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Crystallographic disorder in $[M_2X_8]^{n-}$, $M_2X_4L_4$ and related compounds: chemical and theoretical implications

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Abstract

Orientational disorder occurs in many simple salts and molecular solids, and has been studied by a variety of techniques. A more complex series of compounds, the transition metal complexes of the general types $[M_2X_8]^{n-}$, $M_2X_4L_4$ and $M_2X_4(P\text{–}P)_2$, exhibit an unusual but characteristic form of orientational crystallographic disorder. The metal–metal axis of these complexes often reveals that they have two- or three-fold orientational disorder of the ion or molecule, which gives the appearance of being simply a disorder of the M_2 within a set of halide and phosphine ligands. We provide here a complete tabulation of all such cases and we discuss some of the implications and questions that are thereby raised concerning the chemistry of these compounds.

Introduction

As the number of crystal structures reported continues to increase rapidly, it is becoming clear that disordered structures are not uncommon. Usually a disorder is an unmitigated nuisance, but certain types, one of which we shall review in detail here, are both esthetically appealing and potentially informative about the bonding and chemistry of the compounds in which they occur.

Broadly speaking, and without trying to be too pedantic or encyclopedic, there are three types of disorder. One is the chaotic type (always an unmitigated nuisance), such as solvent molecules that assume many orientations within interstitial holes between the principal molecules. A second type is positional disorder, which occurs when there are more sites available to a set of atoms in a particular structure than the number of atoms to fill them. An early example of positional disorder was observed in the compound CuI_2. The crystals of this salt have a disordered high temperature phase in which each copper ion has access to five sites, a central site and four others. The four additional sites surround the central site in a tetrahedral arrangement at distances of 0.09 nm [1]. Since there are more sites available than copper cations to fill them, there is randomness in the way in which the copper cations are distributed over the five sites. In truly random cases, this can be dealt with by placing fractional atoms at all sites.

The third common type of disorder is orientational disorder. When a polyatomic ion or molecule can assume two or more distinguishable orientations in a lattice, disorder between the orientations may occur. Orientational disorder occurs, for example, in KNCS. In the orthorhombic room temperature structure (*Pbcm*), the anions are ordered in an antiparallel arrangement. At sufficiently high temperatures this salt undergoes a transition, after which the NCS^- anions are still in the same plane, but disordered over two orientations. A representation of the orientation of the anion before and after the transition is shown in Fig. 1. The disorder can be visualized as a 180° rotation of the dumbbell shaped anion about the central carbon. As a result of this transition, the nitrogen and sulfur atoms are no longer distinguishable and a composite atom of [0.5N + 0.5S] replaces each of the individual atoms [2–4].

Another well-known example is provided by the tetrahedral cation NH_4^+ in ammonium chloride where there is a transition from an ordered low-temperature phase to a disordered high-temperature phase. Within any cell, the N–H bonds of the NH_4^+ cation are directed at four of the eight corners of a cube formed by chloride anions. There are two possible orientations for each ion as shown in Fig. 2, but at low temperatures all of

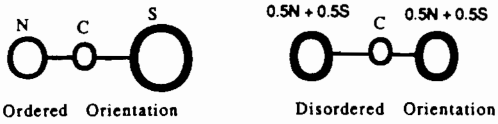

Fig. 1. A representation of the ordered and disordered orientations of NCS^- in KNCS.

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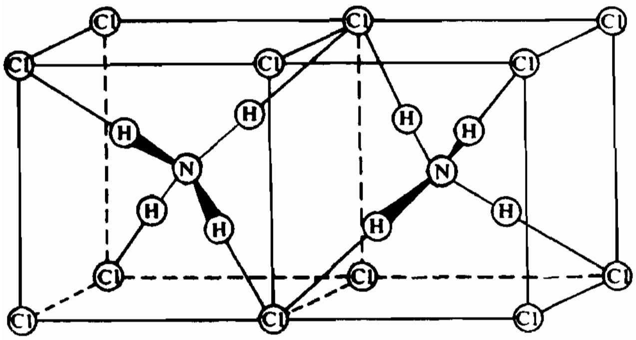

Fig. 2. A representation of the two possible orientations of the NH_4^+ cation in NH_4Cl.

the ions have the same orientation. The transition is due to reorientation of the ammonium cation within the cube of chloride anions. At high temperatures both orientations of the ammonium cation are observed. The change in orientation occurs by a rotation about a two-fold axis of the cation, a flip of 90° [5–7].

The examples mentioned above are just three of a multitude of simple ionic systems that undergo phase transitions involving a low-temperature ordered system and a high-temperature disordered system. There are more complex ionic systems with different degrees of disorder as well as disordered molecular systems, such as the molecular solid cycloheptane with four observed conformations [8].

A special type of orientational disorder

In the two cases just cited, there are several observed orientations of some entire component of the crystal that differ in such a way that it is obvious that the whole thing has been reoriented. Moreover, there are usually two distinct phases, one ordered and the other disordered completely. There are, however, many cases in which a changed orientation of a certain component is obviously only in the positions of some of its atoms (inner ones) but not in the positions of the outer shell atoms. This occurs when the shape of the outer shell is such that two (or more) orientations are tolerable within the crystal and also appear to be superimposable within the resolution of the X-ray diffraction experiment. Roughly speaking, the X-ray diffraction technique, as usually practiced, cannot resolve atoms whose positions differ by <0.6 Å, even when the two are of equal weight. In these cases, it is rare for a phase transition to occur or at least to be observed, and the disordered phase is usually only partially disordered.

Probably the first important example of this situation in inorganic chemistry was the structure of $Fe_3(CO)_{12}$ [9–11]. This molecule resides on an inversion center and to satisfy this, half of the molecules are inversion images of the others, but the two appear superimposed in the electron density map. The disorder is immediately apparent in the positions of the iron atoms, which are seen as six half-iron atoms at the vertices of a 'star of David'. However, the C and O atoms in the two orientations so nearly coincide that only one somewhat blurred set of twelve CO groups can be seen.

It is obvious that this type of disorder is possible because the shape of the molecule, that is, its outer surface, approximates to a high enough symmetry that it can fit into the lattice in two (or more) ways. This is the type of disorder we shall consider in detail for several classes of molecules that have M_2 units or M_4 units in the center, surrounded by ligands that define approximately though not rigorously a more symmetric shape. The case of $Fe_3(CO)_{12}$ is not entirely typical because there is a symmetry element in the crystal that makes the populations of the two orientations *exactly* equal; in other words the disordering is complete. In most of the cases we shall be discussing complete disordering does not occur, and the two (or three) orientations each have a different population.

