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Modelling of metal complexes by the method of molecular mechanics

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ABSTRACT. The review considers various approaches to the conformational analysis of metal complexes within the framework of the method of molecular dynamics and analyses their possibilities and limitations. The limits of the applicability and usefulness of such calculations are outlined.

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I. Introduction

Molecular mechanics constitutes an empirical computational method in which the molecule is regarded as a system of interacting atoms. In this model, electronic ideas are involved implicitly or are absent altogether. The method is also known as the method of atom–atom potential functions, the additive model of interatomic interactions, the molecular force field method, the mechanical model of the molecule, etc.[1] We shall use the term "method of molecular mechanics" (MMM).

Molecular mechanics is one of the most powerful methods applied at the present time in the study of the steric structure of molecules and the estimation of the energies of intramolecular and intermolecular interactions and the properties associated with them. It is applied widely in organic chemistry for the solution of various structural and conformational problems, the calculation of the strain energy, thermochemical properties, and frequencies in vibrational spectra, for the prediction of the rates of chemical reactions and their stereochemical features, for the allowance of the packing effect in condensed media, etc.[2] However, the application of the MMM in the chemistry of metal complex compounds (particularly the compounds of transition metals) is significantly complicated, as a result of which the method has not so far been used very widely.

The main characteristic feature of the MMM applied to metal complexes is the necessity to model the coordination unit, because it is by no means always possible to establish *a priori* the type of coordination polyhedron for a metal with a specified atomic (ionic) radius and a specified coordination number. Here it is necessary to take into account the possibility of the occurrence of different oxidation states of the complex-forming metal and the different structural functions of the ligand.

Furthermore, like any empirical method, the MMM requires the use of a series of parameters, whose correct determination is difficult, particularly in the case of metal complexes, owing to the lack of a sufficient amount of the necessary experimental data. The problem of the selection of the initial approximations for the calculation, which is particularly important for polycyclic chelate compounds, also complicates the conformational analysis of complexes.

In this connection, in the conformational calculations for metal complexes it is necessary to introduce additional hypotheses about the structure of the coordination polyhedron, the nature of the interaction of the ligands with the metal, etc., which is the reason for the wide variety of the modifications of the MMM applied to the chemistry of coordination and organometallic compounds. The choice of a particular model is determined by the information possessed by the investigator and by the problems which he wishes to solve.

This review deals with various approaches to the conformational analysis of metal complexes within the framework of the MMM, their possibilities and limitations are analysed, and the limits of the applicability and usefulness of such calculations are outlined.

We decided not to describe in detail the MMM, its formal features and mathematical apparatus, the form of the potential functions, the technique of the calculation, etc. and also not to consider the advantages and disadvantages of the MMM compared with the experimental and other computational methods for the study of the steric structures and molecules. These questions have been dealt with in detail in numerous publications and in a series of fundamental monographs (see, for example, Refs. 2–4). Here we shall deal with the possibilities of the most "complete" or "correct" (i.e. with the minimum number of simplifications) version of the MMM. The widely used modifications of the MMM, differing mainly in the approach to the modelling of the coordination polyhedron, will be compared and the range of problems solved with their aid will be outlined. The methods for the conformational analysis of many-centre systems (cluster compounds) will be discussed separately.

We thought it desirable to consider also a series of simple mechanical models (strictly speaking not relevant to the MMM), which, on the one hand, are closely related to this method in their "ideology" and, on the other hand, may be useful in certain cases for the study of the steric structures of complex compounds.

Since the problems dealt with in this review have already been considered in a series of other reviews and monographs (see, for example, Refs. 5–7), we shall discuss mainly the results published in 1985–1988. Early studies containing descriptions of the models and

approaches used in subsequent publications as well as the necessary experimental data are an exception.

II. Complete allowance for the deformations of the coordination polyhedron

The MMM is most widely used in the study of the structures of coordination compounds: the prediction and reproduction of the geometry of the complexes, and comparison of the relative stabilities of isomers and structurally similar compounds. In certain branches of the chemistry of metal complexes, studies of this kind have already become fairly systematic. For example, the steric structures of chelate complexes of transition metals with nitrogen-containing ligands have been studied in detail. A review[8] summarises the results of structural and conformational studies of trisalkylenediamine complexes of transition metals with the aid of the MMM—this applies mainly to cobalt(III) complexes, which apparently have in general been studied most thoroughly by this method, and to chromium(III) complexes with five-, six-, and seven-membered chelate rings. The review presents data on the relative stabilities and geometries of the structural isomers and conformers of the above complexes.

An example of the uses of the MMM for the determination of the relative energy factors favouring the existence of particular isomers of complexes is provided by a study[9] of copper(II) complexes with unsubstituted, *N*-monomethyl-, and *N,N*-dimethyl-substituted (*R*)- and (*S*)-alanines. The calculation was performed in accordance with the MM2 program[10] using the parametrisation of Raos et al.[11] in terms of the approximation of the square planar configuration of copper(II). The calculation revealed that the energies of the *cis*- and *trans*-isomers of the $Cu(Ala)_2$ complex are similar and hence that there is a possibility of the presence of the *cis*-isomer in the equilibrium mixture. In complexes with mono- and di-methyl-substituted alanines, the differences between the energies of the *cis*- and *trans*-isomers increase and in the latter case the *cis*-isomers hardly occur. According to the calculation, the complexes containing ligands with the same configuration are more stable.

Similar problems were considered in a study[12] (see also Refs. 11 and 13) of copper(II) bis-*N,N*-dimethylisoleucinates CuL_2. A detailed conformational analysis of the isomers $Cu[(S)\text{-}L]_2$ and Cu[(*S*)-L][(*R*)-L] with the same *trans*-bonding of the aminoacid ligands was carried out. A characteristic of the stability of the isomer, taking into account the contributions of the possible conformations, is the quantity $<G>$†:

$$\langle G\rangle = \frac{\sum_{i=1}^{N} G_i \exp(-G_i/RT)}{\sum_{i=1}^{N} \exp(-G_i/RT)},$$

where G_i is the energy of the *i*th isomer calculated by the MMM. The authors[12] examined 16 conformers but only three of them make the dominant contribution to the quantity $<G>$ [72.4% in the case of the (*S,S*)-isomer ($<G>$ = −1.45 kJ mol^{-1}), which is consistent with experimental data,[16] although the difference between the energies of the diastereoisomers was not in fact reproduced quantitatively.

We may note that the use of the quantity $<G>$ as a characteristic of the relative stability of the complex undoubtedly leads to more correct results than the use of the energy of the steric strain of the most stable conformer frequently employed (see, for example, Timofeeva, et al.[9]) for such estimates.

The MMM can be applied also to the study of complex bioinorganic systems. For example, the possible structures of double-stranded oligonucleotides [*d*(G1−G2−C3−C4−G5−G6−C7−C8)−*d*(G9−G10−C11−C12−G13−G14−C15−C16)] and [*d*(T1−C2−T3−C4−G5−G6−T7−C8−T9−C10)−*d*(G11−A12−G13−A14−C15−C16−G17−A18−G19−A20)]‡ and their complexes with *cis*-diamminedichloroplatinum(II) (antitumour preparations) have been investigated.[17,18] The calculations were carried out by the AMBER program[19] using different force fields whose specific parameters as well as the procedures used to model the coordination polyhedron are unfortunately not indicated by the authors. In conformity with earlier data,[20,21] the addition of the *cis*-$[Pt(NH_3)_2]^{2+}$ fragment to the N atoms of two neighbouring guanosine G5−G6 fragments was considered. It was shown that platination leads to appreciable changes in the structure of the nucleotides: it disturbs the system of stacking interactions in the chain of nitrogen-containing bases, alters the conformation of the monosaccharide as well as the system of intrastrand and interstrand hydrogen bonds in the G5−G6 region, and is accompanied by the formation of a new P=O...H−N hydrogen bond involving a coordinated NH_3 molecule and the phosphate group of guanosine G5. According to the authors,[17,18] the presence of this hydrogen bond and the changes in the steric structure induced by it influence significantly the antitumour activity of platinated oligonucleotides, which in fact explains the observed[22] decrease in this activity in the series of ligands $NH_3 > NH_2R \geqslant NHR_2 \geqslant NR_3$.

Subsequently the same investigators showed[23] that platination of DNA can also lead to the bending of the axis of its helix. Two such "curved" structures have been investigated[23] with the aid of the MMM in relation to the decanucleotide [*d*(TCTCG*G*TCTC)−*d*(GAGACCGAGA)]§. According to the calculation, the stabilisation of both structures is caused by the appearance of yet another hydrogen bond between the second NH_3 ligand and the O atom of the guanosine G6.

The conclusion that both hydrogen bonds play a significant role in the complexes of DNA with various derivatives of diammine dichloroplatinum has been confirmed also by Hambley,[24] who investigated by the MMM the interaction of oligonucleotides with the (*R,R*)- and (*S-S*)-isomer of cyclohexylene-1,2-diammine platinum(II).

