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Mössbauer and Far-Infrared Studies of Tetrahaloferrate Anions of the Type $FeCl_{4-n}Br_n^-$

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The complete series of tetrahaloferrates of the type $[(C_2H_5)_4N][FeCl_{4-n}Br_n]$, where $n = 0$–4, have been synthesized and their vibrational and Mössbauer spectra have been studied. The infrared region from 500 to 33 cm^{-1} was investigated and an attempt was made to assign the observed bands to modes predicted for the complex under study. The far-infrared spectra are consistent with the lowering of the molecular symmetry from T_d to C_{3v} and from T_d to C_{2v}. The Mössbauer spectra of these mixed-ligand complexes indicate a retention of the tetrahedral electronic charge distribution around the Fe^{3+} ion since a narrow, unbroadened single peak is observed for all of the complexes. The isomer shifts (with respect to sodium nitroprusside) fall between the values of +0.54 mm/sec observed for $FeCl_4^-$ and +0.60 mm/sec observed for $FeBr_4^-$ where the absorbers are maintained at liquid nitrogen temperatures. Analyzing the far-infrared and Mössbauer data for these distorted species in the light of other studies we have performed on distorted tetrahaloferrates, it becomes apparent that a reduction in symmetry caused by the presence of mixed ligands does not necessarily result in a reduction of the symmetry of the charge distribution about the central metal ion.

Introduction

In contrast to the considerable amount of Mössbauer data which has recently been accumulated for tetrahaloferrate(III) anions of the type FeX_4^- ($X = Cl$ or Br),[1–2] no such investigation appears to have been reported for a complete series of tetrahedral anions of the type $FeX_{4-n}Y_n^-$. Furthermore while far-infrared and Raman spectral studies have been performed on tetrahalothallates ($TlX_{4-n}Y_n^-$, where $X = Cl$ when $Y = Br$ or I[3]) and on the related zinc(II) anions,[4] no similar investigation appears to have been carried out for a similar series where a transition metal functions as the coordination site.

The purpose of the present work was to extend the Mössbauer and far-infrared studies of distortions in tetrahaloferrate(III) complexes begun earlier in this laboratory. The Mössbauer effect allows a quantitative measure of the degree of chemical bonding of an atom and the far-infrared spectra provide information about the distortion in simple complexes. The detailed bonding information is derived from the covalent interaction of the s electrons with the nucleus which results in measurable changes in the Mössbauer isomer shift (δ). The other parameter derived from Mössbauer spectroscopy, the quadrupole splitting (ΔE_Q), results from the asymmetry of the electronic charge, and together with the far-infrared spectra provides specific information about the electronic and ligand distortion in simple complexes. In the absence of single-crystal structure determinations on mixed tetrahaloferrate complexes, Mössbauer and far-infrared spectroscopy should offer the most rewarding means for studying the bonding and structure of these species.

Experimental Section

Materials.—All reagents and solvents were commercially available and of reagent quality.

Preparation of $[(C_2H_5)_4N][FeCl_4]$ and $[(C_2H_5)_4N][FeBr_4]$.—These complexes crystallized rapidly from absolute ethanol when solutions of the anhydrous ferric halide and the appropriate alkylammonium halide were mixed in the correct mole ratios. They were recrystallized from absolute ethanol, washed with ethanol and ether, and dried *in vacuo*.

Preparation of $[(C_2H_5)_4N][FeCl_3Br]$ and $[(C_2H_5)_4][FeBr_3Cl]$.—Absolute ethanol solutions of the anhydrous iron(III) chloride (or bromide) were treated with tetraethylammonium bromide (or chloride) using 1:1 mole ratios of reactants. The products were purified as above.

Preparation of $[(C_2H_5)_4N][FeCl_2Br_2]$.—Anhydrous iron(II) chloride dissolved in absolute ethanol was oxidized with bromine. Tetraethylammonium bromide dissolved in absolute ethanol was added to the ferrous chloride solution in the 1:1 mole ratio of reactants. The product was worked up as above.

Analyses.—Iron was determined by EDTA titration and total halide was determined by the Volhard procedure. Carbon and hydrogen analyses were determined commercially (G. I. Robertson, 73 West End Ave., Florham Park, N. J.). Analytical data for all of the complexes are shown in Table I.

