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Selenocyanate Complexes of Cobalt(III), Palladium(II), and Platinum(II)[1a,b]

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The synthesis and partial characterization, on the basis of infrared spectra, of the new selenocyanate complexes $K_3[Co(CN)_5NCSe]$, $[Co(NH_3)_4(CN)NCSe]Cl$, $[Co(NH_3)_5NCSe](NO_3)_2$, $[Pd(bipy)(SeCN)_2]$, and $[Pt(bipy)(SeCN)_2]$ are reported. The use of the selenocyanate ion as a bridging ligand in the transition state in oxidation–reduction reactions of coordination complexes is discussed. The type of selenocyanate bonding, M–NCSe or M–SeCN, in the new complexes is contrasted with that found in similarly constituted thiocyanate complexes.

Introduction

Although the behavior of the thiocyanate ion as an ambidentate ligand has been the subject of a number of recent studies, relatively little work has been published concerning the selenocyanate ion, $NCSe^-$. It, too, has been found to function as an ambidentate ligand, being Se-bonded in complexes of metals of class b character,[2] *e.g.*, $K_2[Pt(SeCN)_6]$ and $K_2[Hg(SeCN)_4]$, and N-bonded in complexes of metals of class a character, *e.g.*, $[(CH_3)_4N]_2[Co(NCSe)_4]^{2-4}$ and $K_3[Cr(NCSe)_6]$.[5] A third type of bonding for the selenocyanate ion, as a bridging group, has been reported for AgSeCN,[2] $Hg[Co(NCSe)_4]$,[3,4] and $[Co(py)(NCSe)_2]$ (py = pyridine).[6]

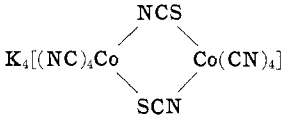
The published results indicate a close similarity in the coordination behavior of the thiocyanate and selenocyanate ions. However, selenocyanate-containing complexes of the majority of the transition metal ions have not yet been prepared. Furthermore, it remains to be demonstrated whether the presence of other ligands in the coordination sphere of a metal ion can affect the nature of the metal–selenocyanate bond, as has been shown to be the case for several thiocyanate complexes.[7] This paper reports the synthesis and partial characterization of several new coordination complexes of the selenocyanate ion and a study of the use of the selenocyanate ion as a bridging ligand in the transition state in oxidation–reduction reactions of coordination complexes.

Experimental

Preparation of Compounds.—Potassium selenocyanate was prepared by the method given in *Inorganic Syntheses*.[8]

$K_3[Co(CN)_5NCSe]$.—This preparation was carried out in a drybox and nitrogen atmosphere. To a solution of 0.33 g. (5 mmoles) of potassium cyanide in 10 ml. of deoxygenated water at 0° was added 0.25 g. (1 mmole) of $Co(C_2H_3O_2)_2 \cdot 4H_2O$. When dissolution was complete, 0.70 g. (1 mmole) of $K_2[Hg(SeCN)_4]$, prepared according to the method of Turco, *et al.*,[4] was added, whereupon the color of the solution changed from reddish yellow to dark red. The solution was filtered, allowing the filtrate to pass directly into 50 ml. of absolute ethanol at 0°. A reddish oil formed which, with standing, crystallized to form a yellow-brown solid. The solid was isolated by filtration, washed with ethanol and ether, both at 0°, and dried *in vacuo* over calcium chloride. The complex was found to be stable with respect to isomerization in the solid state.

Anal. Calcd. for $K_3CoC_6N_6Se$: C, 17.52; N, 20.43. Found: C, 18.04; N, 20.86.



$$\mathbf{K_4[(NC)_4Co\overset{NCS}{\underset{SCN}{\diamond}}Co(CN)_4] \cdot 5H_2O}$$

—This brown bridged complex was isolated as the product of the preceding reaction when 0.51 g. (1 mmole) of $K_2[Hg(SCN)_4]$, prepared according to the method of Turco, *et al.*,[4] was used in place of the $K_2[Hg(SeCN)_4]$.

Anal. Calcd. for $K_4Co_2C_{10}N_{10}S_2H_{10}O_5$: C, 17.44; H, 1.46; N, 20.34. Found: C, 17.41; H, 1.14; N, 20.38.

