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Influence of the molecular configuration on second-order nonlinear optical properties of coordination compounds

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Contents

Abstract

The relationships between structure and nonlinear optical (NLO) properties of coordination compounds in terms of influence of molecular configuration on linear and NLO properties are reviewed. The molecular configurations involved are square pyramidal,

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tetrahedral, square planar, octahedral, sandwich and linear. Based on the experimental results, empirical rules of these relationships have been proposed, which may help the design of new NLO materials from organometallic and coordination compounds.

Keywords: Coordination compound; Molecular configuration; Nonlinear optical properties

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1. Introduction

Due to their varied important applications, the search for nonlinear optical (NLO) materials has continuously attracted attention since the discovery of NLO phenomena in 1961. The practically useful NLO materials thus far are mainly inorganic crystals, which include KH_2PO_4 (KDP), $KTiOPO_4$ (KTP), $LiNbO_3$ (LN), BaB_2O_4 (BBO), etc. A theory called the Anionic Group Theory has been proposed [1] and proved to be a useful guide for the design and discovery of new inorganic NLO materials such as BBO and LBO (LiB_3O_5). Organic NLO materials, on the other hand, have developed rapidly in the last 2 decades [2] due to their higher nonlinearity, faster response and easier structural modification compared with inorganic materials. The Charge Transfer Theory has been proposed [3] to describe successfully the relationship between structure and NLO properties in organic compounds. The concepts of molecular and crystal engineering have been developed [4] in the design of new NLO materials. However, organic NLO materials have encountered also some disadvantages, such as the difficulty to grow single crystals to large sizes, poor environmental stability and poor mechanical strength.

Organometallic compounds (defined here as those which contain at least one direct M–C bond between metal and organic ligands) and coordination compounds (in which the metal and the ligands are connected through M–O, M–N, M–S or M–P bonds) are compounds which combine the features of both inorganic and organic compounds. The study of the NLO properties of these complexes was first reported in the mid-1980s [5,6]. Since then, these studies have become gradually more popular due to their advantages over traditional inorganic or organic materials. For example, organometallic and coordination compounds offer a variety of molecular structures by changing the metals, ligands, coordination numbers and so on. This diversity of molecular structure gives one an oppurtunity to tune the electronic properties of the molecules, and hence to tune the linear and nonlinear optical properties. The metal centre can also behave as either an electron donor or acceptor due to the rich oxidation–reduction properties of the transition metals. Therefore, it can be expected that some novel NLO materials may be found from organometallic or coordination compounds that may combine the features and advantages of both inorganic and organic compounds, and hence may be superior to the existing inorganic and organic NLO materials.

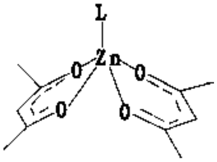
There are three main types of interest in the study of NLO organometallic and coordination compounds thus far. The first interest is to find transparent SHG (second harmonic generation) materials to be used for frequency-doubling of a semiconductor laser. For this purpose, the material should exhibit a large SHG effect and optical transparency both at second-harmonic (SH) and fundamental wavelengths. Secondly, organometallic and coordination compounds may offer some excellent chromophores for synthesis of electro-optical (EO) polymers. In this case, a large value of the product of $\beta\mu$ (where β is the first molecular hyperpolarisability, and μ is the dipole moment) and reasonable thermal stability are required. The third purpose is to find new third order NLO materials. Normally, a large conjugated system is an important factor in achieving this third order effect.

Some excellent NLO studies of organometallic and coordination compounds have been reported. These include some SHG crystals transparent in the visible region, compounds with both large values of β and μ, and materials with a strong third order NLO effect. Several review papers on organometallic NLO materials have appeared [7–9].

The study of the solid state physical properties of organometallic and coordination compounds is a new field [10]. There has been little knowledge about the structure–solid state physical property relationships of these compounds. In the early period, scientists often utilised the principles of the Charge Transfer Theory, which was summarised originally from organic NLO materials, for designing NLO materials with organometallic and coordination compounds. Later, Cheng et al. measured (using the EFISH technique) [11], and Marks calculated [12] the first molecular hyperpolarisability, β, of some types of organometallic compounds, and they studied the correlation between structure and β. Jiang et al. summarised their work on octahedral coordination compounds as SHG materials [13]. All these studies are good examples of attempts to learn about the structure–property correlations in organometallic and coordination compound NLO materials. However, still only little is known. In particular, the role of the metal atoms in intramolecular charge transfer, and the effect of the metals on NLO properties, have remained basically unclear. A comprehensive theory for better understanding and revealing the structure–NLO property relationship in these compounds is still needed.