Mössbauer Measurements.—Mössbauer spectra were taken using an Austin Science Associates drive unit and a 25-mCi source of ^{57}Co in chromium, which gave a line width of 0.28 ± 0.01 mm/sec with a thin nitroprusside absorber. Absorbers contained about 5 mg of iron/cm^2 and were mounted in a Teflon holder maintained at 78°K in a stainless steel dewar. The results were statistically analyzed, assuming Lorentzian line shapes, using an IBM 7040 computer.

Infrared Measurements.—Infrared spectra were recorded on a Beckman IR-11 spectrophotometer, using samples prepared as Nujol mulls. Although scans were made from 500 to 33 cm^{-1}, no bands were observed above 400 cm^{-1} or below 70 cm^{-1}.

Electronic Spectral Measurements.—Electronic absorption spectra were recorded on a Cary Model 15 spectrophotometer.

X-Ray Measurements.—X-Ray powder diffraction photographs were taken with a 11.5-cm Debye–Scherrer camera with filtered Cu Kα radiation. The line intensities were determined by visual comparison with a calibrated intensity scale.

Results and Discussion

The analyses for the mixed tetrahaloferrate complexes presented in Table I support their stoichiometry

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(1) C. A. Clausen, III, and M. L. Good, "Mössbauer Effect Methodology," Vol. IV, Plenum Press, New York, N. Y., 1968, p 187.

(2) P. R. Edwards and C. E. Johnson, *J. Chem. Phys.*, **49**, 211 (1968).

(3) R. A. Walton, *Inorg. Chem.*, **7**, 1927 (1968).

(4) G. B. Deacon, J. H. S. Green, and F. B. Taylor, *Australian J. Chem.*, **20**, 2069 (1967).

TABLE I

ANALYTICAL DATA FOR $[(C_2H_5)_4N][FeCl_{4-n}Br_n]$ COMPLEXES

Compound	% C Calcd	% C Found	% H Calcd	% H Found	% Fe Calcd	% Fe Found	Wt of sample, mg	mequiv of halide Calcd	mequiv of halide Found
$[(C_2H_5)_4N][FeCl_4]$	29.35	29.48	6.11	6.38	17.05	17.20	90.0	1.100	1.092
$[(C_2H_5)_4N][FeCl_3Br]$	25.90	26.21	5.40	5.71	14.98	14.75	110.1	1.186	1.178
$[(C_2H_5)_4N[FeCl_2Br_2]$	23.05	22.98	4.82	4.91	13.39	13.50	105.3	1.012	1.020
$[(C_2H_5)_4N][FeClBr_3]$	20.70	19.86	4.33	4.20	12.11	12.30	95.3	0.828	0.815
$[(C_2H_5)_4N][FeBr_4]$	19.00	19.26	3.96	4.13	11.05	10.9	120.1	0.950	0.945

TABLE II

X-RAY DIFFRACTION POWDER PATTERNS FOR $[(C_2H_5)_4N][FeCl_{4-n}Br_n]$

$[(C_2H_5)_4N][FeCl_4]$ Rel intens	$[(C_2H_5)_4N][FeCl_4]$ d, Å	$[(C_2H_5)_4N][FeCl_3Br]$ Rel intens	$[(C_2H_5)_4N][FeCl_3Br]$ d, Å	$[(C_2H_5)_4N][FeClBr_3]$ Rel intens	$[(C_2H_5)_4N][FeClBr_3]$ d, Å	$[(C_2H_5)_4N][FeCl_2Br_2]$ Rel intens	$[(C_2H_5)_4N][FeCl_2Br_2]$ d, Å	$[(C_2H_5)_4N][FeBr_4]$ Rel intens	$[(C_2H_5)_4N][FeBr_4]$ d, Å
35	7.14	50	7.18	50	7.26	50	7.20	50	7.28
15	6.31	8	6.64	9	6.76	12	6.74	6	6.81
50	4.83	21	6.34	13	6.36	15	6.33	6	6.43
15	4.11	32	4.89	20	4.92	23	4.90	11	4.96
15	3.43	18	4.16	9	4.18	10	4.15	4	4.20
11	3.30	12	3.81	6	3.85	6	3.81	3	3.87
11	3.13	24	3.45	24	3.49	19	3.48	19	3.51
8	3.00	12	3.33	15	3.37	15	3.36	9	3.41
11	2.77	15	3.17	17	3.18	17	3.17	11	3.27
15	1.95	12	3.03	11	3.06	13	3.05	8	3.09
8	1.70	18	2.80	15	2.81	15	2.80	10	2.84
		12	2.32	6	2.66	4	2.71	2	2.76
		6	2.21	6	2.55	4	2.65	2	2.69
		12	2.13	4	2.15	6	2.51	3	2.55
		6	2.07	4	2.08	4	2.31	2	2.36
		24	2.00	24	1.99	4	2.25	2	2.28
		6	1.89	6	1.86	6	2.14	4	2.18
		15	1.74	11	1.73	8	2.07	4	2.09
						10	1.98	5	2.00
						6	1.90	4	1.92
						4	1.76	2	1.78
						4	1.73	2	1.75

