Electron Spin Resonance and Optical Spectroscopic Studies on Cu^{2+} and Co^{2+} in $Cs_2[Zn(N_3)_4]$

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The e.s.r. spectra of crystalline powders of $Cs_2[Zn(N_3)_4]$ containing up to 0.2 mol % of either Cu^{2+} or Co^{2+} have been studied at *Q*- (34 GHz) and *X*-band (9.2 GHz) frequencies at temperatures down to 2 K. Comparison with electronic reflectance spectra at 77 K indicates that in a dehydrated form, the Cu^{2+} ion occupies the zinc site but with compressed tetrahedral geometry. As crystallized however, the crystals contain water and it is suggested that in this case the Cu^{2+} co-ordination is trigonal bipyramidal, having one water molecule in the equatorial plane. For Co^{2+}, optical spectra indicate a distorted tetrahedral geometry and in the e.s.r. spectra the major component is consistent with, but not diagnostic of, this. At least two other minor e.s.r. subspectra are also observed.

The co-ordination of the azide ion has not been extensively studied. The crystal structure of $Cs_2[Zn(N_3)_4]$ [1] and its vibrational spectra [2] have been reported and it was of interest to study the sites occupied by other metal ions introduced into this lattice. It was anticipated that divalent ions would substitute for zinc, which in the parent compound, resides in a distinctly distorted tetrahedral site.[1] In this paper we report the e.s.r. and optical spectra of Cu^{2+} and Co^{2+} in $Cs_2[Zn(N_3)_4]$.

Experimental

Caesium azide (CsN_3) was prepared by metathetical reaction of Cs_2CO_3 with highly concentrated humid hydrazoic acid (HN_3) in a specially designed generator.[3] Zinc oxide was added in portions and in the presence of HN_3 to give a Zn:Cs mole ratio of 1:5. The solution was warmed to 40 °C, filtered and to it was added a small quantity of an aqueous copper(II) sulphate or cobalt(II) nitrate solution. On cooling, the solution deposited crystals after several days. The maximum concentration of the impurity ions is *ca.* 0.2 mol % due to the low solubility of $Cs[Co(N_3)_3]$ and $Cu(N_3)_2$. As crystallized, the Cu^{2+}-doped compound is brown but *in vacuo* over phosphorus pentoxide it converts to a yellow anhydrous form with different optical and e.s.r. spectra. On exposure to moist air the yellow form reverts to a brown colour but the e.s.r. spectra show this to be different from the original compound. We shall refer to the first-formed brown compound as $Cs_2[Zn,Cu(N_3)_4]{\cdot}xH_2O$. We have no evidence for the presence of water in the cobalt-doped compound but it is possible that an octahedrally co-ordinated cobalt site involves co-ordinated water which is not easily removed.

Diffuse-reflectance spectra were measured using a Beckman DK 2A instrument with barium sulphate as reference. The sample was maintained at 77 K in a modified Oxford Instruments CF100 cryostat. E.s.r. measurements at temperatures down to 2 K were made on a Varian E12 instrument at *X* band (*ca.* 9.2 GHz) using a modified Oxford Instruments ESR 10 cryostat. For the copper compounds some additional *Q*-band (34 GHz) measurements were made at temperatures down to 90 K using a Bruker ER-200-D spectrometer with ER078 (38 cm diameter) magnet and ER5102QT low-temperature cavity. Spectra were recorded digitally (2 000 points) employing a Research Machines 380Z computer and simulations were made using the program EPRPOW kindly provided by N. D. Chasteen but with some modification by P. B.[4]

