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An X-Ray Investigation of the Structures of Cadmium Iodide Complexes in DMSO Solutions

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Large-angle X-ray scattering measurements on dimethyl sulfoxide solutions of cadmium iodide and sodium iodide with I:Cd ratios ranging from 2 to 4 show the CdI_4^{2-} complex to be regularly tetrahedral with a Cd–I bond length of 2.790[3] Å. The CdI_3^- complex is pyramidal with a Cd–I bond length of 2.773[3] Å and an I–Cd–I angle of 112.4[8]°. In CdI^+ the Cd–I bond length is further shortened to about 2.75 Å. In the lower complexes DMSO molecules are also coordinated to cadmium.

Large-angle X-ray scattering measurements can be used to obtain information on the structures of solvated ions in solution and on coordination changes taking place when complexes are formed. The present paper, which reports results on the structures of iodide complexes of cadmium in DMSO solutions, forms part of a series of such investigations on halide complexes of Zn(II), Cd(II), Hg(II), Tl(III), and Au(III) in different solvents.[1–5]

Raman and X-ray measurements on aqueous cadmium(II) solutions[6,7] are consistent with an octahedral coordination in the hydrated cadmium(II) ion and with a tetrahedral coordination in CdI_4^{2-}, which is the highest complex formed. Also in DMSO solution the solvated cadmium(II) ion is octahedrally coordinated, as has been shown by X-ray scattering measurements.[8] The six $(CH_3)_2SO$ molecules are bonded to cadmium by their oxygen atoms. From emf and enthalpy measurements Ahrland and Björk[9,10] determined the stability constants for the formation of the complexes CdI^+, CdI_2, CdI_3^-, and CdI_4^{2-} in DMSO solutions and concluded, from the variation of the enthalpy and entropy changes with the stepwise formation of the complexes, that a change from six- to four-coordination takes place in the second step, that is, on the formation of CdI_2. Similar conclusions have been drawn from NMR measurements on ^{113}Cd.[25]

With the use of the stability constants given by Ahrland and Björk[9] the amount of cadmium bound in the different complexes has been calculated as a function of log I^- (Fig. 1). In contrast to what was found for the corresponding complexes of mercury(II) in DMSO solution[11] the ranges of stability are not sufficiently separated to allow the preparation of pure solutions of each of the complexes. Moreover, the CdI_2 complex never occurs as a dominant complex.

In the following, we will accept this distribution of complexes to be at least approximately valid even at the high concentrations used here. The

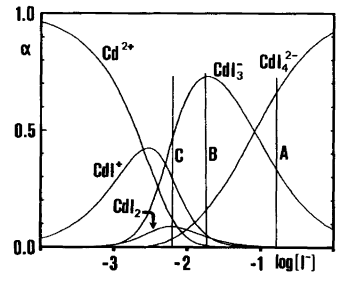

Fig. 1. The fraction, α, of cadmium bound in different complexes in DMSO as a function of the concentration of free iodide. The values are calculated from the stability constants given by Ahrland and Björk.[10]

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compositions of the three solutions chosen for the X-ray scattering measurements are given in Table 1 and are marked in Fig. 1 by vertical lines. In solution A, with a ratio I:Cd = 3.8, the CdI_4^{2-} complex should be dominant although considerable amounts of CdI_3^- should also be present. In solution B, with I:Cd = 3.0, the CdI_3^- complex is predominant with minor amounts of CdI_4^{2-}, CdI_2, and CdI^+ also present. In solution C, with I:Cd = 2.0, significant amounts of all of the complexes are expected to occur, although CdI_3^- and CdI^+ should dominate.

EXPERIMENTAL

Preparation of solutions. The solutions were prepared by adding weighed amounts of CdI_2 (*p.a.*) and NaI (*p.a.*) to DMSO and diluting to a known volume. The compositions were chosen to make the concentrations of iodide the same in the three solutions A, B and C (Table 1). The constant iodide concentration results in approximately equal concentrations of DMSO (Table 1), the difference in composition between the three solutions thus being approximately limited to a replacement of Na^+ by Cd^{2+} ions.