The MMM has been used[25] to elucidate the causes of the experimentally established[26,27] addition of diamminedichloroplatinum to the −A−G− sequence of nucleotides and the absence of adducts of this kind with the −G−A− nucleotides. The trinucleotides [*d*(GT*A*)−*d*(TCC)] and [*d*(GA*G*)−*d*(CTC)] were used as models of DNA and the calculations were performed using the force field specified by Weiner et al.[28]

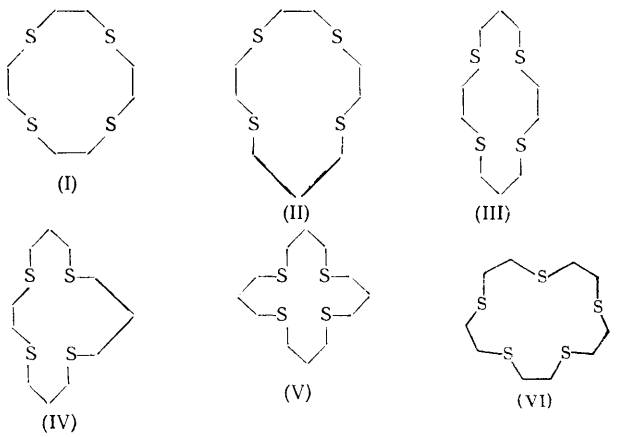
† The authors[12] refer to the quantity $<G>$ as the "Gibbs energy", although in fact it is none other than the enthalpy contribution to the steric component of the free energy of the molecule. For further details about the estimation of the latter with the aid of the MMM, see Kuz'min and co-workers.[14,15]

‡ A = adenosine, G = guanosine, T = thymidine, and C = cytidine.

§ Here and henceforth the asterisks denote the site of addition of *cis*-$[Pt(NH_3)_2]^{2+}$.

The MMM calculation showed that the formation of a complex with the second trinucleotide indicated is more favourable to the extent of 28.1 kJ mol^{-1}. This is explained by the fact that in the case of the $-A-G-$ sequence the complex is stabilised by the formation of the $-NH_3...O$ (guanosine) hydrogen bond (see above). On the other hand, in the case of the reverse sequence of nucleotides such bonding is impossible and the complex is destabilised as a result of the $-NH_3...N$ (adenosine) repulsion.

The MMM is so far used extremely rarely for the quantitative estimation of the influence of the steric factors on the reactivity of metal complexes. As one of the few available examples, one may quote a study[29] of the copper(II) complexes with the ligands (I)–(VI):

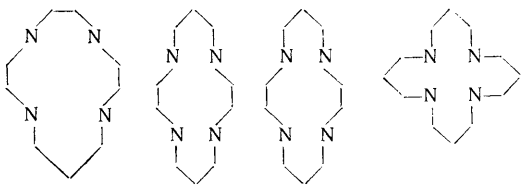


Boyd's program[30] was used for the calculations and the force field was analogous to that employed by Brubaker and Johnson.[6] The calculated structures are fully consistent with those found by X-ray diffraction (XRD).[31]

An attempt was made to subtract from the experimental[32] enthalpies and free energies of formation of the above complexes the calculated energy of the intramolecular strain in the ligands. It was found that the remaining part of the free energy, corresponding to the hypothetical complex free from intramolecular strain (ΔG_{int}), is virtually the same for complexes with the ligands (I)–(V) and amounts to 35.5 kJ mol^{-1}. At the same time, linear relations were observed between the intramolecular strain energy (ISE) calculated by the MMM and the free energy of formation of the complexes with the ligands (I)–(V) and also between the intramolecular strain energy and the logarithms of the rate constants for the dissociation of the complexes with the ligands (II)–(V) in aqueous solution.[33]

It has been concluded[29] that the enthalpies of formation of the above complexes and the enthalpies of activation for the complex formation reactions are predominantly influenced by the intramolecular strain in the ligand when the contribution of the Cu–S interactions is constant. The anomalous behaviour of the complex with the ligand (VI), which is inconsistent with the above relations, can apparently be explained, according to the authors, by the influence of the fifth Cu–S bond not only on the enthalpy components but also on the entropy components of the free energies of formation of the complexes.

The same authors investigated with the aid of the MMM the dissociation in aqueous solution of the complexes $[CoLCl_2]^+$, where L represents the nitrogen-containing macrocyclic ligands (VII)–(X) and their open-chain analogues—1,8-diamino-3,6-diazaoctane (XI) and 1,9-diamino-3,7-diazanonane (XII).



The calculations were performed using the force field of Brubaker and Johnson[6] and Boyd's program.[30]

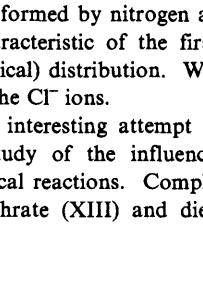
Two model intermediates formed in the hydrolysis of the complexes $[CoLCl_2]^+$ as a result of the removal of one chlorine atom from the initial molecule have been considered.[34] It was assumed that in the first intermediate the geometry of the ligand environment of the cobalt atom remains unaltered, while in the second a new geometry was calculated by means of additional optimisation. The free energy ΔG_{int} was calculated for the second model of the intermediate as had been done by Brubaker and Johnson.[29] It was found that ΔG_{int} is constant for the group of open-chain ligands (~123 kJ mol^{-1}) and the group of tetraazamacrocycles (~137 kJ mol^{-1}). The authors do not explain the difference between these quantities. In our view, the difference is caused by the entropy component of the macrocyclic effect.[35] The authors[34] also analysed in terms of the optimised structure of the intermediate the possibility of the formation of various products of the hydrolysis of the isomeric complexes of (XII).

Continuing these investigations, an attempt was made[36] to model with the aid of the MMM the first hydration shell of the complex cation $[CoLCl_2]^+$, where L is the macrocycle (VIII).

According to the model proposed by the authors,[36] the other molecules (from 1 to 14 molecules) were placed in a random fashion at distances of ~5 Å from the complex and their relative disposition was then found by direct optimisation. Potential functions without an electrostatic component were used.

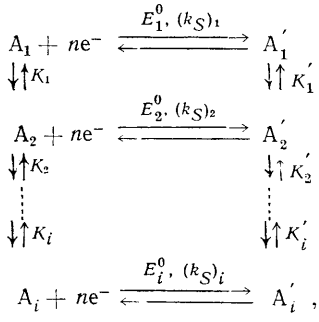
The calculations were performed for 80 different initial positions of the water molecules. The authors note that, as a result of the $-O...H-C-$ interactions, the distribution of H_2O molecules in the plane formed by nitrogen atoms outside the limits of the macrocycle is characteristic of the first hydration shell and not their random (spherical) distribution. Water molecules are more rarely distributed near the Cl^- ions.

An interesting attempt has been made[37] to apply the MMM to the study of the influence of conformational effects on electrochemical reactions. Complexes of divalent and trivalent cobalt with sepulchrate (XIII) and diethylenetriamine (XIV) were investigated.



Cobalt(III) complexes with nitrogen-containing ligands have been fairly frequently investigated by the MMM (see, for example, Brubaker and Johnson[6] and Saito[8]), but the analogous cobalt(II) complexes have been little studied. The force field proposed by Bond et al.,[37] which applies to both these and other complexes, is therefore of independent value. The results obtained reproduce satisfactorily the XRD data.[38,39]

It has been shown that the most stable conformers of complexes with divalent and trivalent cobalt are significantly different [both for the ligand (XIII) and for (XIV)] and the oxidation-reduction process is therefore accompanied by conformational transitions. Thus, according to Bond et al.,[37] the above electrochemical reaction can be represented by the following scheme:



where A_i and A'_i are conformers of complexes in different oxidation states, K_i and K'_i are the constants of the conformational equilibria, E°_i is the standard oxidation-reduction potential, and $(k_S)_i$ is the rate constant for electron transfer.

The authors compared the results of the calculation with the results of a polarographic experiment, but were unable to estimate quantitatively the nature and rates of the conformational transitions.

The calculated and experimental free energies of formation of three structural isomers of cobalt(II) and cobalt(III) complexes with the ligand (XIV) were compared. The results of the calculation did not agree with the experimental data (which is not surprising, since one is dealing with a heterogenous electrode process), but they undergo parallel changes on passing from cobalt(II) to cobalt(III).

The MMM was used similarly[40] to study the electrochemical oxidation-reduction of cobalt complexes with 1,2-propylenediamine. Four structural isomers of the above complexes were investigated. Their calculated enthalpies of formation are satisfactorily correlated with the experimental data. The oxidation-reduction potential of this system was calculated from the difference between the energies of the corresponding cobalt(III) and cobalt(II) isomers. It proved to be ~20 mV, which agrees with experimental polarographic data.

The steric factors governing the stabilities of mixed thiosemicarbazide–carboxylate complexes $CuL_n(TSC)_2$, where TSC = thiosemicarbazide and its phenyl derivatives and L = anions of monocarboxylic ($RCOO^-$, n = 2) and dicarboxylic [$R(COO^-)_2$, n = 1] acids and Cl^-, have been investigated[41] with the aid of the MMM. The calculations were performed using the CONCOORD program pack.[42]

In the series of bisthiosemicarbazide complexes (L = Cl^-), the *trans*-isomers with the diequatorial arrangement of the phenyl groups were found to be more stable. A satisfactory linear relation was observed between the conformational energies and the stability constants of the complexes in aqueous solutions. It was shown that the formation of heteroligand copper(II) thiosemicarbazide-carboxylate complexes is mainly determined by the greater or lesser steric strain in these complexes compared with the corresponding copper(II) bisthiosemicarbazide.

Thus it can be seen from the examples considered¶ that the MMM can be used successfully in the chemistry of metal complexes for the solution of different problems. It not only permits the calculations of the structures and relative stabilities of the complexes which have now come to be regarded as usual, but also it enables one to investigate their functioning and permits a quantitative estimation of the influence of steric factors on their reactivity.

However, we may note that the calculations considered above were performed for compounds with complex-forming metals which have been comparatively thoroughly investigated by the MMM [one may include among them perhaps only cobalt(III) and copper(II)], while in the case of cobalt(II) a preliminary parametrisation was required, which is impossible without an adequate set of experimental data which is difficult to obtain.