$[Co(NH_3)_4(CN)NCSe]Cl$.—To a solution of 0.48 g. (2 mmoles) of $[Co(NH_3)_4(H_2O)CN]Cl_2$ (prepared according to the method of Siebert[9]) in 25 ml. of water was added 0.29 g. (2 mmoles) of potassium selenocyanate, followed by 0.5 g. of activated charcoal. The solution was gradually heated to boiling, then filtered, allowing the filtrate to pass directly into 50 ml. of absolute ethanol at 0°. The yellow precipitate which formed was isolated by filtration, washed with ethanol and ether, and dried *in vacuo* over calcium chloride.

Anal. Calcd. for $CoN_6H_{12}C_2SeCl$: C, 8.19; H, 4.12; N, 28.63. Found: C, 8.27; H, 4.95; N, 27.93.

$[Co(NH_3)_5NCSe](NO_3)_2$.—Five mmoles (1.7 g.) of $(Co(NH_3)_5ONO_2](NO_3)_2$, prepared according to the method of Palmer,[10] was slowly added to a solution of 4.3 g. (30 mmoles) of potassium selenocyanate in a minimum amount of water. The reddish brown precipitate which formed was removed by filtration and dried *in vacuo* over calcium chloride. It was then treated with dimethylformamide to separate the desired product from the red selenium decomposition product. The mixture was filtered and the red filtrate thus obtained was allowed to stand, covered, for 4 days. Ether was then added, whereupon the precipitation of a pink solid occurred. It was isolated by filtration, washed with ethanol and ether, and dried *in vacuo* over calcium chloride. Selenocyanate substitution was not complete, as indicated by the high value obtained for the nitrogen content.

Anal. Calcd. for $CoN_8H_{15}CSeO_6$: N, 30.04. Found: N, 32.16.

$[Pd(bipy)(SeCN)_2]$.—One gram (3 mmoles) of $[Pd(bipy)Cl_2]$ (bipy = 2,2′-bipyridine), prepared according to the method of

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[1] (a) Abstracted in part from the M.S. Thesis of M. Y. A., University of Illinois, 1964; (b) presented at the Fifteenth Delaware Science Symposium, Newark, Del., Feb. 1965; (c) University of Delaware, Newark, Del.

[2] A. Turco, C. Pecile, and M. Nicolini, *Proc. Chem. Soc.*, 213 (1961).

[3] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, **1**, 565 (1962).

[4] A. Turco, C. Pecile, and M. Nicolini, *J. Chem. Soc.*, 3008 (1962).

[5] K. Michelsen, *Acta Chem. Scand.*, **17**, 1811 (1963).

[6] S. M. Nelson, *Proc. Chem. Soc.*, 372 (1961).

[7] J. L. Burmeister and F. Basolo, *Inorg. Chem.*, **3**, 1587 (1964), and references contained therein.

[8] G. R. Waitkins and R. Shutt, *Inorg. Syn.*, **2**, 186 (1946).

[9] H. Siebert, *Z. anorg. allgem. Chem.*, **327**, 63 (1964).

[10] W. G. Palmer, "Experimental Inorganic Chemistry," University Press, Cambridge, England, 1954, p. 535.

Burmeister and Basolo,[7] was added to a solution of 1.0 g. (6 mmoles) of silver nitrate in 15 ml. of water. The resulting mixture was heated on a steam bath until the $[Pd(bipy)Cl_2]$ dissolved, whereupon the silver chloride formed was removed by filtration. After cooling the light yellow filtrate in an ice bath, the small amount of $[Pd(bipy)(ONO_2)_2]$ which precipitated was removed by a second filtration. The addition of 0.88 g. (6 mmoles) of potassium selenocyanate, dissolved in 10 ml. of ice water, to the filtrate resulted in the immediate precipitation of a light reddish orange solid which was collected on a filter, washed with water, ethanol, and ether, and dried *in vacuo* over magnesium perchlorate.

Anal. Calcd. for $PdC_{12}H_8N_4Se_2$: C, 30.50; H, 1.71; N, 11.86. Found: C, 29.71; H, 1.90; N, 11.96.

$[Pt(bipy)(SeCN)_2]$.—This golden yellow complex was prepared by the preceding method, using $[Pt(bipy)Cl_2]$, prepared according to the method of Morgan and Burstall,[11] in place of the $[Pd(bipy)Cl_2]$.

Anal. Calcd. for $PtC_{12}H_8N_4Se_2$: C, 25.68; H, 1.44; N, 9.98. Found: C, 25.56; H, 1.59; N, 9.91.

