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The picrate anion as a versatile chelating counter-ion for the complexation of alkali and alkaline earth metal cations with ionophores: 'The picrate effect'

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Abstract

The special characteristics of the picrate anion as a versatile counter-ion for cation complexation are demonstrated by crystal structures. On the basis of the experimental data reported in the literature a categorization into different modes of picrate/cation interactions is proposed together with the corresponding nomenclature. The results of the present study and the analysis of the picrate versatile interactions may be used for various scientific and commercial applications since picrate is commonly used as a counter-ion in many systems involving extraction and transport of alkali and alkaline-earth metal cations. The data presented here should also be considered for systems involving picrate as counter ion where high efficiency and selectivity towards specific ion are desired. Such systems may be significantly affected from the high diversity of both the coordination and geometry of the picrate-cation interactions.

Alkali and alkaline earth metal cation salts of o-nitro phenolate derivatives are extensively used as model compounds in molecular structure studies of complexes (refs. 1-3), and as standard guests for studies of extraction and transport through membranes of these cations by natural and synthetic ionophores (refs. 4-7). The o-nitro phenolate and its p-nitro derivative are soft and polarizable anions. Such characteristics of the anions are often used to facilitate and increase the extraction and transport of alkali metal cations through solvents of low polarity (refs. 8,9).. All the o-nitro phenolate derivatives, in general, and the picrate anion, in particular, have characteristic intense absorption spectrum in the visible region (300-400nm) due to their aromatic poly-nitro system. The maxima of the absorption spectra are changed in a special manner when a complex is formed (refs. 1-3, 10-12). There is no liquid solution experimental data concerning molecular structure and coordination mode of alkali and alkaline earth metal cations with o-nitro phenolates in salts and complexes. The only available data is obtained from crystallographic studies. Our basic assumption, which is strongly supported by experimental data (ref. 13), is that these crystal structures resemble their structure in solution. Out of all the o-nitro derivatives, picrate salts are most extensively used for determining scales of free energies of complexation. The crystallographic data provide valuable information about the molecular structure of the complexes. In many structures, picrate interacts as mono and bidentate ligand (ref. 13). The preferred binding site is the phenolic oxygen due to ion-ion

interaction. The second binding site is an oxygen of the o-nitro group. In all cases where picrate is bidentate ligand the interaction with the cation is via the phenolic and o-nitro oxygens. The short distance of ~3.5Å between the phenolic and o-nitro oxygens provide an effective bidentate ligand with both charge and dipole binding ability. When additional binding sites are needed, the picrate becomes tridentate ligand and additional o-nitro or p-nitro oxygens are involved in the coordination of the cation (refs. 13,14). In few structures, due to conformational constrains, the picrate is involved in the coordination of the cation as monodentate ligand via o-nitro (ref. 15) or p-nitro (ref. 16) oxygens.Experimental evidences to the coordination ability of the nitro group to alkali metal cations are known (refs. 17-19). Therefore picrate is a versatile mono/bi/tri dentate ligand. It is an integral part of complexes of alkali and alkaline earth metal cations with natural and synthetic ionophores. Another important characteristic of aromatic poly-nitro compounds is their ability to form stable complexes with aromatic hydrocarbons, especially those that are substituted with alkyl groups or are otherwise expected to have electron-donating properties. This behavior is very commonly observed with picric acid, and the complexes therefore are often nicely crystalline solids, which are useful for the separation, purification, and identification of organic compounds. The binding in these complexes results from attractive forces between electron-acceptor polynitro compound and electron-donor substances. Picric acid forms 1:1 π-complexes (charge-transfer) with naphthalene and higher hydrocarbons of higher melting point, lower solubility and more intense color than either component (ref. 20). Therefore, the experimental data demonstrate the versatile binding properties of nitro group as ligand for both charged and neutral substances.

Coordination Modes of Picrate Anion with Cations.

In order to examine the significance of the different conformations and specific cation/counter-ion interactions exhibited by the picrate anion in crystal structures, it should be useful to examine the general case of picrate participation as counter-ion in a complex. The possible experimental binding combinations for picrate are presented in Figure 1. The picrate is a monodentate ligand when it coordinates with the cation via phenolic oxygen, termed as, ph. (fig. 1a), via o-nitro oxygen, termed as, o. (fig. 1b) and via the p-nitro oxygens, termed as, p. (fig. 1c). When the picrate is a bidentate ligand, it coordinates the cation via phenolic and the o-nitro oxygens, termed as, ph,o. (fig. 1d).