In order to perform such calculations for metal complex derivatives, various modifications of the MMM, based on the complete or partial neglect of the nature (type, dynamics) of the coordination polyhedron and on the introduction of additional *a priori* hypotheses about the specificity of the interaction of the metals with the ligands, were developed. Two models were mainly used.

The model of the first type is as follows: the form of the coordination polyhedron is not fixed, only metal–ligand bond lengths being fixed. The force constants of the L–M–L bond angles were close to zero.

In the model of the second type the coordination polyhedron is fixed and the force constants of the L–M–L angles are infinitely large.

Such assumptions naturally make the model more approximate but in many cases the use of approaches of this kind makes it possible to obtain useful information about the steric structure and properties of metal complexes.

III. The "floating point" model

An example of the most logical application of the model of the first type is the modification of the MMM, proposed by Dashevskii, Baranov, et al.,[43] which the authors called the "floating point" method or (on the basis of the mathematical procedure employed) the method of "penalty functions" (Fig. 1).

In this method, the complex forming atom is modelled by the so called "floating point".[43,44] Its interaction with the ligands is described by a penalty function of the type

$$U_{\text{pen}} = \sum_i K(l_i - l_0)^2,$$

where K is an empirical constant—the contribution of the penalty function to the overall target function (for further details, see Baranov et al.[44]), l_i is the distance from the donor atoms of the ligand to an arbitrary "floating" point with the coordinates X, Y,

¶We recall that we are dealing with the most "complete" version of the method, i.e. the calculations were performed taking into account both the deformations of the coordination unit and the non-valence L–M interactions.

and Z, and l_0 is the specified length of the coordinate bond. The summation is carried out over all the possible metal–ligand bonds and the resulting quantity U_{pen} is added to the energy of the intramolecular interactions calculated by the MMM. Next, the minimum in the overall target function is sought with respect to all the conformational parameters of the ligands and the coordinates of the point.

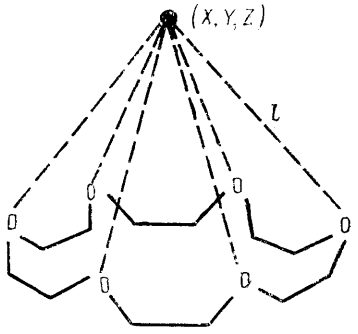


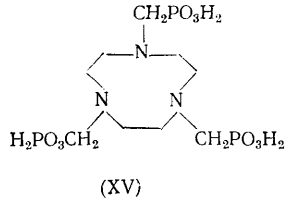
Figure 1. The "floating point" model.

By repeating calculations of this kind for variable values of l_0, one determines the $\Delta E = f(l_0)$ relation, each point of which reflects the energy expended by the ligand on the rearrangement to the conformation characteristic of it in the complex with the cation i separated from the donor atoms by a distance l_{0i}. If the above relation has a deep minimum, then the position of the latter defines the optimum length of the coordinate bond, the geometry of the coordination unit, and the conformation of the chelate rings.

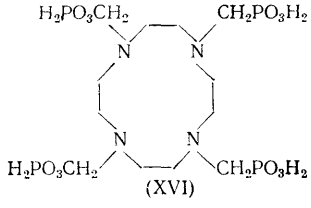
Thus in the method described account is taken only of characteristics such as the metal–donor atom bond lengths. The type of coordination polyhedron is not then fixed and non-valence interactions between the metal and the atoms of the ligand as well as the nature of the deformation of the metal–donor centre bonds are disregarded. An undoubted advantage of the method of penalty functions is the fact that the curves obtained for the variation of the conformational energy of the ligand with the length of the hypothetical coordinate bond can be interpreted in many instances as selectivity curves, using them for the analysis of the possibility of the adaptation of the given ligand to a particular metal cation.[45] We may also note that the above curves reflect to some extent not only the result but also the cause of the conformational rearrangement of the ligand during complex formation.

An example of the use of the "floating point" method may be provided by a study[44] (see also Refs. 43 and 46–48) of the complex-forming properties of tetraphenylmethylenediphosphine dioxide $(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)_2$. The dependence of the conformational energy (taking into account the "penalty") of the complexes ML_3 on the metal–ligand donor atom distance was investigated in this study. It was shown how the structure of the coordination unit varies as a function of l_0: for l_0 = 3 Å, the coordination polyhedron is an almost regular octahedron with a twist-conformation of the chelate rings; for l_0 = 2.5 Å, it is a regular prism with the chelate rings in the chair conformation; for l = 2 Å, it is a distorted octahedron with two chelate rings in the boat conformation and the third one in the twisted chair conformation. It has been stated[44] that these results reproduce satisfactorily the experimental data[49,50] for the structure of the coordination polyhedron in complexes of this kind.

The method of penalty functions is usually employed to investigate the complex-forming capacity of macrocyclic polydentate ligands. Thus a theoretical conformational analysis of the macrocycles (XV) and (XVI) with exocyclic groups containing donor centres (cyclopendants) has been carried out[51] (see also another study by Kabachnik, et al.[52]).



(XV)



(XVI)

Analysis of the dependences of the conformational energy on l_0 (by a procedure similar to that described above) showed that the optimum length of the M–L bond for the ligand (XV) is 1.95 Å. The ligand is then in the hexadentate "twisted basket" conformation. The selectivity of the ligand (XV) in this conformation is significantly greater than that of (XVI) for which the most favourable lengths of the coordinate bonds are in the wide range 1.9–2.2 Å. The maximum denticity of the ligand (XVI) is not achieved. It exhibits a denticity of 5 or 6. According to the calculation, in certain cases [for example in the copper(II) complex[52]] the ligand (XV) is also in the pentadentate conformation, which indicates the possibility of a ready adjustment of the ligand contour of the cyclopendants with respect to the coordination polyhedron characteristic of the metal ion.

The results obtained agree with the experimental data[53,54] for the stability constants of the transition metal and group II metal complexes with the ligands (XV) and (XVI).

The method of penalty functions has also been used[55,56] to estimate the selectivity of the formation of crown-ether complexes. A study was made of the influence of the ring size and of the number and relative positions of the donor atoms on the capacity of macrocyclic complexones for adaptation. It was shown that both an increase in ring size and an increase in the number of donor centres increased the selectivity of macrocyclic ligands. In the first case, the length of the hypothetical coordinate bond corresponding to the optimum conformation of the complex diminishes under these conditions, while in the second it increases. The introduction of conformationally rigid fragments into the ligand diminishes its selectivity. It has been established that analysis of the selectivity curves obtained by the method of penalty functions permits a satisfactory prediction of the relative stabilities of the complexes of crown-ethers with alkali metal ions.

A model similar to the method of penalty functions, which the authors called[57,58] the "hinged model", has been used to investigate the structures of transition metal complexes $M(CO)_6$, $CpM(CO)_n$ (n = 3, 4), $(\eta^4\text{-}C_4H_6)M(CO)_3$, MCp_2, $M[C_5(CH_3)_5]_2$, Cp_2MX_2 (X = H, Cl, CO), and Cp_2MH_3. The calculations were performed in accordance with Boyd's program.[30]

In the model discussed, as in the method of penalty functions, the force constants for the deformation of the angles at the metal atom were assumed to be zero. Thus the form of the coordination polyhedron is not controlled and the ligands bound to the complex-forming agent can rotate freely around the centre ("hinge"). However, in contrast to the "floating point" model, in this modification of the MMM the M–L bond lengths are not varied and their values, taken from X-ray diffraction data, are fixed by specifying higher force constants (the analogue of the "penalty").

The optimum disposition of the ligands corresponds to the minimum in the energy of the non-valence interactions between them (as in the "points on a sphere" model[59]) and the non-valence interactions with the metal atom are not taken into account.

The calculations performed on the basis of the "hinged" model made it possible to reproduce qualitatively the relative disposition of the ligands in the structures most typical for organometallic compounds (half-sandwich, sandwich, and bent sandwich). A satisfactory agreement was achieved between the calculated and experimental ligand–metal–ligand angles (the discrepancies were 5–10°). Certain regular features observed in the structure of π-complexes were reproduced.

The "floating point" ("hinged") model described can apparently be used quite correctly to carry out calculations for complexes with isotropic spherical complex-forming metal cations (alkali and alkaline earth metals—see, for example, Trigub[55] and Kuz'min[56]). On the other hand, its application to transition metal complexes is significantly restricted (as has been justly noted by Slovokhotov, et al.[57]) to the range of compounds for which the principle of the uniform filling of the coordination sphere by the ligands holds. These include, for example, complexes in which the transition metal atom attains the 18-electron inert gas shell environment ("quasi-spherical" ligand environment[60]) and complexes in which "premature" dense filling of the coordination sphere by ligands takes place (for example, π-complexes[57]).

It is noteworthy that consideration of the legitimacy of the assumption of the elasticity of the bond angles (and hence of the applicability of the "hinged" model) is outside the framework of the MMM and should be based on experimental data or on the results obtained by more rigorous computational methods.

When applied correctly, such models, neglecting the elasticity of the bond angles and the metal atom, make it possible, as shown above, not only to estimate the conformational changes in the ligand occurring on complex formation but also to reproduce qualitatively the type of coordination polyhedron and also (using the procedure of "penalty functions") to investigate the process dynamics and the influence of steric factors on the selectivity of the complex formation.

We may note that in all the models examined above no account is taken of non-valence metal–ligand interactions, allowance for which (which naturally requires an additional parametrisation) increases significantly the reliability of the results obtained with the aid of these approaches. When no account is taken of non-valence interactions, a situation may arise, in particular, where the "floating point" coincides with one of the non-donating ligand atoms or is "superimposed" on one of the bonds (which lacks physical significance for understandable reasons).

