

Tableau 3. Valeurs des liaisons électrostatiques et leurs sommes autour des anions

Anion	U(1) <sup>6+</sup>	U(2) <sup>6+</sup>	Cu <sup>2+</sup>	C <sup>4+</sup>	H(1)	H(2)	H(3)	H(4)	H(5)	Σ
O(1)	1,70					0,18			0,19	2,07
O(2)		1,73						0,19	0,05	1,97
O(3)		1,89			0,14					2,03
O(4)	0,40	0,48		1,38						2,26
O(5)	0,79	2×0,68								2,15
O(6)	0,38	0,49		1,37						2,24
O(7)			0,45	1,24						1,79
			0,10							
O(8)		0,55	0,47		0,86					1,99
			0,11							
O(9)			0,43			0,82	0,81			2,06
O(10)			0,40					0,95	0,81	2,16
										Moyenne 2,07

Enfin, dans le Tableau 3, sont groupées les valeurs des liaisons électrostatiques arrivant aux différents atomes d'oxygène, calculées selon la formule de Brown & Wu (1976) pour les atomes lourds et selon celle de Brown (1976) pour les liaisons hydrogène. La somme des valences électrostatiques afférentes à chaque atome d'oxygène reste voisine de deux à l'intérieur des limites généralement acceptées, la valeur moyenne étant égale à 2,07.

#### Références

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). *NRC Crystallographic Programs for the IBM/360 System. World List of Crystallographic Computer Programs*, 2<sup>e</sup> éd., Appendix, p. 52. Utrecht: Oosthoek.

APPLEMAN, D. E. (1956). *Geol. Soc. Am. Bull.* **67**, 1666.

BROWN, I. D. (1976). *Acta Cryst.* **A32**, 24–31.

BROWN, I. D. & WU, K. K. (1976). *Acta Cryst.* **B32**, 1957–1959.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS. Rapport ORNL-TM305*. Oak Ridge National Laboratory, Tennessee.

CESBRON, F., PIERROT, R. & VERBEEK, T. (1970). *Bull. Soc. Fr. Minéral. Cristallogr.* **93**, 550–554.

CHRIST, C. L., CLARK, J. R. & EVANS, H. T. (1955). *Science*, **121**, n° 3144, 472–473.

EVANS, H. T. (1963). *Science*, **141**, n° 3576, 154–157.

GINDEROW, D. & CESBRON, F. (1983a). *Acta Cryst.* **C39**, 824–827.

GINDEROW, D. & CESBRON, F. (1983b). *Acta Cryst.* **C39**, 1605–1607.

*International Tables for X-ray Crystallography* (1974). Tome IV. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEPII*. Rapport ORNL-5138. Oak Ridge National Laboratory, Tennessee.

MAZZI, F. & RINALDI, F. (1960). *Acta Cryst.* **13**, 1139.

MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.

SCHUSTER, P., ZUNDEL, G. & SANDORFY, C. (1976). *The Hydrogen Bond*, p. 406. New York: North-Holland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TOKONAMI, M. (1965). *Acta Cryst.* **19**, 486.

ZACHARIASEN, W. H. (1948). *Acta Cryst.* **1**, 281–285.

ZACHARIASEN, W. H. & PLETINGER, H. A. (1959). *Acta Cryst.* **12**, 526–530.

ZIGAN, F. & SCHUSTER, H. D. (1972). *Z. Kristallogr.* **135**, 416–436.

*Acta Cryst.* (1985). **C41**, 657–660

## Room-Temperature Structure of Ammonium Tetrafluoroferrate(III), NH<sub>4</sub>[FeF<sub>4</sub>]

BY M. LEBLANC, G. FERREY AND R. DE PAPE

Laboratoire des Fluorures et Oxyfluorures Ioniques, ERA 609, Faculté des Sciences, 72017 Le Mans CEDEX, France

AND J. TEILLET

Laboratoire Mössbauer, ERA 682, Faculté des Sciences, 72017 Le Mans CEDEX, France

(Received 4 July 1984; accepted 1 January 1985)