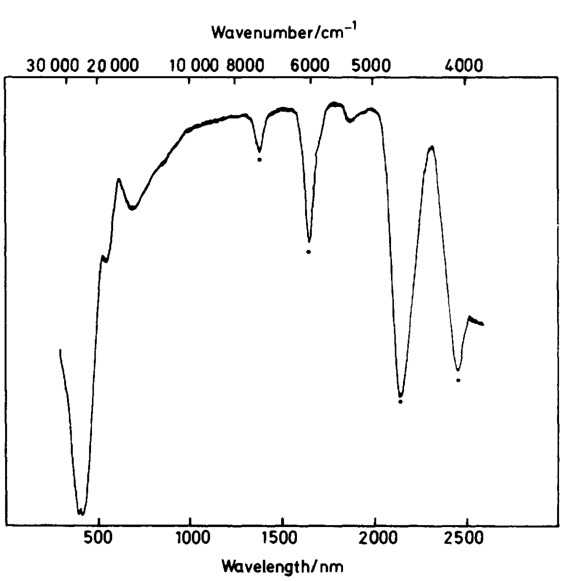

Figure 1. Reflectance spectrum of $Cs_2[Zn,Cu(N_3)_4]$ at 77 K. Bands marked with asterisks are azide vibrational overtones

Results

$Cs_2[Zn,Cu(N_3)_4]$.—The diffuse-reflectance spectrum of the yellow dehydrated material (Figure 1) is dominated by a strong doublet near 25 300 and 23 800 cm⁻¹. In view of its intensity in a crystal containing only 0.08 mol % of Cu^{2+} this feature must be of ligand-to-metal charge-transfer character. Apart from the overtones of the azide vibrations marked by the asterisks, the only other features detected are weak broad bands at 11 560 (shoulder), 14 500, and 18 500 cm⁻¹ which are presumably crystal-field transitions. Below 5 000 cm⁻¹ the intensity of the vibrational overtones precludes the observation of any weak crystal-field bands.

Table. E.s.r. parameters[a]

	$Cs_2[Zn,Cu(N_3)_4]$[b]		$Cs_2[Zn,Cu(N_3)_4]{\cdot}xH_2O$[c]				$Cs_2[Zn,Co(N_3)_4]$[d]
T/K	293	99	252	190	109	19	4.2
g_x	2.055	2.056		2.028	2.016	2.002	6.196
g_y	2.064	2.060		2.150	2.163	2.187	2.913
g_z	2.268	2.275	2.283	2.289	2.292	2.292	1.781
A_x	4	5		73	84	100	116
A_y	4	5		33	40	45	20
A_z	133	141	45	45	36	20	55
WG_x	2.4	2.1			1.2	1.5	
WG_y	2.6	2.1			1.1	1.3	
WG_z	1.9	1.7			0.8	1.5	
WL_x					1.0		
WL_y					0.8		
WL_z					0.75		
α					10	10	

[a] A = hyperfine splittings (10^4 cm^{-1}); WG = Gaussian linewidth and WL = Lorentzian linewidth contribution (mT); α = angle of non-coincidence between g and A tensors about z. [b] Parameters given at 293 K were used in simultaneous simulations at both X and Q band, with the exceptions of A_x, A_y, WG_x, and WG_y which only correspond to the Q-band simulation shown in Figure 2(*a*). They are the least-squares data which best fit the simulated spectrum to the Q-band experimental spectrum; the corresponding data for the X-band spectrum assumed slightly lower linewidths. Because of this slight inconsistency and lack of computing time, the data for 99 K [spectrum of Figure 2(*b*)] were not so rigorously found in so far as the X- and Q-band simulations, though satisfactory as judged by eye, were not simultaneously least-squares fitted by the computer. The differences along the z direction are regarded as quite reliable. [c] Data at 252 and 190 K estimated from spectra; other data as used in simulations of Figure 4. [d] E.s.r. parameters estimated from spectrum.