We have been pursuing research on NLO active organometallic and coordination compounds for 10 years. Hundreds of organometallic and coordination compounds with a variety of metals, ligands and molecular configurations have been designed and synthesised. Their structures and NLO properties (the second or third order properties) were studied. Based on our experimental results, we have found that the molecular steric configuration is a very important factor which strongly influences the molecular electronic property, and hence greatly influences the linear and nonlinear optical properties.

In this paper, we summarise results on organometallic and coordination NLO materials. Based mainly on our own work, as well as some results from other research groups, we propose empirical rules which may help the design of new NLO materials from organometallic and coordination compounds for various applications.



Scheme 1.

2. Square pyramidal configuration

Some organometallic and coordination molecules in which the coordination number is five form a square pyramidal configuration. Molecules of this type are certainly not centrosymmetric, and hence the molecules should exhibit non-zero β values.

We have synthesised a series of this type of compound, L–Zn(acac)$_2$, where L represents a variety of pyridine, urea or thiourea derivatives, and acac stands for the acetylacetate anion. They have a square pyramidal configuration as verified by X-ray single crystal structure analysis (Scheme 1) [14].

Table 1 lists the SHG intensities (with KDP as a reference) and the melting points of these compounds.

It can be seen from Table 1 that 12 of the 15 compounds have shown SHG effects. Such an unusually high percentage (80%) of non-centrosymmetric crystal lattices may result from the low molecular symmetry of this configuration.

Table 1
Structure and properties of zinc bis(acetylacetate) derivatives L–Zn(acac)$_2$

No.	L	M.p. (°C)	Powder SHG (× KDP)
1	H_2O	131–2	0.2
2	Me_2CO	134–5	0.2
3	Py[a]	113–5	0.2
4	2-Pic[b]	119–20	0
5	3-Pic	128–9	0.3
6	4-Pic	150–1	0.25
7	2-H_2N–Py	198–9	0.3
8	4-H_2N–Py	218–9	0.25
9	3-$CH_3C(O)$–Py	115–6	0
10	4-CH_2=CH–Py	198–9	0.6
11	4-NC–Py	150–2	0
12	$H_2NC(O)NH_2$	167–8	0.5
13	(PhNH)C(O)(NH_2)	179–80	1.0
14	$H_2NC(S)NH_2$	225–6	1.0
15	(PhNH)C(S)(NH_2)	172–4	10.0

[a] Py, pyridine.

[b] Pic, picoline.

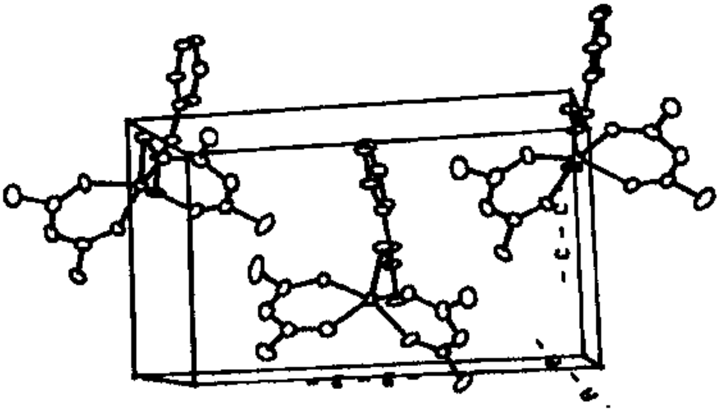


Fig. 1. X-ray crystal structure of $Zn(acac)_2(PhNH)C(S)(NH_2)$.

All of these 15 compounds are completely colourless with the maximum absorption wavelength (λ_{max}) <285 nm in solution. The SHG intensity of most of the compounds in this series is weaker than, or similar to, that of KDP. This excellent transparency and weak SHG effect can be understood by the fact that the metal in the square pyramidal molecule does not form an electron conjugation system with the ligands, and thus is not involved in intramolecular charge transfer.

