ESR Spectra of the Tris((±)chxn)chromium(III) System (chxn = trans-1,2-cyclohexanediamine)[†]

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We report ESR spectra of four diastereoisomeric tris(trans-1,2-cyclohexanediamine)-chromium(III) compounds. Spectra have been obtained from diluted single crystals and powders and also from frozen solutions. All spectra of solid samples have been interpreted in terms of the conventional spin Hamiltonian for an ion having a spin quartet ground state. The zero-field splitting parameters are in the range from $|D| = 0.15$ to 0.457 cm^{-1} for the lel_3 and ob_3 isomers, respectively. The frozen solution spectra exhibit very broad and narrow bands mixed together. We introduce a method for simulating these spectra from powder spectra by averaging over ranges of the zero-field splitting parameters D and E. In this way we can reproduce the gross features of the frozen solution spectra. This work describes the first example of a series of coordination compounds that are conformational isomers distinguishable by means of ESR spectroscopy. Our results are in accordance with the available crystallographic data.

Several transition metal complexes containing chelate organic ligands have the possibility of exhibiting both optical and conformational isomerism. An example is given in Fig. 1, where the Δ-lel_3 and the Λ-ob_3 isomers of Rh((−)-chxn)$_3^{3+}$ are shown. The absolute configuration around the central metal ion is indicated by Δ and Λ, while the lel_3 and the ob_3 designations describe the direction of the carbon–carbon bond as being either paral*lel* or *ob*lique to the three-fold axis, respectively.[1]

If a racemic mixture of a chiral bidentate amine is used as a ligand eight isomers (four racemic pairs) of a tris(diamine) complex are theoretically possible as described below. Many papers concerning this type of isomerisms have appeared in the literature covering studies of closely related compounds. The investigations have included comparisons of absorption spectra, determinations of relative complexity constants and equilibrium isomer distributions. Many structures have been determined by X-ray analysis,[2,3] and interpretation of circular dichroism spectra has made assignments of absolute configurations possible in several cases.[4]

The tris((±)chxn)chromium(III) system consists of two captoptric series (Δ and Λ), each series containing four diastereoisomers lel_3, lel_2ob, ob_2lel and ob_3. These four diastereoisomers are expected to have different chemical and physical properties and therefore of course discernible ESR spectra.

The purpose of the present work is to show that it is actually possible to distinguish the four diastereoisomers of the tris((±)chxn)chromium(III) system by means of ESR spectroscopy. We report single-crystal and powder ESR spectra of these isomers diluted into the diamagnetic Co^{III} and Rh^{III} analogues, and also the frozen solution ESR spectra have been recorded. Since we are primarily interested in the four diastereoisomers we will in the following designate these as the lel_3, lel_2ob, ob_2lel and ob_3 isomers of tris((±)chxn)chromium(III), and will not be concerned with their absolute configurations. We will, however, specify which enantiomers we have used in the experiments.

Experimental

The chromium(III) and cobalt(III) complexes were placed at our disposal by S. E. Harnung[5,6] and the rhodium(III) complexes were supplied by F. Galsbøl.[7]
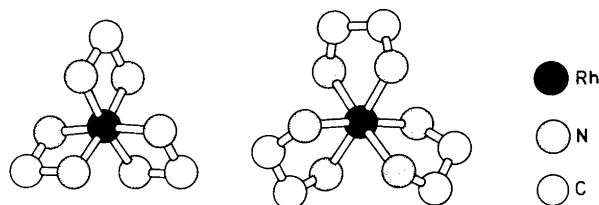

