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Communications

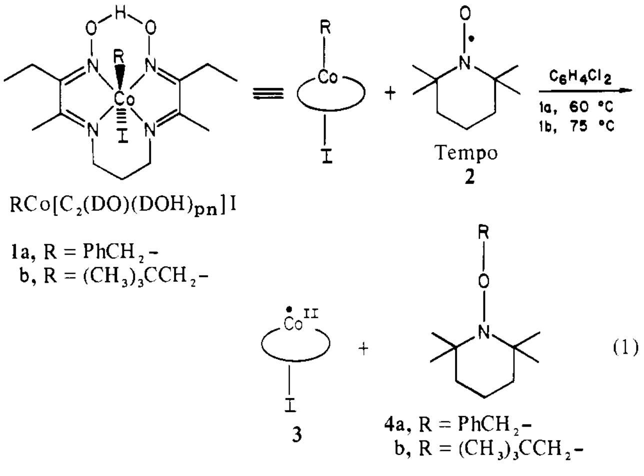
Cobalt–Carbon Bond Homolysis and Bond Dissociation Energy Studies for the Coenzyme B_{12} Analogue $RCo[C_2(DO)(DOH)_{pn}]I$ ($R = PhCH_2–$, $(CH_3)_3CCH_2–$)

Sir:

Facile cobalt–carbon bond homolysis, $R–Co \rightleftharpoons R\cdot + Co^{II}\cdot$ ($K_{eq} = k_1/k_{-1}$), is the key, biochemically unique, first step in the adenosylcobalamin-dependent rearrangement reactions.[1] In spite of this, a lack of suitable R· traps that react selectively with R· but not $Co^{II}\cdot$ has, to date, prevented *reliable* kinetic and $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and thus BDE (bond dissociation energy) measurements[2] in alkylcobalamins[3] under conditions *demonstrating* the proposed homolysis, although Halpern and coworkers have reported considerable success with the kinetic trapping method using the Co(SALOPH) B_{12} model and *n*-BuSH as a selective R· trap.[4]

Our own studies[5] have employed a modification[5d] of Costa's B_{12} model, $RCo[C_2(DO)(DOH)_{pn}]X$ (**1**), which we have shown[5e,f] to be an excellent, ±0.05 V, mimic of the B_{12} Co(III)/Co(II) and base-off Co(II)/Co(I) $E_{1/2}$ values, –0.042[6a] and –0.74 V (SCE),[6b] respectively, while the next closest Schiff base B_{12} model, the cobaloximes, show $E_{1/2} = -0.40$ and -1.14 V (SCE), respectively.[5] Following studies demonstrating that *n*-BuSH, PhSH, $HMn(CO)_5$, and O_2 all undergo rapid redox reactions with $Co^{II}[C_2(DO)(DOH)_{pn}]X$ and are, therefore, unsuitable trapping agents, our efforts turned to the nitroxide free radical 2,2,6,6-tetramethylpiperidinyl-1-oxy or Tempo because of its $E_{1/2} = -0.15$ V (SCE)[7] reduction potential suggesting that it would be more inert to redox reactions with Co(II).

Herein we report product, kinetic, and $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and R–Co BDE (bond dissociation energy) studies for the thermolysis of $RCo[C_2(DO)(DOH)_{pn}]I$ ($R = PhCH_2–$, **1a**; $R = (CH_3)_3CCH_2–$, **1b**) using Tempo as a trapping agent as well as preliminary evidence suggesting that nitroxide traps will be applicable to cobalamins as well.