An attempt to take into account non-valence interactions of the metal–ligand type was undertaken in a study[61] of β-diketonate (β-dik) lanthanide complexes $Ln(\beta\text{-dik})_3L$ (Ln = Eu, Yb; β-dik = acetylacetonate, dipivaloylmethanate; L = water, quinuclidine). The authors[61] consider these complexes as models for the study of the steric factors governing the functioning of lanthanide shift reagents in NMR spectroscopy. A modified[61] MM2 program[10] was used in the calculations. Here the force field was expanded by incorporating in it the force constants of the bonds and bond angles, the barriers to rotation, and the parameters of the van der Waals interactions with participation of Eu and Yb atoms (with the exception of the force constants of the bond angles at the metal atom). The calculated structures of the complexes agree well with those found by the X-ray diffraction method;[62,63] it was shown that the most favourable conformations correspond to the three-bladed propeller form.

It has been suggested[64] that not only non-bonding interactions of the metal atom (without additional parametrisation) but also the form of the coordination polyhedron be taken into account within the framework of the "floating point" model. For this purpose, the penalty function is supplemented as follows:

(1) By quasi-non-valence interactions of the "floating point" with the ligand atoms which are not donor centres, in conformity with the hard sphere approach:

$$F_{r_i^*<r_0} = \begin{cases} 0, & r_i > r_0 \\ U_{\max}, & r_i \leqslant r_0 \end{cases},$$

where r_i is the distance from the "floating point" to the ith ligand atom, r_0 the van der Waals radius of the ith atom, and $U_{\max}$ an empirical constant—the "barrier" to the collision of atoms.

(2) By quasi-elastic angular deformations:

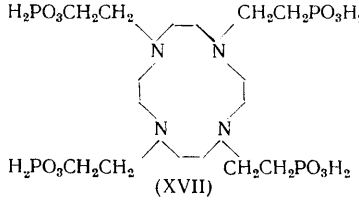
$$U_{\text{def}} = K_2 \sum_i (\alpha_i - \alpha_0)^2,$$

where K_2 is an empirical constant (the contribution of the deformation of bond angles to the overall target function), α_i are the angles formed in the ligand–"floating point"–ligand system, and α_0 are the bond angles characteristic of the donor atoms of the ligands and of the quasi-coordination polyhedron corresponding to the "floating point".

For comparison, the calculation was performed in terms of the approximation described[64] for 18-crown-6, the cryptand[2.2.2.], and the cyclopendant (XVI), which had been investigated previously[43,51] without the refinements indicated. It was shown that such correction of the penalty function influences significantly the form of the dependence of the energy of the molecule on the metal–ligand distance, particularly on the steepness of the walls of the "potential well". Some of the conformations of the ligands indicated, generated previously, proved to be artefacts.

However, one may note that the observed effects are in all probability not associated with the introduction of quasi-elastic angular deformations into the penalty functions; they depend to a large extent on the selection of the initial approximation for the conformational calculations.

Complexes with the cyclopendant (XVIII) have also been investigated:[64]



(XVII)

It was established that the ligand (XVII) [similarly to the ligand (XVI)] in the complex has a folded conformation of the macrocycle while the increase in the length of the exocyclic groups diminishes the selectivity of the complex formation with participation of the ligand (XVII).

There is no doubt that the additional features described increase the applicability of the method of penalty functions, although the "adjustable" character of the coefficients employed nevertheless reduces the correctness of this approach.

IV. The "rigid polyhedron" model

As an example of the use of the model of the second type (see above) we shall consider the approach[65–68] in which the complex-forming atom is modelled by an "ideal" polyhedron. Its configuration is specified on the basis of experimental data referring either to the complex itself or to its analogues and it does not change during the calculations (the lengths of the metal–ligand bonds and the ligand–metal–ligand angles are constant, as a result of which this approach can be referred to as the method of "rigid" or "ideal" polyhedra (the name is conventional because the authors themselves do not name their model). The non-valence interactions of the metal with the ligand atoms as well as the barriers to rotation about the metal–ligand bonds are ignored in this method.

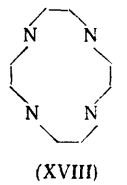
An important component of the above method is the procedure used to search for the initial approximation for the optimisation of the geometry (it is of an especially great current interest for complexes with polydentate ligands forming several chelate rings with common edges). It consists in sorting through all the possible combinations of chelate rings having different conformations taking into account the "rigidity" of the coordination polyhedron. Referring to this process as "assembly on a templet", the authors[65–68] see in it some analogy with templet synthesis. The number of combinations is limited by the steric conditions governing the cross-linking of the chelate rings. A preliminary study is made of the conformational possibilities of the isolated chelate rings and the families of the most favourable conformations and the ways in which they can undergo interconversions are found (see, for example, Pletnev and co-workers[66,69]).

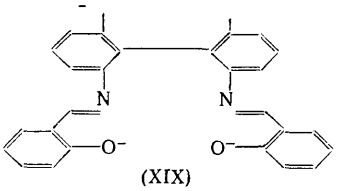
This method of selecting the initial approximation has undoubted advantages—it guarantees the selection of initial approximations which are known beforehand to correspond to the topology of the coordination unit and makes it possible to monitor the configuration of the complex.

The approach described has been applied successfully to the calculation of the structures of various metal complexes using the specially developed FORCON program.[66]

Thus the structure of the cobalt(III) complex of the macrocycle (XVIII) having the composition $[CoL(NO_2)_2]^+$ with the *cis*-octahedral (with respect to the nitro-groups) coordination of cobalt has been calculated[65] (see also Pletnev, et al.[66]). The calculation yielded two structures, one of which (less favourable) agrees well with X-ray diffraction data.[70]

Pletnev, et al.[65] investigated the steric structure and the stability factors of the cobalt complex with the ligand (XIX).

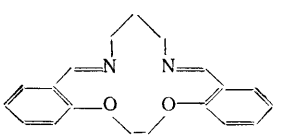

(XVIII)

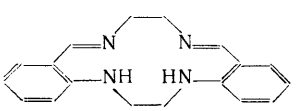

(XIX)

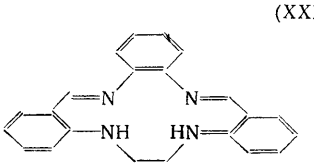
The conformational analysis of the salicylideneamine chelate ring showed that its optimum conformation is non-planar and the deformation of the bond angles is minimal. At the same time, the flattening of the ring does not require much energy expenditure (9.2 kJ mol^{-1}).

The structure of the above complex was calculated in terms of the approximation of the following coordination polyhedra: square, distorted square ("twisted" via the diagonal twist mechanism by 30°), distorted tetrahedron (square "twisted" by 67.6°, which is consistent with the experimental data[71]), and a tetrahedron. Although the results for the distorted tetrahedral structure agree well with experiment, this structure is not most favourable from the standpoint of steric strain in the ligand; the structure of the distorted square, twisted by 30°, is optimal. Evidently the occurrence in the complex of the distorted tetrahedral configuration is determined by the characteristic features of the crystal packing. The authors state that the changes in strain energy on formation of the polyhedron are comparable to the measured enthalpies of the square–tetrahedron interconversion (~20 kJ mol^{-1} [72]) and the contribution of the steric strain in the ligand to the stabilisation of a particular polyhedron should not be neglected.

Complexes of the following macrocyclic reagents have been investigated:[67]


(XX)


(XXI)


(XXII)

Calculations have been carried out for the structures (XX)–(XXII) and the conformations the optimum (from the standpoint of the possibility of coordination) directions of the lone pairs of the donor atoms of the ligands were discovered. The following versions of the geometry of the coordination unit were considered: square, tetrahedral and distorted tetrahedral, bisphenoidal, octahedral, trigonal-bipyramidal, tetragonal-pyramidal, and linear. The formation of square and bisphenoidal complexes is not favourable for the ligand (XX), whereas tetrahedral and distorted tetrahedral complexes cannot be formed for steric reasons. The "capped" (tetragonal-pyramidal) structure of the coordination unit proved to be optimal for complexes of the monoanions of the

tetraazamacrocycles (XXI) and (XXII), while the square structure proved to be optimal for the dianions. The results obtained are in the main consistent with X-ray diffraction data.[73,74] An attempt was made to justify certain extraction properties of the reagents (XX)–(XXII) on the basis of the probable structures of the complexes.[65–68]

The nickel complexes NiL_2 [L = *o*-hydroxyazobenzene (XXIII), *o*-mercaptoazobenzene (XXIV)] with a square-planar configuration of the coordination polyhedron have been examined.[68] The calculated structures of the complexes reproduce satisfactorily the experimental data.[75] The steric factors promoting the formation of six-membered [for the ligand (XXIII)] and five-membered [for the ligand (XXIV)] chelate rings are being interpreted.

Thus the "rigid polyhedron" approach described is entirely suitable for the calculation of the structures of structurally varied metal complexes. Its undoubted advantages include allowance for the configuration of the coordination unit and the corresponding steric organisation of the donor centres of the ligands ("the locus" of the macrocycle according to the authors terminology[65,68]). The method of selecting the initial approximations is also novel.

At the same time, although the approach described takes into account the geometry of the polyhedron it does not consider other characteristics of the complex-forming atom. No account is taken of either the distortions of the coordination polyhedron under the influence of the ligand environment or of the features of the conformational behaviour of the ligands in the field of the non-valence interactions with the central atom or ion. This is probably the explanation of certain inaccuracies in the results, which have been pointed out by the authors themselves.

