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Cobaloximes with Pyrazine and Their Dimetallic Complexes

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Mono- and dinuclear cobaloximes with inorganic anions and pyrazine (Pz) as a base/bridging ligand were synthesized and characterized by ¹H, ¹³C, UV/Vis and IR spectroscopy and X-ray structure analysis. Mononuclear complexes XCo-(dioxime)₂Pz were used as precursors for building homo- and heterodimetallic complexes. The X-ray crystal structures of ClCo(dmgH)₂Pz, ClCo(dpgH)₂Pz, [Co(dpgH)₂(NO₂)₂]Na, and [Co(dmgH)₂(NO₂)₂]₂[Ag]₂·H₂O are reported. [Co(dmgH)₂-(NO₂)₂]₂[Ag]₂·H₂O shows two Ag^I ions in different environments: one is in tetrahedral, whereas the other is in capped trigonal coordination and the metal-organic framework in this molecule shows helical structure. A cyclic voltammetry study in [XCo(dioxime)_2]_2- μ -Pz and XCo(dioxime)_2Pz [dioxime = dmgH (dimethylglyoximato), dpgH (diphenylglyoximato)] is reported. The reduction, Co^{III} to Co^{II} and Co^{II} to Co^I, is found to be more difficult in [XCo(dpgH)_2]_2- μ -Pz than in XCo(dpgH)_2Pz. The CV data have been interpreted in terms of cobalt anisotropy.

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Introduction

Organocobaloximes, initially proposed as models of the B_{12} coenzyme, have now acquired an independent research field because of their rich coordination chemistry and potential application in organic synthesis.^[1] The variation in the N-Co-C bond properties, including its strength, has been described not only in terms of the trans influence of the axial neutral base but also of the steric and electronic properties of the alkyl group.^[2,3] The influence of the equatorial ligands on the axial ligands (cis influence) in dioximates, Costa's model, and iminates (cobalt complexes with tetradentate Schiff bases) has been previously reported.^[2] Such studies are limited in cobaloximes.^[4,5] In recent years the description of spectroscopic data and structure-property relationships and their correlation to Co-C bonds have been most emphasized.^[6] We have shown that spectral correlations are much better understood in terms of field effect; the model takes into account the total effect of cobalt anisotropy of the $[Co(dioxime)_2]^+$ metallabicycle (electronwithdrawing power) and the ring current arising from the delocalization of electron density throughout the [Co(diox- ime_{2}^{+} metallabicycle.^[5,7]

Ligand-bridged complexes are of interest in view of their role as reaction intermediates in inner-sphere electron-transfer processes^[8] and pyrazine has been extensively used as a bridging ligand. Although a number of examples of

the pyrazine-bridged mixed-valence homo- and heterodimetallic complexes of Ru, Fe, and Co are known,^[9] there are few in cobaloxime chemistry.^[10–12] A mixing of two cobalt centers with electron delocalization by pyrazine has been observed in the recently reported pyrazine-bridged organodicobaloximes, [RCo(dioxime)₂]₂-µ-Pz.^[11,12]

Among the electrochemical studies on cobaloximes only few describe a correlation to related cobalt complexes to show the mutual *cis* and *trans* influence.^[13] Recent work has shown that the reduction potential depends upon both the axial and equatorial ligands.^[5,7,14] CV data have been rationalized in terms of cobalt anisotropy and this in turn is affected by the axial ligands; the effect is more distinct when the axial ligand is an inorganic group/atom.^[5,7] A single peak with a very high reduction potential is observed in [RCo(dioxime)₂]₂-µ-Pz, which points to electron delocalization and also shows that the dicobaloximes are more difficult to reduce than the corresponding monocobaloximes.^[12]

In general, the inorganic cobaloximes $XCo(dioxime)_2B$ (B = neutral base) give a better CV curve than organocobaloximes.^[5,7] Also, the changes in NMR chemical shifts in the inorganic complexes are much more marked than in organocobaloximes and these are more effectively rationalized with the field effect.^[4c,5,7,15]

It is therefore interesting and useful to study the pyrazine-bridged dinuclear inorganic cobaloximes, [XCo(diox $ime)_2]_2-\mu$ -Pz. The spectral and CV data in these dinuclear complexes should complement the reported data in [RCo- $(dioxime)_2]_2-\mu$ -Pz. It would also be useful to compare the data with the corresponding mononuclear cobaloximes, XCo(dioxime)_2Pz.

The aim of the present study is (a) to synthesize [XCo-(dioxime)₂]₂-µ-Pz, XCo(dioxime)₂Pz, and XCo(dioxime)₂-

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Scheme 1. Cobaloximes.

Pz-M [M = Cu^I, Ag^I], (b) to verify the validity of our recently proposed field effect model in the interpretation of spectroscopic data in these complexes, and (c) to perform a CV study (Scheme 1).

Results and Discussion

Synthesis

The synthesis of complexes 1 and 4 was easy; an addition of pyrazine to the corresponding aqua complex $ClCo(diox-ime)_2H_2O$ in a 1:2 molar ratio afforded the corresponding dicobaloxime.

