energy is obtained when $\theta = \pi/2$ and the sublattice magnetizations are perpendicular to one another. The magnitude of the vector D_i is approximately equal to $[(\mathbf{g} - 2)/2]\cdot\mathbf{J}$, and the canting is maximized when there exists a large **g** tensor anisotropy in the presence of large intrachain exchange coupling.

Expressions for the parallel and perpendicular *g* values of manganese(III) in a tetragonal field may be derived from perturbation theory:

$$g_{\parallel} = 2 - 2\zeta(1/\Delta_1) \qquad g_{\perp} = 2 - \tfrac{1}{2}\zeta(1/\Delta_2)$$

Clearly the *g* values in moderate to strong ligand fields are nearly isotropic. Since the intrachain exchange coupling is very weak, the contribution from the antisymmetric Dzyaloshinski–Moriya interaction is negligible. As discussed previously, the space group of $Na_2[Mn^{III}(sal)_2(CH_3OH)_2][Mn^{III}(sal)_2]$ is $P\bar{1}$. The manganese sites A and B that make up the unit cell lie on inversion centers, and their Jahn–Teller axes are not collinear. The two sublattices are not chemically equivalent, so there can be no symmetry element that transforms the two sublattice magnetizations into one another. Therefore, the single-ion anisotropy is the dominant contribution to the observed weak ferromagnetism, and in the ordered state $Na_2[Mn^{III}(sal)_2(CH_3OH)_2][Mn^{III}(sal)_2]$ may be tentatively classified as a two-sublattice canted antiferromagnet.

It is interesting to note that the linear-chain compound $(NH_4)_2MnF_5$, which comprises canted, Jahn–Teller-distorted MnF_6^{3-} octahedra, also displays weak ferromagnetism.[3] The relative tilting of the respective octahedra is much less than that observed in $Na_2[Mn^{III}(sal)_2(CH_3OH)_2][Mn^{III}(sal)_2]$, and the intrachain exchange coupling is approximately 30 times larger. Single-crystal magnetic susceptibility measurements determined the canting was due to the single-ion anisotropy, and the canting angle between spins along the chain axis was determined to be 0.83°.

The third linear chain in the A–B series, $(NH_4)_2[Mn^{III}(sal)_2(CH_3OH)_2][Mn^{III}(sal)_2]$ behaves as a one-dimensional Heisenberg antiferromagnet. Unfortunately, the low-temperature behavior is complicated by chain-end effects caused by grinding the sample prior to packing the VSM sample holder, a magnetic impurity, or both. The experimentally determined value of -0.7 cm^{-1} for the intrachain exchange is 3 times larger than that of the sodium salt, but the Mn–Mn separation increases by 0.041 Å and the Mn2–O3 bond distance is 0.063 Å longer. This is consistent with the previous arguments put forth concerning the intrachain exchange in $Na_2[Mn^{III}(sal)_2(CH_3OH)_2][Mn^{III}(sal)_2]$ and the corresponding K^+ salt. Obviously, an additional exchange pathway must be operative. Since the only major structural change between $(NH_4)_2[Mn^{III}(sal)_2(CH_3OH)_2][Mn^{III}(sal)_2]$ and the sodium and potassium salts is the incorporation of a cation capable of hydrogen bonding, the ammonium cation must be involved in enhancing the exchange between the A and B sites. Since there are no good magnetostructural correlations concerning hydrogen bond mediated spin exchange in low-dimensional magnetic systems, testing of this hypothesis is not possible at this time. However, it must be noted that a series of hydrogen-bonded copper(II) dimers exists where anomalously large exchange-coupling constants were determined ($J = -47.5$ cm^{-1}).[23] In these dimers, the exchange pathway is through a short O–H–O linkage.

Conclusions

The linear-chain series described by $(cat)_2[Mn^{III}(sal)_2(CH_3OH)_2][Mn^{III}(sal)_2]$, provides a system in which the effects of the single-ion anisotropy and exchange interaction without changing the axial or equatorial ligation may be observed. The wide range of magnetic behavior found in this series shows that seemingly small structural changes can have a dramatic impact on the magnetic properties of higher spin chains.

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Supplementary Material Available: For **1**–**3**, Tables VI–XVIII, giving complete experimental crystallographic details, anisotropic thermal parameters of all non-hydrogen atoms, fractional atomic positions for hydrogen atoms, complete bond distances, and complete bond angles, and Figures S1–S5, containing additional magnetic data and complete numbering schemes for all atoms (16 pages); Tables XIX–XXI, listing observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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A Molecular Mechanics Model of Ligand Effects. 1. Binding of Phosphites to $Cr(CO)_5$

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Molecular mechanics methods have been employed to compute the minimum energy structures of a series of eight phosphites, including trimethyl phosphite, triethyl phosphite, and triphenyl phosphite, and of their complexes with chromium pentacarbonyl, $Cr(CO)_5$. The MMP2 force field was employed, using the comprehensive computational program BIOGRAF. Substantial changes in lowest energy conformations are seen in the complexes as compared with the free ligands. A major goal of the work was to evaluate the steric contribution to the metal–ligand interaction. As the ligand steric requirement increases, increased van der Waals repulsions between the ligand and the metal carbonyl fragment are largely offset by corresponding increases in van der Waals attractive forces. As a result, neither the overall energy nor net van der Waals interaction energies vary monotonically with increasing ligand steric requirement. The repulsive interactions between the ligand and the metal carbonyl fragment are manifested in bond angle and bond distance changes in the series.

The capacity of ligands, molecules bound to a central metal atom or cluster, to affect the chemical properties of the center is an important consideration in inorganic and organometallic chemistry. Ligand effects are commonly thought to be of two kinds, steric and electronic. Many different approaches have been suggested for separately evaluating these two effects. However, in spite of the substantial attention devoted to this subject, there remains a great deal of uncertainty regarding the best choices of parameters and how they can be best employed in correlating and predicting chemical behavior.

Because of their importance, especially in organometallic systems, phosphorus ligands have been especially throughly studied.[2,3] We will not attempt here to review the enormous

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literature of this field. Steric properties of the ligand can be assessed with the aid of molecular orbital calculations[4] or deduced from structural parameters observed in crystal structures.[5] The most widely accepted approach to assessing ligand steric effects is that suggested by Tolman,[3] who measured so-called cone angles θ for ligands by use of space-filling models. The cone angle represents the apex angle of the cylindrical cone centered 2.28 Å above the P atom and along the 3-fold axis of the ligand. The conical surface is tangent to the outermost van der Waals surface, as represented by the space-filling molecular model of the ligand.

