

JAHN–TELLER DISTORTIONS IN COPPER(II) COMPLEXES AS DETERMINED FROM ESR POWDER SPECTRA

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Received 2 April 1973

Revised manuscript received 15 June 1973

Cations $\text{Cu}(\text{ligand})_6^{2+}$ doped in lattices of non-cubic $\text{Zn}(\text{ligand})_6(\text{anion})_2$ are shown to have ESR powder spectra, corresponding with two types of cations, distorted octahedral and regular octahedral. Upon lowering of the temperature the number of distorted molecules increases. Despite of the non-cubic symmetry the results are essentially similar to single crystal observations and investigations on cubic lattices.

1. Introduction

During recent years the temperature dependence of ESR spectra of hexacoordinated Cu^{2+} -ions in cubic lattices has been discussed in terms of dynamic and static distorted octahedral ligand-field symmetry [1–5]. In magnetically diluted Cu(II) compounds the transition from dynamic to static distortion occurs gradually [3] in contrast with the transition in undiluted compounds [1].

We are studying such distortions in systems where the copper ion is surrounded by six large, monodentate neutral organic ligands, while the lattice symmetry of the host is non-cubic. To see whether the distortion and its temperature dependence vary with the type of the ligand and the anions, we are investigating a large number of copper(II) complexes, diluted in the corresponding powdered zinc(II) and cadmium(II) compounds, by means of ESR spectroscopy between

300 and 80°K. The ligands used contain $\text{S}=\text{O}$, $\text{C}=\text{O}$, $\text{N}=\text{O}$, $-\text{C}\equiv\text{N}$ or N donor sites, the anions are the non-

coordinating perchlorate and tetrafluoroborate ions.

In this paper we report the results obtained on two typical samples, namely Cu^{2+} in hexakis-(tetramethylene sulphoxide) zinc(II) perchlorate, $\text{Zn}(\text{TMSO})_6(\text{ClO}_4)_4$, and in hexakis-(N-methylimidazole) zinc(II) perchlorate, $\text{Zn}(\text{NMIz})_6(\text{ClO}_4)_2$. Results concerning the complete series of compounds will be reported in forthcoming publications.

2. Experimental

Hexakis-(tetramethylene sulphoxide)zinc(II) perchlorate and hexakis-(N-methylimidazole)zinc(II) perchlorate were prepared according to van Leeuwen [6] and Reedijk [7]. Before crystallization of the compounds a few per cent of Cu(II) perchlorate was added.

The compounds were checked for purity by zinc analyses and by recording their infrared spectra. The copper concentrations were not determined analytically, because of the large amount of zinc present.

ESR spectra of the powdered compounds were performed on Varian X- and Q-band instruments as described previously [8].

Simulation of the spectra was carried out with a computer program written by Venable [9]. It was modified by one of the authors by introducing a ratio factor for the contributions to the total intensity of the regular and distorted octahedral structures. The calculations were carried out on the Leyden University IBM 360/65 computer.

3. Results and discussion

At room temperature we obtained spectra of two species in X-band and Q-band for both compounds; i.e., consisting of an intense isotropic spectrum corresponding to an apparently regular octahedrally coordinated Cu^{2+} -ion and a very weak anisotropic spectrum, corresponding to a Cu^{2+} -ion in an axially distorted octahedral ligand field.

The spectra show hyperfine structure due to the copper nucleus. With compounds containing nitrogen-donor ligands, sometimes nitrogen superhyperfine splittings were observed.

On cooling of the sample the isotropic signal gradually disappeared, while the anisotropic signal grew in intensity. Our results are listed in table 1, while some characteristic spectra are given in fig. 1.

A Cu^{2+} -ion in a regular octahedral ligand field would have a 2E_g ground state. According to the Jahn-Teller theorem this state must split, resulting in a distortion of the octahedron. This leaves an orbitally non-degenerate ground state, which is ${}^2B_{1g}$ in the case of tetragonal elongation, this giving rise to an anisotropic ESR spectrum, with two g values [10, 11].

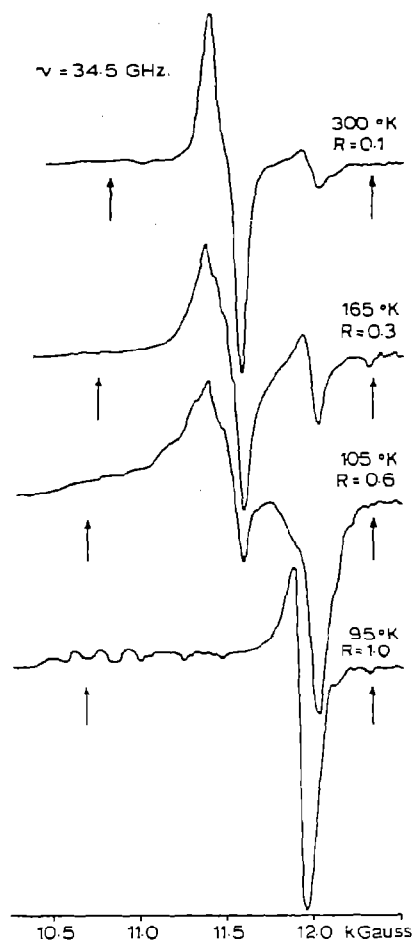


Fig. 1. Q-band ESR spectra of Cu^{2+} in $\text{Zn}(\text{NMIz})_6(\text{ClO}_4)_2$ at different temperatures. (Arrows indicate g_{\parallel} and $g_{\perp} = 2.0$ respectively.)