Fig. 1. A schematic representation of the Δ-lel_3 and Λ-ob_3 isomers of tris((±)chxn)chromium(III) constructed from atomic coordinates. The two complexes are shown with their three-fold axes almost perpendicular to the plane of the paper. For clarity only the atoms necessary to define the geometrical arrangement of the isomers are shown.
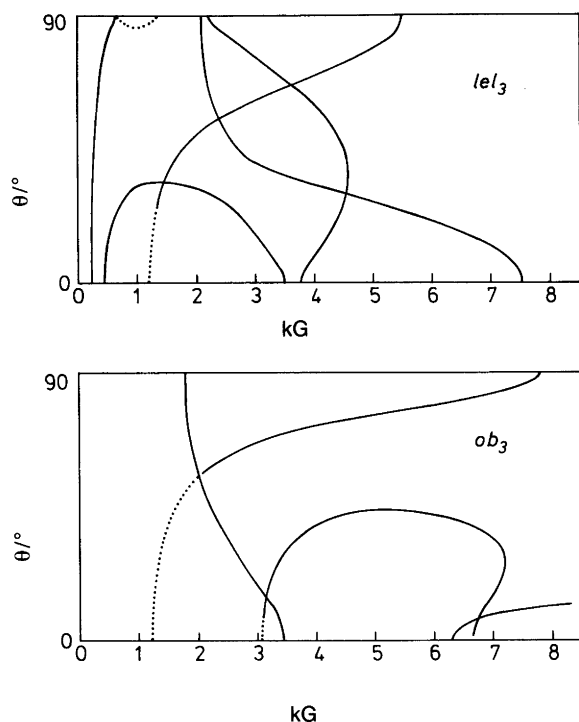
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[†]The recommended IUPAC name is trans-1,2-diaminocyclohexane.

Fig. 2. The solid line (——) illustrates the line positions of the transitions within the quartet ground state as obtained from the single-crystal experiments. The dotted line (·····) is calculated from the parameters in Table 1, since the corresponding transitions are too forbidden to be observed. The microwave frequency used was 9.81 GHz.

Preparation of solid samples for ESR measurements. Λ-[Cr((−)-chxn)₃,λλλ]³⁺ Λ-*ob*₃ and Δ-[Cr((−)chxn)₃,λλλ]³⁺ Δ-*lel*₃ ions were diluted into the analogous Rh(III) compounds by the following procedure: 1.0 g of Rh((−)-chxn)₃Cl₃ · aq (≈1.5 mmol) was dissolved in 50 ml of 0.001 M nitric acid together with 9.0 mg of Cr((−)-chxn)₃Cl₃ · aq (≈15 µmol). The Cr(III)-doped Rh((−)chxn)₃(NO₃)₃ · 3H₂O precipitated upon addition of conc. nitric acid. It was collected on a sintered glass filter washed with 96 % ethanol and dried by suction. Single crystals were grown by the slow evaporation of slightly acidic saturated solutions of the Cr(III)-doped rhodium salts. The crystals obtained in this way were hexagonal needles, some several centimetres long. Δ-[Cr((−)chxn)₂((+)chen),λλδ]Cl₃ · aq Δ-*lel₂ob* and Δ-[Cr((+)chxn)₂((−)chxn),δδλ]Cl₃ · aq Δ-*ob₂lel* were diluted into the analogous Co(III) compounds by a similar procedure. Single crystals were not grown, however. The chromium contents were not analysed, but were assumed to be approximately 1 %.

ESR spectra. Single-crystal ESR spectra were recorded at room temperature with a JEOL JES ME-1X spectrometer by initially placing a single crystal with its longitudinal direction parallel to the magnetic field vector and then rotating it through 90° around an axis perpendicular to the magnetic field vector. This was done by the use of a goniometric arrangement which permitted positional adjustments of the crystal while it was in the cavity. Frozen solution ESR spectra were recorded at liquid nitrogen temperatures with a Bruker ESP 300 spectrometer equipped with an Oxford ESR-900 continuous-flow cryostat by dissolving an amount of the appropriate chloride in a 50/50 % water–glycerol solution (ca. 10⁻³ M). After transfer to an ESR tube the solution was quickly frozen with liquid nitrogen. The spectra of powdered samples at room temperature were also recorded with the Bruker ESP 300 spectrometer. All spectra were obtained at the X-band using a modulation frequency of 100 kHz and amplitudes between 3 and 10 G. The spectra therefore appear as first derivatives of absorptions, as usual. The magnetic field range was 50–15050 G.

