Inorganica Chimica Acta, 126 (1987) 119–124

Studies of Iodine in Nitric Acid and of Iodine Adsorbed onto Silver-Impregnated Silica

FRANK J. BERRY*, ROBERT D. COLLINS

Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT, U.K.

R. V. PARISH and LAILA S. MOORE

Department of Chemistry, The University of Manchester Institute of Science and Technology, P.O. Box 88, Manchester M60 1QD, U.K.

(Received July 16, 1986)

Abstract

A simulation of the initial stages of nuclear-fuel reprocessing has been made by adding potassium iodide to hot nitric acid and sparging with a stream of air. The concentration and nature of the iodine-containing species remaining in the acid have been investigated by use of an iodide selective electrode, a radioactive iodine-125 tracer in conjunction with paper chromatography and column chromatography, differential pulsed polarography and visible region spectroscopy. The residual iodine in the nitric acid was identified as molecular iodine and iodate.

The iodine which was volatilised from the nitric acid by the sparging process was adsorbed onto silver-impregnated silica. Iodine-129 Mössbauer spectroscopy showed that some of the adsorbed iodine underwent conversion to silver iodide and iodine when subjected to moderate thermal treatment.

Introduction

The reprocessing of nuclear fuels involves their initial dissolution in nitric acid followed by distillation and/or sparge treatments to remove the volatile species of which the major component is iodine.

Several isotopes of iodine are produced by the nuclear fission of uranium-235 and during dissolution are liberated to the nitric acid. Although the majority of the iodine is volatilised during the distillation and sparge treatments, some iodine appears to be resistant to removal by volatilisation [1–4]. The trapping of the volatile iodine species may be achieved by a variety of means [5], the most common methods involving scrubbing with sodium hydroxide or hyperazeotropic nitric acid and/or the use of solid silver-containing absorbents. In this respect it is pertinent to note that silver nitrate impregnated amorphous silicic acid beads have been found to be particularly suitable [6, 7] but that their thermal stability, which might have implications for their long-term storage, has received little attention.

This paper describes some investigations of the concentration and characterisation of the iodine remaining in nitric acid following a simplified nuclear fuel reprocessing procedure, and the use of iodine-129 Mössbauer spectroscopy to investigate the thermal stability of the iodine species which are adsorbed onto solid silver-containing silica following volatilisation from the nitric acid solution.

Experimental

Preparation of Samples

Nitric acid (3.06 M, 245 ml) was heated to 90 °C over a period of *ca.* 1 h. A solution (50 μl) containing carrier free sodium iodide-125 (5 mCi) was diluted to 25 ml with aqueous 5×10^{-3} M potassium iodide. Aliquots (5 μl to 5 ml) were made up to 5 ml with aqueous 5×10^{-3} M potassium iodide, added to the nitric acid to give a solution 3.00 M in nitric acid and 1.0×10^{-4} M in potassium iodide, and heated under reflux at 90 °C for 3 h. The solution was sparged with air (125 ml/min) for periods of 60 or 90 min and the volatile iodine species trapped by passing the gas leaving the condenser outlet through four flasks each containing a mixture of 0.4 M sodium thiosulphate solution (75 ml) and 0.4 M sodium hydroxide solution (75 ml). Samples for investigation by polarogaphy were produced on a larger scale (490 ml HNO_3, 10 ml KI solution, 250 ml/min air sparge) without an iodide-125 tracer. The iodine remaining in the nitric acid solution after this procedure is, for the purpose of this work, called residual iodine.

---

*Author to whom correspondence should be addressed.

0020-1693/87/$3.50

For the study of the volatile iodine adsorbed onto silica a solution (10 ml) of iodine-129 as iodide was added to nitric acid (3.06 M, 245 ml) at 90 °C to give a solution 2.93 M in nitric acid and 2×10^{-3} M in iodide. The solution was heated under reflux at 90 °C for 3 h and then sparged with air (125 ml/min) for 2 h. Further sparge treatment at ambient temperature was continued for 15 h. The volatile iodine species were passed at 150 °C over silicic acid beads (1–2 mm diameter) which had been impregnated with 7% silver by immersion in silver nitrate solution as previously described [6]. One portion of the resulting product was heated in air at 200 °C for 12 h (Sample 1) and another in air at 500 °C for 12 h (Sample 2).