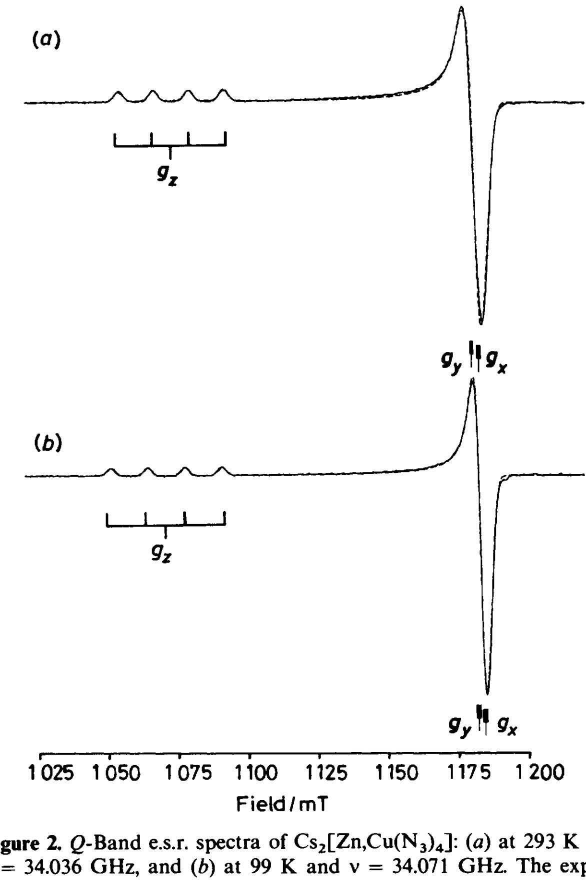

Figure 2. Q-Band e.s.r. spectra of $Cs_2[Zn,Cu(N_3)_4]$: (*a*) at 293 K and ν = 34.036 GHz, and (*b*) at 99 K and ν = 34.071 GHz. The experimental spectra (——) were simulated (----) using the parameters shown in the Table

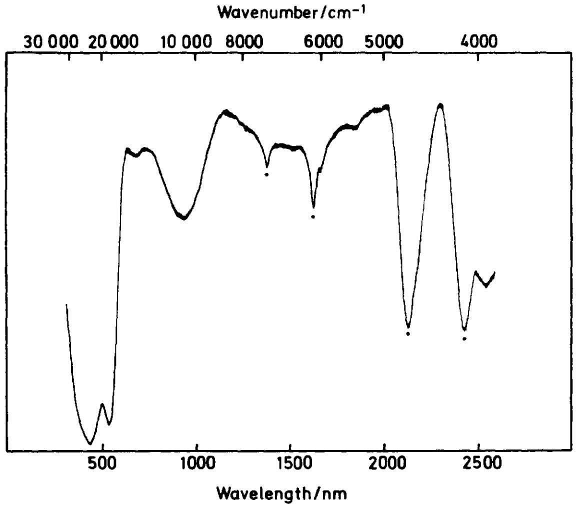

Figure 3. Reflectance spectrum of $Cs_2[Zn,Cu(N_3)_4]{\cdot}xH_2O$ at 77 K. Bands marked with asterisks are azide vibrational overtones

The e.s.r. spectrum of the yellow compound (Figure 2) clearly shows the presence of a single site occupied by a copper(II) ion in an axially symmetric ligand field. Computer simulations of the e.s.r. lineshapes at both X and Q band were used to derive the spin-Hamiltonian parameters shown in the Table, where it may be seen that the spectrum is both slightly rhombic and slightly temperature sensitive.

$Cs_2[Zn,Cu(N_3)_4]{\cdot}xH_2O$.—Both the e.s.r. and optical spectra of the brown hydrated compound are quite different from those of the anhydrous yellow species, although both techniques show variable proportions of minor subspectra characteristic of the anhydrous site.

In the optical spectrum of the brown species (Figure 3) the charge-transfer doublet is split further apart than in the yellow compound to give two distinct bands at 22 700 and 18 500 cm^{-1}. Two broad weaker bands are observed at 10 300 and 6 900 cm^{-1}.