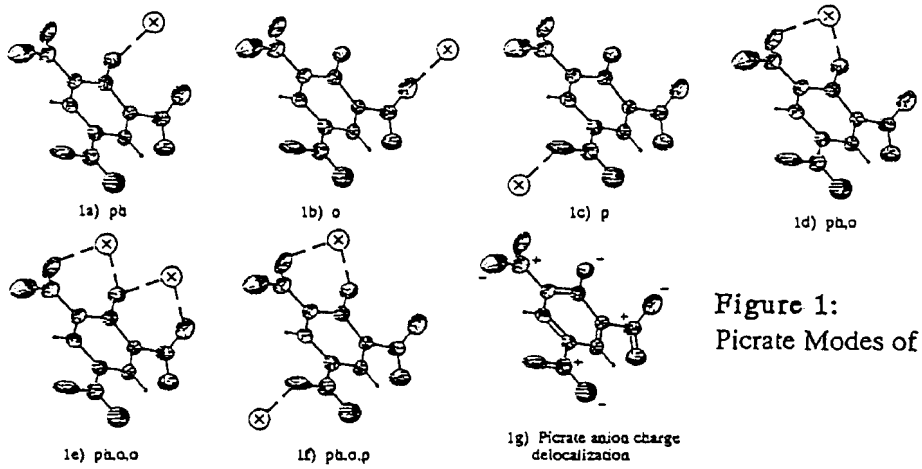

Figure 1:
Picrate Modes of Coordination

When the picrate is a tridentate ligand, it coordinates the cation either by phenolic and the two o-nitro oxygens, termed as, ph,o,o. (fig 1e), or phenolic, o-nitro and p-nitro oxygens, termed as, ph,o,p. (fig.1f). The effective delocalization of the negative charge among the widely separated ortho and para nitro oxygens explain the existence and stability of picrate complexes in which the picrate is completely excluded from the coordination sphere of the cation (fig. 1g).Therefore, the functional group substituents and geometry of the anion are major factors that dictate its interaction modes with the cation (ref. 21).

Anion Tectonics: Anionic Networks with Directional Ligating Properties.

The cation: picrate stoichiometry in mono and bidentate picrate complexes is solely 1:1. When the picrate is tridentate ligand, the stoichiometry is 1:1 for ph,o,p. coordination pattern, while, 2:2 or 2:3 for ph,o,o. coordination pattern. This unusual behavior of the picrate, which is a unique demonstration of anion tectonics, is presented in Figure 2.

Anionic tectons participate in interionic interactions that are strong, specific and directional. The picrate monomer is an essential building block of such

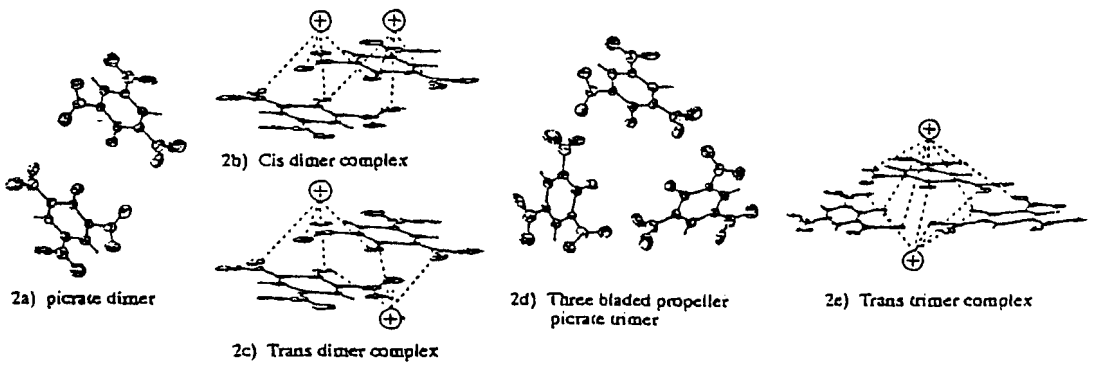

Figure 2: Picrate as Anionic Tecton

network. The buildup of picrate network from monomer via planar dimer to three bladed propeller trimer is presented by picrate tectonics (fig. 2). The picrate dimer (fig. 2a) provides two square coordination patterns with two negative charges. Therefore, it coordinates two alkali metal cations in cis (fig. 2b) or trans (fig.2c) conformation. The cis/trans preference is affected by the coordination number and ionic radius of the cation and the apical ligand geometry and number of binding sites. This is the reason that the LiPicrate monohydrate, in which the apical ligand is a water molecule, is a cis dimer (ref. 20), while the NaPicrate.Dibenzo-14-crown-4 complex, in which the apical ligand is dibenzo-14-crown-4 molecule (fig. 3), is a trans dimer (ref. 22).The three bladed propeller picrate trimer (fig. 2d) has three negative charges. Arrangement of three monovalent cations around such trimer is unfavorable. The trimer provides six binding sites (3 phenolic and 3 o-nitro oxygens) on each side of the propeller plane. This arrangement is favorable for trans complexation of divalent cations (fig. 2e). The Beauvericin.Ba(Picrate)2 complex is a clear demonstration for such

