

# The Structure of Silver(I) Solvate and Sodium Diiodoargentate(I) in Acetonitrile Solution

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Acetonitrile solutions of silver(I) perchlorate and sodium diiodoargentate(I) have been investigated by means of the large-angle X-ray scattering technique. The silver(I) ion is tetrahedrally solvated by four acetonitrile molecules; the Ag–N bond distance is 2.25(1) Å. Diiodoargentate(I) polymerizes to chains in concentrated solution, but it has not been possible in this study to determine the length of these chains; silver is tetrahedrally surrounded by four iodides at a distance of 2.811(2) Å, and the silver–silver distance is 3.02(2) Å. The silver-iodide tetrahedra comprising the chain share edges.

The structural investigations of the silver(I) and diiodoargentate(I) ions in acetonitrile form part of a research programme dealing with solvation and complex formation of copper(I), silver(I) and gold(I) in nitrogen-donor solvents.<sup>1–3</sup> Acetonitrile and pyridine have been used to elucidate the influence of the solvent on complex formation, since both these solvents are nitrogen donors but with different solvating properties. Of the two, pyridine is the more strongly solvating solvent for soft and semi-soft acceptors.<sup>2</sup>

The crystal structure of the solid solvate precipitated from a solution of silver(I) perchlorate in acetonitrile has been reported previously.<sup>4</sup> Silver(I) is tetrahedrally coordinated by four acetonitrile molecules as discrete ions,  $\text{Ag}(\text{CH}_3\text{CN})_4^+$ . Analogous  $\text{Ag}(\text{C}_5\text{H}_5\text{N})_4^+$  ions occur in the complex crystallizing from a pyridine solution of silver(I) perchlorate.<sup>5</sup> Among the group Ib metal perchlorates, only silver(I) perchlorate is soluble enough in acetonitrile and in pyridine to permit LAXS (Large Angle X-Ray Scattering) studies. The solvate structures of copper(I) and gold(I) in acetonitrile and in pyridine solution had to be studied by the EXAFS (Extended X-Ray Ab-

sorption Fine Structure) technique. Copper(I) has been found to be tetrahedrally coordinated in both acetonitrile and pyridine solutions,<sup>6</sup> just as in the solid state;<sup>5,7</sup> the solvates are isostructural with the silver(I) solvates. Gold(I) is also tetrahedrally coordinated by four solvate molecules in acetonitrile and in pyridine solutions,<sup>3</sup> but the solid gold(I) acetonitrile complex is a disolvate.<sup>8</sup>

The neutral silver halides are insoluble in acetonitrile. However, they become soluble in solutions containing silver(I) or halide in large excess, since complex cations or anions are then formed. The following iodide complexes have been shown to occur in acetonitrile solutions:  $\text{Ag}_2\text{I}^+$ ,  $\text{Ag}_3\text{I}^{2+}$ ,  $\text{AgI}_2^-$ ,  $\text{Ag}_2\text{I}_3^-$  and  $\text{Ag}_5\text{I}_6^-$ .<sup>9,10</sup> Owing to the stronger solvating properties of pyridine, the neutral silver halides are soluble in this solvent. In dilute solution, monomeric complexes of the type  $\text{AgL}_n^{(1-n)}$  ( $n = 1-3$ ) and a dimeric complex  $\text{Ag}_2\text{L}^+$  are formed.<sup>2</sup>

The structures of the complexes  $\text{ML}_2^-$  ( $\text{M} = \text{Cu}$  or  $\text{Ag}$  and  $\text{L} = \text{Cl}$ ,  $\text{Br}$  or  $\text{I}$ ) in various solvents have been studied by a variety of methods. Vibrational spectra of these complexes in tributyl phosphate solution have indicated linear coordination.<sup>11</sup> In an early X-ray scattering investigation of  $\text{KAgI}_2$  in a water–acetone mixture, nearly tetrahedral coordination around silver was found.<sup>12</sup>

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Table 1. Composition ( $\text{mol dm}^{-3}$ ), linear absorption coefficient,  $\mu(\text{MoK}\alpha)$  ( $\text{cm}^{-1}$ ) and density,  $D$  ( $\text{g cm}^{-3}$ ), for the investigated solutions.

