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High-field EPR study and crystal and molecular structure of *trans-RSSR*-[CrCl₂(cyclam)]_nX (X=ZnCl₄^{2–}, Cl[–] and Cl[–]·4H₂O·0.5HCl)[†]

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For the first time, HF-EPR (94.5 GHz) spectroscopy has been used to determine crystal field parameters in chromium(III) coordination compounds. The large zero-field splitting parameters of the dark-green photochromic *trans-RSSR*-[CrCl₂(cyclam)]₂ZnCl₄, **1**, the red–purple *trans-RSSR*-[CrCl₂(cyclam)]Cl **2** and the red–purple *trans-RSSR*-[CrCl₂(cyclam)]Cl **4**H₂O·0.5HCl, **3**, where cyclam = 1,4,8,11-tetraazacyclotetradecane, have been obtained. A full analysis of EPR spectra at 94.5 GHz of diluted complexes **1**, **2** and **3** at 300 K revealed that they are extremely sensitive to *D* and *E* values. The rhombic distortion was precisely determined for each compound. For **1**, *g* = 2.01, *D* = -0.305 cm⁻¹, *E* = 0.041 cm⁻¹ and $\lambda = |E/D| = 0.1396$; for **2**, *g* = 2.01; *D* = -0.348 cm⁻¹, *E* = 0.042 cm⁻¹ and $\lambda = |E/D| = 0.1206$ and for **3**, *g* = 1.99, *D* = -0.320 cm⁻¹, *E* = 0.041 cm⁻¹ and $\lambda = |E/D| = 0.1201$ cm⁻¹ and $\lambda = |E/D| = 0.1200$ cm⁻¹. The second the sign of the *D* value for all compounds. These data indicate that at room temperature the crystal field is mainly rhombic and as the temperature decreases, the rhombicity of the *D* tensor increases slightly. These found differences between **1**, **2** and **3** allowed us to establish the importance of the intermolecular interactions in the solid state due to different hydrogen bonding networks in their crystalline arrangement.

Introduction

Most of the EPR measurements on Cr(III) complexes have been carried out at 9.45 GHz, X-band and to a lesser extent at 34.5 GHz, Q-band. However, for Cr(III) when the second-order perturbation is similar to the Zeeman term: $g\beta B \approx |D|$, it is at times difficult to perform even a qualitative assignment of the transitions because many "forbidden" transitions may be present. At a higher magnetic field the Zeeman interaction becomes larger relative to the zero-field splitting (zfs), and since hv is larger, additional transitions become observable,¹ which permits the determination of larger values of zfs.² At high microwave frequency and low temperature $hv > k_BT$ can be achieved, thus increasing spin polarization, *i.e.*, almost all of the spins are in the Zeeman ground state. The changing population of the levels as a function of temperature generates changes in the relative intensity of transitions, thus allowing the determination of the sign of the zfs values.³

In our group three chromium(III) complexes presenting interesting optical and magnetic properties have been isolated.^{4a,5} The photochromism exhibited by the dark-green compound: *trans-RSSR*-[CrCl₂(cyclam)]₂ZnCl₄, **1**, compared to the red–purple *trans-RSSR*-[CrCl₂(cyclam)]Cl. **2** and the red–purple *trans-RSSR*-[CrCl₂(cyclam)]Cl. **3** has been attributed to intermolecular interactions in the crystal packing in which the chromium atoms interact through the zinc atom of the tetrachlorozincate counterion *via* hydrogen bonding.⁵

As a part of a research project on the magnetic characterization of several coordination compounds,⁶ a HF-EPR (at 94.5 GHz) study of magnetically diluted solid samples of 1, 2 and 3 at different temperatures has been carried out. The crystal and molecular structures of 2 and 3 were determined and discussed.

† This paper is dedicated to the memory of Professor Virgilio Beltrán-López.

Experimental

All reagents and solvents had the highest available commercial quality and were used without further purification. Elemental analyses (C, H, N, Cl) were performed in the Chemistry Department at University College London, UK.