Furthermore, the question of the selection of a particular type of coordination polyhedron in the absence of experimental data for the structure of the complex investigated remains open. The authors[67] suggest that various ideal polyhedra should be "sorted through" with comparison of their steric strains, but this approach is also only a palliative.

V. Characteristic features of the modelling of polynuclear complexes

In our view, the attempts to apply the MMM to the study of cluster compounds merit special consideration since allowance for the specific features of the structures of polynuclear complexes involves additional difficulties.

The main problem arising in the application of the MMM to calculations for complexes of this kind consists in the fact that the method requires an unambiguous determination of the orders of the bonds involving the atoms in the molecule, because the deformation of the valence bonds and the non-bonding interactions are described in the MMM by fundamentally different potential functions. Even when X-ray diffraction data are available, in the case of clusters it is frequently impossible to determine unambiguously the metal–metal and metal–ligand bond orders.[76] To overcome these difficulties, it has been suggested,[77] for example, that the interaction of the ligands with the metallic core as a whole and not with specific metal atoms be considered. The concept of an "equipotential surface of the cluster", formed on combining (for further details, see Lauher[77]) the spheres circumscribed around each metal atom (the radii of the spheres correspond to the metal–ligand donor atom bond lengths), has been introduced. Thus the cluster core is replaced by a kind of "superatom".

In the calculation of the energy of the steric strain within the framework of the MMM, additional terms are introduced, taking into account the distance of the ligand from the equipotential surface and the deviation of the ligand axis (for example the C–O bond for carbonyls) from the direction normal to this surface. These contributions are calculated in different ways for the regions corresponding to the bridging and terminal bonding of the ligands (the subdivision of the equipotential surface is based on X-ray diffraction data).

This approach was used to study a series of metal carbonyls with the compositions $Fe_2(CO)_9$, $Co_2(CO)_8$, $Fe_2(CO)_8^{2-}$, $CoFe(CO)_8^-$, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Co_4(CO)_{12}$, $Ir_4(CO)_{12}$, $Fe_4(CO)_{13}^{2-}$, $CoFe_3(CO)_3^{2-}$, $CrFe_3(CO)_{14}^{2-}$, and $Mn_4(CO)_{16}$. The results of the calculations for these complexes (in accordance with Allinger's program[10]) agree well with X-ray diffraction data.[78–82] Furthermore, in the study of these complexes a dependence of the metal–metal bond length on the steric strain energy was noted. Another relatively simple approach was used by Newson and co-workers[83,84]—"interactive molecular graphics"—in the study of the steric structures of clusters. In this model, the dependence of the energy of the steric strain of the molecule on one or two internal coordinates (usually torsional angles) is investigated. The geometry of the remaining part of the complex is then fixed on the basis of X-ray diffraction data. The intramolecular strain energy involved only non-bonding van der Waals interactions (with the parametrisation of DelRe, et al.[85]), while the contributions of metal atoms are disregarded. Despite the evident deficiencies associated with the neglect of a number of important factors, this approach can be used in some cases to estimate steric strain.

Thus the steric hindrance in the complex $Fe_4(CO)_{12}CR$ (R = CH_2, CH_3, CO_2CH_3) caused by the presence of the substituent R was investigated[83] with the aid of the "interactive molecular graphics" (X-ray diffraction data were used[86]). In the determination of the steric hindrance in the cluster, the variable parameter is the torsional angle around the C–R bond, whose magnitude in the optimised conformation agreed with experimental data[86] to within 5°. It was shown that the steric hindrance in the cluster increases significantly when the sp^2-hybridised hydrogen atom in the substituent R is replaced by a sp^3-hybridised hydrogen atom. The dinuclear complexes $[CpMoS(\mu\text{-}S)]_2$, $[C_5(CH_3)_5MoS(\mu\text{-}S)]_2$, and $[(C_2H_4S_2)MoS(\mu\text{-}S)]_2$ were investigated similarly.[84] Scanning with respect to the Mo–S–S–Mo torsional angle revealed the stable conformations of the complex, which proved to be consistent with the experimental ones.[87] It was shown that the stability of the *anti*-isomers of the above complexes is greater than that of the *syn*-isomers.

The interaction of the iron(III) complexes $[Fe_3O(H_2O)_3Piv_6]^+$ (A) and $Fe_6O_2(OH)_2Piv_{12}$ (B) (where Piv = pivaloyl) with the hydroperoxide of dibenzyl ether has also been examined.[88] In the calculation of the steric strain energy, X-ray diffraction data were used[89,90] and the variable parameter was the Fe...O–OR distance.

H

It was shown that the lower catalytic activity of the hexanuclear complex (B) compared with the tetranuclear complex (A) in the hydroperoxide decomposition reaction may be caused by the greatest steric hindrance occurring in the coordination of the latter to the catalytic centre of the complex.

The disadvantages of the models described above include, firstly, the neglect of the metal–metal interaction and also non-bonding metal–ligand interactions and, secondly, the impossibility of carrying out calculations of this kind without X-ray diffraction data.

The approaches described do not allow calculation for the intrinsic metallic core of the cluster although they do take into account the steric effect associated with the influence of the ligand environment.

We may note, however, that even such limited information can in many instances be useful for the elucidation of the causes of the formation of polynuclear complexes with a specific structure.

An attempt to take into account the above interactions in the calculations for polynuclear metal complexes (in the absence of a metal–metal bond) has been undertaken in studies[91,92] of copper complexes of 1,2-dicarboxylic acids with the composition $Cu_2L(OH)_2.2H_2O$ {L = anion of succinic, 4-cyclohexene-1,2-dicarboxylic, 3-methyl-4-cyclohexene-1,2-dicarboxylic, 4-methyl-4-cyclohexene-1,2-dicarboxylic, and *endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acids}. It was shown that the complex $Cu_2L(OH)_2.2H_2O$ can be represented as a superposition of two isomeric structures with bond bidentate-cyclic and bidentate-bridged coordination of the carboxylate groups. With increase in the structural rigidity of the ligand, the contribution of the isomer with the bidentate-cyclic type of coordination increases.

The most correct method of applying the MMM to the study of cluster compounds involves undoubtedly the generation of force fields, including, among other parameters, the force constants for metal–metal bonds and the corresponding constants for the bond and torsional angles. This approach was in fact used by Boeyns and co-workers.[93,94]

Boeyns et al.[93] investigated the complexes $M_2(XYCCH_3)_4$ and $M_2(XYCCH_3)_4L_2$ [M = Rh, Pd, Cd, Cu; X, Y = S, O; L = H_2O, CH_3CSOH, $(CH_3)_2SO$, PPh_3]. A force field, calibrated on the basis of vibrational spectra[95] and including parameters for the above metals, was proposed. Calculations and experimental data led the authors[93] to the conclusion that the metal–metal distance in the above complexes is determined by steric factors both in the presence of the bond (Rh complex) and in its absence (Pd, Cu, and Cd complexes). A change in the nature of the steric influence can lead not only to a lengthening but also to a shortening of the metal–metal bonds.

However, in our view, such categorical conclusions concerning the predominant influence of the steric factor on the lengths of metal–metal bonds are not sufficiently justified. In the study of clusters, it is quite impermissible to neglect, as was done by Boeyns et al.,[93] the electronic factor and in the first place the orbital interactions of the metal atoms.

A similar approach was used in another study by Boeyns[94] to investigate high-order bonds in the complexes $Cr_2(CH_3)_8^{4-}$, $Mo_2(CH_3)_8^{4-}$, $W_2(CH_3)_8^{4-}$, and $Re_2(CH_3)_8^{2-}$. The force constants of the fourth-order metal–metal bonds as well as the parameters of the non-bonding van der Waals interactions were also calculated for the above atoms from experimental data.[96,97] The dependence of the energy of the steric strain of the complexes on the torsional angle of the metal–metal bond was examined. The stabilisation of the unfavourable eclipsed conformation is explained in this instance by the contribution of the δ-bonding component to the Cr–Cr bond (46 kJ mol^{-1}).[94] The properties of triple and quadruple W–W bonds were compared in relation to the complexes $W_2(O_2CC_2H_5)_4$ and $W_2(O_2CC_2H_5)_4(CH_2C_6H_5)_2$ and it was shown that, although the structures of these complexes are similar, the triple bond is significantly more mobile than the quadruple bond. The rotation about the Re–Re triple bond has been investigated[94] for the complex $Re_2Cl_4[P(C_2H_5)_3]_4$. It is claimed that in this case (in the absence of δ-bonding) the occurrence of the eclipsed conformation is caused by steric factors.

However, one cannot agree with all the conclusions reached by Boeyns,[94] because here too the role of orbital interactions has been clearly underestimated. In particular, one can hardly regard as correct the attempt to estimate (especially quantitatively) the effect of the δ-bond with the aid of the MMM.

VI. Simplified "mechanical" and geometrical models

Together with the MMM, simpler approaches based on "mechanical" ideas and geometrical models may be useful in the study of the steric structures of complexes. One of such approaches is the familiar Tolman method of conical angles θ (see, for example, Refs. 98 and 99) (Fig. 2). The method continues to be improved and has found extensive applications in quantitative estimations of steric factors in metal complexes.

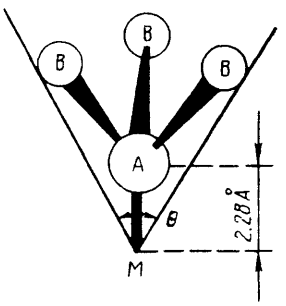


Figure 2. Tolman's conical angle model.

Thus a universal formula has been proposed[100] for the calculation of the conical angles of ligands of the type AB_n (A = atom coordinated to the metal; B = atom linked to A).