$[M_2X_8]^{n-}$ compounds

These ions have a square prismatic structure (Fig. 3). However, the vertical edges (parallel to the M–M unit) are only slightly longer than the edges of the square base and the shape of the ion is very nearly a cube. Thus, it need not be considered surprising that in a crystal some of the nearly cubic anions take up an orientation perpendicular to the one adopted by the majority. We cannot detect this by examining the positions of the X atoms because they are so close to the positions they would have in the dominant or 'correct' orientation, but of course, the very different positions of the metal atoms show us what has happened.

This sort of occurrence was first observed in $K_4[Mo_2Cl_8]$ where 7% of the Mo atoms were found to be on an axis within the 'cube' of Cl atoms that was perpendicular to the axis where the other 93% were found. Interestingly enough, there have been no further observations of this among $[Mo_2Cl_8]^{4-}$ compounds, but it has been seen frequently for compounds containing $[Re_2X_8]^{2-}$ ions. All structures reported (whether disordered or not) are listed in Table 1, and it can be seen that about half of them display disorder. Strictly

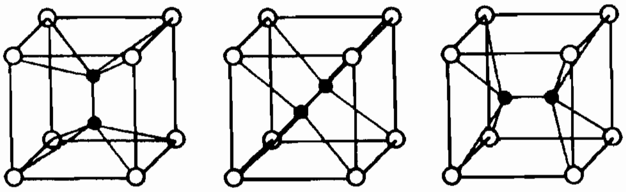

Fig. 3. The three possible orientations of the transition metal core in $[M_2X_8]^{n-}$ salts.

TABLE 1. Orientation disorder observed in $[M_2X_8]^{n-}$ structures

Compound	Occupancy (%)			Reference
$(n\text{-}Bu_4N)_2Re_2F_8 \cdot 2(C_2H_5)_2O$	100			13
$K_2Re_2Cl_8 \cdot 2H_2O$	100			14
$Cs_2Re_2Cl_8 \cdot 2H_2O$	100			15
$(NH_4)_2Re_2Cl_8$	100			16
$(pyH)_2Re_2Cl_8$	100			17–19
$(Me_3\text{-}pyH)_2Re_2Cl_8$	100			20
$(DMFA_2H)_2Re_2Cl_8$	100			21
$(Me_2NH_2)_2Re_2Cl_8$	100			21
$(n\text{-}Bu_4N)_2Re_2Cl_8$	74	26		22
$(PHPr_3)_2Re_2Cl_8$	76	24		23
$(PMePh_3)_2Re_2Cl_8$	61	39		23
$(PPh_4)_2Re_2Cl_8$	100			24
$(Et_4N)_2Re_2Cl_8$	67	17	16	25
$[ReCl_2(depe)_2]_2Re_2Cl_8$	74	26		26
$Cs_2Re_2Br_8$	100			27
$(n\text{-}Bu_4N)_2Re_2Br_8$	62	38		28
$(PMePh_3)_2Re_2Br_8$	82	18		23
$(PPh_4)_2Re_2Br_8$	95	5		29
$(DMAA_2H)_2Re_2Br_8$	57	36	7	30
$(n\text{-}Bu_4N)_2Re_2I_8$	33	33	33	31
$(Ph_4As)_2Re_2(NCS)_8 \cdot 2(CH_3)_2CO$	100			32
$(Ph_4As)_2Re_2(NCS)_8 \cdot 2C_5H_5N$	100			32
$(n\text{-}Bu_4N)_2Tc_2Cl_8$	69	31		33
$(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$	100			34
$K_3Tc_2Cl_8 \cdot nH_2O$	100			35
$K_4Mo_2Cl_8 \cdot 2H_2O$	93	7		12
$[enH_2]_2[Mo_2Cl_8] \cdot 2H_2O$	100			36
$[pipH_2]_2[Mo_2Cl_8] \cdot 4H_2O$	100			37
$(NH_4)_4Mo_2Br_8 \cdot 2H_2O$	100			38
$(NH_4)_4Mo_2(NCS)_8 \cdot 4H_2O$	100			39
$(NH_4)_4Mo_2(NCS)_8 \cdot 6H_2O$	100			39
$(PMePh_3)_2Os_2Cl_8$	63	37		40

$DMFA_2H$: $[(HCON(CH_3)_2)_2H]^+$; $DMAA_2H$: $[(CH_3CON(CH_3)_2)_2H]^+$

speaking, in those that do not, we can only say that there is no disorder in excess of 2%. In six cases there is one secondary orientation (with populations of 5 to 39%), while in two cases there are two secondary orientations each with a different population. In the case of $(n\text{-}Bu_4N)_2[Re_2I_8]$, there is equal population of three orientations, the equality being rigorously required by a three-fold crystallographic axis that coincides with one body diagonal of the I_8 'cube' (which is rigorously only a rhombohedron).

To what extent can we account for this array of structures, ranging from those not detectably disordered to the fully disordered case? Unfortunately we have no satisfactory rationalization (let alone a predicative theory) at present. However, because these are ionic compounds, there is one qualitative idea that probably has merit. Repulsive interactions between the M_2 units inside the cages and other cations outside should influence the orientation of the anions. The most favored orientation will be that in which the outside cations are as far as possible from the faces to which the M atoms are closest. The preference of the $[M_2X_8]^{2-}$ for one or the other of the two perpendicular orientations will then depend on how much coulombic repulsion they entail as compared to that in the preferred orientation. Thus, some correlation of outer cation distribution and the extent of disorder might be anticipated, but since other forces (generically called 'packing' forces) will also be different in different directions, the correlation need not be clear cut, and in fact, it is not.

Unfortunately, the degree of distortion of the octahalide cube does not allow the degree of disorder in the dirhenium axes to be predicted and in some cases it does not even follow this general trend. The compounds $(PPh_4)_2Re_2X_8$ have no disorder for X = Cl and a 95/5 ratio of the two orientations of the metal–metal axis for X = Br. This complex follows the expected trend that more disorder will occur when a more idealized cube of anions is present, but the salts $(PMePh_3)_2Re_2X_8$ have ratios of 61/39 for X = Cl and 82/18 for X = Br for the two orientations of the metal–metal axis [23, 24, 29]. Therefore, the tendency towards two-fold disorder of the dirhenium core appears to depend not only on the extent to which the shape of the $Re_2X_8^{2-}$ anion approaches that of a cube, but also the cation and the extent to which the surroundings will tolerate the tipping of the nearly cubic parallelepiped in a perpendicular orientation. Based on the data available for $Re_2X_8^{2-}$ salts where X = Cl, Br and I, it is not yet possible to predict a priori whether and to what extent a system will be disordered.

As a final point, we note that no disorder has ever been found in compounds containing $[M_2(NCS)_8]^{n-}$ ions. The reason for this appears to be simple. Because the M–M–X angles are typically 102–106° and the M–N–C–S groups are very long, the $[M_2(NCS)_8]^{n-}$ ion is far from cubic, but rather is a flattened square prism. Thus it is impossible for such a species to fit into the appropriate place in the crystal except when oriented in the 'right' direction.