	Ag	I	Na	$\text{ClO}_4$	$\text{CH}_3\text{CN}$	$\mu$	$D$
$\text{AgClO}_4$	0.97			0.97	18.6	3.71	0.97
$\text{NaAgI}_2$	1.22	2.51	1.29		18.3	15.8	1.23

In the present investigation the structures of the species present in 0.97 M  $\text{AgClO}_4$  and 1.2 M  $\text{NaAgI}_2$  solutions in acetonitrile have been studied by LAXS. Raman spectra have also been recorded for these solutions, as well as for a 0.6 M solution of NaI in acetonitrile.

### Experimental

**Preparation of solutions.** A silver(I) solution was obtained by dissolving  $\text{AgClO}_4$  in acetonitrile which had been purified as described previously.<sup>1</sup> For the preparation of a concentrated  $\text{AgI}_2^-$  acetonitrile solution, the highest concentration was obtained using sodium as the cation. AgI was dissolved together with NaI in a molar ratio of 1:1. Data for the solutions studied by LAXS are given in Table 1.

**X-ray scattering experiments.** The X-ray scattering from the free surface of the solutions was measured in a large-angle theta–theta diffractometer of the Seifert GDS type.<sup>13</sup> The solutions

were enclosed in a cylindrical thin-walled glass container in order to avoid evaporation. The absorption of the glass container and its angle dependence have been determined previously.<sup>14</sup>  $\text{MoK}\alpha$  ( $\lambda = 0.7107 \text{ \AA}$ ) radiation was used. The scattered intensities were determined at discrete points in the interval  $4^\circ < \theta < 65^\circ$ , separated by 0.0335 in  $s$ , where  $s = 4\pi\lambda^{-1} \sin\theta$  and the scattering angle is  $2\theta$ . An extrapolation of the intensity data for  $\theta < 4^\circ$  was necessary owing to concave curvature of the meniscus in the glass container. A counting error of 0.35% was achieved by measuring 40 000 counts twice at each sampling point. The fraction of incoherent scattering contributing to the intensity determinations was estimated in the usual manner.<sup>15</sup>

**Data treatment.** The data reduction procedure and corrections applied were as described previously.<sup>15</sup> The experimental intensities were normalized to a stoichiometric unit of volume containing one silver atom. The scattering factors, corrections for anomalous dispersion and values

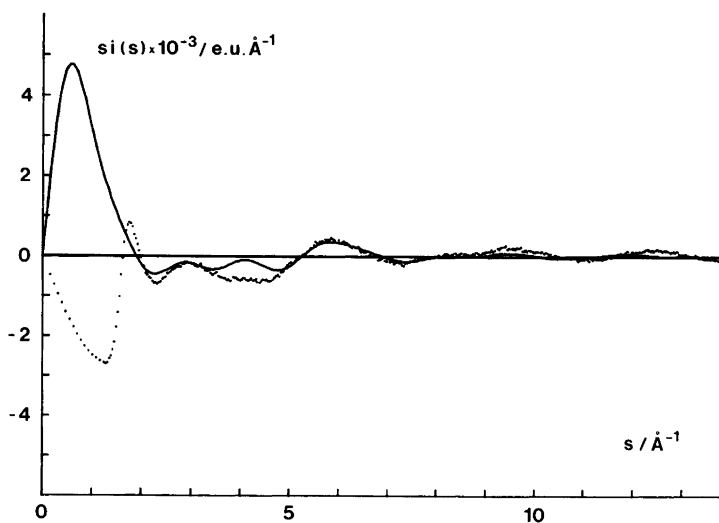


Fig. 1. Experimental  $si(s)$  values (dotted) and values calculated from the model for silver(I) perchlorate (solid line) in acetonitrile solution.