Methods of Investigation

Iodine-125 tracer

The γ- and X-radiations emanating from 2 ml samples of the nitric acid solutions were monitored over periods of 40–80 s using a Nuclear Enterprises Automatic β, γ counter. A standard prepared from 2 μl of the iodide-125 solution diluted to 2 ml with water was used for calibration.

Iodide selective electrode

Samples (5 ml) were mixed with saturated sulphamic acid solution (1 ml) and 60% *v/v* hydrazine hydrate solution (1 ml) to reduce all iodine species to iodide. The cool solutions were made up to 25 ml with an acetate buffer solution composed of ammonium acetate (77 g) and glacial acetic acid (60 ml) in 1000 ml of aqueous solution. After standing for 30 min the solutions were investigated with an Orion 94-53 iodide selective electrode in conjunction with an Orion 90-01 reference electrode.

Column chromatography

Paper chromatography proved unsuccessful as a means of identification of the iodine species in nitric acid; however, column chromatography allowed the resolution of iodide, iodine, and iodate(V). A silica-gel column (25 cm, 70–230 mesh) was used with an n-butanol:acetic acid:water eluant (7:3:10). Using a standard flow rate the eluate was collected for periods of 5 or 10 min and monitored with the β-,γ counter.

Polarography

Samples were investigated at ambient temperature with a Princetown Applied Research model 174A polarographic analyser in conjunction with a model 303 static mercury dropping electrode. The samples were scanned in the potential range +0.2 V to −0.4 V with the polarographic analyser in differential pulse mode. Calibration curves were obtained for iodide and iodate in nitric acid.

Visible region spectrophotometry

The absorbance of nitric acid (3 M) solutions were monitored at 463 nm using a Pye Unicam spectrophotometer calibrated against standard solutions of iodine in nitric acid.

Mössbauer spectroscopy

Iodine-129 Mössbauer spectra were recorded with a Harwell 6000 Series spectrometer and an Ortec hyper pure germanium LEPS detector. The source was $^{66}Zn^{128}Te$ (35 mg) pelleted with LiF, irradiated at 2×10^{14} n cm^{2} s^{-1} for 3 days and allowed to decay for 24 h before use. The source and absorber were both cooled to 4.2 K. The ^{129}I chemical isomer shifts are quoted relative to the source. The low concentration of iodine-129 and low transmission rates mitigated against the acquisition of good quality data. Curve fitting was performed with the asymmetry parameter constrained to zero.

Results and Discussion

(i) Concentration and Nature of Residual Iodine

The total iodine content of nitric acid at different stages of the simulated reprocessing treatment as determined by the iodide selective electrode showed good agreement with those determined by the iodide-125 tracer. The results have important implications for the chromatographic investigations, which will be discussed later, which depend on the behaviour of the ^{125}I tracer accurately reflecting the speciation of all the iodine isotopes in solution. The measurements of residual iodine concentrations indicated that, after 60 min sparge treatment, 13 ± 5% of the iodine initially introduced to the nitric acid remained in solution as residual iodine. Hence the results show that the majority of the iodine is volatilised during the early stages of the sparging process.

The results of the investigations of the nature of iodine in nitric acid by column chromatography are summarised in Fig. 1. The association of the large peak in Figure 1a with iodine is quite reasonable given that iodide is reported [8] to oxidise rapidly in hot nitric acid to molecular iodine. Figure 1b shows that this molecular iodine remains as the major iodine species in nitric acid after heating at 90 °C under reflux for 3 h although the development of the smaller peak, corresponding to a retention time of *ca.* 100 min, can be associated with the growth of an iodate species. Figure 1c shows that following the sparge treatment for 1 h, the concentration of molecular iodine decreases whilst that of iodate increases. The result is to some extent a reflection of the volatilisation of molecular iodine during the sparge process but, given the rapid rate of iodine removal detected by the iodide selective electrode and the iodide-125 tracer, the increase in the iodate