**Abstract.**  $M_r = 149.9$ , orthorhombic,  $Pnma$ ,  $a = 7.559(4)$ ,  $b = 7.575(4)$ ,  $c = 12.754(8)$  Å,  $V = 730(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 2.75$  Mg m<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 4.03$  mm<sup>-1</sup>,  $F(000) = 584$ ,  $R = 0.026$ , 444 unique reflections, hydrothermal growth. The room-temperature structure of NH<sub>4</sub>FeF<sub>4</sub> was solved after correction of the intensities affected by the twinning of the crystal. It is derived from the TlAlF<sub>4</sub> type ( $P4/mmm$ ): infinite [FeF<sub>4/2</sub>F<sub>2</sub>]<sub>n</sub><sup>n-</sup> layers of corner-

sharing FeF<sub>6</sub> octahedra are connected by ammonium ions. The distortion from the aristotype is due to correlated ( $a_p^- b_p^+ c^-$ ) tilts of the FeF<sub>6</sub> octahedra.

**Introduction.** Most of the  $AMF_4$  compounds found in the  $AF-MF_3$  systems ( $A = K, Rb, Cs, NH_4, Tl$ ;  $M = Ti, V, Cr, Mn, Fe, Al, Ga, Sc, In$ ) crystallize with structures derived from the perovskite layer TlAlF<sub>4</sub> type (Brosset, 1938; Nouet, Pannetier & Fourquet, 1981).

Their structural phase transitions (Tressaud, Galy & Portier, 1969; Hidaka, Wood, Wanklyn & Garrard, 1979), and their ferroelastic and/or magnetic properties (Abrahams & Bernstein, 1972; Heger, Geller & Babel, 1971) have been extensively studied. In connection with Mössbauer experiments and electric-field-gradient calculations (Teillet, Calage & Varret, 1982), we have determined the room-temperature structure of  $\text{NH}_4\text{FeF}_4$ .

**Experimental.** Hydrothermal growth (Ferey, Leblanc, De Pape, Passaret & Bothorel-Razazi, 1975), 653 K, 180 MPa, 5M  $\text{NH}_4\text{HF}_2$  solution, ( $\text{NH}_4\text{HF}_2/\text{FeF}_3$ ) = (1/1). Easily cleaved, light-green (001) platelet  $0.28 \times 0.28 \times 0.04$  mm. Data collected on an automatic four-circle Nonius CAD-4 diffractometer,  $\omega$ - $2\theta$  scan mode, sweep  $s = (2.20 + 0.45 \tan 2\theta)^\circ$ , aperture  $D = 3.00$  mm, scanning speed  $v = (20.1166/\text{NV})^\circ \text{min}^{-1}$  with NV integer. Lattice constants based on 15 reflections. Absorption correction by the Gaussian method,  $A_{\text{max}} = 0.787$ ,  $A_{\text{min}} = 0.511$ . Intensity measurement to  $\theta_{\text{max}} = 30^\circ$  within range  $-10 < h < +10$ ,  $-10 < k < +10$ ,  $0 < l < +17$ . Standard reflections 020, 202, 20 $\bar{6}$ , intensity variation 0.50%. 2162 reflections measured, 858 rejected [ $\sigma(I)/I > 0.33$ ], 444 unique [ $|F|/\sigma(|F|) > 6.0$ ],  $R_{\text{int}} = 0.024$ . Structure solved from Patterson synthesis.  $F$  magnitudes used in least-squares refinements: 65 parameters refined; mean  $\Delta/\sigma = 0.025$ , max. = 0.172; secondary-extinction factor  $x = 6.1 \times 10^{-8}$ ; atomic scattering factors for  $\text{N}^0$ ,  $\text{F}^-$ ,  $\text{Fe}^{3+}$  and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); program *SHELX76* (Sheldrick, 1976).

Structural phase transitions in  $\text{AMF}_4$  compounds generally result from concerted rotations of the  $\text{MF}_6$  octahedra. The motions are correlated inside and between the  $[\text{FeF}_4]_n^{n-}$  layers. The tilting mode can be conveniently described by using Glazer's (1975) notation modified by Bulou & Nouet (1982) for layer systems.