Two possibilities were considered for the preparation of complexes **2**, **3** and **5**, **6**:

(a) We have recently synthesized $XCo(dioxime)_2Py$ (X = NO_2 , N_3) complexes by the nucleophilic substitution of the chlorido ligand in ClCo(dioxime)_2Py.^[5,7,15,16] An obvious choice was to follow the same route. However, the reaction of NaN₃ or NaNO₂ with [ClCo(dpgH)₂]₂- μ -Pz (4) did not give the desired compound, but instead a Co^{III} complex was isolated that was sparingly soluble in chloroform and dichloromethane but soluble in methanol/water and acetone/water. The ¹H NMR in [D₆]DMSO showed the absence of a pyrazine peak. It indicated the presence of a salt (discussed later).

(b) The same procedure as used in the preparation of **1** and **4** was followed. The dicobaloximes were formed in good yield. However, this procedure required the preparation of the corresponding aqua complexes, XCo(dioxime)₂-H₂O (**8**, **9**, **11**, **12**).^[17] These were prepared from the corresponding aqua(chlorido)cobaloximes (**7** or **10**) by the nucle-ophilic substitution of the chlorido ligand. Any change in concentration or use of excess NaX led to the formation of a salt along with the desired product. The salt was identical to the product obtained earlier in the reaction of [ClCo(dpgH)₂]₂- μ -Pz (**4**) with NaNO₂ and was identified as [Co(dpgH)₂(NO₂)₂]⁻ by X-ray crystallography (**19**). López et al. have reported a similar type of salt formation in the reaction of ClCo(dioxime)₂B with excess KCN.^[18]

XCo(dioxime)₂Pz (13–18) were prepared by the reaction of the corresponding aqua complexes 7-12 with pyrazine in a 1:1 ratio by slow evaporation of the solvent. These were the only products formed in dilute solution, but in a concentrated solution the precipitation of the dinuclear product (1 or 4) occurred and no mononuclear product was formed. Also a rapid evaporation of the solvent resulted in the formation of a dinuclear complex.

Spectroscopy: Characterization of the Complexes

The ¹H NMR spectra of **1–6** and **13–18** are easily assigned based on the chemical shifts. The signals are assigned according to their relative intensities and are consistent with the related dioxime compounds previously described.^[11] Complexes **1–3** are sparingly soluble in most organic solvents and it took more than 1000 scans to obtain a reasonable ¹H NMR spectrum in CDCl₃. The ¹H values are given in Table 1.

All four protons in the unligated pyrazine are equivalent and appear as a singlet at $\delta = 8.59$ ppm. The ligated pyrazine in **4**–**6** appears as a singlet which is shifted downfield as compared to that of free pyrazine. On the other hand, pyrazine appears as two doublets in **13–18**; the one that is more upfield is assigned to the protons that are in close proximity to the cobaloxime moiety. The ring current of the metallabicycle affects these protons.^[5,7] Hence, their signals are more downfield in **16–18** than in **13–15** because of the lower ring current in the dpgH complexes. ¹H NMR spectroscopy in the region $\delta = 7.5$ –9.0 ppm can easily differentiate between the di- and mononuclear complexes; pyrazine appears as a singlet in the former and as two doublets in the latter.

Spectral Studies

NMR

In the earlier NMR study on cobaloximes XCo(dioxime)₂Py (dioxime = dmgH, dpgH), Py_a and Py_y were

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Table 1. ¹H NMR and yield.

No.	0–H•••0	Pz	dmgH	dpgH/others	Yield (%)
1	_	8.09	2.45	_	89
2	_	8.16	2.42	_	70
3	_	8.18	2.45	_	75
4	18.52	8.66	_	7.82 (d), 7.77 (t), 7.32 (t), 7.18–7.33 (m)	49
5	18.48	8.74	_	7.13–7.29	48
6	18.36	8.63	_	7.14–7.26 (m)	58
13	—	8.33 (d)	2.42	_	60
		8.50 (d)			
14	_	8.35 (d)	2.35	-	58
		8.57 (d)			
15	17.93	8.38 (d)	2.42	-	58
		8.55 (d)			
16 ^[a]	18.57	8.61 (d)	—	7.05–7.28 (m)	80
		8.64 (d)			
17	18.39	8.66 (d)	-	7.16–7.34 (m)	70
		8.72 (d)			
18	18.41	8.60 (d)	-	7.16–7.32 (m)	65
		8.62 (d)			
19 ^[b,c]	18.47	_	_	7.24–7.44 (m)	

[a] 1³C NMR: δ = 154.05, 147.31, 145.46, 129.92, 129.80, 129.31, 128.01 ppm. [b] Recorded in [D₆]DMSO. [c] [Co(dpgH)₂(N₃)₂]⁻ ([D₆]-DMSO): ¹H NMR: δ = 18.59, 7.41 (d, 4 H), 7.39 (d, 8 H), 7.27–7.24 (dd, 8 H) ppm; ¹³C NMR: δ = 151.5, 130.0, 128.7, 127.5 ppm.

found to be the most affected by a change in X.^[5,15] The cobaloximes **13–18** are very similar to pyridine complexes except that pyridine is replaced by pyrazine (pK_a of Pz 1.1,^[19] Py 5.3^[20]). Also, the spectral studies of pyrazinebridged alkyl- (and benzyl-) dicobaloximes have already been reported from our laboratory.^[11,12] Therefore, rather than going into the details about the spectroscopic data and *cis/trans* influence study in the present systems, we want to highlight only the salient points.