Preparation of the compounds

trans-RSSR-[CrCl₂(cyclam)]₂ZnCl₄ (tetragonal) **1**, was prepared as reported in the literature⁴⁶ Elemental analysis for **1**, found: C, 28.30; H, 5.54; N, 13.17; Cl, 33.81%. Calc. for $C_{20}H_{48}Cl_8Cr_2N_8Zn$: C, 28.14; H, 5.67; N, 13.30; Cl, 33.22%.

trans-RSSR-[CrCl₂(cyclam)]Cl (tetragonal) **2**. This compound was prepared by a slight modification of the reported technique for the preparation of *trans* derivative.^{4b} Anhydrous chromium(III) chloride (0.50 g, 5.7 mmol) was extracted with zinc–mercury amalgam into a Soxhlet apparatus and reacted with a boiling ethanolic solution of cyclam (0.74 g, 3.7 mmol) under nitrogen. The reaction time was increased from 1 to 72 h.

Subsequently, a small amount of lithium chloride was added and the reaction mixture was allowed to react for a further 24 h under reflux. Then, the volume was reduced to 1/4 of its original value. The solid formed was recovered and recrystallised from 1 M HCl. Slow evaporation of the solvent produced bright red–purple crystals, which were washed with ice-cold methanol (yield 0.44 g, 1.2 mmol, 60%). Alternatively, crystals of **2** could be grown by slow evaporation of the solution that was used for the purification of crude compound.^{4b} These crystals are stable to air, in contrast to those of **3**. Elemental analysis for **2**, found: C, 33.24; H, 6.75; N, 15.26; Cl, 29.56%. Calc. for C₁₀H₂₄Cl₃CrN₄: C, 33.49; H, 6.74; N, 15.62; Cl, 29.61%.

trans-RSSR-[CrCl₂(cyclam)]Cl·4H₂O·0.5HCl (monoclinic) **3**. Crystals of **3** were grown from the recrystallisation of the *trans*compound reported^{4a} in 1 M HCl (4 °C). Although stable in

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Table 1 Summary of crystallographic data for 2 and 3

Formula	$C_{10}H_{24}Cl_{3}CrN_{4}$, 2	$C_{10}H_{24}Cl_3CrN_4{\cdot}4H_2O{\cdot}0.5~HCl,~{\bf 3}$
Formula weight	358.68	447.15
Color/habit	Red-purple/hexagonal prism	Red-purple/rectangular prism
Crystal size/mm	$0.60 \times 0.32 \times 0.24$	$0.48 \times 0.42 \times 0.30$
Crystal system	Tetragonal	Monoclinic
Space group	$P4_2/m$	$P2_{1}/n$
Z	2	2
T/K	293(2)	293(2)
a/Å	7.6245(7)	6.470(2)
b/Å	7.6245(7)	7.479(2)
c/Å	13.623(1)	21.079(4)
β/°		90.67(2)
$V/Å^3$	792.0(1)	1019.9(5)
<i>F</i> (000)	374	470
$D_{\rm c}/{\rm g~cm^{-3}}$	1.504	1.456
Radiation	Μο-Κα	Μο-Κα
$\lambda/Å$	0.71073	0.71073
μ/mm^{-1}	1.218	1.032
Abs. factor min./max.	0.637/0.747	0.613/0.670
Std. variation (%)	2.8	5.6
$(\sin\theta/\lambda)_{\rm max}/{\rm \AA}^{-1}$	0.7035	0.7035
Final R (on F)	0.031	0.054
Final $w\hat{R}$ (on F^2)	0.070	0.107
Data/parameters	1199/72	2969/184
Residuals min./max./e Å ⁻³	-0.25/0.32	-0.49/0.50

solution, these crystals lose crystallinity almost instantaneously when they are exposed to air.

trans-RSSR-[CoCl₂(cyclam)]Cl \cdot 4H₂O \cdot 0.47HCl (monoclinic) **4** was prepared and crystallised as published.⁷

trans-RSSR-[CoCl₂(cyclam)]Cl (tetragonal), **5** was prepared and crystallised⁸ to get the analogous form of **2**.

trans-RSSR-[CoCl₂(cyclam)]₂ZnCl₄, **6** was prepared by adding a stoichiometric amount of zinc chloride to a solution of **4** and allowing the solution to crystallise out.

