

Dynamic Jahn–Teller effect in a Fe–N₆ cage molecule

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Abstract. Mössbauer spectroscopic studies of [Fe(di(amH)-sar)](NO₃)₄.H₂O where di(amH)-sar represents 1,8 diamino 3,6,10,13,16,19-hexaza bicyclo [6,6,6] icosane in the temperature range of 4.2 to 300 K suggest that it undergoes a dynamic Jahn–Teller effect as revealed from the plots of temperature dependent quadrupole coupling constant, chemical shift and line width values. The spectrum down to 4.2 K, shows a quadrupole doublet with no magnetic hyperfine splitting.

Keywords. Dynamic Jahn–Teller effect; Mössbauer spectroscopy.

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1. Introduction

Any symmetrical non linear molecule having a degenerate orbital electronic state will distort to relieve the degeneracy. High spin Fe²⁺ ion with a ground term ⁵D splits under the influence of octahedral field to produce a low lying orbital triplet (⁵T_{2g}). This degeneracy is lifted by distortions of the ligands as a consequence of Jahn–Teller effect. There are only a few reports [1–6] on such distortions in iron complexes as monitored by Mössbauer spectroscopy. This is mainly due to very low Jahn–Teller energy (E_{JT}) of Fe²⁺ ion. Though EPR is a better technique for probing Jahn–Teller systems this study is made difficult by the non Kramers nature of the Fe²⁺ leading to fast electron relaxation.

Some of the best documented systems in the literature are those of Tanaka *et al* [5]. They have measured the Mössbauer spectra of normal spinels such as FeCr₂O₄, FeV₂O₄ and FeAl₂O₄ in the temperature range of 77 K to 300 K. The Fe²⁺ ion in these lattices are found to exhibit co-operative Jahn–Teller distortions. These spinels in cubic phase have a perfect cubic symmetry around iron and so there is no electric field gradient due to ion distribution resulting in a single Mössbauer line; however, in tetragonal phase the large electric field gradient due to lattice and valency contributions resulted in the appearance of a quadrupole split doublet.

The first reported evidence for the distortion expected of a tetrahedral *d*⁶ configuration comes from tetrahedral tetraethylammonium tetrachloroferrate (II) [6]. The authors have correlated the temperature dependent quadrupole coupling constant to the *E_g* level splitting through an empirical relationship derived for tetrahedral symmetry. Similar kind of

relationship including spin-orbit coupling and covalency effect is available in the literature [7].

A complete theoretical description of the Jahn-Teller effect for the case of the ground E and T terms have been provided by Bersuker *et al* [8] who have theoretically simulated the Mössbauer spectra under linear approximation as well as second order approximation. Under second order approximation a theoretical simulation resulting in a six line pattern having peculiar intensity pattern was reported [8]. But so far there is no experimental evidence of such a spectral pattern due to the influence of Jahn-Teller effect in high spin Fe(II) systems even though such patterns have been observed in the rare earth transition metal ions [9]. Reports say that such a spectrum could only be observed in dilute systems with paramagnetically isolated metal ions [8].

Here we report our findings on the Mössbauer spectral studies of Fe(II) ion encapsulated in a macrocyclic N_6 cage ligand in a highly distorted octahedral environment revealing the presence of dynamic Jahn-Teller distortion. It is necessary to remark that we have noticed the presence of such Jahn-Teller distortion in the same type of N_6 cage ligands bonded to Cu(II) and Ag(II) ions as proven by EPR studies [10-13].

2. Experimental details

The compound $[\text{Fe}(\text{di}(\text{amH})\text{-sar})](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ where $\text{di}(\text{amH})\text{-sar} = 1,8$ diamino 3,6,10,13,16,19-hexaza bicyclo (6,6,6) icosane was prepared by using the reported procedures [14,15]. The compound was deposited in the form of clusters of thin nearly colourless or pale green tablets. The crushed solid can be handled in air for short periods of time without appreciable oxidation to Fe(III).

