3528 *Inorg. Chem.* **1980**, *19*, 3528–3531

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Complex Formation of Nickel(II) and Cobalt(II) with Salicylic Acids. Equilibria and Reaction Mechanisms

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The kinetics and equilibria of the 1:1 chelated complex between Ni(II) and 5-chloro-, 5-sulfo, and 5-nitrosalicylic acids and between Co(II) and salicyclic acid have been studied by the temperature-jump technique at 25.0 °C and ionic strength 0.10 M ($NaClO_4$). Substituent effects on the equilibrium quotient, $K_{eq} = [NiL][H^+]/[Ni^{2+}][HL^-]$, are in the direction of increasing stability with increasing basicity of the ligands. The mechanism involves Me^{2+} and $MeOH^+$ as reactive species, and, while $MeOH^+$ reacts with rates which agree with the dissociative mechanism (no remarkable labilization by the OH^- ligand), the unhydrolyzed cations show rates which are between 2 and 3 orders of magnitude below the *normal* value. This discrepancy is interpreted as due to the structure of the active ligand species, HL^-, which is blocked by an internally bonded hydrogen.

Introduction

The kinetics of formation of nickel(II) and cobalt(II) complexes has been deeply investigated,[1] and the Eigen mechanism,[2] for the formation of labile complexes, is generally accepted for such ions; according to this mechanism, the rate-determining step, taking place with a rate constant k^*, is the release of a water molecule from the inner coordination sphere of the metal and subsequent entrance of the ligand. This step is preceded by a preequilibrium which involves the formation of an outer-sphere ion pair between the metal ion and the ligand, with an equilibrium constant k_{os} (eq 1). Provided the

$$Me(H_2O)_6^{2+} + L \overset{K_{os}}{\rightleftharpoons} Me(H_2O)_6,L^{2+} \underset{k^*_-}{\overset{k^*}{\rightleftharpoons}} Me(H_2O)_5L^{2+} + H_2O \quad (1)$$

first equilibrium is fast and far displaced to the left, the overall second-order observed rate constant is given by $k_{II} = K_{os}k^*$,[3] which in turn can be predicted from the computer K_{os} value[4] and the typical water exchange rate k_{H_2O} of the metal,[5] which is related to k^* through a statistical factor S, i.e., $k^* = Sk_{H_2O}$.[6,7]

Previous investigations[8] of the reaction between Ni(II) and salicylic acid showed that the experimental value for the rate of the complex formation lies about 3 orders of magnitude below the value predicted by the Eigen mechanism. This strong rate reduction has been ascribed to the internal hydrogen-bonded monoanion structure of the ligand and to the presence, in the rate-determining step, of the hydrogen-bond rupture, which is needed to allow the ligand penetration into the inner coordination sphere of the metal center.

In order to gain additional knowledge of this effect we thought it very promising to compare the behavior of a series of substituted salicylic acids, namely, the formation equilibria and mechanism of the nickel(II) complexes with 5-chloro-, 5-sulfo-, and 5-nitrosalicylic acids and of cobalt(II) with salicylic acid. All these ligands bear identical active sites and differ only in their basic strength.

Experimental Section

Chemicals. Salicylic acid (C. Erba; later referred to as H_2SAL), 5-chlorosalicylic acid (Fluka; H_2ClSAL), 5-sulfosalicylic acid (C. Erba; H_2SSAL), and 5-nitrosalicylic acid (Fluka; H_2NSAL) were reagent grade chemicals.

Cobalt(II) and nickel(II) perchlorates were prepared by reacting their carbonates (C. Erba) with aqueous perchloric acid (E. Merck) and recrystallized twice from water. Their stock solutions were analyzed complexometrically.

Stock solutions of the ligands were prepared from weighed amounts. Sodium perchlorate (obtained from NaOH and $HClO_4$) was added to all the solutions in order to maintain a constant ionic strength (for all the solutions, μ = 0.10 M). Bidistilled water was used throughout.

