Chem. Rev. **1980**, *80*, 313–327

Dielectric Behavior and Molecular Structure of Inorganic Complexes

SALVATORE SORRISO

Istituto di Chimica Fisica, Università di Perugia, 06100 Perugia, Italy

Received February 7, 1980

Contents

I. Introduction

A. Purpose of the Review

There is at present an emphasis on the relationship between reactivity and molecular structure.

Most of the information on the latter has been traditionally obtained from dielectric measurements (electric dipole moments and dielectric losses). With this technique, in recent years, many results have been obtained that are very often included in articles of different nature, which are not easy to find even though they are very useful to many workers in very different fields of chemical research.

The present review aims to collect, classify, and, whenever possible, correlate and discuss the relevant experimental results on dielectric measurements with reference to inorganic complexes, on which nothing has been written in the last 10 years. The period covered starts from 1968, when two interesting reviews on dipole moment measurements of inorganic complexes appeared.[1,2]

As far as possible, results on individual compounds will be reduced to a minimum and the accent will be placed on the type of information obtainable in the various cases. This choice is appropriate because the classical texts[3–8] usually do not adequately cover inorganic complexes. In fact, only in the last few years, following the widespread use of this technique in this field,[9–11] have specialized publications appeared.[12,13]

Salvatore Sorriso was born in Licata (Agrigento) in 1936 and studied for his degree in Chemistry at Catania University, where he was Professor of Physical Chemistry in 1964. Since then he has been Professor of Physical Chemistry at the University of Perugia. His current research interests are the study of molecular structure from several points of view. Recently he has turned his attention to the study of dielectric relaxation mechanisms.

The material has been divided in an empirical way, as it cannot be satisfactorily discussed entirely in terms of type of compounds nor entirely in terms of the specific problem involved. In addition, a systematic comparison with the results obtained from other techniques, although it would have been interesting, is not possible here. These results are reported only when necessary.

Finally, quantum-mechanical calculations on the dipole moments and on the conformational aspects of inorganic complexes will not be covered; there is a useful recent review on this topic.[14]

B. Dielectric Measurements in Inorganic Chemistry

The use of electric dipole moments (and in part also of dielectric losses) for studying inorganic complexes is often fraught with even more difficulties, both experimental and theoretical, than is the case for organic substrates. These include the following: the solubility in common nonpolar solvents is often minimal, or almost negligible; the magnitude of the atomic polarization (P_a) to be used may be critical in interpreting the results obtained for low-polarity molecules; series of closely similar molecules are virtually nonexistent—this makes it difficult to obtain reliable group or bond moments necessary for interpreting the experimental results for other molecules; the bonds in each complex have particular individual characteristics (from an electronic point of view).

The problem of the knowledge of group and bond moments is of fundamental importance in the vectorial analysis of a molecule. The greater the similarity, the more the various information to be obtained by means of them is reliable and supported. If these values were not available, the technique would be limited, though nevertheless of extreme interest and usefulness.

On the contrary, the question of atomic polarization should not be exaggerated. In fact, in those cases in which low moment values are predicted (and there are a few in inorganic complexes), it is possible to resort to dielectric loss measurements or to microwave spectroscopy, when possible, for which a knowledge of the atomic polarization is not necessary. On

0009-2665/80/0780-0313$05.00/0

the other hand, for large moments the uncertainty deriving from having assumed the atomic polarization equal to zero is irrelevant.

Notwithstanding these objective difficulties, and all the assumptions which are also necessary (which also pertain to other techniques), dielectric measurements are still widely used with success.[9-11] This is due to the fact that they provide important information on the molecules in the state in which reactions usually occur (i.e. in solution).

As to the inorganic complexes, this information refers to the geometric structure of the complex, the spatial arrangement of ligands, the type of bond and the mobility of its electrons, the detection of equilibria between polyhedral forms, the thermodynamic parameters of conformational and configurational equilibria, the potential energy barriers to internal rotation, and the thermodynamic parameters and time of dielectric relaxation.

Finally, at the present time theoretical moments worked out by means of quantum-mechanical calculations are compared with those obtained experimentally in order to measure the efficiency of the calculations carried out and at the same time the information obtained from them.

II. Chelates

The term "chelate", proposed by Morgan in 1920, refers to the cyclic structure originating from the bonding of a bi- (tri-, tetra-) dentate ligand with a metal ion.

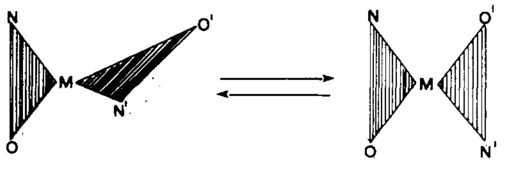
Dipole moment measurements reported in the period covered here are usually concerned with identifying the spatial configuration of the "centre" of such componds, i.e., of the few atoms directly involved in forming these compounds.

The information obtained in this way is very important because magnetic measurements have been found to be often insensitive or not suitable for the purpose. Unfortunately it is generally indicative only, because the structures of such molecules in solution are not known. Consequently it has not yet been possible to extract group and bond moments necessary for studying molecules of unknown structure.

The literature covered is divided according to the ligand type to facilitate a more immediate consultation and because there is no significant difference between the chelates of the few metals studied in this period.

A. Azo and Azomethine Derivatives

These ligands represent one of the widespread types of nitrogen-containing organic compounds capable of forming complexes with the transition metals. The approach used in interpreting the experimental results is based on the relationship between the observed dipole moment and the α value, which is the angle between the two planes NMO and N'MO', **1**. If α approximates to 90°, i.e., the chelate has the tetrahedral configuration, the dipole moment must have the maximum value. On the contrary, if α approximates to 0°, so that the chelate has a planar configuration, in the trans isomer, which is preferred, the dipole moments of the O–M and O'–M bonds and N–M and N'–M bonds compensate one another and the observed moment tends to zero.



a

tetrahedral

b

trans square planar

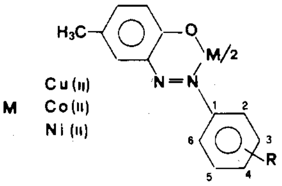
1

TABLE I. Observed Moments,[a] in Benzene, of Some Azo Chelates (2)

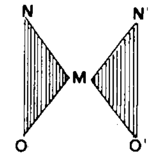
R	μ Cu(II)	μ Co(II)	μ Ni(II)	R	μ Cu(II)	μ Co(II)	μ Ni(II)
H	2.25[15]	3.12[16]	0.98[17]	2-Cl	2.57[15]		1.54[18]
2-Me			0.89[17]	3-Cl		3.48[16]	2.03[18]
3-Me	2.65[15]	3.19[16]	1.47[17]	4-Cl		3.54[16]	2.66[18]
4-Me	3.05[15]	3.26[16]	1.56[17]	2-OMe	3.96[15]	5.30[16]	
2,3-Me_2	1.74[15]	1.98[16]	0.71[17]	3-OMe		3.34[16]	
2,4-Me_2	1.76[15]	2.60[16]	0.84[17]	4-OMe	3.13[15]	3.48[16]	2.91[17]
2,4,6-Me_3	1.14[15]	1.16[16]	0.83[17]				

[a] μ in debye units and $P_a = 0.15P_e$ (P_a and P_e are, respectively, the atomic and electronic polarizations).

Many azo chelates of Co(II), Ni(II), and Cu(II) with various phenyl substituents in different positions have been thoroughly studied (**2** and Table I). It is generally agreed that unsubstituted molecules, in the case of Co(II) and Cu(II) derivatives, have a moment which is high enough to exclude the presence of significant amounts of the centrosymmetric trans-square-planar form, **1b**, having zero dipole moment. (For the cis-planar configuration, see **3**). At the same time, in methyl-substituted derivatives there is a decrease in the moment with an increase in the steric hindrance (Table I), which is much higher in the Co(II) chelates.[16,17] According to the above statement this behavior may be rationalized on the basis of equilibrium **1**, between a tetrahedral and a square-planar form.



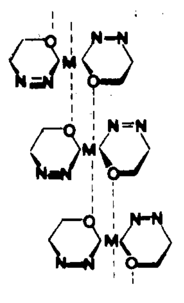
2



cis square planar

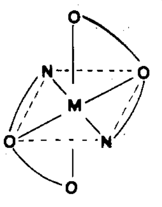
3

From Table I a substantial difference may be seen between the moments of Cu(II) and Co(II) chelates and those of Ni(II). In the first two series the observed moment decreases on increasing the steric and electrostatic effects, while it does not change in the corresponding Ni(II) chelates. This indicates that the tetrahedral form is not predominant. So, taking into account also the increase of the observed moments with the temperature of Ni(II) chelates, an equilibrium between three forms (tetrahedral, trans square planar, and polymeric trans octahedral, **4**) is possible.[17] The position of this equilibrium is affected by the structure of the ligand (electronic and steric effects of the substituents), the nature of the solvent, and the temperature. The presence of the trans-octahedral form (polymeric) in solution is suggested by the fact that the observed moments do not change on introducing bulky substituents in the ortho positions of the phenyl ring. This behavior could not be explained in the presence of only the tetrahedral and trans-planar forms because in this case ortho substituents should shift the equilibrium toward



trans octahedral (polymeric)

4



trans octahedral (monomeric)

5

TABLE II. Observed Moments,[a] in Benzene, of Some Copper(II) Azomethine Chelates (6a)

R	μ	R	μ	R	μ
H	2.77[15]	2,4-Me_2	2.06[15]	2-Cl	2.57[18]
2-Me	1.69[15]	2,4,6-Me_3	1.27[15]	3-Cl	2.55[18]
3-Me	3.37[15]	2-OMe	4.24[15]	4-Cl	2.39[18]
4-Me	3.29[15]	4-OMe	3.60		

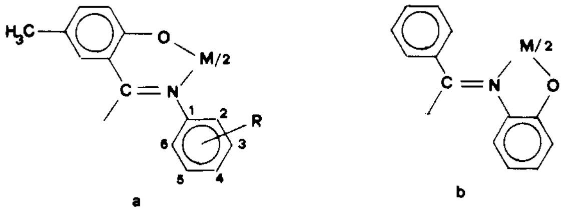
[a] μ in debye units and $P_a = 0.15P_e$.

the planar form, with zero moment. And this is not the situation of Ni(II) complexes, as may be seen from Table I.

On the basis of the above results, in azo chelates of Co(II) and Cu(II) the introduction of a large group such as a methoxy group in the ortho positions of phenyl should shift equilibrium **1** toward a planar configuration. Experimentally, the opposite trend is observed. It is possible[15,16] that an equilibrium between the tetrahedral, trans-octahedral (**5**), and square-pyramidal configurations exists in solution, as has been observed for chelates with ethylenediamine derivatives.[19]

Finally from a comparison of the electric and magnetic moments of the *o*-, *m*-, and *p*-chloro chelates it is suggested that in the case of the Ni(II) chelates supplementary interaction of chlorine with nickel for the ortho compound is absent.[18]

Azomethine chelates are structurally very similar to azo chelates, of which they are iso-π-electronic analogues. They may be divided into two groups, **6**, depending on whether they hydroxyl ortho to the phenyl group is bonded to the aldehyde, **6a**, or to the aromatic amine, **6b**, of the ligand. Table II shows some moments of type **6a**. A series of complexes of this type and analogues has been studied, the results being substantially in agreement.[15,18,20-24] As for the corresponding azo chelates, an equilibrium of type **1** is usually set up in which the steric and electrostatic effects exerted by the groups ortho to the phenyl ring favor planar (or pseudoplanar) forms. In conclusion, the regular variation of the observed dipole moments of azomethine (as well as the corresponding azo) chelates with the stereochemistry of that part of the ligand which is near the metal cannot be explained by an equilibrium between spin states, polymeric association, coordination of the solvent molecules, or acentric pyramidal structure that were considered the reasons for the paramagnetism of the nickel complexes and of the polarity of various azomethine chelates.



6

Eight bis(*N*-alkylsalicylideniminato)beryllium(II) complexes with alkyl groups Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *sec*-Bu, and *t*-Bu have been studied[25] in benzene at 25 °C by means of dielectric loss measurements. The values of atomic polarization were found to range from 28 cm^3 (when the alkyl groups have straight chains) to about 10 cm^3 (when the alkyl groups are branched). This atomic polarization may be attributed to concerted motion of the atoms of the chelate rings. The decrease in the derivatives where the alkyl groups are branched very probably is due to intramolecular steric interactions.

Zinc(II) chelates of *o*-aminobenzeneselenol anils (μ = 2.3–2.75 D)[26] have a tetrahedral structure, as do those of Ni(II) with 4-(aminomethylene)-2-pyrazoline-5-thiones[27] (μ = 3.2–5.1 D) and Co(II) with thiosalicylaldimines[28] (μ = 3.93–6.82 D).

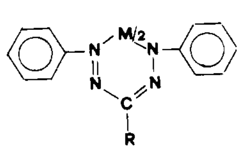
The chelates formed between vanadyl and salicylarylimines adopt a particular configuration, similar to a tetragonal pyramid with the oxygen at the apex,[29] by analogy with the structure found from X-ray measurements.[30]

No significant differences in configuration were found between these chelates, which are derived from *o*-hydroxyaldehyde, **6a**, and those derived from *o*-hydroxyaniline, **6b**. Chelates of the latter type with Cu(II), Ni(II), and Co(II) have been studied[31] (μ = 3.46–5.85 D). In theory, there are three possible configurations: a tetrahedral structure (with a high moment), a trans-octahedral (with a zero moment), and a cis-octahedral one (polymeric, with a high moment). The second and third may be excluded, respectively, on the basis of the observed moments and of the experimental molecular weight (cryoscopy).

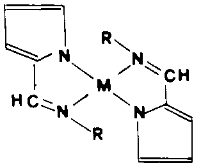
The analogous complexes of Cd(II), Zn(II), and Pb(II)[32] and Co(II) and Mn(II)[33] are also tetrahedral for the same reasons.

B. Derivatives of Formazan and Related Molecules

The tetrahedral configuration in solution is arrived at by exclusion for the chelates between Ni(II), Zn(II),[34] Co(II), Cu(II),[35] and formazans, **7**. As to the Ni(II) chelates it may be observed that the presence of paramagnetism is incompatible[36,37] with a planar structure. Besides, cryoscopic measurements in dioxane rule out the possibility of a polymeric structure, while an octahedral configuration is excluded from the observed moments (1.96–2.48 D).[38] The presence of a tetrahedral structure is in agreement with the fact that the analogous monomeric zinc(II) chelates (for which a planar structure is excluded because of the electronic configuration of the metal (d^{10}), and a tetrahedral one, on the contrary, is very characteristic) have dipole moments similar to those of the nickel complexes.



