[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA RADIATION LABORATORY,[1] LIVERMORE SITE]

The Configuration of the Solvate "Iceberg" About Eu^{+3} in Aqueous and Alcoholic Solutions of $EuCl_3$[2,3]

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Models are proposed for the close-in structure of the solvate about the trivalent europium ion in aqueous and alcoholic solutions of $EuCl_3$. These models satisfy the spectroscopic conditions that (1) the symmetries are D_{2h} and C_{2v}, respectively, (2) there is a single stable configuration about the ion in each case and (3) the close-in arrangements must be very similar. The models are the Eu^{+3} ion in an interstitial position of the ice III lattice for aqueous solutions and in alcoholic solutions a pair of hydrogen bonded alcohol chains drawn in toward the Eu^{+3} ion with possibly one or two nearby chloride ions. These models should be applicable to most of the other rare earths and smaller trivalent ions but probably not to lower valence types.

Introduction

It is well known that ions in polar solvents are solvated to some extent. As yet no direct way is known to determine the actual configuration of the solvated solvent about the ion. Recently, however, the symmetry of the electric field about Eu^{+3} has been determined spectroscopically in solutions of $EuCl_3$ in alcohols and water.[4] It is found to be C_{2v} in alcohols and D_{2h} in water. Since the field must depend on the arrangement of ions and dipoles about the Eu^{+3} ion, the electric field symmetry is a severe criterion which any proposed model must satisfy.

There is other useful information obtained from the spectra. First, since the lines are sharp, either there is a rapid average of several possible configurations or there is one stable one. The former is ruled out at least for alcohol solutions, since these can be cooled to liquid-nitrogen and helium temperatures in the glassy state. In these circumstances, the spectra remain the same except for becoming somewhat sharper. If several different configurations had contributed, these would all have been frozen out separately at helium temperature, resulting in a more complex spectrum than was actually observed.

Secondly, there are no shifts in the positions of the principal lines in going from alcohols to water. Consequently, the close-in ion and dipole configuration must be quite similar in each type of solvent. This in turn implies that there can be only one stable configuration in water solutions as well.

Now, it is known from spectroscopic[5] and electrochemical evidence[6] that aqueous $EuCl_3$ is a strong electrolyte, at least below 1.5 molal. Consequently, the chloride ion will be too far away to affect the field symmetry about the Eu^{+3} ion, and thus the solvate configuration will not contain a chloride ion.

In alcohols, the situation is not as clear. Conductivity evidence from lower valence types indicates that chloride ion association is quite probable. Thus it could happen, for example, that the close-in arrangement is essentially the same in water and alcohols, but the presence of a chloride ion fairly close to the europium ion in alcohols removes the center of inversion present in water, leading to the C_{2v} symmetry. However, it is also conceivable that the powerful field of the europic ion might pull in a sufficient quantity of the polar alcohol to prevent chloride ions from getting close. Both possibilities will be considered.

In the following, we shall try to find models of the solvate "iceberg"[7] which are consistent with criteria and evidence given above.

Examination of Various Solvation Possibilities.—There are at first glance many ways that solvation might occur. Thus, the ion may (a) replace a solvent molecule in the quasi-lattices of the liquid; (b) replace a solvent molecule in the lattice of a solid form of the solvent; (c) fit into the interstices of the liquid quasi-lattices; (d) fit into the interstices of a solid lattice; (e) draw in the solvent so as to give the configuration found in some hydrated crystal; (f) draw in fragments of the lattices mentioned above; (g) replace the H of a water or alcohol molecule in some of the above situations. These possibilities are all based on characteristics of known systems.

There is of course a final possibility (h) the ion may fit into a configuration of the solvent which is quite unlike that of any known system. Such a situation can never be ruled out *a priori*, but it is clearly unprofitable to discuss it any further as there is no point of attack available. Moreover it will be found possible in an intuitively reasonable way to find models which are consistent with the experimental facts and which are examples of the types of systems included in (a)–(g).

We begin our analysis by remarking that of the great number of conceivable systems, few will be consistent with all the spectroscopic and electrochemical evidence. Thus, since Spedding, *et al.*,[6] found that hydrolysis was negligible, (g) is immediately ruled out. Let us examine the others.