$Re_2Cl_6(PEt_3)_2$

This compound presents us with the, so far, unique situation of one compound affording two types of crystals, one fully ordered and the other fully disordered [41]. As first isolated, many years ago, this compound formed monoclinic crystals containing no solvent of crystallization and displaying no disorder. However, crystals grown from toluene contain interstitial toluene molecules and are rhombohedral (space group $R\bar{3}c$). The $\bar{3}$ axis of the crystal passes through the two phosphorus atoms and, as shown in Fig. 4, this results in a 1:1:1 disorder of the Re_2 unit in three directions. The situation is very much like that in $(Bu_4N)_2Re_2I_8$.

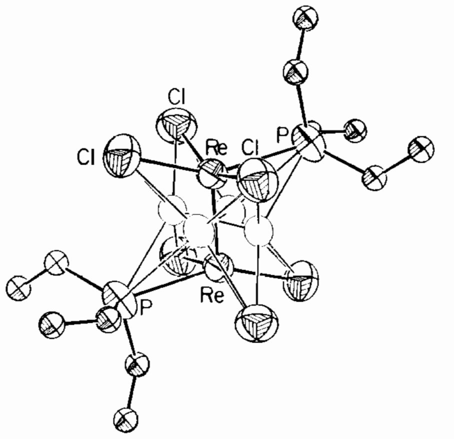

Fig. 4. ORTEP drawing of $Re_2Cl_6(PEt_3)_2$ showing the 1:1:1 disorder of the Re_2 unit.

TABLE 2. Orientation disorder observed in $M_2X_4L_4$ structures

Compound	Occupancy (%)	Reference
$[Re_2Cl_4(PEt_3)_4]ReO_4$	100	42
$Re_2Cl_4(PMe_2Ph)_4$	100	43
$[Re_2Cl_4(PMe_2Ph)_4]PF_6$	100	43
$[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$	100	43
$Re_2Cl_4(PEt_3)_4$	33 33 33	44, 45
$Re_2Cl_4(PMe_3)_4$	100	42
$Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$	43 29 28	42
$Re_2Br_4(P\text{-}n\text{-}Pr_3)_4$	50 32 18	42
$Mo_2F_4(PMe_3)_4$	33 33 33	46
$Mo_2Cl_4(PMe_2Ph)_4$	100	47
$Mo_2Cl_4(PHPh_2)_4$	100	47
$Mo_2Cl_4(PMe_3)_4$	100	48
$Mo_2Cl_4(PEt_3)_4$	33 33 33	47
$Mo_2Cl_4(SEt_2)_4$	100	49
$Mo_2Cl_4(pic)_4 \cdot CHCl_3$	100	50, 51
$Mo_2Br_4(PMe_3)_4$	100	52
$Mo_2Br_4(pic)_4 \cdot CHCl_3$	100	50
$Mo_2Br_4(4\text{-}Bu^tPy)_4 \cdot C_6H_6$	100	51
$Mo_2I_4(NCPh_2)_4$	100	53
$Mo_2I_4(PMe_3)_4$	100	51, 54
$Mo_2I_4(PhCN)_4$	100	53
$Mo_2(NCO)_4(PMe_3)_4$	100	55
$Mo_2(NCS)_4(PMe_3)_4$	100	55
$Mo_2(CH_3)_4(PMe_3)_4$	100	56
$Mo_2(CH_3)_4(PMe_2Ph)_4$	100	56
$W_2Cl_4(PMe_3)_4$	100	48
$W_2Cl_4(P\text{-}n\text{-}Bu_3)_4$	88 8.5 3.5	42
$Mo\text{–}WCl_4(PMe_2Ph)_4$	100	57

$M_2X_4L_4$ complexes

By far the largest class of mixed ligand complexes are those of this $M_2X_4L_4$ stoichiometry, and most of these have $L = PR_3$. Table 2 lists all the structurally characterized compounds that have the arrangement of ligands leading to D_{2d} symmetry. This means that the X and L ligands each occupy alternating corners of the 'cube'. Just as the $M_2X_8{}^{n-}$ ions with true D_{4h} symmetry are nearly cubic, the $M_2X_4L_4$ species, at least for the eight coordinated atoms, come very close to having tetrahedral symmetry. Thus, as the PR_3 ligand is fairly symmetrical, one might anticipate that once again a strong possibility of disorder should exist. And indeed this is the case.

In Table 2 there are nine compounds in which $L = PMe_3$ and only one of them, $Mo_2F_4(PMe_3)_4$, shows disorder. This disorder, however, is of the complete 1:1:1 three-fold type. This may be due to the fact that the PMe_3 ligand is so much larger than the F atom that the molecule is virtually a tetrahedron, as viewed from the outside. In the other eight cases, there are appreciable displacements of the PMe_3 and X ligands from the corners of the 'cube' in the way shown in Fig. 5. This makes the molecule appreciably longer in the direction of the M_2 axis and it can thus fit into the lattice in only the 'right' direction.

In the case of the compounds with PMe_2Ph ligands, there is no possibility of disorder because, as shown in Fig. 6 for one of them, the phenyl groups are all oriented so as to greatly elongate the molecule in the direction of the M_2 axis.

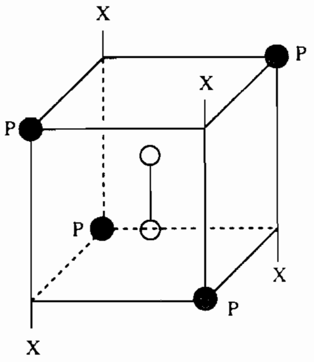

Fig. 5. Schematic representation of $M_2X_4(PMe_3)_4$ demonstrating the appreciable displacements of the PMe_3 and X ligands from the corners of a 'cube'.

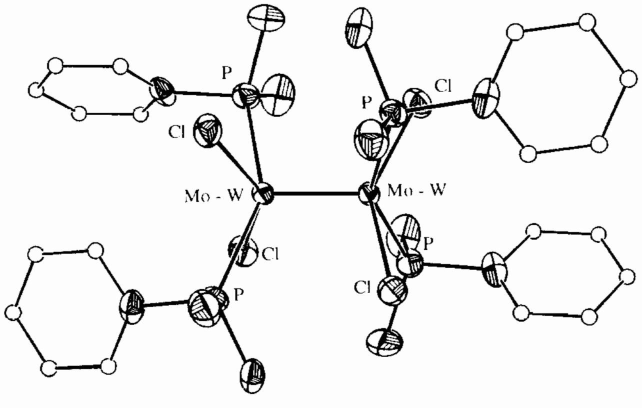

Fig. 6. ORTEP drawing of $Mo\text{–}WCl_4(PMe_2Ph)_4$ showing the orientation of the phenyl groups.