Tolman's approach has the advantage of simplicity and generality. As a parameter in linear free energy relations, it often provides good correlations with rate or equilibrium data. At the same time, the approach has several limitations, some of them noted by Tolman.

1. It is difficult to decide on an appropriate cone angle for complex ligands, in which the van der Waals "surface" is highly irregular. Various approximations for averaging the effects of different R groups in $PR_1R_2R_3$ have been suggested,[4] but the averaged value is often not reflective of the properties of the ligand. In addition, the cone angles for ligands that are highly branched in the β position (for example, $P(i\text{-Bu})_3$) do not adequately reflect the steric effects of this branching.

2. Space-filling models are inflexible, whereas real molecules can undergo sometimes low-energy bending distortions in response to a repulsive interaction.

3. The conformation chosen for a ligand may not be the low-energy one for the free ligand or for the ligand in the bonding situation. In general, the convention in measuring the cone angle has been to choose the conformer that provides the lowest cone angle.

As a result of these limitations, the cone angles for some ligands were in fact estimated by Tolman on the basis of measurements of the equilibrium constant for CO replacement in $Ni(CO)_4$.[3] In addition, alternative values have been suggested for several ligands for which the originally suggested cone angles seem to be inappropriate, e.g., $P(C_6H_{11})_3$,[6] PEt_3,[7,8] or $P(OMe)_3$.[7]

In this series of papers, we explore the use of molecular mechanics methods to assess the steric contributions to ligand–metal interactions. The ultimate goal of the work is to develop a versatile, realistic, and readily employed method for evaluating the steric parameter for any ligand. The steric parameter should be a measure of the steric effect exerted by the ligand in its reactions with a metal center or that exerted when the ligand is bound to a metal center undergoing reaction. There are limitations in the application of a single steric parameter to all situations. Nevertheless, there is great utility in having a single value that serves reasonably well in a variety of contexts, as we will show in later papers in this series.

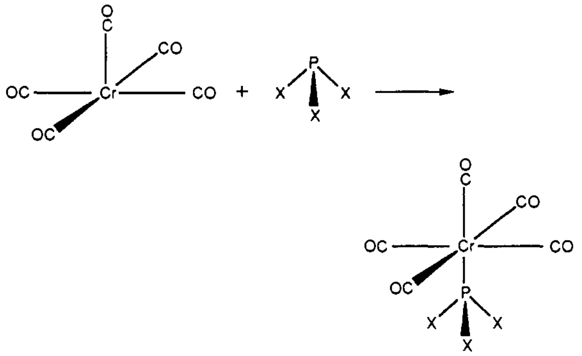
In this first paper, we describe a first step toward our goal, a molecular mechanics model for the interaction of a group of phosphite ligands with a prototypical metal center, $Cr(CO)_5$. The choice of $Cr(CO)_5$ as prototype binding site in this and the studies reported on in following papers is based on several considerations. First, the vibrational potential function for $Cr(CO)_6$, from which we can draw the model for $Cr(CO)_5$, is well-defined. Second, the rotational symmetry of the $Cr(CO)_5$ fragment along the Cr–P bond in the adducts is 4-fold, as opposed to 3-fold or nearly 3-fold for the ligands. This "mismatch" of rotational symmetries helps to ensure that the energy of metal–ligand interaction will not vary greatly with rotation about the Cr–P bond, as might be the case if we had chosen, for example, trigonal $Fe(CO)_4$ as the prototype metal center. Finally, the $Cr(CO)_5$ fragment seems to be reasonably representative of transition-metal binding or reaction sites in terms of the degree of crowding about the metal center.

The Molecular Mechanics Model

In a molecular mechanics model, the structure of a molecule is determined by a set of assumed equilibrium bond distances, bond angles, and dihedral angles and the nonbonding interatomic attractions and repulsions that cause the molecule to distort away from the equilibrium geometry.[9a] The potential energies associated with those distortions are described by a force field consisting of terms for bond stretches, bond bends, and torsions. The model is empirical and highly parametrized. It assumes a set of strain-free, or equilibrium, bond distances, angles, and torsions and functions describing the variation in potential attendant upon departures from the equilibrium geometries.

In the molecular mechanics model, the attractive and repulsive interactions between atoms, generally described as van der Waals interactions, are taken into account only for atoms separated in bonding by at least two atoms. The interatomic interactions between atoms directly bonded or bonded to a common atom are assumed to be already accounted for in the bond-stretching and bond-bending parameters. Aside from the special case of ring systems or intramolecular hydrogen bonding, neither of which concern us here, the van der Waals interactions are the sole factor giving rise to the attractive or repulsive forces that cause the molecule to depart from the assumed equilibrium geometry.

To apply the molecular mechanics model, we consider the binding of a phosphorus ligand, PX_3 at the prototypical metal center, $Cr(CO)_5$:



(1)

We want the change in molecular mechanics energy in this process, ΔE:

$$\Delta E = E_{CrP} - E_{Cr} - E_P \tag{2}$$

Here, E_{CrP}, E_{Cr}, and E_P are the molecular mechanics energies of $Cr(CO)_5PX_3$, $Cr(CO)_5$, and PX_3, respectively. The emphasis in this work is on the *variation* in ΔE as a function of ligand structure.

To evaluate E_{Cr} we must assume a model for $Cr(CO)_5$, i.e., for its geometry, and values for all the bond stretching and bending modes. The force field model we have employed, MMP2, does not contain parameters for the bonds in this fragment.[9b] Similarly, many of the parameters necessary to properly describe the phosphites are not present in MMP2.

To evaluate E_{CrP} we must assume values for many parameters in $Cr(CO)_5PX_3$. It is necessary to choose a force constant and bond distance for the Cr–P bond and values for the associated bending and torsional modes. Formation of the adduct may occasion changes in bond distances and angles within each fragment. For example, the characteristic C_{axial}–Cr–C_{radial} angle

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changes as a result of binding of the phosphorus to Cr. Because detailed force field analyses are not available for these molecules, the choices we make for many parameters are based on analogy with related systems or are made empirically to provide agreement with key experimental data. In evaluating the results of such calculations, it is important to test the sensitivity of the final results to the details of the assumptions. Our goal is to determine a set of relative values for E_{CrP} as the ligand changes that properly reflect the variations in the properties of the ligands. We have therefore tested the sensitivity of the results to the details of the assumptions made, to ensure that the quantitative aspects of the variations are not materially dependent on any assumed value that could plausibly be substantially different from the one chosen.

