Dalton Perspectives

Bond Stretch Isomerism: Fact or Artifact?*

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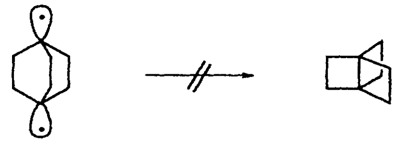
Isomerism, in all its varied forms, transcends the traditional boundaries of inorganic, organic, physical and theoretical chemistry and has captured the imaginations of every generation of research chemist over the past century. Numerous forms of isomerism have been established in which molecules or ions differ in the way the atoms are linked to each other or are arranged in space. The subject of this review is *bond stretch isomerism*, a phenomenon which seems to work against our carefully nurtured chemical intuition in that it involves no change in the geometrical placements of atoms or in rotations of substituent groups, but merely a stretch of one (or possibly more) bonds. In this article we will re-trace the development of the concept of bond stretch isomerism: why it was first proposed, how it has been defined, why evidence for or against it is very difficult to be certain of, why everyone hesitates to believe in it and yet why it is difficult to disprove.

Of central importance to a discussion of isomerism is the magnitude of the energy barrier separating the isomers. In general, the barrier to interconversion of structural alternatives is known to differ widely, from virtually nothing (for small conformational changes) to values of the order of the bond strengths of the constituent atoms (*e.g.* for optical isomers of tetravalent carbon). So, while boat and chair cyclohexane conformers are separated by less than 5 kcal mol^{-1}, optical isomers may be separated by barriers as large as 100 kcal mol^{-1}. This difference in energy barrier has an important practical consequence since two molecules separated by a barrier in excess of 25 kcal mol^{-1} are likely to exist as discrete forms in solution at room temperature, whereas the much smaller energy barriers characteristically separating conformers will ensure their rapid interconversion in room-temperature solutions. It is the difficulty of envisaging that the barrier to interconversion between such similar species as bond stretch isomers could be high enough for them to exist even in the solid state let alone room-temperature solution that makes this topic so controversial.

Background

The term *bond stretch isomerism* was first introduced in 1972 by Stohrer and Hoffmann [1] for systems where two energy minima along a simple bond stretch occurred, and from their calculations they identified a range of hypothetical molecules with this type of double minimum separated by a substantial barrier. The example of tricyclooctane is shown below, in which the bicyclic diradical **I** cannot readily convert into the tricyclooctane **II**.[2] Here, two different states arise due to crossing over of symmetrically dissimilar energy levels and the barrier between the states may be sizable if the interconversion is symmetry forbidden. Schleyer *et al.*[3] have noted similar effects in fused silicon ring systems. Likewise, the existence of hexamethyl(Dewar)benzene **III** may also be attributed to a forbidden transition to its much more thermodynamically stable arene isomer **IV**.



I II

III IV

Related effects also exist in inorganic chemistry, *e.g.* high spin–low spin crossover compounds of the first-row transition metals.[4] A good example is provided by the recent work of Gütlich and Poganiuch[4a] who have demonstrated that certain low-spin iron(II) complexes can be excited to a metastable high-spin state whose lifetime is practically infinite. The high-spin state can be 'pumped' back to the low-spin state by irradiation with red light *via* a double intersystem crossing. Again, rapid interconversion is prevented by a forbidden transition. Another example is provided by Kölle and co-workers [5] who have shown that there are two different forms of $[\{Ru(C_5Me_5)X_2\}_2]$ (X = Cl or Br) which possess substantially different Ru–Ru and Ru–Cl distances and inter-ligand angles; here the effect has been rationalised in terms of an energy barrier between magnetically interacting and non-interacting d^5 metal centres.

The theoretical evidence is quite compelling that under the right conditions there can be two energy minima along a simple bond stretch, but the question remains: can the barrier be large enough for the bond stretch isomers to be stable in solution at room temperature?

The first example of what appeared to be non-hypothetical isomers of this type came from studies of transition-metal complexes, a range of blue and green oxomolybdenum(IV) complexes $[MoOCl_2(PR_3)_3]$ (R = alkyl or aryl) originally reported by Butcher and Chatt[6] in 1970, two years before the expression bond stretch isomers was to be proposed. From spectroscopic data they concluded that the blue and green species had different geometric forms, and a strong band in the 940–955 cm^{-1} region for each complex was attributed to $\nu(Mo{=}O)$. Attention was particularly focused on the dimethylphenylphosphine complex $[MoOCl_2(PMe_2Ph)_3]$ which existed in both the *blue* and the *green* forms. As a preliminary X-ray structure determination of the blue isomer had shown it to have the *cis-mer* configuration **V** it was initially concluded that the green form was the *trans*-dichloro isomer **VI**.[7]

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* *Non-SI unit employed:* cal = 4.184 J.

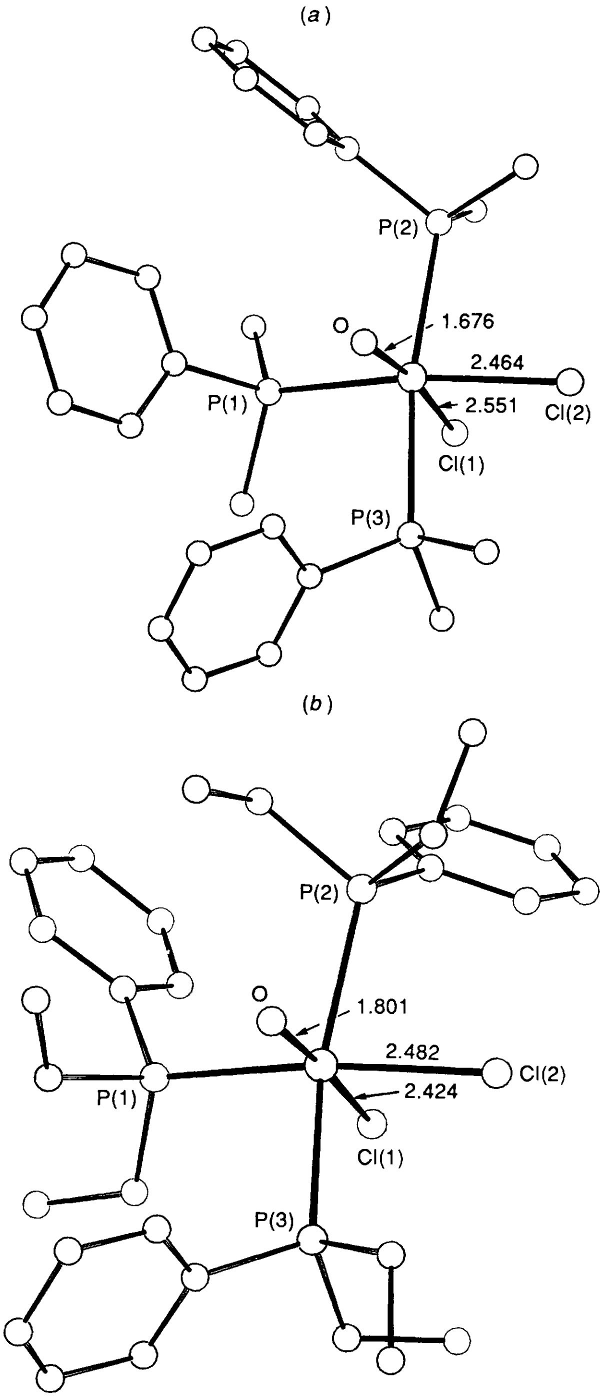
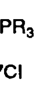
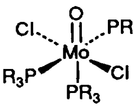


Fig. 1 The *cis-mer* structures observed in X-ray structure analysis of (*a*) the *blue* form of $[MoOCl_2(PMe_2Ph)_3]$ [ν(Mo=O) 954 cm^{-1}], and (*b*) the *green* complex $[MoOCl_2(PEt_2Ph)_3]$ [ν(Mo=O) 940 cm^{-1}]. Distances in Å



V



VI

The blue isomer was considered to be more stable than the green since the latter was rapidly converted into the blue form in warm organic solvents. It is important to emphasise the conviction of these workers that *two* isomers existed over a year before further X-ray evidence was obtained; the IR spectra were particularly significant in the differentiation of the two forms, the blue isomer being readily distinguished from the green in having ν(Mo=O) at 954 cm^{-1} as opposed to 943 cm^{-1} for the green isomer. It was therefore with surprise that Manojlovic-Muir and co-workers[8] discovered that the analogous diethylphenylphosphine complex, only isolated in the *green* form with the characteristic low ν(Mo=O) of 940 cm^{-1}, was not the expected *trans* dichloro isomer but had the *cis*-dichloro configuration established earlier for the *blue* dimethylphenylphosphine complex [ν(Mo=O) 954 cm^{-1}]. From the X-ray data they could find only two significant differences in the structures of the two molecules. First, the dimethylphenyl- and diethylphenyl-phosphines adopt different conformations (Fig. 1). Secondly, the Mo=O distance of 1.801(9) Å in the *green* ethylphosphine complex was very much longer than that of 1.676(7) Å found earlier in the *blue* methylphosphine derivative, and the Mo–Cl bonds *trans* to the M=O group showed the reverse relationship, being 2.424(6) Å in the *green* compound and 2.551(3) Å in the *blue*.