The coordination shift^[21] $\Delta \delta^1 H$ of the Pz_a signal in 13– **18** is very close to the coordination shift $\Delta \delta^1 H$ of the Py_a signal in the corresponding pyridine complexes, indicating further the similarity in the two systems (Table ST2). As H_{α} is affected by the dioxime ring current and cobalt anisotropy, its signal appears more upfield in the dmgH complexes than that of the dpgH complexes in both pyridine and pyrazine complexes.^[4a,11,12] One of the major differences found in the pyridine and pyrazine complexes is the coordination shift of the β -hydrogen signal. It is almost unaltered in the pyrazine complexes, whereas it was shifted downfield (by 0.2-0.3 ppm) in the corresponding pyridine complexes. This is due to the presence of a nitrogen atom instead of a carbon atom at the sixth position in pyrazine. The cobalt anisotropy is less in the pyrazine complexes because of its lower pK_a value and hence it compensates for the β -hydrogen signal downfield shift.

In the $[(R/X)Co(dioxime)_2]_2-\mu$ -Pz complexes, Pz_a is affected by the ring current and the cobalt anisotropy of the two metallabicycles (the factors ring current and cobalt anisotropy work in opposite directions: the Pz_a signal is shifted upfield by the ring current and downfield by the cobalt anisotropy) as compared to one in $(R/X)Co(dioxime)_2Pz$, therefore $\Delta\delta$ of the Pz_a signals should be much larger or even doubled in the former. It is found to be -0.2 to -0.3 ppm in 13–15 and -0.4 to -0.5 ppm in 1–3; however, the difference is unexpectedly small in the corresponding

dpgH complexes (compare **4–6** and **16–18** with Pz_{α} in free pyrazine). This is because of the higher cobalt anisotropy of dpgH, which completely compensates for the upfield shift due to the ring current. Similar compensation is also observed in the mono(pyrazine) complexes (compare **13–15** with **16–18**) as well as in the pyridine complexes XCo(dioxime)₂Py, viz. $\Delta\delta$ of the Py_{α} signals in the dmgH complexes is around –0.3 ppm, whereas it is close to zero in the dpgH complexes.

The pyrazine signals in $[\text{RCo}(\text{dioxime})_2]_2-\mu-\text{Pz}$ were found to be shifted downfield in the dpgH complexes and upfield in the dmgH complexes as compared to the unligated pyrazine.^[11,12] A similar trend is observed in the inorganic complexes **1–6** and $\Delta\delta$ of the Pz_{α} signals in [RCo-(dioxime)_2]_2-\mu-Pz complexes is larger than that in **1–6** because of the higher *trans* effect of the R group with respect to the X.

UVIVis

Three bands, a strong band at 263 nm corresponding to the Co \rightarrow dioxime metal-to-ligand charge transfer (MLCT) and two shoulders around 313 and 330 nm (Co \rightarrow Pz), are observed in **16**. A similar spectrum is obtained in **4** except that the intensity of the band corresponding to Co \rightarrow Pz is significantly increased. This is expected because of the additive factor of the two identical chromophoric groups in the dinuclear complexes. A similar result is found in the dmgH complexes (see Table 2).

In general, organo-cobaloximes exist largely as pentacoordinate species in coordinating solvents like methanol and as hexacoordinate species in chloroform or dichloromethane.^[4a,22] Pyrazine-bridged alkyldicobaloximes show similar behavior to the alkyl(pyridine)cobaloximes.^[11] The base-on/ base-off behavior of organocobaloximes has generally been studied by titration with the base, and the inference is made from the change in shape of the Co–C CT band with the

Compound	UV/Vis	s: λ_{max} [nm]	IR: \tilde{v} [cm ⁻¹]				
-	Co→dioxime (MLCT)	$Co \rightarrow Pz$ (shoulder)	$Co \rightarrow Pz$ (shoulder)	О–Н•••О	C=N	N–O	N–O′
1	224 (sh), 250 (4.32)	292 (3.77)	312 (3.76)	3417.6 (br.)	1563.7	1242.9	1091.4
4	220 (3.71), 258 (4.36)	292 (4.21)	325 (4.30)	3433.0 (br.)	1530.4	1288.5	1139.8
13	256 (4.35)	290 (3.74)	308 (3.69)	3530.0 3446.7	1574.9	1239.9	1094.1
16	263 (4.46)	313 (4.09)	330 (4.04)	3459.8 3421.2	1531.5	1285.6	1136.9
$\begin{array}{c} \textbf{13}{\cdot}Cu^{I}PF_{6}\\ [Co(dpgH)_{2}(N_{3})_{2}]^{-}\end{array}$	230 (4.9	1), 259 (4.52)	3443.5, 1566.4, 1239.3, 1092.3, 845 3438.7, 2025.3, 1383.3, 1136.5				

Table 2. UV/Vis and IR data.

gradual addition of base to the cobaloxime. It has, however, not been possible to obtain a similar information in the present inorganic cobaloximes, because the phenomenon can be monitored by the $Co \rightarrow dioxime$ MLCT band only and this occurs at the same position as in the pyrazine case.

Titration with Cu^IBF₄ Salt

The titration of Cu^+ with a solution of **13** in dichloromethane was monitored by UV/Vis spectroscopy at 233 and 259 nm. The absorbance of the solution increased until 0.5 equiv. of Cu^+ was added (see Figure 1). No spectral change was observed after the addition of 0.5–1.0 equiv. of Cu^+ . This suggests that there is a 2:1 complexation with Cu^+ . Job's plot also suggests a 2:1 complexation (Figure S14).



Figure 1. Cu⁺ addition to a solution of [ClCo(dmgH)₂Pz] (13). The Cu⁺ saturation point is at 0.5 mol-equiv. [ClCo(dmgH)₂Pz] = 1×10^{-5} M (1 mL). [Cu⁺] = 1×10^{-5} M (0.1–1.0 mL).