All Mössbauer measurements were done in a Canberra S-100 Mössbauer spectrometer fitted with a Wissel constant acceleration drive. The spectrum was recorded using 512 channels with a multichannel analyser. The source was $^{57}\text{Co}/\text{Pd}$ (Amersham 50mCi). All velocity calibrations were done by using α -iron foil as the standard. The isomer shift values are reported with respect to metallic iron. Variable temperature measurements were done using an Oxford MD-306 bath type cryostat with a variable temperature tail. Helium was used as the exchange gas in the sample compartment. The sample was mounted on the variable temperature tail, the temperature of which was controlled by an ITC-4 (Oxford) temperature controller. Rh-Fe was used as the temperature sensor which was calibrated in the temperature range from 4.2 K to 300 K. The accuracy of the controller was 0.1 K. All experiments down to 77 K were done using the liquid N_2 as the coolant. In the temperature range 4.2 K to 77 K liquid helium was used. All spectra were fitted by using a computer program MOSFIT with Lorentzian line shapes unless otherwise specified.

3. Results and discussion

The macrocyclic N-donor $[\text{M di}(\text{amH})\text{-sar}](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ forms a stable nearly trigonal prismatic cage complex having a MN_6 chromophore with various divalent metal ions such as Cu^{2+} , Fe^{2+} , Mn^{2+} , Cd^{2+} , Zn^{2+} , Co^{2+} , Mg^{2+} , Ag^{2+} revealing a D_3 symmetry [16-19]. The corresponding Cu^{2+} and Ag^{2+} are found to be Jahn-Teller active ions [10-13].

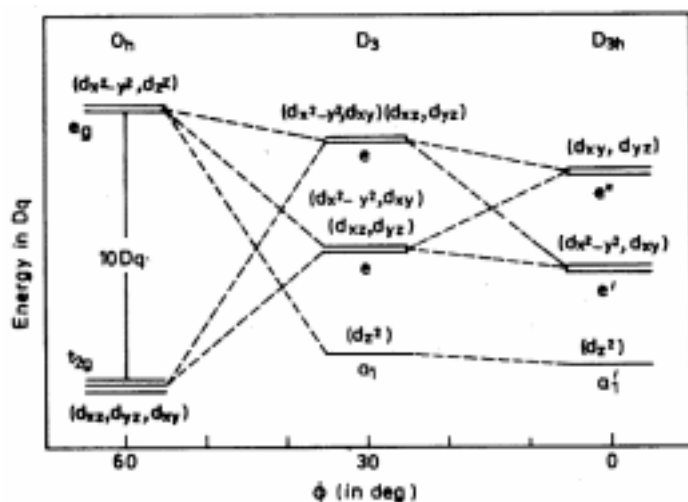


Figure 1. The electronic energy level diagram for the complex $\text{Fe}[\text{di}(\text{amH})\text{-sar}]^{4+}$ under different symmetries.

The single crystal X-ray structure of the $\text{Fe}[\text{di}(\text{amH})\text{-sar}](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ has been reported [16]. The energy level diagram showing the splitting of d -orbitals under different symmetries is given in figure 1. The crystal structure shows that it is distorted into a D_3 symmetry with an intermediate trigonal twist angle $\phi = 29^\circ$ and an average Fe–N bond distance of 2.18 to 2.24 Å. Such distortions are expected to produce the splitting of the ground ${}^5T_{2g}$ parent state to give an orbital singlet ground state. This Fe(II) cage complex exhibits a low spin or high spin state depending upon the nature of the apical substituent [20]. The reported temperature dependent magnetic moment from 4.2 K to 300 K [21] reveals it to be insensitive to temperature in the range 40–300 K. But below 40 K the magnetic moment falls by approximately $1 \mu_B$ (40 to 4.2 K) which is well below the spin only magnetic moment. This type of magnetic moment versus temperature behaviour is attributed to zero-field splitting (D) of essentially the orbital singlet ground state with the z component of the spin quantum number i.e. $M_s = 0$ lying the lowest. The magnetic moment fitting done by the use of a spin Hamiltonian with $S = 2$, gives values: $g = 2.2 \pm 0.01$, and $D = 6.8 \pm 0.1 \text{ cm}^{-1}$. The positive D value indicates the presence of the low lying $S_z = 0$ spin quantum state. The unusual absorption spectrum of $[\text{Fe}(\text{NH}_3)_2\text{-sar}]^{4+}$ in D_2O (pH = 4.5) which displays a weak band centered at ca. $11,000 \text{ cm}^{-1}$ was ascribed to the high spin quintet transition of origin (${}^5T_{2g} \rightarrow {}^5E_g$) split by the dynamic Jahn–Teller distortion of the excited state, suggesting the presence of a degenerate ${}^5T_{2g}$ ground state [20].