7



8

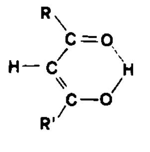
The same results have been found[35] for similar complexes of Ni(II), Co(II), and Zn(II) with *N*-azolylformazans.

Both copper(II) pyrrolecarbaldehyde aryliminates (**8**, with M = Cu and R = Ar)[39,40] and nickel(II) pyrrolecarbaldehyde alkyliminates (**8**, with M = Ni and R = alkyl)[41] exist in apolar solvent in the form of an equilibrium between square-planar and pseudotetrahedral configurations. The position of this equilibrium depends on the steric and electrostatic effects of the group R. The thermodynamic parameters of this equilibrium, in benzene, have been calculated from dielectric measurements[42] starting from the expression $\mu_{obsd} = X\mu_{Zn}^2$, in which μ_{obsd} is the observed moment and X the mole fraction of the tetrahedral form, assuming that the moment of the latter equals the moment of zinc chelate (μ_{Zn}). Apart from this assumption, the results so obtained seem uncertain because of the small temperature range used (15–45 °C) and the few measurements performed. In all cases, the observed increase in moment with temperature (0.2–0.4 D from 15 to 45 °C) indicates the presence of an equilibrium. With regard to thermodynamic aspects of this equilibrium, we observe a constant predominance of the probabilistic conditioning factor (entropy) over the energetic one (enthalpy).

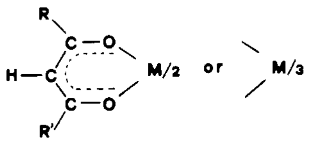
Electronic spectra have been used to obtain independent information on the conformation of these molecules. It has been found that in the complexes of type **8**, in methanol, absorption bands which can be assigned to electron transition in the pseudotetrahedral configuration are absent in the long-wave region. On the contrary, an inflection is observed at 780 nm for the copper pyrrolecarbaldehyde cyclohexyliminate, in which the pseudotetrahedral structure might be favored by the branching of the *N*-alkyl radical. Very probably, the present complexes, with the exception of the cyclohexylimine derivative, show mainly a square-planar configuration in methanol.[41]

C. Derivatives of β-Diketones and Mercapto-β-diketones

These ligands (**9**) bond to metal cations, the metal substituting the alcoholic hydrogen atom available after keto–enol tautomerism, giving rise to a cyclic structure with six atoms, **10**.



9



10

Thallium(I) complexes[43] have been studied. The observed dipole moments (1.87 D for (2,4-pentanedionato)thallium and 1.98 D for (1,3-diphenylpropanedionato)thallium) are in agreement with the assumption that these molecules are monomeric in solution and that thallium–oxygen bonds are only moderately polar (less than 2 D). In both molecules the positive direction is taken as that point away from the metal ion towards the ligand.

The complexes of the type CuL_2 (L indicates a β-diketone molecule) are usually square planar.[44,45] The complex with L = ethyl acetoacetate ion (1.07 D) has been proved to contain 38% symmetric structure (1.73 D) and 62% unsymmetric (0.0 D).[44] In the same way, the moment of the corresponding chelate with $EtOC(O)CH_2C(O)Me$ gave,[45] respectively, 48% and 52%.

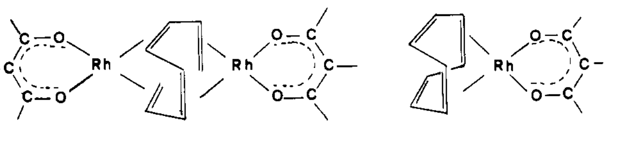
Similar results have been obtained for beryllium bis(β-keto enolate) complexes[46–48] from dielectric measurements and IR spectra.

In the case of fluorinated β-diketone chelates CuL_2 (L = $RCOCH_2COCF_3$, with R = 2-thienyl, Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-BrC_6H_4, and *m*-BrC_6H_4), the presence of a single configuration—the unsymmetric square planar—has been suggested on the basis of the observed moments (2.0–4.3 D, corrected for the contribution due to atomic polarization). Nevertheless, the moments of the two chelates Cu(*p*-$MeC_6H_4CO{=}CHCOCF_3)_2$ and $Cu(C_4H_3SCO{=}CHCOCF_3)_2$, determined at the temperatures of 10, 25, and 40 °C, gave, respectively, the following results: 4.59, 4.54, 4.66 D; 4.85, 4.82, 5.17 D. According to the authors[49] this indicates the absence of a cis–trans equilibrium in solution or, if there is an equilibrium, it has a very small enthalpy variation associated with it. In our opinion the possibility of an equilibrium should not be excluded both by analogy with the results obtained for the zinc(II) chelates[44,45] and because of the fact that from 10 to 40 °C we observe an increase of 0.3 D, which might be significant if the uncertainty in the observed moments is ±0.1 D.

For the following acetylacetonate (L) complexes MnL_3, FeL_3, CoL_3, and CrL_3, both atomic polarization and dipole moments have been found to be independent of the distortion of the octahedral structure.[50] Iron(III), chromium(III), and aluminum complexes do not possess[51] a component of orientation polarization resulting from the existence of a permanent dipole moment in the molecule. Only for the cobalt(III) complex has a possible exception been suggested. However, for aluminum tris(2,4-pentanedionate)[52] a moment value of 1.1 D has also been determined.

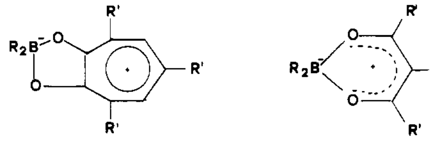
Several complexes containing both β-diketones (L) and other ligands (R) have been studied.

Dielectric loss measurements have shown[53] that (μ-cyclooctatetraene)(2,4-pentanedionato)dirhodium(I) (μ = 0 D) and (2,4-pentanedionato(cyclooctatetraene)rhodium(I) (μ = 0.9 ± 0.1 D) have structures **11**.



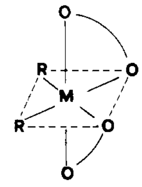
11

The dipole moments of boron chelates[54] with tropolone and 1,3-diketone derivatives, **12**, indicate that the positive charge stabilization decreases in the order tropolone > $(PhCO)_2CH_2$ > $(MeCO)_2CH_2$ moiety.

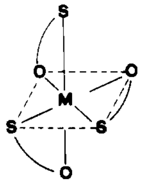


12

Among compounds of the general formula R_2ML_2, a great amount of study has been spent on those of tin. Diphenyl-, dimethyl-, diethyl-, and dibutyltin acetylacetonates, dibenzoylmethanates, and hexafluoroacetylacetonates have moments (2.05–3.86 D)[55] which can be explained only in terms of the predominance of cis-type structure (C_2), **13**. Analogous complexes of tin, titanium, zirconium, and hafnium (6.19–8.15 D)[56,57] have the same stereochemistry.



13



14

Complexes $Re(acac)_2Cl_2$, $Re(acac)_2Br_2$, and $Re(acac)_2I_2$ are monomer and can exist in cis and trans configurations, which can be synthesized by means of different methods.[58] Tropolonate derivatives of these compounds and of tin, titanium, and zirconium have structures very similar to those of the corresponding acetylacetonate ones.[57,59]

No significant difference exists between the chelates of β-diketones and those of mercapto-β-diketones. Many complexes of the latter ligands with the metals Ni(II), Pd(II), Pt(II), Cu(II), and Zn(II) have been studied (general formula ML_2), and also of Cr(III), Fe(III), Co(III), Ru(III), and Rh(III) (general formula ML_3).[60–66] The relatively large moments indicate a cis-square-planar configuration for the nickel, palladium, platinum, and copper complexes, and a fac-octahedral one, **14**, for those of chromium, iron, ruthenium, cobalt, and rhodium. The significantly lower values obtained for the zinc complexes were considered to be consistent with a tetrahedral structure. The copper complexes[64] have moments 0.5–1.0 D lower than the mean value for the corresponding nickel, palladium, and platinum complexes; this decrease of the moment is attributed to significant distortion from the square-planar toward the tetrahedral configuration. It may be useful to know that the solid-state determinations show a cis-square-planar structure each for a palladium and a platinum complex[67] and for four nickel complexes,[68–71] the fac-octahedral for a cobalt[72] and two iron complexes,[73] and a tetrahedral configuration for a zinc(II) complex.[74]

The cis-square-planar and fac-octahedral configurations are two examples of the interesting principle of anti symbiosis.[75–77] According to this principle, in chelates containing ligands with both S and O donors, each S-donor atom has an O-donor atom in a trans position with respect to it for planar and octahedral complexes of class B metal ions.[78-80]

Dielectric loss measurements have been made with the aim of obtaining information on the atomic polarization and on the possible relaxation mechanism[53,57,61,63,81-85] in β-diketone and mercapto-β-diketone chelates. In general, a high atomic polarization has been found, largely due to the bending of the metal-oxygen (sulfur) bonds and in part to the infrared absorption. Very often the order of the relaxation time (τ) is in accordance with increasing bulk of the ligand. For the same ligand and configuration τ is approximately constant with the change of the metal.

From the above results it may be seen that both β-diketone and mercapto-β-diketone chelates have the same structure. Only minor differences are observed between these two classes of compounds.

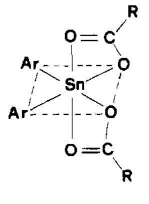
Experimental dipole moments (in D) for copper complexes of fluorinated β-diketones $Cu(RCO{=}CHCOCF_3)_2$ and the corresponding mercapto-β-diketones $Cu(RCS{=}CHCOCF_3)_2$ are, respectively (R, μ_O, μ_S): C_4H_3S, 4.82, 4.96; p-MeC_6H_4, 4.54, 5.12; Ph, 4.01, 4.39; p-BrC_6H_4, 2.47, 2.45. The slightly higher values found for the mercapto derivatives with respect to the β-diketone complexes may be due to the greater electronegativity of oxygen compared to sulfur. This difference may be seen because in the monothio-β-diketone compounds the sulfur is bonded to C-4 of the ligand, i.e., on the side of the square plane farthest from the electron-withdrawing CF_3 group. So the presence of the latter cannot excessively influence the electronic behavior of C–S–M and C–O–M bonds.

Whereas metal chelates of mercapto-β-diketones are usually quite soluble in nonpolar solvents, the corresponding derivatives of β-diketones mostly have low solubilities in the same solvents.

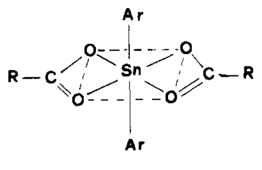
These differences are not too important. In fact, for all metal chelates of both types of ligands it has been found that the dipole moments decrease according to the following order of the R group: p-MeC_6H_4 > 2-thienyl (C_4H_3S) > m-MeC_6H_4 > m-ClC_6H_4 > m-BrC_6H_4 > p-FC_6H_4 > p-ClC_6H_4 > p-C_6H_4 > m,p-$Cl_2C_6H_3$. The vector analysis shows that this variation in the values of the moments with change in the R groups cannot depend only on the magnitude and direction of substituent group moments, but also on the presence of inductive and mesomeric effects. The latter might be relevant because of the electron mobility of the examined systems.

D. Derivatives of Other Ligands

Bis(acyloxy)dialkyl- and bis(acyloxy)diarylstannanes[86] have relatively low dipole moments (1.37 and 1.39 D, respectively), although these molecules contain groups such as Sn—O (μ = 2.7 D) and C═O (μ = 2.4–2.7 D). The low moments of these compounds indicate a mutual compensation and a high degree of symmetry. So an octahedral coordination is very probable, and both cis (**15a**) and trans (**15b**) octahedral configurations with respect to the aryl groups are possible. Vector analysis suggests that structure **15b** is the most probable. This is in agreement with the results obtained by means of IR spectra according to which the introduction of substituents into the para positions of the phenyl has scarcely any influence at all on the state of coordination of the acyloxy groups.



a



b

15

Finally magnetic and electric moments together with EPR, UV, and CD spectra were used in determining the structure of metal chelates of C-hetaryl-substituted monosaccharides.[87]

E. Conclusions

The results of dielectric measurements, many times confirmed by evidence of a different nature, have made it possible to establish some behavior common to different categories of chelates. The most regular are reported below.

The symmetry of the central part of the complex depends essentially on the type of metal and on the stereochemistry of the part of the ligand immediately near it. In other words, the configuration assumed is a compromise between the requirement of the maximum overlapping between the orbitals involved in the bonds and the steric requirements of the ligand.

The configuration of the complexes in solution in general is fairly different from that in the solid state. This is due to molecular packing in the condensed state and not to the influence of the solvent. The latter does not modify the position of the equilibrium, when present.

When an equilibrium between two or more configurations is present, its position is highly conditioned by steric factors connected with the characteristics of the central part of the chelate. In the few equilibria, of which thermodynamic parameters have been determined, it has been found that the entropic conditioning factor is, generally, predominant on the enthalpic one.

Finally, the bonds responsible for the formation of the chelate are not generally very polar and very probably present a considerable degree of covalence.

III. Adducts of the Halides of Group 2–6 Elements as Acceptors

A. General

These complexes originate from a charge transfer between donor (D) and acceptor (A) molecules. In our case the acceptor is an organometallic or inorganic molecule. Given the intrinsic nature of these compounds, the importance of dielectric measurements is obvious. This technique is essentially used for revealing the formation of the complex or any other intermolecular interaction, determining its stoichiometry, estimating the stability, measuring the dipole moments, even when the complexes cannot be isolated, and calculating the charge transferred from the donor to the acceptor.

In practice there are difficulties when the rate, at which the equilibrium between donor and acceptor is established, is low.

Concerning the interpretation of the experimental results, there might be some minor uncertainty due to the unknown atomic polarization of the complex and to the deformation of the structure undergone by the two partners. These difficulties, however, are of no importance because of the high moment of the present complexes.

Literature data can be discussed according to both the donor and acceptor type. Both have advantages and drawbacks. We shall follow the classification according to the type of acceptor because it is more schematic. In addition, a comparison will be made among the various donors.

