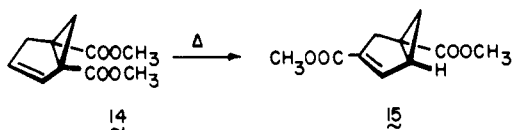


present circumstances. However, it is conceivable that more extended conjugation is able to provide stabilization modes unavailable to simpler molecules. Although this facet of [1,3] sigmatropy seems not to have been purposefully investigated, the reported conversion of **14** to **15** ( $E_a = 26.3$  kcal/mol)<sup>18</sup> serves to illustrate our conceptual analysis. An imidate group is merely the nitrogen analogue of a carboxylate ester and should be capable of comparable stabilization.



What causes **9** to be somewhat more reactive than **8**? A formal possibility derives from the earlier work of Richey and Schull<sup>19</sup> who have demonstrated that a tertiary nitrogen atom exerts an accelerating effect on the [1,3]-sigmatropic behavior of vinylcyclopropanes.

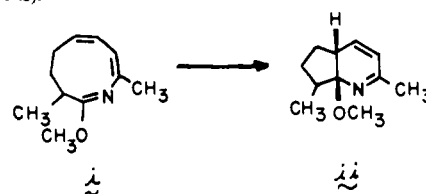
We cannot claim knowledge of the precise extent, if any, to which [1,3] sigmatropy contributes to the thermal bond relocation of **1**, but such a process must now be given explicit consideration.

**Acknowledgment.** We are grateful to the National Science Foundation and Eli Lilly and Co. for support of this research.

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Gary D. Ewing, Steven V. Ley, Leo A. Paquette\*  
 Evans Chemical Laboratories, The Ohio State University  
 Columbus, Ohio 43210  
 Received November 28, 1977

#### A Molecular Chlorine Complex of Cobalt(II). The Crystal Structure of a Dichlorine Sorption Complex of Dehydrated Cobalt(II)-Exchanged Sodium Zeolite A, Co<sub>4</sub>Na<sub>4</sub>-A·4Cl<sub>2</sub>

Sir:

Chlorine gas at ~300 Torr and at 24 (1) °C was sorbed into a single crystal of partially cobalt(II)-exchanged vacuum-dehydrated Co<sub>4</sub>Na<sub>4</sub>-A.<sup>1</sup> A crystallographic analysis indicates that four chlorine molecules are present within the unit cell of the zeolite, each complexed at one end to a cobalt(II) ion and associated at the other to a Na<sup>+</sup> ion. A nearly identical structure was found using diffraction data gathered at -165 (3) °C. The results show that the Cl<sub>2</sub> molecule behaves as a Lewis base to complex strongly, in a bent manner, to the "hard" acid cobalt(II).

The sorption of dichlorine onto cobalt(II)-exchanged zeolite A was initially done to extend work on the Br<sub>2</sub> and I<sub>2</sub> complexes<sup>2</sup> of partially cobalt(II)-exchanged zeolite A. It was anticipated that Cl<sub>2</sub>, like Br<sub>2</sub> and I<sub>2</sub>, would form a linear charge-transfer complex with oxide ions of the zeolite framework.<sup>2,3</sup>

An 85-μm single crystal of partially cobalt(II)-exchanged zeolite A, prepared by methods described before,<sup>4</sup> was lodged in a thin-walled Pyrex capillary and was dehydrated for 2 days at 5 × 10<sup>-5</sup> Torr and 350 °C. After it was allowed to cool to 24 °C, the dry crystal was exposed to ~300 Torr of Cl<sub>2</sub> gas (Matheson, 99.96%) for 1 h. The crystal, still in the chlorine atmosphere, was then sealed in its capillary by torch. It retained the deep blue color of dehydrated Co<sub>4</sub>Na<sub>4</sub>-A.