They immediately questioned the original conclusion that the *green* form of $[MoOCl_2(PMe_2Ph)_3]$ [ν(Mo=O) 943 cm^{-1}] was the *trans* isomer of the *cis*-dichloro *blue* form [ν(Mo=O) 954 cm^{-1}]. Based on the spectroscopic similarity between *green* forms of the PMe_2Ph complex $[MoOCl_2(PMe_2Ph)_3]$ and the *green* PEt_2Ph complex $[MoOCl_2(PEt_2Ph)_3]$ [ν(Mo=O) 943 and 940 cm^{-1} respectively], Chatt *et al.*[8] were forced to the conclusion that the *green* form of the dimethyl complex was not a geometric isomer of the *blue* form [ν(Mo=O) 954 cm^{-1}] but had a similar *cis* configuration. This implied that the difference in the infrared spectra of the two forms of $[MoOCl_2(PMe_2Ph)_3]$, ν(Mo=O) 954 (*blue*) and 943 cm^{-1} (*green*), must be due mainly to a difference in Mo=O bond length; knowing that the *blue* form had a Mo=O length of 1.676(7) Å they deduced that the *green* form (for which they were unable to get crystals) would have a significantly longer Mo=O bond, similar to that of the *green* diethyl analogue of 1.801(9) Å. They gave the name *distortion isomers* to these species because it seemed probable that the differences might arise from different conformations of the phosphines in the highly strained co-ordination polyhedra of the molybdenum. Crystals of the *green* isomer proved very elusive and the first X-ray study of this complex was reported at a conference by Haymore *et al.*[9] This gave a distance of 1.80 Å for Mo=O, but due to serious disorder in the crystals these results were never fully published.

Wieghardt *et al.*[10] have more recently reported a case of apparent bond stretch isomerism in an oxotungsten system, in which the compounds were also found to exist in *blue* and *green* forms, and where in each case the *blue* form has a higher ν(M=O) than the *green*; these are the two forms of the cationic complex of the tridentate ligand *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane (L), $[WOCl_2L]^+$ which have ν(W=O) 980 (*blue*) and 960 cm^{-1} (*green*). They provided the first example of apparent bond stretch isomers where the two compounds studied were perfectly matched, both crystallising with the same counter ion, $[PF_6]^-$, to give isomorphous salts in which crystal-packing effects would be virtually identical. From X-ray structure analyses (Fig. 2) the *blue* compound was shown to have a W–O bond length of 1.719(18) Å, significantly shorter than that of 1.893(20) Å observed in the *green* isomer, although the errors on the parameters were relatively high due to disorder of the counter ion. The isomers are stable in acetonitrile solution for several days with no sign of change of colour.

Cotton *et al.*[11] have also reported studies on *green* $[MoOCl_2(PMePh_2)_3]$ [ν(Mo=O) 945 cm^{-1}] and *blue* $[MoO(NCO)_2(PEt_2Ph)_3]$ [ν(Mo=O) 941 cm^{-1}], two compounds from the original Chatt series. The *blue* compound had a short Mo=O bond length of 1.684(8) Å (mean of two independent molecules), as they had expected from the colour, but they were surprised to find that the *green* chloro compound also had a short Mo=O length of 1.667(4) Å. In an interesting discussion on the implications for bond stretch isomerism they point out that, as the colour trend is towards *green* with increasing bond

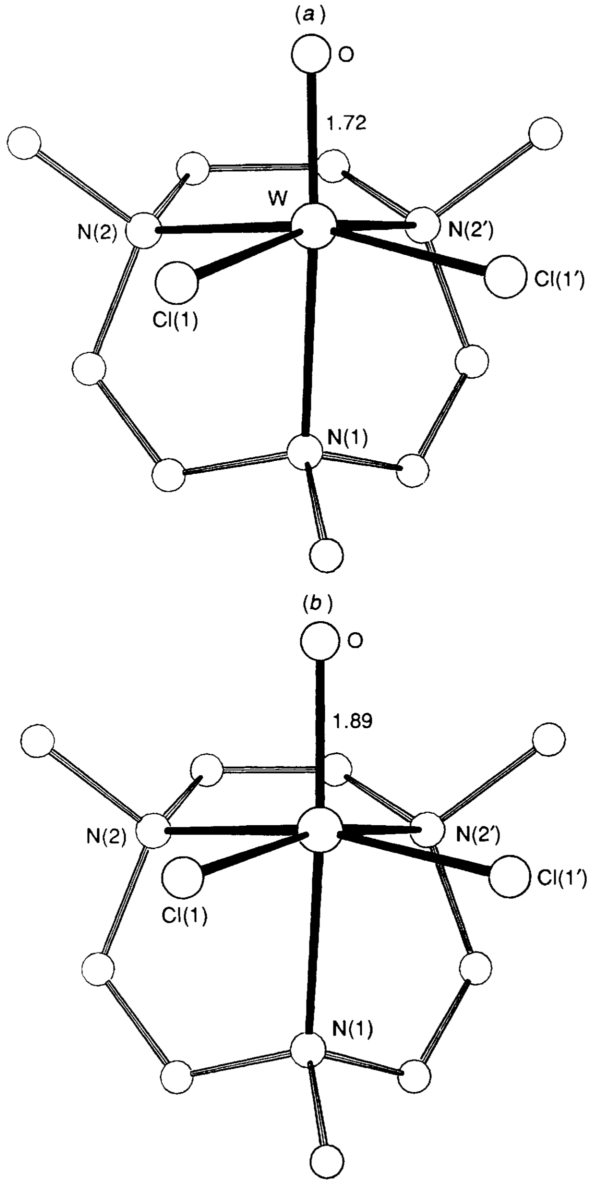


Fig. 2 The structures of the proposed bond stretch isomers of the cationic complex $[WOCl_2L]^+$: (*a*) the *blue* form [ν(W=O) 980 cm^{-1}] and (*b*) the *green* form [ν(W=O) 960 cm^{-1}]

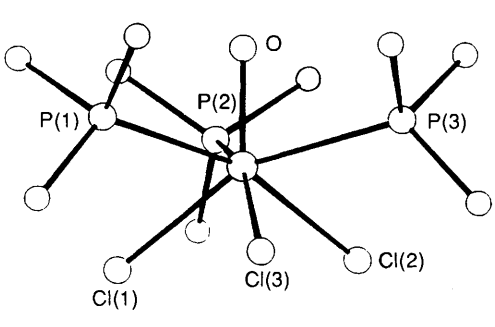


Fig. 3 The monocapped-octahedral structure found for $[NbOCl_3(PMe_3)_3]$

length, were a second isomer of the chloro complex to exist it would be green also and so be undetected during normal laboratory work.

