

namely, $(C_7H_5O_3)_3M \cdot H_2O$ where $M = La, Nd, Sm,$ or Am . This had been found previously only for the case of Nd . The formula for the Pu complex is probably the same because our findings have covered the range of ionic size which includes Pu^{3+} ; we have not, however, been able to produce the compound despite numerous attempts using the published method.³

The kinds of linkages found in the crystal between salicylato and metal ions are relevant to the previous work with stability constants and also suggest the type of interaction which these ions have with humic materials. The chains of metal ions sharing common organic ligands raise the possibility that in solution the molecules are also polynuclear. The presence of numerous types of configurations by which the ligands are attached to the metal not only confirms the cyclic mode of chelation suggested for salicylato ions but also includes many endwise attachments which were proposed to be the case for *p*-hydroxybenzoate ligands. The phenolic hydrogen atom is not expected to be ionized in solutions with $pH < 7$, and the structural evidence tends to confirm this. The one $OH, O(9)$, that is chelated to the metal would seem most likely to be ionized, if any. Evidence that the H atom is *not* ionized is that (1) the $C-OH$ bond is of normal length and equivalent to that in the other salicylato ions, (2) there is a very short $O(9) \cdots O(1)$ contact of 2.399 Å to another ligand, and (3) the $C-O \cdots O$ angle is $112.7(3)^\circ$ which is typical for a phenolic $C-O-H$ angle.

Registry No. $(C_7H_5O_3)_3Sm \cdot H_2O$, 61026-21-9; $(C_7H_5O_3)_3Am \cdot H_2O$, 61026-23-1; $(C_7H_5O_3)_3Nd \cdot H_2O$, 61026-25-3; $(C_7H_5O_3)_3La \cdot H_2O$, 61026-27-5.

Supplementary Material Available: Tables of observed and cal-

culated structure factors (16 pages). Ordering information is given on any current masthead page.

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Metal-Metal Bonding in Reduced Scandium Halides. Synthesis and Crystal Structure of Scandium Monochloride¹

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The synthesis of a number of reduced scandium chlorides is achieved by reaction of excess metal with $ScCl_3$ in sealed Ta tubing above 877 °C for periods of weeks to months. Extreme conditions are necessary because of both the kinetic problems of forming extended metal-metal bonded structures and the fact that $ScCl_{1.5}$ effectively blocks further reaction on metal surfaces below this temperature. Single-crystal x-ray diffraction data showed that a gray-black laminar phase was $ScCl$ with a sheet structure consisting of close-packed homoatomic layers sequenced $Cl-Sc-Sc-Cl$ along $[001]$ ($R\bar{3}m$, trigonal cell; $a = 3.473(2)$ Å, $c = 26.71(4)$ Å, $Z = 6$; $R = 0.088$, $R_w = 0.101$ for 79 independent reflections taken with $Mo K\alpha$ radiation). The phase is thus polytypic (ignoring the difference in metal atom) with $ZrCl$ and isostructural with $ZrBr$ even though there are only two-thirds as many electrons for bonding the double-metal sheets of scandium. The general occurrence of metal-metal bonding in clusters, ribbons, and sheets in transition metal groups 3–5 is considered.

Introduction

Since 1963 a series of publications reporting and disputing the existence of solid, lower chlorides of scandium has appeared. Polyachenok and Novikov^{2a} first reported a relatively large amount of reaction of the metal with the liquid $ScCl_3$ and the formation of the solid phases $ScCl_{2.67}$ and $ScCl_2$, although the means whereby these compositions were established was not given. Corbett and Ramsey^{2b} disputed these results based on thermal analysis data, suggesting the earlier results had been perturbed by reaction with the silica container. In a subsequent publication McCollum and co-workers³ reported on the preparation of solid $ScCl_{1.5}$, scandium sesquichloride, as well as $ScBr_{1.5}$, both of which could be prepared

at elevated temperatures when proper attention was paid to avoiding blockage of the metal surface by product. Subsequent efforts to prepare single crystals of $ScCl_{1.5}$ have revealed a complex and unpredicted⁴ chemistry in the $Sc-ScCl_3$ system. This paper notes some of the chemistry in the region $2.0 \geq Cl:Sc \geq 1.0$ and reports on the single-crystal structure of the stoichiometric monochloride, $ScCl$.