The space group *Pm3m* (no systematic absences) was used throughout this work for reasons discussed previously.<sup>5</sup> Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four-circle Syntex P1 diffractometer, equipped with a graphite monochromator and a pulse-height analyzer. Molybdenum radiation was used for all experiments ( $K\alpha_1$ ,  $\lambda = 0.70930$  Å;  $K\alpha_2$ ,  $\lambda = 0.71359$  Å). The cubic unit cell constant, as determined by a least-squares refinement of 15 intense reflections for which  $20^\circ < 2\theta < 24^\circ$ , is 12.103 (2) Å at 24 (1) °C and 12.099 (7) Å at -165 (3) °C. The 879 unique reciprocal lattice points for which  $2\theta < 70^\circ$ , were examined at 24 (1) °C. Of these only the 333 reflections for which  $I > 3\sigma(I)$  were used for structure

**Table I.** Positional, Thermal,<sup>a</sup> and Occupancy Parameters for Co<sub>4</sub>Na<sub>4</sub>-A·4Cl<sub>2</sub> at 24 (1) °C

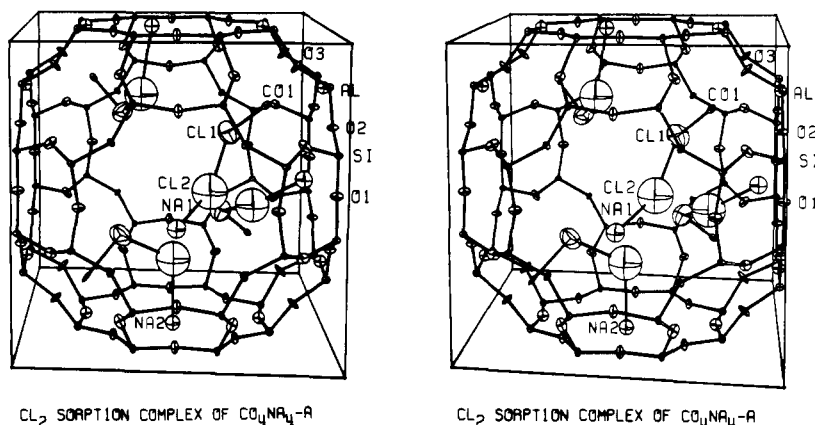
	Wyckoff position	x	y	z	$\beta_{11}^b$ or $B_{iso}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	Occupancy factor
(Si, Al)	24 (k)	0	1819 (2)	3668 (2)	31 (2)	25 (2)	14 (2)	0	0	6 (3)	1 <sup>c</sup>
O(1)	12 (h)	0	2033 (9)	1/2	79 (10)	78 (12)	27 (7)	0	0	0	1
O(2)	12 (i)	0	3014 (5)	3014 (5)	66 (9)	22 (4)	22 (4)	0	0	19 (12)	1
O(3)	24 (m)	1121 (4)	1121 (4)	3264 (5)	61 (4)	61 (4)	58 (7)	87 (11)	-25 (9)	-25 (9)	1
Co	8 (g)	2189 (3)	2189 (3)	2189 (3)	35 (2)	35 (2)	35 (2)	29 (4)	29 (4)	29 (4)	1/2
Cl(1)	8 (g)	3258 (10)	3258 (10)	3258 (10)	245 (14)	245 (14)	245 (14)	-102 (25)	-102 (25)	-102 (25)	1/2
Cl(2)	24 (l)	2329 (81)	3915 (42)	1/2	36 (4)						1/6
Na(1)	24 (l)	713 (71)	4216 (76)	1/2	9 (3)						1/12
Na(2)	12 (h)	0	4270 (92)	1/2	7 (4)						1/12

<sup>a</sup> Positional and anisotropic thermal parameters are given  $\times 10^4$ . Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter. See Figure 1 for the identities of the atoms. The anisotropic temperature factor =  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ . <sup>b</sup> Root-mean-square displacements can be calculated from  $\beta_{ii}$  values using the formula  $\mu_i = 0.225a(\beta_{ii})^{1/2}$ , where  $a = 12.103 \text{ \AA}$ . <sup>c</sup> Occupancy for Si = 1/2; occupancy for Al = 1/2.