Diffraction measurements. The X-ray scattering was measured in a $\theta-\theta$ diffractometer with the X-ray tube and the scintillation counter moving in opposite directions around the sample, which was placed with its surface on the center of the diffractometer. Mo$K\alpha$-radiation ($\lambda = 0.7107$ Å) was used. Monochromatization was achieved by means of a bent and ground single crystal of lithium fluoride placed between the sample and the scintillation counter, which was equipped with a pulse height discriminator. The high absorption in the samples ($\mu = 32-35$ cm^{-1}) eliminated the need for an absorption correction. Corrections for polarization in the sample and in the monochromator were applied and the data were corrected for multiple scattering according to Warren.[12]

The amount of incoherently scattered radiation reaching the counter was estimated from the spectrum of the X-ray tube and was checked by comparing two sets of measurements at high scattering angles with a Zr filter placed before and after the sample, respectively.

The measured intensities, I_{exp}, were scaled by a comparison between the calculated sum of coherent and incoherent scattering and the observed intensities in the region $14.5 < s < 16.5$, where $s = 4\pi\lambda^{-1} \sin\theta$, 2θ being the scattering angle. The reduced intensity values, $i(s)$, were then calculated according to the expression:

Table 1. Compositions of solutions.

a. The concentrations are given as g at l^{-1} (upper figures) and as number of atoms in the stoichiometric unit of volume, V/Å^3 (lower figure).

Solution	I:Cd	Concentrations Cd	I	Na	S	O	C	H	$\frac{V}{Å^3}$
A	3.78	1.33	5.04	2.38	11.20	11.20	22.4	67.2	329.3
		0.264	1	0.47	2.22	2.22	4.44	13.3	
B	2.96	1.70	5.03	1.62	11.28	11.28	22.6	67.7	330.5
		0.34	1	0.32	2.24	2.24	4.48	13.5	
C	2.00	2.49	4.98	–	11.52	11.52	23.0	69.1	333.7
		0.50	1	–	2.31	2.31	4.33	13.9	

b. Calculated concentrations of complexes.

Solution	Concentration mol l^{-1} DMSO	CdI_4^{2-}	CdI_3^-	CdI_2	CdI^+	Cd^{2+}	log[I$^-$]
A	11.2	0.85	0.48	3.6×10^{-3}	4.9×10^{-4}	8.1×10^{-6}	−0.82
B	11.3	0.27	1.24	0.08	0.09	0.01	−1.74
C	11.5	0.09	1.15	0.22	0.74	0.30	−2.20

$$i(s) = KI_{exp}(s) - \sum_{i=1}^{n} n_i\{f_i^2(s)+(\Delta f_i)^2 + I_{incoh}(s)\}$$

where the summation was taken over the number of atoms in the stoichiometric unit of volume chosen for the calculations. K is a normalization factor. Scattering factors, f_i, for the neutral atoms were taken from Cromer and Waber.[13] For H, those of Stewart *et al.* were used.[14] Corrections for the real part, $\Delta f'$ and the imaginary part, $\Delta f''$, of the anomalous dispersion were taken from Cromer.[15] Values for the incoherent scattering for the heavy atoms were those given by Cromer.[16] For H, Compton and Allison's values were used.[17] Corrections for the Breit-Diracfactor were made.[18-20]

Electronic radial distribution functions, $D(r)$, were calculated as

$$D(r) = 4\pi r^2\rho_0 + 2r/\pi \int_0^{s_{max}} si(s)M(s)\sin(rs)\,ds$$

where $M(s)=Z_I^2/f_I^2(s)\exp(-ks^2)$, and ρ_0 is the average scattering density. Here Z_I is the atomic number of iodine and k was given a value of 0.01. The same modification function, $M(s)$, was used in the calculation of peak shapes for the various interactions.[21]

Low-frequency contributions to the $i(s)$ curves giving rise to spurious peaks below 1 Å in the $D(r)$ function, which could not be related to interatomic distances, were removed by a Fourier transformation of the relevant part of the RDFs.