The crystal structures of some hydrated europium salts are known. For example, $Eu(BrO_3)_3 \cdot 9H_2O$[8]

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[2] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[3] Presented before the Physical and Inorganic Division at the 132nd meeting of the American Chemical Society, New York, N. Y., September, 1957.

[4] E. V. Sayre, D. G. Miller and S. Freed, *J. Chem. Phys.*, **26**, 109 (1957), where results in water, methanol and ethanol were reported. Propanol solutions subsequently were found to have the same properties as the two lower alcohols.

[5] S. Freed and H. F. Jacobson, *ibid.*, **6**, 654 (1938).

[6] F. H. Spedding, P. E. Porter and J. M. Wright, THIS JOURNAL, **74**, 2055 (1952).

[7] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

[8] K. H. Hellwege and H. G. Kahle, *Z. Physik*, **129**, 85 (1951). Certain of the polarization properties indicate that the ion may be slightly off this symmetry and in C_2 or C_s.

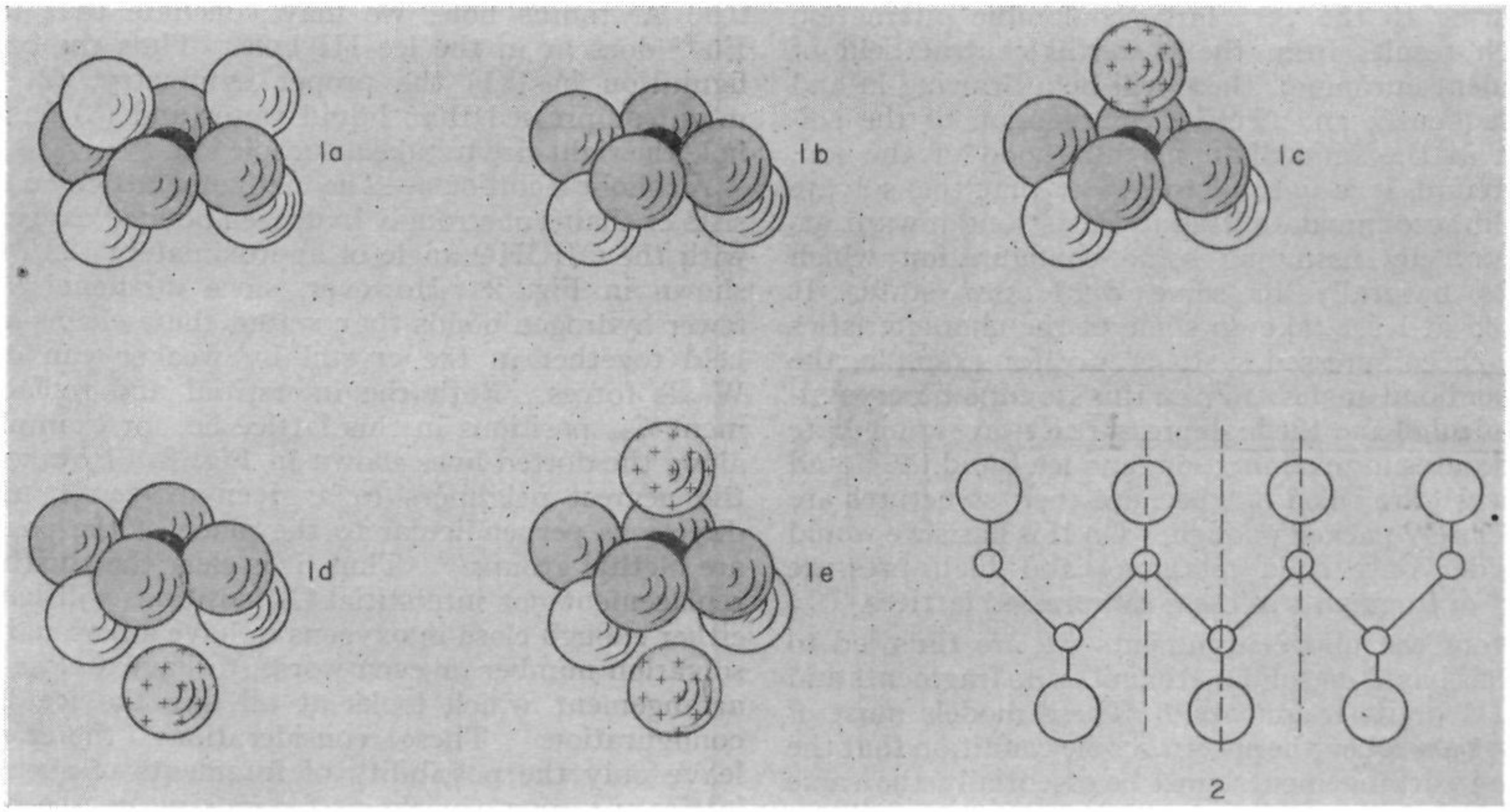

Fig. 1.—Proposed models of the solvate configuration. The gray and white balls represent the oxygens of water in 1a and of alcohol in 1b–1e. The black balls represent the europic ion, and the (+) marked balls the chloride ions. Hydrogens and methyls are not shown. In each figure, the gray balls together with the europic ion lie in one plane, and the white balls—also with the europic ion—lie in another plane which is perpendicular to the first one. The vertical plane containing the europium ion which is perpendicular to the other two is a reflection plane. The (+) marked balls lie directly above or below the europic ion along the twofold axis. In Figs. 1b–1e, the one white and two gray balls on the left form one alcohol chain and the one white and two gray balls on the right form the other chain.

Fig. 2.—A plane from the lattice of crystalline methanol. The small circles represent the oxygens and the large circles the methyls. Any point on the dotted lines is a point of C_{2v} symmetry in the methanol lattice.

and $Eu(C_2H_5SO_4)_3{\cdot}9H_2O$[9] have the Eu^{+3} at positions of D_{3h}, and $EuCl_3{\cdot}6H_2O$[10] has the Eu^{+3} ion at C_2. Not any of these compounds, nor any of the other known cases have the europium ion at positions of the right symmetry. Therefore, (e) is ruled out. This situation is no doubt a consequence of the anions being packed in so much closer to the cation in crystal lattices than in solutions.

