A Jahn-Teller active octahedral metal complex can adopt a distorted molecular structure, in which one axis of the octahedron is either elongated or compressed (Fig. 1) [1]. For quantum mechanical reasons, however, a Jahn-Teller elongated structure is overwhelmingly preferred in practice. For compounds of certain metal ions, notably copper(II), chromium(II) and manganese(III), the resultant structural distortion about the metal centre is severe, with the affected metal-ligand bonds being lengthened by 5-20%. While this is easily detected by structural methods, the direction of a Jahn-Teller distortion also has a great effect on the spectroscopic properties of a metal centre, since it also changes the ordering and occupancy of the metal $d$- atomic orbitals (Fig. 1).

Figure 1 Diagram showing the two possible Jahn-Teller distortions in an octahedral [CuL$_6$]$^{2+}$ complex, and the corresponding splittings of the $d$-energy levels within the copper atom.

Copper(II) compounds represent the best studied Jahn-Teller system [2]. Powder or single crystal X-ray structures of copper(II) compounds, and their EPR spectra, usually clearly demonstrate Jahn-Teller elongated geometries. However, a significant minority of these instead exhibit structural or spectroscopic data implying an “inverse” (i.e. compressed) or “quenched” Jahn-Teller structure. In fact, these apparent anomalies nearly always reflect disorder of a Jahn-Teller elongation over two or three of the unique axes in the molecule. Dynamic disorder of this type can only be detected by in-depth variable temperature diffraction, EPR or single crystal UV/vis experiments. Alternatively, a useful indication of hidden disorder in a powder or single crystal structure can be gained from a TLS analysis of its anisotropic thermal parameters [3]. Although this is easy to carry out using the PLATON program [4], among others, it seems to be rarely done in practise.

This problem is illustrated by [CuL$_2$][BF$_4$]; (L = 2,6-di[pyrazol-1-yl]pyridine), which we have studied in some detail (Fig. 2) [5-8]. At room-temperature, the distribution of Cu–N bond lengths in single crystals of this compound suggests an axially compressed structure along the N–Cu–N vector. However, these bond lengths are temperature-dependent, and gradually resolve themselves upon cooling to a more rhombic coordination geometry. The latter more obviously resembles the Jahn-Teller-elongated structure predicted from its low temperature EPR spectra [7].

Figure 2 View of the complex dication in the crystal structure of [CuL$_2$][BF$_4$]; at 150 K, showing the directions of its two Jahn-Teller disorder orientations; and the temperature dependence of its Cu–N bond lengths between 50-350 K. The lines represent the best fit of these data to a quantum mechanical vibrational surface.

Colour code: C = grey, N = blue, Cu = green

This temperature-dependence reflects dynamic disorder of the Jahn-Teller elongation in this compound, over the two directions indicated in Figure 2. This disorder is slowly frozen out upon cooling, only yielding the ‘true’ molecular structure of the compound at the lowest temperatures. Data like these can be fit to a quantum mechanical model that derives the potential surface for the vibration interconverting the two disorder orientations (Fig. 2) [8]. That gives useful information about the anisotropic crystal strain energies experienced by the molecules in the solid material.

Several copper(II) compounds with apparently anomalous structural or EPR spectra have been analysed in this way. In nearly every case this has led to revision of the original descriptions of the compounds, to static or dynamic disordered Jahn-Teller elongated structures (listed in [2]). However, there are several other such compounds with anomalous distributions of crystallographic metal-ligand bond lengths, whose structures would benefit from re-investigation [2]. Since this is predominantly a structural chemistry project, the Cambridge Crystallographic and
Inorganic Structural databases are invaluable sources of information. Most obviously, they facilitate the location of structurally unusual compounds for further study. The Inorganic Structural database is particularly useful here, in that it contains thermal parameter information that can be used to carry out a quick TLS analysis. It is also important to be able to search quickly and easily for close relatives of a compound under study, such as different salts of a particular complex cation. These can be an invaluable aid to interpretation of what can be quite complicated crystallographic and spectroscopic behaviour in a fluxional Jahn-Teller system.