Experimental Section

Materials. The metal used had been distilled in tantalum and had typical major impurity levels (atomic ppm) of 70 Fe, 250 Ta, <30 individual rare earths, and <800 each C, O, F. Thin foil strips for reduction of $ScCl_3$ were made from cold-rolled scandium sheet which was cut into pieces (4 cm × 1 cm × 0.12 cm), annealed at 750 °C

under vacuum (10^{-6} Torr), and again cold-rolled to a length of 13–14 cm and a thickness of 0.04 mm. The strips were electropolished to remove any hydrocarbon greases and other surface impurities picked up during the cold-rolling process⁵ and then washed with copious amounts of acetone, dried, and stored under vacuum. As an alternate reductant scandium powder (<100 mesh) was made by thermal decomposition of the dihydride. This brittle material was ground to less than 100 mesh, spread out so as to barely cover the bottom of a molybdenum boat, and heated at 750 °C under dynamic vacuum until the system was below discharge ($<10^{-4}$ Torr). The product metal was found to contain H:Sc = 0.091 by vacuum extraction, a value which corresponds to the expected value based on the equilibrium data available for the Sc–H system.⁶

The trihalide was prepared by reaction of the metal with high-purity hydrogen chloride and was vacuum-sublimed in a tantalum jacket as before.⁷ The product after sublimation gave Cl:Sc ratios of 2.99 \pm 0.01 with typical recoveries >99%.

To avoid contamination all reactants and reduced products were stored and manipulated only with standard vacuum-line and drybox techniques. All reactions were carried out in induction-cleaned (1800 °C) tantalum containers which were in turn welded and jacketed in fused silica tubes under vacuum.

Analyses. All wet chemical analyses were done as before³ while the microprobe analyses were performed in this laboratory using an Applied Research Laboratories Model EMX electron microprobe.

Syntheses. The initial preparation of the ScCl phase was through the reduction of ScCl_{1.5} with metal foil. Preparation of ScCl_{1.5} as before³ seemingly leaves a blocked metal surface and stops the reduction process since evidence for a more reduced phase on the foil surface was never found, even with careful and repeated scrutiny. However, under more reducing conditions a number of new phases can be detected by reequilibrating fresh scandium strips with ScCl_{1.5} at temperatures greater than the peritectic melting point of ScCl_{1.5} (877 °C). Several different phases are obtained depending upon various factors: the amount of ScCl_{1.5} used, surface area of the scandium metal, temperature, and especially the length of time the system is allowed to "equilibrate". However, this procedure only gives amounts sufficient for identification by x-ray powder diffraction patterns (Debye–Scherrer) and for microprobe analysis. The latter consistently detected only Sc and Cl in these compounds, but unfortunately contamination by elements lighter than Na, especially C, N, O, and F, cannot be ruled out. The interaction of the electron beam with these compounds to change their composition through loss of ScCl₃ has prevented reproducible reliable quantitative results from being obtained by the microprobe method. Of particular interest was the powder pattern of one of these new phases which resembled those of ZrCl (single-crystal data⁸) and ZrBr (powder data⁹) and which led to this effort to determine whether a monochloride of scandium existed.

In order to overcome the problem of the severely limited yields of these reduced compounds, powdered metal and ScCl₃ were reacted directly. Thus ca. 0.25 g of Sc and 0.4 g of ScCl₃ were added to a 4 cm long, 9 mm o.d. tantalum tube, and this was welded, sealed in a fused-silica jacket, and heated at 800 °C for several weeks. All reactants were completely consumed in the reaction and the product was a mass of black crystalline material analytically determined to have Cl:Sc = 1.04 \pm 0.03 and determined by x-ray powder diffraction to be the scandium monochloride phase. Single crystals were prepared in a similar manner by heating a mixture of Sc powder and ScCl₃ (Cl:Sc = 1.0) at 960 °C for 2 months. The temperature was monitored by a thermocouple attached to the outside of the glass jacket. The reaction tube was cooled at a rate of 1.25°/h to 900 °C and was then air-quenched. The crystals were examined in a specially designed inert-atmosphere box constructed with a nearly horizontal window to facilitate the use of a stereo-zoom microscope.⁸ The crystals were found embedded in a gray-black mass, identified as ScCl₃ by x-ray powder diffraction, which had been molten at temperature. About 80 wt % was the shiny gray-black and easily cleaved ScCl. Two other phases of unknown composition were found in small quantities in separate parts of the tantalum tube implying, of course, that this had not been an isothermal equilibrium experiment at 960 °C.

