%).

When alkylaquocobaloxime was too soluble to isolate, pyridine or another organic base was added to the reaction mixture and alkyl(pyridine)cobaloxime or alkyl(B)cobaloxime was extracted with ether or methylene chloride. The yields obtained by the method with $NaBH_4$ were generally lower than those by alternative method, whereas alkyl iodides were more effective than bromides or chlorides in the preparation of alkylcobaloximes.

Base Substitution Reaction of Alkylaquocobaloxime. The coordinating water in alkylaquocobaloxime is readily displaced by another organic base only by the addition of an equivalent amount of base to the alkylaquocobaloxime. A typical displacement reaction is as follows. Methylaquocobaloxime, 0.967 g (3.00 mmol), was dissolved in 50 m*l* of methanol followed by addition of 0.204 g (3.00 mmol) of

13) N. Yamazaki and Y. Hohokabe, *Chem. Commun.*, **1968**, 829.

imidazole, resulting in immediate color change in the solution from reddish orange to yellow. By concentrating the solution, 1.05 g (94%) of yellow crystals of methyl(imidazole)-cobaloxime was obtained quantitatively.

Alkylcobaloximes prepared in this work are summarized in Table 4. The yields are not given in order to avoid complexity originating from the various preparatory methods.

Measurements. The infrared spectra were taken in KBr pellets with a JASCO, Model IR-G infrared spectrophotometer, and the far-infrared spectra with a JASCO, Model IR-F, far-infrared spectrophotometer.