Heating the dissolved product precipitates the CoL_3 starting material. After the product stands in solution for several hours, a shiny silver solid, Pb, begins to fall from solution.

Synthesis of $Co(NH_2CH_2CH_2SO_2)_3$. Hexaaquonickel(II) chloride and CoL_3 (1.78 g, 0.0062 mol) were mixed in 150 mL of H_2O. This suspension was stirred and heated gently for 1 h in which time the CoL_3 solubilized. The deep brown solution was filtered hot and then again at room temperature to remove unreacted CoL_3. Hydrogen peroxide (10 mL of 30% H_2O_2) was added slowly to the solution. Stirring and gentle heating were continued as a vigorous reaction took place. Gas was evolved as the reaction mixture lightened from brown to yellow-orange over a period of several minutes. Gentle heating and stirring were continued for about 1 h. The precipitate which formed in this time was then collected by filtration, washed with water and then absolute ethanol, and dried in vacuo. The product was bright yellow.

Anal. Calcd for $Co(NH_2CH_2CH_2SO_2)_3$: C, 18.80; H, 4.70; N, 10.97; Cl, 0.00. Found: C, 18.74; H, 4.69; N, 10.87; Cl, 0.44.

The same product was obtained by dissolving solid $Ni[Co(NH_2CH_2CH_2S)_3]_3Cl_2$ or $Pb[Co(NH_2CH_2CH_2S)_3](NO_3)_3$ in 150 mL of water and then adding excess H_2O_2.

Reactions of CoL_3 with H_2O_2. CoL_3 (1.92 g, 6.69×10^{-3} mol) was mixed in 150 mL of H_2O at 0 °C. H_2O_2 (4.00×10^{-3} mol) was then added. The CoL_3 dissolved to form a deep red solution. After 20 min of being stirred the reaction mixture was filtered. A saturated solution of $NaClO_4$ (1.38 g, 2.01×10^{-2} mol) was added to the deep red solution. The solution was refrigerated 2 days in which time a yellow precipitate formed. The precipitate was noncystalline and seemed to form in paper-thin sheets. The precipitate was collected by filtration and washed with about 2 mL of absolute ethanol.

Anal. Calcd for $Co(NH_2CH_2CH_2SO_2)_2(NH_2CH_2CH_2SO)$: C, 19.63; H, 4.95; N, 11.44. Found: C, 20.20; H, 5.30; N, 11.37.

To isolate the red compound, CoL_3 and H_2O_2 are mixed in the same manner as described above except that the solution is concentrated by vacuum evaporation to 30 mL, and 200 mL of acetone rather than $NaClO_4$ is then added. The red compound precipitates out of solution.

Anal. Calcd[19] for $[NH_3CH_2CH_2SH]_2[Co(NH_2CH_2CH_2S)_2O]_2$: C, 19.57; H, 5.21; N, 11.41. Found: C, 19.81; H, 5.32; N, 10.9.

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Registry No. $[Pb(CoL_3)_2](NO_3)_2$, 66551-69-7; CoL_3O_6, 66482-82-4; $Co(NH_2CH_2CH_2SO_2)_2(NH_2CH_2CH_2SO)$, 66482-83-5; CoL_3, 18703-22-5; $[Ni(CoL_3)_2]Cl_2$, 66454-93-1; H_2O_2, 7722-84-1.

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Model for Carbonate Apatite

Sir:

Recently Santos and González-Díaz[1] have assigned parameters to the CO_3 group of carbonate apatite on the basis of highly improbable interpretations of infrared data and correlations of certain ratios with quantitative determinations of constituents. Our primary objection to their model is that for every CO_3 group substituted for a PO_4 group, there is no provision for the fourth oxygen. What happens to it? Does it exist as a large hole? If so, it should markedly affect the density, unit-cell dimensions, and optical properties in ways which they completely failed to explain.