An explanation for the origin of the barrier between the isomers in the molybdenum and tungsten compounds based on extended-Hückel calculations was later published by Jean, Lledos, Burdett and Hoffmann.[12]

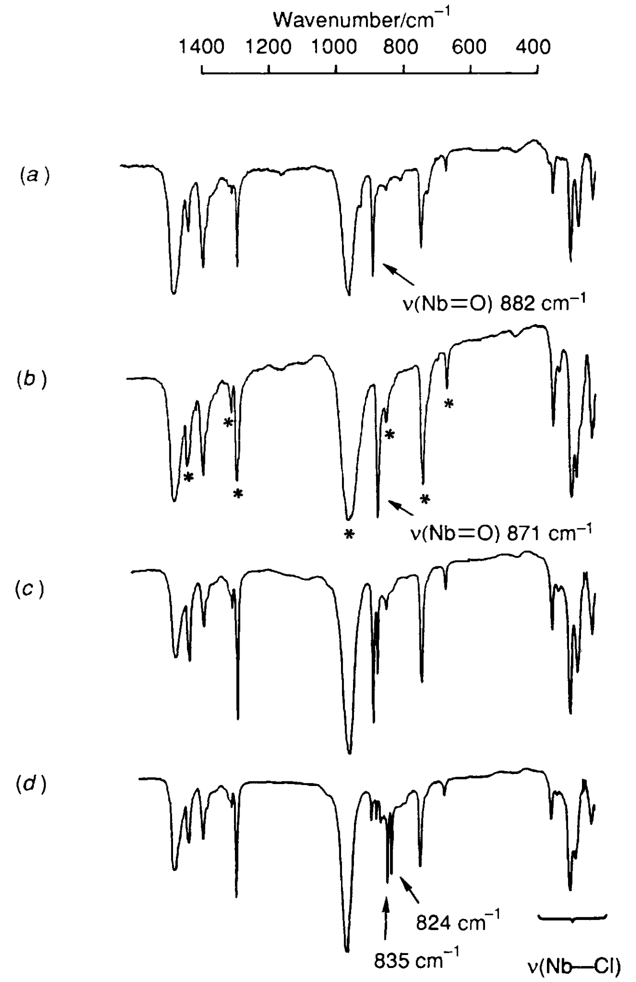


Fig. 4 The IR spectra (Nujol mull, CsI) of the *yellow* and *green* isomers of $[NbOCl_3(PMe_3)_3]$: (*a*) the *yellow* isomer, (*b*) the *green* isomer, (*c*) a mixture of *yellow* and *green* isomers, and (*d*) a mixture of ^{18}O-labelled *yellow* and *green* isomers. The asterisk denotes bands attributable to $Nb-PMe_3$ stretching and bending modes

The $[NbECl_3(PMe_3)_3]$ System (E = O or S)

Our synthetic, spectroscopic, and X-ray structural studies of the niobium(V) complexes $[NbECl_3(PMe_3)_3]$ (E = O or S)[13] appeared to provide the first examples of bond stretch isomerism involving thiometal compounds. They differed from all previous examples in having seven-co-ordination at a d^0 metal centre, the earlier studies having involved an octahedral geometry and d^1 or d^2 configurations at the metal. The early stages of our discovery were very similar to those of the system of Chatt *et al.*[8] The first compound in the series to be structurally characterised was *yellow* $[NbOCl_3(PMe_3)_3]$ which had the capped-octahedral co-ordination shown in Fig. 3, with the three chloro and three organophosphine ligands facially arranged in octahedral sites with the unique oxo ligand capping the 'P_3' face and with a Nb=O length of 1.781(6) Å; this complex was the subject of a short communication reporting it as the first example of a tertiary phosphine adduct of $NbOCl_3$.[14]

Subsequently, the synthesis was repeated using $[NbOCl_3(MeCN)_2]$ instead of $(NbOCl_3)_n$ as the starting material and this gave a green compound which closely resembled the original adduct apart from a slight difference in the IR spectrum; for the *yellow* product ν(Nb=O) was at 882 cm^{-1} and for the new *green* derivative it was at 871 cm^{-1} [Fig. 4(*a*)–(*c*)]. The *green* form could also be obtained upon dissolution of the yellow form in toluene followed by prolonged cooling at −20 °C. Assuming the *green* product to be a geometric isomer of the *yellow* an X-ray structure analysis was undertaken. This showed that the two compounds were not the expected geometric isomers, but

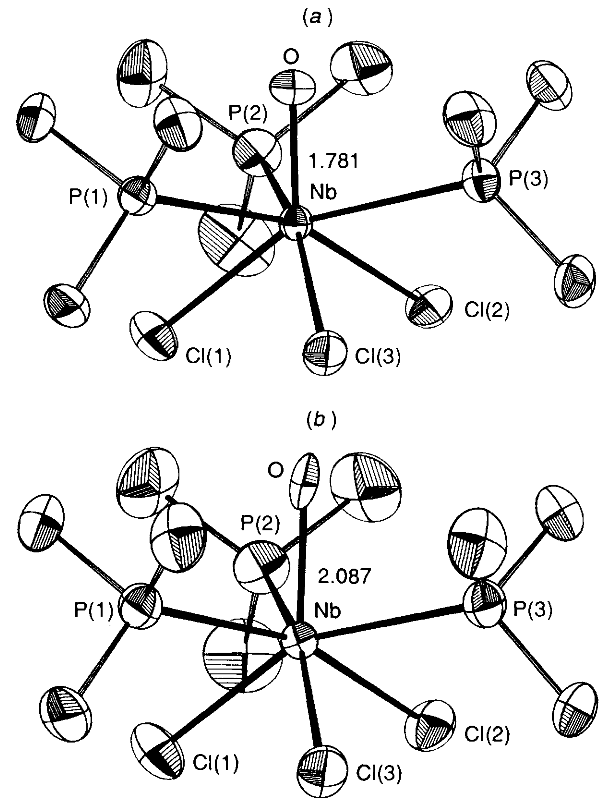


Fig. 5 Comparison of the structures of the *yellow* (*a*) and *green* (*b*) forms of $[NbOCl_3(PMe_3)_3]$ showing the marked elongation of the thermal ellipsoid of the oxygen atom in the *green* form

that the crystals were isomorphous with molecules of very similar overall geometries (even the hydrogen atoms of the methyl groups were in similar sites). However, the extremely long Nb=O distance of 2.087(5) Å in the *green* compound seemed at first to offer an explanation: perhaps this was in fact a hydroxy compound of Nb^{IV}, not an unreasonable idea as the seven-co-ordinate niobium(IV) complex $[NbCl_4(PMe_3)_3]$ was known and is green. The IR spectrum was re-examined but no evidence for a hydroxo group could be found in this, nor in careful ^1H NMR studies, and vibrating-sample magnetometry indicated that the *green* compound was fundamentally diamagnetic whereas a hydroxo complex would have a d^1 configuration and so would be quite evidently paramagnetic. The assignment of the two Nb–O stretches in the IR spectrum was confirmed using ^{18}O-enriched samples of the two species, which gave $\nu(Nb{=}^{18}O)$ at 835 cm^{-1} (calc. 833 cm^{-1}) for the *yellow* form and $\nu(Nb{=}^{18}O)$ at 824 cm^{-1} (calc. 821 cm^{-1}) for the *green* form [Fig. 4(*d*)].

At this stage the possibility of bond stretch isomerism had to be seriously considered, but although everything about our system seemed to fit in with this explanation we continued to search for an alternative.[15] Marked elongation of the anisotropic ellipsoid of the axial oxo atom along the virtual C_3 molecular axis (Fig. 5), and a peak of residual electron density of *ca.* 1.5 e^- in the axial direction 0.51 Å beyond the oxo O atom in the long-bonded *green* compound, offered some hope of a different explanation. The residual peak was clearly due to co-crystallisation of a small amount of a second virtually isostructural molecule with a longer axial bond, because X-ray analysis shows the average structure of the molecules present in the crystal. By systematic testing, the occupancy of the O atom was reduced to 80%, and 20% Cl was assigned to the site of the smaller peak. The parameters of these atoms refined satisfactorily in alternate least-squares cycles, giving a Nb=O distance of 1.929(6) Å and the axial Nb–Cl length of 2.355(8) Å. However, in order to explain the structural and spectroscopic results [*i.e.* different ν(Mo=O)] without invoking bond stretch isomerism, a solid-state model in which 80% of the original *yellow* compound [Nb=O 1.781 Å, ν(Nb=O) 882 cm^{-1}] had co-crystallised with a *geometric* isomer was considered. In this model, the geometric isomer would require a chloro ligand to be in the capping axial site and the oxo ligand [assigned ν(Nb=O) 871 cm^{-1}] replacing it in an octahedral site as shown in Fig. 6(*a*). Detection of the oxygen atom of 20% occupancy required by this model would have been very difficult in the X-ray determination, and completely impossible if an additional rotational disorder of the 20% geometric isomer compound occurred such that each of the three equivalent octahedral sites, fully occupied in 80% of the molecules by the three chloro ligands of the *yellow* isomer, was randomly occupied by the oxo ligand of the geometric isomer in the remaining 20%.