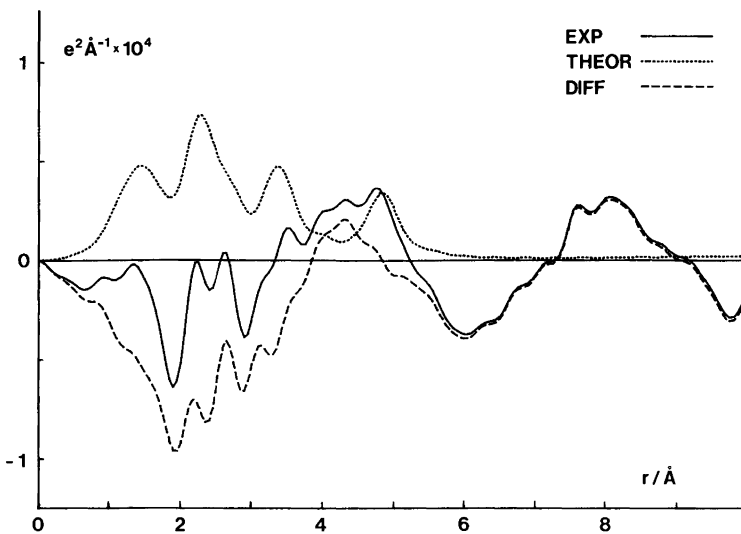


Fig. 2. Experimental radial distribution function,  $D(r) - 4\pi r^2 \rho_0$ , for silver(I) perchlorate in acetonitrile solution, the model function with parameters from Table 2 and the difference between them.

for incoherent scattering were the same as used before.<sup>15</sup> For the silver(I) perchlorate solution, correction was also made for multiple scattering. The reduced intensity curves,  $i_{\text{obs}}(s)$ , multiplied by the scattering variable,  $s$ , are shown in Figs. 1 and 3. The corresponding electronic radial distribution functions (RDF),  $D(r) - 4\pi r^2 \rho_0$ , were obtained by Fourier transformation (Figs. 2 and 4). The same modification as described previously was used.<sup>16</sup> Spurious peaks below 1.5 Å which could not be related to interatomic distances within the acetonitrile molecule or the perchlo-

rate ion were eliminated by a Fourier transformation procedure.<sup>13</sup>

All calculations were carried out using the computer programs KURVLR<sup>17</sup> and STEPLR.<sup>18</sup>

**Raman measurements.** Raman spectra were recorded using d.c. amplification with a D.I. L.O.R. RTI 30 triple monochromator with 3.2  $\text{cm}^{-1}$  spectral bandwidth. The light employed was the 514.5 nm line of a Coherent Radiation Laboratories Innova 90-5 Ar-ion laser.

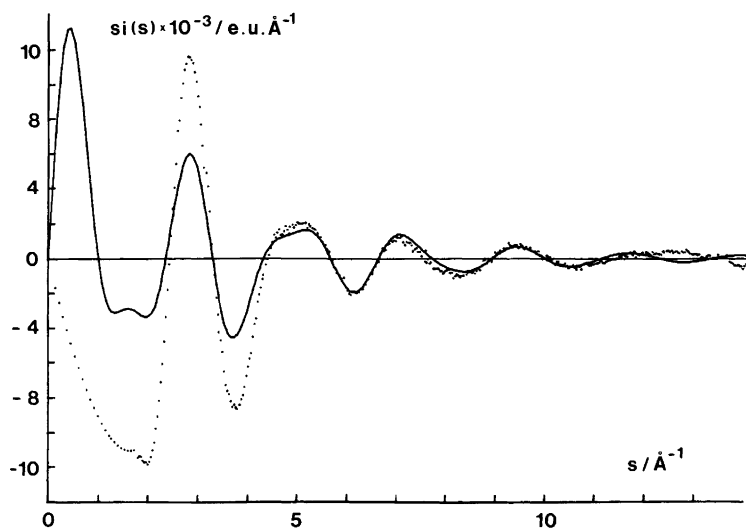


Fig. 3. Experimental  $si(s)$  values (dotted) and values calculated from the model for sodium diiodoargentate(I) in acetonitrile solution.

