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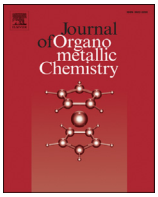

Note

First hyperpolarizability of Ru-half-sandwich complexes: The effect of halogen atom substitution on the ancillary ligand

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ABSTRACT

The first hyperpolarizability (β) of a series of half-sandwich Ru complexes with a mercaptobenzothiazole ligand bearing a halogen atom substitution in the para-position has been investigated by hyper-Rayleigh scattering and quantum chemical calculations. The heterocyclic ligand with a bromine atom in the para position makes it a very good donor and charge flows to the Ru center enhancing the β value of the complex by a factor of 2 compared to the complex with the ligand without the halogen substitution. The resonance (+R) and the inductive (-I) effects exerted by the halogen atom in the para position push electrons in opposing directions in the complex. For the Br and Cl atoms the resonance effect dominates which enables the ligand to donate electrons to the metal center thereby increasing the hyperpolarizability whereas for the fluorine atom, the inductive effect is dominant which reduces the charge flow to the metal and the hyperpolarizability drops even below that of the unsubstituted ligand. This unprecedented halogen atom effect on β of metal complexes is reported.

Introduction

The main objective of synthesizing nonlinear optical (NLO) materials is to achieve thermally and photochemically stable, optically transparent materials with large hyperpolarizabilities. Organometallic complexes have been investigated as a part of the search for new and efficient NLO active materials since they offer flexibility in design and optimization of various important parameters stated above [1–4]. Like organic molecules, organometallic compounds with a donor-π-acceptor motif have been shown to possess large first hyperpolarizability (β) that could be enhanced by modification of the π-bridge or by increasing the donor/acceptor strengths. Heterocyclic ligands such as carbazole, benzimidazole and pyridine have been extensively used as donors in organometallic complexes in order to enhance the first hyperpolarizability of organometallic complexes [5–9].

In addition to the organic groups, ligated metals add one more dimension in the design flexibility of such compounds to produce large nonlinearities [10]. Humphrey et al. [11] explored the effect of different transition metals in a series of organometallic complexes and concluded that 18 valence electron Ni alkynyl complexes have higher β values than 14 valence electron Au alkynyl complexes. It was conjectured that in these complexes the increasing ease of oxidation of the metal center leads to increasing β. They have also shown that when the metal is from the next row as in the case of 18 electron Ru alkynyl complexes, they have higher β values than the 18 valence electron Ni complexes. Among the group 8 metal alkynyl complexes Powell et al. [12] reported that the β value increases from Fe to Ru to Os complexes, which clearly shows that apart from the ease of oxidation, it is the size of the metal valence orbitals that play an important role in the enhancement of β.

We investigated the first order hyperpolarizability of a series of Fe, Ru and Mo based half sandwich complexes [13] where halides were linked directly to the metal. It was expected that iodine substituted metal complex should have the maximum first hyperpolarizability (β) in a particular set of compounds but surprisingly this was not found to be the case. The iodine substituted Ru/Fe complex showed the lowest β value among Cl, Br, and I compounds. This was ascribed to the efficient donation of π electrons of halogen atoms to the metal orbital which match well in energy. Better overlap between the Cl orbitals and metal orbitals as in the case of Fe and Ni make the chloro complexes better nlophores. Gradually the efficiency of electron donation decreases as the size of the halogen atoms and the metal increase and as the energy gap between the interacting orbitals widens.

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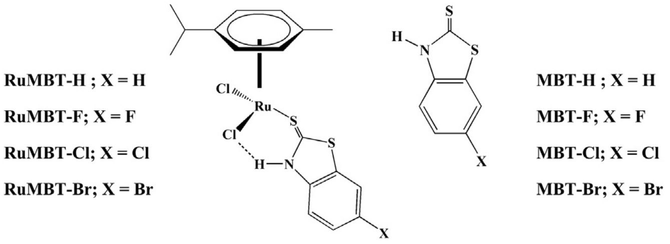

Scheme 1. Chemical structures of Ru-complexes (left) and halogenated mercaptobenzothiazole ligands (right) used in this work.

Herein, we have investigated the effect of a single halogen atom on the molecular hyperpolarizability of a series of half-sandwich Ru complexes where the halogen atom has been attached in the para position of a mercaptobenzothiazole ligand (Scheme 1) which is linked to the metal center.

Experimental

Materials and methods

All the halogenated mercaptobenzothiazole ligands and their corresponding Ru-complexes were synthesized as described in the literature by us [14,15]. The reagents and compounds necessary for the synthesis such as $RuCl_3 \cdot xH_2O$ and 2-mercaptobenzothiazole (MBT) were obtained from Sigma–Aldrich (India). The compounds were characterized fully by NMR spectroscopy, CHNS analysis and high resolution ESI-Mass Spectrometry as reported by us in the literature [14,15]. These crystalline compounds were used for HRS and other optical property measurements. All optical measurements were performed in dichloromethane (DCM).

