above effects. As several conformations of different symmetries would permit d_π-electron delocalization, the D_{4h} symmetry of the solution complex indicated by the ESR spectra should be considered as an approximation of a more complex situation, at least at room temperature. We postpone a discussion of this question until a further more detailed study has been made.

Registry No. $CuCl_2$, 7447-39-4; $NiCl_2(py)_4$, 36829-43-3; $ZnCl_2(py)_2$, 6843-20-5; $CuCl_2(py)_2$, 6831-72-7; $CuCl_2(py)_3$, 73090-54-7; $CuCl_2(py)_4$, 73136-38-6.

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Nature of the Phase Transitions in $[(C_2H_5)_4N]_2MCl_4$ Complexes (M = Co, Cu)

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Single-crystal ESR spectra of undiluted $[(C_2H_5)_4N]_2MCl_4$ (M = Co, Cu) are reported. The spectra of the cobalt complex are quite similar to those of the zinc-doped complex. The spectra of the copper complex are temperature dependent, giving $g_\parallel = 2.29$ and $g_\perp = 2.16$ at room temperature, $g_\parallel = 2.10$ and $g_\perp = 2.29$ at intermediate temperature, and $g_\parallel = 2.46$ and $g_\perp = 2.10$ at 4.2 K. This behavior is interpreted as due to dynamic distortions of the pseudotetrahedral chromophores between two equivalent compressions. A similar behavior is suggested also for the cobalt complex.

Introduction

Transition-metal chloride complexes have attracted much interest as simple models to test theories for the interpretation of the electronic properties.[1-7] It has been found, however, that these simple compounds may have an extremely complicated behavior. Indeed they can exhibit a large variety of stoichiometries and structures, which result in a large variability in the observed spectral and magnetic properties of the complexes.[1,8]

Copper tetrachlorides are now well-known to show thermochromism as a consequence either of phase transitions or of gradual changes in the bond angles and lengths.[9] In the case of $(Et_4N)_2MCl_4$ complexes, phase transitions have been observed and studied also for some other metal ions[10-12] (M = Mn, Fe, Co, Ni, Cu, Zn). In particular it was reported that $(Et_4N)_2NiCl_4$ has a tetragonal structure at room temperature, the Co, Mn, and Zn derivatives being isomorphous.[13] ESR spectra of the cobalt-doped zinc complex have shown that the principal axes of the **g** tensor in the low-temperature phase are disordered, showing the presence of eight magnetically nonequivalent sites.[14] The low-temperature g_z axis is found close to the ⟨110⟩ direction of the room-temperature phase, showing that some rearrangements must have taken place in the chromophores. Similar results were obtained for the pure cobalt compound from magnetic susceptibility data[15] although the *g* values were found to be slightly different. Also the magnetic anisotropy data of the nickel complexes[16] showed abrupt changes indicative of large variations occurring in the crystal structure.

Since ESR spectra of cobalt can be recorded only at low temperature, below the phase transition, it was not possible to follow the dynamics of the phase transition. We have now recorded the ESR spectra of the similar, but not isomorphous, $(Et_4N)_2CuCl_4$ complex and wish to report here the relative results, together with new ESR data on the magnetically undiluted $(Et_4N)_2CoCl_4$, in order to give a more complete model of the nature of the phase transitions in this class of compounds.

Experimental Section

The $(Et_4N)_2CoCl_4$ and $(Et_4N)_2CuCl_4$ complexes were prepared according to the methods reported in the literature.[17]

The crystals of the copper derivative were grown by slow evaporation of concentrated solutions in water or ethanol. From both solvents, yellow crystals of poor quality are deposited, for the most part, in square-tabular form. Single-crystal diffractometer measurements, collected with a Phillips PW 1100 apparatus, using Mo Kα radiation, revealed a tetragonal cell with $a = b = 14.32$ (3) and $c = 12.70$ (2) Å. With these values the most highly developed faces were recognized to be (001). No attempts were done to determine the space group since there is evidence of large disorder in the cell.

