Supramolecular encapsulation of anions in a copper(I) complex

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Mixed ligand copper(I) complexes of 1,10-phenanthroline (phen) and 1,2-bis(diphenyl)phosphinoethane (dppe) have been prepared with different counter ions [ClO$_4$] (1), [BF$_4$] (2), [SO$_4$$^2$] (3), [NO$_3$] (4)]. Based on the $^1$H and $^3$P NMR spectra of these complexes, it is seen that the solution equilibria of the sulfate complex is different from the rest and involves ligand dissociation. Competition experiments show that the nitrate ion is preferred by the cation in solution. Complex 4 has $^1$H NMR features that are different from those observed in complexes 1 and 2. A Cambridge Structural Database study has been taken up to show the uniqueness of phenanthroline in interacting with anions, especially nitrate ions through a preferential (phen)C2-O(nitrate) interaction.

Introduction

Transition metal complexes of N donor heterocyclic ligands are important due to their interesting photophysical properties, relevance in biological systems and more recently in supramolecular chemistry. Chelating ligands such as bipyridine and phenanthroline are typical examples of this class of N-donor ligands extensively used in the synthesis of transition metal complexes. In the context of copper(I) chemistry, 2,9 disubstituted phenanthroline offers enhanced stability for Cu(I) complexes by stabilizing the tetrahedral geometry over the square pyramidal or distorted octahedral geometry required by copper(II) complexes. Since copper(I) is also stabilized by phosphines, mixed donor complexes with phosphines and heterocyclic N donors are attractive in various ways, including enhanced stability and novel photophysical properties. Thus Cu(I) phosphine complexes (with phenanthroline or bipyridine ligands) have been explored for their use as photocatalysts.

The work reported here deals with [Cu(dppe)(phenanthroline)]$^+$ complexes that differ by the identity of the counter ions [ClO$_4^-$ (1), BF$_4^-$ (2), SO$_4$$^2$ (3), NO$_3^-$ (4)], in their composition. The structure of the analogous PF$_6^-$ complex of the present series was crystallographically characterized by Kitagawa et al. They have shown that both dppe and phenanthroline are chelating the copper ion, whereas the counter anion is non-coordinating (I). As the [Cu(dppe)(phenanthroline)]$^+$ series of complexes possess a coordinatively saturated Cu(I) center, the influence of non-coordinating counter anions in the solutions are expected to exert, at best, weak interactions with the cation. The stability of the nitrate ion complex in solution, is greater than that of other anions in this series and suggestive of a supramolecular encapsulation of the ion by the coordinated ligand. To corroborate the results from our NMR studies, we have carried out a database analysis of the available structures from the CSD.

Materials and Methods

All the reactions were carried out under an atmosphere of purified nitrogen, and the solvent dichloromethane was dried with P$_2$O$_5$ and distilled prior to the reaction. Diethyl ether and petroleum ether were distilled before use. Phenanthroline was obtained from Loba-Chemie, dppe was obtained from Aldrich, USA and used as received.

Spectral measurements

$^1$H NMR spectra were recorded on a Bruker ACF 200 MHz spectrometer with tetramethylsilane as the internal reference. $^3$P $^1$H NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer operating at 162 MHz. H$_2$PO$_4$ was used as external reference. FT-IR spectra were recorded in the solid state dispersed in KBr pellets on a Bruker
(EQUINOX 55) spectrometer. The MALDI mass spectra were recorded on a Kratos PCKompact spectrometer using an α-cyanocinnamic acid matrix prepared from a methanol solution of the complexes.