X-Band EPR was used to confirm the purity of the chromium(III) compounds as well as the diamagnetism of the cobalt complexes.

Single-crystal X-ray diffraction

A single crystal of compound 2 was attached to a thin glass fibre using epoxy resin. The data collection and structure refinement follow a routine procedure.

A single crystal of **3** was sealed in a Lindemann capillary filled with HCl–H₂O mother-liquor. The X-ray data collection and the structure refinement followed the procedure described elsewhere.⁷ An empirical absorption correction based on ψ scans^{9b} was applied. The chromium atom of the complex lies on an inversion centre, so that the chloride counterion must have an occupancy of 0.5 in order to preserve charge balance. Since the chloride anion is located on a general position, its occupation and thermal displacement factors were refined by keeping one of them constant and varying the other one alternately.

At an advanced anisotropic refining step, four and three well defined peaks with approximately equal electron densities were located surrounding the water O1 and O2 atoms, respectively. Those peaks near to the water molecule O1 were assigned to the two disordered H atoms, and refined with partial occupancy of 0.5.

For those peaks near the water molecule O2, applying the same restrained refinement used for the chloride ion [O–H distance 0.85(1) Å], the occupation factors for these H atoms added up to 2.24 and gave reasonable values for the thermal parameters $(0.04-0.09 \text{ Å}^2)$. In the final model a fixed site-occupation factor of 0.746 and a refined isotropic temperature were included for each H atom in the partially protonated water molecule. The decision in favour of a partially protonated water instead of an orientationally disordered water molecule was taken based on the significance in the content of Cl⁻.

In both cases the structures were solved using SIR97^{9a} and refined using SHELXL97.¹⁰ A comparison of the details on the crystal data and experimental conditions for **2** and **3** can be found in Table 1.

CCDC reference numbers 195378 and 195379.

See http://www.rsc.org/suppdata/dt/b4/b405789a/ for crystallographic data in CIF or other electronic format.

Solid solutions

The diluted samples for magnetic studies were prepared by slow evaporation of a liquid concentrated solution of **6** containing $\sim 1\%$ (w/w) of **1**, and **5** containing $\sim 1\%$ (w/w) of **2**, and **4** containing $\sim 1\%$ (w/w) of **3**. The obtained solids were finely ground in order to have a homogeneous sample.

EPR measurements

These studies were carried out on polycrystalline samples of 1, 2 and 3, and on solid solutions of their magnetically diluted samples at X-band (9.45 GHz) on a JEOL JES -SX spectrometer operating at 100 kHz. The magnetic field was calibrated with a NMR ES-CE 50 device. The g values were calculated from the accurate measurements of the magnetic field and frequency parameters. The high-frequency (94.5 GHz) spectra were measured at 300, 20 and 10 K, using a novel quasi-optical induction mode spectrometer that was designed and built at the University of St. Andrews, UK. The fit of the powder pattern EPR spectra was performed with a program written by Weihe and coworkers11 which diagonalises the full Hamiltonian matrix with the bases of four S = 3/2 spin functions, eqn. (1). This program can be used to calculate the energies and the transition probabilities, the eigenvalues and eigenvectors, respectively. The resonant fields were determined by the differences of the energy between electronic levels. The SIM program also takes into account the Boltzmann distribution factor in calculating transition probability and signal intensity.

Results and discussion

The complex cation of **2** has crystallographically imposed 2/m symmetry, while the chloride ion lies at a site with $\overline{4}$ symmetry. The configuration for the *trans*-[CrCl₂(cyclam)]Cl has been suggested to be *RSSR*, since it is the most stable for these types of complexes.^{7,12} Moreover, the molecular structure of the cation has been found to have this configuration in the nitrate and bromide salts.^{4a,c} The bright red–purple compound, **2**, shows that the cyclam moiety provides a tetradentate nitrogen ligand, forming with the two axial chlorine ligands a tetragonal bipyramid coordinated chromium complex, which also possesses *RSSR* configuration on the secondary nitrogen atoms (Fig. 1).