The e.s.r. specta [Figure 4(*a*) in particular] clearly show the presence of some Cu^{2+} ions in sites characteristic of the yellow compound, but the majority of the signal is from a temperature-

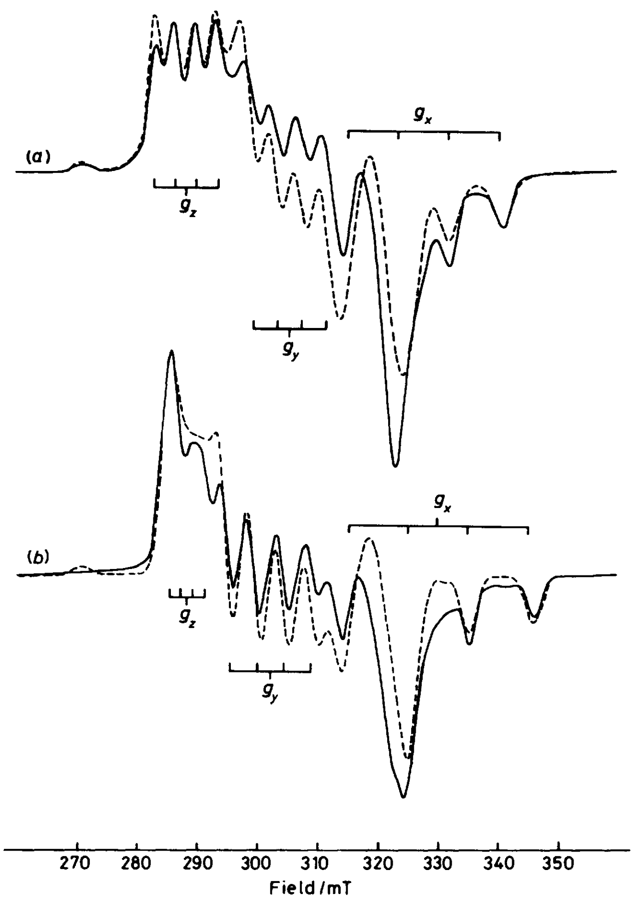

Figure 4. X-Band (9.255 GHz) spectra of $Cs_2[Zn,Cu(N_3)_4]\cdot xH_2O$: (*a*) at 109 K and (*b*) at 19 K. The experimental spectra (——) were simulated (– – –) using the parameters shown in the Table

dependent spectrum having rhombic g values. The relative proportions of the two sites were found to be dependent on the degree of grinding employed in powdering the sample. With light grinding *ca.* 15% of the copper could be attributed to anhydrous Cu sites; however, the Q-band spectrum then showed baseline oscillations typical of incomplete orientational randomization. Additional grinding substantially decreased these but the proportion of the signal from anhydrous sites increased to greater than 30%. This dehydration process could not be reversed by subsequent exposure to moist air, since although the solid then appeared deep brown and lost all trace of the axial e.s.r. signal from the anhydrous copper, the rhombic spectrum of the first-formed brown compound was not reproduced.

The rhombic spectrum of the hydrated copper site at 109 K may be reasonably well simulated assuming the presence of *ca.* 15% of the yellow compound [Figure 4(*a*)]. On cooling, the presence of the yellow compound becomes less obvious because the spectrum more easily saturates especially in the parallel region, as shown in Figure 4(*b*) in which the low-field 'bump' seems to have disappeared for this reason. The spectrum at 19 K and its simulation are shown in Figure 4(*b*); the spectrum at 4.2 K is essentially unaltered from this. The imperfect nature of the fit in the central region of these spectra could result from the presence of a third copper species, though equally it could also arise from inadequacies in the computer simulation. The Hamiltonian parameters used in the simulations are shown in the Table.