Preparation of the complexes

\[ \text{[Cu(C_{26}H_{24}P_{2})(C_{12}H_{8}N_{2})]}CI(C_{6}F_{5}) \] and

\[ \text{[Cu(C_{26}H_{24}P_{2})(C_{12}H_{8}N_{2})]}BF_{4}(2) \]

About 0.04 g of \([\text{Cu(CH}_{3}\text{CN})_{4}] ClO_{4}\) (0.12 mmol) was reacted with 0.05 g (0.12 mmol) of dppp in 10 ml of dichloromethane. After the dissolution of the Cu(I) source, 0.02 g of 1,10 phenantrolin(e monohydrate) (0.10 mmol) was added to the same solution. Addition of phenantrolin(e immediately resulted in a brilliant yellow orange colouration to the reaction mixture. After stirring further for 1 hr, the solvent was removed in vacuum which yielded an oily residue. Addition of diethyl ether to the residue resulted in the formation of complex 1 as a yellow orange free flowing powder in a near quantitative yield. MS (MALDI): m/z = 641.7 (100%) \([\text{Cu(C}_{26}\text{H}_{24}P_{2})(\text{C}_{12}\text{H}_{8}N_{2})]^{+}\), Calcd. 642.5. \(^{1}H\) NMR (CDCl\(_3\), 293 K, ppm) \(\delta = 8.74\) (d, 2H); 8.64 (d, 2H); 8.11 (s, 2H); 7.95 (t, 2H); 7.37 (b, 20H); 2.74 (t, 4H). \(^{31}P\) NMR (CDCl\(_3\), 293 K, ppm) \(\delta = -5.21\).

Similar procedure excepting the use of [Cu(CH\(_3\)CN\(_3\))]BF\(_4\) resulted in the formation of yellow orange free flowing powder of complex 2 in a near quantitative yield. MS (MALDI): m/z = 641.8 (100%) \([\text{Cu(C}_{26}\text{H}_{24}P_{2})(\text{C}_{12}\text{H}_{8}N_{2})]^{+}\), Calcd. 642.5. \(^{1}H\) NMR (CDCl\(_3\), 293 K, ppm) \(\delta = 8.74\) (d, 2H); 8.64 (d, 2H); 8.11 (s, 2H); 7.95 (t, 2H); 7.37 (b, 20H); 2.73 (t, 4H).

\[ \text{[Cu(C}_{26}\text{H}_{24}P_{2})(\text{C}_{12}\text{H}_{8}N_{2})]SO_{4}(3) \] and

\[ \text{[Cu(C}_{26}\text{H}_{24}P_{2})(\text{C}_{12}\text{H}_{8}N_{2})]NO_{3}(4) \]

About 0.015 g of CuSO\(_4\) was dissolved in the 1:1 mixture of water and acetonitrile (10 ml) and stirred for 2 h, with excess of Cu powder. After the reduction (as indicated by the disappearance of the blue colour), the reaction mixture was filtered under N\(_2\) to get a colorless solution of Cu(I) source. To this, 0.05 g of dppp and 0.024 g of 1,10 phenantrolin(e monohydrate) were subsequently added. The resulting yellow orange solution was further stirred for 15 min. and concentrated in vacuum. At this stage a minimum amount of water (~2mL) was remaining together with the pasty yellow residue, which was extracted in dichloromethane. The dichloromethane was removed in vacuum which yielded an oily residue. Addition of diethyl ether and subsequent washing to the residue gave complex 3 as yellow orange free flowing powder in in 85 % yield. MS (MALDI): m/z = 641.9 (100%) \([\text{Cu(C}_{26}\text{H}_{24}P_{2})(\text{C}_{12}\text{H}_{8}N_{2})]^{+}\), Calcd. 642.5. \(^{1}H\) NMR (CDCl\(_3\), 293 K, ppm) \(\delta = 9.1-7.65\) (b, 8 H); 7.26 (b, 20H); 2.69-2.10 (b, 4H). \(^{31}P\) NMR (CDCl\(_3\), 293 K, ppm) \(\delta = -5.7\).

