

## Chromium(II) reduction of halogenocobaloximes containing coordinated pyridine or pyridinecarboxamides : kinetics and mechanism

A. Dayalan<sup>a\*</sup> and V. R. Vijayaraghavan<sup>b</sup>

<sup>a</sup>Department of Chemistry, Loyola College (Autonomous), Chennai-600 034, India

E-mail : adsgp@loyolacollege.edu

<sup>b</sup>Department of Physical Chemistry, University of Madras, Chennai-600 025, India

Manuscript received 23 March 2004, accepted 30 August 2004

The kinetics of chromium(II) reduction of complexes of the type *trans*-[Co(dmgh)<sub>2</sub>(L)X], where dmgh<sup>-</sup> = dimethylglyoximate; L = pyridine (py), nicotinamide (nic-CONH<sub>2</sub>) or isonicotinamide (isonic-CONH<sub>2</sub>), and X<sup>-</sup> = Cl<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup>, was studied in 10% (v/v) CH<sub>3</sub>OH-H<sub>2</sub>O at 27 ± 0.1°C and I = 0.25 mol dm<sup>-3</sup> (LiClO<sub>4</sub>) in the [H<sup>+</sup>] range 0.0001–0.100 mol dm<sup>-3</sup> under pseudo first-order conditions using an excess of the reductant. The inverse dependence of rate on [H<sup>+</sup>] suggests an equilibrium between the protonated and unprotonated forms of the complex, the protonated form reacting slower than the unprotonated form. The rate constants are in the order Cl<sup>-</sup> < Br<sup>-</sup> < I<sup>-</sup> and py ≈ nic-CONH<sub>2</sub> ≈ isonic-CONH<sub>2</sub> for the axial ligands. These observations suggest an inner-sphere mechanism for the reduction of the complexes with bridging by Cr<sup>II</sup> at the oxime-oxygen. Product analysis, done by the cation-H<sup>+</sup> exchange method further supports this conclusion.

Cobalt(III) complexes of dimethylglyoxime, commonly known as cobaloximes, have been extensively studied as model compound<sup>1</sup> for vitamin-B<sub>12</sub>. Cobaloximes exhibit greater tendency for electron-transfer reactions. Kinetics of iron(II) reduction of some cobaloximes showed a rate dependence<sup>2</sup> on [H<sup>+</sup>], indicating the possibility of inner-sphere electron-transfer to cobalt(III). However, it should be of interest to investigate the nature of bridging site when cobalt(III)-dioximes, containing additional ligands with proven bridging efficiency<sup>3</sup> are reduced by powerful reducing agents like Cr<sup>II</sup>. Hence, a study of the kinetics of reduction of cobalt(III)-dioximes containing axial ligands like halide, pyridine or a pyridine carboxamide should be able to ascertain the competitive efficiency of the ligands as the bridging group. This report is a study of the chromium(II) reduction of the complexes of the type *trans*-[Co(dmgh)<sub>2</sub>(L)X].

### Results and discussion

**Kinetic studies :** The kinetics of chromium(II) reduction of all complexes were studied in 10% (v/v) CH<sub>3</sub>OH-H<sub>2</sub>O at 360 nm (where the complexes showed appreciable absorbance and the products showed negligible absorbance) under pseudo first-order conditions, with excess of chromium(II) over the complex as a function of hydrogen ion concentration in the range 0.0001–0.100 mol dm<sup>-3</sup> in nitrogen atmosphere. A linear dependence of pseudo first-order rate constant, *k*<sub>obs</sub>, on Cr<sup>II</sup> was observed. Plot of *k*<sub>obs</sub> vs [H<sup>+</sup>] gave straight lines passing through origin for all complexes indicating no backward or self decomposition reactions. The second-order rate constants, *k* were obtained by dividing *k*<sub>obs</sub> by the concentration of Cr<sup>II</sup> used (Table 1).

It is found that the rate shows an inverse dependence on [H<sup>+</sup>] for all complexes reaching a limiting value at [H<sup>+</sup>] =

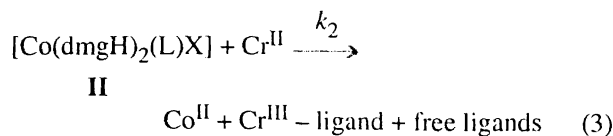
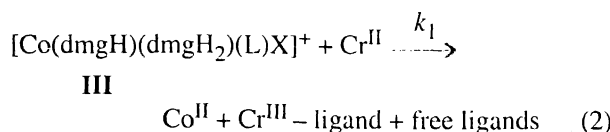
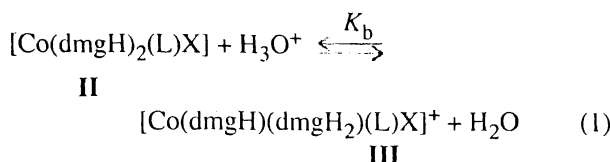
**Table 1.** Second-order rate constants, *k* (dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) for the chromium(II) reduction of halogenopyridinecarboxamidebis(dimethylglyoximate)cobalt(III) complexes as a function of hydrogen ion concentration in 10% (v/v) CH<sub>3</sub>OH-H<sub>2</sub>O at 27 ± 0.1°C