Table I. Equilibrium Quotients for the Investigated Reactions and Dissociation Constants for the Ligands, at 25.0 °C and μ = 0.10 M

			10^6K_{eq}	
ligand	10^3K_{1a},[b] M	K_{2a},[b] M	Ni(II)	Co(II)
H_2SAL	2.04	5×10^{-14}	1.4[a]	0.9
H_2ClSAL	3.10	4×10^{-13}	2.3	
H_2SSAL	3.75	8×10^{-13}	5.0	
H_2NSAL	5.70	7×10^{-11}	4.8	

[a] Taken from ref 8. [b] For K_{1a} and K_{2a}, see the text and ref 8, 13, and 17.

Instrumentation. Spectrophotometric equilibrium data were obtained with a Perkin-Elmer 200 spectrophotometer. pH-metric measurements were performed with a Metrohm E 388 potentiometer equipped with glass and calomel (saturated NaCl bridge) electrodes. The desired acidities for the equilibrium data and the kinetic runs were obtained by adding to the solutions small amounts of $HClO_4$ or NaOH; buffers were avoided in order to have an inert medium with respect to the investigated cations.

Kinetic measurements were performed on a Messanlagen Temperature-jump apparatus (Messanlagen Studiengesellschaft mbH, Göttingen, West Germany) equipped with a Teflon-lined cell (gold electrodes) and connected to a Tektronix (Model 549) storage oscilloscope. A 30-kV discharge gave a 3.4 °C temperature increase.[9]

The temperature after the jump was 25.0 ± 0.1 °C and appeared to be constant during the relaxation effect. Blank experiments with solutions containing all the reagents, including indicator, were run, but the metal or the ligand showed no relaxation effects.

The amplitude of the displacement from the final equilibrium as a function of time was evaluated on photographs taken from the oscilloscope screen; relaxation times were measured from log plots of the displacement vs. time.[9] Each run was replicated three to five times; the relaxation times exhibited a spread of ±10% at most.

Results and Discussion

Formation Constants. Previous investigations showed that

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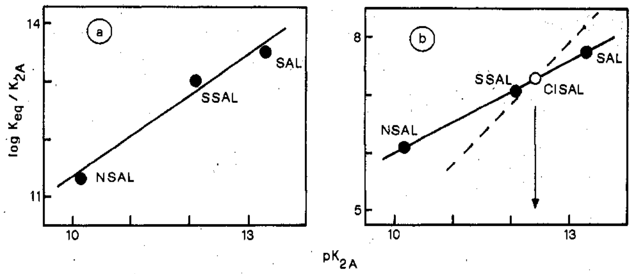

Figure 1. Variation of log (K_{eq}/K_{2a}) as a function of pK_{2a} for the reaction of salicylic acids with Al(III)[13] (a) and Ni(II) (b). For the point concerning H_2ClSAL, see the text.

Co(II) and Ni(II) react with salicylic acid in solution,[8,10,11] with chelate formation, according to eq 2, where HL^- is the

$$Me^{2+} + HL^- \rightleftarrows MeL + H^+ \quad K_{eq} \qquad (2)$$

ligand monoanion, the prevailing ligand species in the pH range investigated (dissociated carboxylic group, undissociated phenolic group). To determine the equilibrium constant K_{eq}, we performed spectrophotometric measurements at λ = 340–380 nm, with solutions containing nickel or cobalt perchlorate ((5.0–30) × 10^{-3} M) and the desired ligand ((0.5–1.0) × 10^{-4} M) brought to μ = 0.10 M and pH between 5.5 and 7.4. At this wavelength a ligand absorption peak is strongly altered upon complexation.

The equilibrium quotients K_{eq}, collected in Table I, have been evaluated with the aid of a modified Benesi–Hildebrand[12] treatment previously described.[8]

Substituents do not affect the stoichiometry of reaction 2 and, for all the reactions investigated, a single 1:1 chelated complex is formed; the substituent role is displayed in the different stability of the complexes, in the expected direction: increased stability with increased basicity (see following paragraph) of the ligand.

Dissociation Constants. Table I collects also the dissociation constants of the ligands. The pK_{1a} value for H_2ClSAL was determined by potentiometric titrations.

The dissociation constant K_{2a} of the phenolic group of H_2ClSAL was estimated according to the following considerations. At a first glance it seems as if the complexes were more stable the higher the acidity of the undissociated ligand. However the complex formation causes the phenolic proton to be expelled. Therefore a comparison should be made not between K_{eq} and K_{1a} but rather between $[MeL]/[Me^{2+}][L^{2-}] = K_{eq}/K_{2a}$ and K_{2a}.[13] A linear relation has been obtained for plots regarding the present data for Ni(II) as well as for the reactions of the same ligands with Al(III)[13] (see Figure 1a, b).

