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Jahn–Teller Distortions of Tris(ethylenediamine)copper(II) Complexes

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ESR spectra between room and liquid helium temperature of a number of Cu(en)$_3^{2+}$ complexes have been interpreted on the basis of dynamic–static Jahn–Teller distortions. On this very same idea assignment of the electronic spectra has also been suggested which can well be operative for all of the complexes with crystallographic D_3 or T_h symmetries reported to date. The possibility of observing the two types of distortions, i.e., trans elongation or compression, has been discussed. From the temperature dependence of the ESR line width, the residence time of the complex in each potential well has been determined. Such a time has been found to be intermediate between the ESR and electronic time scales thus accounting for the experimental data.

Introduction

Jahn–Teller distorted copper(II) complexes have been investigated for many years[1-3] by a large number of different experimental techniques. The first complexes to be studied were of the hexakis(monodentate) type, such as Cu(H$_2$O)$_6^{2+}$ in different lattices, and several of them were in a trigonal site symmetry at room temperature. However it was early recognized that the trigonal field was not very important in the description of the ligand field, but rather distortions along the bond directions, determined by the strong vibronic coupling, were responsible for the observed electronic properties.

Matters have been different for tris(bidentate) complexes possessing a trigonal site symmetry. In this case in fact it was tempting to use the D_3 site symmetry in order to interpret electronic properties, mostly because the first studies have been made by electronic spectroscopy, which cannot discriminate between static and dynamic vibronic interactions. Piper and co-workers studied Cu(bpy)$_3^{2+}$[4] and Cu(en)$_3^{2+}$[5,6] (bpy is 2,2′-bipyridine and en is 1,2-ethylenediamine) and concluded, on the basis of the polarization properties, that the complexes are intrinsically trigonal in the solid. Against this interpretation however stands the fact that the required trigonal distortion is too large, far larger than that observed for the isomorphous cobalt(II) and nickel(II) complexes. Later other studies have been reported both on high-symmetry chromophores, such as Cu(OMPA)$_3^{2+}$ (OMPA is octamethylpyrophosphoramide),[7,8] and on low-symmetry chromophores, such as Cu(bpy)$_3^{2+}$ and Cu(phen)$_3^{2+}$ (phen is 1,10-phenanthroline), in monoclinic or triclinic crystals.[9,10] Whereas a trigonal model again was proposed for the former compound, its inadequacy was underlined for the latter compounds.

We have studied the Cu(en)$_3^{2+}$ complexes with various anions: Cu(en)$_3$SO$_4$ (I),[11,12] Cu(en)$_3$Cu(CN)$_3$ (II),[13] and (Cu,Zn)(en)$_3$(NO$_3$)$_2$ (III). It has been shown by a x-ray analysis that in I and III the copper atoms lie on a D_3 site symmetry,[14,15] while no structure report is available for II. We want to show how all of these complexes are distorted, yielding either elongated or compressed octahedra, and that in every case the electronic properties must be interpreted on the basis of a predominant "tetragonal" distortion superimposed on an essentially cubic situation.

Experimental Section

Preparation of the Complexes. Crystals of I and III were prepared from water solutions, while for II[13] pure ethylenediamine was used as a solvent. Single crystals were obtained by slow evaporation of the solutions. Weissenberg techniques confirmed that I and III were trigonal as described.[14,15] The crystals of I were prisms elongated along c, while those of III were plates parallel to the (100) face.

Optical Spectra. Single-crystal polarized electronic spectra of I in the range 4–300 K were recorded on a Cary 17 spectrophotometer equipped with an Oxford Instruments CF 100 continuous-flow cryostat for liquid helium. A Glan-Thomson prism was used as a polarizer.

ESR Spectra. ESR spectra were recorded on a Varian E-9 spectrometer operating at X-band frequency. Single-crystal spectra were recorded using a goniometer, rotating the crystal by means of a quartz or perspex rod. Low-temperature spectra were recorded with an Oxford Instruments ESR9 continuous-flow cryostat for liquid helium.