[Complex] = 4.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, [Cr<sup>II</sup>] = 2.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, I = 0.25 mol dm<sup>-3</sup> (LiClO<sub>4</sub>)

Complex	[H <sup>+</sup> ] × 10 <sup>4</sup> /mol dm <sup>-3</sup>											
	2	4	6	8	10	40	80	200	400	600	800	1000
[Co(dmgh) <sub>2</sub> (py)Cl]	21.67	21.36	21.07	20.79	20.53	17.67	15.58	14.42	11.57	10.53	9.80	9.69
[Co(dmgh) <sub>2</sub> (nic-CONH <sub>2</sub> )Cl]	21.93	21.58	21.26	20.94	20.67	17.85	16.35	14.90	11.73	10.77	10.15	9.99
[Co(dmgh) <sub>2</sub> (isonic-CONH <sub>2</sub> )Cl]	23.61	23.21	22.83	22.48	22.15	18.73	16.42	15.38	12.37	11.26	10.94	10.59
[Co(dmgh) <sub>2</sub> (isonic-CONH <sub>2</sub> )Br]	26.89	26.03	25.32	24.64	24.07	19.58	17.97	17.23	14.96	14.00	13.66	13.35
[Co(dmgh) <sub>2</sub> (isonic-CONH <sub>2</sub> )I]	30.17	28.85	27.74	26.80	25.99	20.44	19.52	19.09	16.55	15.74	15.38	15.12

0.100 mol dm<sup>-3</sup>. Moreover, the decrease in the second-order rate constant with increase in [H<sup>+</sup>] from 0.0001 to 0.100 mol dm<sup>-3</sup> is about 50–55% of the initial value. For example, the second-order rate constant for the chromium(II) reduction of *trans*-[Co(dmgH)<sub>2</sub>(py)Cl] decreases from 21.67 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at [H<sup>+</sup>] = 0.0001 mol dm<sup>-3</sup> to 9.69 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at [H<sup>+</sup>] = 0.100 mol dm<sup>-3</sup>. The magnitude of change in rate constant with [H<sup>+</sup>] is too large to be attributed to medium effects. Medium effects cause<sup>4</sup> a change in rate about 10–20%.

This behavior is similar to that reported in earlier studies<sup>2</sup> for the iron(II) reduction of cobaloximes. It has been proved that the [H<sup>+</sup>] dependence is not a medium effect, but arises due to acid-base dissociation equilibria, involving the oxime in the complex. Hence, the following reaction sequence may be proposed :



Accordingly, the rate equation may be written as

$$\text{Rate} = k_1 [\text{Co(dmgH)(dmgH}_2\text{(L)X)}^+ [\text{Cr}^{\text{II}}] + k_2 [\text{Co(dmgH)}_2\text{(L)X}] [\text{Cr}^{\text{II}}] \quad (4)$$

Hence, the second-order rate constant, *k* for the reduction of cobaloximes may be expressed in the form :

$$k = \frac{k_1 K_b [\text{H}^+]}{K_b [\text{H}^+] + 1} + \frac{k_2}{K_b [\text{H}^+] + 1} \quad (5)$$

where *K<sub>b</sub>* is the protonation constant and *k<sub>1</sub>* and *k<sub>2</sub>* are the second-order rate coefficients for the reduction of the protonated (III) and unprotonated (II) forms of the complex, respectively.

Eq. (5) may be reduced to eqs. (6) and (7) at high and at low hydrogen ion concentrations, respectively as follows :

$$k = k_1 + \frac{k_2}{K_b [\text{H}^+]} \quad (6)$$

$$k = k_1 K_b [\text{H}^+] + k_2 \quad (7)$$

Hence, according to eq. (6), plot of the second-order rate constants, *k* vs [H<sup>+</sup>]<sup>-1</sup> at high [H<sup>+</sup>] values (0.02–0.10 mol dm<sup>-3</sup>) gave straight lines (Fig. 1) for all complexes, from which the *k<sub>1</sub>* values were obtained from the intercept. Simi-