Note that the molecular mechanics model does not purport to provide a value for the observed energy change that occurs when $Cr(CO)_5$ interacts with PX_3. Such values, as measured, for example, with photoacoustic spectroscopy,[10] measure the enthalpy change in reaction 1. The major source of the observed enthalpy change, formation of the Cr–P bond, makes no contribution to the molecular mechanics energy change, to first order; the zero of energy in the molecular mechanics model of $Cr(CO)_5PX_3$ assumes an equilibrium Cr–P bond length. The energy change ΔE appearing in the molecular mechanics calculation is that occasioned by changes in the sum of all nonbonding interatomic van der Waals interactions and repulsions and the changes in bond distances, angles, and dihedral angles away from the minimum energy values that occur as the system moves to an overall minimum energy structure when $Cr(CO)_5$ and PX_3 are brought together.

The computed energy change ΔE measures different properties of the ligand than are reflected in the value for its cone angle. While van der Waals repulsive forces are present in the calculated van der Waals energy term, so also is the van der Waals attractive interaction. In MMP2 the van der Waals terms are of the so-called exponential-six form proposed by Buckingham,[11] eq 3. For

$$E_{\mathrm{VDW}} = D_0\left\{\left(\frac{6}{\gamma - 6}\right)\exp\left[\gamma\left(1 - \frac{r}{r_0}\right)\right] - \left(\frac{\gamma}{\gamma - 6}\right)\left(\frac{r_0}{r}\right)^6\right\} \tag{3}$$

each pair of interacting atoms the van der Waals interaction is determined by three parameters. D_0 represents the depth of the potential well at the energy minimum, γ is a scaling factor (normally 12.5), and r_0 represents the interatomic distance at which the potential energy is a minimum. In the interaction between two different atom types, geometric mean values of D_0 and arithmetic mean values of r_0 are employed. The attractive terms contribute importantly for atoms at intermediate distances of separation. Thus, for a large, polarizable ligand, the van der Waals attractive forces with the $Cr(CO)_5$ fragment could contribute significantly to the total net molecular mechanics energy of interaction.

Methods Section

All of the molecular mechanics computations were carried out by using BIOGRAF, a comprehensive package of molecular modeling tools developed by Molecular Simulations, Inc., Sunnyvale, CA. The force field model employed is MMP2,[9b] with modifications and additions to the parameter set as described below.

The MMP2 force field includes potential energy terms due to each of the following forms of distortion of the molecule from the equilibrium, strain-free configuration.

1. Bond stretching:

$$E_b = \frac{k_b}{2}(r - r_0)^2[1 + d(r - r_0)] \tag{4}$$

Table I. Added Parameters for MMP2 Force Field

A. Force Constants for Bond Stretching

bond type	k_s, mdyn/Å	r_0, Å
P–O	2.900	1.615
P–Cr	2.000	2.298
Cr–C(sp) radial	2.100	1.895
Cr–C(sp) axial	2.100	1.861
C(sp)–O(sp) radial	17.029	1.131
C(sp)–O(sp) axial	17.029	1.135
O(sp)–LP[a]	4.600	0.600

B. Force Constants for Bond Angle Deformation

bond angle type	k_b, mdyn Å/rad^2	θ, deg
C_{rad}–Cr–C_{rad}	0.550	90.0
C_{rad}–Cr–C_{rad}	0.000	180.0
C_{rad}–Cr–C_{ax}	0.550	90.0
C–C(sp)–O(sp)	0.500	180.0
C_{rad}–Cr–P	0.500	90.0
C_{ax}–Cr–P	0.000	180.0
C(sp)–O(sp)–LP[a]	0.521	180.0
Cr–P–O	0.300	118.0

[a] LP = lone pair.

Here d is a cubic correction term with default value −2, r is the bond distance, and r_0 is the assumed equilibrium bond distance. (In BIOGRAF the potential is modified for large displacements to avoid negative values for dE_b/dr.)

2. Bond bending:

$$E_\theta = \frac{k_\theta}{2}(\theta - \theta_0)^2[1 + d_\theta(\theta - \theta_0)^4] \tag{5}$$

d_θ has a default value of 0.754.

3. Dihedral angle torsions:

$$E_\theta = \sum_{n=1}^{6}\frac{k_\phi}{2}[1 - d_p(\cos n\phi)] \tag{6}$$

Here, k_ϕ is 0.5 times the rotational barrier, n is the periodicity of the potential, and d_p is a phase factor.

4. The van der Waals energies between atoms separated by at least two bonds are expressed in terms of eq 3. In MMP2 the units employed for the energy are kcal mol^{-1}.

Energy minimizations were carried out by using the conjugate gradient method.[12] In general, if one begins with a plausible starting structure, the energy minimum achieved is a local minimum and not the global minimum over the space of all possible conformations of the ligand or complex. To find the global minimum when the conformational space is large, we have used a Monte Carlo search strategy. Typically up to 200 or 300 structures representing variations in any of a set of key dihedral angles were chosen by Monte Carlo methods, and a partial energy minimization was carried out on each. From the results of this initial search, a set of lowest energy structures was selected and fully minimized. The lowest energy structure of this set was then often assumed to represent the global energy minimum. In addition, however, we often also computed the energies of various other conformations that seemed intuitively to be promising. In some cases, we also carried out a molecular dynamics calculation beginning with an energy-minimized structure, followed by a reminimization, to test the possibility of a deeper energy minimum separated by a moderate energy barrier from the starting structure.

Parameters. Table I lists parameters added to MMP2 or representing modifications of the values normally listed therein. Parameters applicable to the $Cr(CO)_5$ fragment were based on the valence force field parameters derived from vibrational studies of $Cr(CO)_6$.[13] It is well-known that in chromium pentacarbonyl complexes, the axial and radial CO groups possess slightly different stretching force constants.[14] For ligands L that engage in weaker π bonding to the metal as compared with CO, the axial CO generally has a slightly higher stretching force constant. However, because the difference between axial and radial CO groups is likely to be small and variable for phosphite-substituted compounds, we

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Table II. Summary of Selected Average Angles (deg) and Distances (Å)