All calculations were carried out by means of the programs KURVLR and PUTSLR.[21]

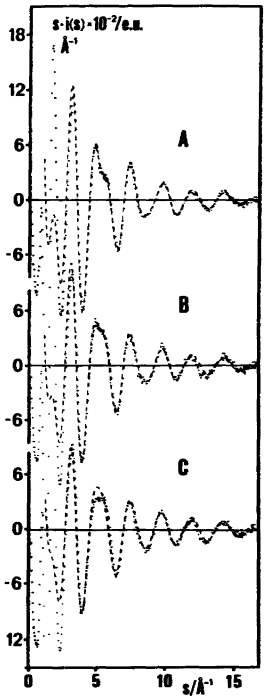

Fig. 2. Observed $si(s)$ values (dots) as a function of $s=4\pi\lambda^{-1}\sin\theta$. Theoretical values (dashed lines), obtained with the use of the parameter values in Table 2, are given for comparison.

ANALYSIS OF THE REDUCED INTENSITY VALUES

The reduced intensities are given as $si(s)$ values in Fig. 2. The calculated electronic radial distribution functions (RDF) are given in Fig. 3.

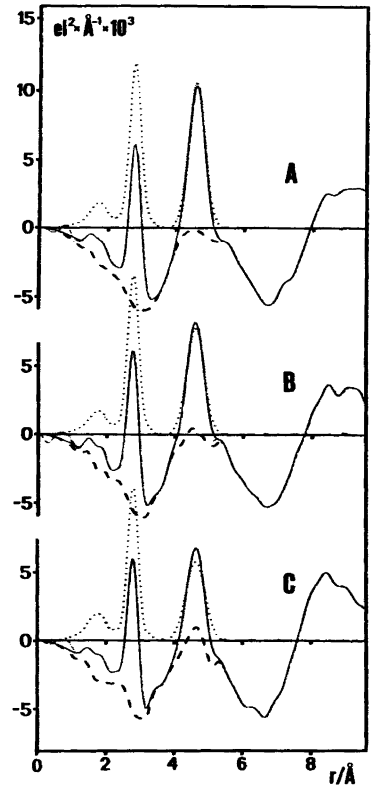

Fig. 3. $D(r)-4\pi r^2\rho_0$ functions (solid lines) for the three solutions investigated. Peak shapes, calculated for intramolecular interactions with the use of the parameter values in Table 2, are given as dotted lines. Dashed lines indicate the difference between the two functions. The dashed-dotted line given for $r<\sim 1$ Å shows the $D(r)-4\pi r^2\rho_0$ function before corrections for low-frequency contributions to the $si(s)$ function.

In addition to peaks, which can be related to intramolecular interactions within the DMSO molecules (S–O: 1.52 Å, S–C: 1.77 Å, O–C: 2.6 Å, C–C: 2.7 Å), two prominent peaks can be distinguished in the RDFs. They appear at 2.8 and 4.5 Å, which are close to expected values for Cd–I and I–I distances within tetrahedral cadmium iodide complexes. More accurate values for these distances were obtained by least squares refinements in which $\sum_i [si_{exp}(s) - si_{calc}(s)]^2$ was minimized.[21] Contributions to $i_{calc}(s)$ were calculated from the known intramolecular distances in the DMSO molecules and from assumed Cd–I and I–I interactions, each characterized by three parameter values, *i.e.* the distance, d, a temperature coefficient, b, and a frequency factor, n.[21] The low-angle scattering data, which are dominated by contributions from intermolecular interactions, were not included in the refinements. For $s > \sim 5$ Å^{-1} the refined parameter values were found to be independent of the lower s limit chosen.