IR

All IR spectra were recorded as solid samples on KBr pellets and are tabulated in Table 3. The mononuclear and pyrazine-bridged dicobaloximes can be distinguished by IR spectroscopy; the O–H···O peak is a sharp doublet in monocobaloximes, whereas it is a broad singlet in the case of dicobaloximes. The O–H···O and C=N peaks appear at lower frequency in dpgH complexes as compared to dmgH complexes because of the higher cobalt anisotropy and lower electron density in the dpgH complexes. The Cu^IPF₆-

bridged complex gives an IR spectrum identical to that of dicobaloxime 1 along with a distinct sharp peak at 845 cm⁻¹ for PF_6^- (Figures S16 and S17).

Cyclic Voltammetry

The cyclic voltammogram (CV) of a cobaloxime shows three types of redox couples: Co^{III}/Co^{II}, Co^{II}/Co^I, and Co^{IV}/Co^{III}. Organo-cobaloximes, in general, give poor CVs and most of the time the Co^{III}/Co^{II} redox couple is not visible. On the other hand, inorganic cobaloximes show relatively better CVs and all the redox couples are prominent. Two common solvents used for the study are dichloromethane and acetonitrile. We have preferred to use dichloromethane because of the higher solubility of the cobaloximes. The cyclic voltammogram of 13 (Figure 2A) shows an irreversible wave in the reductive half at -0.47 V corresponding to Co^{III}/Co^{II} and a quasireversible wave at -1.08 V corresponding to Co^{II}/Co^I. [Interestingly, a CV of 13 recorded in acetonitrile gives a much better plot in which all the peaks are prominent and show the reversible nature (Figure 2B).] In comparison, 16 (Figure 2C) is much more easily reduced, with values at -0.32 and -0.73 V, respectively. In the oxidation half corresponding to Co^{IV}/Co^{III}, 13 and 16 show one reversible wave at +1.25 and 1.38 V, respectively. The CV data are very similar to those of the corresponding pyridine analogues except that the reduction potential values are low and the oxidation halves are high (see Table 3). This agrees well with the pK_a of pyridine and pyrazine.

The CV data for both the oxidative and reductive halves can be rationalized on the basis of the cobalt anisotropy. The higher the cobalt anisotropy, the lower the reduction potential and the higher is the oxidation potential.^[5,7] A comparison of the data in **13** with those in **16** shows that the reduction is easier and the oxidation is more difficult in **16** because of the higher cobalt anisotropy in dpgH complexes than in dmgH complexes. We have made a similar observation in the gH, dpgH, mestgH, and mixed dioxime complexes.^[5,7,15] In view of this it is quite likely that the cobalt anisotropy may be the major factor responsible for the reduction/oxidation process.

We could not record the CV for **1** because of its insolubility in most organic solvents. The CV graph for **4** has three peaks; Co^{IV}/Co^{III} is prominent but Co^{III}/Co^{II} and Co^{II}/Co^I

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No.	Co ^{III} /Co ^{II}					Co ^{II} /Co ^I				Co ^{IV} /Co ^{III}					
	$\begin{array}{l} E_{1/2} \; (\Delta E_{\rm p})^{[{\rm a}]} \\ [{\rm V}] \; ([{\rm mV}]) \end{array}$	$E_{1/2}^{[b]}$ [V]	i _{pc} [μΑ]	i _{pa} [μA]	$i_{\rm pa}/i_{\rm pc}$	$\begin{array}{l} E_{1/2} \; (\Delta E_{\rm p})^{[{\rm a}]} \\ [{\rm V}] \; ([{\rm mV}]) \end{array}$	$E_{1/2}^{[b]}$ [V]	i _{pc} [μA]	i _{pa} [μA]	$i_{\rm pa}/i_{\rm pc}$	$\begin{array}{l} E_{1/2} \; (\Delta E_{\rm p})^{[{\rm a}]} \\ [{\rm V}] \; ([{\rm mV}]) \end{array}$	$E_{1/2}^{[b]}$ [V]	i _{pc} [μA]	i _{pa} [μA]	$i_{\rm pa}/i_{\rm pc}$
4	-0.88 ^[c]	-1.39	0.1	-	_	-1.10 ^[c]	-1.61	0.4	-	_	1.33 (220)	0.82	0.2	8	40.0
13	-0.47 ^[c]	-0.98	15	-	-	-1.08 (320)	-1.59	21	10.7	0.5	1.25 (280)	0.74	26.8	31.2	1.2
13 ^[d]	-0.22 (130)	-0.73	6.1	6.3	1.0	-1.01 (80)	-1.52	11.5	11.5	1.0	1.20 (107)	0.69	9.5	10.0	1.0
16	-0.32 ^[c]	-0.83	11.2	-	-	-0.73 (180)	-1.24	19.0	12.7	0.64	1.38 (120)	0.87	22.3	23.6	1.1
ClCo(dmgH) ₂ Py	$-0.66^{[c]}$	-1.17				-1.12 (200)	-1.63				1.20 (190)	0.69			
ClCo(dpgH) ₂ Py	-0.29 (490)	-0.80				-0.82 (260)	-1.33				1.33 (150)	0.82			

Table 3. CV data in dichloromethane and TBAPF₆ at 0.2 V s⁻¹ at 25 °C.