	$P(OCH_2)_3CCH_3$	$P(OMe)_3$	$P(OEt)_3$	$P(OPh)_3$	P(O-*i*-Pr)$_3$	P(O-*i*-Pr)$_2$(O-*t*-Bu)	P(O-*i*-Pr)(O-*t*-Bu)$_2$	P(O-*t*-Bu)$_3$
				A. Phosphites				
distances								
P–O	1.626	1.633	1.632	1.632	1.632	1.634	1.635	1.637
C–O	1.420	1.417	1.418	1.376	1.422	1.424	1.425	1.426
angles								
O–P–O	100.8	104.3	104.2	103.5	104.7	104.0	103.4	102.1
P–O–C	117.2	118.3	118.5	122.2	120.3	120.9	121.6	122.4
group dihedrals								
P–O–C	179.2	−1.4	4.3	1.9	0.6	−0.5	−3.8	25.3
	179.3	−1.7	6.7	6.8	5.9	−13.4	7.1	25.6
	179.2	−2.5	7.3	−1.9	7.7	−16.9	−12.4	26.3
				B. Complexes				
distances								
P–O	1.627	1.641	1.640	1.643	1.644	1.643	1.647	1.651
C–O	1.420	1.418	1.420	1.378	1.424	1.426	1.428	1.431
Cr–P	2.298	2.311	2.316	2.314	2.322	2.323	2.332	2.339
$Cr–C_{rad}$	1.895	1.895	1.985	1.894	1.894	1.894	1.893	1.894
$Cr–C_{ax}$	1.861	1.860	1.861	1.860	1.860	1.861	1.861	1.861
angles								
O–P–O	100.6	102.6	102.7	103.1	102.6	102.1	103.0	101.5
P–O–C	117.3	120.6	120.9	125.6	124.0	125.1	126.2	127.5
Cr–P–O	117.3	115.6	115.6	115.1	115.6	116.1	115.4	116.6
$C_{ax}–Cr–C_{rad}$	90.0	89.4	89.6	89.4	88.4	88.4	88.4	87.7
$P–Cr–C_{ax}$	179.4	179.8	179.7	179.6	178.6	178.5	179.3	178.8
Cr–C≡O	179.9	179.9	179.7	179.7	179.5	179.4	179.5	179.6
group dihedrals								
Cr–P–O–C	180.0	58.8	58.8	176.3	−45.8	44.1	44.8	−48.2
	178.2	105.1	105.6	−82.6	−103.0	68.9	92.3	−93.7
	179.4	177.2	177.3	−95.4	−148.1	148.8	131.9	−132.9
cone angle	101	107	109	128	130	144	158	172

have assumed that the axial and radial CO stretching force constants are the same. The equilibrium $C_{ax}–Cr–C_{rad}$ angle is assumed to be 90° both in free $Cr(CO)_5$ and in the complexes. While it is known that the equilibrium value for this angle is about 95° in $Cr(CO)_5$,[15] the molecular mechanics energy difference occasioned by the 5° angle change is only 0.03 kcal mol^{-1}. Inasmuch as the $Cr(CO)_5$ fragment energy is a common term in computing all energy differences, the trends in ΔE values are in any case independent of the value chosen. The effects on the computed variations in energies of assuming a slightly higher CO stretching force constant or Cr–C distance for the axial CO group in the complexes are extremely small. In addition to the parameters listed in Table I, we also assumed the following van der Waals parameters for Cr: $r_0 = 2.22$ Å, and $D_0 = 0.468$ kcal mol^{-1}.

To avoid problems with definitions of generalized valence force constants involving cis and trans CO groups about Cr, each C atom of the CO groups was assigned a separate identity, and force constants and equilibrium bond angles with all the other CO groups were specifically assigned.

The Cr–P distance was set by employing an average of eight Cr–P distances in four chromium(0)–$P(OMe)_3$ complexes listed in the Cambridge Structural Database, Version 4.2. We assumed that these distances would be little extended by ligand–metal center repulsive interactions, because of the comparatively small size of $P(OMe)_3$. The Cr–P force constant was set to be slightly smaller than that for Cr–CO, on the grounds that phosphorus ligands in general are bound slightly less strongly than CO.

All dihedral angle torsional barriers involving Cr were set equal to zero. Those of the form C–Cr–P–O we would expect to be very small, because rotation about the Cr–P axis involves rotation of a group with 4-fold symmetry against one with 3-fold symmetry. Barriers in such cases are very small. For dihedral angles of the type Cr–P–O–C, the barriers might be larger, but there are no experimental bases on which to estimate them. In any event, because the van der Waals interactions between the groups bound to phosphorus and between each group and the $Cr(CO)_5$ fragment are substantial, these interactions can be expected to dominate in determining the low-energy conformations and their relative energies, the chief items of interest in this work.

The van der Waals radius and binding energy for Cr were set in recognition of the fact that Cr is formally zerovalent in the complexes under study. A radius for Cr of 2.22 Å is reasonable in comparison with values of C(sp^3) = 1.90 Å, trivalent P = 2.18 Å, Cl = 2.03 Å, and Br = 2.18 Å, employed in the BIOGRAF implementation of MMP2. These values in turn are substantially consistent with Williams' values.[16] Because the Cr atom is centrally located in the $Cr(CO)_5$ complexes, variations in the assumed van der Waals radius for this element have only a very small influence on calculated energies. For example, an increase in the assumed radius to 2.38 Å resulted in changes ranging from 0.03 to 0.06 kcal mol^{-1} in the calculated energies of the complexes and did not significantly influence the relative values.

No account was taken in the calculations of partial charges on the atoms. The principal focus of this work is the steric interaction between ligand and metal center. Inclusion of partial charges, even if it could properly be done, would increase the difficulties in extracting the desired energy terms from the result. Inclusion of partial charges would influence the conclusions regarding steric effects only if the electrostatic contributions resulted in different conformations of the ligands. It seems very unlikely that this would be the case. The explicit inclusion of lone pairs takes appropriate account of the electrostatic repulsive effects of the lone pairs. There are not likely to be other significant partial charge effects. The most recent and detailed Xα molecular orbital studies of $Cr(CO)_6$[17] indicate that the metal carries a slight negative charge and that the charges resident on C and O atoms are small. A similarly low set of partial charges should be present in the $Cr(CO)_5$ complexes.

Values associated with the P–O–C bonds in the phosphites are based on preliminary results from Professor J. P. Bowen.[18] It should be noted that the inclusion of parameters associated with the lone-pair electrons on oxygen is important; they are essential to predicting conformations and rotational barriers in the free ligands.