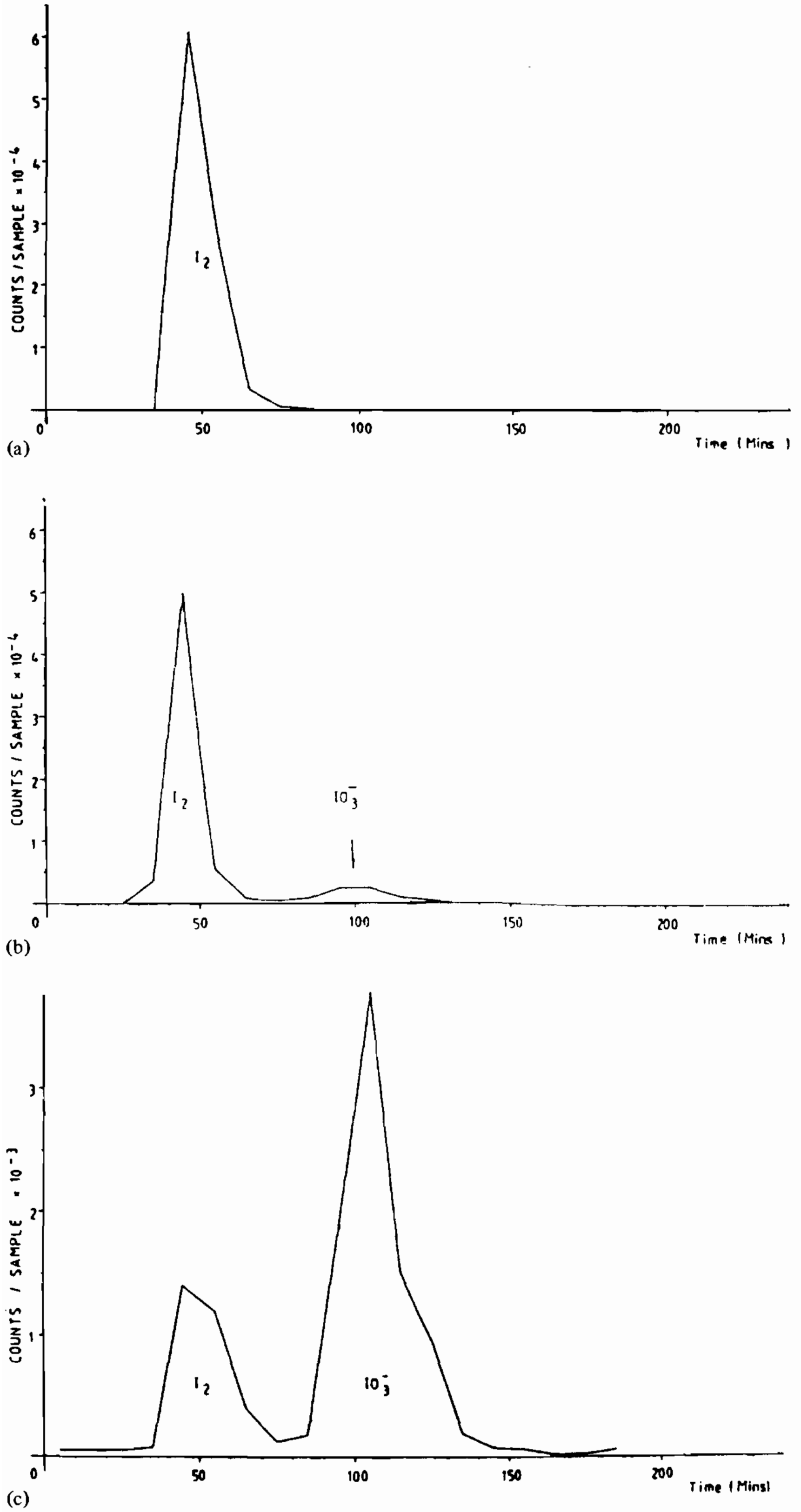

Fig. 1. Column chromatogram of iodine in nitric acid recorded. (a) After addition of potassium iodide solution; (b) after 180 min at 90 °C; (c) after sparge treatment for 60 min.