Table 1
ESR data of two Cu-dopes in Zn lattices^{a)}

	Cu in $\text{Zn}(\text{TMSO})_6(\text{ClO}_4)_2$			Cu in $\text{Zn}(\text{NMIz})_6(\text{ClO}_4)_2$		
	$T = 300^\circ\text{K}$	$T = 180^\circ\text{K}$	$T = 95^\circ\text{K}$	$T = 300^\circ\text{K}$	$T = 165^\circ\text{K}$	$T = 95^\circ\text{K}$
g (av.)	2.19 (1)	2.188(6)	u ^{b)}	2.150(3)	2.147(4)	u
A (av.) ^{c)}	42 (12)	33 (6)	u	48 (5)	55 (5)	u
g_{\parallel}	2.38 (1)	2.40 (1)	2.41(1)	2.277(2)	2.290(6)	2.307(2)
A_{\parallel}	133 (5)	128 (5)	125 (5)	171 (5)	170 (5)	165 (5)
g_{\perp}	2.075(6)	2.07 (1)	2.09(1)	2.061(3)	2.058(3)	2.065(3)
A_{\perp} or $A_{N,\perp}$	br ^{d)}	br	18 (7)	13 (4)	13 (4)	13 (4)
R	0.01	0.3	1.0	0.1	0.3	1.0

a) Uncertainty in the last digit in parentheses; b) u = unobserved; c) A in units 10^{-4} cm^{-1} ; d) br = unresolved.

As pointed out by Ham [11] there are several reasons for the appearance of an isotropic ESR signal.

Phonon assisted rapid hopping between the three different orientations of the tetragonal axis which causes motional narrowing, seems unlikely in this case because of the co-existence of the isotropic and anisotropic lines in our experiments.

At higher temperatures excited vibrational states of the complex itself become more populated. Then it is possible to pass over the energy barriers separating the three distorted configurations. The orientation of the tetragonal axis then varies many times within the time of one ESR transition, which makes it impossible to distinguish between the orientations; this causes an isotropic line to appear.

The thermal population of the excited vibronic singlet level also gives rise to an isotropic line.

Thus a mixed ESR spectrum is expected which consists of an anisotropic line from the vibrational ground state together with an isotropic line with average g - and A -value from the complexes in the excited vibrational states and/or the vibronic singlet level. On cooling, the population of the higher states decreases in favour of the lower states, in both cases. This results in an increase of the intensity of the anisotropic signal at the cost of that of the isotropic one.

Our results in table 1 reveal the values characteristic for oxygen and nitrogen donors respectively. The spectra were calculated by taking into account the contributions of the anisotropic and the isotropic signal by means of a ratio factor R . The total intensity then becomes:

$$R I_{\text{anisotropic}} + (1 - R) I_{\text{isotropic}}$$

In all cases the simulated spectra agreed well with those measured. One example is given in fig. 2.

From the results it can be concluded that our complexes are able to distort dynamically in such a way that they behave as regular octahedral in ESR spectroscopy, in spite of the lack of cubic crystal symmetry and notwithstanding the bulky size and the irregular orientation of the ligands.

It seems that the ligand-field symmetry in these compounds around the Cu^{2+} -ion is just determined by the position of the atoms in the first coordination sphere. In these aspects our results agree with those of Allen et al. [12] on Cu^{2+} surrounded by three bidentate ligands.

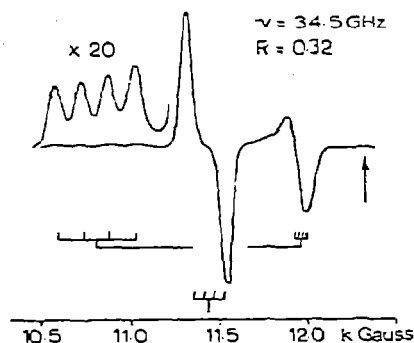


Fig. 2. Simulation of the Q-band ESR spectrum of Cu^{2+} in $\text{Zn}(\text{NMIz})_6(\text{ClO}_4)_2$ at 165°K ($R = 0.32$).

Acknowledgement

We are indebted to Professor P.J. Gellings (Twente University of Technology) for his stimulating interest in this study. Mr. P.G. van den Akker is thanked for doing the ESR measurements. The investigations were supported in part by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.). Part of the work was carried out during the time that one of the authors (J.R.) was at the Department of Chemistry of State University at Leyden.

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