Results

Cu(en)$_3$SO$_4$. The single-crystal polarized electronic spectra of I at liquid-helium temperature, recorded parallel to the room-temperature c crystal axis[15] and orthogonal to it, are reported in Figure 1. They are quite similar to those previously recorded at higher temperatures,[11] except for some sharpening of the bands. The oscillator strength of the transitions however does not appear to have changed in this range of temperatures.

The room-temperature single-crystal ESR spectra show a slight anisotropy,[12,16] with $g_{\parallel} = 2.126$ and $g_{\perp} = 2.110$ and with $g_{\parallel}$ parallel to the trigonal axis. On lowering of the temperature a sudden change is observed at 180 ± 1 K to a completely anisotropic situation.[12] The number of signals for every crystal orientation increases, indicating the presence of three magnetically nonequivalent sites. Three mutually orthogonal rotations and a curve-fitting program, assuming a Lorentzian line shape for the ESR absorption, yielded the principal g values and directions of the three sites. The sites are related by the room-temperature symmetry elements. The g values, which are the same within error for all of the sites, are $g_1 = 2.053$, $g_2 = 2.134$, and $g_3 = 2.159$, and their orientations relative to the room-temperature crystal axes and to the bond directions[17] are reported in Figure 2. The low-temperature polycrystalline powder spectra are reported in Figure 3.

Cu(en)$_3$Cu(CN)$_3$ Polycrystalline powder ESR spectra of II at room temperature are quite similar to the low-temperature spectra of I and can be analyzed with $g_1 = 2.07$, $g_2 = 2.14$, and $g_3 = 2.17$. Lowering the temperature to 77 K affects the bandwidths but does not produce any other measurable effects (Figure 3).

(Cu,Zn)(en)$_3$(NO$_3$)$_2$ The room-temperature polycrystalline powder ESR spectra of III correspond to an isotropic g value of 2.139 and to a hyperfine coupling constant $A = 56 \times 10^{-4}$ cm^{-1}. The single-crystal spectra however show a small anisotropy, with the g value parallel to the c axis equal to 2.153 and $|A| = 68 \times 10^{-4}$ cm^{-1} and $g = 2.129$ and $|A| = 50 \times 10^{-4}$ cm^{-1} in the plane perpendicular to c. On lowering of the temperature an inhomogeneous broadening of the hyperfine components is observed, with the low-field band being the most broadened. Below 70 K the powder spectra become characteristic of a tetragonally elongated copper(II) complex, with $g_{\parallel} = 2.248$, $A_{\parallel} = -168 \times 10^{-4}$ cm^{-1}, and $g_{\perp} = 2.082$. No hyperfine splitting of the high-field component was observed (Figure 3).

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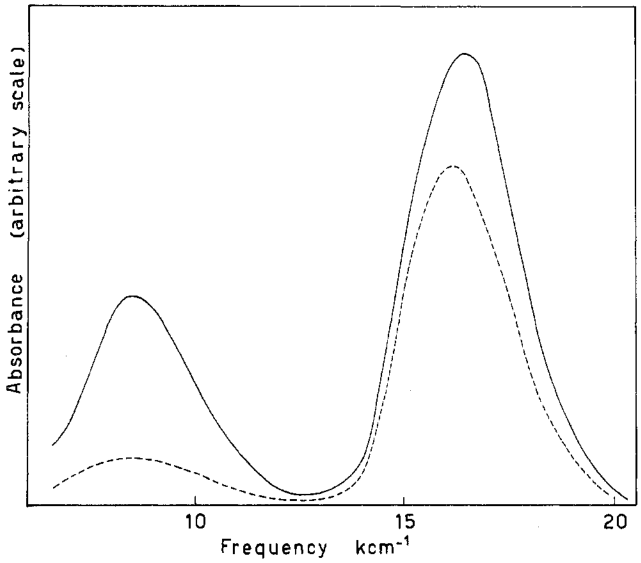

Figure 1. Single-crystal polarized electronic spectra of $Cu(en)_3SO_4$ at liquid helium temperature: ---, electric vector of the incident radiation parallel to *c* of the room-temperature cell; —, electric vector perpendicular to *c*.