Owing to their layered structure, the growth of single crystals is difficult. A crystal of good optical quality, giving sharp spots in Laue diffraction, was selected and studied by the precession method. Cell parameters and systematic absences were determined. The conditions were only  $h00: h \neq 2n$ ,  $0k0: k \neq 2n$ ,  $00l: l \neq 2n$ . Curiously, the derivation of the non-centrosymmetric space group  $P2_12_12_1$  is univocal. In a first step, this group was used for the structure determination but proved to be an artefact due to crystal twinning.

The Patterson synthesis clearly indicated a  $\text{TiAlF}_4$ -type array of  $[\text{FeF}_4]_n^{n-}$  layers. Fe-F interactions further showed that the  $\text{FeF}_6$  octahedra are tilted around all three axes.

The structure was then built, starting from a tilted octahedron, by applying the symmetry elements of the space group  $P2_12_12_1$ . After a proper choice of the origin

from among 16 possibilities [Fe(1) at (0, 0, 0.25)], refinement slowly converged to  $R = 0.047$ ,  $wR = 0.052$ .

Several anisotropic thermal-motion parameters had to be fixed. Moreover the calculated interatomic Fe-F distances showed large deviations from the sum of the ionic radii (1.930 Å), varying between 1.89 and 2.02 Å for equatorial F atoms. In addition, new pseudo-symmetry elements appeared. They are consistent with a centrosymmetric supergroup of  $P2_12_12_1: Pnma$ .

Owing to the ferroelastic properties of  $\text{AMF}_4$  compounds, parameters  $a$  and  $b$  easily interchange under small stresses. We therefore considered the possibility of a twinning of the crystal according to Fig. 1. Intensities were re-analysed (Fig. 2) in the space group  $Pnma$ . The ratio  $r = 9.1$  of  $A$  and  $B$  volumes was estimated from a few unique reflections of  $A$  and  $B$ :  $h0l$  ( $h$  even,  $l$  odd) and  $hk0$  ( $k$  odd).

Intensities corresponding to the larger crystal  $A$  were calculated by using the relation:  $I(hkl)_A = [I_1 - (1/r)I_2] \times [r^2/(r^2 - 1)]$  with  $I_1 = I(hkl)_A + I(khl)_B$  and  $I_2 = I(khl)_A + I(hkl)_B$ . The structure determination was carried out again with this set of corrected data. Fe(1) was positioned at (000); this is the only origin which allows a tilting of the octahedra around the three axes. Refinement of atomic parameters and isotropic thermal parameters easily converged to  $R = 0.043$ ,  $wR = 0.049$ . Further refinements of anisotropic thermal parameters decreased the agreement factor to  $R = 0.026$ ,  $wR = 0.033$ ;  $w = 1/\sigma^2(F)$ . H atoms cannot be

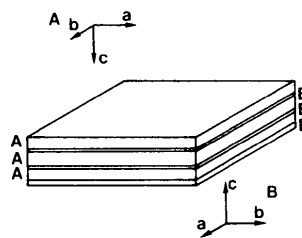


Fig. 1. Imagined view of a possible twinning of the crystal of  $\text{NH}_4\text{FeF}_4$  with stacking sheets  $A$  and  $B$ .

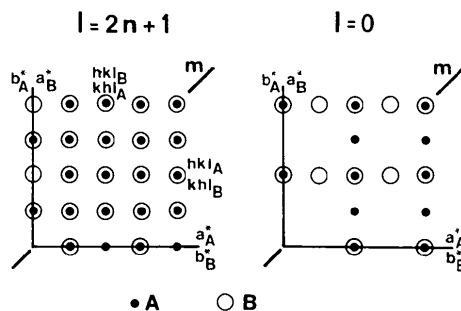


Fig. 2. Effect of the twinning of the crystal on the  $hkl$  reflections; almost equal parameters  $a$  and  $b$  of  $B$  cannot be distinguished from parameters  $b$  and  $a$  of  $A$ .

located, the maximum peak height in the final difference Fourier map being less than  $1.0 \text{ e } \text{Å}^{-3}$ .