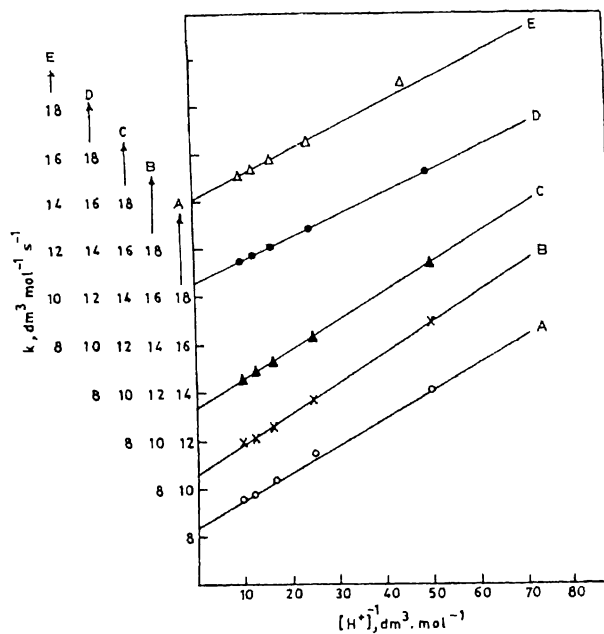
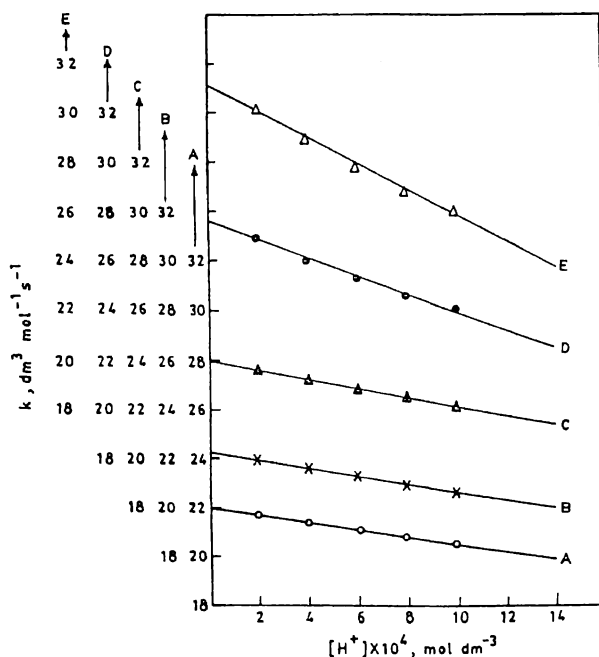


Fig. 1. Chromium(II) reduction of cobalt(III) complexes in 10% (v/v) CH<sub>3</sub>OH-H<sub>2</sub>O at 27 ± 0.1°C. [Complex] = 4.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, [Cr<sup>II</sup>] = 2 × 10<sup>-3</sup> mol dm<sup>-3</sup>, I = 0.25 mol dm<sup>-3</sup> (LiClO<sub>4</sub>). Effect of variation of [H<sup>+</sup>] on the second-order rate constant, *k*: (A) [Co(dmgH)<sub>2</sub>(py)Cl], (B) [Co(dmgH)<sub>2</sub>(nic-CoNH<sub>2</sub>)Cl], (C) [Co(dmgH)<sub>2</sub>(isonic-CoNH<sub>2</sub>)Cl], (D) [Co(dmgH)<sub>2</sub>(isonic-CoNH<sub>2</sub>)Br], (E) [Co(dmgH)<sub>2</sub>(isonic-CoNH<sub>2</sub>)I].

larly the *k<sub>2</sub>* values were evaluated, based on eq. (7), as the intercept of the plot of the second-order rate constants, *k* vs [H<sup>+</sup>] at low [H<sup>+</sup>] values viz. 0.0001–0.001 mol dm<sup>-3</sup> (Fig. 2). The values of *K<sub>b</sub>* were calculated by substituting the values of *k<sub>1</sub>*, obtained from eq. (6), in to the slope of eq. (7). The ratio of *k<sub>2</sub>/K<sub>b</sub>*, thus calculated, agrees well with the slope of eq. (6) for all complexes confirming the validity of the method used. For example, the ratio *k<sub>2</sub>/K<sub>b</sub>* for [Co(dmgH)<sub>2</sub>(py)Cl] is 0.1265, whereas the slope of eq. (6) for the same complex is 0.1205. Moreover, the product of the slopes of eqs. (6) and (7) agrees well with the product of the corresponding intercepts of eq. (6) and (7) for all complexes (Table 2).

Excellent straight fittings, with correlation coefficients ranging from 0.95 to 1.0, were also observed when the second-order rate constants, *k* at the corresponding [H<sup>+</sup>] values were fitted suitably in eqs. (6) and (7) using a suitable



**Fig. 2.** Chromium(II) reduction of cobalt(III) complexes in 10% (v/v) CH<sub>3</sub>OH-H<sub>2</sub>O at 27 ± 0.1°C. [Complex] = 4.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, [Cr<sup>II</sup>] = 2 × 10<sup>-3</sup> mol dm<sup>-3</sup>, I = 0.25 mol dm<sup>-3</sup> (LiClO<sub>4</sub>). Effect of variation of [H<sup>+</sup>] on the second-order rate constant, *k*: (A) [Co(dmgh)<sub>2</sub>(py)Cl], (B) [Co(dmgh)<sub>2</sub>(nic-CoNH<sub>2</sub>)Cl], (C) [Co(dmgh)<sub>2</sub>(isonic-CoNH<sub>2</sub>)Cl], (D) [Co(dmgh)<sub>2</sub>(isonic-CoNH<sub>2</sub>)Br], (E) [Co(dmgh)<sub>2</sub>(isonic-CoNH<sub>2</sub>)I].