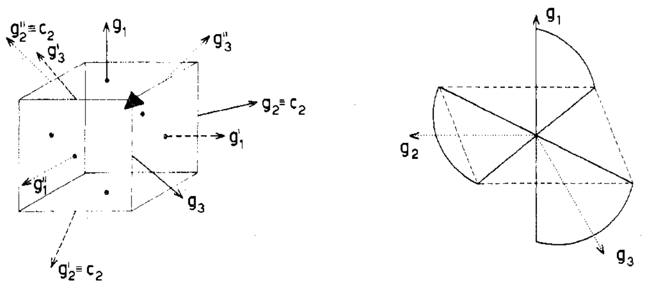

Figure 2. Left: relative orientations of the principal *g* directions of the three distorted sites, referred to the C_3 crystal axis. Right: orientations of the principal *g* directions within the CuN_6 chromophore.

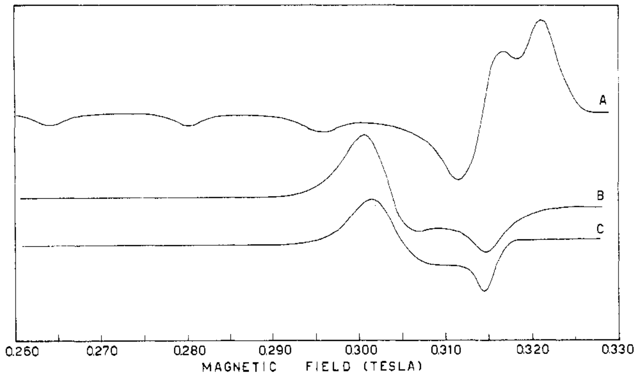

Figure 3. Polycrystalline powder ESR spectra of (A) (Cu,Zn)-$(en)_3(NO_3)_2$ at 4.2 K; (B) $Cu(en)_3Cu(CN)_3$ at room temperature; (C) $Cu(en)_3SO_4$ at 77 K.

Table I. Observed Peak-to-Peak (ΔH_{pp}) Widths of the Lowest Field Component of $g_{\parallel}$ and Calculated Reciprocal Average Lifetime between Jumps over the Potential Barrier (τ^{-1})[a]

T, K	$10^3\Delta H_{pp}$, T	$10^{-6}\tau^{-1}$, rad s^{-1}	*T*, K	$10^3\Delta H_{pp}$, T	$10^{-6}\tau^{-1}$, rad s^{-1}
4.2	3.7		56	4.8	127.5
25	3.75	7.5	62	5.1	162.5
35	3.8	15	65	5.5	206
45	4.1	47.5	71	6.0	263
51	4.3	70	75	6.5	316

[a] τ^{-1} was calculated by the equation of ref 34, assuming effective *g* values 2.446 and 2.036. γ was evaluated from the observed width at 4.2 K, assumed as the natural width of the transition.

The single-crystal spectra become in general quite complicated at low temperature, showing many signals for each orientation in the magnetic field. When the crystal was rotated around the *a* axis, the spectra were found to be symmetrical around the C_3 axis at room temperature. In particular signals are observed in an extreme position, corresponding quite closely to $g_{\parallel}$ of the powder spectra ($g_{\parallel} = 2.249$ and $A_{\parallel} = -168 \times 10^{-4}$ cm^{-1}), making angles of ±53 ± 1° with the C_3 axis. Since the room-temperature space group is $P6_322$[14] and the two copper atoms in the unit cell are related by a binary screw axis, it is expected that a Jahn–Teller distortion generates six magnetically nonequivalent sites in the low-temperature spectra. A situation similar to the present one has been found in cupric insulin single crystals.[18,19] The complexity and the symmetry of the spectra around the C_3 axis are in accord with this view. Due to the large number of overlapping signals in the high-field region it was not possible to perform a detailed analysis of $g_{\perp}$ and in particular it was not possible to detect any deviation of the $g_{\perp}$ values from axial symmetry. The analysis of the low-field region however showed that the angular variation of **g** and of **A** in the *ac* plane conforms to that expected on the basis of the above model.

The variation with the temperature of the bandwidths could be followed only for the lowest field component of $g_{\parallel}$, when the spectra were recorded with the magnetic field parallel to a direction corresponding to this extreme, since the other components are partially overlapped by the signals of other sites. The bandwidths in the range 4–75 K are reported in Table I. Above this temperature the signal becomes too broad to be measured and shifts to higher fields.