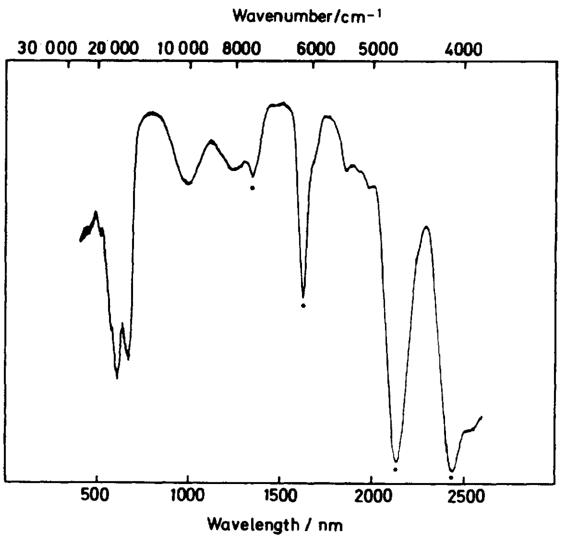

Figure 5. Reflectance spectrum of $Cs_2[Zn,Co(N_3)_4]$ at 77 K. Bands marked with asterisks are azide vibrational overtones

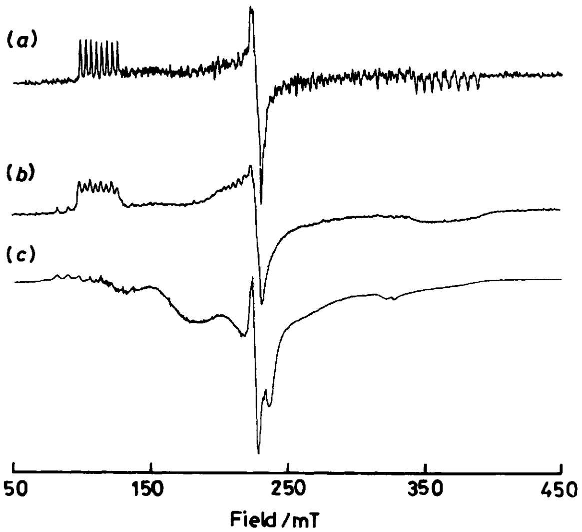

Figure 6. X-Band (9.255 GHz) e.s.r. spectra of $Cs_2[Zn,Co(N_3)_4]$: (*a*) at 19 K and 0.2 μW, (*b*) at 25 K and 0.2 mW, and (*c*) at 2 K and 20 mW

$Cs_2[Zn,Co(N_3)_4]$.—The reflectance spectra of the blue cobalt-doped compound differed slightly in detail from one batch of crystals to another, suggesting the presence of more than one site. A representative spectrum is shown in Figure 5.

No e.s.r. spectra could be recorded above *ca.* 25 K. At or below this temperature only X-band spectra could be obtained and these were characterized by three well resolved features each showing cobalt hyperfine structure. The dominant features were best shown by reducing the temperature and power to minimum levels and are typical of a $S' = \frac{1}{2}$ ground state; see Figure 6(*a*) where unfortunately the effects of inadequate grinding also are seen. The spin-Hamiltonian parameters taken from this spectrum are recorded in the Table. At higher temperatures, or at higher powers with the lowest temperature, this spectrum partially saturates; see Figure 6(*b*) and (*c*). Under such conditions other spectra are seen to be present but in the absence of a clear assignment these will not be discussed.