We have recorded the Mössbauer spectra of this compound in the temperature range of 4.2 K to 300 K. Throughout this temperature range the spectrum essentially consists of a quadrupole split doublet. An isomer shift of 1.3 mm/sec and the quadrupole splitting (ΔE_Q) of 3.39 mm/sec with a line width of 0.48 mm/sec characterized the spectrum at 4.2 K. The observed line width was slightly higher than the natural iron. All these spectral parameters indicate the high spin ground state of the ferrous ion. The expected Jahn–Teller effect due to the second order approximation giving a six line pattern with peculiar intensity distribution as predicted by Bersuker *et al* [8] was not observed in this case.

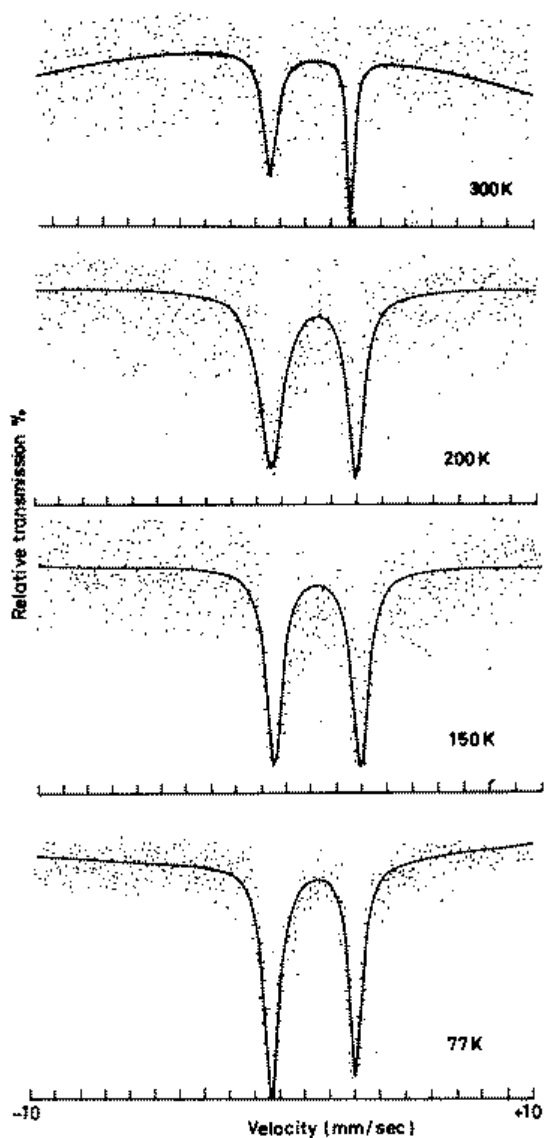


Figure 2. ^{57}Fe Mössbauer spectra of polycrystalline $\text{Fe}[\text{di}(\text{amH})\text{-sar}]^{4+}$ ion at different temperatures in the absence of an external magnetic field. The values of velocities are relative to natural Fe foil.

This may be due to the existence of a non magnetic $S_z = 0$ as the lowest energy state. This level will preferentially be populated at low temperatures which in turn will not produce any magnetic field at the site of the nucleus. Thus the net magnetic field at the site of the nucleus is very low which was further confirmed by a decrease in the magnetic moment at low temperature. A positive value for D again supports this argument.