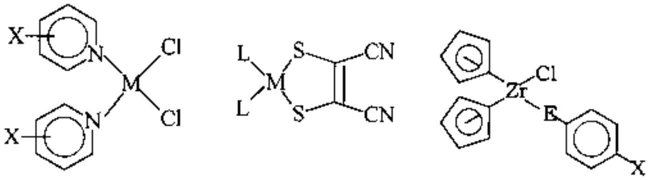
The most interesting result came from compound **15**, which showed a SHG signal ten times as strong as that of KDP. X-ray structure analysis revealed that the molecules in the lattice are arranged in such a way that the directions of their dipole moments are almost parallel (Fig. 1). This compound ($C_{17}H_{22}O_4N_2SZn$) crystallises [15] in the triclinic system, space group $P1$, with $a = 7.418(3)$, $b = 14.356(9)$, $c = 9.143(3)$ Å, $\alpha = 90.05(4)$, $\beta = 91.62(3)$, $\gamma = 86.94(6)°$, $V = 973.2$ Å^3, and $Z = 2$. Attempts to grow large crystals are currently in progress. In this case, β may be small, but the overall NLO effect in the solid state (macroscopic effect) may be strong. This demonstrates the possibility of obtaining a new transparent NLO crystal for frequency doubling of semiconductor lasers from organometallic or coordination compounds with a suitable molecular configuration (Fig. 1).

3. Tetrahedral configuration

We have also synthesised various types of tetrahedral (or pseudo-tetrahedral) compounds, such as in Scheme 2.

Dicyclopentadienyl zirconium(IV) derivatives are especially interesting. Their λ_{max} and powder SHG intensities are listed in Table 2 [16].

Notably, almost all of these compounds are white in colour, except for compound **11** which is yellow. Ten of 11 compounds (91%) have shown SHG signals which are $0.3 \sim 4.5$ times as strong as that of KDP.



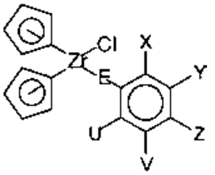
Scheme 2. M = Zn, Cd, and Hg, M’ = Ti or Zr, E = O or S, 2L = 2,2′-bipyridine or 1,10-phenanthroline derivatives, and X = a variety of substituents.

It is not difficult to see that the data in both Tables 1 and 2 have some common features. The compounds are normally transparent in the visible region, and a very high proportion of them crystallise in non-centrosymmetric space groups and hence exhibit SHG signals. In most cases, the SHG signal is weak. However, there is the possibility for a subset of the compounds in these groups to show relatively strong NLO properties in addition to excellent transparency. Actually, a transparent tetrahedral compound, Zn(2-aminopyridine)$_2$Cl$_2$, has been found to show a SHG signal 12 times as strong as that of KDP [17].

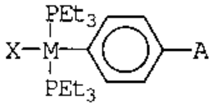
Jiang et al. have also found a very good SHG crystal from a series of tetrahedral complexes, M(Tu)$_2$Cl$_2$ (M = Cd, Pb, Co or Hg, and Tu is thiourea), which showed a powder SHG efficiency similar to that of urea [6].

These data, therefore, demonstrate the possibility to search for transparent SHG materials for frequency doubling of a semiconductor laser from compounds with either square pyramidal or tetrahedral configuration. To achieve this, a metal with

Table 2
Structure, λ_{max} and powder SHG of dicyclopentadienyl monochlorozirconium compounds



No.	E	X	Y	Z	U	V	λ_{max} (nm)	SHG (× KDP)
1	O	H	H	NO_2	H	H	328	2.0
2	O	NO_2	H	H	H	H	–	1.4
3	O	NO_2	H	NO_2	H	H	–	0
4	O	H	H	F	H	H	315	0.15
5	O	F	H	H	H	H	338	2.0
6	O	H	H	Br	H	H	334	0.3
7	O	Cl	H	H	H	H	344	2.0
8	O	H	H	CO_2Pr	H	H	330	1.2
9	S	H	H	F	H	H	316	1.2
10	S	F	F	H	F	F	336	4.5
11	S	F	F	F	F	F	363	0.15



Scheme 3. M = Pd or Pt, X = Br or I, and A = CHO or NO_2.

d^0 or d^{10} electronic structure must be chosen, and different ligands should be utilised and the ligands must be transparent themselves. In addition, various techniques for crystal engineering may be tried to form a favourable molecular arrangement so that the material can show a relatively strong solid state NLO properties.

4. Square planar configuration

Metal ions with d^8 electron structure (such as Ni(II), Pd(II), Pt(II), Ir(I), etc.) often form a square planar molecular configuration with their ligands. The metal ion is normally located in the plane formed by the four coordination atoms of the ligands, and the d_z^2 orbital of the metal can overlap with suitable orbitals of the ligands to form a delocalised electron system.