The various lattices proposed for liquid water[11] apparently do not have either replacement or interstitial positions of the proper symmetry, which eliminates possibilities (a) and (c). As far as the author is aware, very little is known about the structure of liquid alcohol, except that there must be some chain-like structure arising from the hydrogen bonding.

The crystal structures of solid methanol and three of the seven ices are known. For methanol,[12] the structure is D_{2h}^{17}. Reference to the tables[13] shows that there is a series of C_{2v} positions along a certain line in the unit cell, and these positions could be either replacement or interstitial (Fig. 2). We may conclude then that possibilities (b), (d) and (f) are still open for methanol solutions.

For crystalline water, the known structures are D_{6h}^4 for ice I,[14] D_2^5 for ice II[15] and D_{2h}^{26} for ice III.[16] Here the tables[13] show that these ices have neither replacement nor interstitial positions of D_{2h}, ruling out (b) and (d) for all three ices. However, a closer examination of the actual structures shows that of these, ice III has equivalent interstitial positions at either ($^1/_2$, $^1/_2$, $^1/_4$) or ($^1/_2$, $^1/_2$, $^3/_4$)[16] in which the surrounding (eight) oxygens have a strictly D_{2h} position. These eight oxygens constitute a fragment of ice III, and consequently possibility (f) remains open. With respect to the lattice as a whole, of course, we noted that these positions cannot be D_{2h}. However, crystal spectra studies have shown that the closest charge centers primarily determine the spectrum. Thus, in hydrated crystals,[9,17] the rare earth ion sees almost entirely the electric field due to its surrounding hydrate waters rather than that from the whole lattice. On this basis, it is still possible to retain the ice III lattice as an example of (d). To summarize for aqueous solutions, possibilities (d) for ice III and (f) are still open.

So far, we have ruled out everything except placing the ion in interstitial positions of the crystal lattices or surrounding it with fragments of lattices. To narrow down the search still more, we also may reason as follows.