**Discussion.** Final atomic parameters are listed in Table 1.\* Fig. 3 presents the (001) projection; for the sake of clarity the layers at  $z=0$  and  $z=\frac{1}{2}$  are given separately. The structure consists of layers of distorted  $\text{FeF}_6$  octahedra (Table 2) between which ammonium ions are inserted at  $z \approx 0.25$  and  $z \approx 0.75$ .

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39996 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and equivalent isotropic temperature factors ( $\text{Å}^2$ ) (estimated standard deviations in parentheses)

	$x$	$y$	$z$	$B_{\text{eq}}$
Fe(1)	0	0	0	0.72 (16)
Fe(2)	0	0	$\frac{1}{2}$	0.63 (15)
F(1)	0.0364 (6)	$\frac{1}{2}$	-0.0309 (4)	1.81 (16)
F(2)	0.2501 (3)	0.0447 (4)	0.4695 (3)	1.67 (10)
F(3)	0.4492 (6)	$\frac{1}{2}$	0.0187 (3)	1.61 (16)
F(4)	0.0484 (5)	0.0352 (5)	0.1418 (3)	1.94 (13)
F(5)	0.0360 (4)	0.0331 (5)	0.6438 (3)	1.72 (13)
N(1)	0.2880 (9)	$\frac{1}{2}$	0.2562 (7)	2.02 (28)
N(2)	0.2747 (7)	$\frac{1}{2}$	0.7594 (6)	1.83 (30)

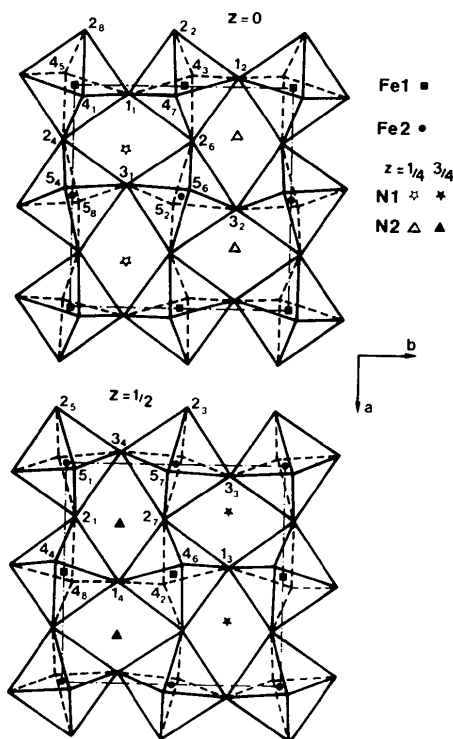


Fig. 3. A (001) projection of the structure of  $\text{NH}_4\text{FeF}_4$ .

Table 2. Selected bond lengths ( $\text{Å}$ ) and angles ( $^\circ$ ) in  $\text{NH}_4\text{FeF}_4$  (e.s.d.'s in parentheses)

Fe(1)—F(1)	1.956 (1)	$\langle \text{Fe(1)—F}_{\text{eq}} \rangle$	1.958
Fe(1)—F(2)	1.959 (2)	$\langle \text{Fe(1)—F} \rangle$	1.927
Fe(1)—F(4)	1.863 (3)		
Fe(2)—F(2)	1.961 (2)	$\langle \text{Fe(2)—F}_{\text{eq}} \rangle$	1.955
Fe(2)—F(3)	1.949 (2)	$\langle \text{Fe(2)—F} \rangle$	1.927
Fe(2)—F(5)	1.871 (4)		
N(1)—F(4)	2.839 (8)	N(2)—F(5)	2.852 (7)
N(1)—F(4)	2.869 (8)	N(2)—F(5)	2.851 (7)
N(1)—F(5)	2.904 (9)	N(2)—F(4)	2.952 (9)
Fe(1)—F(1)—Fe(1)	151.5 (1)		
Fe(1)—F(2)—Fe(2)	149.6 (1)		
Fe(2)—F(3)—Fe(2)	153.2 (1)		