Data Collection. A single-crystal of ScCl of extreme dimensions 0.2 \times 0.15 \times 0.02 mm was used for x-ray data collection at ambient temperature on an automated four-circle diffractometer designed and built in Ames Laboratory.¹⁰ The data set was collected on the basis of a hexagonal unit cell using Mo K α radiation (λ 0.70954 Å)

monochromatized with a graphite single crystal. All data within a sphere defined by $2\theta < 50^\circ$ were collected in the *HKL* and *H \bar{K} L* octants using an ω -scan mode. Peak heights of three standard reflections which were remeasured every 75 reflections did not show any significant change over the data collection period. A total of 227 reflections were observed from a total of 688 reflections checked. Final trigonal cell parameters and their estimated standard deviations were obtained from the same crystal by a least-squares fitting of twice the ω values obtained by left–right, top–bottom beam splitting on Friedel-related pairs of 13 independent reflections randomly distributed in reciprocal space with $2\theta > 25^\circ$; these results were $a = b = 3.473$ (2) and $c = 26.71$ (4) Å. These parameters match those estimated from preliminary oscillation and Weissenberg films. In general the films characteristically exhibited axial streaking and broad diffraction maxima. The data crystal, however, uncharacteristically gave relatively minor axial streaking but still slightly broadened, coherent diffraction maxima, necessitating the ω scan.

Structure Determination. The observed intensities were corrected for Lorentz–polarization effects and the standard deviations were calculated as previously described,¹¹ to give 210 reflections with $I > 3\sigma(I)$. An absorption correction was not considered necessary ($\mu = 48$ cm⁻¹). Examination of the data set revealed the systematic extinction condition $-h + k + l \neq 3n$ which fixes the space group as a trigonal equivalent of a rhombohedral space group. Belov¹² has shown that close-packed structures can have only two *R* space group symmetries, *R* $\bar{3}m$ and *R*3*m*, and the former, with $Z = 6$ and atoms in 6c special positions, was selected in view of the obvious similarity in unit cell dimensions to those of ZrCl⁸ and the earlier observation from powder patterns that ScCl was similar to ZrBr and ZrCl. Appropriate averaging yielded 79 independent reflections for the final data set.

The obvious trial structure based on the ZrCl fractional coordinates resulted in $R = 0.80$ but switching the metal layers ($z' = 0.33 - z$) with respect to packing so that the halogen atoms have prismatic coordination as in ZrBr⁹ gave $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.174$. Conversion to anisotropic thermal parameters gave convergence at $R = 0.088$ and $R_w = 0.111$ where $R_w = [(\sum w(F_o - |F_c|)^2) / \sum w(F_o)^2]^{1/2}$ and $w = \sigma_F^{-2}$. The stronger reflections were observed to have larger values of $w|F_o| - |F_c|$ so the data set was reweighted in ten overlapping groups sorted according to F_o so that $w\Delta^2$ was constant, giving final converged values of $R = 0.088$ and $R_w = 0.101$. Variation of occupation parameters at this point for both scandium and chlorine positions gave converged values of 1.000 (3), indicating no significant deviation from the simple stoichiometry. A final difference Fourier synthesis map was flat to ≤ 0.5 e/Å³ in all regions between atoms and ≤ 2 e/Å³ on atom sites.

Sources of atomic scattering factors for neutral atoms (which included corrections for both real and imaginary parts of anomalous dispersion) and of the computing programs used were referenced before.^{8,13}

Description and Discussion of the Structure

The final parameters together with important distances and angles are given in Table I, while the [110] projection of the structure is shown in Figure 1. Observed and calculated structure factors are available as supplementary material.

The four-layer sheet structure found for ScCl is polytypic with ZrCl (allowing for the change in metal atom) and isomorphous with ZrBr. The basic unit is a sheet composed of four close-packed and tightly bound layers Cl–Sc–Sc–Cl with the usual description of the layering geometry ...|abca|cabcb|cab|... or alternately, in terms of layer sheets, ..ACB.. where the capital letters follow the relative orientation of the outer halide layers of each sheet. The result is antiprismatic coordination of the metal atoms and prismatic coordination of the halogen atoms. The ScCl arrangement is contrasted in Figure 1 with that of ZrCl (...ABC... packing) where there is antiprismatic coordination of halogen.