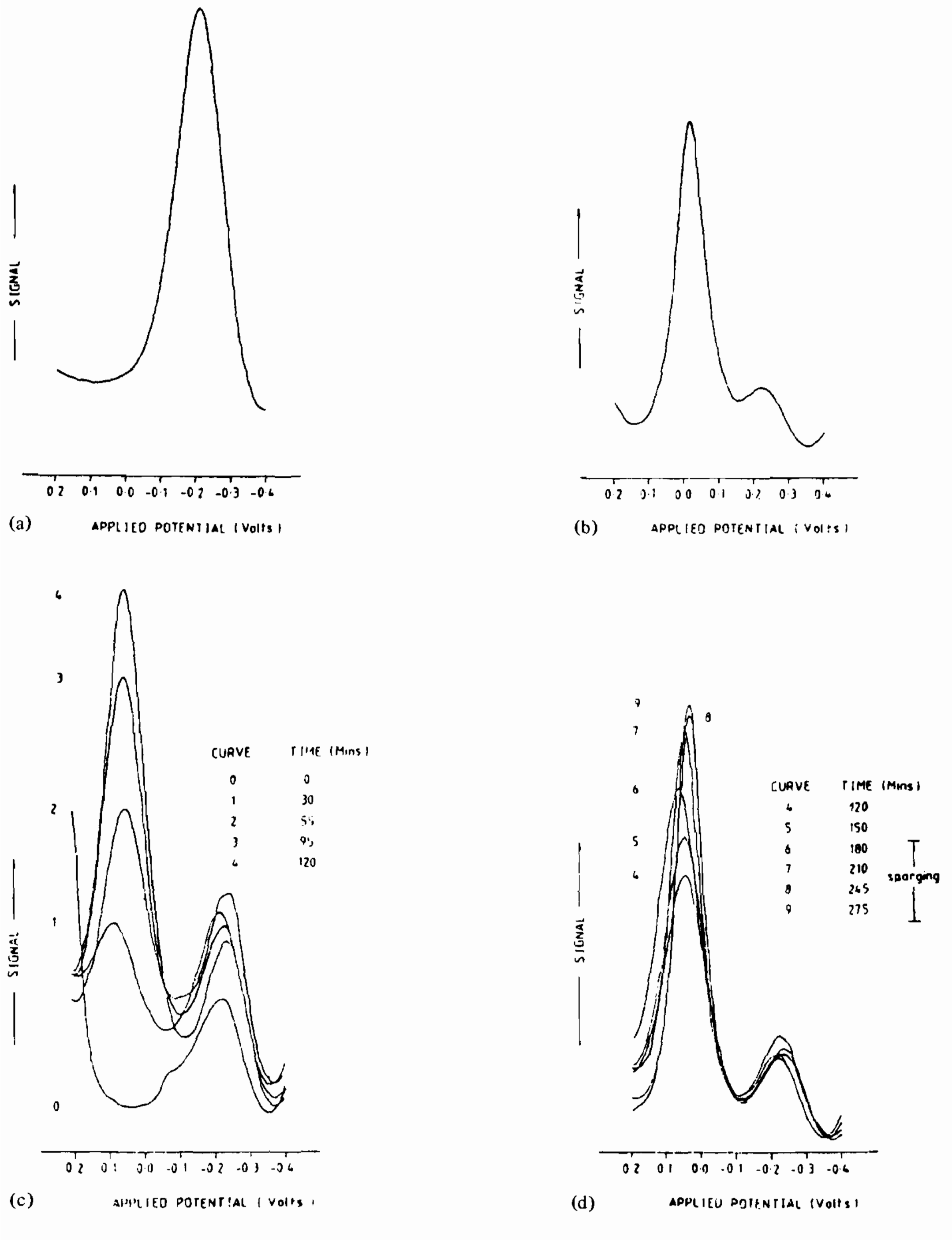

Fig. 2. Differential pulse polarogram of (a) iodide in nitric acid (in the presence of hydrazine hydrate as reductant); (b) iodate in nitric acid; (c) and (d) residual iodine in nitric acid recorded during simulated reprocessing treatment.

concentration may also be associated with the oxidation of some of the iodine during the early stages of the sparge treatment. Although the chromatography results show that residual iodine is present as molecular iodine and iodate, reproduceable quantitative analyses of the I_2/IO_3^- ratios were not obtained.