Results

Description of the spectra of solid samples. The single-crystal experiments resulted in a series of spectra from which it was possible to obtain the line positions of the transitions within the quartet ground state as a function of the angle between the magnetic field vector and the molecular z-axis. This is shown in Fig. 2 for both the *lel*₃ and the *ob*₃ isomers. These two experiments could be interpreted in terms of the conventional spin Hamiltonian [eqn. (1)] for

$$\hat{H} = \mu_B[g_\parallel H_z S_z + g_\perp (H_x \hat{S}_x + H_y \hat{S}_y)] + D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1)\right] \quad (1)$$

an axially symmetric ion having a spin quartet ground state, i.e. effective spin $S = 3/2$, where the zero-field splitting (z.f.s.) is given by $2D$.

The spin Hamiltonian parameters were obtained from a least-squares fit and are shown in Table 1. With these parameters it was possible to simulate[8] the single-crystal experiments; excellent agreement with the experiment was obtained, as is also apparent from Fig. 2.

We conclude from these experiments that both the *lel*₃ and *ob*₃ isomers of Cr((−)chxn)₃³⁺ have axial symmetry, and the symmetry axis is parallel to the longitudinal direction of the crystal. It can also be concluded that if the unit cell contains more than one Cr((−)chxn)₃³⁺ ion, these must

Table 1. Spin Hamiltonian parameters obtained from a least-squares fit of the single-crystal data.

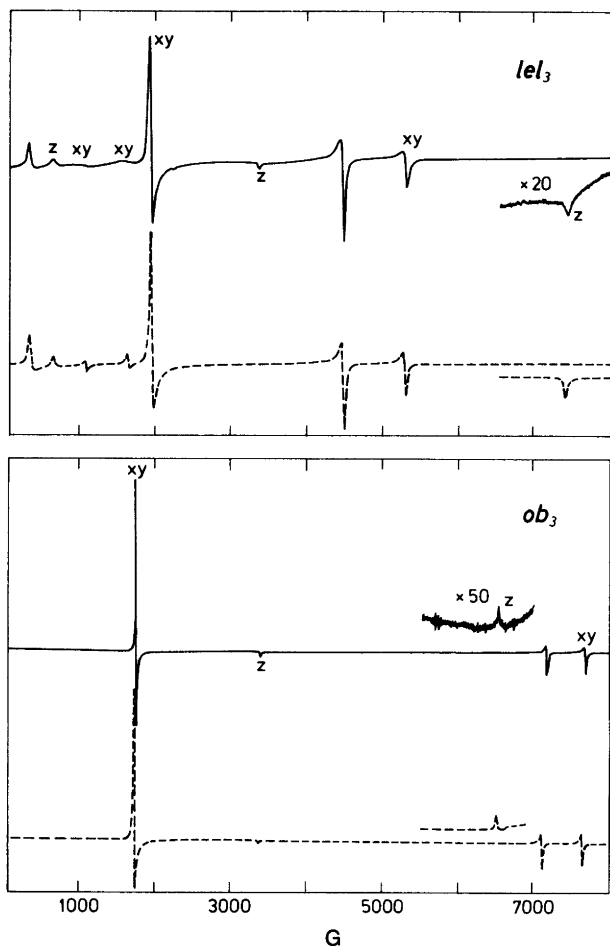| Isomer	$|D|/cm^{-1}$	$g_\parallel$	$g_\perp$	$|A_\perp|/cm^{-1}$
Δ-[Cr((−)chxn)₃,λλλ]³⁺ *lel*₃	0.185	1.980	1.986	–
Λ-[Cr((−)chxn)₃,λλλ]³⁺ *ob*₃	0.457	1.987	1.982	17×10⁻⁴

Fig. 3. ESR spectra of powdered samples at room temperature of the *lel₃* and the *ob₃* isomers are shown (——) together with the spectra simulated from the parameters in Table 1 (-----). In the spectrum of the *lel₃*-isomer the z-transition at $g \approx 2$ is too weak to be observed in the simulated spectrum using the chosen scale. The spectra were recorded with a microwave frequency of 9.37 GHz.