Discussion

A trigonal molecule possessing an E ground state can remove its electronic degeneracy by coupling to an E symmetry vibration.[20] A treatment has been recently provided for trigonal molecules which has shown how the formal results are not too different from those of octahedral symmetry.[21,22]

From the results of the previous section it is apparent that the $Cu(en)_3^{2+}$ ion is subject to large Jahn–Teller distortions. In III the distortion can reasonably be assumed as a tetragonal elongation ($g_{\parallel} > g_{\perp} \simeq 2.0$)[23] of the octahedron, whereas in I the problem is less straightforward since the paramagnetic centers are not diluted and therefore it cannot be established whether the observed *g* values correspond to the molecular *g* values. In case they do correspond (see Figure 2), a tetragonal compression of the octahedron is consistent with the experimental data.[23-26] Indeed, there is no electronic reason which favors one kind of distortion, i.e., elongation or compression of the octahedron, over the other.[27] Cooperative effects[28] must be important for I as is shown by the sudden change of the spectra corresponding to the temperature of a phase transition observed by calorimetric measurements[29] and MCD measurements.[30] These effects might be responsible for stabilizing the compressed chromophores as compared to the elongated ones. The possibility of stabilizing either distortion as a function of crystal forces has already been investigated for the $Cu(NO_2)_6^{4-}$ ions.[31] The hypothesis of a tetragonal compression requires that the cooperative Jahn–Teller effects split the trigonal room-temperature lattice into three lattices, a result confirmed by recent MCD measurements.[30] Within each lattice all of the paramagnetic centers are equivalent so that exchange interactions result in destroying the hyperfine structure but do not change the *g* values.[32] The fact that the lowest *g* values are met quite close to the Cu–N bond directions in I (see Figure 2) gives some support to this interpretation. Since the $g_{\perp}$ values are markedly different from axial symmetry, some additional distortion should be operative, which has been described as cis-distorted octahedral in similar copper(II) complexes.[25,33] The g_1 value is markedly larger than the value of 2.0023 expected for an unpaired electron in the d_{z^2} orbital.[23] The rhombic symmetry and the zero-point motion which makes the three equivalent Jahn–Teller distortions nonorthogonal could account for the large deviation.[34]

As an alternative explanation, the hypothesis suggested for some Cu(NO$_2$)$_6^{4-}$ and Cu(OH)$_6^{4-}$ complexes should be mentioned,[35,36] i.e., that an experimental set of g values consistent with a compressed octahedral geometry could actually be due to elongated octahedra coupled through an antiferrodistortive model.[37] Extension of the model to the present compound would suggest that exchange coupling might be present within each lattice only in the plane of the g_2 and g_3 directions, so that an average occurs between two magnetically nonequivalent copper sites whose elongation directions lie in this plane, more or less orthogonal to each other. It follows that g_2 and g_3 values are not any more the molecular g values, whereas g_1 corresponds to a molecular g value. If, for the sake of simplicity, the molecular **g** tensor is considered as having axial symmetry, the experimental g_1 value can be considered as a $g_\perp$ component, while the g values in the g_2g_3 plane would be

$$g_2^2 = g_\parallel^2 \cos^2 \gamma + g_\perp^2 \sin^2 \gamma$$

$$g_3^2 = g_\parallel^2 \sin^2 \gamma + g_\perp^2 \cos^2 \gamma$$

2γ being the angle made by the $g_\parallel$ directions of the two magnetically nonequivalent molecules; i.e., γ is the angle between the g_2 crystallographic direction and a $g_\parallel$ direction. By taking $g_\perp = g_1 = 2.053$ the preceding equations yield $g_\parallel = 2.236$ and $\gamma = 49°$, which sets the $g_\parallel$ direction quite close to the bond directions. Although this picture represents a chromophore distorted in a manner similar to III with comparable g values, there is no experimental proof in favor of any of the two models.