About 0.02 g of Cu(NO\(_3\))\(_2\) was used as the nitrate source. The cupric nitrate solution dissolved in 10 ml of acetonitrile was stirred with 0.15 g of copper powder for 2 h. After the reduction of the cupric nitrate, 0.065 g of dppp and 0.032 g of 1,10 phenantrolin(e monohydrate) were subsequently added to the colorless solution and the resulting yellow orange solution was further stirred for 15 min. The solvent was removed in vacuum which yielded as in the case of 3 an oily residue which was worked up in a similar fashion to give complex 4 as yellow orange free flowing powder in a near quantitative yield. MS (MALDI): m/z = 642.1 (100%) \([\text{Cu(C}_{26}\text{H}_{24}P_{2})(\text{C}_{12}\text{H}_{8}N_{2})]^{+}\), Calcd. 642.5. \(^{1}H\) NMR (CDCl\(_3\), 293 K, ppm) \(\delta = 8.75\) (m, 4H); 8.16 (s, 2H); 7.95 (t, 2H); 7.37 (b, 20H); 2.74 (t, 4H). \(^{31}P\) NMR (CDCl\(_3\), 293 K, ppm) \(\delta = -5.26\).

\(^{1}H\) NMR titration

About 0.075 g of complex 1 was made up to 10 ml in dichloromethane giving a 0.01 M solution (A). Equimolar concentration of tetrafluoroborate counter anions were synthesized from the direct reaction of the relevant ligands with [Cu(CH\(_3\)CN\(_3\))]BF\(_4\) or [Cu(CH\(_3\)CN\(_3\))]ClO\(_4\) respectively. However, complexes that contain nitrate or sulphate counter anions were synthesized from in situ reduction of the respective Cu(II) salts in acetonitrile (Scheme 1). The products were obtained in pure form by washing repeatedly with diethyl ether. As the complexes 1-4 differ only in the counter anion from the known complex, it is reasonable to expect a

Results and Discussion—Synthesis and spectroscopic characterization

Complexes containing perchlorate or tetrafluoroborate counter anions were synthesized from the direct reaction of the relevant ligands with [Cu(CH\(_3\)CN\(_3\))]BF\(_4\) or [Cu(CH\(_3\)CN\(_3\))]ClO\(_4\) respectively. However, complexes that contain nitrate or sulphate counter anions were synthesized from in situ reduction of the respective Cu(II) salts in acetonitrile (Scheme 1). The products were obtained in pure form by washing repeatedly with diethyl ether. As the complexes 1-4 differ only in the counter anion from the known complex, it is reasonable to expect a...
similar molecular structure in the present study as well. Indeed, the IR spectra of the complexes suggest no coordination of the anion to copper in the solid state [Solid IR data — Anion, v(cm⁻¹): ClO₄⁻, 1093; BF₄⁻, 1064; SO₄²⁻, 1109; NO₃⁻, 1370]

The ratio of ligands was established using ¹H NMR spectra. The MALDI-mass spectral analysis supports the molecular composition derived from the ¹H NMR studies.

¹H NMR of these complexes in CDCl₃ is very informative about their solution structure. The integration of the phenanthroline and dppe signals is always 1:1, thus confirming the retention of the stoichiometry employed for synthesizing these complexes. However, the phenanthroline signals exhibit anion dependent chemical shifts.

Complexes 1 and 2 with ClO₄⁻ and BF₄⁻ counter anions respectively, show identical spectral features (Fig. 1a). Noticeably, the signals due to the protons present at the 2, 9 and 4, 7 positions are close to each other and resonate as two doublets centered at 8.74 ppm and 8.64 ppm respectively. While the 2, 9 signals show an upfield shift (Δδ free-complex 0.5 ppm) with respect to the free ligand, the 4, 7 signals move downfield with a comparable value of Δδ. Whereas the 5, 6 protons, resonate at 8.11 ppm (Δδ = 0.3 ppm), the 3, 8 protons show a triplet at 7.95 ppm (Δδ = 0.3 ppm). The aromatic region of the dppe ligand displays multiplets at 7.36 ppm, whereas the methylenic protons (-CH₂CH₂- of dppe) are magnetically equivalent and appear as a triplet due to coupling with P atoms at 2.74 ppm. All of these facts indicate the formation of a 1:1 complex similar to what is known about the PF₆ complex.