B. Complexes Examined

1. Group 2

Compound $ZnBr_2$, which is apolar in the gas phase,[88] in ethyl ether has a large moment, which depends on the temperature

(8.44 D at 25 °C and 8.92 D at -5 °C).[89] This behavior has been interpreted with the presence of an equilibrium between two forms: one with one molecule of solvent and the other with two. The first is stable at room temperature and the latter at low temperature. However, if we take into account the anisotropy of the solvent, the observed variation might have a different origin.[90]

Mercuric halides also are linear in the gaseous phase[91] and in benzene and in dioxane show definite dipole moments ($HgCl_2$, 1.01 D in benzene and 1.27 D in dioxane; HgI_2, 1.87 D in dioxane).[92a] Taking into account that the value of atomic polarization is 6-7 cm^3 in the gas phase,[92b] very probably these molecules are bent in solution, forming donor-acceptor complexes with the dioxane. The value of 140-160 °C for the angle hal-$\hat{\mathrm{H}}$g-hal has been suggested from theoretical calculations. Previously, however, from Kerr constant measurements some authors[93] argued that the apparent dipole moment may be due to unjustified assumptions on the atomic polarization and suggested that this might be much larger than the 10% or so usually assumed. These objections do not seem to hold because to reduce the dipole moment values to zero, atomic polarization values of more than 20 cm^3 would be assumed and these are very different from the values of 6-7 cm^3 found in the gas phase.[92b]

2. Group 3

Complexes between borane (BH_3) and trimethylamine,[94,95] aziridine,[96] and dimethylphosphine[97] have been studied. The trimethylamine complex, which has been examined also by means of IR, Raman, and microwave spectra,[95] has a moment of 4.45-4.92 D, depending on the method employed and on the state (liquid or gaseous). This molecule has C_{3v} symmetry. From the point of view of the polarity and, consequently, of the charge transferred from the donor to the acceptor, aziridine-borane (4.45 D)[96] and dimethylphosphine-borane (4.78-4.85 D)[97] behave like the trimethylamine complex. This indicates that in all three complexes the moments derive essentially from the charge transfer and not from a rearrangement of the structure of the "partners".

A great deal of complexes, having trihalides of Al,[98-107], B[99,102,109-114] Ga,[99,102,103,115,121] and Tl[117,118] elements as acceptors and amines, ethers, and sulfides as donors, have been studied (Table III). From these works the following information has been obtained, besides that reported at the beginning of the present section.

Concerning the electronic structure of aromatic donors it has been found that, on complexation, the $p\pi$ conjugation between the heteroatom lone pair and the π system of the phenyl is interrupted.[99,100,103] There are two pieces of evidences for this. (i) Benzene has a very intense absorption band (with fine structure) in the region 259-261 nm; this band remains the same in mono derivatives in which the substituent does not conjugate with the π system of the phenyl. Instead, when the conjugation exists (as in amines, ethers, and sulfides), this band is measurably shifted to higher wavelengths and is less intense. After complexation, it appears that the situation existing in unsubstituted benzene and in its noninteracting derivatives is established. (ii) The dipole moments of complexes with donors of the aliphatic series are very close to those for the corresponding complexes with aromatic donors (for the same acceptor). Given this evidence it is reasonable to take the difference between the formation enthalpies of the two complexes (with the same acceptor, but one with an aliphatic donor and the other with an aromatic one) as a measure of the energy of $p\pi$ conjugation in the aromatic amines, ethers, and sulfides.

In addition it has been found that the effect of $p\pi$ conjugation in aromatic amines, ethers, and sulfides is clearly reflected in the complexing reactions. In fact, whenever the energy of that conjugation is of the same order as (or greater than) the formation enthalpy of the complex, the latter cannot be formed. This is the case for the acceptors I_2, $SnCl_4$, and $TiCl_4$.[99]

TABLE III. Complexes of Trihalides of Group 3 Elements

acceptor	donor	ref
$AlBr_3$	ethers	98-102
	amines	98, 99
	sulfides	98, 102, 103
	phosphines	103
	ketones	104
	nitrobenzenes	105
	acetylenic sulfones	106
$AlCl_3$	ethers	99
	amines	99
	sulfides	99
	ketones	107
BBr_3	sulfides	102, 108-110
	amines	104, 109
	ethers	102, 104, 109
	selenides	109
	phosphines	110
BCl_3	ethers	104
	phosphines	103
BF_3	ethers	111, 112
	amines	111, 113
	esters	114
	phosphines	103
$GaBr_3$	amine oxides	115
$GaCl_3$	ethers	99, 102, 116
	amines	99, 116
	sulfides	99, 102, 116
	phosphines	103
	amine oxides	117
$TlCl_3$	tri-*n*-butyl phosphite	118

For sufficiently strong acceptors such as, in general, most of the halogen derivatives of the elements of group 3 the formation enthalpy of the donor-acceptor bond is considerably greater than the energy deriving from the $p\pi$ conjugation. However, this is only the condition necessary to enable the complex to form (it does not mean it is actually formed). From a thermodynamic point of view it is also essential that this energetic factor is predominant over the probabilistic one which, in our case, is against the actual formation of the complex. In fact, the latter presents a lower entropy than the sum of the contributions of the two free "partners".

An analogous $p\pi$ conjugation has been observed in aromatic phosphines. In fact, the dipole moments of the donor-acceptor bonds and consequently the charge transfer are close[103] to one another in complexes between phosphines (aromatic and aliphatic) and $AlBr_3$. However, the values of the heats of formation of the complexes with aromatic phosphines (21.6 kcal mol^{-1})[103] are much lower than those for the complexes with the aliphatic phosphines (33.7 kcal mol^{-1}). Now, the heats of formation of the donor-acceptor bonds being close, it follows that the difference in the heats of formation between the complexes with aliphatic phosphines and those with the aromatic ones might derive from the difference in the rearrangement energy of the phosphines. The rearrangement of aromatic phosphines is the breakdown of $p\pi$ conjugation on complex formation. Other factors, such as steric and inductive effects, are not significant.

Another interesting and controversial topic concerns the relative stability of the complexes as a function of the donor type. For aliphatic R, the following order has been obtained: $R_3N{\cdot}AlBr_3 > R_2O{\cdot}AlBr_3 > R_2S{\cdot}AlBr_3$, in agreement with the calculated overlap integrals of the atoms taking part to the donor-acceptor bond (N-Al 0.48, O-Al 0.42-0.40, S-Al 0.38).[98] The same trend is observed with the acceptor BF_3, which is again in agreement with the overlap integrals (N-B 0.60, O-B 0.54, S-B 0.47).[111] In the case of the acceptor $GaCl_3$ (and also $GaBr_3$, GaI_3, I_2, $SnCl_4$, $TiCl_4$) the order changes: $R_3N{\cdot}GaCl_3 > R_2S{\cdot}GaCl_3 > R_2O{\cdot}GaCl_3$. In this case, the overlap integrals (N-Ga 0.49, O-Ga and S-Ga 0.41)[116] do not account for this partial inversion. The transferred charge and the heat of formation of the complexes (ΔH) are in agreement with the trend of the stability. For example, $\Delta H = -32.3$ (mean), 23.3, and 17.5 kcal mol^{-1}, respectively, for complexes of aliphatic amines, ethers, and sulfides with $AlBr_3$.[99] We feel that in the formation of complexes such as those examined here, it is first necessary to take into account the donor capacity of the organic molecules (for a given acceptor). In addition, for this donor power to become operative, there should be favorable overlap between the oribtals directly involved in the formation of the complex. If both of these factors are taken into account, then the above results (which otherwise appear to be in conflict) become understandable.

It has generally been observed that in complexes not sterically hindered there is a linear proportionality between the degree of charge transfer (μ_{DA}/er, in which μ_{DA} is the dipole moment of the donor-acceptor link, e the electron charge, and r the distance between the centers of the positive and negative charges) and the heat of formation of the donor-acceptor bond.

Some aromatic and heteroaromatic ketones with $AlBr_3$ give rise[104] to complexes $D{\cdot}AlBr_3$ (D is a donor molecule) and $D{\cdot}2AlBr_3$. The first $AlBr_3$ molecule bonds to carbonyl oxygen and the second one probably bonds according to the type of a π complex. However, it is useful to remember that several structures have been proposed for 1:2 complexes between aromatic ketones and chloroaluminum compounds. All these structures have been correlated with experimental data (see ref 107 and references therein).

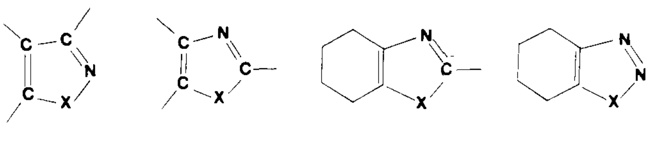
The observed dipole moments for the complexes between $GaCl_3$ and aromatic amine oxides are smaller than those for the corresponding $GaBr_3$ derivatives.[115,117] This may be due to various reasons such as a minor polarity of the donor-acceptor bond, a minor dipolar contribution of the acceptor, and a dissociative effect.

In addition to the halogen derivatives of the elements of group 3B (as acceptors), the corresponding alkyl and aryl derivatives have been studied.[119-123]

The moment and stability of complexes of trimethyl- and triethylaluminum are similar to and slightly lower than the moment and stability of the corresponding triphenylaluminum complexes.[119]

Triphenylboron complexes[120] with pyridine, 2- and 4-picoline, 2,4-lutidine, and Et_3N but does not complex with Pr_2S, Bu_2S, tetrahydropyran, and 2,6-lutidine. Thermodynamic parameters (ΔH, ΔG, ΔS) for the reaction of formation of these complexes have also been determined. In the complexes between trimethyl-, triethyl-, and triphenylboron with pyridines we have a substantial charge transfer (the moments of the donor-acceptor bond are 2.6-3.4 D).[121] The fact that these moments of triethyl- and triphenylboron complexes are comparatively close and the heats of formation (17.6-18.0 kcal mol^{-1}) are the same, within the limits of experimental error, indicates that the energy required to disrupt the pπ conjugation in triphenylboron during formation of the complex with pyridine is not great. With the same donors the triallylboron forms complexes[122] whose stability has the order 3-methylpyridine > pyridine > trimethylamine > 2-methylpyridine. A linear relation has been found between $\Delta\mu$ values (difference in the dipole moments of the complex and the free donor), the activation energies of association processes leading to the formation of the complexes, and the chemical shifts of BCH_2 protons and of ^{11}B.

Finally, interesting results have been obtained[123] on the complexes between the trimethyl derivatives of certain group 3B elements, MMe_3 (M = Al, Ga, In) and the azoles, **16**. The reaction between these two classes of substances gives rise to completely different compounds depending on whether or not the azole contain mobile hydrogen, **16a** and **16b**. In the case where azoles of type **16a** are used, i.e., with mobile hydrogen, this hydrogen of NH group is replaced by the organometallic MMe_2 group and methane is liberated.



a: X = NH ; b: X = NMe, NCH_2Ph, S, $NC_6H_3(NO_2)_2$-2,4

16

3. Group 4

Of the acceptors in this group, it has been $SnCl_4$ that has been studied, almost exclusively, and rarely $SnBr_4$, $TiCl_4$, and $ZrCl_4$. The acceptors $SnCl_4$, $SnBr_4$, and $ZrCl_4$ form complexes with ketones in the ratio of 1:2 (μ = 6.0-7.5 D).[124] The same behavior has been observed among the complexes between SCl_4, $SnBr_4$, and the aldehydes[125] (naphthalenecarboxaldehyde, cinnamaldehyde, furancarboxaldehyde, benzaldehyde, salicylaldehyde), with moments between 5.9 and 6.5 D except for the two complexes with naphthaldehyde which have a zero moment and a 1:1 stoichiometry. In all these adducts the coordination of carbonyl oxygen to the metal halide is evidenced by a large shift (100-150 cm^{-1}) to lower frequency of the carbonyl stretching absorption, in agreement with previous results.[126-129] The spectrum of the two complexes with phthalaldehyde, in solid and in dioxane, does not show any C=O stretching band in the zone of the free aldehydes, indicating that both carbonyl groups are involved in the bond with the metal and explaining, in this way, its stoichiometry. The dipole moment of the acceptors is zero, while that of the aldehydes and ketones is 2.6-3.0 D; therefore the high values observed for the complexes are consistent only with cis octahedral structures. Only in the case of the complexes with naphthalenecarboxaldehyde, which have a zero moment, it is right to suggest a trans octahedral configuration due to the presence of a bulky donor group.[130]

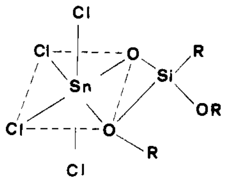
The *same* cis octahedral structure is to be assigned[131] to the six complexes with the general formula $SnCl_4{\cdot}2R_1COOR_2$ (R_1 is an alkyl group and R_2 is an alkyl or aryl), whose moments are about 9.5 D.

For the complex $SnCl_4{\cdot}O_2C_4H_8$ (dioxane) the moment of 2.95 D can be ascribed to the donor-acceptor bond moment only provided the conformation is a tetragonal pyramid. However, such an assignment is arbitrary in the absence of X-ray data. In fact, in the case of molecules such as $SnCl_4$ which have zero dipole moment in the gas phase, the existence of a high dipole moment in a complex can be ascribed to the contribution of a highly polar donor-acceptor bond on the one hand and, on the other, to a change in the structure of the original molecule during complex formation.[132]

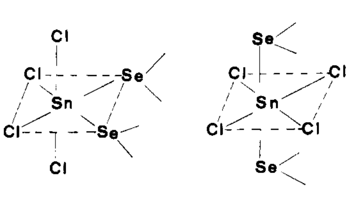
The behavior of the acceptors $SnCl_4$ and $TiCl_4$ with $RS(CH_2)_nSR$, n = 1-10, has been studied through dielectric and calorimetric measurements.[133] The results are analogous to those found above for similar molecules.

Alkoxysilanes with $SnCl_4$ form two types of complexes: $SnCl_4{\cdot}L$ and $SnCl_4{\cdot}2L$. The high values of the dipole moments (5.4-7.2 D) and the high difference ($\Delta\mu$ = 3.5-5.6 D) between dipole moments of the complex and that of the free donor indicate the presence of strongly polarized O-Sn bonds. For the equimolecular complexes a cis octahedral structure, **17**, may be suggested.[134]

(Vinyloxy)anilides (L) give rise to the $SnCl_4{\cdot}2L$ complexes (n = 6.3-9.5 D).[135] The considerable increase in the dipole mo-



17



cis and trans octahedral

18

ment of the complexes compared to that of the donor indicates the formation of a new and highly polarized donor-acceptor bond, of which the oxygen of the carbonyl group is primarily responsible.

Dipole moments and formation constants were calculated for $MCl_4{\cdot}nD$ complexes (M = Sn, Te, Ti; n = 1, 2; D is the donor, ether or sulfide) from dielectric measurements.[136] Limitations of the method with respect to concentration of partners and stability of the obtained complexes are discussed.