For compounds with PR_3 ligands other than PMe_3, namely with PEt_3, $P(C_3H_7)_3$ and $P(C_4H_9)_3$, disorder has been observed in each of the few cases so far examined. Evidently in these compounds the 'sloppiness' in the ethyl, propyl and butyl groups allows some of the molecules to occupy their sites in misoriented fashion. In the case of $Re_2Cl_4(PEt_3)_4$ there is an additional disorder, found nowhere else, namely, the Cl and PEt_3 ligands are randomly exchanged, in addition to a 1:1:1 disordering of the Re_2 units. These molecules are found at sites of crystallographic 432 (O_h) symmetry.

Table 3 lists seven $M_2X_4L_4$ compounds in which the anion, X, is an alkoxide. Only one of these displays disorder, namely, $Mo_2(OC_6F_5)_4(PMe_3)_4$. However, it is of a unique kind. First, the ligand arrangement is not of the D_{2d} type that we have just discussed, but instead is that shown in Fig. 7. Clearly, this allows two orientations of the Mo_2 unit within essentially the same ligand shell, whereas the third orientation would correspond to a different isomer. The two directions are not required by crystal symmetry to be equivalent, but in fact, the two populations are very nearly equal, namely 56% and 44% [58].

TABLE 3. Orientation disorder observed in $M_2X_4L_4$ structures in which the anion is an alkoxide

Compound	Occupancy (%)	Reference
$Mo_2(OC_6F_5)_4(PMe_3)_4$	56 44	58
$Mo_2(O\text{-}i\text{-}Pr)_4(py)_4$	100	59
$Mo_2(OCH_2\text{-}t\text{-}Bu)_4(HNMe_2)_4$	100	59
$Mo_2(OCH_2\text{-}t\text{-}Bu)_4(PMe_3)_4$	100	59
$Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4$	100	59
$Mo_2(O\text{-}i\text{-}Pr)_4(dmpe)_2$	100	60
$Mo_2(OC_6F_5)_4(HNMe_2)_4$	100	61

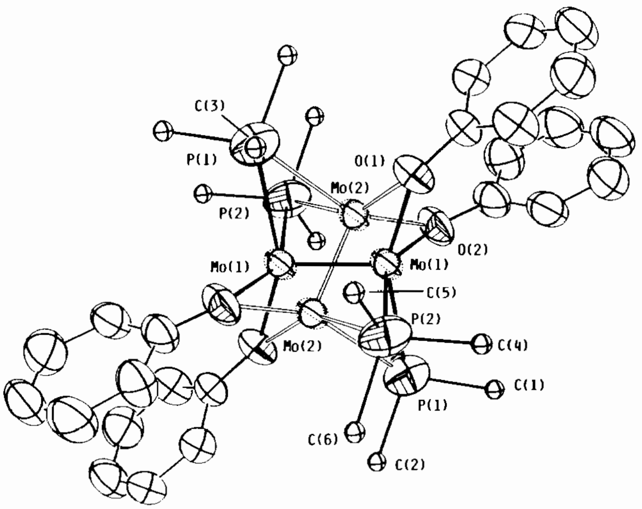

Fig. 7. ORTEP drawing of the disordered molecule $Mo_2(OC_6F_5)_4(PMe_3)_4$ showing the ligand arrangement.

$M_2X_4Y_2L_2$ complexes

Many compounds of this type have been reported, mostly with Mo_2^{6+} and W_2^{6+} cores. Only three have been shown to form disordered crystals, namely $W_2(OSiMe_2Bu^t)_6$ and $W_2Cl_4(NHBu)_2(PR_3)_2$, $PR_3 =$ PEt_3, PMe_3 [62]. In the latter case the molecule lies on a crystallographic position whose symmetry (*mm*) can be satisfied only by having a 1:1 disorder, and refinement proceeded well for such a model. It is said that a 1:1 disorder was also invoked to refine the PEt_3 compound, but here there is no requirement for 1:1 (or indeed any!) disorder. It is not clear why the disorder ratio was not treated as a parameter and allowed to seek an optimum value.

Compounds with two bridging biphosphines

Compounds of the general formula $M_2X_4(P\text{–}P)_2$, where P–P represents a biphosphine ligand of the general type $R_2P(C_nH_m)PR_2$ can occur in one or both of two isomeric forms, as shown schematically in Fig. 8. The α (bischelated) forms have never displayed disorder, but the β (bridged) forms frequently do so. All such compounds that have been characterized structurally are listed in Table 4. It may be noted that when the link between the phosphorus atoms is merely CH_2, disorder has never been observed, even though several of the complexes show appreciable twist angles. In other cases as well there are twisted molecules that show no disorder. It is true, however, that no untwisted molecule displays disorder.

The nature of the disorder is shown for the case of $Mo_2Cl_4(dppe)_2$ in Fig. 9. It should be clear that this would not be possible for an eclipsed molecule. It is also very important to notice that this type of disorder differs from cases already discussed in that each orientation of the M_2 unit exists in a *different molecule*. The two molecules differ most obviously in having opposite directions of twist, but not necessarily equal

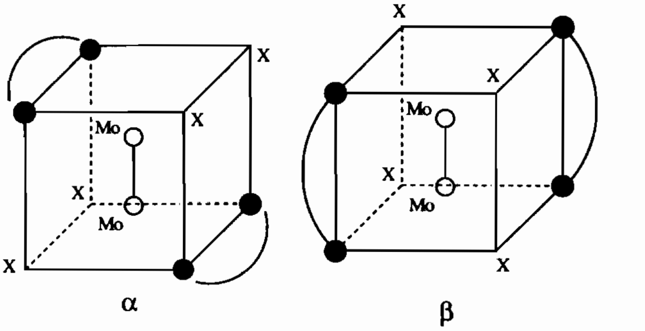

Fig. 8. Schematic representation of the two isomers of $Mo_2X_4(P\text{–}P)_2$: the α chelate form and the β bridged form (shown with an eclipsed geometry for simplicity).