**Table II.** Fractional Coordinate of Cobalt(II), Deviations of Ions from the Six-Ring Planes, and Co<sup>II</sup>-O(3) Distances, in Co<sub>4</sub>Na<sub>4</sub>-A and Its Sorption Complexes

Zeolite <sup>a</sup>	Fractional coordinate of cobalt(III) <sup>b</sup>	Deviations <sup>c</sup> from the (111) plane at O(3), $\text{\AA}$		Co <sup>II</sup> -O(3), $\text{\AA}$ <sup>b</sup>	Ref
		Co <sup>II</sup>	Na <sup>+</sup>		
Co <sub>4</sub> Na <sub>4</sub> -A, dehydrated	0.200 (2)	0.34	-0.56	2.077 (18)	4
Co <sub>4</sub> Na <sub>4</sub> -A·4CO	0.208 (1)	0.53	-0.58	2.113 (15)	4
Co <sub>4</sub> Na <sub>4</sub> -A·4NO <sub>2</sub>	0.208 (2)	0.50	-0.15	2.132 (6)	10
Co <sub>4</sub> Na <sub>4</sub> -A·4C <sub>2</sub> H <sub>4</sub>	0.2106 (2)	0.58	-0.55	2.148 (7)	11
Co <sub>4</sub> Na <sub>4</sub> -A·4C <sub>2</sub> H <sub>2</sub>	0.2111 (3)	0.58	-0.13	2.193 (7)	12
Co <sub>4</sub> Na <sub>4</sub> -A·4C <sub>3</sub> H <sub>6</sub>	0.2124 (3)	0.61	-0.09	2.174 (7)	13
Co <sub>4</sub> Na <sub>4</sub> -A·4Cl <sub>2</sub> at 24 (1) °C	0.2189 (3)	0.73	<i>d</i>	2.244 (6)	This work
Co <sub>4</sub> Na <sub>4</sub> -A·4Cl <sub>2</sub> at -165 (3) °C	0.2207 (4)	0.78	<i>d</i>	2.26 (1)	This work

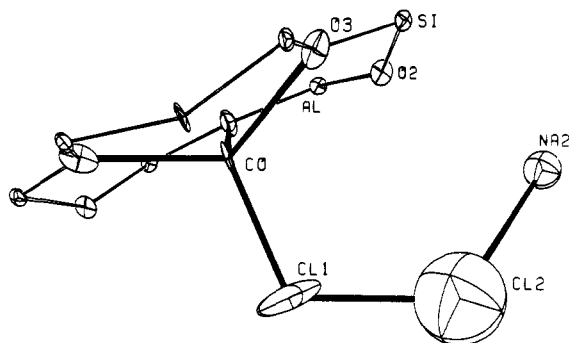
<sup>a</sup> All of these materials are deep blue in color, with the exception of the NO<sub>2</sub> complex which is brown-black. The blue color has been attributed to the near tetrahedral nature of cobalt(II) in these complexes, whether the sorbed molecule is held by a  $\sigma$  or a  $\pi$  interaction. See ref 14. <sup>b</sup> Numbers in parentheses are the esd's in the units of least significant digit given for the corresponding value. <sup>c</sup> A negative deviation indicates that the ion lies on the same side of the plane as the origin, that is, inside the sodalite unit. <sup>d</sup> These ions are located at qualitatively different sites within the zeolite lattice.

**Figure 1.** A stereoview<sup>7</sup> of the chlorine sorption complex of cobalt(II) within Co<sub>4</sub>Na<sub>4</sub>-A·4Cl<sub>2</sub> is shown.

solution and refinement. Of the data at -165 °C, 232 reflections satisfied this 3 $\sigma$  test. Other details of the data collection and reduction are the same as previously described.<sup>6</sup> Full-matrix least-squares refinement using anisotropic thermal parameters for all positions except Cl(2), Na(1), and Na(2), which were refined isotropically, converged to  $R_1 = (\sum |F_o - |F_c|| / \sum F_o) = 0.095$  and  $R_2 = (\sum w(F_o - |F_c|)^2 / \sum wF_o^2)^{1/2} = 0.102$  using the 24 °C data set. Further work to locate the remaining Na<sup>+</sup> ion per unit cell is in progress. The three lowest angle reflections (001), (011), and (111), were deleted from least squares because of apparent extinction. The final positional and thermal parameters are presented in Table I.