 Table 2
 Hydrogen bonding interactions found for 1, 2 and 3

Compound	N–H/Å	H…Cl/Å	N…Cl/Å	N–H…Cl/°	N–H····Cl
1 2 3	0.72(5) 0.85(4) 0.83(3) 0.77(5)	2.73(4) 2.57(4) 2.70(3) 2.65(5)	3.074(3) 3.292(3) 3.340(2) 3.055(3)	112(4) 148(3) 135(2) 115(4)	$N1-H1\cdots Cl2^{a}$ $N4-H4\cdots Cl1^{b}$ $N1-H1\cdots Cl2^{c}$ $N1-H1\cdots Cl2^{d}$
5	0.77(5) 0.81(5)	2.03(3) 2.71(4) 2.49(5)	3.317(3) 3.241(3)	136(4) 155(5)	N1–H1····Cl1 ^e N4–H4····Cl2

Symmetry transformations used to generate equivalent atoms: a-x+1, -y+1, -z, b-x+1/2, -y+1/2, z, c-x+1, -y, -z, d-x+1, -y, -z+1, e_x+1 , y, z.



Fig. 1 ORTEP-like diagram of **2** showing a $[133133]^{13}$ conformation and a distorted octahedral coordination geometry. Thermal ellipsoids are at the 30% probability level; atoms labelled with suffix A are generated by -x+1, -y, -z, atoms labelled with suffix B are generated by -x+1, -y, z and atoms labelled with suffix C are generated by x, y, -z.

The Cr–N ligand and Cr–Cl distances are 2.061(2) and 2.329(6) Å, respectively, agreeing with the literature values.^{4a} The *trans* angles are exactly linear on account of symmetry requirements. The cyclam moiety has the expected geometry and assumes a chair conformation with exact 2/m symmetry. The ligand and the central chromium ion are coplanar, this plane being perfectly perpendicular to the Cl1–Cr–Cl1' axis.

In the crystal lattice four symmetry related *trans*-[CrCl₂(cyclam)]⁺ cations are hydrogen bonded in a tetrahedral fashion to the chloride counterion (Fig. 2 and Table 2).



Fig. 2 View looking down the crystallographic *c* direction of complex 2.

The structure found for *trans*-[CrCl₂(cyclam)]Cl·4H₂O·0.5HCl, **3** is depicted in Fig. 3 and confirms the *RSSR* configuration of the *trans*-[CrCl₂(cyclam)]⁺ cation. This Cr(III) cation is isomorphous to the recently reported *trans*-*RSSR*-[CoCl₂(cyclam)]Cl·4H₂O· 0.47HCl.⁷ The chromium ion is located at a crystallographic centre of symmetry and is surrounded by four N atoms at nearly identical Cr–N distances of 2.061(3) and 2.065(3) Å in the equatorial plane (see Table 3 for selected interatomic distances). The Cr–Cl distance

Table 3 Selected bond lengths (Å) and bond angles (°) for 2 and 3 $$					
2		3			
Cr-N(1) Cr-Cl(1) N(1)-C(1) N(1)-C(2) N(1B) ^b -Cr-N(1)	2.061(2) 2.3295(6) 1.487(3) 1.485(3) 85.1(1)	$\begin{array}{c} \text{Cr-N(1)} \\ \text{Cr-N(4)} \\ \text{Cr-Cl(1)} \\ \text{N(1)-C(2)} \\ \text{C(3)-N(4)} \\ \text{N(4)-C(5)} \\ \text{N(1)-C(7')^{d}} \\ \text{N(1)-Cr-N(4)} \end{array}$	2.061(3) 2.065(3) 2.3292(9) 1.488(5) 1.492(4) 1.482(5) 1.481(5) 85.3(2)		
$N(1C)^{c}-Cr-N(1)$ N(1)-Cr-Cl(1) $N(1A)^{a}-Cr-Cl(1)$ $N(1)-Cr-N(1)^{c}$ $Cl(1)-Cr-Cl(1)^{b}$	94.9(1) 91.7(1) 88.3(2) 180.0 180.0	$\begin{array}{l} N(1)-Cr-Cl(1) \\ N(4)-Cr-Cl(1) \\ N(1)-Cr-N(4')^{d} \\ N(1)-Cr-Cl(1')^{d} \\ N(4)-Cr-Cl(1')^{d} \\ N(1')^{d}-Cr-N(1) \\ N(4')^{d}-Cr-N(4) \\ Cl(1')^{d}-Cr-Cl(1) \end{array}$	92.0(8) 88.7(1) 94.7(1) 88.0(1) 91.3(2) 180.0 180.0 180.0		