Also in the case of III the direction of $g_\parallel$ is quite close to the Cu–N bond directions. The observed angle to the room-temperature C_3 axis is 53 ± 1°, to be compared to the observed angle of 57° between the Ni–N bond directions and the C_3 axis.[14] The difference might be due to different geometrical parameters of the zinc-doped copper complex, but since the bidentate ligand seems to impose restrictions to the possible angular values, it is probable that the difference in angle reflects the lack of axial symmetry of the distorted chromophore, although the in-plane anisotropy could not be detected.

The temperature dependence of the bandwidths is a result of the dynamic Jahn–Teller effects, and it allows the evaluation of the height of the barrier separating the three potential wells. By use of the equation of Hudson[38] and the data of Table I it was possible to calculate the average lifetime between jumps. The values reported in Table I were calculated assuming the observed width at 4 K as the width in the absence of exchange. Assuming that the jumping rate follows the exponential law

$$\tau = \tau_0 \exp(\Delta/kT)$$

Δ, the activation energy for passing over the barrier,[39] can be evaluated as the slope of the least-squares straight line of Figure 4. The calculated value of 102 ± 2 cm^{-1} compares well with the values calculated for other strong Jahn–Teller coupled copper(II) ions.[40] The satisfactory exponential dependence of τ or T^{-1} suggests that the Orbach process[41] is the most important in inducing the transition by the absorption of a phonon.

The electronic spectra deserve some further comment. I and II show quite similar spectra with a band at ~1.6 μm^{-1} and a less intense one at ~0.8 μm^{-1}.[11,13] Spectra similar to the present ones are those of Cu(phen)$_3^{2+}$,[9,10] Cu(bpy)$_3^{2+}$,[4,10] and also Cu(NO$_2$)$_6^{4-}$;[42] III and Cu(OMPA)$_3^{2+}$ on the contrary show only one band at ~1.6 and at ~10 μm^{-1}, respectively.[7,43] The ESR data have now shown that for all of the cases where the x-ray determinations suggested site symmetries D_3 or T_h the copper ions are subject to strong Jahn–Teller coupling resulting in highly distorted chromophores.[11,24] Further, the above estimation of the average lifetime in the distorted potential wells shows that in every case the time scale of the visible photons is far shorter than the time required to jump over the barrier so that the electronic spectra are due to the distorted chromophore. Support for this view comes from the substantial insensitivity of the spectra to changes in temperature and the close similarity of the spectra of distorted chromophores to those of "high-symmetry" ones.[10]

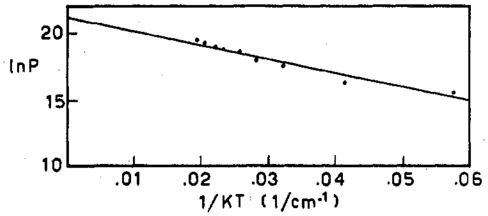

Figure 4. Plot of ln P against $(kT)^{-1}$. $P = \tau^{-1}$ is the reciprocal average lifetime between jumps over the potential barrier.

Regarding the difference of the spectra of Cu(en)$_3^{2+}$ in various environments, we feel that the 0.8-μm^{-1} band of I and II has to be assigned to the transition between the split components of the ^{2}E octahedral term by analogy with the spectra of the distorted complexes[10] while in the case of III this band has to be placed under the envelope of the high-frequency band. The reason for this may be that in the doped lattice Cu(en)$_3^{2+}$ can distort more easily, while in I cooperative effects prevent a large differentiation between the equatorial and axial bond lengths. Similar restrictions may be imposed by the rigid ligands 2,2′-bipyridine and 1,10-phenanthroline. It is worth noting that in diluted hexakis(monodentate) copper complexes which undergo Jahn–Teller distortions the ^{2}E split transition is assumed to be under the envelope of the high-frequency band.[36]

The observed polarization of the low-energy band of I has been assumed as a proof of the essentially trigonal ligand field experienced by the copper ion.[4] If the optical molecular axes were misaligned with respect to the bond axes, polarizations could be expected; for example, if the molecular axes are placed as in Figure 2, the squares of the molecular components parallel to the room-temperature trigonal axis are $0.67y + 0.33z$ and normal to it are $0.50x + 0.16y + 0.33z$. Regarding the actual directions of polarization, they depend on the vibronic functions of the ground and excited states. Until it is possible to obtain experimental vibrational structure on the bands it is not possible to discuss the polarization properties.