The structure obtained at 24 (1) °C was refined with the data collected at -165 (3) °C. Least squares converged quickly and indicated that the structure was essentially the same at the two temperatures. The error indices  $R_1$  and  $R_2$  were 0.108 and 0.120, respectively, after deleting the three lowest angle reflections as before.

Each Cl<sub>2</sub> molecule bridges between a cobalt(II) ion on the threefold axis and a Na<sup>+</sup> ion at an 8-ring site, as can be seen in Figure 1. The three Na<sup>+</sup> ions occupy two crystallographically distinct sites: two of them, at Na(1), are located off the planes of their 8 rings, while the other, at Na(2), is located on this plane. Because there can be no more than three 8-ring



**Figure 2.** One of the four  $\text{Co}^{\text{II}}\text{-Cl}_2\text{-Na}^+$  complexes in the large cavity of each unit cell. Selected bond lengths (in ångströms) are  $\text{Co}^{\text{II}}\text{-Cl}(1)$ , 2.24 (1);  $\text{Cl}(1)\text{-Cl}(2)$ , 2.52 (2);  $\text{Cl}(2)\text{-Na}^+$ , 2.54 (8);  $\text{Co}^{\text{II}}\text{-O}(3)$ , 2.244 (6).  $\text{Co}^{\text{II}}$  is in a tetrahedral environment:  $\text{O}(3)\text{-Co}^{\text{II}}\text{-O}(3)$ ,  $109.6(3)^\circ$ ;  $\text{Cl}(1)\text{-Co}^{\text{II}}\text{-O}(3)$ ,  $109.3(4)^\circ$ .

cations to accommodate the four  $\text{Cl}(2)$  atoms, one ion at  $\text{Na}(2)$  associates itself symmetrically with two  $\text{Cl}(2)$  atoms and remains in the 8-ring plane. Consistent with this are the two  $\text{Na}\text{-Cl}(2)$  distances:  $\text{Na}(1)\text{-Cl}(2)$ , 2.54 (8) Å, and  $\text{Na}(2)\text{-Cl}(2)$ , 2.85 (2) Å.

The cobalt(II) ions are four coordinate; three 6-ring oxide ions of the zeolite framework at  $\text{O}(3)$ , and a chlorine atom at  $\text{Cl}(1)$ , are tetrahedrally disposed about cobalt(II) (see Figure 2). The  $\text{Co}\text{-Cl}(1)\text{-Cl}(2)$  angle,  $114(1)^\circ$ , is quite bent, and the  $\text{Co}\text{-Cl}(1)$  distance, 2.24 (1) Å, is comparable with that found in chloride complexes of cobalt(II).<sup>8</sup> The  $\text{Cl}\text{-Cl}$  bond length is 2.52 (2) Å, 0.53 Å longer than the bond in free  $\text{Cl}_2$ .<sup>9</sup>

In this structure, the cobalt(II) ion lies further from the plane of its three coordinated  $\text{O}(3)$  framework oxide ions than it does in other cobalt(II)-exchanged zeolite A structures (see Table II). The  $\text{Co}^{\text{II}}\text{-O}(3)$  distance of 2.244 (6) Å found in this structure is significantly longer than the same distance reported in dehydrated  $\text{Co}_4\text{Na}_4\text{-A}$  or in its complexes with  $\text{C}_2\text{H}_4$ ,<sup>11</sup>  $\text{C}_2\text{H}_2$ ,<sup>12</sup>  $\text{C}_3\text{H}_6$ ,<sup>13</sup>  $\text{NO}_2$ ,<sup>10</sup> and  $\text{CO}^4$  (see Table II). This indicates that cobalt(II) interacts more strongly with  $\text{Cl}_2$  than it does with the other ligands.

The  $\text{X}_2$  bond lengths ( $\text{X}_2 = \text{I}_2, \text{Br}_2, \text{Cl}_2$ )<sup>3,15,16</sup> are significantly longer in their intrazeolitic charge-transfer complexes than in the uncomplexed molecules.<sup>9</sup> Each halogen molecule forms an axial complex with a framework oxide ion.

In this work, however, instead of oxide ions, dichlorine complexes to cobalt(II); the relatively short  $\text{Co}^{\text{II}}\text{-Cl}$  distance observed, 2.24 Å, as compared with the sum of the appropriate ionic and van der Waals radii,<sup>17</sup>  $0.72 + 1.80 = 2.52$  Å, indicates a strong interaction.