Reaction of $[Co(NH_3)_5NCSe]^{2+}$ with $[Co(CN)_5]^{3-}$.—One mmole (0.37 g.) of $[Co(NH_3)_5NCSe](NO_3)_2$ was dissolved in 20 ml. of deoxygenated water. Five mmoles (0.33 g.) of potassium cyanide was added to the solution, followed by a crystal of $Co(C_2H_3O_2)_2 \cdot 4H_2O$. The addition of the latter resulted in an immediate evolution of ammonia. When the evolution had ceased (0.5 hr.), the solution was filtered and the filtrate allowed to pass into 80 ml. of absolute ethanol at 0°. The solution was allowed to stand, with occasional stirring, for 0.75 hr., during which time a solid precipitated. It was isolated by filtration, washed with ethanol and ether, both at 0°, and dried *in vacuo* over calcium chloride. The analytical and spectral results[12] showed the product to be $K_2[Co(CN)_5OH_2]$.

Anal. Calcd. for $K_2CoC_5N_5H_2O$: C, 21.05; H, 0.71; N, 24.55. Found: C, 20.21; H, 0.88; N, 24.69.

The same product resulted when $[Co(NH_3)_5OH_2](NO_3)_3$, prepared by allowing $[Co(NH_3)_5ONO_2](NO_3)_2$ to aquate, was used in the preceding reaction in place of the $[Co(NH_3)_5NCSe](NO_3)_2$.

Anal. Found: C, 20.34; H, 0.50; N, 24.89.

Reactions with $[M(SeCN)_4]^{2-}$ (M = Pd(II), Pt(II)).—In an attempt to prepare $[Pd(P(C_6H_5)_3)_2(NCSe)_2]$, 0.33 g. (1 mmole) of $K_2[PdCl_4]$ was added to a solution of 0.58 g. (4 mmoles) of potassium selenocyanate in 20 ml. of absolute ethanol. The deep red color which developed was almost identical with that of ethanolic solutions of $[Pd(SCN)_4]^{2-}$. The potassium chloride which precipitated and some unreacted $K_2[PdCl_4]$ were removed by filtration, and the filtrate was cooled in an ice bath. A solution of 0.52 g. (2 mmoles) of triphenylphosphine in 15 ml. of warm absolute ethanol was added to the filtrate, resulting in an immediate decolorization of the solution followed by, ~1 min. later, the precipitation of a shiny white crystalline solid. This was isolated by filtration, washed with water, ethanol, and ether, and dried *in vacuo* over calcium chloride. The analytical and spectral results showed the product to be $[Pd(P(C_6H_5)_3)_4]Cl_2$.

Anal. Calcd. for $PdP_4C_{72}H_{60}Cl_2$: C, 70.51; H, 4.93; N, 0.00. Found: C, 70.98; H, 4.78; N, 0.00.

When either triphenylarsine or 2,2′-bipyridine was used in the above procedure in place of the triphenylphosphine, no reaction was found to take place.

Completely analogous results were obtained when ethanolic solutions of $[Pt(SeCN)_4]^{2-}$ were treated with triphenylphosphine, triphenylarsine, and 2,2′-bipyridine.

Anal. Calcd. for $PtP_4C_{72}H_{60}Cl_2$: C, 65.75; H, 4.60; N, 0.00. Found: C, 65.04; H, 4.56; N, 0.00.

The reaction between $[Pt(SeCN)_4]^{2-}$ and triphenylphosphine was also carried out in dimethylformamide solution. Neither decolorization of the solution nor precipitation took place until ice water was added, whereupon decolorization took place immediately, followed by the precipitation of $[Pt(P(C_6H_5)_3)_4]Cl_2$.

Anal. Found: C, 65.06; H, 4.76; N, 0.00.

Analyses.—All microanalyses were performed by the Microanalytical Laboratory, Department of Chemistry and Chemical Engineering, University of Illinois, under the direction of Mr. J. Nemeth.

Infrared Spectra.—Infrared spectra of Nujol mulls of the complexes prepared were measured on a Perkin-Elmer Model 521 recording spectrophotometer. Either NaCl or CsBr plates were used.

The type of selenocyanate bonding in the complexes was determined on the basis of the position of the selenocyanate C–Se stretching frequency. As has already been noted in the literature,[2,4,5] the shifts of this frequency upon N or Se coordination parallel those exhibited by the C–S stretching frequency of the thiocyanate group upon N or S coordination, *i.e.*, relative to that of uncoordinated $NCSe^-$, as in potassium selenocyanate (558 cm.$^{-1}$),[13] the C–Se stretching frequencies of M–NCSe complexes are shifted to higher wave numbers, those of M–SeCN complexes are shifted to lower wave numbers.