Conclusions

It is now apparent that in tris(bis chelate) copper complexes trigonal symmetry cannot be considered responsible for the spectral properties but that in every case Jahn–Teller distortions are operative which can lead to elongated (or compressed) octahedral stereochemistries. Since vibronic coupling determines distortions along the bond directions, the systems can be better described as tetragonally distorted. Of course it is largely a matter of taste to start from an octahedral or a trigonal description, since the results of vibronic coupling are the same in both cases.

The presence of two or one band in the electronic spectra of such a type of complexes must be related to the ease of distortion of the chromophore in the crystal.

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Registry No. I, 15613-88-4; II, 54927-31-0; $Cu(en)_3(NO_3)_2$, 32696-37-0; $Zn(en)_3(NO_3)_2$, 62571-30-6.

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X-Ray Photoelectron Spectra of Inorganic Molecules. 18.[1] Observations on Sulfur 2p Binding Energies in Transition Metal Complexes of Sulfur-Containing Ligands

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The S 2p binding energies of a series of nickel(II), palladium(II), and platinum(II) complexes of 1,2-ethanedithiol and benzenethiol occur between 163.5 and 161.5 eV. A comparison between data for the square-planar sulfur-bridged polymers $[Ni(SCH_2CH_2S)]_n$ and $[M(SPh)_2]_n$, where M = Ni, Pd, or Pt, and square-planar monomers of the type $Ni(SCH_2CH_2S)L_2$ and $M(SPh)_2L_2$, where L = $C_6H_{11}NC$, PMe_2Ph, or $^1/_2$ dppe, shows that the bridging sulfur atoms usually have S 2p binding energies which are higher than those of sulfur atoms in terminal thiol ligands (i.e., $R\text{–}S_b^- \gtrsim R\text{–}S_t^-$). For the ligand methionine, which contains a thioether moiety, coordination of the sulfur atom to platinum(II) causes a S 2p chemical shift of +1.2eV. However, in methionine complexes of cobalt(II), nickel(II), copper(II), and zinc(II), in which the sulfur atoms are not complexed, the S 2p binding energies (S $2p_{3/2}$ = 163.0 eV) are unchanged from that of the free ligand. Related data for molecules such as $[Fe(SCH_3)(CO)_3]_2$, $[Fe(SC_2H_5)(NO)_2]_2$ and a variety of dithiocarbamate– and dithiene–metal complexes have also been obtained. These results are discussed in the light of some recent XPS results for several sulfur-containing metalloproteins.

Introduction

As a result of our recent work on the x-ray photoelectron spectra of a wide variety of transition metal chlorides and bromides,[1,3,4] we have been able to demonstrate the feasibility of using this technique to differentiate halogen environments in bridging M–X bonds from those in terminal M–X bonds and halide ion X^-. In view of the isoelectronic nature of Cl^- and S^{2-}, we became interested in the possibility that thiol groups ($R\text{–}S^-$) which are bound to a metal center could be differentiated from the related unbound groups. This possibility is of considerable significance in the identification of metal binding sites in metalloproteins, as recent results of the XPS of cobalt and copper plastocyanins[5] and cytochrome *c*[6] have attested. In these two latter studies it was concluded that binding of sulfur (from cysteine or methionine residues) to the metal shifts the S 2p binding energy peaks by ~5 eV to higher energy. The magnitude of this shift is unexpectedly large in view of our previous findings concerning the Cl 2p binding energies of metal chlorides.[7] Although extensive investigations of the S 2p binding energies of organosulfur compounds have been published,[8] no systematic studies have been reported on the S 2p binding energies of stable metal complexes of thiol ligands. It seemed to us that such investigations were essential if conclusions concerning the 5-eV S 2p chemical shifts in plastocyanins and cytochrome *c* were to be substantiated. In the present paper we describe the results of our studies on the XPS of a wide variety of metal complexes of sulfur-containing ligands.

Experimental Section

Metal Complexes. Samples of the nickel(II), palladium(II), and