The reaction stoichiometries determined for $PhCH_2Co[C_2(DO)(DOH)_{pn}]I$ (**1a**) and $(CH_3)_3CCH_2Co[C_2(DO)(DOH)_{pn}]I$ (**1b**) in the presence of Tempo (**2**) are shown in eq 1. For the benzyl complex, **1a** ($\lambda_{max} = 415$ nm, $\epsilon = (9.5 \pm 0.5) \times 10^3$), thermolysis in *o*-dichlorobenzene with 25–170 equiv of Tempo (**2**) proceeds at convenient rates at 60–97 °C with an isosbestic point at 463 nm over at least 75% of the reaction and the formation (eq 1) of 100 ± 4% $Co^{II}[C_2$-

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(1) Recent reviews include: (a) Dolphin, D., Ed. "B_{12}"; Wiley-Interscience: New York, 1982. (b) Zagalak, B., Friedrick, W., Eds. "Vitamin B_{12}, Proceedings of the 3rd European Symposium on Vitamin B_{12} and Intrinsic Factor"; Walter de Gruyter: New York, 1979. (c) Babior, B. M.; Krouwer, J. S. *CRC Crit. Rev. Biochem.* **1979**, *6*, 35. (d) Abeles, R. H.; Dolphin, D. *Acc. Chem. Res.* **1976**, *9*, 114. (e) Golding, B. T. In ref 1a, Chapter 15, p 543. (f) Finke, R. G.; Schiraldi, D. A.; Mayer, B. J. *Coord. Chem. Rev.*, in press.

(2) Reliable use of the kinetic trapping method and the value[4] $\Delta H^{\ddagger}_{-1} \simeq 2$ kcal/mol necessary in the equation $BDE(R–Co) \equiv \Delta H^{\ddagger}_1 - \Delta H^{\ddagger}_{-1} \simeq \Delta H^{\ddagger} - 2$ kcal/mol requires (i) demonstration of the proposed homolysis step via an inverse [Co(II)] rate dependence and (ii) measurement of k_{obsd} vs. temperature under conditions where $k_{obsd} = k_1$, so that $\Delta H^{\ddagger}_1$ and $\Delta S^{\ddagger}_1$ but not composite values are obtained. As noted previously,[4] these requirements were not fully met in previous studies of B_{12}.[3] For some R·, especially sterically crowded ones, $\Delta H^{\ddagger}_{-1} \simeq 2$ kcal/mol may not be valid, and additional $\Delta H^{\ddagger}_{-1}$ measurements are needed.

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(5) Our interests have turned to the kinetic, thermodynamic (R–Co BDE), axial base, corrin conformation, steric, electronic, and radical cage effects influencing this first step following our mechanistic and model studies of the cobalt participation or nonparticipation question in B_{12}-dependent diol dehydratase, where our results support the view that it is the protein, and not participation by the cobalt cofactor as previously thought, that has the major role in the steps following the initial R–Co homolysis:[1f,5a–c] (a) Finke, R. G.; McKenna, W. B. *J. Chem. Soc., Chem. Commun.* **1980**, 460. (b) Finke, R. G.; McKenna, W. B.; Schiraldi, D. A.; Smith, B. L. *J. Am. Chem. Soc.*, in press. (c) Finke, R. G.; Schiraldi, D. A. *Ibid.*, in press. (d) Finke, R. G.; Smith, B. L.; McKenna, W. A.; Christian, P. A. *Inorg. Chem.* **1981**, *20*, 687. (e) Elliott, C. M.; Hershenhart, E.; Finke, R. G.; Smith, B. L. *J. Am. Chem. Soc.* **1981**, *103*, 5558. (f) Finke, R. G.; Smith, B. L., Droege, M. W.; Elliott, C. M.; Hershenhart, E. *J. Organomet. Chem.* **1980**, *202*, C25.

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$(DO)(DOH)_{pn}]I$ (**3**) ($\lambda_{max} = 460$ nm, $\epsilon = (4.6 \pm 0.1) \times 10^3$; $\lambda = 415, 405$ nm, $\epsilon = (3.5 \pm 0.1) \times 10^3$) in comparison to authentic material[8] and ca. 1 equiv[9a] of the $PhCH_2\cdot$ + Tempo radical trapping product, 1-benzyloxy-2,2,6,6-tetramethylpiperidine (**4a**) (GC, NMR, and mass spectroscopy[9b] all in comparison to authentic, isolated material prepared from $PhCH_2MgCl$ + Tempo[9c]). In the case of the neopentyl complex, **1b** ($\lambda_{max} = 405$ nm, $\epsilon = (10.0 \pm 0.5) \times 10^3$), chosen as a case of a sterically demanding[10] alkyl ligand, thermolysis in *o*-dichlorobenzene with 80–200 equiv of Tempo (**2**) at 65–90 °C proceeded with an isosbestic point at 445 nm for at least 1 half-life to produce 1 equiv of $Co^{II}[C_2(DO)(DOH)_{pn}]I$ (**3**) and 1 equiv of 1-(2,2-dimethylpropanoxy)-2,2,6,6-tetramethylpiperidine (**4b**).[9d]