The results, given in Table 2, show a slight decrease in Cd–I distances from2.785[2] Å in the A solution to 2.769[4] Å in the C solution, with the I–I distances remaining practically constant at about 4.60 Å. The ratios between the distances are close to the value expected for a tetrahedral bond angle, $\sqrt{8/3} = 1.632$, although a slight increase in the bond angle with a decreasing I:Cd ratio is indicated (Table 2).

The $si(s)$ values and the peak shapes calculated with the parameter values obtained from the least squares refinements (Table 2) are compared in Figs. 2 and 3 with the experimental values. For the A solution the smooth difference curve obtained after subtracting the calculated peaks from the experimental RDF indicates that the Cd–I and I–I interactions introduced, together with those within the DMSO molecules, satisfactorily account for the intramolecular interactions in the solution. For the B and the C solutions some deviations are left unexplained.

If the results from the least squares calculations are assumed to correspond to weighted averages of the distances in the different cadmium iodide complexes in the solutions, the distances in the individual complexes can be calculated with the use of the concentrations estimated from the stability constants. The resulting values are given in Table 3. Because of the low concentrations of CdI_2 this complex could not be treated separately in these calculations but was assumed to have the same Cd–I distance as CdI^+.

The ratio between the Cd–I and the I–I distances in the CdI_4^{2-} complex given in Table 3 corresponds to an I–Cd–I angle of 110.0[5]° in close agreement with the value 109.5° expected for a regular tetrahedron. In CdI_3^- the corresponding angle is slightly larger, 112.4[8]°, which indicates a slight flattening of the CdI_3 pyramid from that expected for a tetrahedral bonding arrangement. Similar results have been found previously for the corresponding mercury(II) iodide complexes in DMSO solution.[1]

In view of the standard deviations the number of interactions obtained in the least squares refine-

Table 2. Results of least squares refinements of parameter values describing the Cd–I and I–I interactions. Each interaction is characterized by its distance (d Å^2), its temperature coefficient (b Å^2), and its frequency (n) calculated as the number of distances per Cd atom. Standard deviations are given within parentheses.

	Solution A	B	C
d_{Cd-I}	2.785(2)	2.775(3)	2.769(4)
d_{I-I}	4.581(9)	4.60(2)	4.60(3)
d_{I-I}/d_{Cd-I}	1.645	1.658	1.661
b_{Cd-I}	0.0035(6)	0.0031(8)	0.001(1)
b_{I-I}	0.019(2)	0.023(5)	0.03(1)
n_{Cd-I}	3.6(1)	2.7(2)	1.6(2)
n_{I-I}	4.4(6)	2.7(6)	1.5(6)
$(n_{Cd-I})_{calc}$	3.63	3.00	2.06
$(n_{I-I})_{calc}$	4.91	3.22	1.77

Table 3. The derived intramolecular distances in the cadmium iodide complexes. The standard deviations are based on those given in Table 2, but do not include possible inaccuracies in the assumed distribution of complexes.

Complex	d_{Cd-I}	d_{I-I}	Calc. bond angle I–Cd–I
CdI_4^{2-}	2.790(3)	4.57(1)	110.0(5)
CdI_3^-	2.773(3)	4.61(2)	112.4(8)
CdI^+	[2.754]	–	–

ments do not differ significantly from those estimated from the concentrations of the complexes in the solutions (Table 2).

With the use of the parameter values given in Table 3 and the concentrations of the complexes as calculated from the stability constants new least squares refinements were carried out in which only the temperature coefficients, b, for the Cd–I and I–I interactions were adjusted. The resulting b values did not differ significantly between the different solutions and the average values were found to be 0.003[1] Å^2 for b_{Cd-I} and 0.022[5] Å^2 for b_{I-I}.