Although the disordered model gave a convincing explanation of the X-ray structure, the apparent lengthening of the Nb=O bond being readily explained as an artifact of the disorder, it could not explain why in all samples of the *green* isomer only one ν(Nb=O) stretch occurred, at 871 cm^{-1}, and no evidence of the band at 882 cm^{-1} due to the *yellow* isomer (the source of the 80% axial oxo ligand in this model) was ever observed. The *geometric* isomer concept was therefore abandoned and the crystal disorder was explained as due to co-crystallisation of 20% of the tetrachloride $[NbCl_4(PMe_3)_3]$ [Fig. 6(*b*)], thought to arise from some decomposition (in more recent studies a paramagnetic contaminant has been detected). In these structures the bulk of the three tertiary phosphine groups overshadows any axial ligand so that the overall crystal packing would be little affected by replacement of some of the oxo molecules by tetrachloride (Fig. 7).

We concluded that the *yellow* and *green* forms each contained only one oxo species, with the oxygen atom in the axial site [contaminated with the tetrachloride in the *green* case, Fig. 6(*b*)], and although these two species both appeared to have similar ligand distributions on the basis of the X-ray results they nevertheless were clearly distinguishable from their IR spectra. Thus, we were forced back to bond stretch isomerism or some additional, as yet unidentified, contaminant as the only feasible explanations of the different ν(Nb=O) for the *yellow* and *green* forms, which meant that the apparent difference in the Nb=O lengths in the two forms must be real in principle (if not in magnitude) because no other structural difference was observed.

Later, very similar results were obtained for the thioniobium analogues. Pure crystals of an *orange-yellow* and a *green* form of $[NbSCl_3(PMe_3)_3]$ were obtained and were readily distinguished, not only by their colour, but by the marked differences in their IR spectra, ν(Nb=S) occurring at 455 cm^{-1} for the *orange-yellow* form compared to 489 cm^{-1} for the *green* form (Fig. 8).

X-Ray structure analyses of both forms gave the almost indistinguishable structures shown in Fig. 9, the crystals being isomorphous not only with each other but also with the two forms of $[NbOCl_3(PMe_3)_3]$ and the tetrachloride $[NbCl_4(PMe_3)_3]$. Once again the main difference in the two structures observed was centred on the bond lengths. In addition to small differences in the Nb–Cl and Nb–P distances, the Nb=S length of the *orange-yellow* form was 2.196(2) Å and that of the *green* form was 2.296(1) Å. These differences were in the opposite direction from that expected on the basis of the IR stretches which were consistent with the *green* form [ν(Nb=S) 489 cm^{-1}] having a shorter Nb=S length than that of the *orange-yellow* form [ν(Nb=S) 455 cm^{-1}]. This discrepancy in the Nb=S bond length in relation to the IR spectra made us look very closely again at possible disorder models. First, a situation very similar to that known to exist in *green* $[NbOCl_3(PMe_3)_3]$ was considered. The similar number of electrons in sulfur and chlorine atoms mean that signs of disorder in the structures would be almost impossible to detect. Therefore, although the thermal ellipsoids of the two sulfur atoms were normal (Fig. 9), and there was no sign of excess of electron density at the S atom

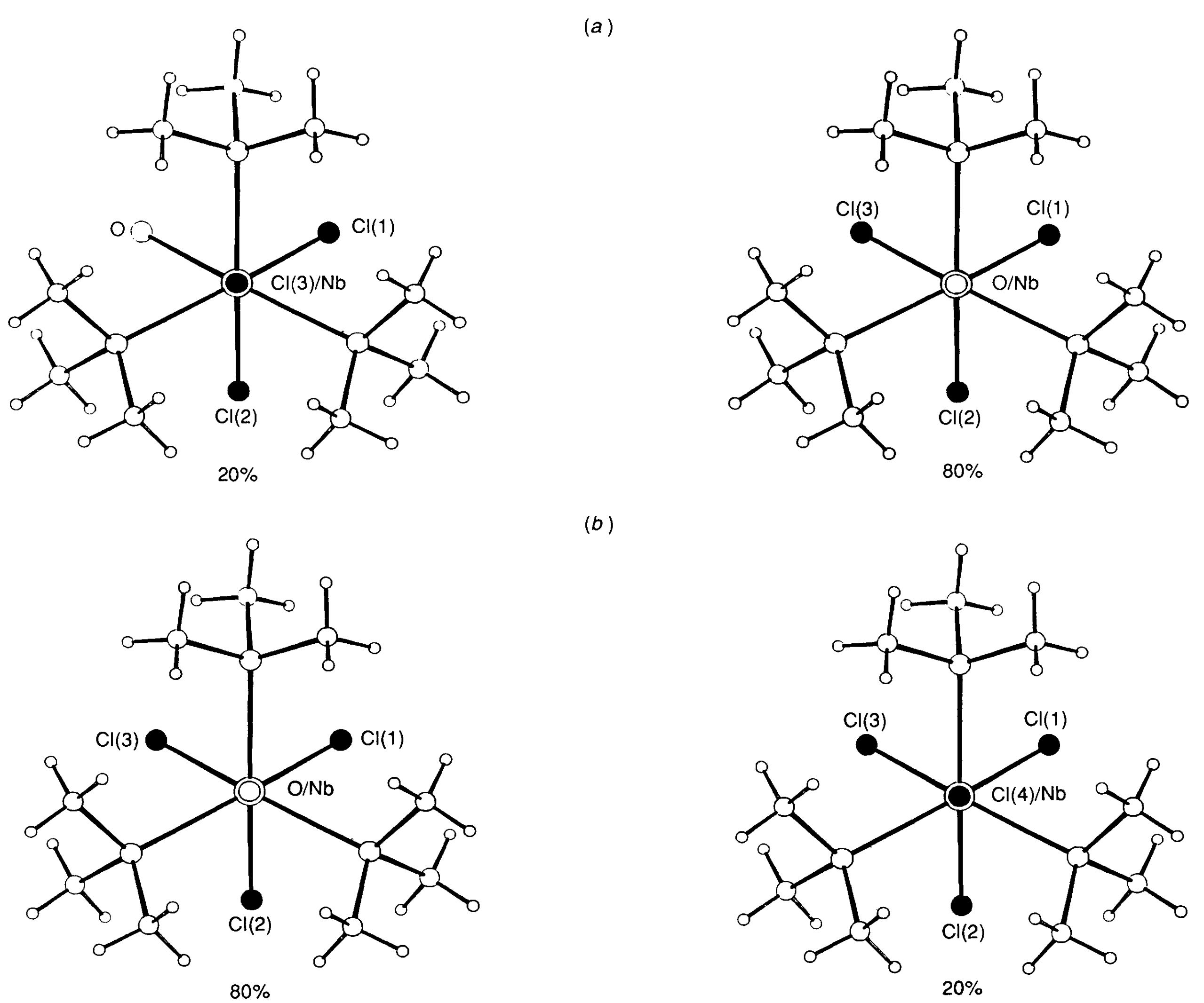


Fig. 6 Disorder models to rationalise the observed crystallographic results on the *green* form of [$NbOCl_3(PMe_3)_3$]: (*a*) 80% of an axial oxo species with 20% of a geometrical isomer (oxygen atom occupying an octahedral site), and (*b*) 80% of an axial oxo species contaminated with 20% of [$NbCl_4(PMe_3)_3$]