Similar formulae have been derived[101] for complex ligands of the type AB'_3, where B′ is a group of atoms. The effective covalent and van der Waals radii of the groups B′ and the conical angles of the ligands AB'_3 have been calculated from the available standardised data[99,102] for phosphorus-containing ligands PB'_3. The conical angles for 610 ligands of the type AB'_3 (A = N, P, As, Sb, Bi, C, Si, Ge, Sn, Pb; B′ = alkyl, cycloalkyl, aryl, alkylaryl, arylalkyl) have been published.[101,103] It was shown that the conical angles for Group IV and V elements are the same in the case of neighbouring elements A and decrease within the Group as the atomic number increases. It was noted that the conical angles depend little on the nature of the metal.

The attempt to extend to organic[104] and organoelement[105] compounds the above system for the description of the steric properties of substituents (ligands) in inorganic compounds is of interest. The attempt was based on the conical angles θ and derivatives of the "degrees of shielding" $\Lambda = \sin^2(\theta/4)$ with respect to these angles. The authors[104,105] derived simple formulae relating these parameters to the covalent radius of the central atom and published their values for various elements (H, B, C, Si, N, P, O, S, the halogens, and the transition metals). Thus a universal scale of steric constants for coordination, organic, and organoelement chemistry has been proposed.[104,105] Its undoubted advantages are

the uniqueness of the approach, a clear-cut geometrical significance of the parameters, and the ability in many instances to describe experimental data correctly.

However, one hardly agrees with the author's view that this system of constants is preferable to the familiar empirical scales of the E_s type, because both can be used only in those cases where the substituent is linked directly to the reaction centre (see, for example, Kuz'min and co-workers[14,15] and Gallo[106]).

Domrachev et al.[107] (see also Refs. 108 and 109) suggest that, not the conical angle, but the solid angle filled by the substituent R be used for the quantitative estimation of the degree of steric shielding of the metal atom in compounds of the type MR_n [R = PPh_3, CPh_3, η^1-Cp, η^5-Cp, CH_3, C_2H_5, CF_3, $C(CH_3)_3$, etc.]. Here the ligand atoms are specified as hard spheres with van der Waals radii. The sum of the solid angles of all the substituents (ligands) is used to estimate the steric strain in the complex. When it is exceeded (4π is the total solid angle), strain in the structure is indicated. The parameter described is satisfactorily correlated with data for the thermal stabilities of the compounds indicated.

In order to achieve a more correct estimation of the "non-valence interactions", it has been suggested[110] that these interactions be considered at the distance from the complex-forming atom where interligand contacts occur. The area S shielded by the ligand on the surface of a sphere with a radius r equal to the length of the metal–ligand bond is used as a steric characteristic of the ligand. The overall ligand environment of the metal is estimated by means of the expression $\sum_i S_i/4\pi r_i^2 \leqslant 1$. The closeness of this parameter to unity indicates, according to the author,[110] the existence of strain in the molecule (see also Refs. 107–109). The values of S calculated for a series of ligands have been published.[110]

Using, within the framework of the approach described, the parameters S, the same author analysed the structures of the metallocenes MCp_n (M = Be, Fe, Cr, V, Ti, Sc, Nd, Sm, Th, Zr, Hf, U; n = 2, 4) and discovered the factors determining whether the η^1- or the η^5-coordination of the cyclopentadienyl group is preferred.[111] This approach has been used[112] to estimate the relative stabilities of various isomers of the complex $Ca(BH_4)_2.2.(CH_3OCH_2CH_2OCH_2CH_2OCH_3)$.

The sum of the solid angles of the ligands (SAS), normalised with respect to 4π, has been used for the quantitative estimation of the steric factors governing the stabilities of uranium complexes with the general formula $U(Cp)X_3L_n$ {X = CNS; n = 1, L = $CH_3OCH_2.CH_2OCH_3$; n = 2, L = $CH_3CON(CH_3)_2$, tetrahydrofuran, $P[N(CH_3)_2]_3O$; X = Cl, Br; n = 1, L = $Ph_2(O)PCH_2P(O)Ph_2$; n = 2, L = $(CH_3)_2CCON(CH_3)_2$, $POPh_3$}.[113] The authors isolated the region of the optimum shielding (SAS = 0.81) of the metal atom (the optimum packing of the ligands in the coordination sphere). With decrease or increase in the degree of shielding, the complexes become unstable.

In the study of lanthanide complexes $LnCp_3(NCR)_2$ (Ln = La, Ce, Pr; R = CH_3, C_2H_5), an additional term taking into account the radius of the metal atom is introduced into the SAS parameter.[114] It was shown that the size of the central atom influences significantly the stability of the complex and that lanthanum compounds are the most stable. The most favourable configuration of the ligand environment, corresponding to the optimum value SAS = 0.72, was discovered.

An attempt has been made[115,116] to use similar ideas not only for the quantitative estimation of the steric effect but also for the prediction of the geometries of the complexes. A model based on the principle of closest packing of the ligands (represented by solid cones with the apex at the centre of the metal atom) in the coordination sphere has been proposed. In terms of mathematical procedures, this approach is a vector analogue of the SAS model (for further details, see Xing-Fu, et al.[115]). Using the conical model, the structures of more than 50 compounds of the type MA_4, MA_3B, MA_2B_2, MAB_2C, and MABCD were calculated (M = actinides, lanthanides, and Group IVB metals). The results agree well with X-ray diffraction data. It has been shown[116] for the formation and dissociation reactions of complexes (see above) that the conical model is applicable to the study of the influence of steric factors on the possible direction of the process. More than 160 lanthanide complexes have been studied with the aid of the conical model.[117]

However, the postulates of the conical model have been developed most fully in the concept of the "coordination site" described in a series of investigations.[118–122] According to this model, not only ligands but also the conical "sites" which they can occupy may be described with the aid of the solid (or conical) angle. A "diagram of levels" is constructed on the basis of the determination in the coordination sphere of the metal atom of "first-order, second-order, etc. 'coordination sites'" (by distributing the Tolman cones in the "holes" within the close packing of the coordination sites of the previous order). The degeneracy of the "levels" in the presence of molecular symmetry and their alteration following the deformation of typical coordination polyhedra have been considered.[118]

The concept of "pre-bonding molecular structure", calculated from the level diagram in terms of the approximation of spherical (the halogens) and disc (Cp) ligands, has been introduced.[19] In order to estimate the correspondence between the ligand and the coordination site, the seat function is introduced:

$$F = \sum_i^m K_i (S_i - \theta_i)^2, \quad F' = \sum_i^m K_i (S_i - \theta_i)^2/\theta_i^2,$$

where m is the number of ligands, K_i the rigidity coefficient, S_i the conical angle of the "site", and θ_i the conical angle of the ligand (K = 1, $S \geqslant \theta$, K = 5, $S < \theta$).

With the aid of the proposed model, it has been possible[118–122] to explain the occurrence of disproportionation reactions, the distribution of ligands between the anion and cation in complex salts, thermolysis, racemisation, and a series of other reactions characteristic of actinide complexes.

However, we may note that all the models described above are suitable only for mononuclear coordination compounds. An approach, similar to that of Lobkovskii[110] and Bagnall and Xing-Fu,[113] based on the construction of projections of the ligands onto a cylindrical surface with a unit radius whose axis coincides with the M–M bond, has been proposed[109] for dinuclear complexes.

A general approach, suitable for polynuclear complexes containing a metal chain or a metallocycle has been put forward.[123] A closed continuous surface covering the metal atoms is constructed in accordance with specific rules. Next, the total area S of this surface is determined as well as its component S_e shielded by the ligands. A characteristic of the degree of shielding of the metallic core is the ratio $K = S/S_e$. Polynuclear complexes of Ti, V, Hg, Ge, Pt, Fe, Mn, and Cr were investigated within the framework of this model. It was shown that, by selecting appropriate ligands, it is possible to achieve the stabilisation of the required structure of the core. It has been suggested that the approach described can be used to study clusters with two-dimensional and three-dimensional structures.

The "frontal steric effect" model has been used successfully[124] to estimate the steric factors governing the stability of complexes. According to this model,[125] the steric effect of the substituent is proportional to the area which it occupies on a spherical surface separating it from the reaction centre. A computational scale of steric constants has been introduced: $R_S = 30 \lg \left(1-\sum_i r_i^2/4L_i^2\right)$, where r_i is the atomic radius of the ith atom in a complex substituent and L_i is the distance from the ith atom to the reaction centre.

This model has been used to investigate the complexes $(R_2PSS)_2M$ (M = Ni, Cu; R = various cyclic and acyclic substituents).[124] Comparison of the calculated results with the stability constants of the complexes[126] showed that, within the framework of individual reaction series, their stability is controlled by the steric factors of the substituents (a satisfactory correlation with the parameter R_S is observed).

An attempt has been made[127] to create on the basis of molecular-mechanical ideas a so called general model of the coordinate bond. According to this model, the length of the metal–donor centre bond is determined by the energy balance of the coordinate bond proper (described by the Morse potential) and the van der Waals interactions in the ligand environment. On the basis of this approach, the authors were able to explain the observed differences between the "long" and "short" Ln–H_2O bonds in the complexes $Ln(C_2H_5SO_4)_3.9H_2O$ and also the variation of the length of these bonds in the La–Lu series.

Table 1. The force fields used in calculations for metal complexes.