While the stoichiometry and observation of 1 equiv of Co(II) product (eq 1) demonstrate that Tempo selectively traps R· in the presence of $Co^{II}\cdot$, control experiments were performed to define the limits of $Co^{II}\cdot$ stability at higher concentrations of $Co^{II}\cdot$ and Tempo and at elevated temperatures, thereby establishing the range of possible kinetic studies. While 1 equiv (1.3×10^{-4} M) of $Co^{II}[C_2(DO)(DOH)_{pn}]I$ (**3**) and 1 equiv of Tempo show little reaction at 80 °C in *o*-dichlorobenzene over ca. 0.5 h, with 50 equiv of Tempo and 100 equiv of Tempo at 80 °C, approximate half-lives of 1 and 0.5 h, respectively, for the growth of an absorption at $\lambda_{max} = 460$ nm were observed. Thus, although TEMPO is not completely inert, the fact that it reacts at nearly diffusion-controlled rates[11] with R· yet is relatively inert at 80 °C to the $Co^{II}\cdot$ radical is, in many respects, remarkable. We are currently examining the products from the $Co^{II}\cdot$ + Tempo reaction as well as other nitroxides that may prove even more stable to $Co^{II}\cdot$.[12]

Reproducible kinetic studies required the use of a high-vacuum Teflon stopcock-fitted 1-cm cuvette to avoid contact of the solution with air, rubber septa, or stopcock grease and the use of low R–Co (and thus $Co^{II}\cdot$) and Tempo concentrations to minimize the bimolecular $Co^{II}\cdot$ and Tempo side reaction. The loss of $PhCH_2Co[C_2(DO)(DOH)_{pn}]I$ (**1a**) at 415 nm and $(CH_3)_3CCH_2Co[C_2(DO)(DOH)_{pn}]I$ (**1b**) at 405 nm was monitored as long as the isosbestic points remained, at least 1 $t_{1/2}$ and generally 2–4 $t_{1/2}$'s in the absence of added $Co^{II}\cdot$ and <200 equiv of Tempo, and was corrected via the straightforward equation[13] $C_t = (A_t - C_0\epsilon_{prod})/(\epsilon_{subst} - \epsilon_{prod})$ for the growth of the overlapping $Co^{II}[C_2(DO)(DOH)_{pn}]I$ (**3**) at 405 and 415 nm. As expected for the prior homolysis followed by Tempo and $Co^{II}\cdot$ competition for the R· intermediate (eq 2 and 3), the apparent[13c] initial rate constant $k_{initial}$

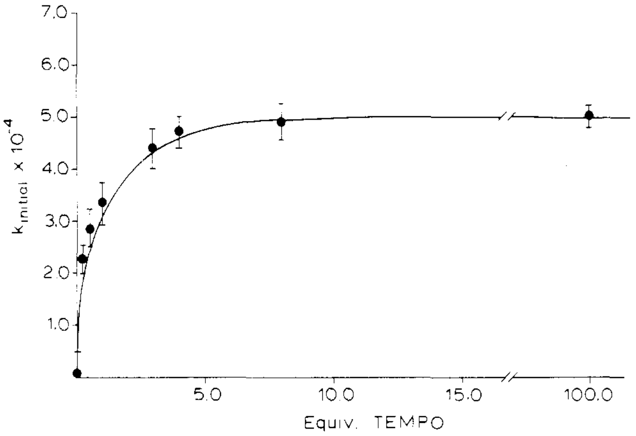
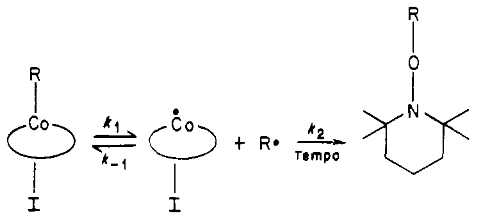


Figure 1. Apparent initial rate constant,[13c] $k_{initial}$ (s^{-1}), vs. equiv of Tempo/equiv of **1a**.