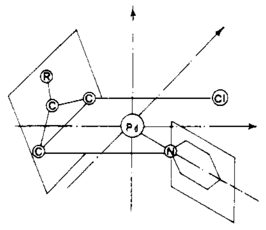
For D = $(C_4H_9)_3P$, $(C_4H_9)_3PO$, $(C_4H_9)_3PSe$, $(C_4H_9)_3PS$, the complexes $SnCl_4{\cdot}D$ (μ = 8.1–11.3 D)[137] are consistent with a trigonal-bipyramidal structure, while the $SnCl_4{\cdot}2D$ (2.36–5.2 D) are found in a mixture of the cis and trans isomers. The same type of complex is obtained between $SnCl_4$ and $R_1R_2R_3AsS$.[138] This behavior of the acceptor $SnCl_4$ seems very common. In fact, also with dialkyl selenides $SnCl_4$ gives rise to $SnCl_4{\cdot}R_2Se$ and $SnCl_4{\cdot}2R_2Se$ complexes. It has been suggested that equimolecular adducts are trigonal bipyramidal and $SnCl_4.2R_2Se$ are mixtures of isomers with cis and trans arrangements of the R_2Se molecules in a octahedral configuration[139] (**18**).

4. Groups 5 and 6

Complexes where group 5 elements are involved, in the period we have reviewed, concern essentially the antimony chlorides (acceptors) and organic carbonyl compounds—aldehydes and ketones (donors). Antimony(V) chloride forms 1:1 complexes with ketones[124] (acetone, methyl ethyl ketone, acetophenone, benzophenone) (μ = 8.3–9.1 D) and with aldehydes[140] (naphthalenecarboxaldehyde, benzaldehyde, salicylaldehyde, cinnamaldehyde, furaldehyde) (μ = 7.7–8.8 D); with phthalaldehyde it gives rise to a 2:1 adduct (9.76 D). These high moments are consistent with octahedral structures. The site donor of the carbonyl compounds (oxygen) has been indicated by the lowering of the stretching frequency of the carbonyl stretching vibration and from the increase in the C–C vibration of the complexed ligand compared to the free one. For these complexes both the initial decomposition temperature and heat of formation ($-\Delta H$) show the following order for the relative stability of the adducts: naphthalenecarboxaldehyde > benzaldehyde > furaldehyde > cinnamaldehyde.

Pyridine N-oxides give rise[141] to 1:1 and 2:1 complexes with $SbCl_3$ and to 1:1 complexes with $SbCl_5$. The dipole moments (8.2–10.5 D) for 1:1 complexes of $SbCl_3$ suggest a bipyramidal-trigonal structure with a lone pair of the central atom in a coordination position. For 2:1 adducts of $SbCl_3$ the observed moments (8.5–11.4 D) are considered too low for an octahedral structure with two donors cis. Therefore, we must consider a certain part of the trans isomer. For the complexes of $SbCl_5$, a C_{4v} structure is suggested. In all these complexes the shift of the (N–O) stretching frequency toward lower frequencies indicates that the coordination takes place through the N–O oxygen.

Complexes of π-allylpalladium chloride[142] ($RC_3H_4PdCl_2$) with pyridine have the structure shown in **19**. The introduction of an amine does not disrupt the π bonding of the allyl group to palladium. In contrast with previous reports, the group moment μ(allyl-Pd), which is of the order 2–2.5 D, goes from the allyl to the metal, i.e., the allyl group carries a positive charge with respect to the metal.



19

Dipole moments together with conductivity measurements in solution and IR spectra[143] of solide complexes $MX_5{\cdot}nL$ (M = Nb, X = Cl, n = 1, 3, 4; X = Br, n = 1, 3; M = Ta, X = Br, n = 1, 3) with amides L = $RCONH_2$ (R = H, Me, Ph) indicate that L bonds to the metal atom through the oxygen atom. The values of M–O bond moments indicate that the basicity of the ligand L increases as R = H < Ph < Me. The dipole moments of the bis(pentane-2,4-dionato)oxovanadium(IV) in benzene (3.27 D) and in dioxane (3.79 D) determined from dielectric loss measurements indicate the presence of the complex $(acac)_2VO{\cdot}$dioxane.[144,145] The relaxation time found for $(acac)_2VO$ in dioxane (130 ps) is much larger than that in benzene (56 ps); this might also be explained by the formation of the adduct with the dioxane. Concerning the configuration of this complex, it has been suggested that very probably the dioxane coordinates via the oxygen to the sixth position of the vanadium, as in the solid.[146]

The results obtained[147-151] on the complexes between $TeCl_4$ (acceptor) and certain donors are not in agreement with each other and, according to some authors, they could seem contradictory. Very probably, this is due to the fact that the configuration of these compounds depends in considerable measure on the environment of the molecules. In benzene, the low conductivity values as well as the magnitude of the observed moments (5.4–8.4 D)[147] of $TeCl_4{\cdot}R_2S$ and $TeCl_4{\cdot}R_2SO$ (R is an alkyl group) indicate that these complexes are molecular compounds of the donor-acceptor type, in which all the Te–Cl bonds are predominantly covalent.

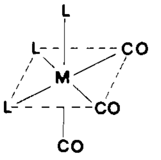
IV. Carbonyls and Nitrosyls

There have been relatively few dipole moment studies on this class of compounds over the past 10 years. Most of the structures of mono- and polynuclear carbonyls and carbonylnitrosyls were examined before 1968.[1,2] In the last few years there has been a more thorough investigation of the outstanding questions left unanswered, such as group and bond moments, as well as the study of some new structures.

For the complexes of general formula $M(CO)_4L_2$, in which L is a monodentate ligand, the dipole moments confirm an octahedral configuration, in solution. In this, the relative arrangement of the L ligands to each other, for which the partial moment is quite high, depends on both the nature of the metal M and of the ligand L.

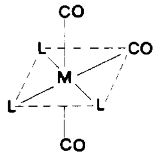
Complexes of the type $M(CO)_4(PMe_2Ph)_2$ with M = Cr, Mo, or W are readily prepared by heating the hexacarbonyl with dimethylphosphine. A cis configuration regarding the relative positions of ligands has been assigned to these complexes (μ = 6.3–7.1 D);[152] only for the chromo derivative a certain isomerization to the trans form may be suggested in solution. The corresponding complexes with L = $AsPMe_2Ph$ (μ = 6.7–7.1 D) are also cis for M = Cr, Mo, and W; that with L = $P(OMe)_2Ph$ and M = Cr is trans with a little cis impurity and that with L = $P(allyl)_2Ph$ is trans (1.1 D). The configuration of these complexes is often obtained from the number and intensity of the carbonyl stretching absorptions. In fact, while cis complexes of this type show a sharp band at highest frequency and a complex of three bands which may not be completely resolved and at least one of which will be intense,[153-156] trans complexes show one intense band and two weaker ones at higher frequencies.

Complexes of the type $M(CO)_3L_3$, with M = Cr, Mo, W and L = PMe_2Ph, $AsMe_2Ph$, PMe_3, $P(OMe)_2Ph$, have been synthesized by substitution of the cycloheptatriene[156] in the complex $M(CO)_3(C_7H_8)$. Of these only the derivatives with $P(OMe)_2Ph$, having a single strong carbonyl band in IR are believed to be of the mer type, **20**. On the basis of the observed moments (7.3–8.3 D) and IR evidence (an intense band and a further more intense one in the carbonyl region) the others may be assigned a facial configuration, **21**.



facial

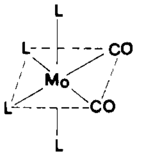
21



meridional

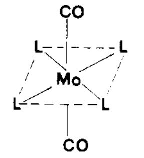
20

For the complexes $Mo(CO)_5L$, *cis*-$Mo(CO)_4L_2$, *fac*-$Mo(CO)_3L_3$ (L = PPh_3, $AsPh_3$, and $SbPh_3$) as well as *cis*- (**22**) and *trans*-$Mo(CO)_2(SbPh_3)_4$ (**23**), the infrared data for stretching as well as deformation vibrations do not clearly explain the difference in stability, the ease of substitution, or the observed dipole moments.[157] In order to get this information, the dipole moments have been utilized by using the model of variable donor–acceptor ability of ligands together with that of nonretention of charges on the metal. A comparison between the L–M–CO group moments has been made by assuming that the same structure is present for all the complexes examined. From these calculations it was found that multiple substitution affects both the L–Mo moment and the Mo–Co one. The critical factors of the stability of these complexes are the donating power of the ligand, which is related to the L–Mo group moment, and the steric effects, which become important whenever large ligands bond to the metal. Finally, in a tentative separation of the σ and π bonding capacities of the ligands examined, it was found that they become more σ donor (π acceptor) in the sequence $PPh_3 > AsPh_3 > SbPh_3$.



octahedral, cis-CO

22



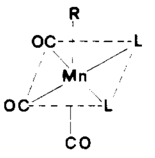
octahedral, trans-CO

23

Carbonyl complexes of general formula $(CO)_5MC(SR)R'$ (with M = Cr, W; R = Me, Et, Ph; R' = Me, Ph) have been thoroughly studied[158] by IR, NMR, electronic and mass spectroscopy, and electric dipole moments (4.53–5.14 D). Various lines of evidence are consistent with an octahedral configuration of these complexes. The higher $\nu(CO)$ stretching frequency, the energy barrier for rotation about the carbene carbon–sulfur bond, the ionization potentials, and the dipole moments show that the capacity of the thiocarbene ligands to transfer charge along L–M–CO is intermediate between that of alkoxycarbene and aminocarbene ligands.

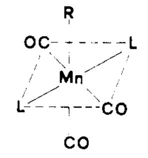
An increasing capacity of ligands to transfer charge on the $W(CO)_5$ group is suggested[159] from the observed dipole moments of the compounds $(CO)_5W[C(OMe)Me]$ (3.75 D), $(CO)_5W[C(SeMe)Me]$ (4.82), $(CO)_5W[C(SMe)Me]$ (4.95) and $(CO)_5W[C(NHMe]$ (6.34).

Dipole moments have been utilized[160] for finding the configuration of the compounds obtained by the reaction of *cis*-$MeMn(CO)_4L$ or *cis*-$MeCOMn(CO)_4L$ with the ligands L = $P(OCH_2)_3CMe$, PPh_2H; PPh_2Me, $P(OPh)_3$, PEt_3; $PPhMe_2$, $P(OMe)_3$. For the first group of ligands the single product $MeCO(CO)_3L_2$, with a facial configuration **24**, has been obtained; with the second group a meridional-trans complex, **25**, $MeCOMn(CO)_2L_2$, is obtained; and with the third group facial complexes are obtained which rapidly rearrange to meridional ones, **25** and **26**. These conclusions are further supported by the infrared and NMR spectral properties of the complexes examined.



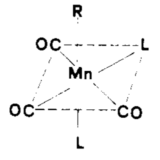
facial

24



meridonal, trans-L

25



meridional, cis-L

26

Information has been obtained[161] on the charge transferred in formation of the bond Co–M' (covalent) and Fe–M'' (coordinative), (M' and M'' are elements of groups 4B and 5B, respectively), from a comparative study of the two series of molecules $(CO)_4CoM'X_3$ and $(CO)_4FeM''X_3$, where X = Cl, OMe, Ph, or an alkyl group. On the assumption that the central metal remains electronically neutral after complexation, the charge transfer τ (in terms of electrons) in the bond M–M' (or M–M''), is connected to the group moment by eq 1, in which d and d' are the M–M' (M–M'') and M–C distances (in Å), respectively.

$$\tau = \mu_{(CO)_4MM'}\left(\frac{4}{4d + d'}\right) \tag{1}$$

Another virtually linear relationship has been found between $\mu_{(CO)_4MM'}$ (or $\mu_{(CO)_4MM''}$) and the average stretching frequency, $\nu(CO)_{av}$. From $\mu_{(CO)_4MM'} = f[\nu(CO)]$ plot a relationship, (2), has been obtained for calculating the charge transfer.

$$\tau = \frac{\nu_0 - \nu(CO)_{av}}{142 \pm 10} \tag{2}$$

In (2) ν_0 is the hypothetical CO stretching frequency in the absence of ligands. Given the various assumptions in obtaining these two relations, the values calculated in this way acquire an interesting significance only when they are utilized for a comparison within a homologous series. So, it is found that, for the same X the charge transferred to the transition metal is always greater in the coordination bond $M\text{–}M''X_3$ than in the covalent one. For a highly electronegative X (X = Cl) the charge transferred along the bond M'' → M tends to zero, when this is in the opposite direction, M' → M, in the covalent bond. This difference in behavior is explained if we remember the different origin of the electrons that are present in the M'–M and M''–M σ bonds.

The effect of the ligands bonded to the tin on the nature of the Co–Sn[162] and Fe–Sn[163,164] bonds has been established from the group moments. It has been shown that the charge transfer in these bonds is determined more by the electronic properties of the ligands than by the nature of the central metal and the structure of the complexes.

The group moments $\mu(L \pm M)$, where M = Co, Fe and L = PPh_3, have been extracted[165] from the values observed for $CoCONO(PPh_3)_2$ and $Fe(NO)_2(PPh_3)_2$ assuming 0.5 D for $\mu(M \pm CO)$ and 1.0–1.3 D for $\mu(M \pm NO)$. The μ values obtained assuming tetrahedral structures [$\mu(L \pm Co)$ = 3.3 D and $\mu(L \pm Fe)$ = 3.7 D] are much smaller than the calculated ones (~8 D) for an exclusively dative L → M bond. This was ascribed to the strong metal-to-ligand back-bond. Taking the same group moments a vectorial analysis has been carried out[166] on the molecules π-$(CH_2CXCH_2)FeCONOL$ (X and L are, respectively: H, CO; H, PPh$_3$; Me, CO; Cl, CO; Br, CO).

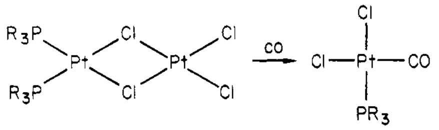
In the complexes π-tetracarbonyl(monoolefin)iron, π-LFe(CO)$_4$, (with L = *trans*-PhCH=CHCOMe, *trans*-PhCH=CHCOPh, *trans*-PhCH=CHCHO, CH$_2$=CHCHO) it has been found[167] that the ketone maintains the conformation present in the free ligand, while the aldehyde gives both rotamers, in equilibrium. As regards the latter equilibrium, from IR measurements the enthalpy change (ΔH) for the interconversion s-cis $\rightleftarrows$ s-trans is: π-(CH$_2$=CHCHO)Fe(CO)$_4$ $\neq$ 943 ± 200 cal mol^{-1} and π-(PhCH=CHCHO)Fe(CO)$_4$ 1066 ± 200 cal mol^{-1}. In the complexes π-LFe(CO)$_3$ the same ligands bond to the iron via the π doublet of the olefinic ligand and the carbonylic one.[168]

Analysis of the electric moments of bis(1,3-butadiene)carbonyliron, bis(2,3-dimethyl-1,3-butadiene)carbonyliron, bis(1,3-cyclohexadiene)carbonyliron, bis(1,3-butadiene)(trimethyl phosphite)iron, and (trimethyl phosphite)tetracarbonyliron allows an assessment of the magnitude of the μ(Fe$\overset{+}{-}$CO) group moment (ca. 2 D) in these molecules.[169]

Dipole moments and IR and NMR spectra have been used to identify the structure of the octahedral (cis and trans) complexes Ru(CO)$_2$L$_2$X$_2$ (where L = organo derivatives of group 5B and 6B elements; X = Cl, Br, or I).[170] The cis isomers show dipole moments which fall distinctly into three groups, enabling the exact assignment of the three possible cis CO structures to be made. Group and bond moments are also derived.