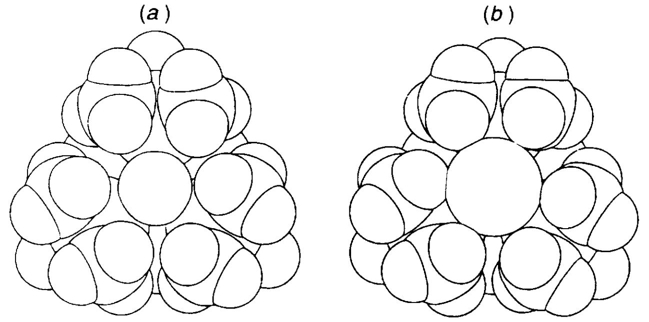


Fig. 7 Comparison of computed space-filling models of (*a*) the *yellow* oxo complex [$NbOCl_3(PMe_3)_3$] and (*b*) the *green* tetrachloride [$NbCl_4(PMe_3)_3$] showing how replacement of the axial oxygen atom by a chloride ligand has negligible effect on the external features of the molecule

in the *green* structure, the possibility that this long-bonded form contained some co-crystallised [$NbCl_4(PMe_3)_3$] or other S/Cl disorder could not be ruled out. Using similar arguments to those employed for the [$NbOCl_3(PMe_3)_3$] case (see above), the possibility that the *green* form of [$NbSCl_3(PMe_3)_3$] consisted of a geometric isomer disordered with the tetrachloride, or alternatively of a pure *green* geometric isomer three-fold disordered (Fig. 10), was considered. Both these models fitted the spectoscopic data, giving an explanation of the different ν(Nb=S) stretches of the *orange-yellow* and *green* forms, but they left unexplained the axial bond length of the *green* compound which was too short (even allowing for the differences in oxidation state) to be a single Nb–Cl length, 2.296 compared to 2.409 Å in the tetrachloride. Simple disorder of the *orange-yellow* form with the tetrachloride [as shown in Fig. 6(*b*) for the oxo complex], feasible from the crystallography, would not readily explain the observed differences in ν(Nb=S) between the *orange-yellow* and *green* forms. As the spectra had been recorded in Nujol mull, some solid-state effect, produced by the presence of tetrachloride in the crystals, seemed to be for this model the only explanation of the different spectra; if this were correct it would be expected that in solution both forms would show the same ν(Nb=S). However, the spectrum of a mixture of *orange-yellow* and *green* forms recorded in CH_2Cl_2 solution gave the two characteristic ν(Nb=S) stretches found in the Nujol mull spectra, Fig. 8(*c*). The differences in ν(Nb=S) between the *orange-yellow* and *green* forms of [$NbSCl_3(PMe_3)_3$] clearly did not arise from a solid-state artifact, and we were forced back to considering the possibility that these could be genuine examples of bond stretch isomers, regardless of whether or not the *green* form was contaminated with tetrachloride.

Recent Work on the [$Mo(O)Cl_2(PR_3)_3$] System

While our work was in progress three other groups turned

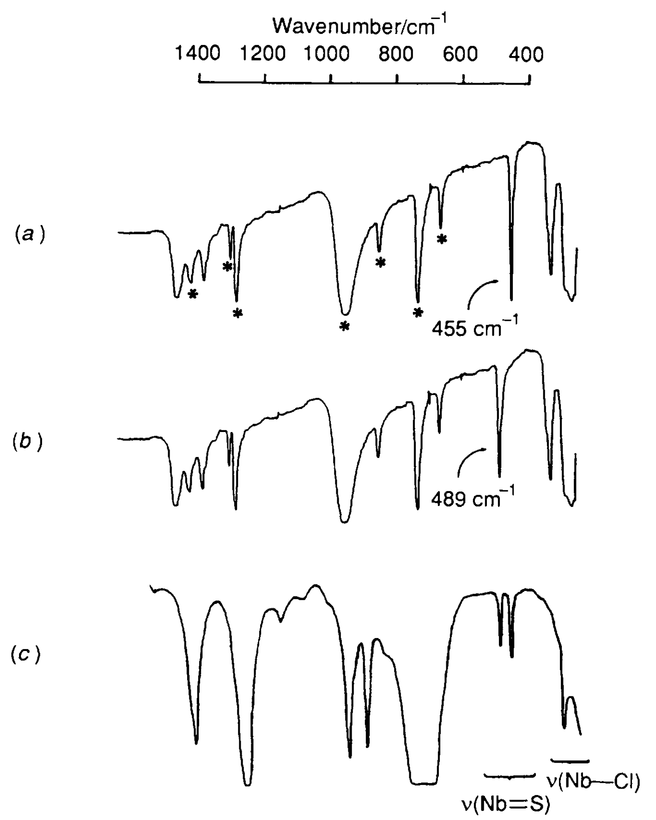


Fig. 8 The IR spectra of the *yellow-orange* and *green* isomers of [$NbSCl_3(PMe_3)_3$]: (*a*) the *yellow-orange* form (Nujol mull, CsI), (*b*) the *green* form (Nujol mull, CsI), (*c*) a mixture of *yellow-orange* and *green* forms in CH_2Cl_2 solution. The asterisk denotes bands attributable to Nb–PMe_3 stretching and bending modes

critical eyes to the problem of bond stretch isomerism. Enemark,[16] Parkin[17] and Hall[18] and their co-workers, unknown to each other, were re-examining the original Chatt [$MoOCl_2(PMe_2Ph)_3$] system. The first two groups concluded that the reported apparent lengthening of the Mo=O bonds in the *green* form was due to co-crystallisation of the *blue* form with the *yellow* trichloride [$MoCl_3(PMe_2Ph)_3$]. The findings caused an upsurge of confidence that at last a conventional explanation of the surprising phenomenon of bond stretch isomerism had been found. Song and Hall[18] say that the Parkin findings gave them 'sufficient courage' to publish their theoretical evidence from *ab initio* calculations that, for [$MoOCl_2(PMe_2Ph)$], only the *blue* short-bond form should exist. However, none of these groups offered an explanation for the two *different* ν(Mo=O) values found for the *blue* and *green* forms of [$MoOCl_2(PMe_2Ph)_3$] as first reported, but Enemark and co-workers,[16] who paid the Chatt observation particular attention, concluded that the original assignment of ν(Mo=O) at 954 cm^{-1} in the IR spectrum of the *blue* form of [$MoOCl_2(PMe_2Ph)_3$] was incorrect as they could find no evidence of it in their own spectra. However, their comment that 'the two different M=O bond lengths reported for a pair of distortional isomers suggest two different M=O bond orders [and] it is therefore not surprising that different M=O stretching frequencies have been reported for each of the distortional isomers within a pair' implies that in earlier work two stretches were sought after the X-ray analyses, whereas in all cases the existence of some type of isomerism has been proposed on the basis of IR evidence *before* the X-ray results on both isomers were available (see above).

Parkin and co-workers[17] initially investigated the solid-state structure of [$MoOCl_2(PMe_3)_3$], the trimethylphosphine analogue of the Chatt compounds, reported[19,20] to exist in *blue* and *green* forms. They found that crystals of the *green* form had two independent molecules per asymmetric unit with Mo=O bond lengths of 1.698(8) and 1.866(7) Å. Thinking this compound provided the ideal system for the study of two bond stretch isomers, within one crystal, they expected to find two absorptions in the IR spectrum corresponding to the *long* and *short* isomers, but found only one at 950 cm^{-1}. To check their original X-ray findings they looked at a second crystal, from a new batch, and were surprised to find two new M=O lengths, 1.772(12) and 2.154(8) Å. The earlier observation[21] of contamination in *green* [$NbOCl_3(PMe_3)_3$] by *ca.* 20% of the isomorphous tetrachloride [$NbCl_4(PMe_3)_3$] prompted an explanation of the discrepancies between the two sets of 'Mo=O' bond lengths as due to co-crystallisation of small quantities of the isostructural trichloride [$MoCl_3(PMe_3)_3$] with the oxo compound [$MoOCl_2(PMe_3)_3$].

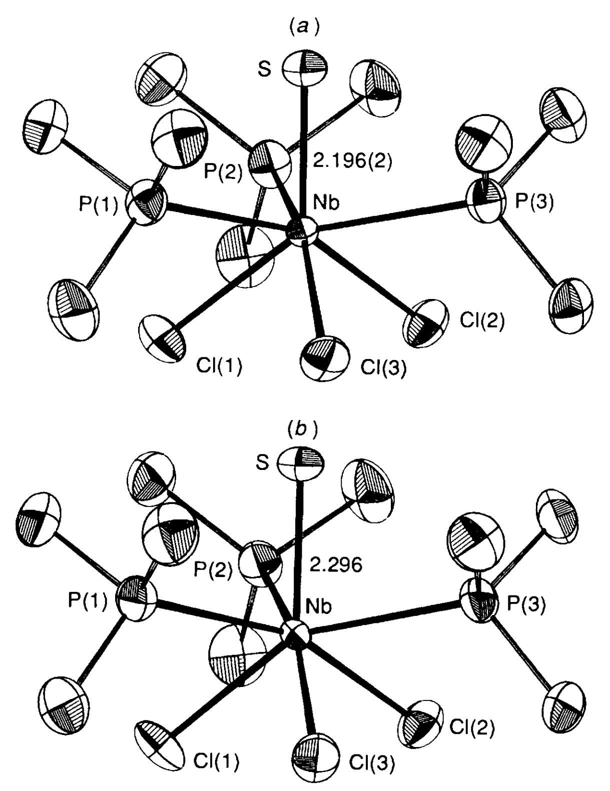


Fig. 9 Comparison of the monocapped-octahedral structures observed for (*a*) the *yellow-orange* form of [$NbSCl_3(PMe_3)_3$] [ν(Nb=S) 455 cm^{-1}], and (*b*) the *green* form of [$NbSCl_3(PMe_3)_3$] [ν(Nb=S) 489 cm^{-1}], showing that there is no distortion of the thermal ellipsoid of the *green* form