They completely disregarded the proposal by McConnell[2] that $3PO_4 \rightarrow 4CO_3$, thus preserving the "oxygen lattice" essentially intact. In fact, Santos and González-Díaz consider merely the model of Elliott[3] and thus disregard all other models that are to be found in the mineralogical literature on apatite (including carbonate apatite) which are summarized in 1973 in book form.[4] The types of substitution in apatite appear to be very complex—in addition to the mechanism for replacement of phosphate ions by carbonate. For example, it has been postulated[5] that combined water can enter the structure in several ways: (i) H_2O can replace (OH) at (0, 0, $^1/_4$), (ii) vacancy of a tetrahedral P can result in (H_4O_4), and/or (iii) calcium can be replaced by H_3O^+.

Although Santos and González-Díaz appear to accept (i) they completely disregard (ii) and (iii), following Elliott in this respect. Nevertheless, Simpson[6] has greatly augmented the arguments of McConnell[5] by obtaining evidence in partial confirmation and has suggested what modifications of the unit-cell dimension (a) would be probable for each configuration. It is known, for example, from Foreman's[7] study (by neutron diffraction) of $Ca_3Al_2(D_4O_4)_3$, that the volume of the unit cell increases significantly with $(ZO_4) \rightarrow (H_4O_4)$ and, despite Elliott's disparaging remarks, this type of substitution is now recognized among many silicate and phosphate minerals.[8]

With respect to the infrared absorption spectra, the interpretations of Santos and González-Díaz are highly spectulative for reasons stated in 1966,[9] as well as a recent study: "The fact that the doublet is not observed at first with high CO_2 content (Fig. 4A), and appears only at low CO_2 content, supports, in our opinion, McConnell's (1952b) hypothesis that $CO_3{}^{2-}$ groups in the apatite are in two different orientations "perpendicular" and "parallel" to the c axis (both groups are, in fact, tilted at ~32 °C)."[10] In connection with their consideration of quantitative relationships of constituents, the following remarks seem pertinent: "In the present study the line of best fit is having a slope of −0.5328, therefore [the] more probable mode of substitution was $4CO_3$ for $3PO_4$ as suggested by McConnell (1952)."[11]

Finally, if there is such a substance as "B carbonate apatite"—which we seriously doubt, believing that both

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mineral and biologic types can be explained in terms of the theory proposed by McConnell—Santos and González-Díaz[1] surely have not proposed the correct formula for it. Their sixth (final) formula, $Ca_{10-x}(PO_4)_{6-5x/4}(CO_3)_{3x/2}(HPO_4)_{x/4}(OH)_{2-x/4}(H_2O)_{x/4}$, is out of balance by 1.5 electrons when $x = 1$. Thus, we conclude that they have befuddled a somewhat complex topic.

Registry No. Carbonate apatite, 12286-89-4.

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Concerning the Mechanism of Uncatalyzed Cis to Trans Isomerization of $[Pt(PEt_3)_2RX]$ Complexes

Sir:

In a series of papers[1] we have suggested a dissociative asynchronous mechanism (see Scheme I) for the spontaneous cis to trans isomerization of *cis*-$[Pt(PEt_3)_2RX]$ (X = halide ions; R = alkyl or substituted aryl groups) in protic solvents. Such a mechanism involves as a rate-determining step the breaking of the Pt–X bond to yield a 14-electron 3-coordinate T-shaped species. This is converted to its "trans-like" counterpart, which subsequently links with the halide ion to give the trans product. In all the cases the isomeric equilibrium was found to lie well to the trans form. The derived rate law:

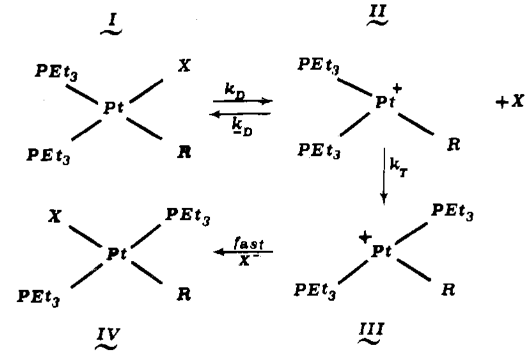
$$k_i = \frac{k_D k_T}{k_{-D}[X^-] + k_T} \qquad (1)$$

accounts for the mass law retardation produced by small amounts of added halide ions and for the linearity of the plots of k_i^{-1} vs. $[X^-]$. While we are well aware of the great propensity for the metal to undergo bimolecular substitutions and are familiar with the fact that, in most of the known cases (except for photochemical reactions), a catalyst was required to produce isomerization,[2] we still favor the dissociative mechanism for the above reactions for the following reasons.