Analogous measurements have been made on the complexes [IrX$_3$(CO)L$_2$], where X = Cl, Br, or I, L = PMe$_2$Ph, AsMe$_2$Ph, obtaining[171] similar results.

The cis configuration of the complexes PtX$_2$(CO)PR$_3$ (where X = Cl, Br, or I and R = alkyl or aryl group), obtained by scission of the corresponding dimer (eq 3), has been suggested (μ = 9.1–9.65 D).[172] In the complexes PtCl$_2$(CO)PR$_3$, with PR$_3$ = Ph$_3$P, (C$_6$H$_{11}$)(C$_6$H$_5$)$_2$P, (C$_6$H$_{11}$)$_2$(C$_6$H$_5$)P, the carbonyl stretching frequency of the (C$_6$H$_5$)$_3$P complex is highest and that of the (C$_6$H$_{11}$)$_3$P complex is lowest. Presumably, the less basic (C$_6$H$_5$)$_3$P competes most effectively for the metal d electrons, thus reducing donation of metal d electrons into the antibonding orbitals of carbon monoxide.



(3)

V. Sandwich Complexes and Related Molecules

The structures of the parent molecules have been known for a long time.[173] In the period covered here few dipole moment studies have been carried out on the derivatives; most refer to ferrocene.

A. Iron and Chromium Complexes

A thorough discussion of the present position for various (benzene)-, (thiophene)-, and other (arene)chromium tricarbonyl compounds has appeared.[174,175] The vector analysis of the observed moments reveals that the arene–Cr(CO)$_3$ group moment depends on the nature of the arene substituent in a precise manner. An almost monotonic relationship has been found between increase in the ligand–metal bond moment (excluding the contribution of the substituent) compared to that of the unsubstituted complex and the carbonyl stretching frequency. This is explained by the fact that the bigger this increase the greater the charge transfer from the ligand to the metal and, consequently, the metal d$_\pi$ → CO π^* electron donation must be higher. Conformationally it has been found that for the tricarbonyl(aniline)chromium [and tricarbonyl(*p*-phenylenediamine)chromium] complex a conformer with the two hydrogen atoms pointing toward the center of the molecule (in the eclipsed form **27**) is present.

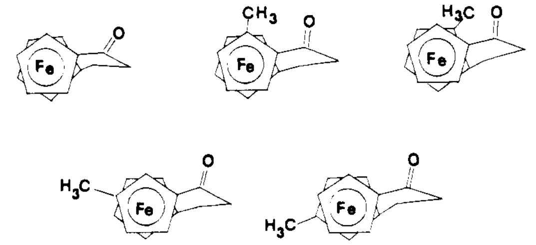
eclipsed staggered

27

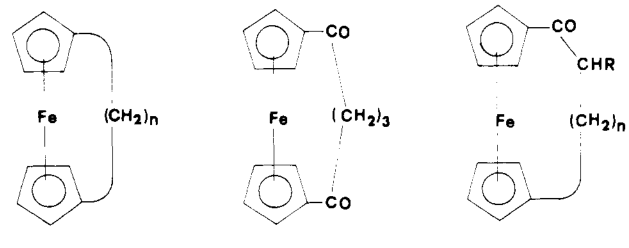
Dipole moments and CO stretching frequencies suggest that, for unsubstituted (arene)tricarbonylchromium complexes LCr(CO)$_3$, with L = diphenyl, fluorene, and *cis*-stilbene, the π basicity to be considered is that of the ring directly united to the metal and not that of the arene as a whole. In general the substituent effect in para-substituted diphenyltricarbonylchromium complexes (L = 4-methyl-, 4-amino-, and 4,4′-dimethyldiphenyl), in which the tricarbonylchromium group is bonded to the substituted phenyl ring, is markedly weaker than that in the corresponding (benzene)tricarbonylchromium complexes.

2-Ferrocenylmethylene-1,3-indandione has a moment of 2.03 D,[176] to be compared to 1.17 for 2-benzylidene-1,3-indandione.[177] In agreement with this the two carbonyl stretching frequencies show a significant shift ($\Delta\nu_1$ = −12 and $\Delta\nu_2$ = −13 cm^{-1} in CH$_2$Cl$_2$; $\Delta\nu_1$ = −7 and $\Delta\nu_2$ = −8 cm^{-1} in CCl$_4$) when compared with 2-benzylidene-1,3-indandione. This evidence led to the suggestion that in the former compound there is a contribution of extreme polar forms having negative charge on the oxygen.

The temperature dependence of the NMR spectra and the dipole moments as well as the circular dichroism[178] of the "ferrocene band" indicate that in [3]ferrocenophanes (**28**) the methyl in the α position determines the configuration of the bridge between the two cyclopentadienyl rings while that in the β has no influence. Consequently the activation energy of the inversion decreases in the same order. The conformational aspects of many bridged and nonbridged ferrocene derivatives, **29**, have been examined by other authors.[179] The interesting results obtained for the bridged complexes cannot be summarized briefly. As concerns nonbridged complexes, a comparison between the moments of benzene derivatives and those of the corresponding ferrocene derivatives shows that, with the exception of acetyl- and benzoylferrocenes, the ferrocenyl compounds are more basic. Acetyl- and benzoylferrocenes (1,1′ diderivatives) may exist in two conformational situations, meso



28



29

(**30a**) and racemic (**30b**).[180] Since the dipole moments of these compounds are compatible with the moment of the racemic bis(1,2)(1′,2′)-(α-ketotetramethylene)ferrocene and not with the corresponding meso isomer, it was inferred that 1,1′-diacylferrocenes exist mainly in *d* and *l* configuration. The potential energy barrier to internal ring rotation was calculated to be highest for the meso structure.

a, meso **30** b, racemic

The problem of the presence or otherwise of the internal rotation of ferrocene, about which contrasting opinions exist,[181–186] has been explored closely by means of the examination of the behavior of some 1,1′-dihalo derivatives (halogen = Cl, Br, or I) in apolar solvents.[180,187–189] Measurements of the dielectric constant for a wide temperature range have shown clearly that, in benzene and in *n*-decane, the internal rotation of the cyclopentadienyl rings is restricted. This suggests that in the parent molecule the internal rotation is completely free. From the point of view of the energy barrier to internal rotation, the moment values at the various temperatures have been treated in two ways, assuming that (i) the interaction between the two rings takes place through the carbon and hydrogen atoms and (ii) that the only existing interaction takes place through the two halogens. The values of the potential energy for the rotation and their trend have shown that the real situation, in polar solvent, lies somewhere between the two shown in the calculation, i.e. (i) and (ii).[189]

B. Complexes of Other Metals

Several complexes of the type $(\pi\text{-}C_5H_5)_2MX_2$ (M = Ti or Zr, X = NCS, OCN, or Cl) have been studied in various solvents.[190] The dipole moments show that $\mu[(\pi\text{-}C_5H_5)_2Ti(NCS)_2]/\mu[(\pi\text{-}C_5H_5)_2TiCl_2] = \mu[(\pi\text{-}C_5H_5)_2Zr(NCS)_2]/\mu[(\pi\text{-}C_5H_5)_2ZrCl_2$, suggesting that the titanocene and zirconocene complexes have the same structure and bond type of thiocyanate ion. IR measurements[190,191] show that the NCS groups bond via the nitrogen atom. On the other hand, it is found that $\mu[(\pi\text{-}C_5H_5)_2Ti(OCN)_2]/\mu[(\pi\text{-}C_5H_5)_2TiCl_2 \neq \mu[(\pi\text{-}C_5H_5)_2Zr(OCN)_2]/\mu[(\pi\text{-}C_5H_5)_2ZrCl_2]$. This may indicate that the structure of the complexes and/or the bonding of the cyanate ion are different in titanocene and zirconocene. These results together with those obtained from IR measurements may indicate that titanocene cyanate most likely contains N-bonded groups, whereas those in the zirconocene cyanate are most likely O-bonded. The high dipole moment of the complexes $(C_5H_5)_2TiCl_2$ (6.25 ± 0.39 D in benzene[192] and 5.8 ± 0.3, in dioxane[190]), $(C_5H_5)_2ZrCl_2$ (5.90 ± 0.38, in benzene[192] and 4.87–4.93 ± 0.03, in benzene[193]), and $(C_5H_5)_2HgCl_2$ (4.66 ± 0.03, in benzene[193]) makes it possible to conclude that these compounds have a tetrahedral configuration, with an angular arrangement of the cyclopentadienyl rings, connected by a "central" σ bond.[192,193] Such a structure has been suggested also on the basis of the electron-diffraction measurements.[194,195]

The (C_5H_5)–Ti bond moment in $(C_5H_5)_2TiCl_2$ (3.1–3.2 D) and in $(C_5H_5)TiCl_3$ (2.8–2.9 D) has been calculated[196] from the observed dipole moments of $(C_5H_5)_2TiCl_2$ (6.1 D), $(C_5H_5)TiCl_3$ (4.31 D), and $(C_5H_5)_2TiCl$ (4.23 D), and it has been deduced that $(C_5H_5)_2TiCl$ does not form a centrosymmetric association in benzene solution.

The problem regarding the kind of bond existing in these types of complexes has been tackled by studying tetracyclopentadienylzirconium and -hafnium complexes.[193] For these compounds, on the basis of the NMR and IR spectra it was impossible to establish the configuration unequivocally.[197] In fact, the presence in the NMR spectra of a sharp singlet of the protons is in agreement with the assumption of a highly symmetrical structure, with four equivalent rings. On the contrary, IR spectra show a greater number of bands than is required for this configuration. The high values of the dipole moment (3.41–3.79 D) indicate asymmetric structures and agree with results obtained for the zirconium derivative from X-ray measurements.[197] On the basis of the structural parameters we are led to believe that three cyclopentadienyl rings are connected to the metal by a normal σ bond.

Still on the subject of this kind of molecule, the NMR and ESR spectra suggest[198] that, in the $(C_5H_5)V(C_7H_7)$ complex, the carbon atoms in the pentatomic ring are more negatively charged than those in the heptatomic one. This is in agreement with the fact that the metallation takes place predominantly in the pentatomic ring.[199] The same is true for the corresponding chromium compound, even though the reaction is more difficult,[200] while with the titanium derivative the metallation is again quick but takes place in the heptatomic ring. On the basis of dipole moments (1.6 ± 0.1, 1.2, and 1.0 D, respectively, for the titanium, vanadium, and chromium derivatives)[201] we can establish that the behavior of these complexes is a consequence of the fact that the negative charge on the carbon atoms in the heptatomic ring increases in the order Cr < V < Ti. Finally, concerning the true precise structure of these molecules, the moment values, which would have been extremely useful, cannot be used because of their uncertainty due to the fact that the atomic polarization has not been taken into account. The effect of this contribution can, in fact, be critical for such low moments.

VI. Unclassifiable Complexes

This section reports results on some less easily classifiable complexes. Many of these are recognizable in their similarity to the charge-transfer complexes (see section III on the molecular adducts) since they produce donor–acceptor type bonds. We have put them in a separate section because they have been studied differently.

The classification is made according to the central element. Unfortunately, because of the paucity of information available, it is not possible to have details of the characteristics of the various groups of the periodic table, as we should have wished.

A. Compounds with Group 2B Elements

The dipole moments of the complexes of type $MX_2 \cdot 2$pyridine, where M = Zn and X = Cl, M = Cd and X = I, in benzene and dioxane have values in the range 8.4–9.2 D, consistent with both a tetrahedral and cis-square-planar structure.[202,203] There is evidence (X-ray structure and diamagnetic character of the complex in the solid state)[204–206] that indicates that the zinc complex is monomeric and that the bonds around the central atom have an almost tetrahedral arrangement. The closeness of the moments of the zinc and cadmium derivatives suggests the same configuration for the latter compound too. On this the results of vibrational spectra[207] and dielectric polarization measurements are in agreement.[208,209] In these two complexes, measurements of the Kerr constant show that the two pyridine rings are parallel to each other and assume an equal spatial arrangement, where φ = 51–60° (φ = 0° for the structure having the two C_5N rings coplanar).