Therefore a value of K_{2a} for H_2ClSAL has been assumed (4 × 10^{-13} M) in order to place the corresponding point (open circle of Figure 1b) on the common linear behavior (the dotted line represents the variation of K_{eq}/K_{2a} as a function of the variation of K_{2a} for H_2ClSAL).

Kinetics and Mechanism. Each run involved solutions containing the metal (C_{Me} = (1.0–10.0) × 10^{-3} M), ligand ((1.0–10.0) × 10^{-3} M), and bromothymol blue (3.0 × 10^{-5} M) brought to the desired acidity (pH 6.2–7.4) and ionic strength (μ = 0.10 M). A wider pH range of study was prevented at the high end by interference from precipitation and at the low end by too small relaxation effects. The perturbation, by the temperature jump, of eq 2 involves a proton; therefore, the relaxation could be conveniently followed by monitoring the variation, at 615 nm, of the acid–base indicator (HIn).[8]

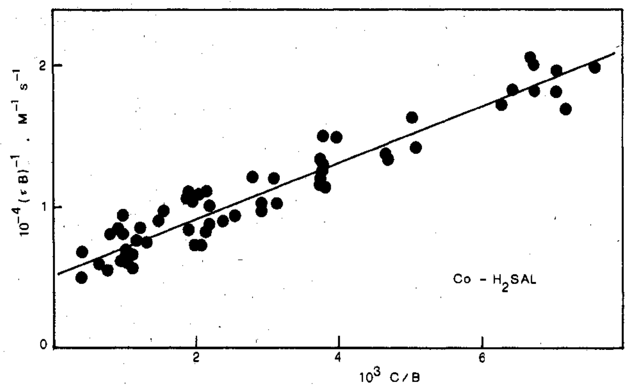

Figure 2. Variation of $(\tau B)^{-1}$ as a function of $K_h/[H^+]$ (or C/B; see eq 9) for the reaction of Co(II) with salicylic acid.

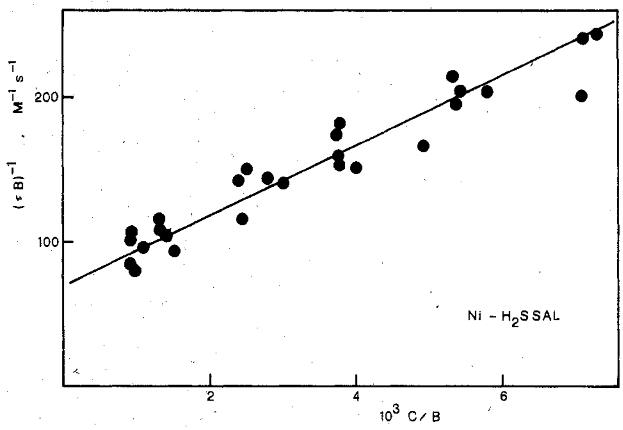

Figure 3. Variation of $(\tau B)^{-1}$ as a function of $K_h/[H^+]$ (or C/B; see eq 9) for the reaction of Ni(II) with 5-sulfosalicylic acid.

Kinetic and equilibrium experimental results were in agreement with the reaction scheme shown by eq 3–6. This

$$Me^{2+} + HL^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} MeL + H^+ \quad k_{12}/k_2 = K_{eq} \qquad (3)$$

$$K_h \Big\downarrow\!\Big\uparrow H^+$$

$$MeOH^+ + HL^- \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} MeL \quad k_{34}/k_{43} = K_{eq}/K_h \qquad (4)$$

$$H_2L \overset{K_{1a}}{\rightleftharpoons} HL^- + H^+ \overset{K_{2a}}{\rightleftharpoons} L^{2-} + 2H^+ \qquad (5)$$

$$HIn \rightleftharpoons In^- + H^+ \quad K_{In} \qquad (6)$$

scheme consists of two parallel reactions (3) and (4) coupled with a number of fast proton-involving equilibria. It has been demonstrated[14] that for this type of system the net rate of formation of MeL, $\vec{V}$, is given by eq 7 where $v_3°$ and $v_4°$ are