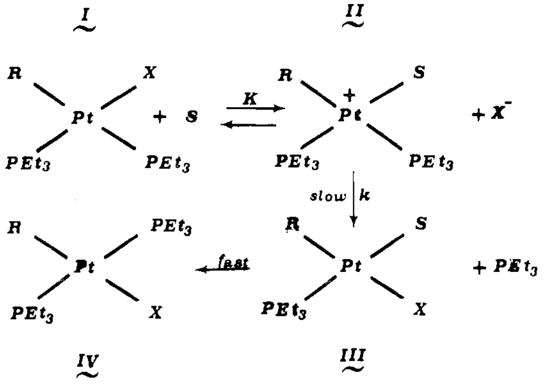
(a) The addition of small amounts of X^- inhibits the rate of isomerization (k_i, s^{-1}) but does not affect the rate of halide substitution by the solvent (k_S, s^{-1}).

(b) The rates of solvolysis of Br in *cis*-$[Pt(PEt_3)_2RBr]$ are dramatically reduced by the increasing steric crowding produced by ortho alkyl substituents on the coordinated aromatic ring (e.g., 10^3k_S (s^{-1}, 30 °C): 6.000, R = Ph; 54.4, R = *o*-MeC_6H_4; 16.2, R = *o*-EtC_6H_4; 0.19, R = 2,4,6-$Me_3C_6H_2$) and approach the rates of isomerization (k_i values) which in contrast are not affected significantly.[1c] In the complex *cis*-$[Pt(PEt_3)_2(2,4,6\text{-}Me_3C_6H_2)Br]$ in which steric congestion is at its peak, isomerization and bromide substitution proceed at the same rate.

Scheme I



Scheme II



(c) Large values of enthalpy and entropy of activation are associated with isomerization in agreement with a dissociative mode of activation, while the low $\Delta H^{\ddagger}$ and the largely negative $\Delta S^{\ddagger}$ found for solvolysis fit well in the simplified picture of an associative mechanism.

(d) Cis–trans isomerization is particularly sensitive to factors controlling bond dissociation, viz., the nature of the halide ion and changes in the electron density at the reaction center, brought about by para substituents on the aromatic ring.[1b] The same factors hardly affect the rates of solvolysis.

Such findings (a–d) give unmistakable evidence that the solvolysis step is not rate determining for the isomerization and suggest the dissociative mechanism as the most reasonable interpretation, unless one objects to three-coordinate (i.e., 14 electron) Pt^{II} intermediates, which we do not.

Very recently Louw[3] has proposed an alternative mechanism (see Scheme II) for isomerization, which assumes a fast preequillibrium between *cis*-$[Pt(PEt_3)_2RX]$ and a solvento intermediate II followed by a rate-determining step in which the halide added or released from the starting material removes the phosphine ligand on II. A fast reentry of PEt_3 on III produces isomerization. Unfortunately, the rate law derived from this mechanism by Louw

$$k_i = \frac{kK}{K + [X^-]} \qquad (2)$$

is incorrect and should be

$$k_i = \frac{kK[X^-]}{K + [X^-]} \qquad (3)$$

which does not fit the experimental observations.

Although this alone must rule out Louw's mechanism, it is useful to add some other comments, since the assessment of the new mechanism appears to have been made while ignoring all the experimental evidence available. Halide retardation can be very important if the halide ion competes effectively with another reaction pathway in capturing a reaction in-