These results led Parkin and co-workers to question the original structural evidence for bond stretch isomerism in the analogous Chatt dimethylphenylphosphine complexes, *blue* and *green* [$MoOCl_2(PMe_2Ph)_3$]. When the syntheses were repeated they isolated crystals which varied in colour from *blue*, through *blue-green*, to *emerald green*, and they showed that the colour change was associated with increasing contamination with a paramagnetic material thought to be *yellow* [$MoCl_3(PMe_2Ph)_3$]. By analysing the ^1H NMR spectrum of the bulk samples they estimated the fractional composition [$MoOCl_2(PMe_2Ph)_3$]:[$MoCl_3(PMe_2Ph)_3$] corresponding to the apparent lengths found in the X-ray analysis. They expanded these data by deliberately crystallising from a solution containing a 10:1 ratio of these two complexes; this gave *emerald green* crystals with an apparent 'Mo=O' bond length of 1.789(3) Å and an estimated composition [$MoO_{0.97}Cl_{2.03}(PMe_2Ph)_3$]. Thus, they were able to draw up a graph of apparent 'Mo=O' length as a function of estimated composition, and show that a 'continuum' of observed 'Mo=O/Mo–Cl' lengths arise from crystals of *blue* [$MoOCl_2(PMe_2Ph)_3$]

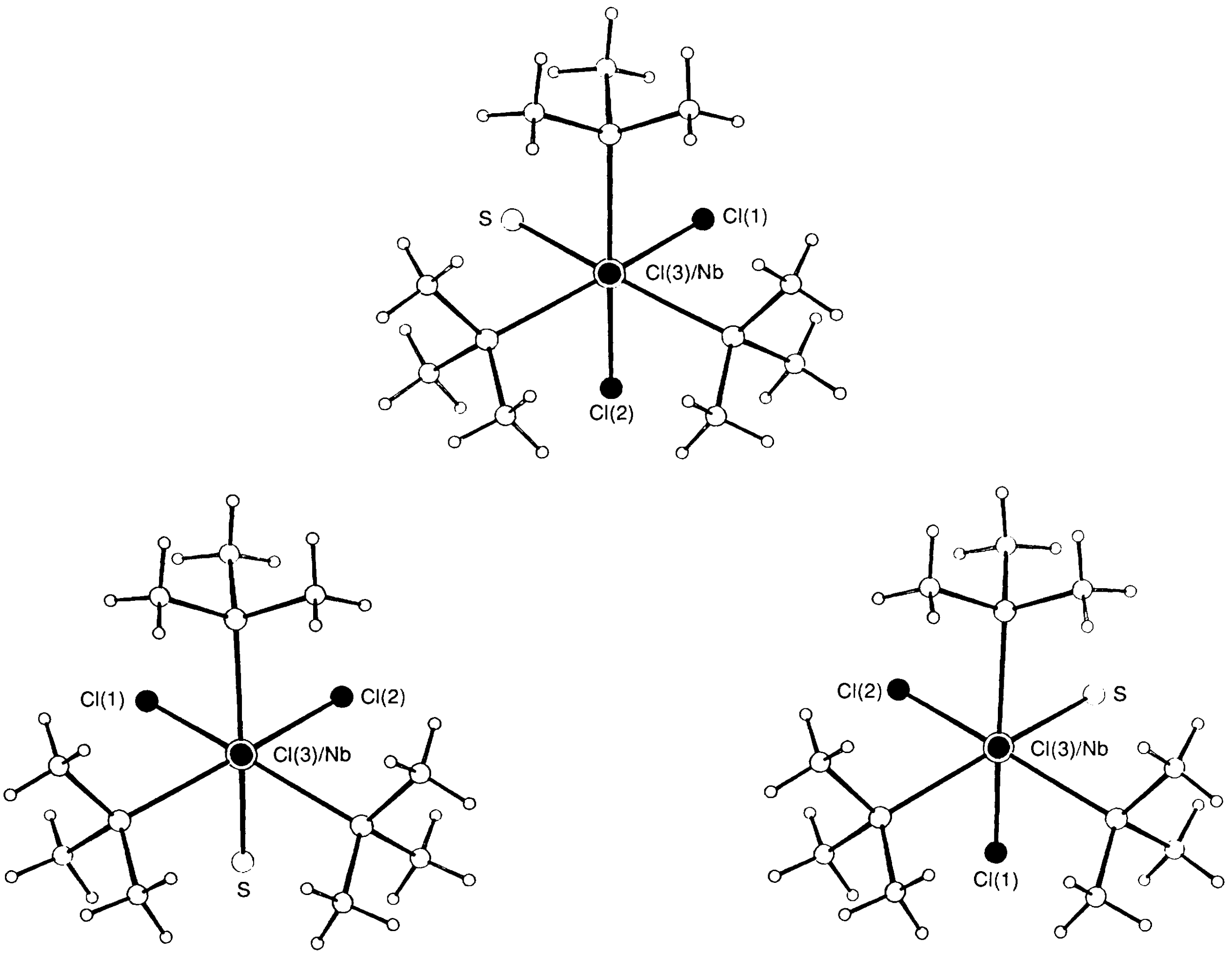


Fig. 10 A three-fold disorder model for a pure geometrical isomer of [$NbSCl_3(PMe_3)_3$] which would fit the spectroscopic data, but requires a longer bond length for the axial ligand than observed

present in different proportions with *yellow* [$MoCl_3(PMe_2Ph)_3$], Fig. 11(*a*).

Parallel results from Enemark and co-workers provide overwhelming evidence that in *green* [$MoOCl_2(PMe_2Ph)_3$] the contaminant of their *blue* [$MoOCl_2(PMe_2Ph)_3$] is the *yellow* [$MoCl_3(PMe_2Ph)_3$]. They prepared *blue* and *green* [$MoOCl_2(PMe_2Ph)_3$] and *yellow* [$MoCl_3(PMe_2Ph)_3$] by similar methods to those in the literature. By thin-layer chromatography they separated the *green* form of '[$MoOCl_2(PMe_2Ph)_3$]' into *blue* [$MoOCl_2(PMe_2Ph)_3$] and *yellow* [$MoCl_3(PMe_2Ph)_3$] in a 65:35 ratio. The elemental analysis of their *green* mixture gave a higher percentage of chlorine than expected for pure [$MoOCl_2(PMe_2Ph)_3$], and they pointed out that this slight discrepancy was also present in the original data reported by Chatt. They were entirely able to rationalise the spectra of the *green* compound as a summation of the spectra due to their *blue* form and the *yellow* trichloride. For their *blue* compound they showed that a band at 944 cm^{-1} is undoubtedly due to the Mo=O stretch as it is found at 943 cm^{-1} in the Raman spectrum, and the same stretch is always present in the *green* form; in direct contrast to Chatt they found no peak in the IR at 954 cm^{-1} for the *blue* form.

The results of these two groups demonstrated clearly that evidence of *bond lengthening* from X-ray single-crystal analysis must be treated with caution. However, the shape of the graph of apparent bond lengthening against estimated composition obtained by Parkin and co-workers[17] seems to overestimate the effect of very small amounts of chloride contaminant. It is extremely steep in the low-chloride region [Fig. 11(*a*)] indicating a lengthening of the Mo=O bond by minute amounts of co-crystallised Mo–Cl, which is excessive on crystallographic grounds. For example, when a crystal contains *ca.* 0.66 Mo=O and 0.33 Mo–Cl in the *trans* position, there would be approximately the same electron density at the oxo as at the chloro site, so that a bond length of about 2.04 Å would be expected, intermediate between the two extremes of 1.675 and 2.400 Å for the *blue* oxide and the *yellow* trichloride. In contrast, a length of *ca.* 2.2 Å is obtained from the reported curve, demonstrating that the estimated chlorine contents are too low. This is not unexpected due to the uncertainties inherent in attributing the same composition to the single crystals as that estimated for the bulk sample. The authors point out that alternative estimation by internal correlation using systematic variation of site occupancies of fixed O and Cl atoms gave different results.