For both compounds, the crystals were oriented on a Perspex rod for ESR measurements, according to the extinction properties of polarized light.

ESR measurements down to liquid-helium temperature were performed with the apparatus described previously.[18]

Results

Single-Crystal ESR Spectra of Pure $(Et_4N)_2CoCl_4$. The ESR spectra of single crystals of pure $(Et_4N)_2CoCl_4$, recorded at 4.2 K, were found to be qualitatively in agreement with those of the zinc-doped complex.[14] In particular several signals were observed for a particular orientation of the crystal in the static magnetic field. The lines are broad ($\Delta H_{pp} \simeq 400$ G) so that large overlap of the line occurs, preventing an accurate determination of the *g* values. The lowest *g* value, $g = 2.40$, is observed in the (001) plane, quite close to the ⟨110⟩ direction. Contrary to the value used for the calculation of the susceptibility, this value is quite close to that observed in the

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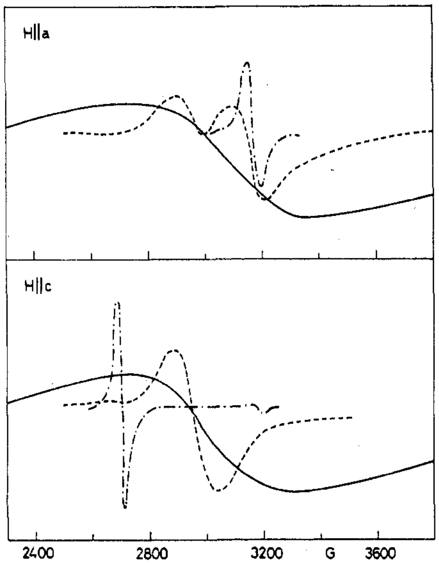

Figure 1. Single-crystal ESR spectra of $(Et_4N)_2CuCl_4$ at various temperatures recorded with the static magnetic field parallel to *c* (bottom) and to *a* (top): (—) 296 K; (---) 152 K; (-·-·-) 4.2 K. The spectra with the static magnetic field parallel to *b* are always equivalent to those of *a*.

zinc lattice, and also the principal direction appears to be within error identical with that of the zinc-doped complex.[14] Along ⟨110⟩ also the highest *g* value of 4.89 was observed, again suggesting that the actual *g* values of the undoped complexes resemble those of the doped ones. The angular dependence of *g* values is quite similar to that found for the zinc-doped complex.[14]

The components of the g^2 matrix were obtained by least-squares methods from only two rotations along the ⟨001⟩ and ⟨110⟩ axes, respectively. In the latter case, two sites, related by a tetragonal axis, are observed. This symmetry relation allowed us to consider the two series of signals as obtained from two independent rotations along orthogonal axes lying in the (001) plane and to evaluate two independent sets of g^2_{ii} values.[19]

Tensor diagonalization gave the following *g* values: $g_1 = 5.23$, $g_2 = 4.62$, and $g_3 = 2.35$, whose directions are close, within experimental error to those previously reported.[14]

Single-Crystal ESR Spectra of Pure $(Et_4N)_2CuCl_4$. Room-temperature ESR spectra show only very large bands ($\Delta H_{pp} \simeq 550$ G (parallel to *c*) and $\Delta H_{pp} \simeq 650$ G (orthogonal to it)). The ESR spectra agree with the tetragonal structure with $g_c = 2.29$ and $g_a = g_b = 2.16$. Two phase transitions have been described for this compound,[12] one in the range 260–205 K and the other in the range 205–130 K. For a temperature in the range of the second transition, two signals are neatly resolved in the (001) plane with extreme *g* values at 2.29 and 2.10, respectively (Figure 1). The angular dependence of the g^2 values in this plane is shown in Figure 2. No variation was observed parallel to *c*, i.e., $g_c = 2.29$, except a sharpening of the band. For temperatures below 130 K, with the field parallel to *c*, one intense signal is observed at $g = 2.46$, with residual signals at $g = 2.29$ and 2.10. At 4.2 K only the signal at $g = 2.46$, with some residual intensity at $g = 2.10$, is seen. The relative intensity of the two signals depends on the cooling mechanism. The high-field spectrum has a minimum intensity for a slow cooling. For the field parallel to ⟨100⟩ or ⟨010⟩, at the second phase transition, one intense signal at $g = 2.10$ is observed, together with a large signal at 2.29 and a small intensity signal at 2.46. At lower temperatures, only the two extreme *g* values are observed. These signals do not shift for a rotation along the *c* axis. The $g_\parallel$ and $g_\perp$ values correspond well to the extreme *g* values seen in polycrystalline powder spectra of the complex at liquid-helium temperature.