TABLE 4. Orientation disorder observed in β-$M_2X_4(P\text{–}P)_2$ structures

Compound	Torsional angle	Occupancy (%)		Reference
$Re_2Cl_4(dppe)_2$	45	93.5	6.5	63
$Re_2Cl_4(depe)_2$	42.1	100		64
$Re_2Cl_4(dppee)_2$	60	80	20	65
$Re_2Cl_4(dppm)_2$	56	100		66
$Re_2Cl_4(dpae)_2$	not given	86	14	67
$Re_2Cl_4(dppa)_2$	47	100		68
$Mo_2Cl_4(dppe)_2$	30.5	87	13	69
$Mo_2Cl_4(dmpm)_2$	0	100		70
$Mo_2Cl_4(dppp)_2$	18	100		71
$Mo_2Cl_4(dmpe)_2$	40	90	10	72
$Mo_2Cl_4(dmpe)_2$	33.8	96	4	73
$Mo_2Cl_4(depe)_2$	41.4	100		64
$Mo_2Cl_4(dppb)_2$	23	100		74
$Mo_2Cl_4(dppee)_2$	25	83	17	75
$Mo_2Cl_4(dppm)_2$	0	100		76
$Mo_2Cl_4(tdpm)_2$	20	100		77
$Mo_2Cl_4(bppm)_2$	0	100		78
$Mo_2Cl_4[(R,R)\text{-DIOP}]_2$ (Δ)	−78	89	11	79
$Mo_2Cl_4[(R,R)\text{-DIOP}]_2$ (Λ)	87	89	11	79
$Mo_2Br_4(dppb)_2$	22	100		74
$Mo_2Br_4(dmpe)_2$	36.5	100		73
$Mo_2Br_4(dppm)_2$	0	100		77
$Mo_2Br_4(dppe)_2$	31	74	26	80
$Mo_2Br_4(arphos)_2$	30.3	76.5	23.5	81
$Mo_2I_4(dppe)_2$	28	100		82
$Mo_2I_4(dppe)_2$	0	100		82
$Mo_2I_4(dppe)_2$	26	100		82
$Mo_2I_4(dppm)_2$	0	100		83
$Mo_2(NCS)_4(dppm)_2$	13.3	100		76
$W_2Cl_4(dppe)_2$	31.3	93	7	84
$W_2Cl_4(dppm)_2$	17.3	100		85
$W_2Cl_4(dippp)_2$	75.9	100		86

arphos: 1-diphenylphosphino-2-diphenylarsinoethane; bppm: (2*S*,4*S*)-*N*-(tert-Butoxycarbonyl)-4-[(diphenylphosphino)-methyl] pyrrolidine; depe: 1,2-bis(diethylphosphino)ethane; (*R*,*R*)-DIOP: (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane; dippp: 1,3-bis(diisopropylphosphino)propane; dmpe: 1,2-bis(dimethylphosphino)ethane; dmpm: 1,2-bis(dimethylphosphino)methane; dpae: 1,2-bis(diphenylarsino)ethane; dppa: bis(diphenylphosphino)amine; dppb: (2*S*,3*S*)bis(diphenylphosphino)butane; dppe: 1,2-bis(diphenylphosphino)ethane; dppee: *cis*-1,2-bis(diphenylphosphino)ethylene; dppm: 1,2-bis(diphenylphosphino)methane; dppp: 1,3-bis(diphenylphosphino)propane; tdpm: tris(diphenylphosphino)methane.

angles, in general, nor do any of their other dimensions correspond exactly. Such a disordered crystal may be described as a solid solution of one rotational isomer in another. When we take this point of view it is natural to ask whether both rotational isomers are capable of existence outside of the crystal.

Only for $Mo_2Cl_4[R,R\text{-DIOP}]_2$ has it been shown that both isomers can exist independently in solution. It should not be surprising that the ratio is different in solution (1.7) from that in the crystal (8.1) [79]. In the crystal the two twist angles are 87° and −78°.

Miscellaneous other types

In addition to the fairly general classes of disordered compounds presented above and in Tables 1–4, there are several other types that it is appropriate to mention.

The cluster molecule $Mo_4Cl_8(PEt_3)_4$ also has been shown to form crystals with a two-fold disorder [87]. An ORTEP drawing of the core of this molecule is shown in Fig. 10. In the structure 92% of the Mo_4 rectangles are in one orientation and 8% are in an orientation perpendicular to the main one. The positions of the ligands are approximately the same for both orientations. The same type of disorder was earlier observed in the four-membered Re_4 ring in the molecule $(n\text{-}Bu_4N)_2[Re_4Cl_8(\mu\text{-}O)_2(\mu\text{-}OMe)_2]$ with the occupancy of the secondary orientation only 3% [88].

The structure of $Re_2H_8(PPh_3)_4$ with four bridging hydrides has been determined and the facile exchange of terminal and bridging hydrogen atoms investigated by variable temperature ^1H NMR spectroscopy. The Re–Re axis is disordered with 96% of the molecules in the major orientation and 4% in the minor orientation. The rapid exchange of the bridging and terminal hydrogen atoms in this complex could be due to an internal flip of the Re–Re bond within the ligand cage [89]. However, there are other possible mechanisms and there is no direct proof for any one mechanism.

The internal flip mechanism is also relevant to the disordered structure of $Mo_2(OC(CF_3)_3)_4(NMe_2)_2$. The disorder present in this complex (69/31) is still the only reported example of disorder of an M_2 unit within an M_2X_6 molecule [90].

Causes and consequences

The existence of the disordered structures reviewed above raises interesting questions about the how as well as the why of disordering, and also about whether any chemically significant conclusions or consequences can be drawn from the observations. At present there are many questions and foreseeable experiments but few answers and completed experiments. Thus, this concluding section will be brief, but, nonetheless, it adds an important perspective to the subject.

We know why the disorders *can* occur: because two or three of the same or similar molecules can fit reasonably well in two or three ways into the same crystal structure. We do not understand very well why the disorders *do* occur. That is, why do some members of a given class of compounds show no disorder, others

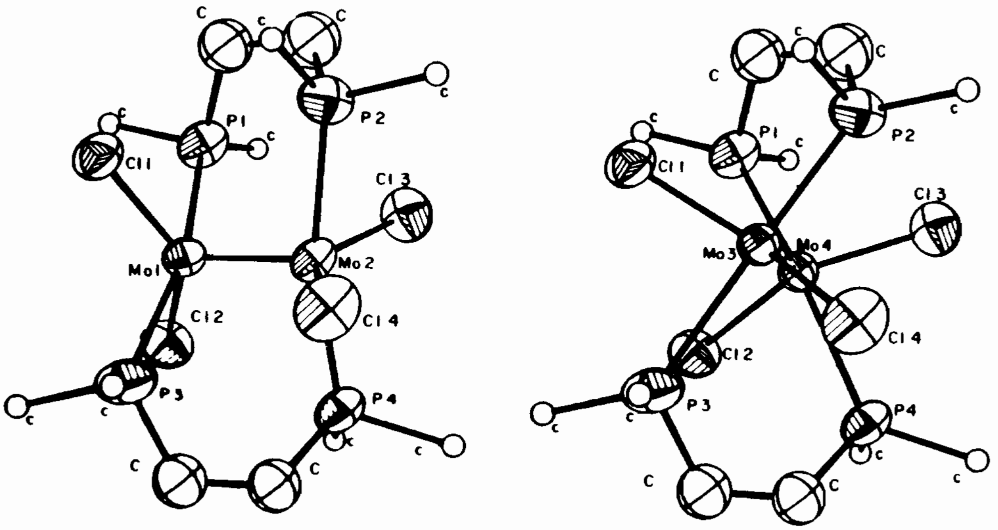

Fig. 9. Drawings of the core of the structure of $Mo_2Cl_4(dppe)_2$ showing how the Mo(1)–Mo(2) and Mo(3)–Mo(4) units form bonds to sets of *trans*-P_2Cl_2 ligands.

