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Non-covalent interactions between anions and a cationic rhenium diamine complex: structural characterization of the supramolecular adducts

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The behavior of the new cationic complex [Re(CN^{t}Bu)(CO)$_3$(N–N)]$^+$ (N–N = 1,2-phenylenediamine) toward several inorganic anions (X$^-$) has been investigated both in solution (by ^{1}H NMR) and in the solid state (by X-ray diffraction), and the results show the formation of supramolecular adducts featuring N–H···X hydrogen bonds.

The hydrogen bond interactions between the N–H groups of chelated diamine ligands and the negative end of polar molecules have been found to be crucial in several instances. Thus, such interactions stabilize the pericyclic transition state proposed to occur in hydrogen transfer to ketones mediated by Noyori-type catalysts[1] and determine the nucleobase preference displayed by the anti-cancer areneruthenium complexes recently reported by Sadler.[2] Regarding solid state structures, Guilera and Steed have found that hydrogen bonds between ethylenediamine (en) N–H groups and terephthalate (tph) oxygens provide the inter-chain linkage in $[Zn(en)(tph)]_\infty$ coordination polymers.[3] The hydrogen bonds between the keto oxygens of the ester groups and the N–H groups of 1,2-phenylenediamine appear to be the major driving force in determining the observed conformation of organometallic $[Mo(CO)_2(MeOOC–C{=}C–COOMe)_2(N–N)]$ fumarate and maleate complexes.[4]

Non-covalent interactions between chelated diamines and external, *i.e.* non-coordinated, anions have been less studied, although their occurrence in the solid state was noticed in early works.[5] Very recently, Yu, Xu and coworkers reported the unusual photoelectric properties shown by $[Co(en)_3]_2(Zr_2F_{12})(SiF_6)\cdot 4H_2O$, a compound containing a hydrogen-bonded assembly of discrete $[Co(en)_3]^{3+}$, $(Zr_2F_{12})^{4-}$, and $(SiF_6)^{2-}$ ions, in which the N atoms serve as H-bond donors and the F atoms as H-bond acceptors.[6] The study of second-sphere interactions between anions and metal complexes of several ditopic ligands is an area of great current interest.[7]

We set out to devise a simple system where such interactions could be examined for the case of chelated diamines. Therefore, we focused on mononuclear complexes with a single diamine chelate. The N–H groups of amines are weak H-bond donors compared with those of amides, pyrroles, *etc*. Amine-based anion receptors are, in fact, protonated macrocyclic polyamines, which interact with anions by a combination of electrostatic attraction and hydrogen bonds (Fig. 1a illustrates the encapsulation of halide anions by the diammonium polymacrocycles termed *catapinands*, the first synthetic organic hosts for anionic species).[8] Coordination as a chelate to a cationic transition metal center closes the diamine ring and provides the positive charge. The resulting complex can be thought of as a simple model of the mentioned protonated macrocyclic polyamines (Fig. 1b).

For our study, we have targeted the new compound *fac*-[Re(CN^{t}Bu)(CO)$_3$(1,2-(NH$_2$)$_2$C$_6$H$_4$)]BAr$'_4$ (Ar$'_4$ = 3,5-bis(trifluoromethyl)phenyl) (**1**), featuring (a) 1,2-phenylenediamine ligand, more rigid than the more widely employed alkanediamines such as ethylenediamine, (b) BAr$'_4$ as counteranion, aiming to minimize its competition with the external anion for the interaction with the N–H groups[9] and, at the same time, to afford a high solubility in low-polarity organic solvents, in which the presumedly weak anion–diamine interactions could be observed, (c) a cationic metal fragment, $\{Re(CO)_3\}^+$, relatively inert regarding substitution reactions, without additional strong hydrogen-bond donor groups, and devoid of ligands able to engage in strong intra- or intermolecular hydrogen bonding with the amine N–H groups, (*i.e.*, ligands with high hydrogen-bond acceptor character). *t*-Butyl isocyanide was selected as the neutral monodentate ligand to block the remaining coordination position because (d) it cannot act as a hydrogen-bond acceptor, and (e) exploratory experiments revealed that it was more resistant to substitution by anions than other monodentate ligands such as pyridines, phosphines, *etc*. The choice of an organometallic complex with a hydrophobic periphery, and whose preparation is carried out in anhydrous organic solvents, helps to prevent the presence of molecules of water and thus to limit the complexity of the structure.