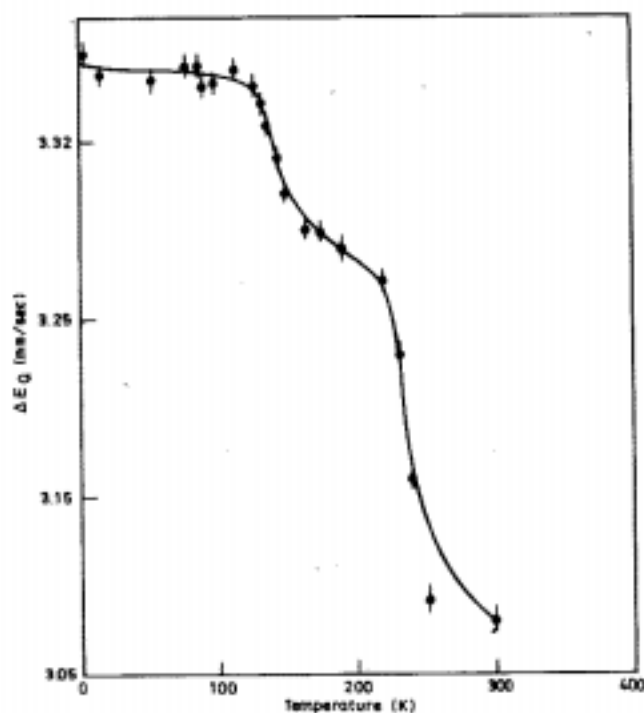


Figure 3. Variation of quadrupole coupling constant (ΔE_Q mm/sec) with temperature for $\text{Fe}[\text{di}(\text{amH})\text{-sar}]^{4+}$ ion.

The high temperature spectra need some comments. We have analysed the temperature dependence of quadrupole coupling constant, isomer shift and the line width in the temperature range of 4.2 to 300 K. Four representative spectra are given in the figure 2. The following observations are made from the plot of these parameters:

- (i) the quadrupole coupling constant decreases with increase in temperature as shown in figure 3 revealing a transition temperature of 140 K;
- (ii) the line width is the largest at the transition temperature of approximately 145 K (figure 4); there is also an increase in line width at temperatures higher than the transition temperature after an initial fall;
- (iii) the isomer shift generally decreases on increasing the temperature except for the presence of a maximum around the transition temperature (figure 5).

It is clear from all three parameters – quadrupole splitting, isomer shift and line width – that there is a definite transition temperature around 140–145 K. It may be noted that the spinels [5] have a high temperature cubic phase with a perfect cubic symmetry (no quadrupole coupling constant) and a low temperature tetragonal phase with a high electric field gradient, consequently leading to large quadrupole coupling constant. Even though we notice similar observations in the case of this macrocyclic iron complex, the kind of

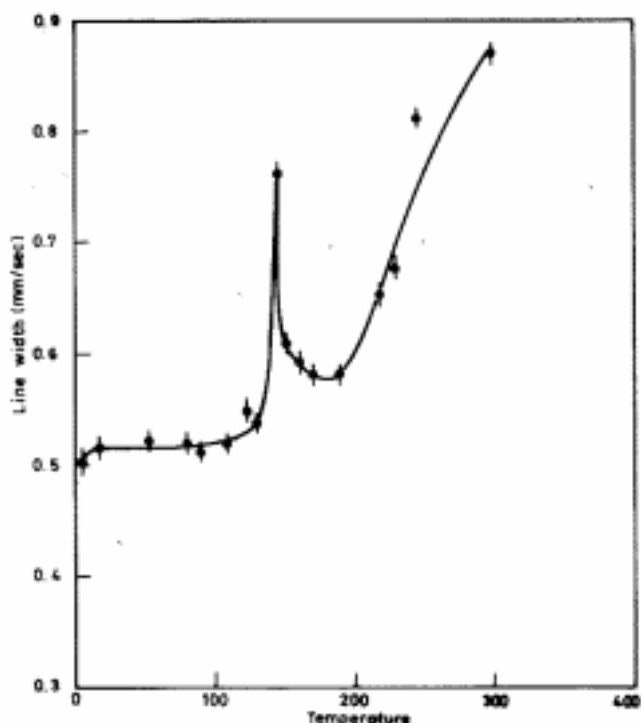


Figure 4. Variation of line width (FWHM mm/sec) as a function of temperature for $\text{Fe}[\text{di}(\text{amH})\text{-sar}]^{4+}$ ion.