Table 2. Spin Hamiltonian parameters obtained from powder spectra.

Isomer	$|D|/\text{cm}^{-1}$	$|E|/\text{cm}^{-1}$	g
Cr((±)chxn)₃³⁺ *lel₂ob*	0.22	0.04	1.98
Cr((±)chxn)₃³⁺ *ob₂lel*	0.29	0.05	1.98

chxn)₃³⁺ ions in the unit cell. Since it was not immediately obvious how to assign the lines to transitions within the quartet ground state, several ESR spectra were simulated with $0.2 < D < 0.4$ cm⁻¹ and $0 \le E \le 1/3$ D (since $3E > D$ merely corresponds to a different choice of x-, y- and z-axes) until approximate matches were reached. The spin Hamiltonian parameters given in Table 2 were then obtained by slightly adjusting these preliminary parameters until the simulated spectrum was in reasonable agreement with the experimental one. Because of the relatively broad lines any anisotropy in the g-tensors could not be deter-

be magnetically equivalent, i.e. have parallel three-fold axes.

The powder ESR spectra of the *lel₃* and *ob₃* isomers are shown in Fig. 3, together with the spectra simulated from the parameters in Table 1 (without hyperfine coupling, however). These spectra of course contain no new information as compared to the single-crystal experiments. However, they neatly illustrate how to interpret a powder spectrum as an adequately weighted sum of single-crystal spectra.[9] The powder spectra (not shown in this paper) of the *lel₂ob* and *ob₂lel* isomers clearly show that neither isomer is axial, and the spectra must be interpreted in terms of a spin Hamiltonian accounting for their lack of a principal axis of rotation by including the term $E(\hat{S}_x^2 - \hat{S}_y^2)$ in eqn. (1); the z.f.s. is thus given by $2(D^2 + 3E^2)^{1/2}$. When the spectra are compared with those of the axial *lel₃* and *ob₃* isomers an appreciable line broadening is observed. This makes the interpretation more difficult, as the broad lines might be due to the existence of several non-equivalent Cr((±)-
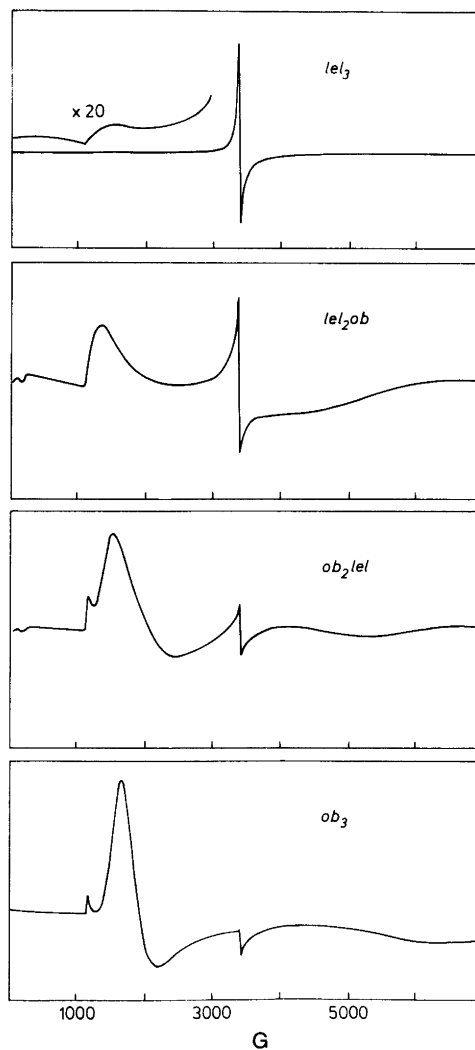