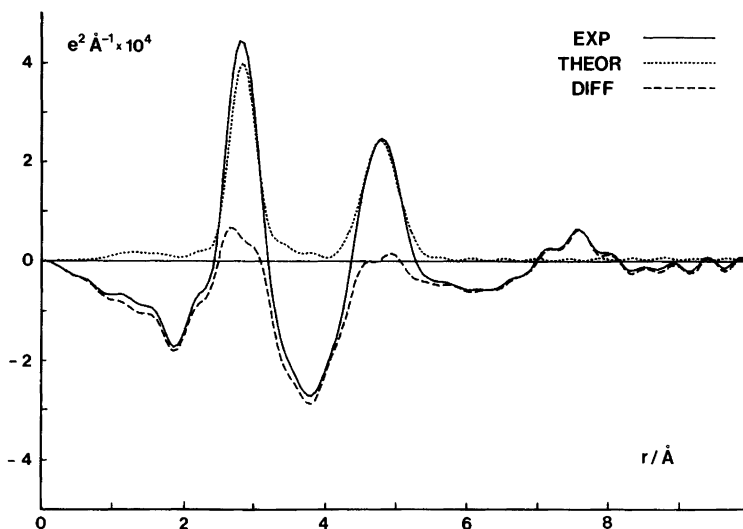


Fig. 4. Experimental radial distribution function,  $D(r) - 4\pi r^2 \rho_0$ , for sodium diiodoargentate(I) in acetonitrile solution, the model function with parameters from Table 3 and the difference between them.

## Results

**Scattering measurements.** For the  $\text{AgClO}_4$  solution, peaks corresponding to Ag–N, Ag–C(1) and Ag–C(2) of the coordinated  $\text{C}(2)\text{H}_3\text{C}(1)\text{N}$  molecules were found at 2.2, 3.4 and 4.8 Å, respectively, in the RDF (Fig. 2). The distances to silver and the N–N distance, together with temperature factor coefficients, were refined in the range  $4.5 \leq s \leq 13.0 \text{ \AA}^{-1}$  (Table 2). The frequencies of the distances were kept fixed. Fixed values were also introduced for the interatomic distances within the free acetonitrile molecule and the perchlorate ion.

The RDF for the  $\text{NaAgI}_2$  solution shows two distinct peaks at 2.8 and 4.8 Å (Fig. 4). The first peak corresponds well to the Ag–I distance found in the zinc blende structure of solid AgI, viz. 2.812 Å.<sup>19</sup> The size of the peak indicates four Ag–I distances; tetrahedral coordination would then be preferred by Ag(I). The second peak must be attributed to the I–I distances. Least-squares refinements were performed in the range  $4.5 \leq s \leq 12.0 \text{ \AA}^{-1}$  for the Ag–I and I–I distances as well as the temperature coefficients (Table 3). The frequencies of the distances were refined separately. The rather low number of I–I distances indicates that the iodine atoms are shared between the silver atoms. A polynuclear structure consisting of  $\text{AgI}_4$  tetrahedra is therefore most probable, which in turn implies that rather short Ag–Ag distances should occur. A separate

refinement of the Ag–Ag distance together with the temperature coefficient and frequency of the distance was carried out and the Ag–Ag distance of 3.0 Å found implies that the tetrahedra must indeed share edges.

Sodium is weakly solvated in acetonitrile (see below). In all refinements for the  $\text{NaAgI}_2$  solution, fixed values were used for the species  $\text{Na}(\text{CH}_3\text{CN})_6^+$ . The Na–N distance was assumed to be 2.5 Å, and the coordination around sodium was assumed to be octahedral. Fixed values were also introduced for the interatomic distances within acetonitrile, and the Ag–N distance for the acetonitrile molecules coordinated at the ends of the chain was taken to be 2.3 Å.