drastic changes observed in the case of FeCr_2O_4 and FeV_2O_4 [5] is not seen here. It may be due to the fact that the molecule already has got a distorted D_3 symmetry and the Jahn–Teller stabilization energy is very small. In the plot of the ΔE_Q vs T shown in figure 3, we could see a distinct transition temperature region around 140 K at which the value of quadrupole coupling constant starts decreasing sharply; this could be explained by considering the molecule passing from one potential well to the other having a small energy barrier, as a manifestation of the dynamic Jahn–Teller effect. At this temperature, kT may be equal to E_{JT} ; hence at room temperature the frequency with which the molecules reorient between different structures is much faster than the frequency with which the electric field gradient direction changes. Thus the quadrupole coupling constant is reduced. But at low temperatures of the order of 140 K the reorientation frequency will be slower in favor of the structure with large electric field gradient and hence the ΔE_Q value increases. At temperatures lower than 140 K the structure of the molecule will be completely frozen out and it will be static in one potential well leading to almost constant ΔE_Q values as seen in figure 3. Moreover, the larger ΔE_Q at lower temperatures is indicative of the distorted structure.

It is interesting that the temperature dependent line width and isomer shift show similar kind of transition temperature but more distinctly as seen in figures 4 and 5. The increased line width values from 200 K to 300 K and reduced recoil free fraction are indicative of the dynamics in the molecule. The isomer shift vs temperature plot also shows an increase

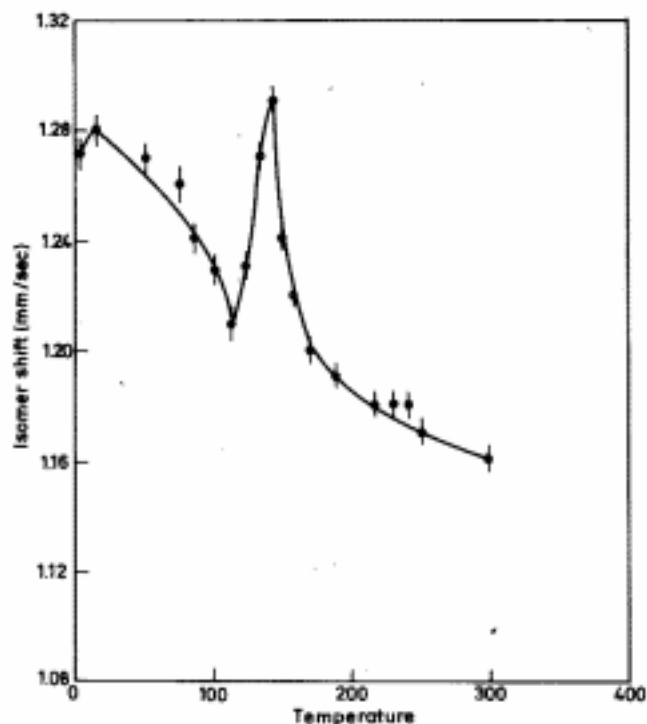


Figure 5. Variation of isomer shift (δ mm/sec) as a function of temperature for $\text{Fe}[\text{di}(\text{amH})\text{-sar}]^{4+}$ ion.

in the value at around 145 K and then decreases on further heating. All these plots are found to be similar to the earlier observations of the dynamic Jahn–Teller effect in the spinels, FeCr_2O_4 and FeV_2O_4 [5]. The exception is the line width. The line width plots in both FeCr_2O_4 and FeV_2O_4 are found to be maximum at the transition temperature and decreases on further heating. Thus we conclude that dynamic Jahn–Teller effect operates in the case of this cage complex although the clarity exhibited by spinels [5] is not found here. This may be due to the distorted D_3 symmetry of $\text{Fe}[\text{di}(\text{amH})\text{-sar}].(\text{NO}_3)_4.\text{H}_2\text{O}$ molecule as compared to the simple cubic symmetry of spinels at room temperature.

The high temperature spectral patterns need an additional explanation. From figure 2, it can be seen that at 300 K the doublet is clearly asymmetric; the low velocity component of the quadrupole doublet is not only broad but its amplitude is smaller than that of the other. But on cooling, the amplitude of the former increases with a concomitant decrease in linewidth. At 150 K the components of the doublet have equal intensities with almost similar linewidths. But around 77 K, the reverse trend sets in the amplitude. Such behaviour may not be ascribed to Goldanskii–Karyagin effect since the asymmetry is not present at all temperatures. Moreover, in the case of Goldanskii–Karyagin effect, asymmetry in general is expected to increase with the decrease of temperature. An alternative explanation of this observation may come from the Blum–Tjon’s theory of relaxation [22]. According to this theory, two different possibilities of fast relaxation exist, one in which the fluctuating magnetic field acts parallel to the quadrupole tensor axis and in another these