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[9] E. V. Sayre and S. Freed, *J. Chem. Phys.*, **24**, 1213 (1956). The *lattice* has the Eu^{+3} at C_{3h}, but the *close-in water molecules*, which dominate the electric (crystal) field, have a D_{3h} configuration. The reported spectrum is essentially D_{3h} with very weak C_{3h} contributions.

[10] K. H. Hellwege and H. G. Kahle. *Z. Physik*, **129**, 62 (1950).

[11] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

[12] K. J. Tauer and W. N. Lipscomb, *Acta Cryst.*, **5**, 606 (1952).

[13] "Int. Tables for X-Ray Crystallography," Vol. I, I.U.C., Birmingham, 1952.

[14] See, for example, S. W. Petersen and H. A. Levy, *Acta Cryst.*, **10**, 70 (1957).

[15] R. L. McFarlan, *J. Chem. Phys.*, **4**, 60 (1936).

[16] R. L. McFarlan, *ibid.*, **4**, 253 (1936).

[17] K. H. Hellwege, *Nachr. Akad. Wiss. Göttingen, Math-Physik. Kl.*, 58 (1947).

Owing to the very large coulombic interaction which results from the powerful central field of trivalent europium, there will be a drawing in and consequently an effective compression of the solvent in the immediate neighborhood of the ion. Therefore, it is natural to expect that this solvate would accommodate itself to this strong inward attraction by assuming some configuration which exists naturally in some *compressed* state. It should at least take on some of the characteristics of such compressed systems. say for example, the proper bond angles. From this standpoint, crystalline alcohol and the high pressure ices are immediate candidates for examination, and ice I and the liquid lattices[18] are ruled out because their structures are not closely packed enough. On this basis we would consider only solid methanol and high pressure ices[19] or fragments of these compressed lattices.

From the above arguments we are thus led to models based on solid methanol or its fragments and ice III or its fragments.[19] These models must of course also obey the spectroscopic condition that the close-in arrangements must be essentially the same in both solvents. We therefore suggest the following models as being the most consistent with presently available data.

Aqueous Solutions.—For aqueous solutions, the proposed close-in solvate configuration is that of the eight water molecules in ice III which surround a europic ion placed in the position ($^1/_2$, $^1/_2$, $^1/_4$)[16] or its equivalent ($^1/_2$, $^1/_2$, $^3/_4$). This structure, pictured in Fig. 1a, has four close-in oxygens which are hydrogen bonded to four others which are also very close. As noted before, the europic ion is in a position of D_{2h} with respect to these eight molecules alone. However, it is likely that the total hydration number is somewhat higher than eight.[20] Whether the less tightly bound outer layers[21] perpetuate the ice III structure or have any permanent or even definite configuration apparently cannot be determined at this time. The spectra give an indication only of the close-in arrangement.

It remains to show that this D_{2h} hole in ice III is of the proper size to accept a europic ion. Assuming that the lattice dimensions and the packing diameter of the oxygen atoms in ice III[16] are not affected by the presence of Eu^{+3}, it is found that a spherical object of radius 0.91 Å. will just fit. However, the accepted ionic radius of trivalent europium[22] is very close to this, namely, 0.96 Å. Considering the crude nature of the calculation for the hole size or alternatively that only a 2.5% increase in the oxygen packing diameter will give a 0.96 Å. radius hole, we may conclude that the Eu^{+3} does fit in the ice III hole. Thus the configuration has (1) the proper symmetry, (2) is more compressed than liquid water and (3) has a hole the right size to take a europic ion.

Alcoholic Solutions.—The methanol lattice[12] consists of chains of strongly hydrogen bonded oxygens with the OHOHO angle of approximately 122°, as shown in Fig. 2. However, since methanol has fewer hydrogen bonds than water, these chains are held together in the crystal by weaker van der Waals forces. Both the interstitial and replacement C_{2v} positions in this lattice lie, for example, along the dotted lines shown in Fig. 2. However, the nearest neighbors to a given oxygen in the directions perpendicular to the plane of the paper are methyl groups.[12] Thus, it is clear that neither replacement nor interstitial C_{2v} positions will have either enough close-in oxygens to have a reasonable solvation number or even worse, to have a close-in arrangement which looks at all like the ice III configuration. These considerations, therefore, leave only the possibility of fragments of such a lattice, *i.e.*, parts of chains for making up the solvate configuration. It is reasonable to suppose that these chains, which exist loosely in the liquid, would assume the zig-zag form characteristic of the compressed solid.