Results

Molecular mechanics calculations were carried out for a series of phosphite ligands and for their $Cr(CO)_5$ complexes. The values for selected bond distances and angles in the computed structures of the free ligands and $Cr(CO)_5$ complexes are listed in Table II. In the free phosphites, the dihedral angle between the plane defined by the pseudo-3-fold axis through the phosphorus and the P–O

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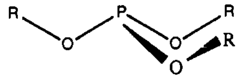
Table III. Miminized Energies (kcal)

	$P(OCH_3)_3CCH_3$	$P(OMe)_3$	$P(OEt)_3$	$P(OPh)_3$	$P(O\text{-}i\text{-}Pr)_3$	$P(O\text{-}i\text{-}Pr)_2(O\text{-}t\text{-}Bu)$	$P(O\text{-}i\text{-}Pr)(O\text{-}t\text{-}Bu)_2$	$P(O\text{-}t\text{-}Bu)_3$
				A. Phosphites				
E_T	20.31	9.91	10.94	8.17	21.78	25.68	29.72	34.51
E_b	0.89	0.42	0.61	1.31	0.97	1.22	1.46	1.74
E_θ	1.74	2.47	2.30	6.11	4.48	4.78	5.20	6.09
E_ϕ	9.30	1.73	1.85	−18.45	10.40	14.11	18.19	22.49
E_{VDW}	8.38	5.29	6.17	19.20	5.93	5.57	4.88	4.13
				B. $Cr(CO)_5P(OR)_3$				
E_T	13.96	7.25	7.21	10.76	19.86	25.19	31.99	38.59
E_b	0.86	0.61	0.77	1.61	1.31	1.61	2.03	2.38
E_θ	1.75	3.59	4.09	10.66	8.55	10.37	13.57	15.84
E_ϕ	9.31	5.20	4.31	−10.30	14.40	18.32	21.76	26.31
E_{VDW}	2.04	−2.16	−1.96	8.79	−4.40	−5.11	−5.37	−5.94
				C. $\Delta E = E_{complex} - E_{phosphite} - E_{Cr(CO)_5}$				
ΔE_T	−4.14	0.45	−1.52	4.80	0.29	1.72	4.48	6.29
ΔE_b	−0.03	0.19	0.16	0.30	0.34	0.39	0.57	0.64
ΔE_θ	0.01	1.12	1.79	4.55	4.07	5.59	8.37	9.76
ΔE_ϕ	0.01	3.47	2.46	8.15	4.00	4.21	3.57	3.82
ΔE_{VDW}	−4.13	−5.24	−5.92	−8.20	−8.12	−8.47	−8.04	−7.86

bond and that defined by the P–O–C plane is a prominent feature. We will in the future refer to this as the *group dihedral*. In the free ligands, group dihedrals are not far from 0^0, corresponding to the P–O–C plane vertical, with the organic group "up", as illustrated in **1**. This means that the oxygen lone pairs are directed



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"down" and outward with respect to the 3-fold axis that passes through phosphorus. There is some uncertainty about the lowest energy conformations of phosphites in solution or in the liquid state,[19] but the computed minimum energy configuration for $P(OMe)_3$ corresponds to one of the proposed minimum energy forms.

In the $Cr(CO)_5$ complexes, the lowest energy conformations of the ligands may differ substantially from those of the free ligand. Figure 1 shows the computed minimum energy structures of $P(OEt)_3$ and $Cr(CO)_5P(OEt)_3$. In the complex, one of the alkoxy groups is oriented in approximately the position characteristic of the free ligand, but the other two are substantially twisted. Inspection of the data for the group dihedrals in Table II shows that this is a characteristic of several of the complexes. In general, the computational results fairly well reflect the results from a variety of structural studies.[7]

The molecular mechanics energies of the energy-minimized structures are listed in Table III. Total energies as well as the separate components of the energy are listed for both the free ligands and the complexes. The corresponding energies for $Cr(CO)_5$ are $E_T = E_{VDW} = -2.21$ kcal mol^{-1}, with all other energy terms zero.

Discussion

Structural Parameters. The X-ray crystallographic structure for $Cr(CO)_5P(OPh)_3$ is the only one reported for a phosphite–$Cr(CO)_5$ complex.[22] Although no parameters were adjusted to improve the fit between the computed and observed structures, the agreement is quite good; the values of the more prominent bond distances and angles are compared in Table IV.

Table IV. Comparison of Computed and Observed Structural Parameters for $Cr(CO)_5P(OPh)_3$ (Average Deviations or Estimated Uncertainty for Single Values in Parentheses)

parameter	molecular mechanics	X-ray structure[22]
distances, Å		
P–O	1.643 (0.002)	1.598 (0.009)
O–C	1.378 (0.002)	1.399 (0.006)
Cr–P	2.314	2.309 (0.001)
$Cr–C_{rad}$	1.894 (0.001)	1.896 (0.004)
$Cr–C_{ax}$	1.860	1.861 (0.004)
angles (averages), deg		
O–P–O	103.1 (3.8)	100.0 (3.2)
P–O–C	125.6 (0.5)	126.7 (2.9)
Cr–P–O	115.1 (2.5)	117.8 (4.2)
$C_{ax}–Cr–C_{rad}$	89.4 (0.8)	88.3 (1.2)
$P–Cr–C_{ax}$	179.6	176.1 (0.1)
group dihedrals, deg		
	176.3	175.9 (0.3)
	−82.6	−50.3 (0.3)
	−95.4	−36.2 (0.3)

Table V. Bond Distances (Å) in Coordinated Trialkyl Phosphites[a]

phosphite	P–O	O–C	no. of bonds
$M–P(OCH_2)_3C–R$	1.580 ± 0.016	1.464 ± 0.011	45
$M–P(OMe)_3$	1.587 ± 0.036	1.435 ± 0.066	369
$M–P(OEt)_3$	1.580 ± 0.022	1.422 ± 0.072	84
$M–P(O\text{-}i\text{-}Pr)_3$	1.606 ± 0.023	1.465 ± 0.035	60
$M–P(OPh)_3$	1.600 ± 0.026	1.397 ± 0.031	357

[a] From Cambridge Structural Database, Version 4.2.

To obtain more general insights into the structural aspects of phosphite–metal complex interactions, we have gathered statistical data from the Cambridge Structural Database (CSD),[23] Version 4.2, for metal complexes of several of the phosphites modeled in the present work. The particular metal and the complexity and degree of steric crowding at the metal center all vary. Our intent in examining these data is to focus on variations in structural parameters characteristic of the ligands, to discern if there are regular trends and to discern the extent to which particular structural parameters of the ligand exhibit sensitivity to the forces operating in the complexes.