$$\vec{V} = (v_3° + v_4°)\frac{\vec{\delta} v_3 - \overleftarrow{\delta} v_3}{v_3°} \qquad (7)$$

the rates at equilibrium in either direction, or exchange rates, for paths 3 and 4, respectively, and $\delta\vec{v}_3$ and $\delta\overleftarrow{v}_3$ are excess rates in either the forward and backward directions. Equation 7 holds near equilibrium, i.e., when δ, the difference between the *actual* concentration and the *equilibrium* concentration of MeL, is small. With these conditions eq 8 can be derived.[15]

$$\tau^{-1} = -\vec{V}/\delta \qquad (8)$$

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Table II. Kinetic Parameters for the Reaction of Ni(II) and Co(II) with Salicylic Acid and Ni(II) with Substituted Salicylic Acids at 25.0 °C and $\mu = 0.10$ M

reacn	k_{12}, $M^{-1}\,s^{-1}$	k_{34}, $M^{-1}\,s^{-1}$	k_{21},[b] $M^{-1}\,s^{-1}$	k_{43},[b] s^{-1}
Ni-SAL[a]	70 ± 15	$(6.3 \pm 1.0) \times 10^4$	5.0×10^7	17
Ni-ClSAL	90 ± 15	$(4.7 \pm 0.5) \times 10^4$	3.9×10^7	7.8
Ni-SSAL	70 ± 15	$(2.4 \pm 0.3) \times 10^4$	1.4×10^7	1.8
Ni-NSAL	80 ± 20	$(5.1 \pm 1.0) \times 10^4$	1.7×10^6	0.4
Co-SAL	$(5.0 \pm 1.0) \times 10^3$	$(2.1 \pm 0.5) \times 10^6$	5.6×10^9	900

[a] Taken from ref 8. [b] k_{21} and k_{43} are computed from forward and equilibrium constants.

Equations 7 and 8, when applied to the reaction sequence (3)–(6), yield expression 9 for the relaxation time, τ,[8,15] where

$$(\tau B)^{-1} = k_{12} + k_{34}C/B \qquad (9)$$

the meaning of B and C has been already specified.[8] Furthermore[14] $C/B = K_h/[H^+]$, and therefore a plot of $(\tau B)^{-1}$ against $K_h/[H^+]$ should be linear with intercept k_{12} and gradient k_{34}. The following equilibrium constants were adopted: $K_h(\text{Co(II)}) = 3.8 \times 10^{-10}$ M,[16,17] $K_h(\text{Ni(II)}) = 3.8 \times 10^{-10}$ M,[16,17] $K_w = 1.58 \times 10^{-14}$ M^2,[18] and $K_{In} = 9.0 \times 10^{-8}$ M.[19]

Figure 2 reports the data concerning the reaction of Co(II) with salicylic acid, and, as an example, Figure 3 shows the trend for the reaction of Ni(II) with H_2SSAL. The derived kinetic parameters are collected in Table II.

According to the described Eigen mechanism, the value of k_{12} can be computed from the corresponding ion-pair constant K_{os}[4,20,21] ($\simeq 2$ M^{-1}),[22] the water exchange rate at the coordination sphere of the metal ($k_{H_2O} \simeq 2.7 \times 10^4$ s^{-1} for Ni^{2+} and $\simeq 2.4 \times 10^6$ s^{-1} for Co^{2+}),[23,24] and a statistical factor S ($S = 0.2$, which accounts for the competition of the incoming ligand with bulk water).[6]