Interestingly, the nitrate complex, 4, shows a very different proton NMR spectrum. Firstly, virtual equivalence of the 2, 9 and 4, 7 protons of the phenanthroline moiety is observed. The signals that are observed as two doublets, in complexes 1 and 2, become a multiplet at 8.75 ppm. However, other signals (due to protons at 5, 6 and 3, 8 positions) possess comparable chemical shift values to those of complexes 1 and 2. Similarly the chemical shift values of the dppe signals are identical to those of complexes 1 and 2 (Fig. 1b). Clearly, the nitrate ion
has interactions with the phenanthroline moiety and has caused significant shifts in the proton resonances.

The $\text{SO}_4^{2-}$ containing complex 3, displays significantly different $^1\text{H}$ NMR signals, and shows a drastic broadening compared to the other complexes in this series (Fig. 1c). In addition, there are signals at 9.1 ppm, 8.30 ppm, and 7.85 ppm, indicating the presence of free phenanthroline due to dissociation. It is to be noted that the overall integration between the phenanthroline and the dppe signals fits the expected 1:1 ratio on the basis of the stoichiometry used for synthesis. The interaction of the sulfate anion with the cation is presumably by coordination to copper and displacement of the phenanthroline from its coordination sphere.

Thus the $^1\text{H}$ NMR experiments reveal three different categories of complexes. While the perchlorate and tetrafluoroaborate containing complexes are similar to the non-interacting hexafluorophosphate complex, sulphate and nitrate anions are different. The doubly charged sulphate is able to disrupt the coordination sphere, but the nitrate has weak interactions with the phenanthroline (vide infra).

The $^{31}\text{P}$ NMR of all these complexes displays a singlet at -5 ppm except in the case of the sulphate anion where broad signals are observed. While the FWHM for complex 3 is 530 Hz, complex 4 exhibits a relatively sharp signal (FWHM = 360 Hz). Furthermore, the complex 3 shows minor signals at -10 ppm, indicating the presence of monodentate forms of dppe ligand. The occurrence of a relatively sharp singlet in the negative region for the other anions is in contrast to the usual observation of a broad peak between 0-10 ppm, a characteristic feature of the chelating dppe fragment. This suggests that the species in solution is not the chelated species that is found in the solid state. A bridging dppe or a chelated dppe that is exchanging rapidly on the NMR time scale with a bridging dppe describes the structure better. Since the proton NMR presents a sharp signal for the complexes, 1, 2 and 4 we suggest an equilibrium that is rapid on the NMR time scale and one that predominantly favours the structure having a bridging dppe.

Relative stabilities of complexes 1-4

NMR titration experiments were performed in order to compare relative stabilities of these interactions in the systems 1-4 (Fig. 2). It was found that the addition of the nitrate anion to the complexes 1, 2 and 3 resulted in a spectrum indicative of the formation of 4. Addition of the perchlorate ion to 4 did not result in the formation of 1. In other cases also, a similar observation was made suggesting the greatest stability for the complex formed by the nitrate anion. The structure where both phenanthroline and dppe are bound to the copper is indeed the most stable one and the nitrate is interacting with the phenanthroline in a non-covalent fashion.