Square planar organometallic compounds were among the first organometallic SHG materials due to the existence of this delocalisation. Some excellent examples can be seen in Scheme 3.

In these compounds, the *trans*-X–M(PEt_3)$_2$ group functions as an electron donor, which donates an electron to the *para*-substituent through the aromatic system. These compounds exhibit β values in the range of 0.5 to 3.8×10^{-30} esu, depending on the acceptor strength of A and the nature of M or X [18].

All of these square planar coordinated compounds are deeply coloured due to d–d excitation. Therefore it is hard to utilise this type of compound as SHG crystals for a semiconductor laser. However, it is highly possible for them to be used as chromophores in EO or photorefractive polymers provided that they exhibit large value of $\beta\mu$ and that they are not ionic compounds.

On the other hand, square planar complexes have exhibited very interesting third order NLO properties. Almost all the organometallic or coordination compounds which show strong third order NLO properties thus far are from this type of compound. These include metallophthalocyanines [19–21], metal dithiolenes [22], and platinum-containing conjugated polymers [23], etc. Perry, Marder and coworkers have found that phthalocyanine complexes bearing heavy atoms or paramagnetic groups, or in solvents containing heavy atoms, showed optical limiting enhanced triplet-state absorption [20]. Underhill and coworkers have reported that some metal dithiolenes possess large values of the nonlinear refractive index, n_2, and sufficiently good figures of merit for device applications in all-optical switching [22]. Recently, we have observed the excited state enhancement of the third order optical nonlinearity in a square planar coordination compound [24].

5. Octahedral configuration

The octahedron is a common configuration in organometallic and coordination molecules. Many metals (with either a fulfilled or unfulfilled d orbital) may take this configuration with their ligands. Since the coordination number is six, there can be many choices for the ligands.

Jiang and coworkers were among the earliest researchers to investigate the NLO properties of the coordination compounds. They were very interested in octahedral complexes since they suggest that octahedral complexes combine the features of two different types of NLO materials, i.e. the inorganic distorted octahedron oxides (such as KTP and $LiNbO_3$) and organic conjugated compounds. They studied octahedral cadmium complexes with some simple ligands such as thiourea or its derivatives systematically, and found some very interesting materials. For example, $Cd(Tu)_2ICl$ and $Cd(Tsc)_2Cl_2$ (Tu is thiourea, and Tsc is thiosemibazide) have shown powder SHG efficiency of the order of KTP and urea, respectively, and they are all transparent in the visible region [25].

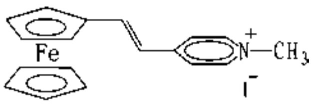
Another type of octahedral complex featured in early SHG studies is metal pyridine (or bipyridine) σ-complexes. For example, $[ReCl(CO)_3(2,2'\text{-bipyridine})]$ and $[Re(CF_3SO_3)(CO)_3(2,2'\text{-bipyridine})]$ both had powder SHG efficiencies about twice that of urea [26]. Another series of pyridine derivatives, $[W(CO)_5(NC_5H_4X)]$, was studied systematically with $X = H$, CHO, $COCH_3$, C_6H_5 or NH_2. The λ_{max} of the electronic spectra varied from 256 to 440 nm, depending on X, and β values were in the order of 10^{-30} esu [27].

6. Sandwich configuration

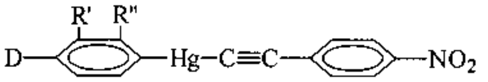
Ferrocene derivatives have drawn great attention for their NLO properties due to their great stability, cheap source, and easy chemical modification. The highest powder SHG efficiency (220 times that of urea) among organometallic and coordination compounds, thus far, is a ferrocenyl containing salt [28] (see Scheme 4).

The measurement of β of ferrocene derivatives by the EFISH technique [11] revealed that the ferrocenyl group functions as an electron donor with a strength similar to a methoxy group (CH_3O-).

Due to strong d–d excitation, all these ferrocenyl derivatives are deeply coloured, with λ_{max} around 500 nm. As a result, the frequency of the laser used for the measurement of either SHG or β is normally as long as 1907 nm. Therefore, although this type of compound may show a very strong SHG effect, it is hard for



Scheme 4.



D = I, Br, Cl, MeO, EtO, H_2N, MeHN, Me_2N or NO_2;
R' = H or Me;
R" = H or Me.