Table I. $\Delta H^{\ddagger}{}_1$ and $\Delta S^{\ddagger}{}_1$ Values for the Thermolysis of Benzyl and Neopentyl R–Co Complexes

system	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\dagger}$, eu	ref
R = Benzyl			
$PhCH_2Co[C_2(DO)(DOH)_{pn}]I$	27.9 ± 0.8	8 ± 2	this work
$PhCH_2Co$[SALOPH]py	23.6 ± 1.0	1 ± 3	4a
$PhCH_2Co$[cobalamin]	24.6 ± 0.6	12 ± 2	3
$PhCH_2Co$[cobinamide]	26.9 ± 0.5	9 ± 2	3
R = Neopentyl			
$(CH_3)_3CCH_2Co[C_2(DO)(DOH)_{pn}]I$	32.2 ± 2.0	18 ± 6	this work
$(CH_3)_3CCH_2Co$[SALOPH]py	20.3 ± 0.6	−6 ± 3	4a
$(CH_3)_3CCH_2Co$[cobalamin]	23.4 ± 0.2	2.6 ± 0.1	3
$(CH_3)_3CCH_2Co$[cobinamide]	32.1 ± 0.1	17.3 ± 0.4	3



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(2)

$$-d[\mathbf{1}]/dt = \frac{k_1k_2[\text{Tempo}][\mathbf{1}]}{k_{-1}[\text{Co(II)}] + k_2[\text{Tempo}]} = k_{obsd}[\mathbf{1}] \qquad (3)$$

$$1/k_{obsd} = 1/k_1 + k_1[\text{Co(II)}]/k_1k_2[\text{Tempo}] \qquad (4)$$

increased with increasing [Tempo] until k_2[Tempo] >> k_{-1}[$Co^{II}\cdot$] (eq 3) and a rate zero order in [Tempo] was observed, $-d[\mathbf{1a}]/dt = k_1[\mathbf{1a}]$ (Figure 1) (69 °C). The [Co(II)]/

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(8) Prepared by the Co(I) + Co(III) redox reaction of $(OC)Co[C_2(DO(DOH)_{pn})]$[5d] and $ICo[C_2(DO(DOH)_{pn})]I$[5d] in CH_3OH under N_2 followed by removal of the solvent.

(9) (a) Although some decomposition of the $PhCH_2ONC_9H_{18}$ product, **4a**, appears to occur on the injector port, 84 ± 10% was detected by GC. (b) ^1H NMR (benzene-d_6): δ 6.8 (m, 5 H), 4.95 (s, 2 H) 0.9–1.5 (m, 18 H). Mass spectrum: parent *m/e* 247.19 (±0.01); calcd 247.19. (c) Hill, C. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 870. (d) ^1H NMR (benzene-d_6): δ 1.6 (s, 9 H), 1.8–1.9 (d, 6 H (collapses to singlet at ~50 °C)), 1.6–2.2 (m, 6 H), 4.2 (s, 2 H). Using $T_c = 50$ °C and $k_c = \pi(\Delta\nu)/2^{1/2}$ gives $k_c = 53\ s^{-1}$ and $\Delta G^{\ddagger} = 21$ kcal/mol.[9e] (e) Günther, H. "NMR Spectroscopy"; Gleason, R. W., translator (Engl.); Wiley: New York, 1980; Chapter 8, pp 239–244. (f) In the absence of nitroxide, neopentyl iodide is observed, the amount of which decreases to zero at 100 equiv of nitroxide. The mechanism of this reaction is under a separate investigation: Finke, R. G.; Mayer, B. J.; Molinero, A. A., experiments in progress.