Table 3. Rotation ( $^\circ$ ) of the Fe—F vectors around the  $a$ ,  $b$ ,  $c$  axes [Fe(1) at (0, 0, 0) and Fe(2) at (0, 0,  $\frac{1}{2}$ )] (e.s.d.'s  $\sim 0.1^\circ$ )

Vectors	Rotation axis		
	$a$	$b$	$c$
Fe(1)—F(11)	11.7		8.3
Fe(1)—F(24)		11.6	10.0
Fe(1)—F(41)	8.4	11.4	
Fe(2)—F(21)		11.6	10.0
Fe(2)—F(34)	7.2		11.4
Fe(2)—F(51)	7.8	8.5	

The rotations of octahedra are antiphase along  $c$  and  $a$  but in phase along  $b$ . The  $a$  and  $b$  tiltings are identical in successive layers. According to the Bulou notation, the mode of tilting is  $a_p^- b_p^+ c^-$ .

This differs from that of the room-temperature homologues  $\text{RbFeF}_4$  and  $\text{CsFeF}_4$  ( $a_p^+ b_p^+ c^0$ ) (Abrahams & Bernstein, 1972; Babel, Wall & Heger, 1974).

The presence of strong N—H...F hydrogen bonds in  $\text{NH}_4\text{FeF}_4$  probably induces the new type of complex tilting  $a_p^- b_p^+ c^-$ . Four axial F atoms approach N at  $d < 2.87 \text{ Å}$  and two others at  $2.90 \text{ Å} < d < 2.96 \text{ Å}$ . The tilting angles around the three axes vary between 7 and  $12^\circ$  (Table 3). As a consequence, the F—F—F angles between equatorial F atoms [F(24)—F(11)—F(26) or F(11)—F(24)—F(31)] are close to  $110$  or  $70^\circ$  and the octahedra are somewhat distorted.

The electric-field gradient at the Fe sites was recalculated with a polarizable point-charge model. The calculated F polarizability,  $0.9 \text{ Å}^3$ , does not differ from that of other  $\text{AMF}_4$  compounds (Teillet *et al.*, 1982). The results with the space group  $Pnma$  are consistent with experimental data. The difference between the calculated quadrupolar shifts of Fe(1) and Fe(2) is  $0.06 \text{ mm s}^{-1}$ ; this value is in qualitative agreement with the room-temperature spectrum consisting of only one quadrupole doublet with narrow lines (Menil, Tressaud, Sabatier & Le Flem, 1977; Teillet, Ferrey, Leblanc & Varret, 1978). These parameters showed large unexplained discrepancies when the space group  $P2_12_12_1$  was used (Teillet *et al.*, 1982).

The authors are indebted to Dr J. Pannetier and Y. Calage for helpful discussions and to Professor Hardy (Université de Poitiers) who allowed the data collection.

## References

- ABRAHAMS, S. C. & BERNSTEIN, J. L. (1972). *Mater. Res. Bull.* **7**, 715–720.
- BABEL, B., WALL, F. & HEGER, G. (1974). *Z. Naturforsch. Teil B*, **29**, 139–148.
- BROSSET, C. (1938). *Z. Anorg. Allg. Chem.* **239**, 301–304.
- BULOUE, A. & NOUET, J. (1982). *J. Phys. C*, **15**, 183–196.
- FEREY, G., LEBLANC, M., DE PAPE, R., PASSARET, M. & BOTHOREL-RAZAZI, M. (1975). *J. Cryst. Growth*, **29**, 209–211.
- GLAZER, A. M. (1975). *Acta Cryst.* **A31**, 756–762.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- HEGER, G., GELLER, R. & BABEL, D. (1971). *Solid State Commun.* **9**, 335–340.
- HIDAKA, M., WOOD, I. G., WANKLYN, B. M. & GARRARD, B. J. (1979). *J. Phys. C*, **12**, 1799–1807.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MENIL, F., TRESSAUD, A., SABATIER, R. & LE FLEM, G. (1977). *Mater. Res. Bull.* **12**, 983–988.
- NOUET, J., PANNETIER, J. & FOURQUET, J. L. (1981). *Acta Cryst.* **B37**, 32–34.
- SHELDRIK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.
- TEILLET, J., CALAGE, Y. & VARRET, F. (1982). *J. Phys. Chem. Solids*, **43**(9), 863–869.
- TEILLET, J., FEREY, G., LEBLANC, M. & VARRET, F. (1978). *Solid State Commun.* **27**, 1083–1084.
- TRESSAUD, A., GALY, J. & PORTIER, J. (1969). *Bull. Soc. Fr. Minéral. Cristallogr.* **92**, 335–338.