A tetrahedral structure can be suggested from the moments even for the analogous complexes (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)cadmium(II) iodide, CdI_2TMED,[203] and $ZnCl_2 \cdot L_2$,

TABLE IV. Observed Moments[a] and Inferred Configurations of Some Organotin(IV) Complexes

complex	μ	X group	co-ord no.	arrang of X	ref
$X_2Sn(NCS)_2$	6.2	Bu	4	tetrah	212
$X_2Sn(NCS)_2$	5	Ph	4	tetrah	212
$X_2Sn(NCS)_2$(bpy)[b]	13.3	Bu	6	trans	212
$X_2Sn(NCS)_2$(bpy)	7.2	Ph	6	cis	212
$X_2Sn(NCS)_2$(*o*-phen)	15.0	Bu	6	trans	212
$X_2Sn(NCS)_2$(*o*-phen)	6	Ph	6	cis	212
$X_2Sn(NCS)_2$(*o*-phen)	6	NCS	6	trans	212
$X_2Sn(NCS)(Ox)$	7.8	Bu	5	cis	212
$X_2Sn(NCS)(Ox)$	6.20	Ph	5	cis	212
$X_2SnCl(Ox)$	4.76	Ph	5	cis	212
$X_2Sn(Ox)_2$	5.48	Ph	6	cis	212
$X_2Sn(Ox)_2$	4.63	Bu	6	cis	212
$BuSnX_3$(bpy)	10.2	NCS	6	trans	213
$PhSnX_3$(bpy)	10.0	NCS	6	trans	213
$BuSnX_3$(*o*-phen)	10.1	NCS	6	trans	213
$PhSnX_3$(*o*-phen)	8.9	NCS	6	trans	213
$BuSn(NCS)(Ox)_2$	9.1		6		213
$PhSn(NCS)(Ox)_2$	8.4		6		213
$BuSnCl(Ox)_2$	7.69		6		213
$PhSnCl(Ox)_2$	7.4		6		213
$BuSnCl_3$(bpy)	9.8		6		213
$BuSnCl(2\text{-}SpyO)_2$	7.63		6		213
$BuSnCl(2\text{-}SpyO)_2$	5.0		6		213
$BuSnCl(2\text{-}SpyO)_2$	5.0		6		213
$PhSnCl(2\text{-}SpyO)_2$	7.49		6		213
$Bu_2SnCl_2(Bu_3PO)_2$	>11.9	Bu	6	trans	214
$Bu_2SnCl_2(Ph_3PO)_2$	>11.0	Cl	6	cis	214
$Bu_2SnCl_2(Ph_3AsO)_2$	>12.5	O	6	cis	214
$Bu_2Sn(NCS)_2(Ph_3AsO)_2$	7.4	all ligands	6	trans	215
$Bu_2Sn(NCS)_2(Bu_3PO)_2$	7.4	all ligands	6	trans	215
$Ph_2Sn(NCS)_2(Ph_3AsO)_2$	5.8	all ligands	6	trans	215
$Ph_2Sn(NCS)_2(Bu_3PO)_2$	6.0	all ligands	6	trans	215

[a] In benzene, determined by means of Higasi method;[211] μ in D. [b] Bpy = α,α'-bipyridyl; *o*-phen = *o*-phenanthroline; Ox = oxinate; 2-SpyO = 2-pyridinethiol 1-oxide.

with L a substituted phenylhydrazine.[210]

B. Compounds with Group 4A Elements

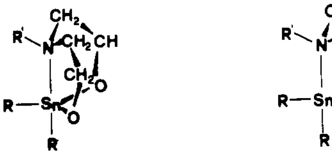
Tetra-, penta-, and hexacoordinated tin complexes have been studied thoroughly from the point of view of the configuration[211-221] in solution and in the solid state. Regarding the results obtained from dielectric measurements, in Table IV we have a drawing of the main molecules and the structure deduced from the observed dipole moments. We must state in advance that in solution the NCS ligand is monodentate and utilizes a lone pair of the sulfur and not of the nitrogen to bond to the central atom, as can be deduced by the absence of the CN stretching vibration band in the region 2005–2035 cm^{-1}.

From Table IV we can see, apart from the NCS ligands that are always in a trans arrangement, that the other ligands assume a relative position depending on their nature and that of the other ligands present. We notice that the complexes between $R_2Sn(NCS)_2$ and the *o*-phenanthroline or 2,2′-dipyridyl reveal a change from trans C–Sn–C bonds in dibutyl compounds to cis C–Sn–C bonds in divinyl and diphenyl compounds; on the contrary, the corresponding R_2SnCl_2 complexes are all trans.

From the moments of the complexes Bu_2SnCl_2(*o*-phen) (11.3 D),[216] Bu_2SnCl_2 (4.37 D),[216] and $Bu_2Sn(NCS)_2$ (6.2 D)[212] we can calculate a moment of 13.5 D for the complex $Bu_2Sn(NCS)$(*o*-phen) whose observed moment is 15.0 D. The difference between the observed and calculated moment can be mainly due to an increased $N^+{\equiv}CS^-$ character for the isothiocyanate group in the octahedral structure with respect to the tetrahedral one.

Regarding the pentacoordinated complexes R_2SnXOx (Ox = oxinate), the theoretical moments, calculated from the group and bond moments, are consistent with trigonal-bipyramidal structures with the R groups cis to each other. The NMR, IR, and UV results,[216-219] not in agreement with this, are unanimously interpreted in favor of a bipyramidal structure but with the groups trans to each other. Against this interpretation it could be affirmed that, in the case of R trans to each other, the angle of the chelate ring (74°)[200] would allow a large distortion of the bipyramidal configuration.

In the hexacoordinated tin complexes the compounds[221] $R_2SnX(OC_2H_4)_2$ and $R_2SnX(SC_2H_4)_2$, in which X = NH, NMe, NEt, NPh, have been studied. The NMR spectra and the dipole moments (2.56–4.16 D) are consistent with octahedral structures **31**, chosen from various theoretical ones.



31

C. Compounds with Group 8 Elements

A zero moment[222] in benzene indicates unequivocally a symmetric trigonal-bipyramidal structure for the complex $RuCl_3(AsPh_3)_2$, with three chlorine atoms in the equatorial plane and two triphenylarsine ligands along the *z* axis, in a trans position to each other. Such a structure had been found from the same evidence for the complex $CoCl_3(PEt_3)_2$. Trigonal-bipyramidal structures are common for electronic configurations d^0, d^8, and d^{10} and quite rare for configurations d^5, which is the one present.[224]

Ruthenium also forms many hexacoordinated, neutral and monomeric complexes with tertiary phosphines and arsines.[225-230] Among these the dipole moments for the three complexes $RuCl_3(AsPh_3)_2(py)$ (7.54 D), $RuCl_3(AsPh_3)(py)_2$ ((7.69 D), and $RuCl_3(AsPh_3)$(bipy) (7.6 D) have been determined.[231] If we compare these moments with those found for similar molecules, whose structures have been verified,[225,229,232-234] we can suggest the following octahedral configurations. In the first complex the chloride groups are mer with a trans arrangement of the arsine groups. In the other two compounds a mer arrangement of the chlorine atoms and a cis arrangement of the pyridine rings are again observed.

The same problem of the relative arrangement of the ligands in the ambit of the hexacoordinated and tetracoordinated structure has been tackled with the complexes of rhodium, iridium,[235] palladium, and platinum.[236] The structure of rhodium and iridium derivatives[235] $MCl_3(SEt_2)_3$ may be derived in the following way. If we assume that the partial moments Cl–M–SEt_2 (M = Rh or Ir) and Cl–Pt–SEt_2 are of the same order, taking the value 9.5 D for the complex[237] *cis*-$PtCl_2(SEt_2)_2$, we arrive, via a simple vector calculation, at the values 6.7 and 11.6 D, respectively, for the mer and fac isomers of the two complexes in question. Now, since there have been observed moments of 5.1–5.2 D, we deduce that they have a mer-type configuration. This structure is also suggested for the complex $RhCl_3(SMe_2)_3$, whose observed moment is 4.72 D. The quality of the results obtained is also shown from indirect proofs. In fact the complexes $RhCl_3(SEt_2)_3$ and $IrCl_3(SEt_2)_3$ are isomorphous[238] to each other and structurally very similar to a $RuCl_3(SEt_2)_3$, for which a mer configuration was suggested from ESR measurements.[239] The other, more valid, evidence has been obtained from ^1H NMR spectra.[235] Fac isomers of complexes of this type have three equivalent dialkyl sulfide molecules while the mer isomers present these ligands in two different environments; more precisely, two equivalents in a trans position to each other and a third trans with respect to the chlorine atom. Less univocal is the proof of the IR spectra of these molecules at low frequency (400–90

cm^{-1}). Group theory indicates that in MX_3L_2 complexes (X = halogen; L = ligand) three normal modes involving metal-halogen stretching would be expected to be active for the mer configuration, and only two for the fac configuration. Now, rhodium mer isomers generally show[240] three such modes while the mer isomers of iridium have two rather than the expected three bands. Consequently, for the iridium complexes it is often not possible to distinguish between mer and fac isomers on the basis of the number of the metal-halogen stretching vibrations.

For the tetracoordinated complexes of palladium and platinum[236] [$MX_2(TeEt_2)_2$, where X = Cl, Br, or I] having moments of 1.8-1.9 D, the problem consists in seeing whether the structure is cis and/or trans in solution. Since the situation, from this point of view, is not very clear, it is useful to cite other results. So ^1H NMR spectra show the presence of only one isomer in solution for all complexes except $PtBr_2(TeEt_2)_2$ for which a second, very short-lived, isomer is evident. In phenyl chloride Raman spectra are in agreement with a trans configuration. In the solid state, IR spectra suggest the presence of a trans isomer for the complexes $PtI_2(TeEt_2)_2$, $PdBr_2(TeEt_2)_2$, and $PdI_2(TeEt_2)_2$ and a cis for the other three. Gathering together all this evidence, the only satisfactory situation seems to be a trans structure which, as shown by the nonzero dipole moments, must be partly distorted.

Acknowledgments. We are indebted to Consiglio Nazionale delle Ricerche, Rome, for financial support. We also acknowledge the precious collaboration of Mrs. M. R. Trubbianelli and Mr. M. Cesari in preparing the manuscript and the drawings.