**Table 2.** Second-order rate coefficients, *k*<sub>1</sub> and *k*<sub>2</sub> (dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) and protonation constant *K*<sub>b</sub> (dm<sup>3</sup> mol<sup>-1</sup>) for the chromium(II) reduction of halogenopyridinecarboxamidebis(dimethylglyoximate)cobalt(III) complexes in 10% (v/v) CH<sub>3</sub>OH-H<sub>2</sub>O at 27 ± 0.1°C [Complex] = 4.0 × 10<sup>-4</sup> mol dm<sup>3</sup>, [Cr<sup>II</sup>] = 2.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, I = 0.25 mol dm<sup>-3</sup> (LiClO<sub>4</sub>)

Complex	<i>k</i> <sub>1</sub>	<i>k</i> <sub>2</sub>	<i>K</i> <sub>b</sub>
[Co(dmgh) <sub>2</sub> (py)Cl]	8.44	21.95	173.55
[Co(dmgh) <sub>2</sub> (nic-CoNH <sub>2</sub> )Cl]	8.62	22.25	190.94
[Co(dmgh) <sub>2</sub> (isonic-CoNH <sub>2</sub> )Cl]	9.35	23.98	221.55
[Co(dmgh) <sub>2</sub> (isonic-CoNH <sub>2</sub> )Br]	12.47	27.58	299.10
[Co(dmgh) <sub>2</sub> (isonic-CoNH <sub>2</sub> )I]	14.10	31.20	397.78

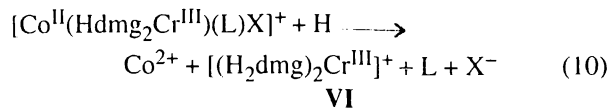
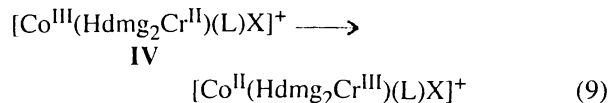
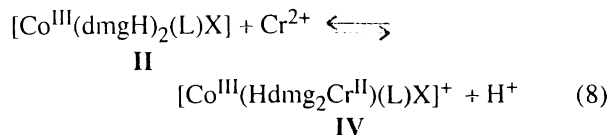
program in C++. The various parameters viz. *k*<sub>1</sub>, *k*<sub>2</sub> and *K*<sub>b</sub> thus computed agreed well with those obtained graphically.

It may be noted that eq. (5) represents the extent to which the second-order rate coefficients *k*<sub>1</sub> and *k*<sub>2</sub> contribute to the overall second-order rate constant, *k* for the reaction at different [H<sup>+</sup>]. For example, the fractional contribution of *k*<sub>1</sub> to the second-order rate constant, *k* for [Co(dmgh)<sub>2</sub>(py)Cl] in the [H<sup>+</sup>] range 2 × 10<sup>-4</sup>–1 × 10<sup>-1</sup> vary from 0.021 to 0.907 and that of *k*<sub>2</sub> in the reverse order viz. 0.979 to 0.093 for the same [H<sup>+</sup>] range. Moreover, the magnitude of

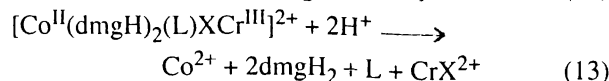
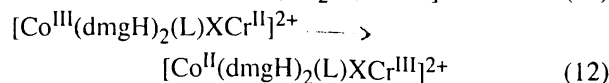
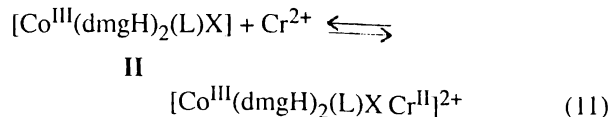
the second-order rate coefficients *k*<sub>1</sub> and *k*<sub>2</sub> follows the order *k*<sub>1</sub> < *k*<sub>2</sub>, with *k*<sub>2</sub> values being more sensitive to halide variation than the *k*<sub>1</sub> values, suggesting a greater sensitivity to halide variation for the unprotonated form (II) of the complex. The *k*<sub>2</sub> values follow the trend in rates Cl<sup>-</sup> < Br<sup>-</sup> < I<sup>-</sup> for the axial halogen complexes and py ≈ nic-CoNH<sub>2</sub> ≈ isonic-CoNH<sub>2</sub> for the substituted pyridine. The observed [H<sup>+</sup>] dependence of *k* and the values of *k*<sub>1</sub> and *k*<sub>2</sub> indicate that the unprotonated form (II) is reduced at a faster rate than the protonated form (III). Such behavior is characteristics of an inner-sphere reaction.