Symmetry transformations used to generate equivalent atoms: ${}^{a}-x + 1$, -y, -z. ${}^{b}-x + 1$, -y, z. ${}^{c}x$, y, -z. ${}^{d}-x + 1$, -y, -z + 1.



Fig. 3 ORTEP-like diagram of **3** showing a $[133133]^{13}$ conformation and a distorted octahedral coordination geometry. Thermal ellipsoids are at the 30% probability level and primed atoms are generated by crystallographic $\overline{1}$ symmetry (1-x, -y, 1-z).

is 2.329(9) Å, modifying the ideal octahedron to a tetragonally distorted coordination array.

The cyclam moiety exists in a chair conformation with the fivemembered chelate rings adopting a twist conformation, whereas the six-membered chelate rings are in a chair conformation.

In the crystal lattice the *trans*- $[CrCl_2(cyclam)]^+$ cations stack along the *b* direction (Fig. 4) and are held together by N–H···Cl hydrogen bonds. The channels left by this arrangement are filled by chloride ions (arising from the counterion of the complex and the hydrochloric acid used for crystallisation) and the protonated solvate water molecules, forming a rather complicated hydrogen bonding network, in which all possible hydrogen bonds are formed (Table 2).

The structural characterisation of **1** has already been published^{4*a*} and showed the same absolute configuration on the secondary nitrogen atoms; the same [133133] arrangement¹³ as observed for **2** and **3**.



Fig. 4 View of the unit cell of 3 looking down the crystallographic *b* direction.

It should be noted that in the case of 1, there is a crystallographic array which includes the chromium and zinc from the tetrachlorozincate hydrogen bonded counterion, Fig. 5, Table 2.



Fig. 5 View looking down the crystallographic *c* direction for $1.^{4a}$

From the above results it can be shown that **1**, **2** and **3** have similar molecular geometry but different hydrogen bonding networks.

X-Band EPR spectra at room temperature

Another important difference among 1, 2 and 3 in the solid state is shown by their X-band EPR spectra of their polycrystalline samples which have different effective g values. A very broad isotropic peak is centred at g = 1.991 for 1 and 3; while 2 shows a rhombic-like spectrum: g = 4.309, 3.107 and 1.223. Since the spectra, Fig. 6, are very broad with high exchange magnetic interactions (linewidth >500 G) little can be said about their local magnetic environments.



Fig. 6 X-Band EPR spectra of the polycrystalline samples 1, 2 and 3 at 300 K.

 Table 4
 Spin-Hamiltonian parameters of 1, 2 and 3 obtained by simulation of their X-band EPR spectra at 293 K

Complex	g	$ D /cm^{-1}$	E/cm^{-1}
1	1.99	0.305	0.04
2	1.99	0.310	0.05
3	1.99	0.305	0.04
3	1.99	0.305	0.04

The solid-state interactions are very important in these compounds; in fact, when **1** was irradiated ¹⁴ with an X-ray source (using regular X-ray diffraction powder doses), its colour changed from dark green to a dark grey-greenish, and the original EPR spectrum changed showing a "burning hole-like" effect on the original broad signal. New peaks appeared, a singlet at g = 2.003 and a multiplet centered at g = 2.217. The former is assigned to a radical species while the latter, to a Cr(III) cation. It is important to mention that when **2** and **3** were irradiated with the same X-ray source, no change was observed in their EPR spectrum.