Discussion

The inverse linear relationship between the e.s.r. parameters $|A_{\parallel}|$ and $g_{\parallel}$ for variation of the total charge on a given ligand donor set around copper(II), *e.g.* CuN_4, is well established.[5] Similar relationships have been noted for planar copper(II) complexes with the electron-donating ability of ligands,[6] or the apical co-ordination of basic solvent molecules.[7] However, for a series of pseudo-tetrahedral complexes these effects were dominated by the correlation between $|A_{\parallel}|$ and $g_{\parallel}$ for the degree of twist from planar towards tetrahedral co-ordination. The $g_{\parallel}$ for the yellow copper azide studied here is significantly higher, while the $|A_{\parallel}|$ value is significantly lower, than that expected for a planar $[CuN_4]^{2-}$ donor set. Reference to the paper by Yokoi and Addison[8] establishes that these parameters are the co-ordinates of a point very close to the line associated with CuN_4 dipyrromethene complexes, and correspond to a dihedral angle of *ca.* 65°. Furthermore the $g_{\parallel}$ value is related by these authors to the lowest two *d–d* bands in the electronic spectrum and for $g_{\parallel} = 2.275$ we therefore predict bands close to 11 000 and 15 000 cm^{-1}. These are in good agreement with our experimental data for the yellow copper azide. Assuming the energy-level ordering to be that generally accepted[9] for $[CuCl_4]^{2-}$, the relative energies of the *d* orbitals are $d_{xy} > d_{xz},d_{yz} > d_{x^2-y^2} > d_{z^2}$, and the observed bands are assigned as 11 560 ($d_{xy},d_{yz} \longrightarrow d_{xy}$), 14 500 ($d_{x^2-y^2} \longrightarrow d_{xy}$), and 18 500 cm^{-1} ($d_{z^2} \longrightarrow d_{xy}$), all three of which are allowed when spin-orbit coupling is included in D_{2d} symmetry. We conclude that for the yellow compound the copper substitutes for the normal zinc site, which itself departs somewhat from tetrahedral symmetry,[1] but quite naturally distorts that site by compression a little less than one third of the way towards planar. Comparison may be made with a recent study on $[CuCl_4]^{2-}$ in $Cs_2[Zn,CuCl_4]$ and other hosts[10] which emphasized how the tendency of Cu^{2+} to seek a planar environment may be balanced by the lattice effects of a tetrahedral hole in the host structure. Our lower *g* values and higher energy electronic transitions indicate that, relative to the halide site in $Cs_2[Zn,CuCl_4]$, the pseudo-halide site in $Cs_2[Zn,Cu(N_3)_4]$ more readily distorts away from tetrahedral on substitution by the copper(II) ion.

The nature of the brown copper azide compound is indicated by the fact that it is formed by crystallization from an aqueous solution, but subsequently quite readily loses water to form the yellow compound. There is no *X*-ray crystallographic, analytical, infrared, or Raman evidence that water is present in the host compound $Cs_2[Zn(N_3)_4]$,[1,2,11] in related compounds $M_2[Zn(N_3)_4]$ (M = K or Rb),[11] or in the cobalt-doped compound $Cs_2[Zn,Co(N_3)_4]$.[12] The presence of water therefore, together with the Jahn–Teller requirement for the copper(II) ion to avoid tetrahedral co-ordination either by assuming a square arrangement or a co-ordination number greater than four, reasonably leads to the proposal that water is actually a ligand to copper(II) in this brown compound. This proposal is supported by the e.s.r. spectra. At the lowest temperature, one of the *g* values is almost 2.000 which is consistent with a d_{z^2} ground state which would be appropriate for a trigonal bipyramidal geometry in which one water molecule has entered the co-ordination sphere. The *g* tensor is not axial, however, implying that such water would lie in the equatorial plane, rather than on the axis. Tyagi *et al.*[13] have recently described a CuN_5 chromophore with a rhombic *g* tensor in which NH_3 similarly has entered the equatorial plane. Such a geometry, with two modes of azide co-ordination, would also account for the observation of two charge-transfer bands in the optical spectrum (Figure 3).

As the temperature is raised two observations may be noted. First, all components of the *g* and *A* tensors change until, at the maximum temperature for which we have a resolved spectrum (190 K), the 'unique' axis of *g* has rotated through 90° though the *g* tensor is now even further from axial. The largest *A* component is not along this new direction as it would be if the ground state were purely $d_{x^2-y^2}$ and we assume now a very strong mixing between d_{z^2} and $d_{x^2-y^2}$. The most rapid part of this e.s.r. spectral change occurs in the region between 60 and 110 K. Second, at the higher temperatures there is a rapid loss of resolution due to line broadening and loss of hyperfine structure such that above 190 K it is no longer possible to assign three *g* values. No definite proposal can be made for these changes on the e.s.r. evidence alone but we assume them to be structural in nature and possibly, at the higher temperature, fluxional also.