VII. References

(1) Osipov, O. A.; Garnovskii, A. D.; Minkin, V. I. *Zh. Strukt. Khim.* **1967**, *8*, 913.
Garnovskii, A. D.; Osipov, O. A.; Minkin, V. I. *Russ. Chem. Rev.* **1968**, *37*, 763.
(3) Böttcher, C. J. F. "Theory of Electric Polarization"; Elsevier: London, 1952.
(4) Le Fèvre, R. J. W. "Dipole Moments"; Methuen: London, 1953.
(5) Smith. J. "Electric Dipole Moments"; Butterworth: London, 1955.
(6) Smyth, C. P. "Dielectric Behaviour and Structure"; McGraw-Hill: New York, 1955.
(7) Davies, M. "Some Electrical and Optical Aspects of Molecular Behaviour"; Pergamon: Oxford, 1965.
(8) Minkin, V. I.; Osipov, O. A.; Zhdanov, Yu. A. "Dipole Moments in Organic Chemistry"; Plenum: New York, 1970.
(9) McClellan, A. L. "Tables of Experimental Dipole Moments"; W. H. Freeman: San Francisco and London, 1963.
(10) Garnovskii, A. D.; Osipov, O. A.; Minkin, V. I. "Spravochnik po Dipol'nym Momentam (Reference Book on Dipole Moments)"; Izv. Vysshaya Shkola: Moscow, 1971.
(11) McClellan, A. L. "Tables of Experimental Dipole Moments"; Rahara Enterprises: El Cerrito, CA, 1974; Vol. 2.
(12) Moody, G. J.; Thomas, J. D. R. "Dipole Moments in Inorganic Chemistry"; Arnold: London, 1971.
(13) Osipov, O. A.; Garnovskii, A. D.; Minkin, V. I. "Dipol'nye Momenty v Khimii Kompleksnykh Soedinii"; Izv. Rostov University: Rostov-on-Don, USSR, 1976.
(14) De Brouckère, G. *Adv. Chem. Phys.* **1978**, *37*, 203.
(15) Kogan, V. A.; Osipov, O. A.; Shcherbak, S. N.; Zhuchenko, T. A. *Zh. Obshch. Khim.* **1968**, *38*, 1607.
(16) Kogan, V. A.; Shcherbak, S. N.; Osipov, O. A. *Zh. Obshch. Khim.* **1971**, *41*, 165.
(17) Kogan, V. A.; Osipov, O. A.; Shcherbak, S. N. *Dokl. Akad. Nauk SSSR* **1971**, *199*, 384.
(18) Kogan, V. A.; Shcherbak, S. N.; Osipov, O. A. *Zh. Obshch. Khim.* **1971**, *41*, 382.
(19) Sacconi, L.; Ciampolini, M.; Speroni, G. P. *Inorg. Chem.* **1965**, *4*, 1116.
(20) Kogan, V. A.; Kochin, S. G. *Zh. Strukt. Khim.* **1969**, *10*, 340.
(21) Tumakova, Zh. A.; Minkin, V. I.; Osipov, O. A. *Zh. Obshch. Khim.* **1969**, *39*, 1387.
(22) Kurbatov, V. P.; Osipov, O. A.; Kovalenko, K. N.; Tikhonova, A. S. *Russ. J. Inorg. Chem.* **1968**, *13*, 404.
(23) Kurbatov, V. P.; Osipov, O. A.; Kovalenko, K. N. *Russ. J. Inorg. Chem.* **1968**, *13*, 228.
(24) Kurbatov, V. P.; Osipov, O. A.; Kovalenko, K. N. *Zh. Obshch. Khim.* **1968**, *38*, 2194.
(25) Angel, R. L.; Hayes, J. W.; Radford, D. V. *J. Chem. Soc., Faraday Trans. 2*, **1975**, 81.
(26) Garnovskii, A. D.; Minkina, L. S.; Sakhashchik, L. V.; Kurbatov, V. P.; Osipov, O. A. *Zh. Obshch. Khim.* **1971**, *41*, 1884.
(27) Osipov, O. A.; Minkina, L. S.; Garnovskii, A. D.; Kvitko, I. Ya.; Kurbatov, V. P.; Sof'ina, E. M. *Zh. Obshch. Khim.* **1972**, *42*, 926.
(28) Minkina, L S.; Lin'kova, V. P.; Kurbatov, V. P.; Osipov, O. A. *Zh. Obshch. Khim.* **1973**, *43*, 1819.
(29) Kogan, V. A.; Lempert, L. E.; Osipov, O. A.; Nemirov, G. V.; Nyrkova, A. N. *Russ. J. Phys. Chem.* **1969**, *43*, 21.
(30) Dodge, R. P.; Templeton, D. H.; Zalkin, A. *J. Chem. Phys.* **1961**, *35*, 55.
(31) Garnovskii, A. D.; Osipov, O. A.; Minkin, V. I.; Orlova, L. D.; Kuznetsova, L. I. *Dokl. Akad. Nauk SSSR* **1968**, *178*, 598.
(32) Garnovskii, A. D.; Orlova, L. V.; Osipov, O. A.; Minkin, V. I.; Kukushkina, I. I. *Zh. Obshch. Khim.* **1968**, *38*, 1845.
(33) Orlova, L. V.; Garnovskii, A. D.; Osipov, O. A.; Minkin, V. I. *Zh. Obshch. Khim.* **1968**, *38*, 1167.
(34) Garnovskii, A. D.; Bednyagina, N. P.; Kuznetsova, L. I.; Panyushkin, V. T.; Osipov, O. A.; Ogloblina, R. I.; Novikova, A. P. *Russ. J. Inorg. Chem.* **1969**, *14*, 924.
(35) Garnovskii, A. D.; Osipov, O. A.; Bednyagina, N. P.; Kuznetsova, L. I.; Kostromina, A. S.; Kurbatov, V. P.; Panyushkin, V. T.; Ogloblina, R. J.; Serebryakova, N. V. *Dokl. Akad. Nauk SSSR* **1969**, *184*, 1132.
(36) Bailar, J. C.; Bush, D. H., Eds. "The Chemistry of Coordination Compounds"; Reinhold: New York, 1956.
(37) Nyholm, R. S. *Usp. Khim.* **1963**, *32*, 354.
(38) Osipov, O. A.; Garnovskii, A. D.; Minkin, V. I. *Zh. Strukt. Khim.* **1968**, *8*, 913.
(39) Minkin, V. I.; Osipov, O. A.; Verkhodova, D. Sh. *Zh. Neveg. Khim.* **1966**, *11*, 2829.
(40) Osipov, O. A.; Minkin, V. I. In "Proceedings of the 9th International Conference on Coordination Chemistry", St. Moritz-Bad; Schneider, W., Ed.; Verlag Helv. Chim. Acta: Basle, 1966, 521.
(41) Holm, R. H.; Chakravorty, A.; Theriat, L. J. *Inorg. Chem.* **1966**, *5*, 625.
(42) Verkhodova, D. Sh.; Osipov, O. A.; Minkin, V. I. *Russ. J. Inorg. Chem.* **1969**, *14*, 494.
(43) Moore, C. Z.; Nelson, W. H. *Inorg. Chem.* **1969**, *8*, 143.
(44) Maijs, L. *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* **1973**, *4*, 497; *Chem. Abstr.* **1974**, *80*, 7308s.
(45) Maijs, L. *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* **1976**, *4*, 474; *Chem. Abstr.* **1977**, *86*, 11062y.
(46) Maijs, L.; Vevere, I.; Strauss, I. *Latv. PSR Zinat. Akad. Vestis, Ser. Kim.* **1972**, *4*, 486; *Chem. Abstr.* **1972**, *77*, 158251g.
(47) Maijs, L. *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* **1972**, *2*, 245; *Chem. Abstr.* **1972**, *77*, 40338n.
(48) Maijs, L.; Khvoles, A. R.; Vevere, I. *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* **1974**, *4*, 474; *Chem. Abstr.* **1974**, *81*, 160871k.
(49) Das. M.; Livingstone, S. E. *Inorg. Chim. Acta* **1975**, *14*, 267.
(50) Maijs, L. *Latv. PSR ZINAT. Akad. Vestis, Kim. Ser.* **1973**, *4*, 498; *Chem. Abstr.* **1974**, *80*, 7310m.
(51) DiCarlo, E. N.; Logan, T. P.; Stronski, R. E. *J. Phys. Chem.* **1968**, *72*, 1517.
(52) Nelson, R. D., Jr.; White. C. E. *J. Chem. Phys.* **1969**, *73*, 3439.
(53) Le Fèvre, R. J. W.; Radford, D. V.; Saxby, J. D. *Inorg. Chem.* **1969**, *8*, 1533.
(54) Balaban, A. T.; Bally, Iana; Minkin, V. I.; Usachev, A. I. *Tetrahedron* **1977**, *33*, 3265.
(55) Moore, C. Z.; Nelson, W. H. *Inorg. Chem.* **1969**, *8*, 138.
(56) Serpone, N.; Fay, R. C. *Inorg. Chem.* **1969**, *8*, 2379.
(57) Hayes, J. W.; Nelson, W. H.; Radford, D. V. *Aust. J. Chem.* **1973**, *26*, 871.
(58) Courrier, W. D.; Lock, C. J. L.; Turner G. *Can. J. Chem.* **1972**, *50*, 1797.
(59) Nelson, W. H.; Aroney, M. J. *Inorg. Chem.* **1973**, *12*, 132.
(60) Eddy, L. P.; Hayes, J. W.; Livingstone, S. E.; Nigam, H. L.; Radford, D. V. *Aust. J. Chem.* **1971**, *24*, 1071.
(61) Das, M.; Livingstone, S. E.; Filipczuk, S. W.; Hayes, J. W.; Radford, D. V. *J. Chem. Soc., Dalton Trans.* **1974**, 1409.
(62) Das, M.; Livingstone, S. E. *J. Chem. Soc., Dalton Trans.* **1975**, 452.
(63) Filipczuk, S. W.; Hayes, J. W.; Radford, D. V.; Das, M.; Livingstone, S. E. *J. Chem. Soc., Dalton Trans.* **1975**, 886.
(64) Das, M.; Livingstone, S. E.; Mayfield, J. H.; Moore, D. S.; Saha, N. *Aust. J. Chem.* **1976**, *29*, 767.
(65) Das, M.; Livingstone, S. E.; *J. Chem. Soc., Dalton Trans.* **1977**, 662.
(66) Livingstone, S. E.; Oluka, J. E. *Aust. J. Chem.* **1976**, *29*, 1913.
(67) Shugan, E. A.; Shokol'nikova, L. M.; Livingstone, S. E. *Zh. Strukt. Khim.* **1967**, *8*, 550.
(68) Kutschabsky, L.; Beyer, L. *Z. Chem.* **1971**, *11*, 30.
(69) Sieler, J.; Thomas, P.; Uhlemann, E.; Höme, E. *Z. Anorg. Chem.* **1971**, *380*, 160.
(70) Siiman, O.; Titres, D. D.; Cowman, C. D.; Fresco, J.; Gray, H. B. *J. Am. Chem. Soc.* **1974**, *96*, 283.
(71) Craig, D. C.; Das, M.; Livingstone, S. E.; Stephenson, N. C. *Cryst. Struct. Commun.* **1974**, *3*, 2353.
(72) Ollis, J.; Das, M.; James, V. J.; Livingstone, S. E.; Nimgirawath, K. *Cryst. Struct. Commun.* **1976**, *5*, 679.
(73) Hoskins, B. F.; Pannan, C. D. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 409.
(74) Hoskins, B. F.; Pannan, C. D. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 405.
(75) Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712.
(76) DeStefano, N. J.; Burmeister, J. *Inorg. Chem.* **1971**, *10*, 998.
(77) Jorgensen, C. K. *Inorg. Chem.* **1964**, *3*, 1201.
(78) Holm, R. H. *Prog. Inorg. Chem.* **1972**, *14*, 241.
(79) Gordon, J. S.; O'Connor, M. J.; Holm, R. H. *Inorg. Chim. Acta* **1971**, *5*, 381.
(80) Livingstone, S. E. *Coord. Chem. Rev.* **1971**, *7*, 59.
(81) Dasgupta, S.; Smyth, C. P. *J. Am. Chem. Soc.* **1967**, *89*, 5532.
(82) DiCarlo, E. N.; Stronski, R. E.; Varga, C. E. *J. Phys. Chem.* **1969**, *73*, 3433.
(83) Haigh, J.; Sutton, L. E. *Chem. Commun.* **1970**, 296.
(84) DiCarlo, E. N.; Watson, E., Jr.; Varga, C. E.; Chamberlain, W. J. *J. Chem. Phys.* **1973**, *77*, 1073.

(85) Hayes, J. W.; Le Fèvre, R. J. W.; Radford, D. V. *Inorg. Chem.* **1970**, *9*, 400.

(86) Gur'yanova, E. N.; Syutkina, O. P.; Panov, E. M.; Kocheshkov, K. A. *Zh. Obshch. Khim.* **1974**, *44*, 1974.

(87) Zhdanov, Yu. A.; Osipov, O. A.; Grigor'ev, V. P.; Garnovski, A. D.; Alekseev, Yu. E.; Gontmakher, N. M.; Alekseeva, V. G.; Yusman, T. A.; Zaletov, V. G.; et al. *Koord. Khim.* **1977**, *3*, 3; *Chem. Abstr.* **1977**, *86*, 140356w.

(88) Akishin, P. A.; Spiridinov, V. P. *Kristallografiya*, **1957**, *2*, 475.

(89) Bonnet, P. *J. Chim. Phys. Phys.-Chim. Biol.* **1968**, *65*, 1701.

(90) Bonnet, P.; Barriol, J. *J. Chim. Phys. Phys.-Chim. Biol.* **1971**, *68*, 1703.

(91) Buchler, A.; Stauffer, J. L.; Klemperer, W. *J. Chem. Phys.* **1964**, *40*, 3471.

(92) (a) Reger A.; Eliezer, I. *J. Chem. Phys.* **1971**, *54*, 3902; (b) Braume, H.; Linke, R. *Z. Phys. Chem.* **1935**, B31, 13.

(93) Le fèvre, R. J. W.; Radford, D. V.; Ritchie, G. L. D.; Saxby, J. D. *Aust. J. Chem.* **1966**, *19*, 1615.

(94) Odom, J. D.; Barnes, J. A.; Hudgens, B. A.; During, J. R. *J. Phys. Chem.* **1974**, *78*, 1503.

(95) Cassoux, P.; Kuczkowski, R. L.; Bryan, P. S.; Taylor, R. C. *Inorg. Chem.* **1975**, *14*, 126.

(96) Akerfeldt, S.; Wahlberg, K.; Hellström, M. *Acta Chem. Scand.* **1969**, *23*, 115.

(97) During, J. R.; Hudgens, B. A.; Li, Y. S.; Odom, J. D. *J. Chem. Phys.* **1974**, *61*, 4890.

(98) Romm, I. P.; Gur'yanova, E. N. *Zh. Obshch. Khim.* **1968**, *38*, 1927.

(99) Romm, I. P.; Gur'yanova, E. N.; Kocheshkov, K. A. *Tetrahedron* **1969**, *25*, 2455.

(100) Romm, I, P.; Kharlamova, E. N.; Gur'yanova, E. N. *Zh. Obshch. Khim.* **1973**, *43*, 891.

(101) Romm, I. P.; Shakhgel'diev, M. A.; Gur'yanova, E. N. *Zh. Obshch. Khim.* **1977**, *47*, 975.

(102) Ganyushin, L. A.; Gur'yanova, E. N.; Romm, I. P. *Zh. Obshch. Khim.* **1978**, *48*, 2478.

(103) Romm, I. P.; Sadykova, E. M.; Gur'yanova, E. N., Kolli, I. D. *Zh. Obshch. Khim.* **1973**, *43*, 728.

(104) Romm, I. P.; Belen'kii, L. I.; Gur'yanova, E. N.; Tovbin, Yu. K. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, *11*, 2478.

(105) Orlova, L. N.; Suvotov, B. A.; Zetkin, V. I. *Zh. Strukt. Khim.* **1976**, *17*, 389.

(106) Puchkova, V. V.; Gur'yanova, E. N.; Laba, V. I.; Prilezhawa, E. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1973**, *5*, 1156.

(107) Starowieyski, K. B.; Pasynkiewicz, S.; Sporzynski, A. *J. Organomet. Chem.* **1976**, *117*, 117.

(108) Armstrong, R. S.; Aroney, M. J.; Hector, A.; Le Fèvre, R. J. W. *J. Chem. Soc. B* **1968**, 1203.

(109) Gol'dshtein, I. P.; Gur'yanova, E. N.; Kucheruk, L. V.; Kremer, E. D. *Zh. Obshch. Khim.* **1978**, *48*, 2568.

(110) Romm, I. P.; Galuashvili, Zh. S.; Gur'yanova, E. N. *Zh. Obshch. Khim.* **1976**, *46*, 2445.

(111) Romm, I. P.; Sevast'yanova, T. G.; Gur'yanova, E. N.; Kolli, I. D.; Rodionov, R. A. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1968**, *38*, 1881.

(112) Topchii, V. A.; Borovikov, Yu. Ya. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1969**, *39*, 2627.

(113) Sevast'yanova, T. G.; Romm, I. P.; Gur'yanova, E. N.; Kolli, I. D. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1969**, *39*, 1152.

(114) Topchii, V. A.; Borovikov, Yu. Ya. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1970**, *40*, 1323.

(115) Sanchez, A.; Casas, J. S.; Sordo, J.; Masaguer, J. R. *J. Inorg. Nucl. Chem.* **1978**, *40*, 357.

(116) Gur'yanova, E. M.; Romm, I. P.; Gol'dshtein, I. P. *Zh. Obshch. Khim.* **1969**, *39*, 754.

(117) Masaguer, J. R.; Sanchez, A.; Casas, J. S.; Sordo, J.; Castineiras, A. *J. Inorg. Nucl. Chem.* **1978**, *40*, 355.

(118) Chuchalin, L. K.; Peshchevitskii, B. I.; Kuzin, I. A.; Grankina, Z. A.; Dulepov, E. V. *Zh. Strukt. Khim.* **1968**, *9*, 213.

(119) Galuashvili, Zh. S.; Romm, I. P.; Gur'yanova, E. N.; Korneev, N. N.; Kocheshkov, K. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, *12*, 2713.

(120) Romm, I. P.; Galuashvili, Zh. S.; Gur'yanova, E. N.; Sheverdina, N. I., "Khim. Elementoorg. Soedin."; Danilov, S. N., Ed.; Nauka: Leningrad, USSR, 1976; pp 6–10; *Chem. Abstr.* **1977**, *86*, 29273c.

(121) Galuashvili, Zh. S.; Romm, I. P.; Gur'yanova, E. N., Viktorova, I. M.; Sheverdina, N. I.; Kocheshkov, K. A. *Dokl. Akad. Nauk SSSR* **1972**, *207*, 99.

(122) Bogdanov, V. S.; Baryshnikova, T. K.; Kiselev, V. G.; Mikhailov, B. M. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1971**, *41*, 1537.

(123) Garnovskii, A. D.; Okhlobystin, O. Yu.; Osipov, O. A.; Yunusov, K. M.; Kolodyazhnyi, Yu. V.; Golubinskava, L. M.; Svergun, V. I. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1972**, *42*, 910.

(124) Paul, R. C.; Chadha, S. L. *J. Inorg. Nucl. Chem.* **1969**, *31*, 1679.

(125) Paul, R. C.; Singal, H. R.; Chadha, S. L. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3205.

(126) Paul, R. C.; Chadha, S. L. *J. Inorg. Nucl. Chem.* **1969**, *31*, 1673, 2753.

(127) Paul, R. C.; Chadha, S. L. *Spectrochim. Acta Part A*, **1967**, **23A**, 1243, 1249.

(128) Paul, R. C.; Chadha, S L. *Aust. J. Chem.* **1969**, *22*, 1381.

(129) Lappert, M. F. *J. Chem. Soc.* **1962**, 542.

(130) Beattie, I. R.; Hulme, R.; Rule, L. *J. Chem. Soc.* **1965**, 1581.

(131) Borovikov, Yu. Ya. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1969**, *39*, 1633.

(132) Vasil'eva, V. N.; Yatskovskaya, M. A.; Medvedev, S. S. *Dokl. Akad. Nauk SSSR* **1969**, *187*, 797.

(133) Gol'dshtein, I. P.; Kharlamova, E. N.; Gur'yanova, E. N. *Khim. Seraorg. Soedin., Soderzh. Neftyakh Nefteprod.* **1972**, *9*, 134; *Chem. Abstr.* **1975**, *82*, 90953.

(134) Kolodyazhnyi, Yu. V.; Grishchenko, A. S.; Pushkareva, K. S.; Osipov, O. A. *Zh. Obshch. Khim.* **1972**, *42*, 1351.