Fig. 4. Frozen solution ESR spectra of all four diastereoisomers (ca. 10⁻³ M in 50/50 % water–glycerol) recorded at 80 K and with a microwave frequency of 9.36 GHz.
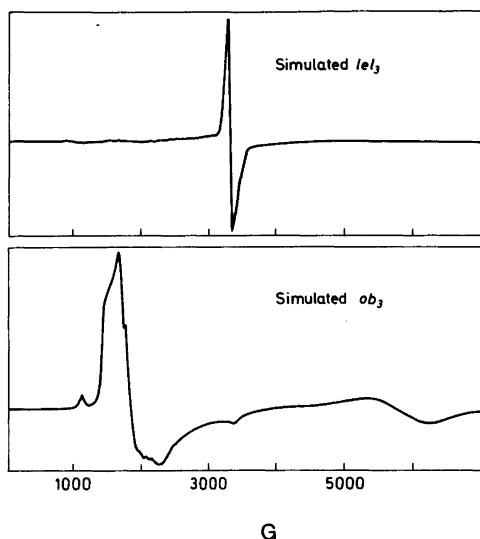
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Fig. 5. Attempts to simulate the frozen solution ESR spectra of the *lel*$_3$ and the *ob*$_3$-Cr((−)chxn)$_3$$^{3+}$ isomers by averaging around 1800 and 1000 spectra, respectively. Top: the spectrum was obtained by adding spectra with $0.01 \leq D \leq 0.06$ cm^{-1} in steps of 0.001 cm^{-1}, and for each value of D, $D/10 \leq E \leq D/5$ in steps of 0.0001 cm^{-1}. Bottom: the spectrum was obtained by adding spectra with $0.300 \leq D \leq 0.368$ cm^{-1} in steps of 0.002 cm^{-1}, and for each value of D, $0.000 \leq E \leq 0.050$ cm^{-1} in steps of 0.001 cm^{-1}. The bandshape function used in both simulations was a first-derivative lorentzian with a linewidth of 27 G. The figure should be compared with the experimental *lel*$_3$ and *ob*$_3$ spectrum in Fig. 4.

mined, just as the zero-field splitting parameters could only be obtained with poor accuracy.

Description of the spectra of frozen solutions. Frozen solution ESR spectra are shown in Fig. 4. Comparing these with the analogous powder spectra it is immediately conspicuous that an extensive line broadening and a loss of fine structure have occurred. The frozen solution spectra are rather uncharacteristic although still clearly discernible. In the spectrum of the *lel*$_3$ isomer a weak shoulder appears from ca. 1100 G. This shoulder is also seen in the rest of the spectra, and it gains intensity relative to the signal at $g \approx 2$ through the series *lel*$_3$, *lel*$_2$*ob*, *ob*$_2$*lel* and *ob*$_3$. The spectrum of the *lel*$_2$*ob* isomer contains a broad signal extending from about 3350 to 6000 G. A similar signal is observed in the spectra of the *ob*$_2$*lel* and *ob*$_3$ isomers, where it has successively moved toward higher field. Both the *ob*$_2$*lel* and *ob*$_3$ isomers have a relatively sharp signal at $g \approx 6$ corresponding to the m_s transition $-3/2 \rightarrow +3/2$.

Simulation of frozen solution spectra. We have only tried to simulate the frozen solution spectra of the *lel*$_3$ and the *ob*$_3$ isomers. Here a somewhat different approach was adopted. The zero-field splittings were found by a comparison of the line positions of identifiable transitions to be slightly less than those of the diluted powders. At the same time it was evident from the ESR spectra that the ions in the frozen solutions were not all strictly axial, since the m_s transition $-3/2 \rightarrow +3/2$ has gained substantial intensity. The dissimi-

larities of the linewidths within the same spectrum indicated that the Cr((−)chxn)$_3$$^{3+}$ ions are situated in different environments (*vide infra*). The frozen solution spectra were thus simulated according to eqn. (2), which corresponds to

$$I(H) = \underset{N(\beta,\lambda)}{\int_D \int_E \int_\beta \int_\gamma \int_\alpha} \sum_{\sigma=1} P_\sigma(\alpha,\beta,\gamma) F_\sigma(H_\sigma;H) \sin\beta \, d\alpha \, d\beta \, d\gamma \, dD \, dE \quad (2)$$

a powder spectrum with an additional integration over the z.f.s. parameter space. In eqn. (2) H_σ is the resonance magnetic field for the transition numbered σ, $F_\sigma(H_\sigma;H)$ is a bandshape function centred at H_σ, and $P_\sigma(\alpha,\beta,\gamma)$ is the transition probability for this transition. All the integrations are, however, performed as simple summations. The result of applying this procedure is shown in Fig. 5, and the spin Hamiltonian parameters used in the simulations are given in the figure caption. The reason for this approach is discussed later: until now it suffices to observe the similarities of the simulated and the experimental spectra.