The C–N and C–Se stretching frequencies of the new complexes are shown in Table I. There were determined by comparing the infrared spectra of Nujol mulls of the complexes in question with those of analogous halogeno complexes, *e.g.*, $K_3[Co(CN)_5NCSe]$ *vs.* $K_3[Co(CN)_5Br]$. None of the latter exhibited any interfering absorption in the C–Se stretching range.

Discussion

Whereas the predominant theme in previously published studies concerning selenocyanate coordination complexes has been an emphasis on the analogous coordination behavior of the selenocyanate and thiocyanate ions, the results of this study provide several examples of dissimilar behavior. This is, perhaps, best shown by the comparisons afforded by Tables II and III.

The formation of $[Co(CN)_5OH_2]^{2-}$ in reaction 2 could have resulted from either a prior aquation of the oxidant, since it was found that $[Co(NH_3)_5OH_2]^{3+}$ could be used as the oxidant in this reaction, or an aquation of the anticipated $[Co(CN)_5SeCN]^{3-}$ product. The formation of the thiocyanate bridges in the product of reaction 3 is believed to result from further reaction of the initially formed $[Co(CN)_5NCS]^{3-}$, whereby cyanide groups on adjacent $[Co(CN)_5NCS]^{3-}$ ions are displaced by the sulfur atoms of the thiocyanate groups. Evidence for the fact that the bridging groups are thiocyanates, rather than cyanides, is seen in the fact that the complex exhibits only two C–N stretching bands (Table I). If both bridging and terminal cyanide groups were present, as well as terminal thiocyanates, at least three C–N stretching bands should have been found.

In reaction 4, the mercury(I) selenocyanate, which is believed to be the initial reduction product of the reaction, could not be isolated before decomposition took place, nor could it be prepared by simple metathetical reactions between mercury(I) and selenocyanate ions. The stability of $[Co(CN)_5NCSe]^{3-}$ offers an example of nonsymbiotic behavior, while the stability of $[Co(CN)_5SCN]^{3-}$ is an example of the

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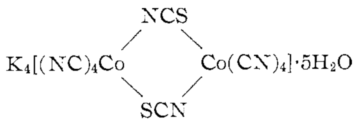
(11) G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 965 (1934).

(12) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 166.

(13) H. W. Morgan, *J. Inorg. Nucl. Chem.*, **16**, 367 (1961).

TABLE I

C–N AND C–Se STRETCHING FREQUENCIES OF SELENOCYANATE COMPLEXES OF COBALT(III), PALLADIUM(II), AND PLATINUM(II) (CM.$^{-1}$)

Compound	ν_3 (C–N)	ν_1 (C–Se)
$K_3[Co(CN)_5NCSe]$	2127 s (–CN) 2124 s (–CN) 2095 w (–CN) 2072 s (–NCSe)	664 w
$[Co(NH_3)_4(CN)NCSe]Cl$	2140 m (–CN) 2105 s (–NCSe)	607 w
$[Co(NH_3)_5NCSe](NO_3)_2$[a]	2116 s	624 m
$[Pd(bipy)(SeCN)_2]$[b]	2116 s 2112 s	523 w 518 w
$[Pt(bipy)(SeCN)_2]$[b]	2135 s 2125 s	532 w 527 w
 $K_4[(NC)_4Co\genfrac{}{}{0pt}{}{NCS}{SCN}Co(CN)_4]\cdot 5H_2O$	2180 s (Co–NCS–Co) 2120 s (–CN)	

[a] Cotton, *et al.*,[3] have pointed out that analogous *iso*thiocyanato and *iso*selenocyanato complexes exhibit C–N stretching frequencies within 10 cm.$^{-1}$ of each other. The C–N stretching frequency of $[Co(NH_3)_5NCS](NO_3)_2$ has been determined to be 2120 cm.$^{-1}$ [M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 6412 (1959)]. [b] Splitting of C–N and C–Se stretching modes due to the *cis* configurations of the complexes.