Calculations

Quantum chemical calculation of hyperpolarizabilities of Ru(II) complexes and the corresponding ligands were carried out. The GAUSSIAN 09 program [16] was used for DFT as well as TDDFT calculations for MBTX and their corresponding Ru-complexes. Geometry optimization (by DFT), dipole moment of the ground and relevant excited states, electronic transition energy, first hyperpolarizability calculation were carried out using 6-31 + G* basis set for C, H, O, N, S, halogens and Los Alamos National Laboratory 2 double-ζ (LANL2DZ) basis sets for Ru transition metal. CAM-B3LYP functional within the polarized continuum model (PCM) was used to take into account the solvent effect in both DFT and TDDFT calculations. Recently it has been shown [17] that CAM-B3LYP functional predicts the properties in a charge transfer process correctly. In a computational paper Tian et al. [18] have done TDDFT calculations of β values of a series of Ru-coordinated dithienylperfluorocyclopentene (DTE) complexes using 6-31G(d,p) basis set and CAM-B3LYP functional. They have used continuum solvation model in their calculation. On the other hand, Coe et al. [19] have computed first hyperpolarizability of some two dimensional Ru(II) based organometallic chromophores containing electron donor acceptor ligands using B3LYP/6-31 + G(d) level of theory and found partial agreement in prediction of trends between calculations and experiment. Our choice of functional and basis set is based on the conclusions provided in these reports. The comparison between the key X-ray structural parameters and the DFT optimized geometry was done. The C-X (where X = H, F, Cl, and Br) bond distances obtained from the X-ray crystal structure published earlier [14,15] are 0.926, 1,365, 1.739 and 1.894 A, respectively, which agree well with the bond distances of 1.085, 1.355, 1.747, and 1.899 A, obtained from the calculated optimized geometry of the compounds using CAM-B3LYP functional with 6-31 + G(d) basis.

Results and discussion

UV–vis spectra

UV–Vis spectra of MBT-X ligands (Fig. 1) show an intense absorption band at ~330 nm along with another low intensity band, at ~235 nm. Following the assignment of UV bands of mercaptobenzothiazole and mercaptobenzimidazole ligands and their rhenium complexes by AlHokbany et al. [20], the intense band at ~330 nm could be assigned to a n-π* transition where the lone pair of electrons of the S atom belonging to the benzothiazole ring is involved. The other band below 300 nm appears to be due to a π-π* transition localized on the benzothiazole ring. The ~330 nm band of the MBT-X ligands shifts to longer wavelengths to ~340 nm in RuMBT-X complexes. The calculated area under ~340 nm band in RuMBT-X complexes is significantly greater in magnitude than that calculated for MBT-X ligands under the ~330 nm band. This increase in the absorbance in RuMBT-X complexes is due to charge transfer between MBT-X ligands and the Ru metal. There is another noticeable broad band (peak wavelength ~440 nm) of very low intensity, which is due to Laporte forbidden d–d transitions. The relevant band areas reported in Table 1 were obtained by fitting the absorption profiles to Gaussian functions.

First hyperpolarizability (β) of Ru-complexes

First hyperpolarizability (β) of Ru half-sandwich complexes and their corresponding ligands were measured by the HRS technique

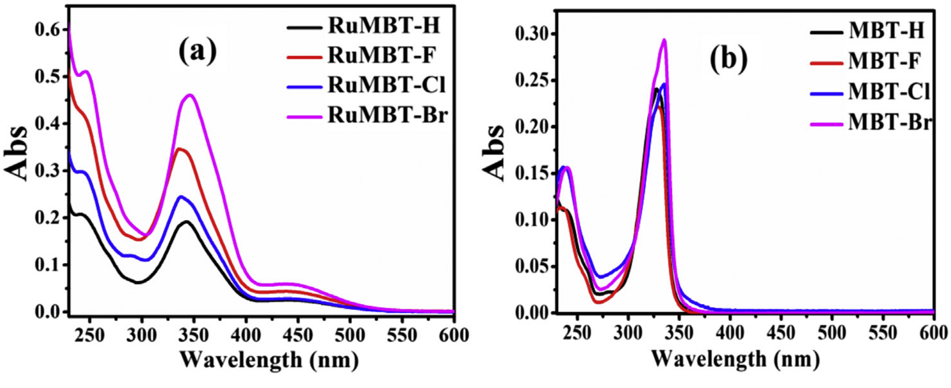

Fig. 1. UV–VIS spectra of (a) RuMBT-X complexes (recorded at ~ 10^{-5} M) and (b) MBT-X ligands (at ~ 10^{-4} M).