Table V shows data for average P–O and O–C bond distances in complexes of several phosphites. The distances do not vary much from one ligand to the other, nor do they differ from the average values suggested as typical of isolated P–O–C groups.[24] The angular variables are displayed in Table VI. Here the data are presented as normalized distributions over the range of observed angles. The average P–O–C or O–P–O angle in a given phosphite group is considered. Other than for complexes of $P(OMe)_3$ and $P(OPh)_3$, too few data are available to draw conclusions other than to note that the average deviations in the angles

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(19) A conformer represented as **1** is thought to be in equilibrium with conformers of C_1 or C_s symmetry, in which two ligands have group dihedrals in the range 0 to ±60°, the third is "down", with a group dihedral angle around 180°.[20,21]

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(24) Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier Scientific Publishing: New York, 1974.

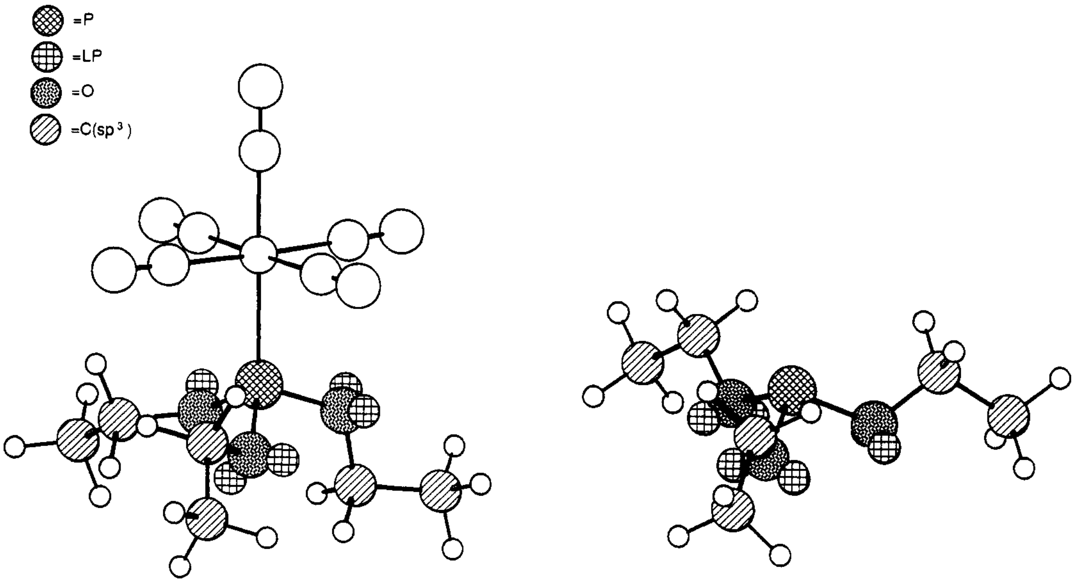

Figure 1. Comparison of the computed minimum energy structures for $P(OEt)_3$ and $Cr(CO)_5P(OEt)_3$.

Table VI. Normalized Data for Phosphite Angles (deg) in Complexes[a]

	fraction of fragments				
angle	$P(OCH_2)_3CR$	$P(OMe)_3$	$P(OEt)_3$	$P(O\text{-}i\text{-}Pr)_3$	$P(OPh)_3$
		Average OPO Angles			
96	0.000	0.016	0.000	0.100	0.025
98	0.130	0.244	0.071	0.400	0.210
100	0.600	0.358	0.071	0.400	0.437
102	0.270	0.293	0.464	0.100	0.252
104	0.000	0.089	0.357	0.000	0.059
106	0.000	0.000	0.036	0.000	0.017
tot. no. of ligands	15	123	28	20	119
av	101.2 ± 1.4	101.2 ± 4.5	103.5 ± 1.7	100.2 ± 1.3	100.8 ± 1.8
		Average POC Angles			
114	0.070	0.000	0.000	0.000	0.000
116	0.800	0.008	0.000	0.000	0.000
118	0.130	0.016	0.000	0.000	0.008
120	0.000	0.154	0.000	0.050	0.008
122	0.000	0.228	0.036	0.400	0.092
124	0.000	0.203	0.357	0.350	0.336
126	0.000	0.171	0.179	0.100	0.294
128	0.000	0.081	0.107	0.000	0.151
130	0.000	0.033	0.071	0.050	0.084
132	0.000	0.041	0.071	0.050	0.025
134	0.000	0.041	0.071	0.000	0.000
136	0.000	0.016	0.107	0.000	0.000
tot. no. of ligands	15	123	28	20	119
av	117.3 ± 0.8	124.7 ± 5.6	127.2 ± 4.4	124.8 ± 2.6	126.2 ± 2.4

[a] From Cambridge Structural Database, Version 4.2.

are in all cases rather large. This is to be expected; the potential energies associated with bending modes are much lower than those for stretching. The data for $P(OPh)_3$ and $P(OMe)_3$ complexes are presented in histogram format in Figure 2. These figures show that, while there is little or no difference in the distribution of O–P–O bond angles, the P–O–C bond angles are distributed to larger values for the bulkier ligand $P(OPh)_3$. Further, the range of P–O–C angles is larger than the range of O–P–O angles in both cases.

Consistent with these empirical observations, the calculated O–P–O angles in the free ligands and complexes, Table II, show very little variation across the series. Furthermore, the computed values are close to 103°, observed to be characteristic of coordinated phosphites.[25] The P–O–C angles, on the other hand, vary over a much wider range in both the free ligands and complexes; the variation is substantially larger in the complexes.

It might have been expected that increased repulsive interaction between the ligand and the $Cr(CO)_5$ fragment would result in variations in the Cr–P–O angle. The assigned force constant for the Cr–P–O bending mode, 0.3 mdyn Å rad^{-2}, is small enough so that this could serve to relieve repulsions. However, changes in these angles are coupled to changes in O–P–O angles; any relief of steric repulsions by a net increase in Cr–P–O angles must necessarily be accompanied by corresponding net decreases in the O–P–O angles, with consequent increases in intraligand repulsions. Because the alkoxy groups vary in their dispositions in the complexes, as measured by the group dihedrals, Table II, steric repulsions can be relieved by tilting with respect to the Cr–P axis. This tilting is reflected in an increasing scatter in the values for the Cr–P–O angles as the ligand grows increasingly bulky. For example, the three Cr–P–O angles in the computed structure for $Cr(CO)_5P(OPh)_3$ are 118, 114, and 113° (the corresponding values in the crystal structure are 123, 120, and 111°).[22] In the

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(25) Michael, G.; Kaub, J.; Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 502.