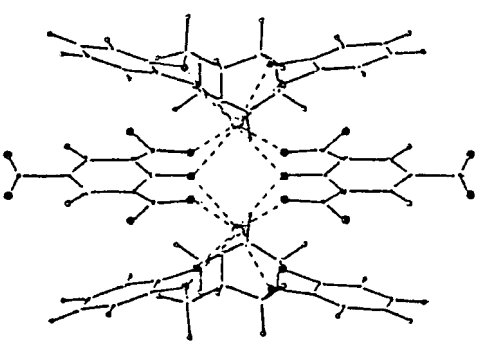

Figure 3: Dibenzo-14-Crown-4 NaPicrate Complex Crystal Structure.

complex (ref. 23). While the ph,o,o. coordination mode propagates from picrate dimer to picrate trimer, the ph,o,p. coordination mode remains solely as monomer. This is probably due to the p-nitro coordination site which is responsible for the formation of head to tail complex, as demonstrated by the KPicrate complex (ref. 14). The ph,o,o. coordination mode is more flexible in its coordination ability. Therefore, it is involved both in picrate dimer and trimer formation The resonance structures in Figure 4 illustrate the preferred coordination modes of the picrate with alkali and alkaline earth metal cations. The most favorable site is the negatively charged phenolic oxygen. Simultaneous interactions with o-nitro and p-nitro oxygens lead to the formation of favorable bi ph,o., tri ph,o,o. and ph,o,p. dentate ligands.The o-nitro and p-nitro oxygens are favorable coordination modes because of the charge localization on these oxygens as demonstrated in figure 4. Therefore, multidentate anions, such as, picrate, provide a highly favorable enthalpy and entropy of interaction with the cation.

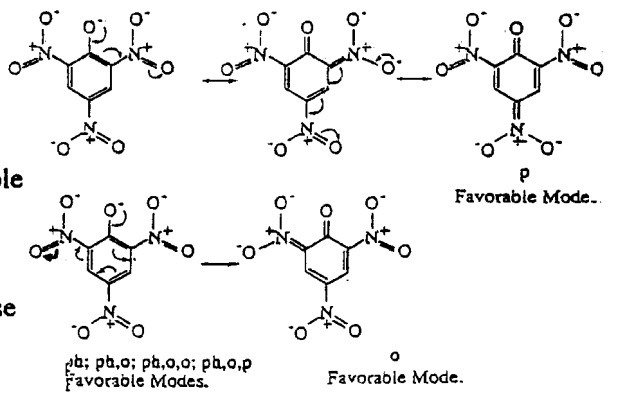

Figure 4: Picrate Anion Resonance Structures and Favorable Coordination Modes

Cation Extraction and Membrane Transport Extractability and Selectivity

The systematic study of alkali and alkaline earth metal cation picrate complexes provides a model for understanding how counter-ions affect the cation extraction and transport selectivities (ref. 21). On one hand, the picrate versatile nature which provides many interacting combinations with cations and ligands might be regarded as advantage, enabling the cation to form optimal complexes. In addition, the effective delocalization of the negative charge over the aromatic polynitro system explain the existence and stability of the picrate complexes in which the picrate is completely excluded from the cation coordination sphere. On the other hand, this chelating versatility of the picrate might be regarded as disadvantage because the picrate may provide additional binding sites for unfavored cations to saturate their coordination sphere. Therefore, more stabilized unfavored complexes are formed, which both contribute to increased extractability of undesirable cations and decrease in the extraction selectivity of the desired cation. The highly polarizable aromatic polynitro system might be regarded as advantage in increasing extractability and transport rate of alkali and alkaline earth metal cation salts in hydrophobic organic solvents and membranes. This is one of the main reasons for the extensive use of picrate salts in extraction and transport experiments. On the other hand, the picrate ability to form stable complexes with aromatic hydrocarbons and amines might be regarded as disadvantage when picrate salts are used in natural and synthetic membrane selectivity measurements. We can't exclude the possibility that the picrate will interact with hydrocarbon, aromatic and amine moeities in natural and synthetic membranes, causing morphological changes in their structure which result in selectivity changes. The intimate

involvement of the picrate in the coordination of alkali and alkaline earth metal cations as demonstrated above explains observations that the cation specificity of natural and synthetic ionophores, such as, valinomycin (refs. 3, 24,25), beauvericin (ref.23), dibenzo-18-crown-6 (ref. 26) and dibenzo-14-crown-4 (ref.27), in extraction and membrane trasport depends on the species of anions present .

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