and the X-ray powder data for these complexes (shown in Table II) provide evidence for the existence of the discrete $FeCl_{4-n}Br_n^-$ species. A comparison of the interplanar spacings and the relative intensities of the lines for $FeCl_{4-n}Br_n^-$ with those for $FeCl_4^-$ and $FeBr_4^-$ indicates that all the compounds are pure single phases. The X-ray data also show that these five compounds consist of three isomorphous sets, *i.e.*, (A) $FeCl_4^-$, (B) $FeCl_3Br^-$ and $FeClBr_3^-$, and (C) $FeCl_2Br_2^-$ and $FeBr_4^-$. In a similar series of compounds, $[(C_2H_5)_4N][TlBr_{4-n}I_n]$, Matthews and Walton[5] showed that the five compounds consist of two isomorphous sets, *i.e.*, (A) $TlBr_2I_2^-$, $TlBrI_3^-$, and TlI_4^- and (B) $TlBr_4^-$ and $TlBr_3I^-$.

TABLE III

CHARGE-TRANSFER SPECTRA OF $[(C_2H_5)_4N][FeCl_{4-n}Br_n]$ IN ACETONITRILE

Compound	Concn, M	Absorption max, kK ($\epsilon_{max} \times 10^{-3}$ in parentheses)
$[(C_2H_5)_4N][FeCl_4]$	0.461×10^{-4}	27.58 (7.7), 32.12 (7.5), 37.25 sh, 42.00 (13.4) [27.45 (7.4), 31.8 (7.6), 36.8 sh, 41.2 (11.9)][a]
$[(C_2H_5)_4N][FeCl_3Br]$	0.823×10^{-4}	27.58 (5.1), 32.30 (5.4), 41.20 (8.9)
$[(C_2H_5)_4N][FeCl_2Br_2]$	0.95×10^{-4}	25.45 (4.4), 27.50 (4.7), 34.99 (6.2), 38.58 (7.4)
$[(C_2H_5)_4N][FeClBr_3]$	0.936×10^{-4}	21.75 sh, 26.00 (4.6), 33.90 sh, 37.78 (7.5)
$[(C_2H_5)_4N][FeBr_4]$	0.125×10^{-3}	21.45 (5.8), 23.65 sh, 25.6 (5.9), 31.55 sh, 36.10 (10.2) [21.20 (5.8), 23.6 sh, 25.5 (6.0), 31.5 sh, 35.65 (10.5)][a]

[a] From ref 6 in dichloromethane.

The room-temperature charge-transfer spectra of the mixed tetrahaloferrate species in solution are further evidence that the compounds are not mixtures of the $FeCl_4^-$ and $FeBr_4^-$ anions (Table III). The excellent agreement of the data reported in Table III for $FeCl_4^-$ and $FeBr_4^-$ with that reported by Day and Jørgensen[6] implies that there is negligible dissociation of these species in solution. The concentration *vs.* absorption curves for all compounds were linear, indicating a close adherence to Beer's law behavior. Bird and Day[7] have assigned the charge-transfer spectra of $FeCl_4^-$ and $FeBr_4^-$ to electron transitions from orbitals predominantly ligand in character to orbitals which are almost entirely metal. The greater number of bands in $FeBr_4^-$ as compared to $FeCl_4^-$ has been attributed to the increase in the spin–orbit coupling constant of the bromide ion. One would therefore also expect to observe the appearance of fine structure in the mixed halides. The absence of

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[5] R. W. Matthews and R. A. Walton, *J. Chem. Soc., A*, 1639 (1968).