Each scandium atom in ScCl has three metal neighbors in the next layer at 3.22 Å, six metal neighbors in the same layer at 3.47 Å, and three chlorine neighbors in the opposite layer at 2.59 Å (Table I). The two different short metal–metal distances, 3.22 and 3.47 Å, indicate strong metal–metal bonding between the metal layers and a somewhat lower bond

Table I. Final Atom Parameters, Interatomic Distances, and Angles in ScCl^a

Atom Parameters ^b							
	<i>x</i>	<i>y</i>	<i>z</i>	$B_{11} = B_{22}$	B_{33}	$B_{12} = \frac{1}{2}B_{11}$	$B_{13} = -B_{23}$
Sc	0	0	0.2137 (1)	0.9 (1)	3.8 (2)	0.45 (5)	0
Cl	0	0	0.3914 (1)	1.0 (1)	3.8 (2)	0.50 (5)	0

Distances, Å			
Intralayer		Interlayer	
Sc-Sc	3.473 (2)	Sc-Sc	3.216 (6)
Cl-Cl	3.473 (2)	Cl-Cl	3.695 (8)
		Sc-Cl	2.591 (4)

Interlayer Angles, Deg			
Defining the antiprismatic coordination of Sc		Defining the prismatic coordination of Cl	
Sc-Sc-Sc	65.3 (1)	Cl-Cl-Cl	56.1 (1)
Cl-Sc-Sc	104.7 (1)	Cl-Cl-Sc	96.4 (1)
Cl-Sc-Cl	84.1 (2)	Sc-Cl-Sc	84.1 (2)

^a The cell is trigonal, space group $R\bar{3}m$, with $a = 3.473$ (2) Å, $c = 26.71$ (4) Å, and $Z = 6$. $R = 0.088$; $R_w = 0.101$ (79 reflections).

^b The general thermal parameter expression used is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

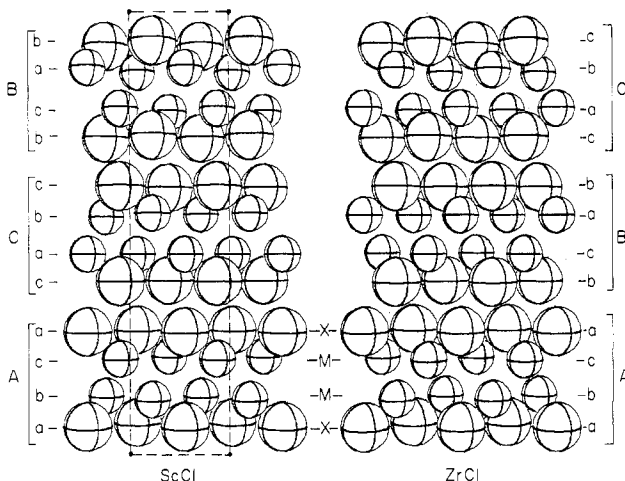


Figure 1. Projections along [110] of the structures of ScCl (left) and ZrCl⁸ (right). The lower case letters refer to relative positions of close-packed layers along [001]; the capital lettering, to packing of four-layer sheets. Arbitrary isotropic temperature factors were used.

order for the metal-metal bonds between atoms in a layer, the latter separation of course being dictated by the Cl-Cl period in the planar sheets. In hcp scandium metal the metal-metal distances are 3.26 and 3.31 Å for inter- and intralayer distances, respectively, the difference arising because of a small distortion from the ideal c/a ratio for close-packed structures.¹⁴ The distortion in ScCl is even greater but chemically reasonable since each metal layer is now adjacent to a chlorine layer. The 8% difference in scandium-scandium distances and corresponding angular distortions indicates the degree of approximation necessary in a description of the double-metal layer structure in terms of metal octahedra (trigonal antiprisms) each of which shares six edges.