Table 2. Interatomic distances,  $d(\text{\AA})$ , temperature factor coefficients for the distances,  $b(\text{\AA}^2)$ , and frequency of the distances relative to one silver atom,  $n$ , for  $\text{AgClO}_4$  in acetonitrile solution. The refined parameters are those with e.s.d.'s in parentheses.

Distance	$d$	$b$	$n$
Ag–N	2.25(1)	0.004(1)	4.0
Ag–C(1)	3.37(2)	0.006(2)	4.0
Ag–C(2)	4.83(4)	0.012(5)	4.0
N–N	3.65(9)	0.01	6.0
Cl–O	1.44	0.005	4.0
O–O	2.35	0.01	6.0
N–C(1) (solvent)	1.14	0.0015	1.0
N–C(2) (solvent)	2.63	0.0015	1.0

Table 3. Interatomic distances,  $d$  (Å), temperature factor coefficients for the distances,  $b$  (Å<sup>2</sup>), and frequency of the distances relative to one silver atom,  $n$ , for NaAgI<sub>2</sub> in acetonitrile solution. The refined parameters are those with e.s.d.'s in parentheses.

Distance	$d$	$b$	$n$
Ag-I	2.811(2)	0.0049(3)	3.99(6)
Ag-Ag	3.02(2)	0.007(5)	0.7(2)
I-I	4.76(1)	0.024(2)	3.3(2)
Ag-N	2.3	0.005	0.1
Na-N	2.5	0.005	6.0
Na-C(1)	3.6	0.010	6.0
Na-C(2)	5.0	0.015	6.0
N-N	3.5	0.010	12.0
N-N	5.0	0.010	3.0
N-C(1) (solvent)	1.14	0.0015	1.0
N-C(2) (solvent)	2.63	0.0015	1.0

There remain peaks at 2.6 Å for both solutions after subtraction of the theoretical RDF; these peaks probably originate from the bulk structure. It has been proposed that acetonitrile molecules form dimers,<sup>20</sup> and the peaks at 2.6 Å would then refer to the distance between the two acetonitrile units within these dimers.

**Raman measurements.** Raman spectra of the AgClO<sub>4</sub>, NaAgI<sub>2</sub> and NaI solutions in acetonitrile were recorded in the C-N stretching frequency region 2220 to 2320 cm<sup>-1</sup>. Coordination of acetonitrile molecules to an acceptor causes  $\nu(\text{CN})$  to shift to a higher frequency in most cases.<sup>21,22</sup> In pure acetonitrile,  $\nu(\text{CN})$  was observed at 2253 cm<sup>-1</sup>. In AgClO<sub>4</sub> solution a new band appeared at 2272 cm<sup>-1</sup> which has been assigned to the  $\nu(\text{CN})$  stretch for acetonitrile molecules coordinated to Ag<sup>+</sup>. For the NaAgI<sub>2</sub> and NaCuI<sub>2</sub> solutions a shoulder was observed on the band at 2253 cm<sup>-1</sup>. By subtracting the spectrum of pure acetonitrile from the spectrum in question, a band at 2267 cm<sup>-1</sup> was found for the NaAgI<sub>2</sub> so-

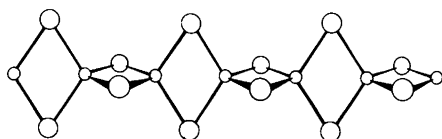


Fig. 5. Structural model for the  $[\text{AgI}_2]_n$  complex in acetonitrile.

lution. A similar shoulder is observed in the spectrum of the NaI solution. After subtraction, a band at 2265 cm<sup>-1</sup> is observed which must be assigned to the acetonitrile molecules coordinated to Na<sup>+</sup>. The 2267 cm<sup>-1</sup> band observed for the NaAgI<sub>2</sub> solution most probably arises from solvated sodium ions, while no band is observed for acetonitrile molecules coordinated to the diiodoargentate complex present in the solution.