Diluted samples of 1, 2 and 3 were studied at 300 K at 9.45 GHz. Their spectra are similar, showing well defined lines from zero to 10000 G, with no hyperfine structure. As a first approximation, all the spectra may be described as isotropic with g = 1.99. Thus, the spin-Hamiltonian that describes these spectra is typical for systems with S = 3/2:

$$\check{H} = g\beta BS + D\left(S_z^2 - \frac{1}{3}S\left(S+1\right)\right) + E\left(S_x^2 + S_y^2\right)$$
(1)

where the first term corresponds to the electronic Zeeman and the second and third terms correspond to zero-field splitting: axial (*D*) and rhombic (*E*) components. It has been assumed that the principal axes of the *g* tensor and the *D* tensor are parallel to the molecule axes.^{15,16}

These spectra were simulated, and the results for compound **1** are shown in Fig. 7.



Fig. 7 Experimental and simulated X-band EPR spectra (top) and the angular variation of the resonance position plot (bottom) for compound 1 diluted in a cobalt(III) matrix.

The Hamiltonian parameters found for 1, 2 and 3 are listed in Table 4.

X-Band EPR at low temperature

Measurements carried out at 123 K for **1**, **2** and **3** showed no change relative to the room-temperature spectra.

Since in these systems the zfs energy term is approximately of the same magnitude as the Zeeman energy, $hv \approx zfs$, it is possible to observe a large number of signals in a wide range of magnetic field, including close to zero magnetic fields and off-axis resonances ("looping transitions"), which are of particular importance when we consider the powder spectra¹⁷ as they correspond to noncontinuous resonance lines in the considered ranges of θ and ϕ , *i.e.* they are closed transitions that generate signals off the axis. Then,

HF-EPR (94.5 GHz) at room temperature

In EPR spectra at 94.5 GHz for systems of S = 3/2 the condition $g\beta B \gg |D|$ is satisfied and at this limit the resonance lines appear more resolved and in general the HF-EPR spectrum is much simpler than that obtained at X-band.¹⁹ This is a great advantage since the spectra can be more easily calculated and readily interpreted. Working at high frequencies the situation $zfs/h\nu \approx 0.1$ is reached, and under these conditions it is possible to separate "forbidden" ($\Delta M_s = \pm 2, \pm 3$) from "allowed" ($\Delta M_s = \pm 1$) transitions.²⁰ Thus, perturbation theory at second-order approximation²¹ leads to the fact that zero-field parameters can be easily obtained directly from the spectrum. Additionally, the spectrum is extremely sensitive to the values of *D* and *E*, thus allowing an accurate determination of these parameters, Fig. 8.



Fig. 8 Position of the signals ($\Delta M_s = \pm 1$) in the HF-EPR ($\nu = 94.5$ GHz) spectrum in a rhombic field, g = 2.00, |D| = 0.3 and E = 0.04 cm⁻¹ obtained from our theoretical calculations.

From all these theoretical calculations, it was possible to simulate the experimental HF-EPR spectra of diluted 1, 2 and 3 samples obtained at 300 K. The results for compound 1 are shown in Fig. 9. The *D* and *E* parameters for compounds 1, 2 and 3 are listed in Table 5.



Fig. 9 Powder HF-EPR spectra at 300 K (top) and its angular variation diagram for **1** diluted into a cobalt(III) matrix (bottom).

HF-EPR (94.5 GHz) at low temperature

In order to verify the sign of the D and E parameters, measurements at low temperature were carried out. This can be explained by the Boltzmann distribution. At low temperature the difference between

 Table 5
 Spin-Hamiltonian parameters of 1, 2 and 3 obtained by simulation of their HF-EPR (94.5 GHz) spectra at different temperatures

Compound	T/K	W-Band (94.5 GHz)				
		g	$ D /cm^{-1}$	E/cm^{-1}	D/E	
1	293	2.01	-0.305	0.041	0.1396	
	10	1.99	-0.292	0.0515	0.1759	
2	293	1.99	-0.320	0.041	0.1281	
	10	1.99	-0.292	0.0499	0.1709	
3	293	2.01	-0.348	0.042	0.1206	
	10	1.98	-0.290	0.0519	0.1789	

the population of the energy levels is large enough to show differences in the relative intensity of the transitions of fine structure.