Hence, the chromium(II) reduction of the unprotonated form (II) of the cobaloximes may be considered stepwise as :

*Oxime bridged chromium(II) reduction of unprotonated (II) complexes :*

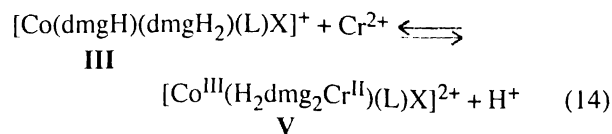


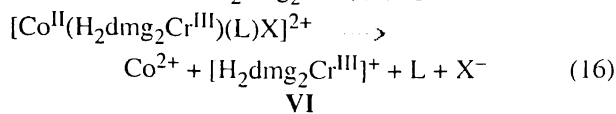
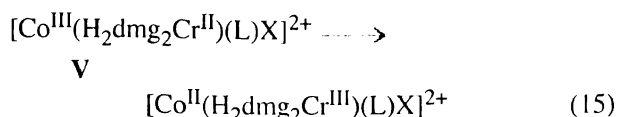
*Halogen bridged chromium(II) reduction of unprotonated (II) complexes :*



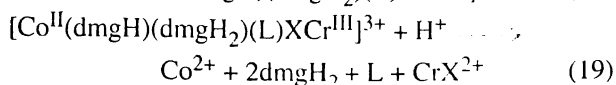
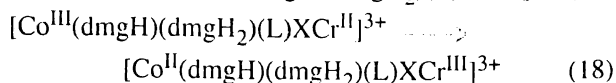
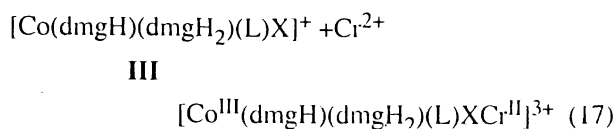
Similarly, the reaction scheme for chromium(II) reduction of the protonated form (III) of the cobaloximes may be written as :

*Oxime bridged chromium(II) reduction of protonated (III) complexes :*





Halogen bridged chromium(II) reduction of protonated (III) complexes :



The equilibrium constants for the formation of the precursor (eqs. (8) and (11)) should be greater for the unprotonated form than for the protonated form of the complex (eqs. (14) and (17)). Such mode of binding of the metal ion to the coordinated oxime has been reported in literature<sup>5</sup>. Eqs. (10), (13) and (19) represent the fast dissociation of the successor complexes followed by the protonation of the oxime liberated.

**Product analysis :** The product analysis was carried out in 10% (v/v) CH<sub>3</sub>OH-H<sub>2</sub>O medium. The first fraction, eluted with water, contained 25–35% free oxime but no chromium (Table 3). Typical UV spectra of this fraction (10 ml aliquots collected at different intervals of elution) are shown in Fig. 3(a). This fraction also found to contain free halides to the extent of 65–75% estimated as silver halides. Hence, the considerable percentage of free oxime and halides detected in this fraction may be attributed to partial halide bridging.

The second fraction, obtained by eluting with 0.5 mol

dm<sup>-3</sup> HClO<sub>4</sub> contained 95–100% pyridine or pyridine carboxamides indicating that the amide group of pyridine carboxamides is not very much involved in bridging. The UV spectra of different aliquots are shown in Fig. 3(b). Cobalt analysis of this fraction showed more than 95% Co<sup>II</sup> and chromate analysis of the same second fraction indicated about 20–30% Cr<sup>III</sup> (Table 3) which could be due to CrX<sup>2+</sup>. High percentages of pyridine or pyridine carboxamides detected in the second fraction suggests that amide bridging is negligible.

The third fraction, eluted with 1.0 mol dm<sup>-3</sup> HClO<sub>4</sub>, showed characteristic UV spectra common for all complexes [Fig. 3(c)] which could be attributed to Cr-dioxime. The molar ratio of chromium to oxime was found to be 1 : 2 (Table 3) confirming the formula (VI) proposed for the product formed as a result of chromium(II) bridging with the cobalt(III) complex at oxime.

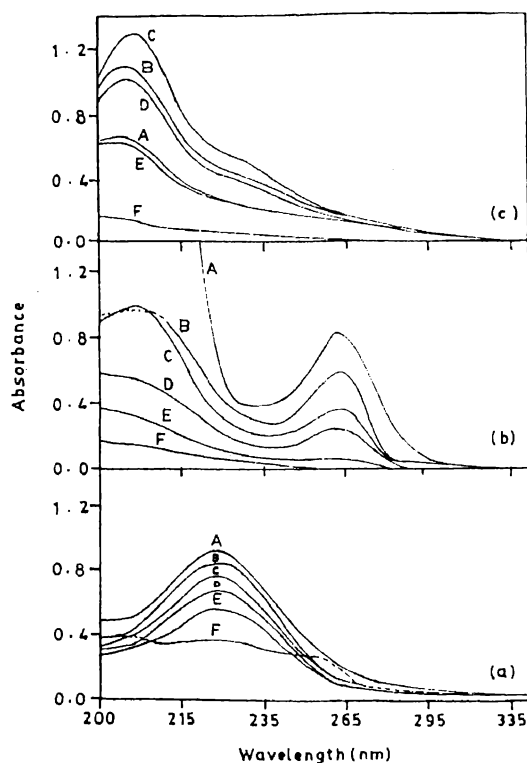
Hence, the inverse [H<sup>+</sup>] dependence on the rate of reduction, and the product analysis suggest that the chromium(II) reduction of the cobalt(III)-dioxime proceeds predominantly through oxime bridging possibly with partial halide and negligible amide bridging.