directions are perpendicular to each other. In the first case the high velocity component of the doublet becomes broadened with reduced amplitude at higher temperature. But in the second case it is the low velocity component that will have the property of larger linewidth and reduced amplitude at high temperatures. The second condition is satisfied in the case of $\text{Fe}[\text{di}(\text{amH})\text{-sar}]^{4+}$ and hence we suggest that the fluctuating magnetic field is approximately perpendicular to the quadrupolar tensor axis. This effect could be attributed to the spin lattice relaxation at high temperature due to spin orbit coupling from the 5D ground state of high spin Fe(II). Finally, a decrease in ΔE_Q , an increase in linewidth followed by a decrease in isomer shift at high temperatures above ~ 230 K may well represent a dynamically active Jahn–Teller effect though no quantitative explanations can be offered.

4. Conclusion

Mössbauer spectroscopy has been used to probe the dynamic Jahn–Teller effect in Fe(II) system having a D_3 symmetry which has a very small E_{JT} value. The variable temperature Mössbauer spectroscopy also gives evidence to the direction of the quadrupole tensor with respect to the magnetic field. These two were found to be perpendicular to each other in the case of $\text{Fe}[\text{di}(\text{amH})\text{-sar}](\text{NO}_3)_4 \cdot \text{H}_2\text{O}$. No hyperfine split six line pattern could be observed in the spectrum because of the fact that at low temperatures the low lying $M_s = 0$ of the z component of the spin quantum number is substantially populated.

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References

- [1] F S Ham, *Phys. Rev.* **160**(2), 328 (1967)
- [2] F S Ham, W M Schwarz and M C M O'Brien, *Phys. Rev.* **185**(2), 548 (1969)
- [3] P Bonville, C Garcin, A Gerard, P Imbert and G Jehanno, *Phys. Rev.* **B23**(9), 4310 (1981)
- [4] K K P Srivastava, *Phys. Rev.* **B29**(9), 4890 (1984)
- [5] M Tanaka, T Tokoro and Y Aiyama, *J. Phys. Soc. Japan* **21**(2), 262 (1966)
- [6] T C Gibb and N N Greenwood, *Tech. Rep. IAEA (Vienna)* **50**, 6989 (1966)
- [7] R Ingalls, *Phys. Rev.* **A133**, 787 (1964)
- [8] I B Bersuker, S A Borshch and I Ya Ogurtsov, *Phys. Status Solidi*, **B59**, 707 (1973)
- [9] O A Yakovleva, *Hyperfine Interactions* **56**, 1503 (1990)
- [10] T K Kundu and P T Manoharan, *Chem. Phys. Lett.* **241**, 627 (1995)
- [11] T K Kundu and P T Manoharan, *Chem. Phys. Lett.* **264**, 338 (1997)
- [12] T K Kundu and P T Manoharan, *Mol. Phys.* (communicated)
- [13] T K Kundu, R Bruyndonckx, C Daul and P T Manoharan, *Inorg. Chem.* (in press)
- [14] J M Harrowfield, G A Lawrance and A M Sargeson, *J. Chem. Educ.* **62**, 804 (1985)

- [15] R J Geue, T W Hambley, J M Harrowfield, A M Sargeson and M R Snow, *J. Am. Chem. Soc.* **106**, 5478 (1984)
- [16] P Comba and A M Sargeson, L M Engelhardt, J M Harrowfield, A H White, E Horn and M R Snow, *Inorg. Chem.* **24**, 2325 (1985)
- [17] P Comba and A M Sargeson, *Aust. J. Chem.* **39**, 1029 (1986)
- [18] P Comba and A M Sargeson, *Phosphorous and Sulphur* **28**, 137 (1986)
- [19] S J Strach and R J Bramley, *Chem. Phys.* **88(12)**, 7380 (1988)
- [20] L L Martin, K S Hagen, A Hauser, R L Martin and A M Sargeson, *J. Chem. Soc. Chem. Com.* 1313 (1988)
- [21] L L Martin, R L Martin, K S Murray and A M Sargeson, *Inorg. Chem.* **29**, 1387 (1990)
- [22] M Blume and J A Tjon, *Phys. Rev.* **165(2)**, 446 (1968)