ANALYSIS OF THE RADIAL DISTRIBUTION FUNCTIONS

The major contributions to the structured intermolecular interactions in the solutions are likely to come from the packing of the large I^- ions and the DMSO molecules. Since the three solutions were all made to contain equal concentrations of iodide and, therefore, also approximately equal concentrations of DMSO, it seems reasonable to assume that the intermolecular interactions will differ only slightly between them. If the intermolecular interactions in the A solution are approximated by a model in which $CdI_{3.6}$, DMSO, and Na^+ are assumed to occupy spherical holes, with radii equal to 4.7, 2.8 and 1.4 Å, respectively, in an evenly distributed electron density, the calculated $si(s)$ values lead to the RDF shown in Fig. 4. A comparison with the experimental values shows deviations in the $si(s)$ function in the low-angle region and in the RDF in the regions around 5 Å and around 9 Å. If the difference curve, given by the dashed line in Fig. 4, is used as an approximate correction curve for the intermolecular interactions in all the solutions, the shape functions for the complexes in the solutions can be derived.[26]

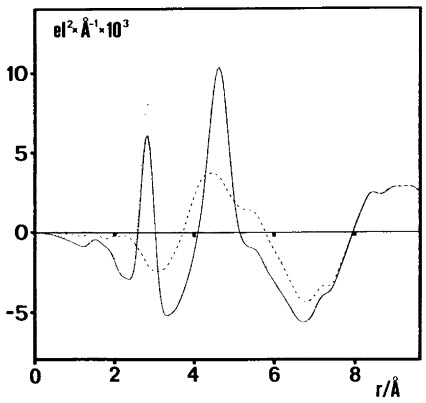

Fig. 4. The electronic radial distribution function $D(r)-4\pi r^2\rho_0$ for the A solution (solid line) compared with a curve (dotted line) calculated with the use of the parameter values in Table 2, with the intermolecular interactions approximated by assuming the complexes to occupy spherical holes in an even electron distribution. The difference between the experimental and the calculated curve is given by the dashed line.

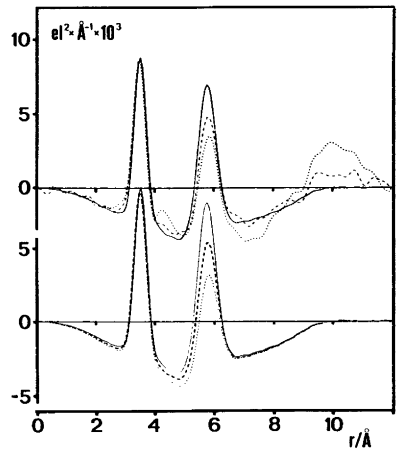

Fig. 5. Derived shape functions for the Cd–I complexes in the A (solid line), the B (dashed line) and the C (dotted line) solutions. In the lower part, calculated shape functions, which have been obtained with the use of the parameter values in Table 3 and the concentrations of complexes in Table 1, are given for comparison.

The shape functions for the cadmium iodide complexes in the three solutions derived in this way are compared in Fig. 5. The calculations are referred to a stoichiometric unit of volume equal to the average volume per I^- ion. The curves in Fig. 5 clearly illustrate the changes in intramolecular interactions within the cadmium iodide complexes when Na^+ ions in the A solution are replaced by Cd^{2+} ions. The first peak, resulting from the Cd–I interactions, changes its position only very slightly towards shorter distances, in agreement with the results obtained in the least squares refinements (Table 2). The area under the peak is unchanged which shows that the number of Cd–I distances per I atom does not change.

Each I^-, therefore, forms one bond to a Cd^{2+} ion in the C solution as it does in the A solution. This shows that polynuclear complexes do not form, a conclusion which is supported by the absence of other peaks in the derived shape functions, which can possibly be related to such complexes.