**Bridging efficiency of the ligands in cobaloximes :** The hard and soft acid characteristics of the metal ions in their complexes can be considered as the basis to explain the reactivities of the cobalt(III) complexes. For examples, the rates of halogen bridged inner-sphere chromium(II) reductions of the soft acids [Ru(NH<sub>3</sub>)<sub>5</sub>X]<sup>2+</sup> and [Rh(NH<sub>3</sub>)<sub>5</sub>X]<sup>2+</sup> followed the order<sup>6</sup> of reactivity : Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup>. Hence, the same order of reactivity is expected for the chromium(II) reduction of halogenocobalt(III)-dioximes, which are also soft acids, if the electron-transfer occurs through halide bridging. But, the observed order of reactivity, viz. I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup> is not in favor of electron-transfer mediated by dominant halide bridging. This is further supported by the product analysis, which indicated high percentages of free ha-

**Table 3.** Products recovered (μmole) for the chromium(II) reduction of *trans*-halogenopyridinecarboxamidebis(dimethylglyoximate)cobalt(III) complexes in 10% (v/v) CH<sub>3</sub>OH-H<sub>2</sub>O

[Complex] = 50 μmole, Cr<sup>II</sup> = 50 μmole, [H<sup>+</sup>] = 0.01 mol dm<sup>-3</sup> and *t* = 0.25 mol dm<sup>-3</sup>

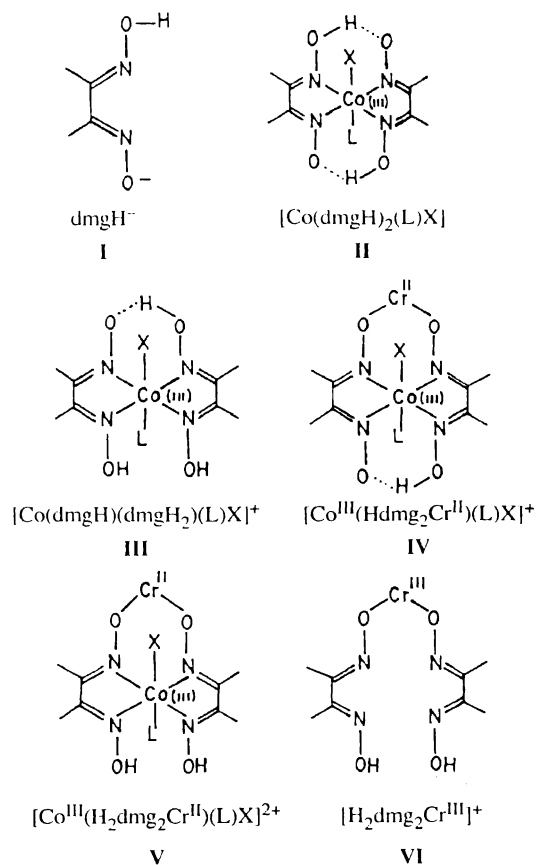
Complex	dmgH <sub>2</sub>	AgX	Cr-X <sup>2+</sup>	Pyridine (or) pyridine carboxamide	Cr-dioxime		Co <sup>II</sup>
					Oxime	Cr <sup>III</sup>	
[Co(dmgH) <sub>2</sub> (py)Cl]	23.2	38.1	11.7	49.8	76.3	38.7	47.8
[Co(dmgH) <sub>2</sub> (nic-CONH <sub>2</sub> )Cl]	26.4	37.2	12.6	49.6	73.4	36.9	48.4
[Co(dmgH) <sub>2</sub> (isonic-CONH <sub>2</sub> )Cl]	27.9	37.9	11.6	47.8	71.1	35.7	47.6
[Co(dmgH) <sub>2</sub> (isonic-CONH <sub>2</sub> )Br]	29.3	36.7	12.1	47.5	70.2	35.3	49.6
[Co(dmgH) <sub>2</sub> (isonic-CONH <sub>2</sub> )I]	35.8	34.4	15.3	47.4	64.3	31.9	47.7



**Fig. 3.** Product analysis for the chromium(II) reduction of *trans*-[Co(dmgH)<sub>2</sub>(nic-CONH<sub>2</sub>)Cl] in 10% (v/v) CH<sub>3</sub>OH. [Complex] = 1 × 10<sup>-4</sup> mol dm<sup>-3</sup> (25 ml), [Cr<sup>II</sup>] = 1 × 10<sup>-4</sup> mol dm<sup>-3</sup> (25 ml). Products eluted with (a) water, (b) 0.5 mol dm<sup>-3</sup> HClO<sub>4</sub>, (c) 1.0 mol dm<sup>-3</sup> HClO<sub>4</sub>. UV spectra of 10 ml aliquots (A-F) collected at different intervals of elution.

lides viz. 65–75% eluted in the first fraction.