The scandium-chlorine distance observed, 2.59 Å, compares closely with 2.58 Å in ScCl₃¹⁵ even though the latter involves octahedral coordination about scandium(III). Intralayer Cl-Cl distances are 3.47 Å while interlayer Cl-Cl distances are 3.70 Å, very appropriate distances between chlorine atoms bound to common scandium atoms and for weak van der Waals interactions between halogen sheets, respectively. The weak interlayer binding in this and related compounds is of course

Table II. Some Distance Comparisons for the Polytypic ScCl and ZrCl and the Metals (Å)

Type	Distances, Å			
	ScCl	ZrCl ^a	Sc ^b	Zr ^b
M-M interlayer	3.22	3.09	3.26	3.18
intralayer	3.47	3.42	3.31	3.23
M-Cl	2.59	2.63		
Cl-Cl interlayer	3.70	3.61		
intralayer	3.47	3.42		

^a Reference 8. ^b Estimated standard deviations are all ≤ 0.01 Å.

responsible for their graphitic properties and easy physical damage. The larger thermal parameters exhibited normal to the layers (Table I) parallel very closely the behavior found for ZrCl⁸ and are taken to be a manifestation of crystal imperfection in the weakly bound direction. An error resulting from the lack of an absorption correction is considered unlikely here as (a) this correction was carried out for ZrCl with the same results and (b) the ellipsoid elongation is in the direction of the thin dimension of the crystal platelet, contrary to the usual evidence for an absorption error.

A remarkable feature of the ScCl structure is that it is polytypic with ZrCl (and isostructural with ZrBr) even though there are formally only *two* rather than *three* electrons per metal involved in binding the double-metal sheets. The effects of this reduction are discernible particularly in the interlayer metal-metal separation (Table II), even when the difference in core radii is allowed for; on the other hand, intralayer metal bonding changes are largely obscured by the nearly fixed period of the chloride layers. Some charge redistribution in the metal-metal bonding is probable on the transition from ZrCl to ScCl, in part because of the change in second nearest neighbors. Such a change seems implicit in the XP spectra of ZrCl and ZrBr⁹ where only the packing is changed. The apparent effects of second nearest neighbors are also evident in the physical properties; ScCl is much less graphitic and is more brittle and easy to cleave than ZrCl, while its sensitivity to oxygen and moisture is appreciably greater.

The two types of packing observed in these zirconium and scandium monohalides may arise from a competition between electrostatic second nearest neighbor effects in the case of ZrBr and ScCl vs. a predominance of polarizability of the chlorine layer by the adjacent metal layer in ZrCl which provides an alternate second nearest neighbor potential. The antiprismatic chlorine coordination in ZrCl places each chlorine atom 180° in the [113] direction from a second nearest neighbor metal atom so that polarization effects must predominate. However, in ZrBr and ScCl, both with somewhat greater a lattice parameters, the prismatic halogen coordination positions each halogen atom directly over a second nearest neighbor metal atom in the neighboring sheet along the [001] direction and provides a direct electrostatic interaction with the positive ion cores of the metal atoms.

Although the ScCl₃-Sc phase study is not complete in the region $2.0 \geq \text{Cl:Sc} \geq 1.0$, crystal structure determinations are presently under way on two more of the plethora of phases that exist. Evidence of strong metal-metal interactions in isolated groups and extended chains of scandium in these compounds is already in hand. This system seems to provide the ideal opportunity to study the correlation between structure and degree of reduction, in other words, localized (cluster) vs. extended electron delocalization. Two implications of these results are immediately apparent. First, the results for many of the lanthanide-halogen systems merit a closer inspection and reappraisal. Perhaps prior expectations have placed too much emphasis on the divalent state. Born-Haber cycles, which do not (or cannot) allow for stabilization energies

resulting from metal-metal interactions, do not provide useful guidelines. A hint of a more reduced chemistry has existed for several years in the $\text{GdCl}_3\text{-Gd}$ system where the very incongruently melting $\text{GdCl}_{1.5}$ forms;⁷ this is a compound containing elongated metal octahedra sharing edges to form chains.¹⁶ The present results together with the checkered history of published results of the Sc-ScCl_3 system (cf. Introduction) should give experimentalists due caution regarding kinetic barriers in seemingly tractable systems even at as high as 877 °C, the temperature where decomposition of $\text{ScCl}_{1.5}$ seemingly first allows access to so much new chemistry. We have found evidence for a similar chemistry in the Y-YCl_3 and La-LaCl_3 systems where previous work did not provide any direct evidence for reduced phases,^{17,18} and a preliminary note on the formation of GdCl and TbCl , isostructural with ZrCl , has just been published by Simon et al.¹⁹

The second more speculative implication may involve the 4d and 5d metal-halogen systems for niobium and tantalum. Their cluster chemistry is well-known but perhaps a kinetic, not a thermodynamic, barrier there limits the formation of extended metal-metal bonded structures which would be similar to those in ScCl and ZrCl . It remains to be seen whether these will be manifest as ZrX -type structures with four electrons per atom in the band, as $\text{M}^{\text{V}}\text{X}_2$ structures which are isoelectronic in the metal-metal bonding of ZrX or, perhaps most likely, as intermediate states with extended metal-metal bonding in more nearly one-dimensional aggregates (ribbons, strings, dimers, etc.), as these can better accommodate the greater number of anions.