[6] P. Day and C. K. Jørgensen, *J. Chem. Soc.*, 6226 (1964).

[7] B. D. Bird and P. Day, *J. Chem. Phys.*, **49**, 392 (1968).

TABLE IV

VIBRATIONAL FREQUENCIES OF THE $FeX_{4-n}Y_n^-$ ANIONS[a]

Anion	Vibrational bands obsd, cm^{-1}	Band assignments
$FeCl_4^-$	388 vs	γ(Fe–Cl)
	137 m	δ(Cl–Fe–Cl)
$FeCl_3Br^-$	391 vs, 350 s	γ(Fe–Cl)
	296 s	γ(Fe–Br)
	135 w, 117 sh	δ(Cl–Fe–Cl)
	268 m, 245 sh	. . .
$FeCl_2Br_2^-$	385 s, 348 sh	γ(Fe–Cl)
	296 s, 266 sh	γ(Fe–Br)
	126 m, 115 sh	δ(Cl–Fe–Cl)
	74 m	δ(Br–Fe–Br)
	244 w, 222 w	. . .
$FeClBr_3^-$	384 s	γ(Fe–Cl)
	295 vs, 270 sh	γ(Fe–Br)
	120 m, 73 m	δ(Br–Fe–Br)
	244 w, 222 w	. . .
$FeBr_4^-$	294 vs	γ(Fe–Br)
	98 m	δ(Br–Fe–Br)

[a] Samples run as Nujol mulls.

an increase in the number of bands in the mixed halides may be due to the broadness of the peak which occurs between 35 and 31 kK, preventing the resolution of other bands at room temperature.

The far-infrared data obtained for the tetrahaloferrate anions are shown in Table IV, and a representative spectrum of $FeCl_3Br^-$ is shown in Figure 1. Previous work has shown[8] that the iron–chloride stretches occur above 300 cm^{-1} and that the iron–chloride bending modes occur below 150 cm^{-1}. The asymmetric iron–bromide stretching mode has been reported to occur at 290 cm^{-1}.[9] The assignments of the vibrational bands in Table IV are based on these reported values and the predicted symmetry of the complexes. The assignments for $FeCl_4^-$ and $FeBr_4^-$ are straightforward for T_d symmetry where two bands would be predicted as indicated in the table. As the molecular symmetry of a four-coordinated species is lowered from T_d to C_{3v}, the number of infrared-active bands increases from 2 to 6. In the resulting pseudotetrahedral FeX_3Y^- species, two γ(Fe–X) modes are predicted.

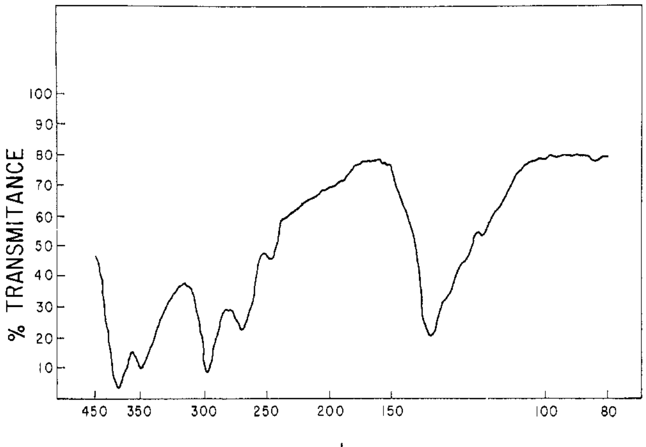

Figure 1.—Far-infrared spectra of crystalline $[(C_2H_5)_4N][FeCl_3Br]$.

TABLE V

MÖSSBAUER DATA FOR FeX_4^-, FeX_3Y^-, AND $FeX_2Y_2^-$ ANIONS

Anion	Isomer shift (δ),[a] mm/sec	Γ, mm/sec[b]
$FeCl_4^-$	+0.539	0.38
	+0.55[c]	. . .
$FeCl_3Br^-$	+0.542	0.40
$FeCl_2Br_2^-$	+0.578	0.43
$FeClBr_3^-$	+0.590	0.45
$FeBr_4^-$	+0.607	0.43
	+0.62[c]	. . .