At low temperature, if D is positive, the energy levels will become more populated with a concomitant increase in the intensity of the central transition while the side transitions become less intense in the spectrum, if there are no other changes in the relaxation processes. In the case where D has a negative value, the energy diagrams are inverted; therefore, the side transitions are now more intense.^{19,21,22}

EPR spectra at 94.5 GHz of complexes 1, 2 and 3 were also obtained at 10 K. The comparison of the spectra obtained at different temperatures shows that there is a magnetic dependence as the temperature decreases, Fig. 10.



Fig. 10 HF-EPR (94.5 GHz) spectra of **1** at variable temperature showing a slight magnetic dependence as temperature decreases.

The experimental and simulated spectra at 10 K for 1 are shown in Fig. 11.

From the spectral analysis and theoretical calculations, the best fit at 293 K zero-field splitting parameters is, for 1, D = -0.305 cm⁻¹,



Fig. 11 Experimental and simulated HF-EPR (94.5 GHz) spectra of 1 at 10 K (see Table 5).

E = 0.041 cm⁻¹, $\lambda = |E/D| = 0.1396$. At 10 K both zero-field parameters D = -0.292 cm⁻¹ and E = 0.0515 cm⁻¹ change; thus, $\lambda = |E/D| = 0.1759$ increased, indicating a larger rhombic distortion as the temperature decreased. This behaviour appeared in all complexes.

An article²³ dealing with the determination of the crystal field parameters of *trans*-[CrCl₂(cyclam)]Cl at X-band EPR in frozen water–ethylene glycol solution appeared recently. It is interesting to note that the values reported by these authors: g = 1.99, |D| =0.470 cm⁻¹ and E = 0.068 cm⁻¹ are higher than ours. This could be explained by changes in the environment of the cation, since in that case the EPR measurements were performed on frozen solutions.

It is clear that the series of compounds: *trans-RSSR*-[CrCl₂(cyclam)]_nX, where $X = ZnCl_4^{2-}$, Cl⁻ and Cl⁻·4H₂O·0.5HCl are distinct in the solid state. They have the same *trans-RSSR*configuration of the coordinated ligand and the molecular structure of the cations are practically the same. However, we have shown by crystal analysis, that these compounds have different hydrogen bonding networks due to different supramolecular interactions. Thus, the differences in *g* values in the spectra of the polycrystalline samples at X-band EPR and in the spectroscopic parameters, *D* and *E*, found for **1**, **2** and **3** can be attributed to these supramolecular interactions. It has been recognized that hydrogen bonding is responsible for important magnetic interactions in the solid state.

Conclusions

The series of compounds: *trans-RSSR*-[CrCl₂(cyclam)]_nX, where $X = ZnCl_4^{2-}$, Cl⁻ or Cl⁻4H₂O·0.5HCl were characterised by EPR spectroscopy. X-Band EPR spectra were highly broadened. Our calculations revealed that the HF-EPR (94.5 GHz) spectra are extremely sensitive to the *D* and *E* values and the full analyses of the spectra of **1**, **2** and **3** at room temperature showed clear differences in their zero-field splitting parameters, revealing that they have different rhombic distortion. As the temperature was decreased (10 K), *D* and *E* changed slightly, producing a larger rhombicity in all cases. The HF-EPR study at low temperature allowed us to confirm unambiguously the sign of *D*, which in all cases was found to be negative.

The differences in the effective g values observed in the EPR spectra of the polycrystalline samples permitted the characterisation and identification of compounds 1, 2 and 3. Additionally, they allowed us to establish the importance of intermolecular interactions in the solid state as they have different hydrogen bonding networks in their crystalline arrangements.

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