It is possible to make a model having a close-in arrangement of the oxygens essentially the same as in ice III. It consists of two alcohol chains with approximately the correct OHOHO bond angles which are drawn in toward the Eu ion, as illustrated in Fig. 1b. The O–O distances of these chains will be shorter than in the crystal lattice, but this is reasonable in view of the drawing in effect of the europic ion's field. Because of steric hindrance between methyl (or ethyl) groups of the two chains, the two outermost oxygens are forced down out of the plane containing the other four and the europium ion. The twofold axis is perpendicular to this plane. This structure has both the required C_{2v} symmetry and a close-in configuration similar to ice III's; it does not involve ion association.

In the event of chloride ion association, as is most likely, the same configuration of alcohol chains will serve as a basic structure. Thus if a single chloride ion is involved, it could go along the twofold axis either as in Fig. 1c or Fig. 1d. Both these structures also have C_{2v} symmetry, although the field on the Eu^{+3} is best balanced in 1c. In case ion association is strong enough to involve two chloride ions, the configuration of 1b with one chloride ion above and one below, as shown in Fig. 1e, will have the proper symmetry and satisfy the other criteria as well.

The above configurations are clearly not as closely related to the crystal lattice as in the aqueous case.

Conclusions.—On the basis of the above considerations, the author feels that ice III and 1c (or possibly 1e) are the most reasonable models for the structures of the solvate in aqueous and alcoholic solutions of $EuCl_3$ which can be advanced at this time. These considerations should also be

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[18] About which little concrete structural evidence is available anyway.

[19] Although the high pressure ices other than ices II and III are good candidates too, we can say nothing about them at this time for lack of crystal structure data.

[20] Various estimates of this hydration number have been made. They range, for example, from 18 (R. Robinson and R. Stokes, "Electrolyte Solutions," Butterworths, London, 1955, p. 61) to 33 (D. G. Miller, *J. Phys. Chem.*, **60**, 1296 (1956)).

[21] They are less tightly bound because the central field emanating from the ion falls off very rapidly with distance.

[22] W. H. Zachariasen, "The Actinide Elements," Vol. IV-14A, National Nuclear Energy Series, McGraw-Hill Book Co., New York, N. Y., 1954, p. 769, Chapter 18.

valid for the chlorides[23] of all the other rare earths which will fit inside the ice III hole and for any smaller trivalent ions, provided no hydrolysis occurs. These models satisfy all the necessary criteria mentioned at the beginning and are consistent with all the other evidence presented above. However, lower valence types with a weaker coulombic interaction will pull in the solvent to a somewhat lesser extent, and larger ions may badly distort the configurations. As a result the symmetry and structure may well be different in these cases.[24]

It cannot be claimed that the structures proposed *must* be the actual ones present, but they seemed to be the most probable ones consistent with the currently available information.

Acknowledgments.—The author wishes to acknowledge the very considerable contributions of Dr. E. V. Sayre of Brookhaven National Laboratory to this discussion. The above notions are the result of an extended interchange of ideas with Dr. Sayre on various possible models consistent with the spectra. The author also wishes to thank Drs. Simon Freed, Allan Zalkin and Donald Sands for their aid in various aspects of this investigation.

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[23] The bromides, iodides, perchlorates, etc., should be similar to the chloride. However, the spectrum of aqueous $Eu(NO_3)_3$,[5] for example, shows that some sort of complexing or ion association occurs, and in such circumstances these models will not apply.

[24] Thus in an (unpublished) experiment on alcoholic solutions of $PrCl_3$, E. V. Sayre and D. G. Miller have found that *two* distinct solvate configurations are frozen out at liquid helium temperature. The Pr^{+3} ion has a larger ionic radius (1.00 Å.) than Eu^{+3}, and thus might be too large for the proposed configurations. Unfortunately, the lines were too broad for any detailed electric field symmetry analysis.