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(13) (a) An error analysis[13b] based on this equation shows an estimated ±10% error in $[\mathbf{1a}]_t$, which propagates as a ±15% error in k_{obsd}. (b) Bevington, P. R. "Data Reduction and Error Analysis for the Physical Sciences"; McGraw-Hill: New York, 1969. (c) The apparent $k_{initial}$, taken as the apparent initial slope of a ln ($[\mathbf{1a}]_0/[\mathbf{1a}]_t$) vs. time plot, is ill-defined, in that it refers to unknown [$Co^{II}\cdot$] and [Tempo] values, since the true $k_{initial}$ is where [$Co^{II}\cdot$] = 0 (and [Tempo] = $[\text{Tempo}]_{initial}$) and thus $k_{initial}$ (=k_{obsd}) = k_1 (eq 3, 4). The $k_{initial}$ values and Figure 1 clearly illustrate that the desired conditions of zero-order [Tempo] have been reached, however, and the figure has been included for this reason.

[Tempo] dependence predicted by eq 4 was also verified for **1a** at 78.0 °C and at [Co(II)]/[Tempo] ratios of 0, 0.026, 0.047, and 0.097 and k_1 and k_{-1}/k_2 values comparable to those available in the literature[14] were obtained from the slope and intercept, respectively, $k_1 = (1.7 \pm 0.9) \times 10^3\ \mathrm{s^{-1}}$ and $k_{-1}/k_2 = (2 \pm 1) \times 10$, although the range and precision of the data were limited by the growth of the overlapping peak at 460 nm from the reaction of $\mathrm{Co^{II}}\cdot$ + Tempo.

Under conditions with excess nitroxide where $k_{\mathrm{obsd}} = k_1$ (eq 3 and Figure 1) the temperature dependence of k_1 was obtained at 11 temperatures over a 60–90 °C range for $\mathrm{PhCH_2Co[C_2(DO)(DOH)_{pn}]I}$ and at 6 temperatures over a 65–90 °C range for $\mathrm{(CH_3)_3CCH_2Co[C_2(DO)(DOH)_{pn}]I}$, $\Delta H^{\ddagger} = 27.9 \pm 0.8$ kcal/mol, $\Delta S^{\ddagger} = 8 \pm 2$ eu and $\Delta H^{\ddagger} = 32.2 \pm 2.0$ kcal/mol, $\Delta S^{\ddagger} = 18 \pm 6$ eu, respectively,[15] to yield the first estimates of the $\mathrm{R{-}Co[C_2(DO)(DOH)_{pn}]I}$ bond energies ($\simeq \Delta H^{\ddagger} - 2$ kcal/mol)[2] of 26 ($\mathrm{R = PhCH_2{-}}$) and 30 ($\mathrm{R = (CH_3)_3CCH_2{-}}$) kcal/mol. The available $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, including Schrauzer and Grates' estimates for cobalamins and cobinamides with O_2 as a trap, make an interesting comparison (Table I). Especially interesting are the observations that (a) the $\mathrm{RCo[C_2(DO)(DOH)_{pn}]I}$ complexes with their weak $\mathrm{I^-}$ axial ligands show the same $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values within experimental error as those for the base-off alkylcobinamide complexes and (b) the alkylcobinamide and $\mathrm{RCo[C_2(DO)(DOH)_{pn}]I}$ complexes exhibit a neopentyl vs. benzyl ΔBDE (ΔBDE ≡ BDE(neopentyl) – BDE(benzyl)) of only 4–5 kcal/mol. Clearly the B_{12} model chosen and the effect of the axial base are significant, and a collaborative program to determine the solid-state structures vs. the $\mathrm{RCo[C_2(DO)(DOH)_{pn}](base)^+X^-}$ R–Co BDEs for a series of alkyls and bases is under way.[16] In the case of cobalamins, preliminary experiments show, as expected on the basis of the similar $E_{1/2}$ values for $\mathrm{Co^{II}[C_2(DO)(DOH)_{pn}]^+}$ and $\mathrm{Co^{II}}$ $B_{12(r)}$, that $B_{12(r)}$ is relatively stable to nitroxides and that 1.0 equiv of $B_{12(r)}$ is produced by the thermolysis of benzylcobalamin in the presence of a nitroxide.[17] Studies of this and other alkyl cobalamins and cobinamides will be reported in due course.