[a] δ relative to sodium nitroprusside with precision ±0.015 mm/sec, where the samples are at 77°K. [b] Peak width at half-height, with precision of ±0.03 mm/sec. [c] From ref 2, at 77°K.

In the spectra of $FeCl_3Br^-$ the two bands appearing at 361 and 350 cm^{-1} can be assigned with certainty to the two predicted γ(Fe–Cl) bands. Similarly the bands appearing at 295 and 270 cm^{-1} in the spectra of $FeBr_3Cl^-$ can be assigned to the two predicted γ(Fe–Br) bands although the assignment of the absorption band at 270 cm^{-1} must be considered tentative because of the appearance of other bands in this region whose origin is uncertain. The symmetry of $FeCl_2Br_2^-$ would be predicted to be C_{2v} and the assignment of the γ(Fe–Cl) and γ(Fe–Br) bands can be considered certain except for the band at 266 cm^{-1}. For the mixed-halide species considerable uncertainty exists in the unambiguous assignment of δ(Fe–X) and δ(Fe–Y). All of the mixed-halide complexes exhibit bands below 135 cm^{-1} which arise either from these bending modes or from lattice modes. The "extra" or unassigned bands in the mixed tetrahalides could arise from several different sources including crystal field splitting of degenerate vibrations and overtone or combination bands. Similar unassigned bands have been recently reported by Walton[3,10] in the infrared spectra of $[(C_2H_5)_4N][TlCl_3I]$ and $[(C_2H_5)_4N][TlBr_3I]$. Some observed frequencies are between the known stretching and bending modes, and their appearance cannot be explained on symmetry requirements. Deacon, *et al.*,[4] also observed the same phenomenon in the infrared spectra of $[(C_2H_5)_4N]_2[ZnX_3Y]$, where X = I when Y = Br and X = Br when Y = I.

The Mössbauer data obtained for the tetrahaloferrate anions are shown in Table V, and a representative spectrum for $[(C_2H_5)_4N][FeCl_3Br]$ is shown in Figure 2. The appearance of a single nonbroadened line in the Mössbauer spectra of all the complexes indicates the absence of an electric field gradient at the iron nucleus and implies a symmetric electric charge distribution about the iron atom. This result is predicted for the $FeCl_4^-$ and $FeBr_4^-$ anions, since the infrared data have shown that the iron atom is in a perfect tetrahedral environment where the sum of the electron density in four equal sp^3 orbitals would lead to a symmetric charge distribution. In the anions of C_{3v} symmetry ($FeCl_3Br^-$ and $FeBr_3Cl^-$) and of C_{2v} symmetry ($FeCl_2Br_2^-$) one would predict the presence of an electric field gradient at the iron nucleus which should produce a

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(8) L. A. Woodward and M. J. Taylor, *J. Chem. Soc.*, 4473 (1960).

(9) R. J. H. Clark and T. M. Dunn, *ibid.*, 1198 (1963).

(10) R. A. Walton, *Inorg. Chem.*, **7**, 640 (1968).

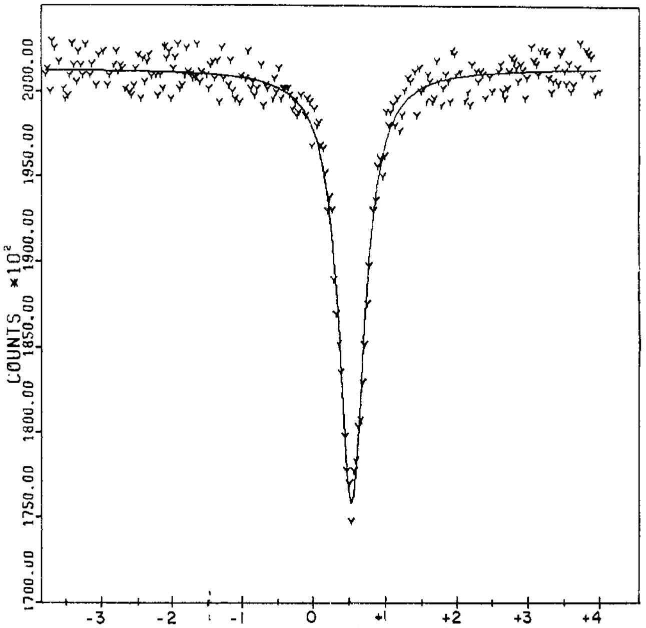

Figure 2.—Mössbauer spectra of $[(C_2H_5)_4N][FeCl_3Br]$.