Discussion

Genarally, ESR spectra of monomeric chromium(III) compounds can be considered well understood, and this can in part be attributed to the large amount of experimental data that are available for analysis.

Naturally occurring chromium consists primarily of four isotopes of which ^{53}Cr (9.50 %) is the only one having a non-zero nuclear spin ($I_{Cr} = 3/2$). Hyperfine structure is seldom observed, however, and instead it results in some line broadening. This is due to the relatively small hyperfine coupling constant of chromium(III) when compared, for example, to the congeneric molybdenum(III).[10] Since the zero-field splitting of chromium(III) complexes usually lies within the range of 0–2 cm^{-1} the X-band ESR spectra typically contain more than enough features to allow an accurate determination of all the parameters in the spin Hamiltonian.

Structures and ESR spectra. It should be emphasized that none of the tris((±)chxn)chromium(III) isomers has been characterized by single crystal X-ray work. The crystal structures of some of the diamagnetic solid solvents are known, however, and we assume isomorphism where appropriate, as specifically shown by X-ray powder diffraction for the *lel*$_3$ isomers.[11] The results of our single crystal experiments are in accordance with the crystallographic data, from which it is known that both the *lel*$_3$ and the *ob*$_3$-Rh((−)chxn)$_3$(NO$_3$)$_3$ · 3H$_2$O isomers crystallize with a hexagonal unit cell, $P6_3$, containing two Rh((−)chxn)$_3$$^{3+}$ ions, both of which are situated on three-fold axes.[12,13] We have demonstrated that these two three-fold axes are parallel, and therefore of course both parallel to the longitudinal direction of the crystal.

Using the single-crystal spectra as a starting point it is immediately possible to assign the signals in the powder

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spectra of the lel_3 and the ob_3 isomer as being due to $Cr((-)chxn)_3^{3+}$ ions having their three-fold axis parallel or perpendicular either to the magnetic field (as indicated in Fig. 3 by z and xy, respectively) or to some intermediate orientation. Before discussing the spectra of the two rhombic isomers the linewidth of, in particular, the ob_3 isomer deserved attention. Remembering that the six ligators are nitrogen [to which superhyperfine coupling (usually only observed as line broadening) can be expected, since ^{14}N (99.63 %) has a nuclear spin ($I_N = 1$)], the very narrow signals must be indicative of a very strict axial symmetry and a well ordered structure. In fact by examination of the second-derivative spectrum the two outermost ^{53}Cr hyperfine lines are observed on the xy transition at ca. 1700 G, and allow an estimate of the hyperfine coupling constant $A_\perp$. This is also given in Table 1.

The structures of lel_2ob and ob_2lel-$Co((\pm)chxn)_3(NO_3)$ · aq have unfortunately not been determined by X-ray crystallography, and only the structure of Λ-lel_2ob-$Co((\pm)$-chxn$)_3$Cl$_3$ · 5H$_2$O is available.[14] Therefore it is known that the complex cation only has an approximate two-fold axis. This is in accordance with the ESR spectra, which clearly illustrate that neither the lel_2ob nor ob_2lel isomer has axial symmetry. This, of course, merely conforms to simple considerations of molecular geometry.