[a] vs. Ag/AgCl. [b] vs. Fc/Fc⁺. [c] Values refer to E_{pc} . [d] Value is in CH₃CN.



Figure 2. Cyclic voltammograms of **13** in dichloromethane (DCM) (A), in CH₃CN (B), and **16** in DCM (C) with 0.1 M (nBu_4N)PF₆ as supporting electrolyte at 0.2 V s⁻¹ at 25 °C.

are not; however, the differential pulse voltammogram (DPV) clearly shows reduction. The pyrazine-bridged benzyl dpgH complex, [PhCH₂Co(dpgH)₂]₂Pz, also showed a poor CV in the reduction half.^[12] The Co^{III}/Co^{II} and Co^{II}/ Co^I values in **4** are -0.88 and -1.10 V, respectively. The Co^{II}/ Co^I reduction potential is much lower than the corresponding value in [PhCH₂Co(dpgH)₂]₂Pz (-1.41 V). This is expected because of the higher cobalt anisotropy in **4**. Similarly, the oxidation potential Co^{IV}/Co^{III} is higher (+1.33 V) in **4** than in [PhCH₂Co(dpgH)₂]₂Pz (+1.12 V).

X-ray Crystallographic Studies

Description of Structures 13 and 16

The "diamond" diagrams of molecular structures **13** and **16** along with selected numbering schemes are shown in Figures 3 and 4, respectively. Selected bond lengths, bond angles, and structural parameters are given in Table 4. The crystal structure of **13** contains two molecules in its asymmetric unit. As there is a structural variation, they are numbered as **13-I** and **13-II** and the crystal data are given separately (Table 4).^[23] Cobalt is in a distorted octahedral geometry with four nitrogen atoms of the dioxime in the equatorial plane and pyrazine and Cl axially coordinated. The cobalt atom deviates +0.013 and +0.028 Å from the

mean equatorial CoN₄ plane toward the neutral pyrazine ligand in **13-I** and **13-II**, respectively, while the deviation is -0.016 Å in **16**. The positive sign means the deviation is towards the axial base group.^[2]



Figure 3. Molecular structure of $ClCo(dmgH)_2Pz$ (13-I and 13-II) with two molecules in the asymmetric unit. The hydrogen atoms of the C–H bonds are omitted for clarity.



Figure 4. Molecular structure of $ClCo(dpgH)_2Pz$ (16). The hydrogen atoms of the C–H bonds are omitted for clarity.

The Co–Cl [2.2332(9), 2.2262(10), and 2.2185(10) Å] and Co–N5 [1.958(3), 1.967(3), and 1.961(3) Å] bond lengths in **13-I**, **13-II**, and **16** are very similar to their those of the corresponding ClCo(dioxime)₂Py cobaloximes (dioxime = dmgH or dpgH). This indicates that the bond length does not change with a slight difference in the *cis* or *trans* influence.^[2a,5] However, the Co–Cl [2.252(1) Å] and Co–N5 [1.981(3) Å] bonds are significantly longer in ClCbl.^[24]

		13	16	16·2DCM	19	$[Co(dmgH)_2(NO_2)_2]_2Ag_2^{[a]}$
	Col	Co2				
CoCl [Å]	2.2332(9)	2.2262(10)	2.2185(10)	2.2174(10)		
Co–N(ax) [Å]	1.958(3)	1.967(3)	1.961(3)	1.963(3)	1.943(3), 1.948(4)	1.937, 1.940; 1.940, 1.940
X-Co-N5 [°]	179.12	178.11	177.62(9)	179.15(9)	180	177.0, 180
<i>d</i> [Å]	+0.013	+0.028	-0.016	+0.054	0.0	0
	4.14	1.04	1.62	11.38	ca. 0	0
τ [°]	81.34	72.63	86.38	82.60	90, 0	ca. 90

Table 4. Selected bond lengths, bond angles, and structural data.

[a] Ag1-O8 2.426(6), Ag1-O10 2.428(6), Ag2-O3 2.548 (6), Ag2-O6 2.352(6), Ag2-O11 2.698(5), Ag2-O12 2.383(6), Ag2-O13 2.337(5) Å.

The pyrazine ring is almost parallel to the dioxime C–C bonds and the twist angles $(\tau)^{[25a]}$ are 81.34, 72.63, and 86.38° in **13-I**, **13-II**, and **16**, respectively. The butterfly bending angle $(a)^{[25b]}$ in **13-I** and **13-II** is 4.14 and 1.04°, respectively, while it is 1.62° in **16**.

When 16 is crystallized with dichloromethane, the singlecrystal analysis shows two dichloromethane molecules in the unit cell and its molecular structure differs from 16 (Figure S22). The Co–Cl and Co–N bond lengths are 2.2174(10) and 1.963(3) Å and comparable to the values in 16; however, *a* (11.38°) and *d* (+0.054 Å) are larger and the twist angle is smaller (82.60°). These changes are the results of crystal packing forces due to the extensive H-bonding and π -interaction.

Description of Structure 19

The characterization of **19** by X-ray analysis shows it to be $[Co(dpgH)_2(NO_2)_2]Na$ (Figure 5). An extensive hydrogen-bonding network results in large solvent-accessible voids of about 211 Å³.