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Intermolecular Metal–Metal Bonds and Solubility of Some Nickel and Palladium Complexes of *vic*-Dioximes[1]

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The effect of the strength of intermolecular metal–metal bonds on the solubility of twelve nickel(II) and palladium(II) complexes of *vic*-dioximes was studied. Metal–metal bond lengths were measured in the nickel and palladium complexes of dimethylglyoxime, nioxime, heptoxime, α-furildioxime, α-benzildioxime and in nickel 3-methylnioxime and nickel 4-methylnioxime. All of these complexes, except palladium heptoxime, have the same crystal structure as nickel dimethylglyoxime. Palladium heptoxime still has a structure containing metal chains. Molar solubilities in water, chloroform and 1,2-dichlorobenzene are compared with the metal–metal bond lengths. No correlation was found because of the wide variation in the nature of the ligands. The solubility products of the nickel(II) complexes of dimethylglyoxime, nioxime, 4-methylnioxime, 3-methylnioxime and heptoxime were measured at 25.0° and at 40.0°. Values of ΔF^0, ΔH^0 and ΔS^0 were calculated. Excluding nickel dimethylglyoxime, the solubility product increases with increasing metal–metal bond length. The solubility product of nickel dimethylglyoxime seems to be unusually large and shows that this product depends on the nature of the ligand as well as on the metal–metal bond length.

Introduction

Godycki and Rundle[3] have determined the crystal structure of nickel dimethyglyoxime. They found that the square planar molecules are stacked one above another, 3.24 Å. apart, so that the nickel atoms lie in a straight row that extends throughout the length of the crystal. They proposed that weak intermolecular nickel–nickel bonds exist, thus forming a chain of nickel atoms that is responsible for the well known selectivity of dimethylglyoxime as a gravimetric reagent for nickel(II) and palladium(II). Copper dimethylglyoxime, which has almost identically the same molecular structure as nickel dimethylglyoxime but packs differently in the crystal so that no –Cu–Cu– bonds are possible, is soluble in water. Thus, the metal chains contribute enough stability to the crystal of nickel dimethylglyoxime so that it is insoluble in water and the unique packing tends to prevent coprecipitation. On the basis of the relative solubilities of nickel dimethylglyoxime and copper dimethylglyoxime, Rundle[4] has estimated that the metal chains in the nickel complex contribute about 10 kcal./mole to the stability of the crystal.

The existence of metal–metal interaction in nickel dimethylglyoxime has been confirmed by Yamada and Tsuchida[5] from measurements of the dichroism of the nickel, platinum and copper complexes of dimethylglyoxime. It also has been shown that the Magnus green salt, $[Pt(NH_3)_4][PtCl_4]$, and the complex $[Au^{III}(DH)_2][Au^{I}Cl_2]$ (where DH^- is the anion of dimethylglyoxime) contain chains of metal–metal bonds of comparable length,[4,6,7] and that other *vic*-dioxime[8] complexes of nickel, palladium and platinum have the same structure as nickel dimethylglyoxime.[3,9,10]

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[1] No. XXI in a series on "Chemistry of the *vic*-Dioximes." Previous paper in this series is No. XX, *J. Org. Chem.*, in press (1958). Abstracted from dissertation submitted by Dennis W. Barnum to graduate faculty of Iowa State College in partial fulfillment of requirements for the degree of Doctor of Philosophy, 1957.

[2] Shell Development Co., Emeryville, Calif.

[3] L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

[4] R. E. Rundle, THIS JOURNAL, **76**, 3101 (1954).

[5] S. Yamada and R. Tsuchida, *ibid.*, **75**, 6351 (1953).

[6] S. Yamada, *ibid.*, **73**, 1579 (1951).

[7] M. Atoji, J. W. Richardson and R. E. Rundle, *ibid.*, **79**, 3017 (1957).

[8] The prefix *vic*- is an abbreviation for *vicinal*, and a *vic*-dioxime is one in which the oxime groups are on adjacent carbon atoms. Nioxime and heptoxime are the trivial names for 1,2-cyclohexanedionedioxime and 1,2-cycloheptanedionedioxime, respectively.

[9] A. G. Sharpe and D. B. Wakefield, *J. Chem. Soc.*, 281 (1957).

[10] J. Pech, M. Polster and A. Rezabek, *Chem. Listy*, **43**, 180 (1949); *C. A.*, **44**, 9295c (1950).