Interpretation of frozen solution spectra. The ESR spectra of the frozen solutions are, as mentioned earlier, rather uncharacteristic. However, a careful examination reveals several trends which we have already described. They can all be explained by assuming that the z.f.s. increased on going from the lel_3 isomer to the ob_3 isomer as in Fig. 4. We have an explanation for the appearance of the frozen solution spectra. Before we undertake this discussion it is worthwhile emphasizing that the frozen solution spectra of the $Cr((\pm)chxn)_3^{3+}$ isomers are by no means unique. In particular, the spectrum of the lel_3 isomer exhibits features which seem to be characteristic of all chromium(III) compounds having small z.f.s. values.[15] We suggest that their appearance is due to the existence of a multitude of slightly different sites within the structure of the frozen solution. The difference, for example, being due to each site having a different hydrogen-bonding arrangement. This explanation suggests the possibility of simulating the ESR spectra by assuming different kinds of $Cr((\pm)chxn)_3^{3+}$ ions, and this is the basis for the special approach in the simulations of the frozen solution spectra of the lel_3 and the ob_3 isomer. The difference in the linewidths in the experimental spectra can in this way be attributed to the fact that the positions of the z-transitions (at $g \approx 2$ and $g \approx 6$) are rather insensitive to variations of D and E, while the positions of the xy and intermediate transitions are strongly dependent upon these parameters.[9] We are, of course, aware of the limitations of this model. The parameters used in our simulation are difficult to assess, and also the weighting of the individual spectra are hard to justify. It is, however, very difficult to give a physically reliable procedure, one reason being that

even a small geometrical distortion of an axially symmetric ion may give rise to a large rhombic z.f.s. parameter. This is the reason for the differences between the experimental and the simulated spectra, and therefore our weighting schemes are only to be regarded as first approximations.

Conclusion

It has been possible to interpret the powder ESR spectra of all four diastereoisomers of tris$((\pm)chxn)$chromium(III), and thus all the spin Hamiltonian parameters have been obtained. We have also given a possible explanation of the general appearance of the frozen solution spectra and indicated a way to interpret and thus simulate these spectra. We are of the opinion that the most probable explanation of the appearance of the frozen solution spectra is the existence of several inequivalent sites in the structure of frozen solutions.

The spectra of the four diastereoisomeric tris$((\pm)chxn)$-chromium(III) complexes are the first examples of such a series of coordination compounds being distinguished by ESR spectroscopy. This could in part be due to the difficulties in preparing all the paramagnetic isomers as well as suitable diamagnetic solid hosts.

References

1. *Nomenclature of Inorganic Chemistry*, Butterworths, London 1971.
2. Saito, Y., Ed., *Absolute Configurations of Metal Complexes Determined by X-ray Analysis*, Osaka 1977.
3. Saito, Y., Ed., *Absolute Configurations of Metal Complexes Determined by X-ray Analysis*, Osaka 1984.
4. Saito, Y. *Coord. Chem. Rev. 13* (1974) 305.
5. Harnung, S. E. and Laier, T. *Acta Chem. Scand., Ser. A 32* (1978) 41.
6. Harnung, S. E., Søndergaard, B., Craeser, I., Maegaard, H., Pfenninger, U. and Schäffer, C. E. *Inorg. Chem. 15* (1976) 2123.
7. Galsbøl, F., Steenbøl, P. and Søndergaard, B. *Acta Chem. Scand. 26* (1972) 3605.
8. Bang, E., Eriksen, J., Glerup, J., Mønsted, L., Mønsted, O. and Weihe, H. *Acta Chem. Scand. 45* (1991) 367.
9. Pedersen, E. and Toftlund, H. *Inorg. Chem. 13* (1974) 1603.
10. Jacobsen, C. J. H. and Pedersen, E., *Inorg. Chem. 30* (1991) 4477.
11. Andersen, P., Galsbøl, F., Harnung, S. E. and Laier, T. *Acta Chem. Scand. 27* (1973) 3973.
12. Miyamae, H. and Saito, Y. *Acta Crystallogr., Sect. B 33* (1977) 860.
13. Kuroda, R., Sasaki, Y. and Saito, Y. *Acta Crystallogr., Sect. B 30* (1974) 2053.
14. Sato, S. and Saito, Y. *Acta Crystallogr., Sect. B 33* (1977) 860.
15. E.g. Andersen, P., Døssing, A., Glerup, J. and Rude, M. *Acta Chem. Scand. 44* (1990) 346.