The results of the investigation of residual iodine species in nitric acid by differential pulse polarography are shown in Fig. 2. The polarographic waves displayed by iodide in nitric acid, recorded after reducing all iodine species to iodide by addition of sulphamic acid and hydrazine hydrate (Fig. 2a),

TABLE I. Iodine-129 Mössbauer Parameters Recorded at 77 K from Iodine Adsorbed onto Silver-Impregnated Silica

Sample	δ (ZnTe) (mm s^{-1})	e^2qQh^{-1} (MHz)	Area ratio
1 Heated at 200 °C	−0.08(5)		1
(12 h) in air	−0.05(20)	+425(100)	3.8(10)
2 Heated at 500 °C	+0.73(50)	−1890(100)	1
(12 h in air)	+0.37(20)	+322(100)	5.6(10)

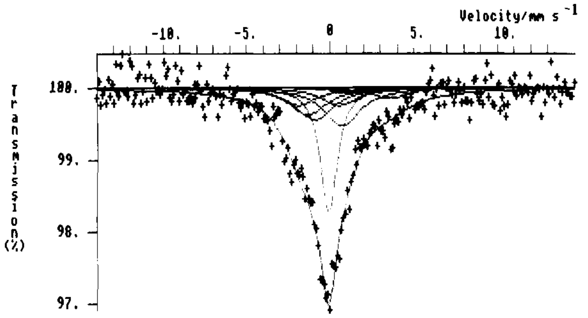

Fig. 3. Iodine-129 Mössbauer spectrum recorded from iodine adsorbed onto silver-impregnated silica and heated at 200 °C.

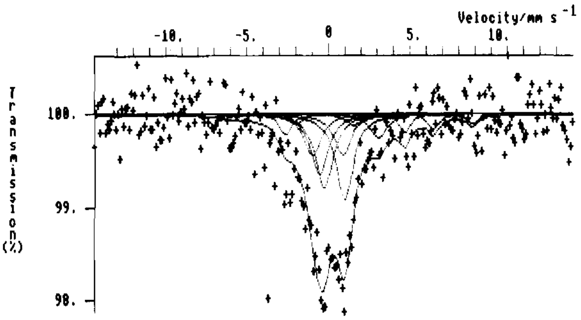

Fig. 4. Iodine-129 Mössbauer spectrum recorded from iodine adsorbed onto silver-impregnated silica and heated at 500 °C for 12 h.

and iodate in nitric acid (Fig. 2b) enabled the growth in iodate concentration during the sparge treatment to be monitored (Fig. 2(c) and (d)). The results clearly show the increase of the iodate species during the simulated reprocessing treatment and the resistance of some iodide to oxidation. The data thereby endorse the results recorded by column chromatography.

Visible region spectroscopy showed that the initial addition of the potassium iodide solution to nitric acid gives a molecular iodine content close to the 12.7 μg/ml which would be expected for a 10^{-4} M iodide solution confirming that all the iodide was rapidly oxidised to molecular iodine. The results also showed a slow decrease in the molecular iodine content as it is slowly converted to iodate and a rapid decrease through volatilisation during sparging.

(ii) Iodine Trapped in Sodium Thiosulphate Solution

The volatile iodine species trapped in the sodium thiosulphate scrub solution was found as expected [9] to be present as iodide.