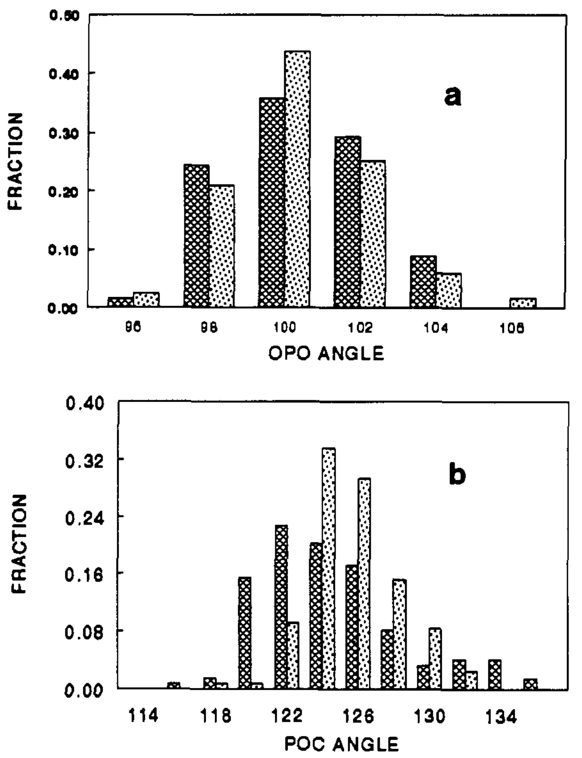

Figure 2. Distribution of (a) O–P–O and (b) P–O–C bond angles in complexes of $P(OMe)_3$ and $P(OPh)_3$. The darker shading represents $P(OMe)_3$ data (data from Cambridge Structure Database, Version 4.2).

computed structures, the average deviation in the Cr–P–O angles varies from less than 1° for $P(OMe)_3$ to 8° for $P(O\text{-}t\text{-}Bu)_3$.

Other expected variations in angle are observed; the C_{ax}–Cr–C_{rad} angle grows smaller as the ligand grows increasingly bulky. At the same time, the Cr–P distance increases, from 2.298 Å for $P(OCH_2)_3CCH_3$ to 2.339 Å for $P(O\text{-}t\text{-}Bu)_3$. The decrease in C_{ax}–Cr–C_{rad} angle and increase in Cr–P distance are due entirely to variations in steric forces; the same equilibrium values for each quantity were assumed for all phosphites.

Energy Changes. The total energy change upon complex formation varies in the expected manner with increasing steric requirement of the ligand, as reflected in the cone angle, Table III: from –4.14 kcal mol^{-1} for the bicyclic ligand $P(OCH_2)_3CCH_3$ to +6.29 kcal mol^{-1} for the bulkiest ligand, $P(O\text{-}t\text{-}Bu)_3$. Variation in the individual components of each overall energy change are, however, quite revealing. It is noteworthy that the change in van der Waals energy in each case is negative. This means that the attractive components of the interatomic interactions between all the atoms of the ligand with all the atoms of the $Cr(CO)_5$ fragment are, in the aggregate, larger than the repulsive terms, *for all ligands in the series*. To provide a clear perspective on the changes in the components of the energy across the series, we show each component as a function of the cone angle, Figure 3. The total energy change, ΔE_T, increases regularly with increasing cone angle, except for the anomalously large values for $P(OPh)_3$. The source of this anomaly is the torsional energy change. The torsional parameters associated with the –OPh group are such that complex formation produces an exceptionally large increase in E_ϕ. Except for the anomaly in the $P(OPh)_3$ torsional term, the variation in ΔE_T is reflected in the variation in ΔE_θ. There is not a strongly secular variation in ΔE_b, ΔE_ϕ, or ΔE_{VDW}.

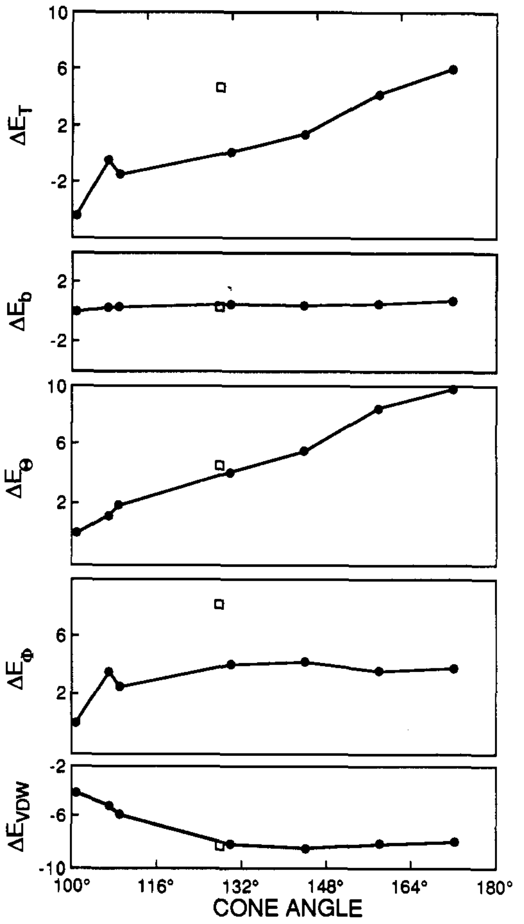

Figure 3. Variation in the computed components of the energy change upon formation of $Cr(CO)_5P(OR)_3$ complexes as a function of the $P(OR)_3$ ligand cone angle. The open squares represent the data for $Cr(CO)_5P(OPh)_3$.

At or near the equilibrium ligand–metal bonding distance, to which the ligand is constrained by the Cr–P stretching force constant, variations in ligand structure result in more or less compensating variations in the repulsive and attractive components of the van der Waals energy; both increase with increasing ligand bulk. The increasing attractive component, resulting from the larger number of contributing atoms in the ligand, has the effect of drawing the ligand more tightly to the $Cr(CO)_5$ fragment. At the same time, increased branching in the groups bound to the oxygens increases the repulsive interactions, not only within the ligand but also between the ligand and the $Cr(CO)_5$ fragment. The repulsive interactions are relieved through an opening of the P–O–C angles, because the alkoxy groups in the bound ligand are oriented in such a way that an opening of this angle does not increase the intraligand repulsions as much as it relieves the repulsions with $Cr(CO)_5$. Thus, E_θ is the one energy term that increases more or less monotonically with increasing cone angle. An additional avenue for relieving the repulsive interactions is tilting of the ligand. As described above, this tilting grows increasingly obvious as ligand bulk increases.