The once totally uninteresting chemistry of the Sc-ScCl_3 system now seems just the opposite, rich and full of fascinating

synthetic, structural, and physical problems for investigation.

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Crystal and Molecular Structure of Ferricenium Tetrachlorobismuthate

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Ferricenium tetrachlorobismuthate, $(\text{C}_5\text{H}_5)_2\text{FeBiCl}_4$, crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.998$ (5) Å, $b = 17.449$ (4) Å, $c = 7.569$ (4) Å, $\beta = 98.46$ (5)°. There are four molecules in the unit cell. Reflection intensities were measured by the θ - 2θ scan method with a Picker FACS-1 automated diffractometer, Mo $K\alpha$ radiation, and a graphite monochromator. For 1374 data with $F^2 > 3\sigma(F^2)$, $R_1 = 0.030$ and $R_2 = 0.037$. The Bi atom is coordinated by six chloride ions in an irregular octahedral array; two pairs of Cl^- ions form halogen bridges with neighboring Bi ions resulting in an infinite chain of edge-sharing octahedra. There are six independent Bi-Cl bond distances: 2.50 (1) and 2.52 (1) Å to nonbridging chlorines and 2.70 (1), 2.75 (1), 2.95 (1) and 3.10 (1) Å to bridging chlorines. The bridging Cl-Bi-Cl bond angles are 80.3 and 83.9°; the ten nonbridging Cl-Bi-Cl bond angles range from 85.9 to 99.3°. The axial Cl-Bi-Cl bond angles are 166.0, 174.5, and 175.9°. The ferricenium cations stack between the polymer chains with cyclopentadiene rings in the eclipsed conformation, unlike the pure ferrocene molecule which shows staggered rings. The average C-C distance in the rings is 1.40 (2) Å, the distance between ring centers is 3.40 (2) Å, and the Fe-ring center distance is 1.70 (2) Å.

Introduction

The crystal structure of ferricenium tetrachlorobismuthate, $(\text{C}_5\text{H}_5)_2\text{FeBiCl}_4$, has been determined as part of an investigation of compounds formed between group 5 halides and ferrocene. In addition to the possibility of uncovering a novel derivative of ferrocene, studies of group 5 halide compounds have revealed interesting structural effects, such as halogen bridging³ and infinite-chain structures.^{4,5} The distance from the Fe atom to the center of the cyclopentadiene ring is also of some interest, particularly in a nonsubstituted ferricenium compound where steric influences would be less significant.

Diffraction Data

The cell dimensions and data collection details are given in Table I.

The material was isolated as black crystals by reaction of a 1:1 molar ratio of ferrocene and BiCl_3 in acetone. A single crystal was

mounted along its needle (c) axis. Weissenberg and precession data revealed systematic extinctions for $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$), characteristic of space group $P2_1/c$. The same crystal was placed on a Picker FACS-1 four-circle diffractometer; a scintillation counter was used to measure the scanned intensities. Unit cell dimensions were refined by a least-squares program from the diffractometer setting angles of 12 reflections measured manually. A set of three standard reflections (004, 600, 800) was checked after every 200th scan in order to test for instrumental stability and crystal decay; no systematic variation in the intensities was observed.

Standard deviations were assigned to each reflection on the basis of counting statistics where $\sigma = (C + \sigma^2(B))^{1/2}$. The standard deviation of the background count, $\sigma(B)$, was determined as the maximum value of the quantities $\sigma(B) = (t_c/2t_b)(B_1 + B_2)^{1/2}$ or $\sigma(B) = (t_c/2t_b)|B_1 - B_2|$, where t_c and t_b are the scan counting time and background counting time, respectively, and C is the number of counts recorded during the scan. The weighting parameters, w , used in the least-squares refinement were calculated as $w = 1/\sigma^2$. A "p" factor of 0.06 was