Metal	Ligand atoms	Allowance for the contributions of different interactions to the conformational energy				Refs.
		val	angle	tors	nb	
Co	H, C, N, O, S, B, P, Cl	+	+	+	+	[6]
	H, C, N	+	+	−	−	[37]
Cu	H, C, N, O, S, B, P, Cl, F	+	+	+	+	[6]
	H, C, O	+	−	−	+	[93]
Ni	H, C, N, O, S, B, P, Cl, F	+	+	−	+	[6]
Cd	H, C, O, S, P	+	+	+	+	[93]
Rh	H, C, O, S, P	+	+	+	−	[93]
Pd	H, C, O, S, P	+	+	+	+	[93]
Cr	C	+	−	−	−	[94]
Mo	C	+	−	−	−	[94]
W	C	+	−	−	−	[94]
Re	H, C, P, Cl	+	−	−	−	[94]
Eu	H, C, N, O	+	+	+	+	[61]
Yb	H, C, N, O	+	+	+	+	[61]

Notation adopted: val—bond deformations: angle—bond angle deformations; tors—torsional strain; nb—non-bonding interactions; + parameters are present; −parameters are absent.

A novel mechanical model has been used[128] to investigate the elementary steps in the synthesis-decomposition reactions of diarenechromium compounds. The $Cr(\eta^6\text{-}C_6R_6)_2$ (R = H, CH_3) molecules were represented by three-particle systems in which the benzene rings were represented by toroids of rotation. The metal–ligand interactions were described by the Morse potentials and the non-valence interactions by functions of the Lennard-Jones type. In all probability, this approach can be applied in a qualitative analysis of the stabilities and structures of the given systems.

As can be seen from the examples examined, the simplified mechanical models of complexes can be employed only in those cases where the steric strain of the molecules is determined primarily by the non-valence interactions between the ligands. In all probability, such approaches cannot be used correctly if the behaviour of the complexes is influenced significantly also by the structures and conformational characteristics of the ligands which are modelled, as a rule, by hard cones or spheres in such approaches. The mechanical models described can be used only when the principle of uniform filling of the coordination sphere by the ligands holds.

Thus analysis of the literature on the application of the MMM to the study of steric factors regulating the structures and properties of transition metal complexes shows that calculations of this kind make it possible to obtain much useful information. The method of molecular mechanics is at present available for the study of a wide range of compounds with various metals (Table 1 presents data for the known force fields). It is important to emphasise that, when the method is used correctly, a satisfactory agreement is achieved with the experimental results and in many instances it becomes possible to predict the properties of complexes.

References

1. V G Dashevskii *Konformatsionnyi Analiz Organicheskikh Molekul* (Conformational Analysis of Organic Molecules), Izd. Khimiya, Moscow, 1982, 272 pp.
2. A Warshel *Semiempirical Methods for the Calculation of Electronic Structure* (Translated into Russian), Izd. Mir, Moscow, 1980, Vol. 1, p. 172 [this may well be a reference to a review by this author in *Mod. Theor. Chem.*, 1977, 7 133 (Ed.)]
3. V G Dashevskii *Konformatsionnyi Analiz Makromolekul* (Conformational Analysis of Macromolecules), Izd. Nauka, Moscow, 1987, 288 pp.
4. U Burkert, N L Allinger *Molecular Mechanics* (Translated into Russian), Izd. Mir, Moscow, 1986, 364 pp.
5. K Rassmussen *Lecture Notes in Chemistry*, Springer-Verlag, Berlin, 1985, Vol. 37, p. 1
6. G R Brubaker, D W Johnson *Coord. Chem. Rev.*, 1984, **53**(1) 1
7. C J Hawkins *Absolute Configuration of Metal Complexes* (Translated into Russian), Izd. Mir, Moscow, 1974, 430 pp.
8. Y Saito *J. Mol. Struct.*, 1985, **126** 461
9. T V Timofeeva, A A Kurganov, V A Davankov, Yu T Struchkov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, (11) 2484
10. N L Allinger *J. Am. Chem. Soc.*, 1977, **99**(25) 8127
11. N Raos, S R Niketic, V Simeon *J. Inorg. Biochem.*, 1982, **16**(1) 1
12. N Raos, V Simeon *Croat. Chem. Acta*, 1984, **57**(5) 1217
13. N Raos, V Simeon *Croat. Chem. Acta*, 1983, **56**(1) 79
14. V E Kuz'min, D V Pozigun, R N Lozitskaya, G L Kamalov *Teor. Eksp. Khim.*, 1986, **22**(3) 366
15. V E Kuz'min, G L Kamalov, R N Lozitskaya, et al., Manuscript deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 05.03.84, No. 1408-84 Dep.
16. V A Davankov, S V Rogozhin, A A Kurganov, L Ya Zhucova *J. Inorg. Nucl. Chem.*, 1975, **37**(1) 369

17. J Kozelka, G A Petsko, S J Lippard, G J Quigley *J. Am. Chem. Soc.*, 1985, **107**(13) 4079
18. J Kozelka, G A Petsko, S J Lippard, G J Quigley *Rev. Port. Chem.*, 1985, **27**(1–2) 378
19. P K Weiner, P A Kollman *J. Comput. Chem.*, 1981, **2**(3) 287
20. J H J Denhartog, C Altona, et al. *J. Am. Chem. Soc.*, 1984, **106**(5) 1528
21. B VanHemelryck, E Guittet, G Chottard, et al. *J. Am. Chem. Soc.*, 1984, **106**(10) 3037
22. M J Clear, J D Hoeshele *Bioinorg. Chem.*, 1973 **2**(1) 187
23. J Kozelka, G A Petsko, G J Quigley, S J Lippard *Inorg. Chem.*, 1986, **25**(8) 1075
24. T W Hambley *Inorg. Chim. Acta*, 1987, **137**(1) 15
25. T W Hambley *J. Chem. Soc., Chem. Commun.*, 1988, (3) 221
26. A M J Fichtinger-Schepman, J L VanderVeer, J H J DenHartog, et al. *Biochemistry*, 1985, **24**(3) 707
27. J L VanderVeer, H VandenElot, J H J Denhartog *Inorg. Chem.*, 1986, **25**(12) 4567
28. S J Weiner, P A Kollman, et al. *J. Comput. Chem.*, 1986, **7**(1) 230
29. G R Brubaker, D W Johnson *Inorg. Chem.*, 1984, **23**(11) 1591
30. R H Boyd *J. Chem. Phys.*, 1968, **49**(19) 2574
31. V B Pett, L L Diaddario, E R Dockal, et al. *Inorg. Chem.*, 1983, **22** 3661
32. C J Hillary, T F Them, R E Tarscott *Inorg. Chem.*, 1980, **19**(1) 102
33. L L Diaddario, L L Zimmer, et al. *J. Am. Chem. Soc.*, 1979, **101**(13) 3511
34. D W Johnson, G R Brubaker *Inorg. Chim. Acta*, 1986, **119**(2) 131
35. K B Yatsimirskii *Teor. Eksp. Khim.*, 1980, **16**(1) 34
36. G R Brubaker, Shi Chen-Xi, D W Johnson *Inorg. Chim. Acta*, 1987, **134** 15
37. A M Bond, T W Hambley, M R Snow *Inorg. Chem.*, 1985, **24**(12) 1920
38. I I Creaser, R J Geue, et al. *J. Am. Chem. Soc.*, 1982, **104**(22) 6016
39. F D Sancillo, L F Druding, D M Lukaszewski *Inorg. Chem.*, 1976, **15** 1626
40. A M Bond, T W Hambley, D R Mann, M R Snow *Inorg. Chem.*, 1987, **26** 2257
41. D V Pozigun, T V Koksharova, V E Kuz'min, et al. *Dokl. Akad. Nauk Ukr. SSR, Ser. B*, 1988, (6) 61
42. D V Pozigun, V E Kuz'min *Zh. Strukt. Khim.*, 1988, **29**(1) 171
43. V G Dashevskii, A P Baranov, T Ya Medved', M I Kabachnik *Dokl. Akad. Nauk SSSR*, 1983, **270**(2) 355
44. A P Baranov, V G Dashevskii, T Ya Medved', M I Kabachnik *Dokl. Akad. Nauk SSSR*, 1985, **281**(3) 607
45. V G Dashevskii, A P Baranov, M I Kabachnik *Usp. Khim.*, 1982, **51** 2117
46. V G Dashevskii, A P Baranov, T Ya Medved', M I Kabachnik *Teor. Eksp. Khim.*, 1977, **13**(3) 340
47. A P Baranov, V G Dashevskii, T Ya Medved', M I Kabachnik *Teor. Eksp. Khim.*, 1977, **13**(4) 488
48. V G Dashevskii, A P Baranov, T Ya Medved', M I Kabachnik *Teor. Eksp. Khim.*, 1979, **15**(3) 255
49. W Hewertson, B T Kilbourn, R H B Mais *J. Chem. Soc., Chem. Commun.*, 1970, **15**(3) 952
50. A E Kalinin, V G Andrianov, Yu T Struchkov *Zh. Strukt. Khim.*, 1976, **17**(1) 153
51. M I Kabachnik, V G Dashevskii, T Ya Medved', A P Baranov *Teor. Eksp. Khim.*, 1985, **21**(6) 660
52. M I Kabachnik, M Yu Antipin, B K Shcherbakov, et al. *Koord. Khim.*, 1988, **14**(4) 536
53. B M Polikarpov, B K Shcherbakov, F I Bel'skii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, (7) 1669
54. M I Kabachnik, T Ya Medved', F I Bel'skii, S A Pisareva *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, (4) 844
55. L P Trigub, Candidate's Thesis in Chemical Sciences, Odessa, 1986, 130 pp.
56. V E Kuz'min *Mezhmolekulyarnoe Vzaimodeistvie i Konformatsii Molekul* (Intermolecular Interaction and Molecular Conformations), Izd. NTsBI Akad. Nauk SSSR, Pushchino, 1987, p. 75
57. Yu L Slovokhotov, T V Timofeeva, Yu T Struchkov *Zh. Strukt. Khim.*, 1987, **28**(4) 3
58. T V Timofeeva, Yu L Slovokhotov, Yu T Struchkov *Dokl. Akad. Nauk SSSR*, 1987, **294**(5) 1173
59. D Kipert *Inorganic Stereochemistry* (Translated into Russian), Izd. Mir, Moscow, 1985, 280 pp.
60. Yu L Slovokhotov, Yu T Struchkov *J. Organomet. Chem.*, 1984, **277** 143
61. D J Brecknell, D J Raber, D M Ferguson *J. Mol. Struct.*, 1985, **124** 343
62. E D Watkins, J A Cunningham, T Phillips *Inorg. Chem.*, 1969, **88**(1) 29
63. E Bye *Acta Chem. Scand., Ser. A*, 1974, **28**(7) 731
64. M I Kabachnik, A P Baranov, T Ya Medved' *Teor. Eksp. Khim.*, 1986, **22**(6) 655
65. I V Pletnev, Yu A Zolotov, L A Gribov *Dokl. Akad. Nauk SSSR*, 1984, **276**(5) 1144
66. I V Pletnev, Yu A Zolotov, L A Gribov, M M Raikhshtat *Koord. Khim.*, 1985, **12**(2) 216
67. I V Pletnev, Yu A Zolotov, L A Gribov *Koord. Khim.*, 1986, **12**(2) 185
68. S B Savvin, L A Gribov, M M Raikhshtat *Koord. Khim.*, 1986, **12**(8) 1044
69. A V Pletnev *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1987, **28**(4) 399
70. Y Iitaka, S Shina, E Kimura *Inorg. Chem.*, 1974, **13**(12) 2886
71. L H Pignolet, R P Taylor, W DewHorrocks *J. Am. Chem. Soc.*, 1969, **91**(20) 5457
72. M J O'Connor, R E Ernst, R H Holm *J. Am. Chem. Soc.*, 1968, **90**(17) 4561
73. L G Armstrong, L F Linday, et al. *Inorg. Chem.*, 1977, **16**(7) 1665
74. E N Maslen, L M Engelhardt, A H White *J. Chem. Soc., Dalton Trans*, 1974, (16) 1799
75. S M Aldoshin, V A Alekseenko, L O Atovmyan, et al. *Koord. Khim.*, 1975, **1**(8) 1075
76. S P Gubin *Khimiya Klasterov: Osnovy Klassifikatsii i Stroenie* (The Chemistry of Clusters: Principles of Classification and Structure), Izd. Khimiya, Moscow, 1987
77. J W Lauher *J. Am. Chem. Soc.*, 1986, **108**(7) 1521
78. F A Cotton, J M Troup *J. Chem. Soc., Dalton Trans.*, 1974, (8) 800
79. G G Sumner, H P Klug, L E Alexander *Acta Crystallogr.*, 1964, **17**(6) 732
80. H B Chin, M B Smith, et al. *J. Am. Chem. Soc.*, 1974, **96**(16) 5285
81. F A Cotton, J M Troup *J. Am. Chem. Soc.*, 1974, **96**(13) 4155