The second prominent peak in the derived shape functions, which corresponds to the I – I interactions within the complexes, is reduced in size when the Cd^{2+} concentration is increased, reflecting the decrease in the number of I^- ions in the Cd^{2+} coordination sphere. A comparison with shape functions calculated with the use of the parameter values in Table 3 for a distribution of complexes given by the stability constants, and arbitrarily assigning a radius of 4.8 Å to all cadmium iodide complexes, shows a satisfactory agreement with those derived (Fig. 5) and thus confirms the parameter values derived in the least squares refinement process.

In the shape function derived from the solution B and, much more pronounced, in that derived from the C solution, two new peaks are indicated at about 2.3 and 3.3 Å, that is, at distances close to those expected for Cd – O and Cd – S interactions involving DMSO molecules coordinated to cadmium. The contributions from interactions between cadmium and coordinated DMSO molecules are small compared to those of the heavy atom interactions Cd – I and I – I, and a precise evaluation of the number of coordinated DMSO molecules does not seem possible. The result of such an evaluation would depend also on how well the distribution of complexes in these concentrated solutions is described by the stability constants used. It seems reasonable to assume, however, that in CdI_3^- a DMSO molecule is coordinated at the fourth corner of the tetrahedron. A significant improvement in the agreement between observed and calculated *si(s)* values was in fact obtained for the A and the B solutions when CdI_3DMSO^- was used rather than CdI_3^- for the least squares refinements.

In order to separate more clearly the intramolecular Cd – DMSO interactions, the derived shape function for the Cd – I complexes in the C solution is given in Fig. 6 after subtracting contributions from Cd – I and I – I interactions. The peaks corresponding to the Cd – O and the Cd – S distances in oxygen coordinated DMSO molecules are now clearly indicated. They are compared with peak shapes calculated for Cd – O and Cd – S distances of 2.3 and 3.4 Å, which have been found in the

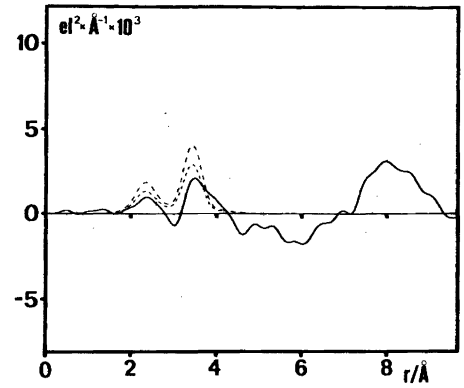

Fig. 6. The derived shape function for the C solution after subtracting Cd – I and I – I interactions. Calculated peak shapes for Cd – O and Cd – S interactions are given for comparison, assuming an average number of 2.0 (short dashes) or 2.8 (long dashes) DMSO molecules coordinated to each Cd^{2+} ion. The dotted line shows the original $D(r)-4\pi r^2\rho_0$ function for the C solution.

crystal structure of $[Cd((CH_3)_2SO)_6](ClO_4)_2$,[27] and assuming an average of 2.0 or 2.8 DMSO molecules bonded to each Cd^{2+} ion. If all complexes contain 4-coordinated Cd^{2+}, the average number of DMSO molecules bonded to the metal ion would be 2.0, while a value of 2.8 would be expected if Cd^{2+} and CdI^- were 6-coordinated. The comparison confirms the presence of DMSO molecules coordinated to Cd in the lower complexes. In view of the uncertainties involved it does not, however, seem possible to distinguish between a six- or a four-coordination in the CdI^+ complex.

CONCLUSIONS

The X-ray scattering data on the DMSO solutions of cadmium iodide complexes show conclusively that the CdI_4^{2-} complex is regularly tetrahedral. The CdI_3^- complex is pyramidal with an I – Cd – I bond angle of 112.4(8)°, that is, slightly larger than the tetrahedral angle of 109.5°. For the lower complexes DMSO molecules are shown to be coordinated to cadmium but the scattering data are not sufficient for a quantitative evaluation of the number of coordinated DMSO molecules in the different complexes.