The crystal structure contains two cobaloxime molecules in its asymmetric unit and has two Na⁺ as counter cations. The two cobaloxime molecules are structural isomers and differ only in their orientation of the NO₂ group; one is above the dioxime unit [with a Co–N_{ax} distance of 1.943(3)] and the other is above the O–H···O unit [Co–N_{ax} distance 1.948(4) Å]. Of the two units, one has a positional disorder of the NO₂ group attached to Co2. The Co–NO₂ distances are comparable to those of NO₂Cbl [1.942(6) Å]^[24] and $[Co(dmgH)_2(NO_2)_2]^-$ [1.945(3) Å]^[26] indicates no *cis* influence.

Description of the Structure of $[Co(dmgH)_2(NO_2)_2]_2$ - $[Ag]_2 \cdot H_2O$

The molecular structure shows the silver atoms in two distinct environments: a pseudo-four-coordinate and a pseudo-five-coordinate arrangement are displayed. A "diamond" picture of the unique portion of this structure is shown in Figure 6. Two cobaloxime units are repeated in three dimensions, linked by bridging Ag atoms, to form a 3D coordination polymer. The two silver atoms are in different coordination spheres: one is in a tetrahedral environment and the other is in a capped trigonal environment, as demonstrated in Figure 7.

We see two crystallographically inequivalent silver centers arranged linearly, whose differences arise from the binding mode of Ag. Ag1 is in a tetrahedral environment bridged by four oxygen atoms; two sets of symmetry-equivalent oxygen atoms are present. One set belongs to two nitro groups and the other set to two dioxime units. The Ag1– O bond lengths are 2.426(6) and 2.428(6) Å, respectively.



Figure 5. Molecular structure of $[Co(dpgH)_2(NO_2)_2]Na$ (19). Counter cations and hydrogen atoms of the C–H bonds are omitted for clarity.



Figure 6. Molecular structure of [Co(dmgH)₂(NO₂)₂]₂[Ag]₂·H₂O.



Figure 7. Ag1 and Ag2 coordination environment in $[Co(dmgH)_2\text{-}(NO_2)_2]_2[Ag]_2\text{-}H_2O.$

Ag2 has a (3+1) capped trigonal coordination sphere with four oxygen atoms. Three short bonds [Ag2–O6 2.352(6), Ag2–O12 2.383(6), Ag2–O13 2.337(5) Å] with bridging NO₂ groups and a water molecule form the trigonal geometry (slightly deviated from the planar geometry). The longer bond Ag2–O3 [2.548(6) Å] is with the dioxime oxygen atom; O11 acts like a chelating atom and has a weak interaction with Ag2 at a distance of 2.698(6) Å to generate a five-member silver-containing ring.^[27]

In the solid state, these tetrahedral building blocks and cobaloxime units are linked together by the oxygen atom of the coordinated nitro group into a novel 2D helical structure along the *a*-axis. A right-handed helix present in the crystal structure is shown in Figure 8a. The helix is formed through four Ag–O bonding interactions (O8–Ag1–O8 and O6–Ag2–O12) along the 2_1 screw axis (Figure 8b). Only one of the oxygen atoms of each nitro group takes part in the formation of the helix. Each coil of the helix contains six cobaloxime residues and six Ag atoms and the distance between the coils is 42.91(1) Å. Also it shows a 2D metalorganic framework (Figure S23) and an infinite zigzag coordination polymer (Figure S24).



Figure 8. (a) Space-filling view of the right-handed helix of $[Co(dmgH)_2(NO_2)_2]_2[Ag]_2 \cdot H_2O$. (b) 2D helical assembly along the *a*-axis. Some of the atoms have been omitted for clarity.

Conclusions

Procedures were developed for the synthesis of monoand dinuclear inorganic cobaloximes with pyrazine. The changes observed in NMR and CV are much more prominent than in organocobaloximes and these are more effectively rationalized with the field effect, a model proposed recently by us. Electron delocalization throughout the two metallabicycles through pyrazine is observed in the NMR and CV studies. $[XCo(dioxime)_2]_2-\mu$ -Pz complexes are more difficult to reduce than $XCo(dioxime)_2$ Pz. Mononuclear pyrazine complexes behave similarly to the corresponding pyridine complexes. $[Co(dmgH)_2(NO_2)_2]_2[Ag]_2\cdot H_2O$ shows two Ag^I ions in different environments: one is tetrahedral whereas the other is in a capped trigonal coordination, and the metal-organic framework in this molecule shows helical structure.