Since the nitrate anion induces this change it can be inferred that a solution structure is one where two anions of uni-negative charge are comfortably encapsulated, in a dimeric complex. Nitrate anion being planar in shape and smaller in size (in terms of thermochemical radii), fits into the cavity more readily than the other anions in this series. As the solution IR studies suggest the presence of a non-coordinating nitrate ion (with a band at 1358 cm$^{-1}$), inclusion should principally result only from the non-covalent interactions, (vide infra). In other words, the presence of nitrate could drive the equilibrium towards a structure in which there is a suitable cavity.
A plausible explanation for the solution behavior of complexes 1-4

Various models can be invoked to explain the anion dependent proton and phosphorus NMR of solutions of these complexes.

a) Ionic model

As the stoichiometry of the ligands suggests, the ligands present in the complexes offer a tetrahedral coordination for Cu(I) to give a [Cu(N-N)(P-P)]⁺ coordination unit. In principle one expects no perturbation of the molecular cation, a closed shell species, by the anion. However, from the results presented it is clear that the counter anion has considerable influence on the solution behavior of the [Cu(phenanthroline)(dppe)]⁺ cation. A purely ionic model is insufficient to explain all the observations.

b) Covalent model

The counter anions might form covalent bonds to the metal centers. For such situations, it is necessary that the anion replace the Cu-N or Cu-P bonds to enter the coordination sphere. Formation of a covalent bond resulting in a five coordinate Cu(I) is highly unlikely. In this case, where multidentate ligands such as bipyridine are present, we assume the probability to be quite small. But, probably due to its high ionic charge, sulfate forms a bond to the metal center and pushes out the phenanthroline (Scheme 2). The ¹H NMR of the sulfate complex indicates free phenanthroline signals in the NMR spectrum, which is not observed in other cases. Formation of free phenanthroline can be readily explained if intrusion of the sulfate ion into the coordination sphere of copper(I) causes expulsion of phenanthroline.

c) Supramolecular model

The ³¹P NMR spectrum of complexes 1-3 suggests the presence of bridging dppe in solution. Although the solid state structure of the analogous complex in this series has a chelating dppe, possibility of having dppe in the bridging mode in solution is quite high due to dissociation in solution. As shown in Scheme 3, Cu(I) complexes possessing a chelated dppe, undergo ring opening to form a bridged species. Such dimeric complexes offer a suitable molecular cavity for ion inclusion. This might be particularly important in the case of solvents having a low-dielectric constant.

Kitagwa et al. have recently illustrated the formation of such cavities in the case [(Cu-dppe)₂[hat-(CN)₆]]²⁺ (hat refers to hexaazatriphenylene hexacarbonitrile) core. In this system, there are 3 copper atoms, situated in the molecular plane of the [hat-(CN)₆]⁻ ion. The three dppe ligands are coordinating to three Cu(I) centers in the chelating mode. Hence the six phenyl rings of the three dppe ligands create concave cavities on each side of the planar [hat-(CN)₆]⁻ unit into which two anions are trapped (Fig. 3). Similarly Pilloni et al. have shown that the [Cu₂(dpptp)₂X₂]₄ (dpptp = bis(diphenylthiophosphoryl)ferrocene) are capable of trapping anions without a covalent bond.

Along similar lines, we propose the formation of a bridged structure that would lead to a cavity in which anions are housed. It has recently come to light that the presence of a partial positive charge on carbons can result in "anion-π interactions." Highly electronegative groups on an aromatic ring like F or...
heteroatom substitution can cause sufficient depletion of electron density from the ring to aid anion complexation. In these systems, non-coordinating anions can interact with the ligand and influence the solution behavior of the molecular cation to different extents. In fact, a second possibility is along the lines of our earlier proposal based on work we had carried out with dppe complexes of copper(I). The arrangement of phenyl rings of the bridging dppe can create hydrophobic environments above and below the Cu-Pa plane that are suitable for anion encapsulation through weak C-H···π interactions. To probe the probabilities of these two interactions occurring in established structures, a database analysis was carried out with the Cambridge Structural Database (CSD).