The bridging efficiency of pyridine carboxamides was demonstrated<sup>5</sup> for the chromium(II) reduction of pyridine-carboxamidopentaamminecobalt(III). The second order rate constants for the amide bridged electron-transfer reaction were found to be  $3.3 \pm 0.2 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for [Co(NH<sub>3</sub>)<sub>5</sub>(nic-CONH<sub>2</sub>)]<sup>3+</sup> and  $17.4 \pm 0.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for [Co(NH<sub>3</sub>)<sub>5</sub>(isonic-CONH<sub>2</sub>)]<sup>3+</sup>. The higher rate constants for the reduction of cobalt(III) complexes of isonicotinamide have been attributed to its greater conjugation effect. Accordingly, one should expect a much higher rate constant, at least of the order of 10<sup>2</sup>, for the chromium(II) reduction of halogenocobalt(III)-dioximes containing axial isonicotinamide than the corresponding nicotinamide complex, if the reductions were mediated through the amide group. However, the observed trend in rates: py ≈ nic-CONH<sub>2</sub> ≈ isonic-CONH<sub>2</sub> suggests that the reduction of the cobalt(III) complexes through amide bridging is not predominant. This is further evidenced by high percentages viz. 95–100% of pyridine or pyridine carboxamides detected in the



second fraction in the product analysis (Table 3).

The preference for oxime bridging must provide a pathway of lower energy than bridging by the axial ligands. The Co–N bond length in cobaloximes may be considered to support this observation. The equatorial Co–N bond length in the tetraza macrocyclic complexes of cobalt(III) differs little from those in the cobalt(II) analogues<sup>7</sup>. Hence, the change from Co<sup>III</sup> to Co<sup>II</sup> in their complexes should involve minimum Franck-Condon barrier if bridging involves equatorial oxime.

### Experimental

*Preparation of the complexes* : E. Merck samples of cobalt(II) chloride, dimethylglyoxime, pyridine and pyridine carboxamides were used for the synthesis of the complexes. Cobalt(II) bromide was prepared by the addition of a calculated amount of 40% aqueous HBr to cobalt(II) carbonate and evaporating the resulting solution to dryness. All complexes were synthesised by adopting the methods reported earlier<sup>8</sup> and characterised by physical methods such as elemental analysis, UV-Visible, IR and <sup>1</sup>H NMR spectral studies.

**Preparation of chromium(II) perchlorate :** Chromium(II) perchlorate solution was prepared by the zinc amalgam reduction<sup>9</sup> of an aqueous solution of  $\text{Cr}(\text{ClO}_4)_3$ , obtained by dissolving electrolytic grade E. Merck chromium powder in  $0.2 \text{ mol dm}^{-3} \text{ HClO}_4$  in nitrogen atmosphere. The reaction completed in 3 to 4 h giving a sky blue solution of  $\text{Cr}(\text{ClO}_4)_2$ . The concentration of  $\text{Cr}^{\text{II}}$  was estimated by reaction with excess  $\text{Fe}^{\text{III}}$  solution in nitrogen atmosphere and estimating the  $\text{Fe}^{\text{II}}$  produced using standard  $\text{KMnO}_4$ . The concentration of the free acid present in the  $\text{Cr}^{\text{II}}$  solution was determined by measuring the pH of the known volume of the solution diluted suitably. Required volumes of the chromium(II) solutions were withdrawn using deaerated hypodermic syringes fitted with stainless steel needle and injected into deaerated complex solution fitted with serum cap. The chromium(II) solution was preserved under nitrogen atmosphere and fresh chromium(II) solutions were prepared frequently.

**Stoichiometric studies :** The stoichiometry of chromium(II) reduction of all the complexes was determined spectrophotometrically by estimating the amount of pyridine or pyridine carboxamide and cobalt(II) liberated for every mole of  $\text{Cr}^{\text{II}}$  added. The ratio of  $\text{Cr}^{\text{II}}$  added to pyridine (or pyridine carboxamide) and  $\text{Co}^{\text{II}}$  liberated was found to be 1 : 1 : 1 confirming the 1 : 1 stoichiometry of the reaction with respect to the reductant and the cobalt(III) complex.

**Kinetic studies :** The kinetics of chromium(II) reduction of the complexes in 10% (v/v)  $\text{CH}_3\text{OH}-\text{H}_2\text{O}$  was studied using applied photophysics model-1705 stopped flow spectrophotometer. Solutions of the complexes, perchloric acid (of the required concentration) and lithium perchlorate (to adjust the ionic strength to  $0.25 \text{ mol dm}^{-3}$ ) were deaerated and thermostated in one compartment and the  $\text{Cr}^{\text{II}}$  solution was injected and thermostated in the other deaerated compartment. The solutions were injected into the mixing chamber at a pressure of 40 psi. The reactions were followed by monitoring the decrease in absorbance of the complex at 360 nm and  $27 \pm 0.1^\circ\text{C}$  in the time scale sampling interval of 2–50 ms. The absorption output was digitalised with a data lab model 902 transient recorder, equipped with a variable input sensitivity and variable sampling interval and was monitored by Trio-model CS-1562 A oscilloscope. Several data points were collected for each run and at least six kinetic runs were made for each value of the rate constant. The data were stored and analysed by a computer. The kinetic plots were done on graphic plotter to get the pseudo first-order rate constants,  $k_{\text{obs}}$ .