The reflectance spectrum of the cobalt-doped crystals (Figure 5) is typical of a distorted tetrahedral species although it is often difficult to distinguish co-ordination geometries of cobalt(II) from reflectance spectra alone. The e.s.r. spectra clearly show evidence of high-spin cobalt(II) in more than one site. The spin-Hamiltonian parameters of the dominant spectrum, shown in Figure 6(*a*), are similar to those reported for a pseudo-tetrahedral symmetry, slightly distorted in the case of a CoN_2O_2 centre reported by Horrocks *et al.*[14] and very distorted in the case of a $CoNSCl_2$ centre reported by Desideri *et al.*[15] They are thus readily assigned to the zinc site. However one frequently sees either much smaller hyperfine structure or no hyperfine structure at all from tetrahedral cobalt(II)[15,16] and since the Hamiltonian parameters in question are also not unlike those of $[Co(acac)_2(H_2O)_2]$ (acac = acetylacetonate; tetragonally elongated octahedron)[17] or cobalt(II) in zinc formate[18] (tetragonally compressed octahedron), or cobalt(III) plus a hydrogen atom in sapphire[19] (trigonal prism), they cannot be regarded as definitive for this geometry.

Acknowledgements

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References

1 G. F. Platzer and H. Krischner, *Z. Kristallogr.* 1975, **141**, 363.

2 W. Dobramysl, H. P. Fritzer, L. Harland, and S. F. A. Kettle, *Spectrochim. Acta, Part A*, 1977, **33**, 221.

3 B. Kolbesen, Diplomarbeit, Technische Universitat, Graz, 1967.

4 P. Beardwood, Ph.D. Thesis, University of London, 1983.

5 J. Peisach and W. E. Blumberg, *Arch. Biochem. Biophys.*, 1974, **165**, 691.

6 H. Yokoi and T. Kishi, *Chem. Lett.*, 1973, 749.

7 J. I. Zink and R. S. Drago, *J. Am. Chem. Soc.*, 1972, **94**, 4550.

8 H. Yokoi and A. W. Addison, *Inorg. Chem.*, 1977, **16**, 1341.

9 J. Ferguson, *J. Chem. Phys.*, 1964, **40**, 3406.

10 R. J. Deeth, M. A. Hitchman, G. Lehmann, and H. Sachs, *Inorg. Chem.*, 1984, **23**, 1310.

11 W. Dobramysl, H. P. Fritzer, and S. F. A. Kettle, *Spectrochim. Acta, Part A*, 1975, **31**, 905.

12 W. Neissl, Diplomarbeit, Technischen Universitat, Graz, 1980.

13 S. Tyagi, B. Hathaway, S. Kremer, H. Stratemeier, and D. Reinen, *J. Chem. Soc., Dalton Trans.*, 1984, 2087.

14 W. DeW. Horrocks, jun., J. N. Ishley, B. Holmquist, and J. S. Thompson, *J. Inorg. Biochem.*, 1980, **12**, 131.

15 A. Desideri, A. A. G. Tomlinson, and J. B. Raynor, *J. Inorg. Biochem.*, 1980, **12**, 221.

16 A. Bencini, I. Bertini, G. Canti, D. Gatteschi, and C. Luchinat, *J. Inorg. Biochem.*, 1981, **14**, 81.

17 A. Bencini, C. Benelli, D. Gatteschi, and C. Zanchini, *Inorg. Chem.*, 1980, **19**, 3027.

18 H. Abe, *J. Phys. Soc. Jpn.*, 1977, **43**, 82.

19 B. F. Gachter, H. Blum, and Hs. H. Gunthard, *Chem. Phys.*, 1973, **1**, 45.

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