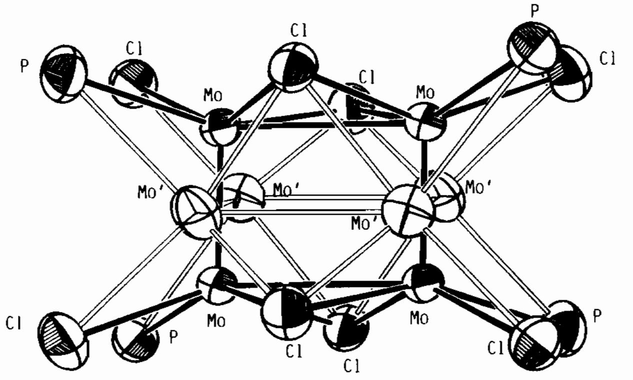

Fig. 10. ORTEP drawing of the $Mo_4Cl_8P_4$ core of the molecule $Mo_2Cl_8(PEt_3)_4$.

a two-fold disorder and still others a three-fold disorder.

It has often been assumed but never truly proved that the phenomenon is under thermodynamic control. This would mean, in the simplest case, that at a given temperature the extent of disorder should be determined by the free energy (ΔG_D) of giving a mole of molecules the 'wrong' orientation within a sea of molecules having the correct orientation. Of course, this is a non-cooperative model, valid only at infinite dilution and will certainly have to be modified to take account of cooperativity at many of the levels of disorder actually found. Generally speaking, the value of ΔG_D should depend on $\Delta H_D - T\Delta S_D$, where ΔH_D is the energetic cost of having a mole of misoriented molecules and ΔS_D is mainly attributable to the many permutations of the 'wrong' orientations over all the available positions.

Many experiments can be envisioned to test for thermodynamic control, but the only one carried out so far is the repeated preparation and structural characterization of the compound $(n\text{-}Bu_4N)_2Re_2Cl_8$ at ambient temperature, where it has been found that the same level of disorder is always observed, within *c.* 0.5%.

Whether or not the level of disorder is under thermodynamic control, there are interesting and as yet unanswered questions about how the disorder arises. One possibility, that *could* account for all known results, is that the disorder grows in as the crystals grow. In other words, as new molecules (or ions) come from solution to strike a growing crystal face, they are more likely to stick (and then be covered up) in one orientation than in another or others. Thus the end result, as observed by X-ray crystallography, is determined by the surface energetics and kinetics of the growth process.

Another possibility is that reorientation of molecules (ions) within the crystal can and does occur after it is formed, and that in some period of time, inversely proportional to the exponential of the activation energy for reorientation, the observed level of disorder will be obtained, regardless of the level that occurs during the growth process. While this may seem plausible in a few cases, generally speaking it does not seem reasonable that the large, knobby or spikey molecules typical of these substances could manage to turn by *c.* 90° within the confines of their crystal sites at any noticeable rate. In other words, in most cases their orientations are almost certainly 'locked in' once they become part of the interior of the crystal. Thus, we would have to believe that in nearly all, if not all cases

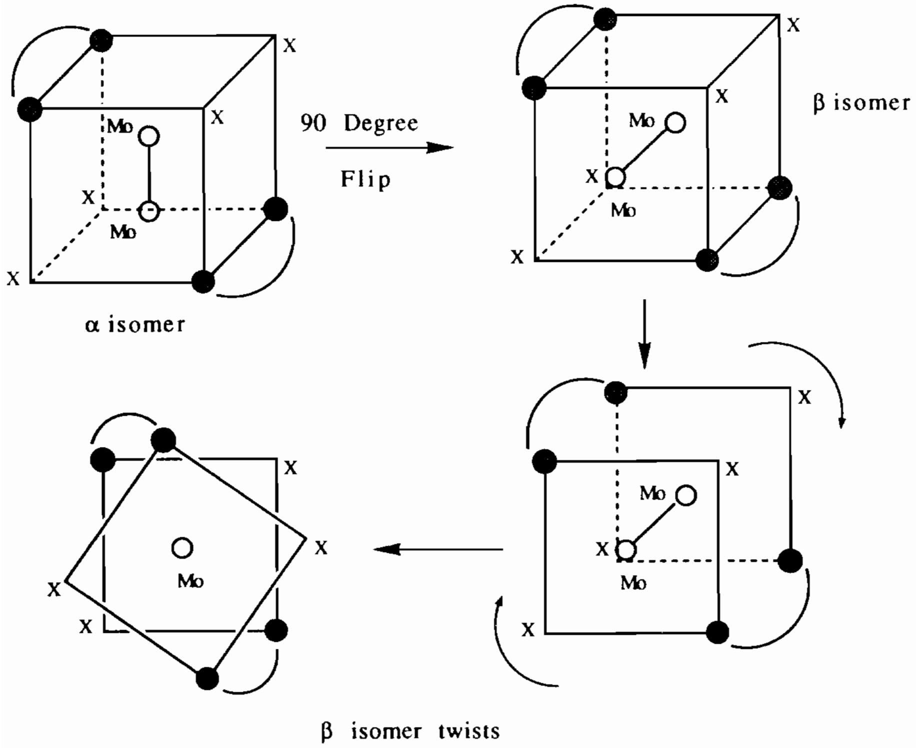

Fig. 11. The internal flip of the Mo_2 unit within the ligand cage in the α to β conversion of $Mo_2X_4(P\text{–}P)_2$.

the disorder level results from the surface thermodynamics and kinetics that govern crystal growth.

Unless there is some other process that has some likelihood of occurring within a formed crystal! Could there be such a process, and what might it be? To answer this question we must examine some chemistry dating back about a decade.

When the first compounds $M_2X_4(P\text{–}P)_2$ were made, it was found that in general there are two isomeric forms, as shown in Fig. 8. The α forms are generally less stable than the β forms and complete or nearly complete $\alpha \rightarrow \beta$ conversion occurs on heating [91, 92]. It was then found that the $\alpha \rightarrow \beta$ conversion processes are unimolecular, showing no dependence on the concentration of additional X^- ions or P–P molecules [93, 94]. Finally, however, the observation was made that α-$Mo_2Cl_4(dppe)_2$ could be converted cleanly and without decomposition in the solid state to the β isomer [95]. Moreover, in 1988 it was shown that $\alpha \rightarrow \beta$ conversion proceeds stereospecifically for $Mo_2X_4(P\text{–}P')_2$ type molecules, where P–P′ represents a diphosphine with distinguishable ends [96]. From all this evidence it was concluded that the $\alpha \rightarrow \beta$ process proceeds as shown in Fig. 11, where the crucial, rate-determining step is an internal flip of the Mo_2 unit within the ligand cage, followed by a moderate twist about the new Mo_2 direction to give the relaxed β isomer.