We therefore re-examined Parkin's data using internal correlation to obtain a more representative estimation of the fraction of trichloride actually present in the crystal studied as opposed to that of the bulk sample. The *trans*-Mo–Cl length was more sensitive to composition than was the corresponding *cis* value, decreasing from 2.528(1) Å in Parkin's pure *blue* form of the oxo complex to a mean of 2.427(1) Å for the two mutually *trans*-Mo–Cl lengths in the *yellow* trichloride. We assumed the differences in length between the two extremes to be approximately linearly related to composition and, as only chlorine atoms were involved in the calculations, this was reasonable. Three data points were omitted, the first two and the last, as for these the difference in individual *trans*-Mo–Cl lengths from those of the adjacent extremes (*i.e.* pure *blue* oxo and *yellow* trichloride) were less than 3σ and therefore of very low

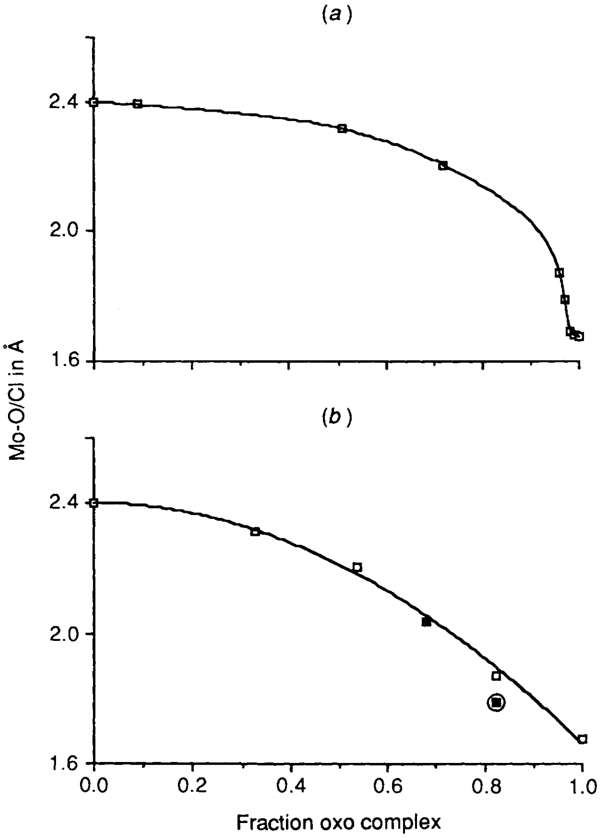


Fig. 11 The variation of Mo–O/Cl lengths observed in [$MoOCl_2(PMe_2Ph)_3$] as a function of fraction of oxo complex: (*a*) estimated by ^1H NMR study of the bulk sample, and (*b*) by internal correlation from the X-ray results (recalculated from ref. 17); assuming a mixture of the oxo complex and [$MoCl_3(PMe_2Ph)_3$]

significance. From this approach, much higher estimated chloride fractions were obtained for the remaining data points than from the original bulk sample estimates and the change in 'Mo=O/Cl' bond length followed a more gradual and plausible curve, Fig. 11(*b*). Significantly, the estimated Mo=O/Cl length of *ca.* 2.04 Å for equal electron density at the two sites fits well onto this new curve (black square). Although Parkin's conclusion that apparent 'Mo=O' bond lengthening results from chloro contamination is indisputable, these internal correlation results are important in clearly demonstrating a more reasonable magnitude for the effect. Caution, therefore, is necessary in the use of the original graph as demonstrating extreme bond lengthening by minute amounts of contaminant. For example, it might be thought that co-crystallisation of 4% chloride can cause an apparent Mo=O lengthening of 0.2 Å; however, the point on which this is based ('Mo–Cl/O' length 1.871 Å) appears from the length of its *trans*-Mo–Cl to have closer to 20% chloro contamination. It is puzzling that the one 'compound' made by deliberate co-crystallisation from a solution containing both the *yellow* trichloride and the *blue* [$MoOCl_2(PMePh_2)_3$] gives an anomalous point (circled) lying well below the curve of the others.

In view of the co-crystallised [$NbCl_4(PMe_3)_3$] present in our *green* [$NbOCl_3(PMe_3)_3$] sample, we decided to reinvestigate the thioniobium system where any disorder of this type could not be directly detected from one structure determination but where, if there were an undetected mixture of two components present in the *green isomer*, the proportion might change between successive preparations. So far, two additional batches of suitable crystals have been examined and significantly, although the bulk sample showed only the ν(Nb=S) of 489 cm^{-1} characteristic of the *green* isomer, the single crystals had a somewhat brown tint; the X-ray structure analyses of these two crystals showed very much shorter Nb=S lengths (2.225 and 2.219 Å) than that of 2.296 Å in the original X-ray analysis of the *green* isomer. This implies that the *green* form of [$NbSCl_3(PMe_3)_3$], like its oxo analogue, contained a proportion of co-crystallised tetrachloride thus allowing the apparent Nb=S bond length to vary depending on the fraction of tetrachloride present. An important conclusion is that any lingering expectation of explaining the differences in ν(Nb=S) as due to a disordered pure geometric isomer with chloride in the axial site may be dismissed because the major component in these crystals must have an axial sulfide to explain the short and variable axial lengths observed; as only one stretch [ν(Nb=S) 489 cm^{-1}] is present in all these cases it must be attributed to this axial Nb=S, not to an undetected Nb=S in an octahedral site. Thus, unexpectedly, the demonstration of disorder in the *green* form of [$NbSCl_3(PMe_3)_3$] makes it *more* difficult to rule out bond stretch isomerism in these compounds.

Playing the devil's advocate with our own crystallographic results for the thioniobium system we sought to explain them as due to co-crystallisation of the *orange-yellow* form with different proportions of tetrachloride. This meant that, for this exercise, we suspended any consideration of the differences in ν(Nb=S), as Parkin had done in his consideration of the molybdenum systems. The difference of 0.0456 Å between the mean octahedral Nb–Cl length in the tetrachloride (2.4527 Å) from that in the *orange-yellow* form were used to estimate the fractional composition of the mixtures by the method outlined above, although in this case the differences in M–Cl lengths are very small so that the estimates are of limited accuracy. The fraction of chloride in these samples, estimated in this way, ranged from 0.09 to 0.26 in the original '*green* isomer', and when plotted against observed axial 'Nb–S/Nb–Cl' length a fairly gentle curve is obtained. The plot is useful in confirming how contamination is contributing to apparent bond lengthening but cannot be a true representation of the situation as we have deliberately neglected the IR evidence that in these three *green* forms [all with ν(Nb=S) 489 cm^{-1}] it is *not* the *orange-yellow* form [ν(Nb=S) 455 cm^{-1}] that is co-crystallised with the tetrachloride but the second form [ν(Nb=S) 489 cm^{-1}] for which no Nb=S bond length will be available until we have isolated it free from tetrachloride contamination.

Summary and Conclusions

From the results on the oxomolybdenum and the thioniobium systems it has been clearly established that the apparent bond differences observed from X-ray structure analyses of pairs of 'bond stretch isomers' are artifacts of unresolved disorder of the components of co-crystallisation with the isomorphous higher chlorides; the Nb–O differences in the two forms of [$NbOCl_3(PMe_3)_3$] must be treated with caution although in this case the disorder was resolved. Furthermore, it has recently been shown that the *green* oxotungsten complex [$WOCl_2L$]$^+$ of Wieghardt and co-workers also suffers from some contamination.[22] The accumulated evidence supports the very persuasive argument that *ipso facto* the phenomenon of bond stretch isomerism is an artifact of contamination. However it may not be that simple, as there remain a number of unanswered questions.