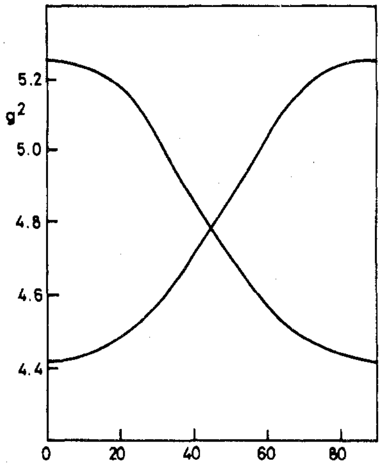

Figure 2. Angular dependence of the g^2 values in the (001) plane. The curve corresponds to the least-squares fit of the experimental points.

Discussion

The *g* values of $(Et_4N)_2CuCl_4$ at 4.2 K are typical of compressed tetrahedral copper(II) chromophores,[20] and in particular they compare well with those of $Cs_2(Cu,Zn)Cl_4$ complexes.[21] These considerations suggest that, although they were obtained from undiluted complexes, they are quite close to, if not identical with, the molecular values. Therefore a compressed tetrahedral copper coordination is well established for the low-temperature phase.

The spectra of the intermediate-temperature phase (205–130 K) reveal the presence of at least two sites, one with $g_a = g_c = g_\perp = 2.29$ and $g_b = g_\parallel = 2.10$ and the other with $g_b = g_c = 2.29$ and $g_a = 2.10$. The two sites are related by a tetragonal axis, so that a $g_\parallel$ value lies in the (001) plane. The fact that two sites are observed is indicative that intermolecular exchange interactions are not large enough to determine exchange narrowings of the signals;[22] therefore the *g* values must be considered as molecular values.

They are rather unusual for pseudotetrahedral copper(II) complexes[23] for which the observed pattern has always been $g_\parallel > g_\perp$. As such, they induce us to suspect that an averaging process between magnetically nonequivalent sites is operative. This has indeed been found to be the case for several octahedral copper(II) complexes with $g_\parallel < g_\perp$ in the solid state.[22] Since the signals of individual molecules are resolved, the averaging process must not be intermolecular, but intramolecular. In other words, the complexes are experiencing a dynamic rearrangement in this temperature range, which is fast on the ESR time scale. The comparison with the values of the low-temperature phase gives a simple model for this rearrangement. According to this, the site which has, e.g., $g_a = g_c = 2.29$ is experiencing a dynamic hopping between two compressions of the tetrahedron parallel to *a* and *c*, respectively. When *a* is the compression axis, the corresponding *g* value would be $g_\parallel = 2.46$, with $g_\perp = 2.10$ along *b* and *c*. When *c* is the compression axis, $g_\parallel = 2.46$ would be along *c* and $g_\perp = 2.10$ along *a* and *b*. The average along *c* and *a* would be 2.28, while g_b would be 2.10, in good agreement with the

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experimental values. Similar considerations apply to the other site.

Since these changes in the ESR spectra are concomitant with phase changes, they may be well accompanied by an onset of order in the Et_4N^+ cations. It is apparent that cooperative effects are occurring, which couple the distortions in one chromophore to those of the neighboring ones.