From these results and their interpretation, it is possible to discern how variations in properties of the phosphite ligand affect the total energy of its interaction with the prototypical metal carbonyl binding site, $Cr(CO)_5$. The expected increase in repulsive interactions with the metal center with increasing ligand bulk is not evident from the computed van der Waals energy changes. The repulsive term is compensated for by increasing attractive van der Waals interactions between the ligand and $Cr(CO)_5$. For this reason, the total energy change, which increases monotonically with cone angle in the series, reflects increasing repulsive interactions only indirectly, via the bond-bending energy terms.

It is possible that the results of the calculations place too much importance on the attractive component of the interatomic van der Waals interactions. The expression of the van der Waals energy as the sum of pairwise atomic potentials has limitations.[26] In addition, no explicit account is taken of the nature of the intervening space in computing the van der Waals interactions between widely separated atoms.[27] While these limitations might

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(26) (a) Morgenau, H.; Kestner, N. R. *Theory of Intermolecular Forces*; Pergamon: Oxford, England, 1969. (b) Hobza, P.; Zahradnik, R. *Intermolecular Complexes*; Elsevier: Amsterdam, 1988; Chapter II.

affect the quantitative accuracy of the results, the wide-ranging successes of molecular mechanics methods suggest that they are not sources of serious error.

The calculations of energy changes based on molecular mechanics implicitly assume that the process occurs in the gas phase. The presence of the solvent might alter the relative energies of different conformations of the free ligand or in the complex, but the energies associated with these changes would be small. The major differences in ΔE_T would arise from the fact that both the ligand and the $Cr(CO)_5$ fragment would be surrounded by solvent molecules, with which there would be weakly attractive van der Waals interactions. For complex formation to occur, some portion of this solvent sheath must be removed, to expose the fraction of the surface necessary to permit the Cr–P bond to form. The $Cr(CO)_5$ fragment is in fact a strong Lewis acid, and is known to bind even such weakly basic solvent molecules as hexane with enthalpies of interaction on the order of 10 kcal mol^{-1}.[10b] This term, however, is a constant for the series as the ligand varies, and so need not concern us in this discussion.

The same variations in van der Waals attractive interactions that operate between the ligand and $Cr(CO)_5$ as the ligand grows larger and more complex operate also in the interactions between the ligand and solvent molecules. Thus, the energy required to "prepare" the ligand for complex formation with $Cr(CO)_5$, by exposing the binding site, should vary in the same direction as the attractive component of the van der Waals interaction with $Cr(CO)_5$ once complex formation has occurred. While the magnitude of the contribution from the solvent term will in general not be the same as for $Cr(CO)_5$, the attractive van der Waals terms in the complex might be partially countered by corresponding terms in the ligand–solvent interaction. In this case, experimental measures of the enthalpies of ligand interactions with $Cr(CO)_5$ in solution would more strongly reflect changes in the repulsive van der Waals terms than do the computed values for total energy change. Experimental studies on both the gas-phase and solution systems could provide a test of this question. It should be kept in mind that the molecular mechanics model for a series such as under consideration here does not take account of variations in the metal–ligand bond strength occasioned by variations in ligand electronic properties. Thus, a comparison of the enthalpies of interaction of a series of phosphites with $Cr(CO)_5$ with the calculated values of ΔE_T would not be appropriate without taking account of variations in the strain-free donor character of the phosphites. This variation should be small for the acyclic trialkyl phosphites.

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Contribution from the Department of Chemistry, School of Science and Engineering, Waseda University, Tokyo 169, Japan, and Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274, Japan

Synthesis, Crystal Structure, and Solvolysis Reaction of a H–T 3,3-Dimethylglutarimidate-Bridged Binuclear Platinum(II) Complex, $[Pt_2(NH_3)_4(C_7H_{10}NO_2)_2](NO_3)_2 \cdot H_2O$

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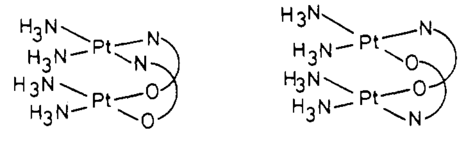
Synthesis and crystal structure of a 3,3-dimethylglutarimidate-bridged platinum complex (**1**) are reported. **1** is a binuclear structure with two 3,3-dimethylglutarimidate ligands bridging in a head-to-tail (H–T) manner. Each platinum atom is coordinated with two amine ligands in the cis position, a deprotonated nitrogen atom, and an oxygen atom of the 3,3-dimethylglutarimidate ligands. The Pt–Pt separation within the complex cation is 2.939 (1) Å. Although the ^{13}C spectrum of **1** in D_2O measured immediately after dissolution corresponds to the solid structure, the spectrum gradually changes to an unknown one, which indicates that the binuclear structure is not stably retained in D_2O. From ^{13}C and ^{195}Pt NMR spectroscopy in D_2O and DMSO-d_6, it turns out that the solvolysis reaction occurs in solution and the binuclear complex changes to a mononuclear one. Compound **1** crystallizes in the monoclinic space group $C2/c$ with $a = 36.933$ (7) Å, $b = 10.473$ (1) Å, $c = 14.070$ (4) Å, $\beta = 105.28$ (2)°, $V = 5249.8$ (9) Å^3, and $Z = 8$. Anisotropic refinement of all nonhydrogen atoms converged to the residuals $R = 0.059$ and $R_w = 0.045$ ($w = 1/\sigma^2(F)$).

Introduction

Recently, amidate- or lactamate-bridged binuclear or tetranuclear platinum complexes have attracted the interest of many chemists because of the novel redox chemistry of these complexes involving the unusual Pt(III) oxidation state. Binuclear complexes of the formula $[Pt^{II}_2A_4L_2]^{2+}$ (A is NH_3 or (en)/2 and L is deprotonated amidate or lactamate ligand)[2-5] are oxidized to $[Pt^{III}_2A_4L_2XX']^{4+}$[6-8] (X and X′ are axial ligands such as NO_3^- or NO_2^-) or to tetranuclear mixed-valent platinum blues $[Pt^{II}_3Pt^{III}A_8L_4]^{5+}$[9-11] and platinum tans $[Pt^{II}_2Pt^{III}_2A_8L_4]^{6+}$.[12-14]

Chart I



head-to-head (H–H) isomer   head-to-tail (H–T) isomer

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[1] (a) Waseda University. (b) Toho University.

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