The internal flip mechanism for the $\alpha \rightarrow \beta$ isomerization raises the question of whether internal flips can occur in $M_2X_nL_{8-n}$ species generally. If so, it could constitute the ‘other’ process whereby the level of disorder can change within a formed crystal. At this point, we do not know for certain if this is true. In the $\alpha \rightarrow \beta$ isomerizations, the activation energies were 20–30 kcal mol^{-1}, which would mean that thermodynamic equilibrium could be reached in a period of seconds to days [94].

Clearly, the type of experiment that needs to be done in order to assess the correctness of such a mechanism will involve obtaining in some way (several can be imagined), a crystal with a level of disorder that does not correspond to the thermodynamic value for some temperature and pressure (T and P) and then observing the change in level as a function of time. For practical reasons this may well mean choosing T to be at or above room temperature and P to be one atmosphere. Experiments along these lines are underway in this laboratory.

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References

1 S. Miyake, S. Hoshino and T. Takenada, *J. Phys. Soc. Jpn.*, *7* (1952) 19.

2 H. P. Klug, *Z. Kristallogr. Kristallgeom., 85* (1933) 215.

3 C. Akers, S. W. Peterson and R. D. Willett, *Acta Crystallogr., Sect. B, 24* (1968) 1125.

4 Y. Yamada and T. Watanabe, *Bull. Chem. Soc. Jpn., 36* (1963) 1032.

5 P. Dinichert, *Helv. Phys. Acta, 15* (1942) 462.

6 A. A. Boiko, *Sov. Phys. Crystallogr., 14* (1970) 156.

7 N. G. Parsonage and L. A. K. Staveley, *Disorder in Crystals,* Clarendon, Oxford, 1978.

8 J. H. Brookeman and F. A. Rushworth, *J. Phys. C, 9* (1976) 1043.

9 C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc., 88* (1966) 1821.

10 C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc., 91* (1969) 1352.

11 F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc., 96* (1974) 4155.

12 J. V. Brencic and F. A. Cotton, *Inorg. Chem., 8* (1969) 7.

13 G. Henkel, O. Peters, W. Preetz and J. Skowronek, *Z. Naturforsch., Teil B, 45* (1990) 469.

14 F. A. Cotton and C. B. Harris, *Inorg. Chem., 4* (1965) 330.

15 F. A. Cotton and W. T. Hall, *Inorg. Chem., 16* (1977) 1867.

16 P. A. Koz'min, M. D. Surazhskaya and T. B. Larina, *Sov. J. Coord. Chem., 5* (1979) 593.

17 V. A. Kuznetzov and P. A. Koz'min, *Zh. Strukt. Khim., 4* (1963) 55.

18 V. A. Kuznetzov and P. A. Koz'min, *J. Struct. Chem., 4* (1963) 49.

19 W. K. Bratton and F. A. Cotton, *Inorg. Chem., 8* (1969) 1299.

20 W. R. Robinson, *Ph.D. Thesis,* Massachusetts Institute of Technology, Cambridge, 1966.

21 P. A. Koz'min, A. S. Kotel'nikova, M. D. Surazhskaya, T. B. Larina, S. A. Bagiror and T. V. Misailova, *Sov. J. Coord. Chem., 4* (1978) 1183.

22 F. A. Cotton, B. A. Frenz, B. R. Stults and T. R. Webb, *J. Am. Chem. Soc., 98* (1976) 2768.

23 F. A. Cotton, A. C. Price, R. Torralba and K. Vidyasagar, *Inorg. Chim. Acta, 175* (1990) 281.

24 F. Weller, K. Jausen and K. Dehnicke, *Acta Crystallogr., Sect. C, 43* (1987) 2437.

25 K. Gelman, N. S. Grigoriev, F. A. Cotton, S. V. Kryutchkov and L. Falvello, *Koord. Khim., 17* (1991) 1230.

26 F. A. Cotton and L. M. Daniels, *Inorg. Chim. Acta, 142* (1988) 255.

27 F. A. Cotton, B. G. DeBoer and M. Jeremic, *Inorg. Chem., 9* (1970) 2143.

28 H. W. Huang and D. S. Martin, *Inorg. Chem., 24* (1985) 96.

29 F. A. Cotton and K. Vidyasagar, unpublished results.

30 P. A. Koz'min, *Sov. J. Coord. Chem., 12* (1986) 647.

31 F. A. Cotton, L. M. Daniels and K. Vidyasagar, *Polyhedron, 7* (1988) 1667.

32 F. A. Cotton and M. Matusz, *Inorg. Chem., 26* (1987) 3468.

33 F. A. Cotton, L. M. Daniels, A. Davison and C. Orvig, *Inorg. Chem., 20* (1981) 3051.

34 W. K. Bratton and F. A. Cotton, *Inorg. Chem., 9* (1970) 789.

35 F. A. Cotton and L. W. Shive, *Inorg. Chem., 14* (1975) 2032.

36 J. V. Brencic and F. A. Cotton, *Inorg. Chem., 8* (1969) 2698.

37 I. Leban and P. Segedin, *Inorg. Chim. Acta, 85* (1984) 181.

38 J. V. Brencic, I. Leban and P. Segedin, *Z. Anorg. Allg. Chem., 427* (1976) 85.

39 A. Bino, F. A. Cotton and P. E. Fanwick, *Inorg. Chem., 18* (1979) 3558.

40 F. A. Cotton and K. Vidyasagar, *Inorg. Chem., 29* (1990) 3197.

41 F. A. Cotton and K. Vidyasagar, *Inorg. Chim. Acta, 166* (1989) 105.

42 F. A. Cotton, J. G. Jennings, A. Price and K. Vidyasagar, *Inorg. Chem., 29* (1990) 4138.

43 F. A. Cotton, K. R. Dunbar, L. R. Falvello, M. Thomas and R. Walton, *J. Am. Chem. Soc., 105* (1983) 4950.

44 F. A. Cotton, B. A. Frenz, J. R. Ebner and R. A. Walton, *J. Chem. Soc., Chem. Commun.,* (1974) 4.

45 F. A. Cotton, B. A. Frenz, J. R. Ebner and R. A. Walton, *Inorg. Chem., 15* (1976) 1630.

46 F. A. Cotton and K. J. Wiesinger, *Inorg. Chem., 31* (1992) 920.

47 F. A. Cotton, L. M. Daniels, G. L. Powell, A. J. Kahaian, T. Smith and E. F. Vogel, *Inorg. Chim. Acta, 144* (1988) 109.