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Registry No. **1a**, 87319-52-6; **1b**, 87319-53-7; **2**, 2564-83-2.

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(15) The k_1(obsd) values ($\mathrm{s^{-1}}$, ±15%) and temperatures (±0.5 °C) are as follows. (a) For **1a**: 5.9×10^{-3} at 90.5 °C; 5.0×10^{-3} at 88.0 °C; 3.4×10^{-3} at 86.0 °C; 2.3×10^{-3} at 83.0 °C; 1.3×10^{-3} at 78.5 °C; 1.7×10^{-3} at 78.0 °C; 6.8×10^{-4} at 72.0 °C; 4.4×10^{-4} at 69 °C; 3.0×10^{-4} at 64.5 °C; 2.4×10^{-4} at 64.0 °C; 1.8×10^{-4} at 60.5 °C. (b) For **1b**: 2.4×10^{-3} at 90.0 °C; 1.3×10^{-3} at 83.0 °C; 6.7×10^{-4} at 77.0 °C; 2.7×10^{-4} at 72.0 °C; 2.3×10^{-4} at 71.0 °C; 8.7×10^{-5} at 65.0 °C.

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Alkali-Metal Insertion in the Pyrochlore Structure

Sir:

Intercalation or insertion reactions of alkali metals with transition-metal oxides or chalcogenides have been the subject of considerable research in recent years.[1–4] These reactions formally involve reduction of transition-metal ions with the change in charge being compensated by diffusion of alkali-metal cations into a host structure (eq 1). Ideally only small

$$A + M^nX_y \rightarrow A^+M^{n-1}X_y \tag{1}$$

structural changes occur on insertion, which allows the reactions to be readily reversed by oxidation. The reaction rates, which are often fast at room temperature, are limited by the rate of alkali metal ion diffusion into the host structure. Many van der Waals bonded layer compounds such as graphite, $\mathrm{TiS_2}$, or $\mathrm{MoO_3}$ are able to accommodate a wide variety of ions because the weak interlayer bonding allows easy interlayer expansion and reorientation of the layers to create favorable sites for the inserted ions. More rigid, three dimensionally bonded hosts are also capable of insertion reactions with alkali metals, but the size and site requirements are more critical. Most of the oxide systems studied to date are lithium specific.[4–7] Insertion of the larger alkali metals in such oxides is not common. The recently synthesized hexagonal $\mathrm{WO_3}$[8] is the most versatile host for the larger alkalis, yielding compounds with the limiting formula $\mathrm{A_{1/3}WO_3}$ (A = Na, K, Rb, Cs).[9] In this paper we report the insertion of A = Na, K, Rb in the defect pyrochlore compounds $\mathrm{ANbWO_6}$ to give the corresponding $\mathrm{A_2NbWO_6}$. This is the largest stoichiometry change in an oxide for insertion reactions with these alkali metals.

The full pyrochlore stoichiometry is $\mathrm{A_2B_2X_6X'}$, and a wide variety of compositions are known with various permutations of large A cations (Na, K, Rb, Cs, Ca, Cd, Tl, Pb, Sc, Lu, Yb, etc.), smaller B cations (Ti, Nb, V, W, Ta, Re, Ru, etc.), X (O or F), and X′ (O or F).[10–15] The structure may be conveniently thought of as a $\mathrm{B_2X_6}$ framework composed exclusively or corner-shared $[\mathrm{BX_6}]$ octahedra interleaved with an $\mathrm{A_2X'}$ network as shown in Figure 1. The ideal structure is cubic with space group $Fd3m$ and eight formula units per unit cell. The A, B, and X′ ions occupy the special positions 16d, 16c, and 8b, respectively. The X ions occupy the 48f positions. The A ion is linearly coordinated to two X′ and six approximately coplanar X ions. The X′ ion is coordinated tetrahedrally to four A ions. Defect pyrochlores have been synthesized with stoichiometries $\mathrm{A_2B_2X_6}$,[16] $\mathrm{AB_2X_6}$,[17–20] and

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