Raman spectra of the NaAgI<sub>2</sub> solution show a band at 109 cm<sup>-1</sup> in the lower frequency region which must be assigned to the symmetric Ag-I stretching mode. For an apparently linear AgI<sub>2</sub><sup>-</sup> complex occurring in tributyl phosphate, the corresponding frequency is 132 cm<sup>-1</sup>.<sup>11</sup> The lower frequency in acetonitrile must originate from a higher coordination number, which is consistent with the formation of AgI<sub>4</sub> tetrahedra. The intensity of this symmetric stretching frequency is rather low, and consequently the weaker asymmetric stretching frequency could not be detected at all. Dilution of the NaAgI<sub>2</sub> solution resulted in decreased intensity of the band at 109 cm<sup>-1</sup>, as expected. The integrated intensity, however, did not decrease proportionally with concentration. Below ~0.1 M, tetrahedral coordination of iodide to silver no longer occurs. No bands in the range 120–200 cm<sup>-1</sup> were observed which could be assigned to  $\nu(\text{Ag-I})$  originating from a monomeric AgI<sub>2</sub><sup>-</sup> complex.

## Discussion

The structure of the silver(I) acetonitrile solvate in solution differs only slightly from the structure in the solid state. The crystal structure consists of discrete Ag(CH<sub>3</sub>CN)<sub>4</sub><sup>+</sup> and ClO<sub>4</sub><sup>-</sup> ions. The four almost linear acetonitrile molecules are tetrahedrally coordinated to the silver ion. In the solid state, the Ag-N distance varies between 2.18 and 2.33 Å, with an average of 2.26 Å. The Ag-N distance found in solution, 2.25 Å, is in the middle of this range. The N-C(1) distance, 1.12 Å, does not differ much from that in the solid state. The angle NC(1)C(2) seems to deviate slightly more from linearity in solution than in the solid state, although the difference is hardly significant.

The atomic arrangement in the solid is a consequence of a compromise between intramolecular and intermolecular forces leading to the lowest state of energy. The large range of Ag-N dis-

tances observed in the solid state is due to the fact that the silver-acetonitrile interaction is rather weak, so that packing forces then have greater influence.<sup>4</sup> A more ideal value for the Ag-N distance is found in solution, since the intermolecular forces in this case are much weaker than in the solid state.

The structural model proposed for the diiodoargentate complex is shown in Fig. 5. A chain of  $\text{AgI}_4$  tetrahedra sharing edges is formed. Acetonitrile molecules are probably coordinated at the ends of the chain, yielding a stoichiometric ratio of 1:2 for silver:iodide. The length of the chain, however, is presumably not the same in all complexes. The structure may vary from di- to polynuclear. The refined frequency factors for Ag-Ag and I-I indicate a trinuclear structure, but the frequency of Ag-I is representative of a longer chain. No band for acetonitrile molecules coordinated to silver was observed in the Raman spectrum. Consequently, few chain ends are available for coordination of solvent molecules and the chains may therefore be rather long.

The I-I distance found disagrees with that calculated for a regular tetrahedron with an Ag-I distance of 2.81 Å, which should be 4.59 Å. Consequently the  $\text{AgI}_4$  tetrahedra must be distorted. The value of 4.76 Å is valid for the iodine atoms bridging silver atoms separated by a distance of 3.0 Å. The former distance should be the most rigid I-I distance and consequently that with the lowest temperature coefficient. Both shorter and longer I-I distances must occur, but their higher temperature coefficients make it impossible to separate them from each other. There are no peaks in the RDF between 5 and 7 Å which can be assigned to large Ag-Ag, Ag-I or I-I distances (Fig. 4). This is probably a consequence of very large temperature coefficients for the longer distances, since the flexibility within the chain is large.