A value k_{12}(calcd) $\simeq 1.1 \times 10^4$ M^{-1} s^{-1} for NiL formation and $k_{12} \simeq 1 \times 10^6$ M^{-1} s^{-1} for CoL can be computed for "normal" behavior. Higher values are obtained if a statistical factor $S = 0.75$ is assumed.[25] The computation of k_{34} needs the knowledge of the water-exchange rate at the $MeOH^+$ center. It has been demonstrated that the presence of the OH^- ligand labilizes the coordination sphere of the hydrolyzed species with respect to the parent ion for trivalent metal ions such as Fe(III),[7,26] Al(III),[27,28] or Ga(III).[29] On the contrary, such labilization seems to be much less pronounced in the case of divalent metal ions: for example, comparable rates for Cu^{2+} and $CuOH^+$ have been obtained.[30] In the case of Ni(II) and Co(II) the hydrolyzed $NiOH^+$ or $CoOH^+$ ions have not been found as reactive species almost universally; therefore, for these species the water-exchange rate should be of the same magnitude as for the unhydrolyzed ones. Thus the calculated k_{34} values should be comparable to the corresponding k_{12} values. If we compare the experimental and computed values, good agreement can be noticed for $NiOH^+$ and $CoOH^+$ (the differences lie within the generally accepted discrepancies for such comparison); on the contrary, the experimental k_{12} values, for both nickel and cobalt, lie more than 2 orders of magnitude below the "normal" computed values. This noticeable reduction can be ascribed to the presence of an internal hydrogen bond in the ligand-reactive species which blocks the reaction site; therefore, the reaction involves a bimolecular interaction of the metal species attacking the internally hydrogen-bonded ligand species as the rate-determining step.

This behavior is not unique and has been previously observed for complex formation reactions with ligands in which the reaction site is blocked by a proton,[1a,31] especially when the proton forms an internal hydrogen bond as in the case of the reactions of La^{3+} with pyridineazo ligands,[32] of Ni^{2+} with hydroxyazo ligands,[33-35] or of Cu^{2+} with hydroxy ketones.[30]

On the contrary, the much greater basicity of $NiOH^+$ and $CoOH^+$[33,34] makes easier the release of the blocking H^+ with subsequent opening of the ligand sites and the rate-determining step appears to be the substitution between coordinated water molecules and the ligand at the metal center.

Turning now to the present results, the substituents on the different ligands affect mainly the acidity of the phenolic groups (K_{2a} values) whereas the carboxylic group acidity is varied to a much lesser extent (K_{1a} values). The independence of the k_{12} (see the values for Ni^{2+} in Table II) of the ligand basicity suggests that the rate-determining step concerns the hydrogen-bond rupture, before the release of the phenolic proton, followed by a fast chelation ring closure with the proton release. In this context it is worth mentioning that the protolysis reaction rate of salicylate monoanion with OH^- turns out to be abnormally low (about 3 orders of magnitude lower than the diffusion-controlled limit which is common for most of this kind of reactions)[36] and this effect has been ascribed to the strong intramolecular hydrogen bridge.

The strength of the hydrogen bond, which must be loosened in the rate-determining step, is nearly the same; in fact it is related to the carboxylato group basicity, i.e., the K_{1a} values which lie close together for all the ligands investigated. If, on the contrary, a slow step in the chelation ring closure would bring about a possible reduction of rate,[32] this process (which involves phenolic proton explusion) should be slower the higher the K_{2a} value. Thus the independence of k_{12} of such a parameter allows us to exclude this possibility.

It is worth mentioning that the strong rate reduction for the unhydrolyzed species allows the evaluation of the reactivities of $NiOH^+$ and $CoOH^+$; these values suggest that the labilizing effect of the OH^- ligand is in these cases very limited. In conclusion, the present metal ions, which generally follow a dissociative mechanism, in some reactions show abnormally high or low reactivities. In the former case the internal-con-

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jugate-base mechanism, ICB,[37] is operative, in the latter the ligand, blocked by a proton, is responsible for the retardation. This behavior seems to be always operative when an internal hydrogen bond at the reaction site is present, for which we propose the designation "internal hydrogen bond mechanism".

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Registry No. H_2ClSAL, 321-14-2; H_2SSAL, 97-05-2; H_2NSAL, 96-97-9; H_2SAL, 69-72-7; Ni^{2+}, 14701-22-5; Co^{2+}, 22541-53-3.

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Crystal Structure of Ferric Molybdate, $Fe_2(MoO_4)_3$

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Single crystals of $Fe_2(MoO_4)_3$ have been grown by hydrothermal techniques from 0.75 M HCl solution and by flux techniques from K_2MoO_4–MoO_3–B_2O_3. $Fe_2(MoO_4)_3$ crystallizes in the space group $P2_1$ with $a = 15.693$ (3) Å, $b = 9.235$ (1) Å, $c = 18.218$ (4) Å, and $\beta = 125.21$ (1)°. Full three-dimensional least-squares isotropic refinement using counter diffractometer data converged to $R = 0.041$ ($R_w = 0.055$) for 2464 observed independent data. The relationship of this structure to that of $Sc_2(WO_4)_3$ is discussed. Magnetic susceptibility measurements are indicative of an antiferromagnetic material with an ordering temperature below 80 K ($\Theta = -62.7$ K).