Cambridge structural database analysis

In order to probe the generality of anion interactions with phenanthroline complexes, the database analysis included all structures having nitrate and the 1,10-phenanthroline framework. As there is only one heteroatom substitution in the ring, the number of complexes having π interactions with phenanthroline, as found with triazine is quite small as expected. Of the 122 structures containing a nitrate anion in conjunction with phenanthroline, only eight of the complexes had one of the nitrate oxygen atoms at an average distance of 3.5 Å from the ring carbons forming a π complex - as suggested by Frontera et al. (See Fig 4). However, innumerable anion-carbon short contacts i.e. anion carbon distances less than the sum of the Van der Waals distances of C and O (r_C-O ≤ 3.22 Å) were observed. The preference for the anion to reside near the carbon atom C2, rather than near other carbons, C3 or C4 is very clear. In most of the structures, the anion was found closer to carbon atom 2 (71 hits) than to any other carbon (38 hits for C3 and 47 hits for C4). The anion approaches the carbon at an acute angle with respect to the centroid X indicating the presence of the well established C-H-O interaction. Ab Initio molecular orbital calculations on phenanthroline provide an explanation for the preference exhibited by the anion for C2. Calculated charges show the presence of positively charged carbons next to the N and positive charges on all the H atoms of phenanthroline. On coordination to a positively charged metal ion, the positive charge on carbon atoms adjacent to the N atoms are enhanced but other carbons still bear a net negative charge. The utility of the database analysis was borne out by examination of systems with other anions and phenanthroline. Tetrafluoroborate, hexafluorophosphate and perchlorate also indicate a large number of short contacts with the C adjacent to the N, although the percentage of short contacts in these structures to C2 was less than that found for the nitrate ion. Surprisingly, only ten structures with sulfate and phenanthroline have been characterized. Among these structures, only four short contacts were observed between carbons of phenanthroline and sulfate oxygens.

To find out if nitrate has a greater preference for phenanthroline compared to phenyl rings as in PPh₃, a search of nitrate ion containing structures with phenyl groups were probed for short contacts. Only 134 hits (short contacts between nitrate and C of arene ring) were registered in 644 structures (containing both nitrate and phenyl groups). The reduced ratio of short contacts to number of available structures emphasizes the enhanced preference of the anion for phenanthroline in comparison with a phenyl group. Interestingly, the interaction of a nitrate with bipyridine reveals a similar trend. A detailed analysis of all anions with bipyridine and phenanthroline is underway.
Conclusions
The results suggest supramolecular interaction of the counter anion with the ligand in solution, which is an important finding. Most studies involving C-H...π interactions discuss the solid state structural data. The present results suggest that these effects persist in solution. They also point out the flexibility of the Cu(I) center in optimizing the coordination environments and the choice of ligands. The stoichiometry of the ligands, present in the [Cu(dppe)(phenanthroline)]+ series of complexes offers a tetrahedral coordination for the Cu(I) center with a [Cu(N-N)(P-P)] coordination unit. However, the solution behavior and spectroscopic features of these complexes reveal the flexibility in the structure leading to the formation of a bridged dimer in the presence of counter ions. 1H and 31P NMR experiments reveal that in solution, two anions of negative charge interact very differently from a doubly charged anion like sulfate. Apparently, the two nitrate ions can interact with the coordinated phenanthroline more effectively than the sulfate which will not be able to span the two bridged copper(I) centers present. The presence of sulfate leads to disruption of the structure by formation of covalent bonds and dissociation of the phenanthroline unit. The database study is useful in confirming the dearth of sulfate ions interacting with the phenanthroline. It also confirms the preference of the anions for the carbon adjacent to the nitrogen, which is consistent with the chemical shift Δδ in the proton attached to the same carbon.

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References
14 Cambridge Structural Database, version 5.23, April 2002. Search criteria were the following: (a) Occurrence of the 1,10-phenanthroline framework and nitrate in the structure registered a hit. (b) C-O contacts were considered short if the distance between C and O was less than 3.22 Å. (c) π interactions were those with an oxygen perpendicular to the plane of the aromatic ring at a distance of 3.5 Å.
16 Ahuja R & Samuelson A G, Unpublished results.