At higher temperatures only one very broad signal is detected in the (001) plane. It is not clear whether this is due to a broadening of the bands which overlap each other or to an averaging process operative in the (001) plane. It is worth mentioning that single-crystal-polarized electronic spectra do not show appreciable variation of the band maxima in the range 77–300 K, suggesting that the interconversion is slow on the time scale of the technique. In the absence of X-ray structural data it is not possible to go further with the analysis. However the comparison with the behavior of the $(Et_4N)_2CoCl_4$ derivative can be of help.

In the X-ray crystal structure of $(Et_4N)_2NiCl_4$ at room temperature, which is isomorphous to the cobalt analogue,[13] there is evidence of disorder of the tetraethylammonium cations, and also the thermal ellipsoids of the chlorine atoms are large if compared to the values seen for instance in Cs_3CoCl_5.[24] The site symmetry at the metal atom is D_{2d}, with the Cl–Ni–Cl angle around the S_4 axis of 106.83°, so that the chromophore can be described as an elongated tetrahedron. However the previous results by Carlin[14,15] and the present ones show that at low temperature the unique axis is found in the plane perpendicular to the room-temperature S_4 axis. We use here the term unique axis in a loose sense, since the spectra are actually orthorhombic, as was found also for the cobalt-doped zinc lattice.[14] What we suggest is that the room-temperature structure shows a dynamically distorted chromophore hopping fast between two equivalent distortions. At low temperature the rate of jumping between the two equivalent distinct potential energy minima is diminished until it is actually frozen out. In order to have an idea of the nature of the low-temperature structure, it is perhaps useful to consider the room-temperature structure of $(Me_4N)_2CoCl_4$,[25] which shows Cl–Co–Cl angles of 113 and 111°, indicating a slightly compressed chromophore. This would be in accord with the proposed mechanism by which the observed elongated tetrahedra of $(Et_4N)_2CoCl_4$ are actually due to rapid interconversion between two compressed tetrahedra.

In the case of copper the expected distortions from the tetrahedral angle are presumably larger. For comparison it may be mentioned that the Cl–Cu–Cl angles in Cs_2CuCl_4 are 131 and 127°.[26] The larger deviation may be responsible for the different unit cell structures at room temperature. When the hopping rate becomes sufficiently slow, the chromophore is frozen out into one of the two distortions. In so doing, it influences the nearest neighbors so that an ordered domain is formed. The dimensions of the domain depend on the freezing mechanism so that one or more signals of different intensity can be seen in the single-crystal spectra. This behavior has been observed also for some Jahn–Teller-distorted octahedral copper(II) chromophores.[22,27–29] It is however apparent that the distortions with the unique axis parallel to the room-temperature tetragonal axis must be more stable, so that in general this is the largest domain formed.

The irregular formation of the domains may be responsible for the large range of temperature along which the phase transition occurs. We have observed too a noteworthy hysteresis in the ESR experiment in the sense that the temperatures at which the changes in the spectra occur are largely different if they are recorded during cooling or warming.

Now we make a final comment on the g values of $(Et_4N)_2CoCl_4$. Contrary to the results of magnetic anisotropy experiments,[15] we find that the g values of the pure and zinc-doped cobalt complexes are substantially similar; the differences may be due to experimental uncertainty in our data. In particular the g_z value is identical with that seen in the zinc lattice so that the distortions of the tetrahedron must be extremely similar in the two lattices. Using a method we have developed for the calculation of the g values of high-spin cobalt(II) complexes[30] and the angular overlap parameters used by Horrocks for other $CoCl_4^{2-}$ chromophores,[31] we find a good agreement with the experimental data. The calculated g values are $g_1 = 5.08$, $g_2 = 4.26$, and $g_3 = 2.27$, on the basis of the geometrical coordinates of the $(Me_4N)_2CoCl_4$ structure, so that it can be assumed as reasonable that the frozen-out chromophores are similar in the Me_4N and Et_4N complexes.

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Registry No. $(Et_4N)_2CoCl_4$, 6667-75-0; $(Et_4N)_2CuCl_4$, 13927-32-7.

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