*Acta Cryst.* (1985). **C41**, 660–663

## Verfeinerung der Kristallstruktur des Ammoniumtriiodids, $\text{NH}_4\text{I}_3^*$

VON K.-F. TEBBE UND B. FRECKMANN

*Institut für Anorganische Chemie der Universität zu Köln, Greinstrasse 6, D-5000 Köln 41, Bundesrepublik Deutschland*

UND M. HÖRNER, W. HILLER UND J. STRÄHLE

*Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, Bundesrepublik Deutschland*

(Eingegangen am 27. Dezember 1983; angenommen am 1. Januar 1985)

**Abstract.**  $M_r = 398.75$ , orthorhombic,  $Pnma$ ,  $a = 10.854$  (3),  $b = 6.620$  (1),  $c = 9.595$  (3) Å,  $V = 689.4$  Å<sup>3</sup>,  $D_x = 3.841$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 13.34$  mm<sup>-1</sup>,  $F(000) = 680$ ,  $T = 293$  K. The crystal structure has been confirmed and has been refined by full-matrix least squares to  $R_F = 0.038$  for 597 observed reflections [ $|F_o| \geq 4\sigma(F_o)$ ]. In addition to former investigations, the H positions have been located. The extreme asymmetry of the triiodide ion [I(1)–I(2) 3.114 (2), I(2)–I(3) 2.797 (2) Å,  $\angle$ I(1)–I(2)–I(3) 178.55 (5)°] is mainly caused by asymmetrically distributed hydrogen bonds. The relation between the total length of the triiodide ion and its asymmetry is discussed.

**Einleitung.** Die Kristallstruktur des Ammoniumtriiodids konnte frühzeitig geklärt werden (Mooney, 1935). Im Vergleich mit dem isotypen Caesiumtriiodid  $\text{CsI}_3$  (Runsink, Swen-Walstra & Migchelsen, 1972) liegt hier ein noch stärker asymmetrisches Triiodid-Ion vor.

Inzwischen wurde die Struktur bereits mit dem Ziel verfeinert, die extreme Asymmetrie des Triiodid-Ions zu bestätigen (Cheesman & Finney, 1970). Als Ursache wurden die unsymmetrische Umgebung des Triiodid-Ions im Kristall genannt und im besonderen Wasserstoffbrücken zum Ammonium-Ion auf Grund der Iod–Stickstoff–Abstände vermutet (vgl. auch Yoshioka, Nakamura & Chihara, 1983), ohne dass letzteres infolge der erreichten Genauigkeit ( $R = 0,183$  für 516 unabhängige Reflexe, Filmmethoden, Weissenberg-Goniometer) direkt nachgewiesen werden konnte. Zu Klärung haben wir die Kristallstruktur des  $\text{NH}_4\text{I}_3$  erneut verfeinert und die Begründung für die Verzerrung des hier vorliegenden Triiodid-Ions der Erwartung entsprechend in der Verteilung der Wasserstoffbrücken-Bindungen erkannt.

**Experimentelles.** Zunächst unbeabsichtigte Darstellung der Verbindung bei Versuchen zur Gewinnung von Polyiodiden der Ammin-Komplexe des Cobalts; Identifizierung und Charakterisierung über röntgenographische Pulver- und Einkristallmethoden;

\* Untersuchungen an Polyhalogeniden. 7. Teil 6: Tebbe (1983).