48 F. A. Cotton, M. W. Extine, T. R. Felthouse, B. W. Kolthammer and D. G. Lay, *J. Am. Chem. Soc., 103* (1981) 4040.

49 F. A. Cotton and P. E. Fanwick, *Acta Crystallogr., Sect. B, 36* (1980) 457.

50 J. V. Brencic, L. Golic, I. Leban and P. Segedin, *Monatsh. Chem., 105* (1974) 142.

51 K. J. Ewing, S. I. Shupack and A. L. Rheingold, *Polyhedron, 9* (1990) 1209.

52 M. D. Hopkins, W. P. Schaefer, M. J. Bronikowski, W. Woodruff, V. Miskowski, R. Dallinger and H. B. Gray, *J. Am. Chem. Soc., 109* (1987) 408.

53 F. A. Cotton and R. Poli, *J. Am. Chem. Soc., 110* (1988) 830.

54 F. A. Cotton and R. Poli, *Inorg. Chem., 26* (1987) 3228.

55 F. A. Cotton and M. Matusz, *Inorg. Chem., 27* (1988) 2127.

56 F. A. Cotton and K. J. Wiesinger, *Inorg. Chem., 29* (1990) 2594.

57 F. A. Cotton, L. R. Falvello, C. A. James and R. L. Luck, *Inorg. Chem., 29* (1990) 4759.

58 F. A. Cotton and K. J. Wiesinger, *Inorg. Chem., 30* (1991) 750.

59 M. H. Chisholm, K. Folting, J. C. Huffman and R. J. Tatz, *J. Am. Chem. Soc., 106* (1984) 1153.

60 M. H. Chisholm, J. C. Huffman and W. G. Van Der Sluys, *J. Am. Chem. Soc., 109* (1987) 2514.

61 R. G. Abbott, F. A. Cotton and L. R. Falvello, *Inorg. Chem., 29* (1990) 514.

62 (a) D. C. Bradley, M. B. Hursthouse and H. R. Powell, *J. Chem. Soc., Dalton Trans.,* (1989) 1537; (b) M. H. Chisholm, C. M. Cook, J. C. Huffman and W. E. Streib, *J. Chem. Soc., Dalton Trans.,* (1991) 929.

63 F. A. Cotton, G. G. Stanley and R. A. Walton, *Inorg. Chem., 17* (1978) 2099.

64 F. L. Campbell, F. A. Cotton and G. L. Powell, *Inorg. Chem., 24* (1985) 4384.

65 M. Bakir, F. A. Cotton, L. R. Falvello, K. Vidyasagar and R. A. Walton, *Inorg. Chem., 27* (1988) 2460.

66 T. J. Barder, F. A. Cotton, K. R. Dunbar, G. L. Powell, W. Schwotzer and R. A. Walton, *Inorg. Chem., 24* (1985) 2550.

67 J. Ferry, J. Gallagher, D. Cunningham and P. McArdle, *Polyhedron, 8* (1989) 1733.

68 M. T. Costello, D. R. Derringer, P. E. Fanwick, A. C. Price, M. I. Rivera, E. Scheiber, E. W. Siurek III and R. A. Walton, *Polyhedron, 9* (1990) 573.

69 P. A. Agaskar and F. A. Cotton, *Inorg. Chem., 23* (1984) 3383.

70 F. A.. Cotton, L. R. Falvello, W. S. Harwood, G. L. Powell and R. A. Walton, *Inorg. Chem., 25* (1986) 3949.

71 F. A. Cotton, L. R. Falvello, D. R. Root, T. Smith and K. Vidyasagar, *Inorg. Chem., 29* (1990) 1328.

72 F. A. Cotton and G. L. Powell, *Inorg. Chem., 22* (1983) 1507.

73 F. A. Cotton and G. L. Powell, *Inorg. Chem., 24* (1985) 177.

74 P. A. Agaskar, F. A. Cotton, I. F. Fraser, L. Manojlovic-Muir, K. W. Muir and R. D. Peacock, *Inorg. Chem., 25* (1986) 2511.

75 M. Bakir, F. A. Cotton, L. R. Falvello, C. Q. Simpson and R. A. Walton, *Inorg. Chem., 27* (1988) 4197.

76 E. H. Abbott, K. S. Bose, F. A. Cotton, W. T. Hall and J. C. Sekutowski, *Inorg. Chem., 17* (1978) 3240.

77 F. L. Campbell, F. A. Cotton and G. L. Powell, *Inorg. Chem., 23* (1984) 4222.

78 J. D. Chen and F. A. Cotton, *Inorg. Chem., 29* (1990) 1797.

79 J. D. Chen, F. A. Cotton and L. R. Falvello, *J. Am. Chem. Soc., 112* (1990) 1076.

80 P. A. Agaskar and F. A. Cotton, *Rev. Chim. Miner., 22* (1985) 302.

81 F. A. Cotton, P. E. Fanwick, J. W. Fitch, H. D. Glicksman and R. A. Walton, *J. Am. Chem. Soc., 101* (1979) 1752.

82 F. A. Cotton, K. Dunbar and M. Matusz, *Inorg. Chem., 25* (1986) 3641.

83 F. A. Cotton, K. Dunbar and R. Poli, *Inorg. Chem., 25* (1986) 3700.

84 F. A. Cotton and T. R. Felthouse, *Inorg. Chem., 20* (1981) 3880.

85 J. A. Canich and F. A. Cotton, *Inorg. Chim. Acta, 142* (1988) 69.

86 M. D. Fryzuk, C. G. Kreiter and W. S. Sheldrick, *Chem. Ber., 122* (1989) 851.

87 F. A. Cotton and M. Shang, *J. Cluster Sci., 2* (1992) 121.

88 J. D. Chen and F. A. Cotton, *J. Am. Chem. Soc., 113* (1991) 5857.

89 F. A. Cotton and R. L. Luck, *Inorg. Chem., 28* (1989) 4522.

90 R. G. Abbott, F. A. Cotton and L. R. Falvello, *Polyhedron, 9* (1990) 1821.

91 S. A. Best, T. J. Smith and R. A. Walton, *Inorg. Chem., 17* (1978) 99.

92 J. R. Eber, D. R. Tyler and R. A. Walton, *Inorg. Chem., 15* (1976) 833.

93 I. F. Fraser, A. McVitie and R. D. Peacock, *J. Chem. Res., S,* (1984) 420.

94 P. Agaskar, F. A. Cotton, D. R. Derringer, G. L. Powell, D. R. Root and T. J. Smith, *Inorg. Chem., 24* (1985) 2786.

95 P. Agaskar and F. A. Cotton, *Inorg. Chem., 25* (1986) 15.

96 F. A. Cotton and S. Kitagawa, *Polyhedron, 7* (1988) 463.