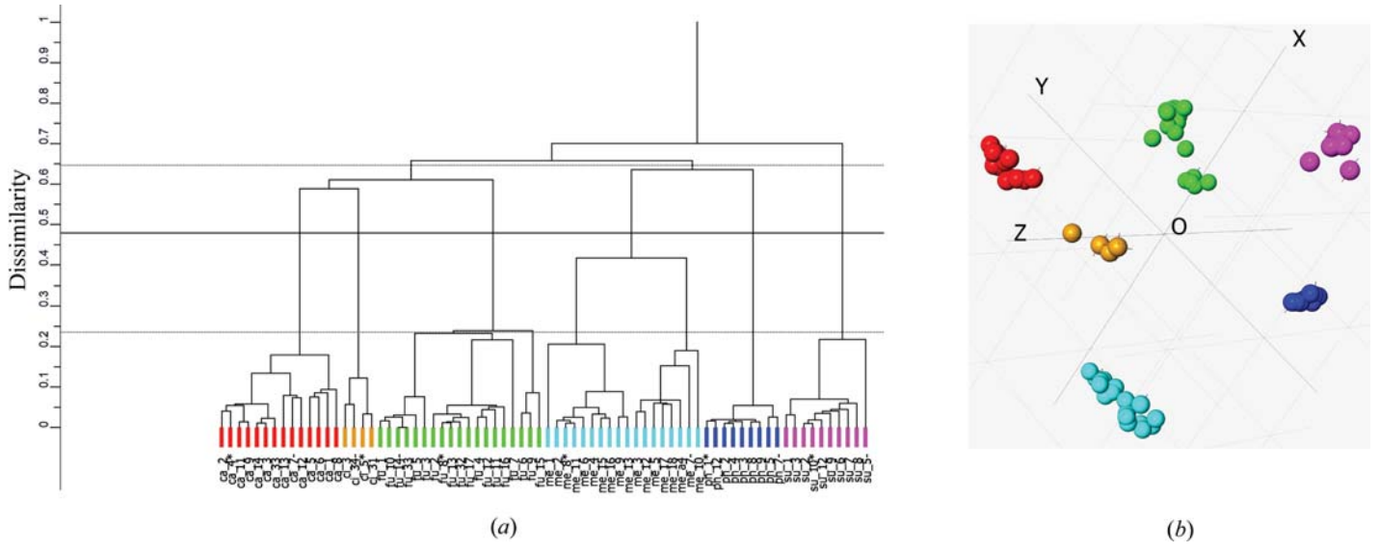

Figure 3.8.13
(*a*) The dendrogram generated from 74 Raman spectra without background corrections applied. Labelling from the left-hand side, the red samples are carbamazepine, the orange are cimetidene, the green are two forms of furosemide, the light blue is mefenamic acid, the dark blue is phenilbutazone and the purple at the right-hand side is sulfamerazine. (*b*) The MMDS plot. The sphere colours are taken from the dendrogram. This representation shows clearly discrete clusters in correspondence with those generated by the dendrogram.

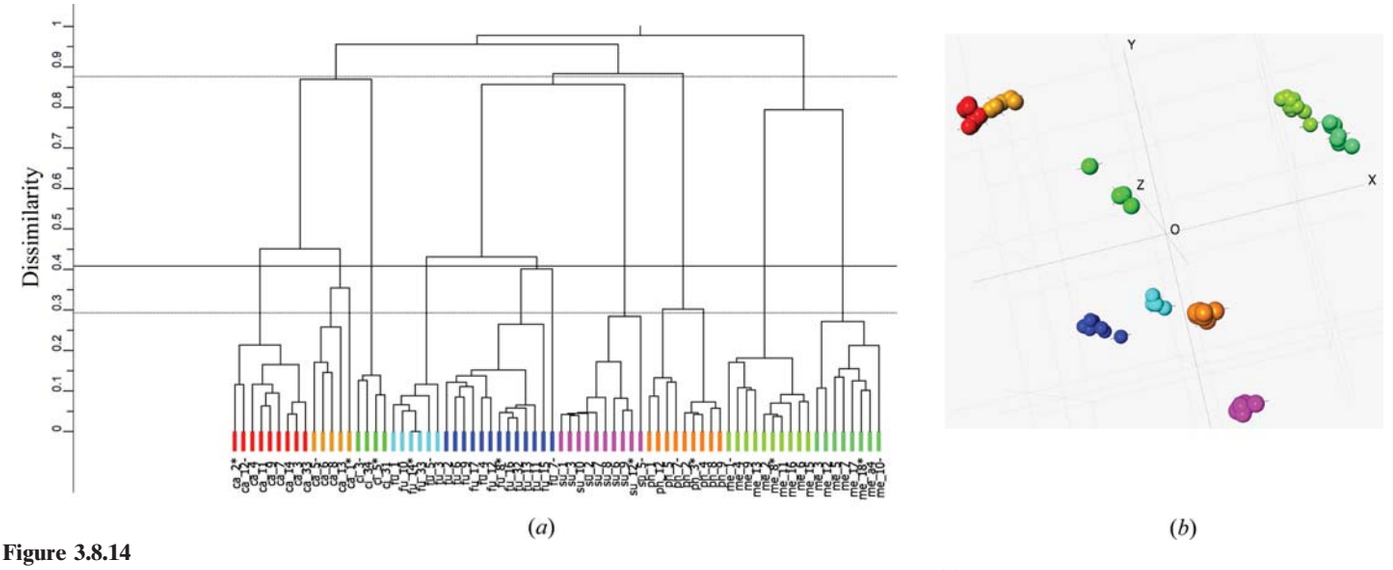

Figure 3.8.14
Clustering the 74 Raman spectra without background corrections applied using first-derivative data. (*a*) The dendrogram. Labelling from the left-hand side, the red and orange entries are carbamazepine; the green are cimetidene; the light blue and dark blue are two forms of furosemide; the purple are sulfamerazine; the brown are phenilbutazone and the right-hand light and dark green are two forms of mefenamic acid. (*b*) The MMDS plot. The clusters are well defined but the orange and red (both carbamazepine) are very close to each other.

For further details of this method with organic samples, see Dong *et al.* (2008).

3.8.8. Using spectroscopic data

There is no reason why the methodology described in this chapter cannot be used for other 1D data sets, *e.g.* Raman, IR, NMR and near-IR spectroscopies, although different data pre-processing is usually required. Raman spectroscopy is well suited to high-throughput screening: good-quality spectra can be collected in a few minutes, and sample preparation is straightforward and flexible, although the resulting spectra are not always as distinct as the PXRD equivalents (Mehrens *et al.*, 2005; Boccaleri *et al.*, 2007).

As an example we show the results of cluster analysis carried out on samples of carbamazepine, cimetidene, furosemide, mefenamic acid, phenilbutazone and sulfamerazine using Raman spectroscopy. A total of 74 samples were measured on a LabRam HR-800/HTS-Multiwell spectrometer at room temperature, equipped with a backscattering light path system of a light-emitting diode laser (785 nm, 300 mW) as an excitation source and an air-cooled charge-coupled device detector. A 20-fold superlong working distance objective lens was used to collect the backscattered light. The spectra were acquired with 5.84 cm^{-1} spectral width and at least 30 s exposure (Kojima *et al.*, 2006). The spectra had backgrounds subtracted but no other corrections were carried out.

The initial clustering is shown in Fig. 3.8.13(*a*) with the default cut level in the dendrogram. There are six clusters: labelling from the left-hand side, the red are three polymorphs of carbamazepine; the orange are cimetidene; the green cluster contains three polymorphs of furosemide; the light blue contains three poly-