(135) Shergina, N. I.; Chipanina, N. N.; Skvorsova, G. G.; Stepanova, Z. V.; Shostakovskii, M. F. *Dokl. Akad. Nauk SSSR* 1969, *184*, 108.

(136) Shcherbakova, E. S.; Gol'dshtein, I. P.; Gur'yanova, E. N.; Peisakhova, M. E.; Aleinikov, V. I.; Gorbanev, A. I. "Fiz-Khim. Issled. Metall. Metalloved. Primen."; Novikev, I. I., Shelest, A. E., Eds., Nauka: Moscow, 1974; pp 59–70.

(137) Kucheruk, L. V.; Gol'dshtein, I. P.; Kuranshin, I. Ya.; Gur'yanova, E. N.; Pudovik, A. N. *J. Gen. Chem. USSR* (*Engl Transl.*) **1977**, *47*, 2179.

(138) Gol'dshtein, I. P.; Galyametdinov, Yu. G.; Gur'yanova, E. N.; Gel'fond, A. S.; Chernokal'skii, B. D.; Kocheshkov, K. A. *Dokl. Akad. Nauk SSSR*, **1976**, *226*, 1076.

(139) Gol'dshtein, I. P.; Smolentsev, A. V.; Gur'yanova, E. N.; Kataeva, L. M. *Zh. Obshch. Khim.* **1977**, *47*, 1199.

(140) Paul, R. C.; Singal, H. R.; Chadha, S. L. *J. Chem. Soc. A*, **1969**, 1849.

(141) Masaguer, J. R.; Castano, M. V.; Casas, J. S.; Bermejo, M. R.; Sordo, J. *Inorg. Chim. Acta* **1976**, *19*, 139.

(142) Levanda, O. G.; Kartsev, G. N.; Ignat'eva, S. I.; Moiseev, I. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, *5*, 1077.

(143) Masaguer, J. R.; Bermejo, M. R. *An. Quim.* **1973**, *69*, 1099.

(144) Aroney, M. J.; Chio, H.; James, J. M.; Le Fèvre, R. J. W.; Pierens, R. K.; Skamp, K. R. *J. Chem. Soc., Dalton Trans.* **1972**, 712.

(145) Aroney, M. J.; Angel, R. L. *Aust. J. Chem.* **1975**, *28*, 1137.

(146) Dichmann, K.; Hamer, G.; Nyburg, S. C.; Reynolds, W. F. *Chem. Commun.* **1970**, 1295.

(147) Gol'dshtein, I. P.; Gur'yanova, E. N.; Volkov, A. F.; Peisakhova, M. E. *J. Gen. Chem. USSR* (*Engl. Transl.*) 1973, *43*, 1655.

(148) Greenwood, N. N.; Straughan, B. P.; Wilson, Anne E. *J. Chem. Soc. A* **1968**, 2209.

(149) Katsaros, N.; George, J. W. *J. Inorg. Nucl. Chem.* **1969**, *31*, 3503.

(150) Peisakhova, M. E.; Gol'dshtein, I. P.; Gur'yanova, E. M.; Shcherbakova, E. S. *Zh. Obshch. Khim.* **1973**, *43*, 159.

(151) Peisakhova, M. E.; Gol'dshtein, I. P.; Gur'yanova, E. N.; Kocheshkov, K. A. *Dokl. Akad. Nauk SSSR* **1972**, *203*, 1316.

(152) Jenkins, J. M.; Moss, J. R.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 2793.

(153) Jenkins, J. M.; Verkade, J. G. *Inorg. Chem.* **1967**, *6*, 2250.

(154) Paiblanc, R.; Bigorgne, M. *Bull. Soc. Chim. Fr.* **1962**, 1301.

(155) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

(156) Adams. D. M. "Metal-Ligand and Related Vibrations"; Edward Arnold: London, 1967; p 97.

(157) Barbeau, C.; Turcotte, J. *Can. J. Chem.* **1970**, *48*, 3583.

(158) Fisher, E. O.; Leupold, M.; Kreiter, C. G.; Müller, J. *Chem. Ber.* **1972**, *105*, 150.

(159) Fisher, E. O.; Kreis, G.; Kreissl, F. R.; Kreiter, C. G.; Müller, J. *Chem. Ber.* **1973**, *106*, 3910.

(160) Maples, P. K.; Kraihanzel, L. S. *J. Am. Chem. Soc.* **1968**, *90*, 6645.

(161) Kahn, O. *Justus Liebigs Ann. Chim.* **1970**, *5*, 75.

(162) Wuyts, L. F.; Van Der Kelen, G. P. *J. Organomet. Chem.* **1975**, *97*, 453.

(163) Kolodyazhnyi, Yu. V.; Skripkin, V. V.; Kolobova, N. E.; Garnovskii, A. D.; Lokshin, B. V.; Osipov, O. A.; Anisimov, K. N.; Gruntfest, M. G. *Zh. Strukt. Khim.* **1972**, *13*, 160.

(164) Sorriso, S.; Distefano, G.; Foffani, A. *J. Organomet. Chem.* **1973**, *47*, 139.

(165) Sorriso, S.; Lumbroso, H. *C. R. Hedb. Seances Acad. Sci., Ser. C*, **1970**, *270*, 1071.

(166) Sorriso, S.; Cardaci, G.; Murgia, S. M *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1972**, *27*, 1316.

(167) Sorriso, S.; Cardaci, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1041.

(168) Sorriso, S.; Cardaci, G. *J. Organomet. Chem.* **1975**, *101*, 107.

(169) Lumbroso, H.; Bertin, D. M. *J. Organomet. Chem.* **1976**, *108*, 111.

(170) John, P. *Chem. Ber.* **1970**, *103*, 2178.

(171) Shaw, B. L.; Smithies, A. C. *J. Chem. Soc. A*, **1968**, 2784.

(172) Smithies, A. C.; Rycheck, M.; Orchin, M. *J. Organomet. Chem.* **1968**, *12*, 199.

(173) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, 1960; pp 385–90.

(174) Lumbroso, H.; Segard, C.; Roques, B. *J. Organomet. Chem.* **1973**, *61*, 249.

(175) Lumbroso, H.; Liegeois, C.; Brown, D. A.; Fitzpatrick, N. J. *J. Organomet. Chem.* **1979**, *165*, 341.

(176) Agramat, I.; Weiler-Feilchenfeld, H.; Loewenstein, R. M. *Israel J. Chem.* **1969**, *7*, 555.

(177) Weiler-Feilchenfeld, H.; Loewenstein, R. M. J.; Agramat, I.; Bergmann, E. D. *Israel. J. Chem.* **1969**, *7*, 99.

(178) Falk, H.; Hofer, O. *Monatsch. Chem.*, **1970**, *101*, 477.

(179) Lumbroso, H.; Pigenet, C.; Lentzner, H. L.; Watts, W. E. *Tetrahedron* **1972**, *28*, 111.

(180) Sorriso, S.; Lumbroso, H. *Tetrahedron* **1970**, *26*, 2695.

(181) Fisher, E. O.; Pfab, W. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1952**, *7*, 377; Eiland, P. F.; Pepinski, R. *J. Am. Chem. Soc.* **1952**, *74*, 4971.

(182) Dunitz, J. D.; Orgel, L. E. *Nature* (*London*) **1953**, *171*, 121. Dunitz, J. D.; Orgel, L. E.; Rich, A. *Acta Crystallogr.* **1956**, *9*, 373.

(183) Haaland, A.; Nilsson, J. E. *Acta Chem. Scand.* **1968**, *22*, 2653.

(184) Seibold, E. A.; Sutton, L. E. *J. Chem. Phys.* **1955**, *23*, 1967.

(185) Akishin, P. A.; Rambidi, N. G.; Bredikhina, T. N. *J. Struct. Chem. USSR* (*Engl. Transl.*) **1961**, *2*, 443.

(186) Bohn, R. K.; Haaland, A. *J. Organomet. Chem.* **1966**, *5*, 470.

(187) Sorriso, S.; Cardaci, G.; Murgia, S. M. *J. Organomet. Chem.* **1972**, *44*, 181.

(188) Sorriso, S. *J. Organomet. Chem.* **1979**, *179*, 205.

(189) Riemschneider, H. *Chem. Ber.* **1956**, *89*, 155.

(190) Jensen, A.; Christiansen, V. H.; Hansen, J. F.; Litowski, T.; Burmeister, J. L. *Acta Chem. Scand.* **1972**, *26*, 2898.

(191) Burmeister, J. L.; Deardorff, E. A.; Jensen, A.; Christiansen, V. H. *Inorg. Chem.* **1970**, *9*, 58.

(192) Giddings, S. A.; Best, R. J. *J. Am. Chem. Soc.* **1961**, *83*, 2393.

(193) Kharlamova, E. N.; Brainina, E. M.; Gur'yanova, E. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 2621.

(194) Alekseev, N. V.; Ronova, I. A. *Zh. Strukt. Khim.* **1966**, *7*, 103.

(195) Ronova, I. A.; Alekseev, N. V.; Struchkov, Yu. T.; Gapotchenko, N. I. *Zh. Strukt. Khim.* **1970**, *11*, 3.

(196) Yakovleva, N. A.; Soloveichik, G. L.; Bulychev, B. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 1409.

(197) Bochvar, D. A.; Gambaryan, N. P.; Brainina, E. M.; Freidlina, R. Kh. *Dokl. Akad. Nauk. SSSR* **1968**, 183, 1324.

(198) Rettig, M. F.; Stout, C. O.; Klug, A.; Farnham, P. *J. Am. Chem. Soc.* **1970**, *92*, 5100.

(199) Groenenboom, C. J.; de Liefde Meijer, H. J.; Jellinek, F. *Recl. Trav. Chim. Pays-Bas*, **1974**, *93*, 6.

(200) Fisher, E. O.; Breitschaft, S. *Chem. Ber.*, **1966**, *99*, 2905.

(201) Groenenboom, C. J.; de Liefde Maijer, H. J.; Jellinek, F. *J. Organomet. Chem.* **1974**, *69*, 235.

(202) Aroney, M. J.; Le Fèvre, R. J. W.; Vaughan, H. J. *J. Chem. Soc. A*, **1970**, 2224.

(203) Armstrong, R. S.; Aroney, M. J.; Filipczuk, S. W.; Pierens, R. K. *J. Mol. Struct.* **1975**, *29*, 117.

(204) Gill, N. S.; Nyholm, R. S.; Barclay, G. A.; Christie, T. I.; Pauling, P. J. *J. Inorg. Nucl. Chem.* **1961**, *18*, 88.

(205) Abraham, M. H.; Parrett, F. W. *Can. J. Chem.* **1970**, *48*, 181.

(206) Htoom, S.; Ladd, M. F. C. *J. Cryst. Mol. Struct.* **1973**, *3*, 95.

(207) Goldstein, M.; Unsworth, W. D. *J. Mol. Struct.* **1972**, *14*, 451.

(208) Schafer, M.; Curran, C. *Inorg. Chem.* **1965**, *4*, 623.

(209) Jain, S. R.; Soundararajan, S. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1255.

(210) Mau-Kuen, L.; Novakovskii, M. S.; Orlov, V. D. *Zh. Strukt. Khim.* **1969**, *10*, 75.

(211) Higashi, K. *Bull. Inst. Phys. Chem. Res.* (*Tokyo*) **1943**, *22*, 805.

(212) Mullins, M. A.; Curran, C. *Inorg. Chem.* **1968**, *7*, 2584.

(213) Mullins, F. P. *Can. J Chem.* **1970**, *48*, 1677.

(214) Mullins, F. P. *Can. J. Chem.* **1971**, *49*, 2719.

(215) Mullins, F. P. Curran, C. *Can. J. Chem.* **1975**, *53*, 3200.

(216) Mullins, M. A.; Curran, C. *Inorg. Chem.* **1967**, *6*, 2017.

(217) Westake, A. H.; Martin, D. F. *J. Inorg. Nucl. Chem.* **1965**, *27*, 1579.

(218) Huber, F.; Kaiser, R. *J. Organomet. Chem.* **1966**, *6*, 126.

(219) Kawakami, K.; Okawara, R. *J. Organomet. Chem.* **1966**, *6*, 249.

(220) Schlemper, E. O. *Inorg. Chem.* **1967**, *6*, 2012.

(221) Tzschach, Von A.; Pönicke, K. *Z. Anorg. Allg. Chem.* **1974**, *404*, 121.

(222) Manoharan, P. T.; Mehrotra, P. K.; Taquikhan, M. M.; Andal, R. K. *Inorg. Chem.* **1973**, *12*, 2753.

(223) Jensen, K. A.; Nygaard, B.; Pedersen, C. J. *Acta Chem. Scand.* **1963**, *17*, 1126.

(224) Muetterties, E. L.; Schum, R. A. *Qt. Rev., Chem. Soc.* **1966**, *20*, 245.

(225) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945.

(226) Natarajan, K.; Poddar, R. K.; Agarwala, U *J. Inorg. Nucl. Chem.* **1976**, *38*, 249.

(227) Ruiz-Ramirez, L.; Stephenson, T. A.; Switkes, E. S. *J. Chem. Soc., Dalton Trans.* **1973**, 1770.

(228) Dwyer, F. P.; Humpoletz, J. E.; Nyholm, R. S. *Proc. R. Soc. London* **1946**, *80*, 217.

(229) Chatt, J.; Shaw, B. L.; Filed, A. E. *J. Chem. Soc.* **1964**, 3466.

(230) Chatt, J.; Leigh, G. J.; Mingos, D. M. P.; Paske, R. J *J. Chem. Soc. A*, 1968, 2636.

(231) Muscarella, J. C.; Crook, J. R. *J. Chem. Soc., Dalton Trans.* **1978**, 1152.

(232) Jenkins, J. M.; Lupin, M. S.; Shaw, B. L. *J. Chem. Soc. A*, **1966**, 1407.

(233) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1963**, 6017.

(234) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 34, 896.

(235) Allen, E. A.; Wilkinson, W. *J. Chem. Soc., Dalton Trans.* **1972**, 613.

(236) Cross, R. J.; Green, T. H.; Keat, R. *J. Chem. Soc., Dalton Trans.* **1976**, 382.

(237) Jensen, K. A. *Z. Anorg. Chem.* **1935**, 225, 97.

(238) Fergusson, J. E.; Karran, J. D.; Seevaratnam, S. *J. Chem. Soc.* **1965**, 2627.

(239) Chatt, J.; Leigh, G. J.; Storace, A. P. *J. Chem. Soc. A*, **1971**, 1380.

(240) Chatt, J.; Leigh, G. J.; Mingos, D. M. P. *J. Chem. Soc. A*, **1969**, 1694.