TABLE II

A COMPARISON OF OXIDATION–REDUCTION REACTIONS OF ANALOGOUS THIOCYANATE AND SELENOCYANATE COMPLEXES

	Oxidant[a]	Postulated intermediate or activated complex	Products
(1)[b]	$[Co(NH_3)_5NCS]^{2+}$	$[(H_3N)_5Co^{III}–NCS–Co^{II}(CN)_5]^-$	$[Co(CN)_5SCN]^{3-} + [Co(OH_2)_6]^{2+} + NH_3$
(2)	$[Co(NH_3)_5NCSe]^{2+}$	$[(H_3N)_5Co^{III}–NCSe–Co^{II}(CN)_5]^-$	$[Co(CN)_5OH_2]^{2-} + [Co(OH_2)_6]^{2+} + NH_3 + NCSe^-$
(3)	$[Hg(SCN)_4]^{2-}$	$[(NCS)_3Hg^{II}–SCN–Co^{II}(CN)_5]^{5-}$	$[(NC)_4Co<^{SCN}_{NCS}>Co(CN)_4]^{4-} + Hg_2(SCN)_2$
(4)	$[Hg(SeCN)_4]^{2-}$	$[(NCSe)_3Hg^{II}–SeCN–Co^{II}(CN)_5]^{5-}$	$[Co(CN)_5NCSe]^{3-} + Hg_2(SeCN)_2(?)$

[a] The reductant used in each reaction was $[Co(CN)_5]^{3-}$. [b] The existence of the postulated intermediate or activated complex in this reaction is supported by the results of a kinetic study by Halpern and co-workers [J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **85,** 2517 (1963); J. Halpern and S. Nakamura, "Proceedings of the Eighth International Conference on Coordination Chemistry," Springer-Verlag, Vienna and New York, 1964, p. 271. The product of the reaction has been isolated by Burmeister [J. L. Burmeister, *Inorg. Chem.*, **3,** 919 (1964)].

TABLE III

A COMPARISON OF SUBSTITUTION REACTIONS OF ANALOGOUS THIOCYANATE AND SELENOCYANATE COMPLEXES[a]

Substrate[b]	Entering ligand	Product[c] (X = S)[d]	Product[c] (X = Se)
$[M(XCN)_4]^{2-}$	2,2′-Bipyridine	$[M(bipy)(NCS)_2]$	No reaction
$[M(XCN)_4]^{2-}$	$P(C_6H_5)_3$	$[M(P(C_6H_5)_3)_2(NCS)_2]$	$[M(P(C_6H_5)_3)_4]^{2+}$
$[M(XCN)_4]^{2-}$	$As(C_6H_5)_3$	$[M(As(C_6H_5)_3)_2(NCS)_2]$	No reaction
$[M(bipy)(OH_2)_2]^{2+}$	NCX^-	$[M(bipy)(NCS)_2]$	$[M(bipy)(SeCN)_2]$

[a] Identical conditions (see Experimental section) employed in the reaction of a given ligand with analogous substrates. [b] M = Pd(II), Pt(II). [c] The thiocyanate- and selenocyanate-containing complexes shown were found to be stable with respect to isomerization. [d] Reference 7.

symbiotic behavior of ligands, as discussed by Jørgensen.[14]

The subject of the coordination behavior of ambidentate ligands is a complicated one, as exemplified by the numerous explanations proposed in the literature[7] to account for the coordination behavior of the thiocyanate ion. Each is substantiated by experimental evidence, yet none remotely approaches universal applicability. One of the more recent of these, by Wojcicki and Farona,[15] involves the postulate that an increase in the negative charge at the metal favors the formation of an M–NCS linkage, *e.g.*, $[Mn(CO)_5SCN]$ *vs.* *cis*-$[Mn(CO)_3(py)_2NCS]$ and $[Cr(CO)_5NCS]^-$. This argument can be used to rationalize the bonding in $[Co(CN)_5NCSe]^{3-}$, but not in $[Co(CN)_5SCN]^{3-}$ if the primary function of the cyanide ion is to be considered to be that of a strong Lewis base. The explanation of Wojcicki and Farona conflicts with that of Pearson,[16] who has suggested that the sulfur atom in the thiocyanate ion is soft (polarizable) and will prefer to coordinate with soft acids (class b metals), whereas the nitrogen atom is hard (nonpolarizable) and coordinates

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(14) C. K. Jørgensen, *Inorg. Chem.*, **3**, 1201 (1964).

(15) A. Wojcicki and M. F. Farona, *ibid.*, **3**, 151 (1964); "Proceedings of the Eighth International Conference on Coordination Chemistry," Springer-Verlag, Vienna and New York, 1964, p. 262.