The crystal structures of several compounds with a silver:iodide ratio of 1:2 consist of discrete infinite chains of  $\text{AgI}_4$  tetrahedra with shared edges, e.g.  $[\text{N}(\text{CH}_3)_4][\text{AgI}_2]^{23}$  and  $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3][(\text{AgI}_2)_2]^{24}$ . It is therefore plausible that chains of the same kind are also formed in solution, although the length of the chain is smaller. The Ag-I distance varies between 2.76 and 2.86 Å in these solid compounds. As mentioned before, more ideal interatomic distances are obtained in solution and consequently the dis-

tance 2.81 Å for Ag-I is the most favourable. The same distance is also found in solid AgI (zinc blende form),<sup>19</sup> in which ideal tetrahedral coordination is achieved.

As is evident from thermodynamic measurements, these polynuclear chain complexes are not formed in dilute acetonitrile solutions.<sup>10</sup> In such solutions, complexes with a silver:iodide ratio of 1:2 are mononuclear. The formation of polynuclear complexes probably starts at ~0.1 M, with the chains increasing in length as the concentration is raised.

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## References

1. Ahrland, S., Nilsson, K. and Tagesson, B. *Acta Chem. Scand., Ser. A* 37 (1983) 193.
2. Ahrland, S., Ishiguro, S.-i. and Persson, I. *Acta Chem. Scand., Ser. A* 40 (1986) 418.
3. Ahrland, S., Nilsson, K., Persson, I., Yuchi, A., Penner-Hahn, J. E. and Hodgson, K. O. *Inorg. Chem. Submitted for publication.*
4. Nilsson, K. and Oskarsson, Å. *Acta Chem. Scand., Ser. A* 38 (1984) 79.
5. Nilsson, K. and Oskarsson, Å. *Acta Chem. Scand., Ser. A* 36 (1982) 605.
6. Persson, I., Penner-Hahn, J. E. and Hodgson, K. O. *Inorg. Chem. Submitted for publication.*
7. Csöregi, I., Kierkegaard, P. and Norrestam, R. *Acta Crystallogr., Sect. B* 31 (1975) 314.
8. Bergerhoff, G. *Z. Anorg. Allg. Chem.* 327 (1964) 139.
9. Coetzee, J. F., Campion, J. J. and Liberman, D. R. *Anal. Chem.* 45 (1973) 343.
10. Luehrs, D. C. and Abate, K. *J. Inorg. Nucl. Chem.* 30 (1968) 549.
11. Waters, D. N. and Basak, B. *J. Chem. Soc. A* (1971) 2733.
12. Dallinga, G. and Mackor, E. L. *Recl. Trav. Chim. Pays-Bas* 75 (1956) 796.
13. Levy, H. A., Danford, M. D. and Narten, A. H. *Data Collection and Evaluation with an X-Ray Diffractometer Designed for the Study of Liquid Structure*, Report ORNL-3960, Oak Ridge National Laboratory, Oak Ridge, TN 1966.
14. Persson, I., Sandström, M., Goggin, P. L. and Mosset, A. *J. Chem. Soc., Dalton. Trans.* (1985) 1597.

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15. Sandström, M., Persson, I. and Ahrland, S. *Acta Chem. Scand., Ser. A* 32 (1978) 607.
16. Sandström, M. and Johansson, G. *Acta Chem. Scand., Ser. A* 31 (1977) 132.
17. Johansson, G. and Sandström, M. *Chem. Scr.* 4 (1973) 195.
18. Molund, M. and Persson, I. *Chem. Scr.* 25 (1985) 197.
19. *NBS Circular 539* (1959), Vol. 9, p. 48.
20. Sadlej, J. *Spectrochim. Acta, Part A* 35 (1979) 681.
21. Storhoff, B.N. and Lewis, H.C. *Coord. Chem. Rev.* 23 (1977) 1.
22. Reedijk, J., Zuur, A.P. and Groeneveld, W.L. *Recl. Trav. Chim. Pays-Bas* 86 (1967) 1127.
23. Peters, K. and von Schnering, H.G. *Acta Crystallogr., Sect. C* 40 (1984) 789.
24. Thackeray, M.M. and Coetzer, J. *Acta Crystallogr., Sect. B* 31 (1975) 2341.

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