Scheme 5.

them to find applications as SHG materials. Instead, they may behave as an effective chromophore for EO or photorefractive polymers.

Third order NLO properties have also been observed in some sandwich metallocene complexes [29].

7. Linear configuration

The linear configuration is less common, and exists in complexes of only very few metals. Mercury is one such metal. We have synthesised 12 arylmercuric nitrophenylacetylides which have a linear configuration as shown below [30] (Scheme 5).

Their first molecular hyperpolarisability, β, was determined by the solvatochromism technique, and some by the EFISH method, to be of the order of 10^{-29} esu. There is no linear relationship between the electronic property of the substituent (D) and the value of β, indicating that an effective intramolecular charge-transfer from D to nitro group does not exist [31]. Table 3 compares β and λ_{max} of one of these organomercury complexes with some other organic compounds which bear the same donor (NH_2) and acceptor (NO_2). It can be seen that the mercury complex (no. **5**) possesses a rather high β value, which is higher than that of *p*-nitroaniline (no. **1**) and 4-amino-4′-nitro-biphenyl (no. **2**), and almost the same as that of 4-amino-4′-nitro-tolane (no. **3**). Its λ_{max} is much shorter than that of all other molecules in Table 3 by about 70 nm or more [32].

Therefore, these organomercury compounds with a linear molecular configuration may represent a new approach to solve the conflict between increasing nonlinearity and improving transparency. Further research is needed to give a satisfactory explanation.

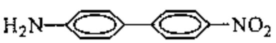
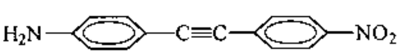
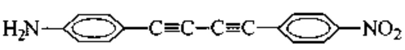
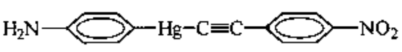
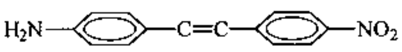
8. Concluding remarks—empirical rules

The influence of several molecular configurations on the NLO properties and the transparency in organometallic and coordination compounds have been discussed. These have not yet included such configurations as triangular planar and triangular bipyramidal which have hardly been encountered in NLO studies so far, and thus are not included here.

Many factors may influence the linear and nonlinear optical properties of organometallic and coordination compounds. However, the molecular configuration is definitely one such important factor, as demonstrated above. From the above discussion, we may be able to draw some empirical rules which may act as guidelines for the design of different types of metal-containing NLO materials for different applications.

1. To design new SHG materials completely transparent in the visible region for frequency doubling of semiconductor lasers, metallic complexes should meet the following requirements:
    1.1. The central metal atom or cation should possess a d^0 or d^{10} electronic structure.
    1.2. The organic ligands must themselves be transparent in the visible region.
    1.3. Tetrahedral, square pyramidal, octahedral or linear configurations may be suitable.
    1.4. Different ligands (donors and acceptors, respectively) should be used to form the complexes. In particular, this must be the case for octahedral and linear configurations.
    1.5. A method for crystal engineering (such as the existence of hydrogen bonding or chirality, etc) [4] may be utilised to facilitate a favourable molecular alignment. This is especially important for tetrahedral or square pyramidal compounds.

Table 3
Comparison of β and λ_{max} of an organomercuric compound with other organic aromatic compounds possessing similar groups

Compound	β ($\times 10^{-30}$ esu)	λ_{max} (nm)
	16.7	378
	17.8	378
	24	379
	28	384
	26.4	307
	260	402

2. To design molecules with high $\beta\mu$ values as a chromophores for preparation of polymeric EO or photorefractive materials, the best configuration is square planar. For this purpose, the metal cation should normally possess a d^8 electronic structure, and the two sides of the metal cation should be occupied by donor and acceptor ligands, respectively. On the other hand, the ferrocenyl sandwich compounds may also behave as this type of material, though their $\beta\mu$ value may not be very high.
3. To design the third order NLO materials square planar and sandwich complexes have good configurations. In this case, an absence of molecular centrosymmetry is not required, but extensive electron delocalisation is preferred.

Organometallic chemistry and coordination chemistry are mature disciplines. On the other hand, very limited knowledge about the correlation between the structure and the solid state physical properties of organometallic and coordination compounds has been available thus far. Since these compounds exhibit features of both inorganic and organic compounds, they have been expected to be new candidates for electronic and optical materials. Therefore, the study of structure–property relationships is of great importance, and will attract more attention from the experimental and theoretical chemists as well as the physicists. We anticipate that a more comprehensive and more useful theory will be developed in the near future.

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