The thioniobium system presents the best case to illustrate the evidence that bond stretch isomerism may after all be a fact. Although it is now clear that the *green* form of [$NbSCl_3(PMe_3)_3$] [ν(Nb=S) 489 cm^{-1}] is not a pure compound, its properties cannot be explained as due to its being a mixture of the *orange-yellow* form [ν(Nb=S) 455 cm^{-1}] with the *green* tetrachloride (*i.e.* a parallel explanation to that accepted for the oxomolybdenum case) unless some explanation can be found for the difference in the observed stretch frequencies between the *orange-yellow* and *green* forms. It is not a solid-state artifact because the two stretches are also present in solution. It must therefore be concluded that the *green* form contains a different

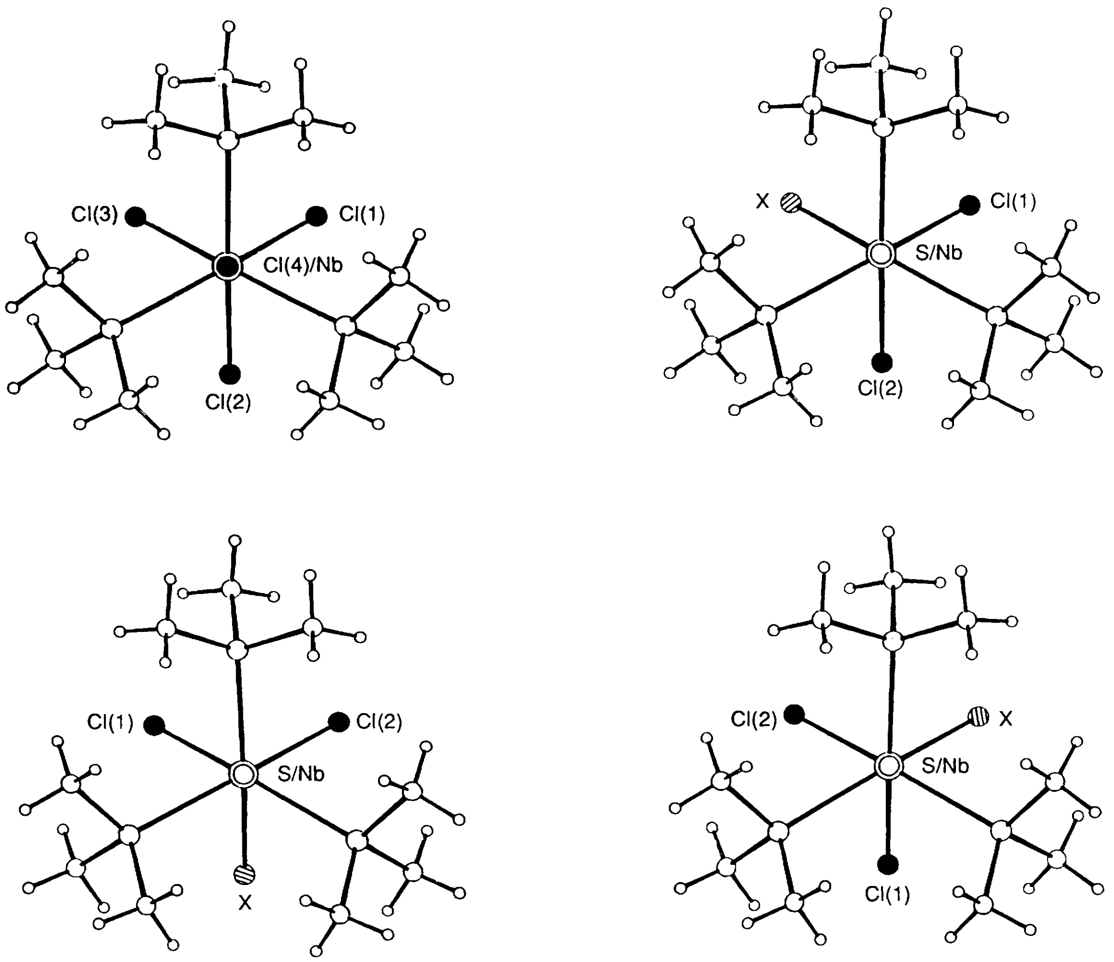


Fig. 12 The type of disorder model that might be the explanation of the difference in ν(Nb=S) in the *green* isomer. One of the chloro ligands has been replaced by another ligand X (such as OH or SH); this molecule might be three-fold disordered in addition to being contaminated with some [$NbCl_4(PMe_3)_3$]

thioniobium species from that in the *orange-yellow*, and yet the X-ray structure analysis shows no structural distinction between the two apart from slight bond length differences. In particular, the nature of the established disorder confirms that the thio ligand in this mystery species must be in the axial (face-capping) site as it is in the *orange-yellow* form, so that the difference in stretch frequency from that of the *orange-yellow* form is not explained by it being a geometric isomer with the thio ligand in an octahedral site. There appears to be only one other possibility, apart from bond stretch isomerism: does the unknown thioniobium species have some undetected difference in the non-sulfur ligand set? This cannot be dismissed on crystallographic grounds because, for example, replacement of one of the chlorides by a thiolate ligand (possibly generated during decomposition to the tetrachloride) would be undetectable if accompanied by a three-fold disorder involving interchange of the sulfur and chlorine sites (Fig. 12). Another possibility is that one of the chlorides is replaced by a hydroxide arising from partial hydrolysis. However, neither of these explains the observation that for *green* thioniobium compounds the chlorine analyses are consistently high: the presence of up to *ca.* 20% tetrachloride would not explain this if one of the three chloride ligands had been replaced by OH or SH.

Clearly in the thioniobium system the presence of chloride contaminant in the '*long bonded*' *green* form has not proved to be sufficient evidence to rule out bond stretch isomerism. Unexpectedly, it in fact makes the case for this type of isomerism quite hard to disprove. In the earlier work on this system the bond lengthening which appeared to be present in the *green* form was an embarrassment to the case because on the basis of the *infrared* spectra the *orange-yellow* form [ν(Nb=S) 455 cm^{-1}] was expected to have a longer Nb=S bond than that of the *green* [ν(Nb=S) 489 cm^{-1}]; it is now clear that the Nb=S bond length for the [$NbSCl_3(PMe_3)_3$] '*green*' isomer is as yet unknown and may be *shorter* than that in the *orange-yellow* isomer. It is an interesting corollary that it seems probable that this high-frequency species may also prove to be *orange-yellow* in colour as the observed *green* coloration for this form may be entirely due to the *green* tetrachloride with which it co-crystallises.

At this stage the only evidence of bond stretch isomerism that still appears to be irrefutable is spectroscopic. Although X-ray studies are essential evidence demonstrating the existence of species with virtually indistinguishable structures, the evidence of bond lengthening from these data is either suspect or wrong in all the known cases. However, there is strong spectroscopic evidence in at least two cases, the oxo- and thio-niobium systems, that nevertheless two 'isomers' do exist and probably do differ in their Nb=E lengths because the two ν(Nb=E) stretches are different in each case. As it has clearly been demonstrated that evidence of co-crystallisation of a contaminant does not rule out bond stretch isomerism in the niobium system it may be argued that the case against it in the oxomolybdenum system, which appears to be widely accepted without question, is in fact still not proven. For example, it might turn out to be that the *blue* form of [$MoOCl_2(PMe_2Ph)_3$] [ν(Mo=O) 941 cm^{-1}] obtained by Enemark, both by direct synthesis and by purification of the *green* form, is not the same isomer as the *blue* form reported by Chatt [ν(Mo=O) 954 cm^{-1}]. It is an intriguing alternative to the conclusion that Chatt misassigned the ν(Mo=O) for his *blue* isomer to ask whether this system may, as possible for the thioniobium system, have two *bond stretch* isomers of the same colour, both *blue*, and differing in their stretch frequencies. Further support for this may be gleaned from a comparison of the structure observed by X-ray analysis of the Chatt *blue* isomer by Manojlovic Muir with that of the *blue* form studied by Parkin and co-workers which shows very different Mo–Cl lengths *trans* to the Mo=O bond, 2.551(3) and 2.528(1) Å respectively.

Thus, overall it may be concluded that rationalisation of *bond stretch isomerism* as a mere solid-state artifact does not fit all the observations so far reported. However the evidence is that, if the phenomenon is a fact, chemists will be faced with the daunting challenge of spotting the isomers even though they are structurally almost identical and have the same colour. It may emerge that the reason the only examples of this controversial form of isomerism so far proposed have all had co-crystallised contaminant is because it is only the resultant (and possibly irrelevant) colour difference produced when one form partially decomposes that has led to two forms being identified.

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