(16) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

with hard acids (class a metals). Using this theory, it would appear that the cyanide groups in [Co(CN)$_5$-NCSe]$^{3-}$ enhance the hard character of cobalt(III) by the withdrawal of d$_\pi$ electron density into their vacant π^* orbitals, thereby reinforcing the tendency of the cobalt to bond to the hard nitrogen end of the selenocyanate, while in [Co(CN)$_5$SCN]$^{3-}$ the cyanide groups convert the cobalt(III) into a soft metal by strong σ donation of electron density, thereby making the bond to the soft sulfur end of the thiocyanate the preferred one—conclusions which seem to be mutually exclusive.

If the π-bonding explanation of Turco and Pecile[17] is used to rationalize the bonding in the [M(bipy)-(SeCN)$_2$] and [M(bipy)(NCS)$_2$] complexes, the conclusion reached is that the π-bonding factor is of lesser importance in the selenocyanate complexes, whereas, by virtue of the parallel behavior of their infrared frequencies, π bonding would be expected to be of comparable importance for both. In point of fact, the only over-all bonding trend observed is that observed for the selenocyanate complexes which, in all of the complexes prepared thus far, exhibit the "normal" class a N-bonded, class b Se-bonded bonding pattern.

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[17] A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

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Thermal Decomposition of Barium and Strontium Trisoxalatoferrates(III)[1]

BY P. K. GALLAGHER

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Thermogravimetric, differential thermal, and effluent gas analyses were performed on $Ba_3[Fe(C_2O_4)_3]_2\cdot 8H_2O$ and $Sr_3[Fe(C_2O_4)_3]_2\cdot 2H_2O$. These results were compared with those of the individual oxalates and with a physical mixture having the same metallic ratio as the complex oxalates. The stoichiometry of the decomposition was found to be highly complex, involving at least four changes in the oxidation state of the iron. At an intermediate stage, a considerable fraction of the total iron has the usual oxidation state of +4.

Introduction

It was suggested by Derbyshire, *et al.*,[2] that the calcination of a coprecipitated barium–iron(III) oxalate produced stoichiometric barium ferrate(IV) ($BaFeO_3$). By analysis of the X-ray pattern of this material and comparison with that of barium titanate, they further concluded that barium ferrate(IV) had a cubic perovskite structure at room temperature. Other investigators have prepared a material approaching this composition by calcining the mixed oxides or carbonates and have discussed its properties and possible structure.[3-6] The magnetic and electrical properties of the analogous strontium compound have been more extensively studied.[7-10] Confirmation of the actual existence of iron(IV) has been provided by measurements of the Mössbauer effect for the strontium[11] and barium[12] compounds. All the aforementioned studies, with exception of those of MacChesney, *et al.*,[9,11] have employed nonstoichiometric material and, therefore, possible preparation of the stoichiometric compound by simple calcination of the complex oxalate has great interest.

The nature and stoichiometry of the thermal decomposition of such an alkaline earth–iron(III) oxalate is likely to be complex because of the probable changes in the oxidation state of iron. Iron(III) oxalate is readily photoreduced to iron(II) oxalate and such a reduction might occur during the thermal decomposition. The data of Derbyshire[2] require iron(IV) at 700° while MacChesney[9] has shown that above about 1000° the iron is predominantly trivalent. In this work, thermogravimetric (t.g.a.), differential thermal (d.t.a.), and effluent gas analysis (e.g.a.) were performed on the individual barium, strontium, and iron(III) oxalates as well as on the coprecipitated barium or strontium trisoxalatoferrates(III). Similar experiments were per-

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[1] Presented at the Symposium on the Chemical Reactivity of Solids, American Chemical Society, Ann Arbor, Mich., Nov. 12–13, 1964.

[2] S. W. Derbyshire, A. C. Fraker, and H. H. Stadelmaier, *Acta Cryst.*, **14**, 1293 (1964).

[3] M. Erchak, I. Frankuchen, and R. Ward, *J. Am. Chem. Soc.*, **68**, 2085 (1946).

[4] W. W. Malinofsky and T. Kedesdy, *ibid.*, **76**, 3090 (1954).

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[8] T. R. Clevenger, *J. Am. Ceram. Soc.*, **46**, 207 (1963).

[9] J. B. MacChesney, R. C. Sherwood, J. F. Potter, and H. J. Williams, to be published.

[10] C. Brisi, *Ric. Sci.*, **24**, 1858 (1954).

[11] P. K. Gallagher, J. B. MacChesney, and D. N. E. Buchanan, *J. Chem. Phys.*, **41**, 2429 (1964).

[12] P. K. Gallagher, J. B. MacChesney, and D. N. E. Buchanan, Paper FA11, National Meeting of the American Physical Society, New York, N. Y., Jan. 28, 1965; to be published.