82. M R Churchill, F J Hollander, J P Hutchinson *Inorg. Chem.*, 1977, **16** 2697
83. J M Newsam, J S Bradley *J. Chem. Soc., Chem. Commun.*, 1985, (12) 759
84. J M Newsam, T R Halbert *Inorg. Chem.*, 1985, **24**(4) 492
85. G DelRe, E Gavuzzo, E Giglio, et al. *Acta Crystallogr., Sect. B*, 1977, **33** 3289
86. J S Bradley, G B Ansell, E W Hill *J. Am. Chem. Soc.*, 1979, **101** 7417
87. M Rakowski, D L DuBois, M G VanderVeer, R C Halianger *Inorg. Chem.*, 1981, **20**(9) 3064
88. D V Pozigun, V E Kuz'min, G L Kamalov *IX Vsesoyuznoe Soveshchanie "Fizicheskie i Matematicheskie Metody v Koordinatsionnoi Khimii": Tezisy Dokladov. Novosibirsk* (The IXth All-Union Conference on "Physical and Mathematical Methods in Coordination Chemistry": Abstracts of Reports. Novosibirsk), Novosibirsk, 1987, Vol. 2, p. 275
89. A B Blake, L R Fraser *J. Chem. Soc., Dalton Trans.*, 1975, (3) 193
90. N V Gerbeleu, A S Batsanov, et al. *Dokl. Akad. Nauk SSSR*, 1987, **293**(2) 364
91. D V Pozigun, V E Kuz'min, G L Kamalov *VII Vsesoyuznyi Simpozii po Mezhmolekulyarnomu Vzaimodeistviyu i Konformatsiyam Molekul: Tezisy Dokladov. Pushchino* (The VIIth All-Union Symposium on Intermolecular Interaction and Molecular Conformations: Abstracts of Reports. Pushchino), Pushchino, 1986, p. 144
92. D V Pozigun, V E Kuz'min, G L Kamalov *Koord. Khim.*, 1990, **16** 380
93. J C A Boeyns, F A Cotton, S Han *Inorg. Chem.*, 1985, **24**(12) 1750
94. J C A Boeyns *Inorg. Chem.*, 1985, **24**(24) 4149
95. V M Miskowski, W P Schaefer, B Sadeghi, et al. *Inorg. Chem.*, 1984, **23**(8) 1154
96. A P Sattelberger, J P Fackler *J. Am. Chem. Soc.*, 1977, **99**(4) 1258
97. P R Sharp, D Astruc, R R Schrock *J. Organomet. Chem.*, 1979, **182** 477
98. C A Tolman *J. Am. Chem. Soc.*, 1970, **92**(10) 2596
99. C A Tolman, D W Reuter, W C Seidel *J. Organomet. Chem.*, 1976, **117** 30
100. N S Imyanitov *Koord. Khim.*, 1985, **11**(8) 1041
101. N S Imyanitov *Koord. Khim.*, 1985, **11**(9) 1171
102. C A Tolman, W G Seidel, L W Gosser *J. Am. Chem. Soc.*, 1974, **96** 53
103. N S Imyanitov *Koord. Khim.*, 1986, **12**(2) 161
104. N S Imyanitov *Zh. Org. Khim.*, 1987, **23**(5) 916
105. N S Imyanitov, G I Shmelev *Zh. Obshch. Khim.*, 1987, **57**(10) 2161
106. R Gallo *Progress in Physical Organic Chemistry*, Wiley, New York, 1983, Vol. 14, p. 115
107. G A Domrachev, L N Zakharov, Yu A Shevelev *Usp. Khim.*, 1985, **54**(8) 1260 [English translation in *Russ. Chem. Rev.*, 1985(8)]
108. L N Zakharov, G A Domrachev, Yu T Struchkov *Zh. Strukt. Khim.*, 1983, **24**(3) 75
109. S N Titova, V T Bychkov, et al. *Inorg. Chim. Acta*, 1981, **50**(1) 71
110. E B Lobkovskii *Zh. Strukt. Khim.*, 1983, **24**(2) 66
111. E B Lobkovsky *J. Organomet. Chem.*, 1984, **277**(1) 53
112. E B Lobkovskii, A N Chekhlov, M D Levicheva, L V Titov *Koord. Khim.*, 1988, **14**(4) 543
113. K W Bagnall, Li Xing-Fu *J. Chem. Soc., Dalton Trans.*, 1982, (7) 1365
114. Li Xing-Fu, S Eggers, U Korf, et al. *Inorg. Chim. Acta*, 1985, **100**(1) 183
115. Li Xing-Fu, Xu Ying-Ting, Feng Xi-Zhang *Inorg. Chim. Acta*, 1986, **116**(1) 75
116. Li Xing-Fu, Feng Xi-Zhang, Xu Ying-Ting, et al. *Inorg. Chim. Acta*, 1986, **116**(1) 85
117. Feng Xi-Zhang, Guo Ao-Ling, et al. *Polyhedron*, 1987, **6**(5) 1041
118. Li Xing-Fu, Shen Tian-Gi, et al. *Inorg. Chim. Acta*, 1987, **129**(2) 227
119. Li Xing-Fu, Shen Tian-Gi, Guo Ao-Ling, et al. *Inorg. Chim. Acta*, 1987, **129**(2) 235
120. Li Xing-Fu, Sun Peng-Nian, et al. *Inorg. Chim. Acta*, 1987, **129**(2) 245
121. Li Xing-Fu, Guo Ao-Ling *Inorg. Chim. Acta*, 1987, **131**(1) 129
122. Li Xing-Fu, Guo Ao-Ling *Inorg. Chim. Acta*, 1987, **134**(1) 143
123. L N Zakharov, G A Domrachev, Yu N Saf'yanov *Dokl. Akad. Nauk SSSR*, 1987, **293**(1) 108
124. V V Ovchinnikov, V I Galkin, et al. *Zh. Obshch. Khim.*, 1988, **55**(2) 357
125. V I Galkin, R A Cherkasov *Reakts. Sposobn. Org. Soedin.*, 1981, **18** No. 1(65) 111
126. V V Ovchinnikov, A R Garifzyanov, V F Toropova, R A Cherkasov *Zh. Obshch. Khim.*, 1982, **52**(6) 1323
127. Feng Xi-Zhang, Xu Ying-Ting, Sun Peng-Nian *Can. J. Chem.*, 1988, **66**(1) 109
128. G A Domrachev, L N Zakharov, Yu A Shevelev, G A Razuvaev *Zh. Strukt. Khim.*, 1986, **27**(2) 14