The long  $\text{Cl}\text{-Cl}$  bond indicates that its bond order has been reduced upon complexation to cobalt(II). This can occur (1) when charge is delocalized from an occupied bonding orbital on  $\text{Cl}_2$  into an empty cobalt(II) orbital, or (2) when charge on cobalt(II) delocalizes into an empty antibonding dichlorine orbital. The highest occupied molecular orbitals in dichlorine are  $3p\pi_g^*$ ,  $3p\pi_u$ , and  $3p\sigma_g$ .<sup>18</sup> Dichlorine could be acting as a  $\sigma$  donor from  $3p\pi_u$  to, perhaps, the empty cobalt(II) 4s orbital, the lowest unoccupied cobalt(II) orbital of proper symmetry. The order of the dichlorine bond might also be decreased by a  $3d\pi_{\text{Co}} \rightarrow 3d\pi_{\text{Cl}_2}$  back-bonding interaction.

The observations, (1) that the color of the crystal did not change upon the sorption of  $\text{Cl}_2$  and (2) that the approach distances between the cobalt ion and the zeolite framework are relatively long, indicate that cobalt(II) has not been oxidized to cobalt(III) by  $\text{Cl}_2$ . The first observation indicates also that the 3d structure of cobalt(II) has not been qualitatively altered by coordination to  $\text{Cl}_2$ .

The  $\text{Na}^+\text{-Cl}(2)$  distances (2.54 and 2.85 Å) average to less than the sum of the corresponding ionic and van der Waals

radii,<sup>17</sup>  $0.97 + 1.80 = 2.77$  Å. The  $\text{Na}^+\text{-O}$  distances (2.96 and 2.57 Å) are both more than the sum of the corresponding radii,  $0.97 + 1.32 = 2.29$  Å. This indicates that the larger  $\text{Cl}^0$  atoms, which are more polarizable than oxide ions, can interact strongly with  $\text{Na}^+$ .

**Acknowledgments.** This work was supported by the National Science Foundation (Grant No. CHE76-81586). We are indebted to the University of Hawaii Computing Center.

**Supplementary Material Available:** Final positional, thermal, and occupancy parameters for the structure at  $-165(3)^\circ\text{C}$  (Supplementary Table 1) and listings of the observed and calculated structure factors for both structures (Supplementary Tables 2 and 3) (8 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) The nomenclature refers to the contents of the unit cell. For example,  $\text{Co}_4\text{Na}_4\text{-A}$  represents  $\text{Co}_4\text{Na}_4\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$  with the zeolite A structure.
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V. Subramanian, Karl Seff\*

Chemistry Department, University of Hawaii  
Honolulu, Hawaii 96822

Tor Ottersen

Department of Chemistry, University of Oslo  
Oslo, Norway

Received October 31, 1977

## A Stereoelectronic Effect in Hydrogen Atom Abstraction from a Substituted Cyclohexyl Radical

Sir:

Since the pseudoaxial and pseudoequatorial protons of the  $\beta$  positions of cyclohexyl radical in its chair-like conformation are stereochemically nonequivalent with respect to the semi-occupied  $p$  orbital, they should exhibit different reactivity toward reagents capable of abstracting hydrogen atoms. Two reports of such reactivity differences have recently appeared. Agosta and Wolff<sup>1</sup> observed preferential intramolecular transfer of the pseudoaxial  $\beta$ -hydrogen atom in biradicals generated photochemically from bicyclo[3.2.1]octan-6-ones. A contrary result was reported by Livant and Lawler<sup>2</sup> who studied the disproportionation of cyclohexyl radicals by the CIDNP technique and obtained evidence for the selective loss of pseudoequatorial  $\beta$ -hydrogen atoms. The discord between these reports prompted the present study of the stereochemical course of reactions of an appropriately substituted, conformationally locked<sup>3</sup> cyclohexyl radical **4**.

The radical **4** was generated by thermolysis of the *tert*-butyl peroxyglyoxalate **2b**. Catalytic hydrogenation of 4-*tert*-