quadrupole splitting in the spectra or at least a broadening of the absorption line which would be indicative of an unresolved quardupole splitting. The absence of either one of these effects in the mixed-halide anions indicates that the difference in bonding between a bromide and a chloride ligand in the tetrahaloferrates is not enough to distort the tetrahedral charge distribution.

The isomer shift values obtained for $FeCl_4^-$ and $FeBr_4^-$ as shown in Table V are in excellent agreement with those reported by Edwards, *et al.*[2] The decrease in the positive isomer shift (δ) in the tetrahaloferrates as the number of chlorides in the coordination sphere increases indicates an increase in the s-electron density at the iron nucleus. This decrease in δ with an increase in the number of chlorides is just opposite from what one would predict based upon covalency considerations. As the degree of covalency in the metal–ligand bond increases, an increasing fraction of σ-electron density is transferred to the iron, causing a decrease in δ. Edwards, *et al.*,[2] have shown that the Fe–Br bond is more covalent than the Fe–Cl bond, and thus one would expect that the isomer shift for $FeCl_4^-$ should be more positive than that for $FeBr_4^-$. The smaller amount of s-electron density at the iron nucleus in $FeBr_4^-$ as compared to $FeCl_4^-$ can be accounted for if the π-bond formation in these complexes is considered in addition to the σ-bond formation. Based upon the crystal structure determination for $[(C_6H_5)_4As][FeCl_4]$, Zaslow, *et al.*,[11] postulated the existence of π-bond formation to account for the short Fe–Cl bond distance. The π bond would result from the overlap of lone pairs of p electrons on the halides with partially filled $3d_{xz}$, $3d_{xy}$, and $3d_{yz}$ orbitals of iron which are of the same symmetry. Since the capability of this type of bond formation has been shown to be greater for bromides than for chlorides,[12] the 3d orbital electron density would be greater in $FeBr_4^-$ than in $FeCl_4^-$. This 3d orbital electron density partially shields the 4s-electron density from the nucleus, thus accounting for the reduction in s-electron density at the iron nucleus in $FeBr_4^-$ relative to $FeCl_4^-$. This enhanced shielding effect from (p → d) π-bond formation accounts for the increase in isomer shift with an increase in the number of bromides as is observed in Table V.

[11] B. Zaslow and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957).
[12] M. S. Whitehead and H. H. Jaffé, *Theoret. Chim. Acta*, **1**, 209 (1963).

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A Mössbauer Study of the Thermal Decomposition of Potassium Tris(oxalato)ferrate(III)

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Mössbauer spectroscopy has been used to follow the thermal decomposition of $K_3Fe^{III}(C_2O_4)_3 \cdot 3H_2O$ in air and *in vacuo*. After dehydration at about 120°, a binuclear complex containing the anion $(C_2O_4)_2Fe^{II}OxFe^{II}(C_2O_4)_2^{6-}$ (Ox = quadridentate oxalate group) is formed. This complex then decomposes above 380° *via* Fe_3O_4 to either Fe_2O_3 (in air) or Fe (*in vacuo*).

Introduction

Several workers have recently studied the thermal decomposition of potassium tris(oxalato)ferrate(III) and the analogous tris-oxalate complexes of chromium, manganese, and cobalt.[1–4] For the iron complex,[3] infrared spectra have been recorded at the plateaus of the thermogravimetric analysis (tga) curve, but the decomposition products have not been conclusively identified, nor has the mechanism of decomposition been discussed.

[1] W. W. Wendlandt, T. D. George, and K. V. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **21**, 69 (1961).
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[4] L. A. Funes and W. W. Wendlandt, *Arch. Bioquim. Quim. Farm. Tucuman*, **12**, 113 (1965).