Introduction

Molybdates and tungstates of trivalent metal ions, $M_2(XO_4)_3$, have been classified[1] according to the coordination polyhedra about the metal atoms. In particular, molybdates of the smaller lanthanides as well as those of Al, Cr, Fe, Sc, and In are reported[1] to form with the C-type structure, characterized by tetrahedral MoO_4 groups and six-coordinated trivalent metal ions. The prototype of this structure is the orthorhombic tungstate $Sc_2(WO_4)_3$, described by Abrahams and Bernstein.[2]

Of the molybdates, structure determinations have been reported for $In_2(MoO_4)_3$[3] and $Fe_2(MoO_4)_3$,[4] which are described as crystallizing in the space group $P2_1/a$. Monoclinic $Fe_2(MoO_4)_3$ has also been reported[5] to reversibly transform to an orthorhombic form at 518 °C.

We have grown single crystals of ferric molybdate of suitable size and quality for X-ray diffraction studies by both high-temperature flux and hydrothermal techniques and present the results of our structure refinement of this compound. A preliminary report of this work has been presented.[6]

Experimental Section

Synthesis and Crystal Growth. Nutrient material was prepared by mixing stoichiometric aqueous solutions of reagent grade ferric nitrate and ammonium molybdate, boiling the mixture gently for 30 min, and then filtering the precipitate. The solid product was dried at 110 °C, ground thoroughly, and sintered overnight at 800 °C. The resulting yellow-green powder gave an X-ray powder diffraction pattern identical with that reported in the literature.[5] This nutrient proved to be far superior to stoichiometric mixtures of Fe_2O_3 and MoO_3 since it eliminated any free Fe_2O_3 upon which $Fe_2(MoO_4)_3$ is prone to nucleate.

After preliminary experiments using the high-temperature flux technique, a flux consisting of 13.35 mol % K_2MoO_4, 13.35 mol % MoO_3, and 73.30 mol % B_2O_3 was selected. Optimum conditions for the growth of $Fe_2(MoO_4)_3$ by this technique require that a 4–6 mol % solution of the nutrient in this flux be soaked for 12–24 h at 800 °C and then cooled at 15 °C/h to ambient temperature. The resulting crystals, separated from the flux by boiling water, were yellow-green and, for the most part, exhibited a largely bladelike habit. Occasionally, some of these crystals formed as well-defined rectangular tablets with beveled edges.

Initial attempts to grow single crystals of $Fe_2(MoO_4)_3$ by the hydrothermal technique were based on a method developed by Klevtsov.[7] Charges of 50 mg of a stoichiometric mixture of the component oxides (1:3 Fe_2O_3:MoO_3) along with a mineralizer charge of 0.02–0.20 mL of a 6 wt % $FeCl_3$ solution were sealed in 5-mm-diameter gold tubes 5 cm long and contained in cold-seal autoclaves (TemPress MRA 114R) operating at 3–60 kpsi and 450–480 °C. It was found that, under these conditions, successful growth runs could last only 2 days due to the deterioration of the gold capsules in the highly acidic halide mineralizer. For optimal growth period and for elimination of nucleation and contamination problems the precipitated nutrient material was substituted for the oxide mixture and the mineralizer (which hydrolyzes to form Fe_2O_3) was changed to a 0.25–0.75 M HCl solution. At pressures below ~28 kpsi, transparent, strongly pleochroic, lemon yellow–green crystals form up to 0.30 mm in maximum dimension. These crystals often exhibit the characteristic rectangular tablet habit of flux-grown crystals. At pressures above this range, large (1–2 mm) green crystals form. Precession photographs indicate, however, that these "crystals" are often twinned and are in most instances nearly polycrystalline.

Magnetic Susceptibility. Magnetic data were recorded in the temperature range 84–303 K with a Faraday balance of the type described by Morris and Wold.[8] Absence of ferromagnetic impurities

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