Experimental Section

General: Cobalt chloride hexahydrate, dimethylglyoxime (SD Fine Chemicals, India), and pyrazine (Aldrich Chemical Company) were used as received. Diphenylglyoxime (Lancaster Chemicals) was washed with methanol before use. Silica gel (100-200 mesh) and distilled solvents were used in all chromatographic separations. ClCo(dmgH)₂H₂O,^[28] ClCo(dpgH)₂H₂O,^[29] ClCo(dmgH)₂Pz,^[18] and ClCo(dpgH)₂Pz^[18] were prepared according to the literature procedure. ¹H and ¹³C NMR spectra were recorded with a JEOL JNM LA 400 FT NMR spectrometer (400 MHz for ¹H and 100 MHz for ¹³C) in CDCl₃ solution with TMS as internal standard. NMR spectroscopic data are reported in ppm. UV/Vis spectra were recorded with a JASCO V-570 spectrophotometer in dichloromethane (dry) and methanol (dry) at 298 K. IR spectra were recorded with KBr pellets in the range 4000–650 cm⁻¹ using a Vertex-70 Bruker Spectrophotometer. Elemental analysis was carried out at the Regional Sophisticated Instrumentation Center, Lucknow (see Table ST1). Cyclic voltammetry measurements were carried out using a BAS Epsilon Electrochemical workstation with platinum working electrode, Ag/AgCl reference electrode (3 M KCl), and a platinum wire counter electrode. All the measurements were performed in 0.1 M $nBu_4N(PF_6)$ in dichloromethane (dry) at a concentration of 1 mm of each complex. In addition, in a separate series of experiments, an internal reference system (ferrocene/ferrocenium ion) was used. Under the conditions used, the reversible Fc/Fc⁺ potential occurred at 0.51 V versus the Ag/AgCl electrode. X-ray Structural Determination and Refinement: Orange crystals were obtained by slow evaporation of the solvent {acetone/hexane for 13 and 16; chloroform/methanol/hexane for 19; dichloromethane/acetone for [Co(dmgH)₂(NO₂)₂]₂[Ag]₂·H₂O}. Single-crystal Xray data were collected at 100 K with a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallogra*phy*.^[30a] The data integration and reduction were processed with SAINT^[31] software. An empirical absorption correction was applied to the collected reflections with SADABS^[32] using XPREP.^[33] All the structures were solved by direct methods using SIR-97^[34] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97^[30b] program package. All non-hydrogen atoms were refined anisotropically in all the structures. The hydrogen atoms of the OH group of oxime were located on difference Fourier maps and were constrained to those difference Fourier map positions. The hydrogen atom positions or thermal parameters were not refined but were included in the structure factor calculations. The pertinent crystal data and refinement parameters are compiled in Table 5. CCDC-299539, -299540, -299541, -299543, and -299544 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cam-

Synthesis

data_request/cif.

[ClCo(dmgH)₂]₂-µ-Pz (1): Pyrazine (0.14 mmol, 0.01 g), dissolved in acetone (1 mL), was added to a clear brown solution of

bridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/

Table 5. Crystal data and structure refinement details.

	13	16	19	[Co(dmgH) ₂ (NO ₂) ₂]Ag
Empirical formula	$(C_{12}H_{18}Cl_1Co_1N_6O_4)_2$	C ₃₂ H ₂₆ Cl ₁ Co ₁ N ₆ O ₄	C ₂₉ H ₂₄ Co ₁ N ₆ Na _{1.5} O ₁₄	C ₂₄ H ₄₆ Ag ₃ Co ₃ N ₁₈ O ₂₆
Formula mass	809.41	652.97	773.96	1503.19
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_{1}/c$	$P\bar{1}$	C2/c
a [Å]	10.0217(7)	9.953(7)	9.6382(10)	23.6052(24)
b [Å]	21.7874(16)	24.6908(16)	12.9620(13)	15.5292(17)
c [Å]	15.5993(11)	11.8723(8)	16.5136(17)	14.3357(15)
a [°]	90	90	73.438(2)	90
β[°]	107.352(10)	102.212(10)	83.668(2)	115.993(2)
γ [°]	90	90	75.135(2)	90
V [Å ³]	3251.0(4)	2852(2)	1909.7(3)	4723.4(8)
Z	4	2	2	4
$\rho_{\rm calcd.} [\rm mg m^{-3}]$	1.654	1.521	1.346	2.114
$\mu \text{ [mm^{-1}]}$	1.251	0.746	0.535	2.355
F (000)	1664	1344	791	2984
Crystal size [mm]	$0.31 \times 0.23 \times 0.21$	$0.32 \times 0.25 \times 0.21$	$0.26 \times 0.19 \times 0.16$	$0.32 \times 0.17 \times 0.12$
Index ranges	$-8 \le h \le 13,$	$-12 \le h \le 13,$	$-12 \le h \le 10,$	$-23 \le h \le 31,$
	$-28 \le k \le 28,$	$-32 \le k \le 31,$	$-17 \le k \le 15,$	$-20 \le k \le 14,$
	$-20 \le l \le 19$	$-15 \le l \le 9$	$-19 \le l \le 21$	$-18 \le l \le 19$
Reflections collected	20450	18797	12682	15455
Independent reflections	7392	7024	9048	5832
Gof on F^2	1.046	1.101	1.056	1.116
Final R indices	$R_1 = 0.0510$	$R_1 = 0.0528$	$R_1 = 0.0866$	$R_1 = 0.0650$
$[I > 2\sigma(I)]$	$wR_2 = 0.1137$	$wR_2 = 0.1070$	$wR_2 = 0.2173$	$wR_2 = 0.1188$
R indices (all data)	$R_1 = 0.0748$	$R_1 = 0.0787$	$R_1 = 0.1119$	$R_1 = 0.1007$
	$wR_2 = 0.1273$	$wR_2 = 0.1414$	$wR_2 = 0.2449$	$wR_2 = 0.1522$
Data/restraints/parameters	7392/0/441	7024/0/397	9048/0/488	5832/0/342

FULL PAPER

ClCo(dmgH)₂H₂O (7) (0.29 mmol, 0.10 g in 10 mL of MeOH). An immediate precipitation occurred. The solution was stirred for several hours to ensure complete precipitation. The yellow precipitate was filtered, washed with acetone, and dried in vacuo over phosphorus pentoxide. Yield 0.091 g (89%) with respect to pyrazine.

 $[ClCo(dpgH)_2]_2-\mu-Pz$ (4): The same procedure as in 1 was used except that $ClCo(dpgH)_2H_2O$ (10) (0.20 g, 0.34 mmol) was dissolved in acetone (2 mL) and methanol (1 mL). Yield 0.096 g (49%) with respect to pyrazine.