The Cd – I bond length decreases from 2.790[3] Å in CdI_4^{2-} to 2.773(3) Å in CdI_3^- and is further

shortened to about 2.75 Å in CdI^+. These values are close to values found in crystal structures where Cd^{2+} is four-coordinated: 2.723–2.823 Å (av. 2.774 Å) in $RbCdI_3H_2O$[22] and 2.693–2.865 Å (av. 2.83 Å) in the $Cd_2I_6^{2-}$ anion,[23] and also in previous X-ray scattering measurements on cadmium iodide complexes in water solution:[6,7] 2.79 Å in CdI_4^{2-} and 2.80 Å in CdI^+. In the crystal structure of CdI_2 the cadmium is octahedrally coordinated by 6 I^- at distances of 2.98 Å.[24]

The solvated cadmium ion has previously been shown to be octahedrally surrounded by DMSO molecules[8] and a coordination change therefore takes place somewhere during the stepwise addition of I^- ions. Obviously, this change is completed in CdI_3^-. However, since the number of coordinated DMSO molecules in the CdI^+ and the CdI_2 complexes could not be determined, the exact location of the coordination change cannot be derived from the scattering data.

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REFERENCES

1. Gaizer, F. and Johansson, G. *Acta Chem. Scand. 22* (1968) 3013.
2. Sandström, M. and Johansson, G. *Acta Chem. Scand. A 31* (1977) 132.
3. Sandström, M. *Acta Chem. Scand. A 31* (1977) 141.
4. Sandström, M. *Acta Chem. Scand. A 31* (1977) 627.
5. Maeda, M., Ohtaki, H. and Johansson, G. *Bull. Chem. Soc. Jpn. 47* (1974) 2229.
6. Tsurumi, M., Maeda, M. and Ohtaki, H. *Denki Kagaku 45* (1977) 367.
7. Ohtaki, H., Maeda, M. and Ito, S. *Bull. Chem. Soc. Jpn. 47* (1974) 2217.
8. Sandström, M., Persson, I. and Ahrland, S. *Acta Chem. Scand. A 31* (1977) 607.
9. Ahrland, S. and Björk, N. O. *Acta Chem. Scand. A 30* (1976) 249.
10. Ahrland, S. and Björk, N. O. *Acta Chem. Scand. A 30* (1976) 257.
11. Ahrland, S., Persson, I. and Portanova, R. *To be published.*
12. Warren, B. E. *X-Ray Diffraction*, Addison-Wesley 1969.
13. Cromer, D. T. and Waber, J. T. *Acta Crystallogr. 18* (1965) 104.
14. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys. 42* (1965) 3175.
15. Cromer, D. T. *Acta Crystallogr. 18* (1965) 17.
16. Cromer, D. T. *J. Chem. Phys. 50* (1969) 4857.
17. Compton, A. H. and Allison, S. K. *X-Rays in Theory and Experiment*, Van Nostrand, New York 1935.
18. Breit, G. *Phys. Rev. 27* (1926) 362.
19. Dirac, P. A. M. *Proc. R. Soc. London A 111* (1926) 405.
20. Dwiggins, C. W. and Park, D. A. *Acta Crystallogr. A 27* (1971) 264.
21. Johansson, G. and Sandström, M. *Chem. Scr. 4* (1973) 195.
22. Natarajan Iyer, M., Faggiani, R. and Brown, I. D. *Acta Crystallogr. B 33* (1977) 129.
23. Orioli, P. L. and Ciampolini, M. *J. Chem. Soc. Chem. Commun.* (1972) 1280.
24. *Struckturbericht Bd3* 1933/35, p. 23.
25. Drakenberg, T., Björk, N. O. and Portanova, R. *Personal communication.*
26. Johansson, G., Pettersson, L. and Ingri, N. *Acta Chem. Scand. A 32* (1978) 407.
27. Sandström, M. *Acta Chem. Scand. A 31* (1977) 519.

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