(iii) Iodine Adsorbed onto Silver-Impregnated Silica

The iodine adsorbed onto silver-impregnated silica and heated at 200 °C (Sample 1) gave an iodine-129 Mössbauer spectrum (Fig. 3) from which the presence of two different iodine species could be identified (Table I). One component, representing *ca.* one third of the total spectrum area, gave a single line with a chemical isomer shift, δ −0.08 mm s^{-1}, similar to that expected for the iodide ion [10] and close to that reported for silver iodide [11, 12]. The second component has a small positive quadrupole coupling constant and is consistent with iodine in a positive oxidation state. Ionic iodates(V) give rather large quadrupole coupling constants, *ca.* 1000–1100 MHz [10], and iodine-(III) compounds usually give considerably larger values of e^2qQh^{-1}, *ca.* 2000–3000 MHz [10]. Given the chemistry involved, an iodine(V) species such as $AgIO_3$ or I_2O_5 does not seem unlikely [13]. In this respect it is interesting to note that the reaction of iodine vapour with solid silver nitrate has been reported [14] to result in the formation of silver iodide and silver iodate. It is unfortunate that the Mössbauer spectrum of silver iodate has yet to be reported.

The iodine adsorbed onto the silver-impregnated silica and heated at 500 °C (Sample 2) gave a spectrum (Fig. 4) in which two components could also be identified. The major component is probably the same as the iodine(V) species observed in the previous sample but the second component has ^{129}I Mössbauer parameters, δ 0.73 mm s^{-1}, e^2qQh^{-1} −1890 MHz, similar to those reported for molecular iodine [10]. Although a thorough analysis of the spectrum is complicated by overlapping of the peaks there appears to be little evidence for the presence of silver iodide. The results suggest that the silver iodide formed in Sample 1 undergoes a thermally induced transformation to molecular iodine when heated at 500 °C for 12 h.

Conclusion

When iodide is added to hot nitric acid it is converted to molecular iodine rapidly and quantitatively. Slow oxidation to iodate(V) subsequently occurs. On sparging with air *ca.* 90% of the molecular iodine is volatilised. The volatile iodine trapped on silver-nitrate impregnated silica is probably present as a mixture of silver iodide and silver iodate after heating to 200 °C. Subsequent treatment at 500 °C gives rise to the formation of molecular iodine at the expense of the silver iodide.

Acknowledgements

We thank British Nuclear Fuels PLC for financial support and Drs. Hawkrigg and Holmes for valuable discussions.

References

1 J. C. Mailen and D. L. Hormer, *Nuclear Technology, 33*, 260 (1970).
2 *U.S. Patent 3803295* (1974) to G. I. Cathers and C. J. Shipman.
3 *U.S. Patent 3914388* (1975) to G. I. Cathers and C. J. Shipman.
4 P. M. Bryant and B. F. Warner, 'Control of Iodine in the Nuclear Industry', International Atomic Energy Agency Technical Reports Series No. 148, Vienna, 1973.
5 D. W. Holliday, 'Oak Ridge National Laboratory Report ORNL/TM-6350', Oak Ridge National Laboratory, Tennessee, 1979.
6 J. G. Wilhelm and H. Scheuttelkopf, *Proceedings of the 11th AEC Air Cleaning Conference, CONF-700816*, Atomic Energy Commission, 1970, p. 568.
7 J. G. Wilhelm and H. Scheuttelkopf, *Proceedings of the 12th AEC Air Cleaning Conference, CONF-720823*, Atomic Energy Commission, 1972, p. 540.
8 E. Heinrich, R. Hufner and A. Sahm, *International Symposium on Management of Waste Gases from Nuclear Facilities*, International Atomic Energy Agency Report No IAEA-SM-245/16, Vienna, 1980.
9 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 3rd edn., Wiley Interscience, London, 1972, p. 453.
10 N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy', Chapman and Hall, London, 1971, p. 470.
11 A. N. Murin, B. G. Lur'e and Yu. S. Grushko, *Sov. Phys. - Solid State, 9*, 1429 (1967).
12 P. Junod, H. Hediger and W. Kundig, *Photogr. Sci. Eng., 20*, 47 (1976).
13 N. N. Greenwood and A. Earnshaw, 'Chemistry of the Elements', Pergamon Press, Oxford, 1984, p. 1009.
14 K. C. Patil, C. N. Rao, J. W. Lacksonnen and C. E. Dryden, *J. Inorg. Nucl. Chem., 29*, 407 (1967).