**Product analysis :** To a deaerated complex solution (25

ml of  $1 \times 10^{-4} \text{ mol dm}^{-3}$ , 2.5  $\mu\text{mol}$ ), was injected a known volume of the  $\text{Cr}^{\text{II}}$  solution (2.5  $\mu\text{mol}$ ) and allowed to react for 30 s in nitrogen atmosphere. The reaction mixture was exposed to air and passed through dowex 50W-X8,  $[\text{H}^+]$  cation exchange column (3 cm and long 1 cm diameter), maintained at  $5^\circ\text{C}$  by circulating ice cold water. Gradient-elution technique, using water (50 ml),  $0.5 \text{ mol dm}^{-3} \text{ HClO}_4$  (100 ml) and  $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$  (100 ml), was employed to separate the products. The products were analysed spectrophotometrically. Typical UV spectra of various fractions, obtained at different intervals of elution, are shown in Fig. 3. However, greater quantities of the complexes (50  $\mu\text{mol}$ ) and the  $\text{Cr}^{\text{II}}$  solution (50  $\mu\text{mol}$ ) were used for the quantitative estimation of the products formed (Table 3).

The first fraction containing the free oxime, eluted at the time of charging the column followed by washing with water, was estimated spectrophotometrically ( $\lambda_{\text{max}} = 226 \text{ nm}$ ;  $\epsilon_{\text{max}} = 15400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). The halide present in this fraction was estimated gravimetrically as silver halide.

Similarly, free pyridine or pyridine carboxamides, detected in the second fraction, eluted with  $0.5 \text{ mol dm}^{-3} \text{ HClO}_4$ , were estimated from their characteristic measured UV absorptions in  $0.5 \text{ mol dm}^{-3} \text{ HClO}_4$  ( $\lambda_{\text{max}}$ , nm( $\epsilon_{\text{max}}$ ,  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )) : py = 256 (5500); nic- $\text{CONH}_2 = 263$  (5420) and isonic- $\text{CONH}_2 = 265$  (5200)}. Cobalt(II) present in this fraction was estimated as follows : The solution was neutralised with solid NaOH and evaporated to dryness. About 2 ml of 50% ammonium thiocyanate was added. The cobalt thiocyanato complex formed was extracted and made upto 100 ml with acetone. The absorbance of the solution was measured at 625 nm ( $\epsilon = 1864 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). Chromium(III), present in the third fraction, was estimated by chromate analysis and nitrogen by micro-Kjeldahl method.

### Acknowledgement

The authors are thankful to Dr. T. Balakrishnan, Head, Department of Physical Chemistry, Dr. P. Maruthamuthu, Head, Department of Energy, University of Madras, Rev. Fr. Dr. Francis M. Peter, S. J., Secretary and Rev. Fr. Dr. V. Joseph Xavier, Principal, Loyola College, Chennai.

### References

1. M. S. A. Hamza, C. D. Benfer and R. van Eldik, *Inorg. Chem.*, 2000, **39**, 3777; B. Grossman and A. Haim, *J. Am. Chem. Soc.*, 1971, **93**, 6990; C. K. Poon, *Coord. Chem. Rev.*, 1973, **10**, 1.
2. P. N. Balasubramanian and V. R. Vijayaraghavan, *Inorg. Chim. Acta*, 1980, **38**, 49.

Dayalan *et al.* : Chromium(II) reduction of halogenocobaloximes containing coordinated pyridine *etc.*

3. F. Nord Meyer and H. Taube, *J. Am. Chem. Soc.*, 1968, **90**, 1162.
4. J. H. Worrell, R. A. Goddard and R. Blauco, *Inorg. Chem.*, 1978, **17**, 3308.
5. A. Bakac and J. H. Espenson, *Inorg. Chem.*, 1980, **19**, 242; A. L. Crumbliss, J. T. Bowmann, P. L. Gas and A. T. McPhail, *J. Chem. Soc., Chem. Commun.*, 1973, 415; A. C. Dash, R. K. Nanda and K. Das, *Indian J. Chem., Sect. A*, 1991, **30**, 617.
6. N. M. Samus and A. V. Ablov, *Coord. Chem. Rev.*, 1979, **28**, 203.
7. H. A. O. Hill, "Inorganic Biochemistry", ed. G. L. Eichhorn, Elsevier, p. 1067.
8. V. R. Vijayaraghavan and A. Dayalan, *J. Indian Chem. Soc.*, 1992, **69**, 383.
9. G. Ali and N. A. Lewis, *Inorg. Chim. Acta*, 1990, **165**, 5.