[XCo(dioxime)₂]₂- μ -Pz (2, 3, 5, 6). (a): A solution of NaNO₂ (0.03 g, 0.43 mmol) in water (2 mL) was added to a refluxing suspension of 4 (0.53 g, 0.43 mmol) in methanol (30 mL). The reaction mixture was further refluxed for 0.5 h. The solvent was evaporated to 2–5 mL. The product isolated was a salt and did not contain the pyrazine unit. (b): The complexes were prepared from the corresponding aqua complexes according to the method outlined for 1 and 4 (Scheme 2).



Scheme 2.

XCo(dmgH)₂H₂O (8, 9):^[35] These compounds were synthesized by the nucleophilic substitution of the chlorido ligand by X⁻ in ClCo(dmgH)₂H₂O (7). In a typical experiment, a solution of NaNO₂ (0.03 g, 0.43 mmol) in water (2 mL) was added to a refluxing suspension of ClCo(dmgH)₂H₂O (7) (0.15 g, 0.43 mmol) in methanol (30 mL). The reaction mixture was further refluxed for 0.5 h. The solvent was evaporated to 2–5 mL and a sufficient amount of water was added to precipitate the compound; the precipitate was filtered and dried over phosphorus pentoxide. Yield (0.12 g, 77%).

XCo(dpgH)₂H₂O (11, 12): The same procedure as outlined for XCo(dmgH)₂H₂O was used. Two products, a salt and the desired compound **11**, were formed. The salt was identified as [Co-(dpgH)₂(NO₂)₂] by X-ray crystallography (**19**). However, when a dilute solution of NaNO₂ (0.03 g, in 10 mL) was treated with ClCo(dpgH)₂H₂O (**10**) (0.25 g, 0.43 mmol) in methanol/acetone (1:1, 30 mL) (**11**), the desired product was formed exclusively. Yield (0.145 g, 71%).

XCo(dmgH)₂Pz (13–15): Pyrazine (0.084 g, 1.05 mmol) dissolved in acetone (5 mL) was added to a clear brown solution of

 $N_3Co(dmgH)_2H_2O$ (0.34 g, 1.00 mmol) in acetone (70 mL). The solution was stirred for 1 h and kept aside for slow evaporation of the solvent. The needle-shaped brown crystals, formed after 2–3 d, were filtered and air-dried. Yield 60%. (a): When acetone was less than 70 mL, an immediate precipitation occurred and the compound identified was the dinuclear complex 3 (see above). (b): The use of methanol always led to the formation of a mixture of mono-and dinuclear complexes.

 $XCo(dpgH)_2Pz$ (16–18): These were prepared from the corresponding aqua complexes according to the method outlined for 13–15. Yield 80%.

Heterodimetallic Complexes

Reaction of Cu^IX (X = BF₄, PF₆, ClO₄) with ClCo(dmgH)₂Pz: When CuBF₄ was added dropwise to ClCo(dmgH)₂Pz (13) (both taken in dry dichloromethane), a dark red precipitate formed, which was completely insoluble in dichloromethane. (A similar kind of precipitation occurred with other Cu^I salts also.) The precipitate dissolved instantaneously upon the addition of 2–3 drops of acetonitrile and the color changed to yellow. The precipitate was totally insoluble in most noncoordinating solvents and hence it could not be characterized by CV, NMR spectroscopy, or crystallographic studies.

Reaction of Ag^{I}(PF_{6}) with XCo(dmgH)₂Pz: The addition of Ag^{I} to 13 or 16 in dichloromethane/acetone immediately formed a white precipitate of AgCl, whereas the addition of an acetone solution of AgPF₆ to 14 gave an orange-yellow precipitate. In an effort to grow a single crystal by the layering process, most of the salt precipitated from the solution but a few orange crystals appeared on the inside wall of the tube. X-ray analysis of one of these crystals showed it to be [Co(dmgH)₂(NO₂)₂][Ag]₂H₂O. The complex may have formed during the crystallization process or because of a small impurity of [Co(dmgH)₂(NO₂)₂]Na in 14. However, this compound can be reproduced with addition of an AgPF₆ solution to [Co(dmgH)₂-(NO₂)₂]Na salt in acetone.

Attempted Synthesis of Mixed Dicobaloximes ClCo(dmgH)2-Pz-Co(dpgH)₂Cl (20): The synthesis of 20 turned out to be unexpectedly complicated. The procedure used in the synthesis of 1-6 did not afford the required product, for example the reaction of 10 with 13 (1:1) or the reaction of 7 with 16 (1:1) in chloroform formed 4 instead of the desired complex (20). The same reactions in acetone/ methanol afforded 1 as the exclusive product. It is very difficult to offer any conclusive evidence for the formation of 4 or 1. It is, however, possible that 4 is thermodynamically the more stable product and arises from the intermediate ClCo(dpgH)2-Pz-Co(dmgH)₂Cl, a kinetically controlled product. [We have, however, not been able to isolate this compound, even at low temperatures (see Scheme S1).] Similarly, all efforts to synthesize other combinations like ClCo(dmgH)₂-Pz-Co(dpgH)₂nPr and MeCo(dmgH)₂-Pz-Co(dpgH)₂Cl also failed, although many procedures were tried (see Supporting Information).

Supporting Information (see footnote on the first page of this article): Representative figures of UV/Vis, IR, NMR spectra, and X-ray metal-organic framework for the subject compounds.

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