Preparation of **1** was easily accomplished from [ReBr(CO)$_5$] *via* thermal reaction with the diamine to afford [ReBr(CO)$_3$(1,2-(NH$_2$)$_2$C$_6$H$_4$)]. Reaction of this complex with silver triflate afforded [Re(OTf)(CO)$_3$(1,2-(NH$_2$)$_2$C$_6$H$_4$)], reaction of which with NaBAr$'_4$ and *t*-butyl isocyanide yielded **1** (see Scheme 1).

Compound **1** was characterized analytically and by IR and NMR (^{1}H and ^{13}C) spectroscopy. Its IR spectrum in the 2200–1800 cm^{-1} region displayed, besides the pattern diagnostic of a *fac*-M(CO)$_3$ moiety, a medium intensity band at 2187 cm^{-1} (in CH$_2$Cl$_2$ solution) due to the coordinated isocyanide.

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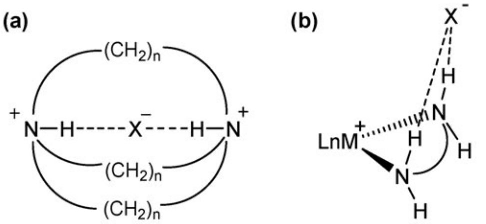
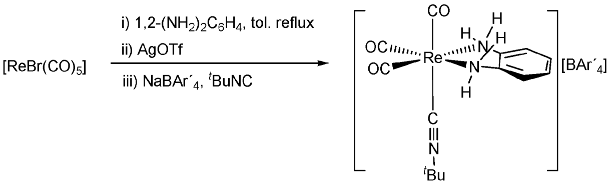


Fig. 1 Anion binding by **(a)** diammonium catapinand; **(b)** diamine cationic metal complex.

The solution behavior of **1** toward several anions (added as tetrabutylammonium salts) was studied by IR and ^1H NMR. Compound **1** was stable against ligand dissociation in the presence of Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, ReO_4^- and ClO_4^- anions. Dissociation of the monodentate isocyanide ligand (found by us in other compounds)[10] can be easily detected by IR, since free NC^tBu gives rise to a band at 2139 cm^{-1} in CH_2Cl_2 solution.

Fast anion exchange was found in every case, and the titration profiles in CD_3CN (attempts to study the anion binding in CD_2Cl_2 were thwarted by precipitation of the adducts), displayed in Fig. 2, were constructed plotting the chemical shift of the midpoint of the AA′BB′ N–H multiplet against the amount of anion added. These data were used to calculate the 1 : 1 binding constants,[11] which were found to be very small, indicating weak interactions. The relative values of the binding constants correlate with the ability of the different anions to act as H-bond acceptors (Cl^-: 77 ± 15 M^{-1}, Br^-: 48 ± 6 M^{-1}, I^-: 20 ± 2, HSO_4^-: 19 ± 2 M^{-1}, NO_3^-: 26 ± 2 M^{-1}, ReO_4^-: 24 ± 2 M^{-1}, ClO_4^-: 18 ± 3 M^{-1}). Attempts to study the behavior of **1** towards more basic anions, such as fluoride, dihydrogenphosphate or acetate led to the precipitation of a black solid and the vanishing of the ^1H NMR diamine signals, indicating decomposition of the rhenium complex. Although we have not studied this process, we note that 1,2-phenylenediamine transition metal complexes are prone to undergo redox chemistry,[12] which could account for the formation of paramagnetic, NMR-invisible species. We are not aware of previous solution studies of diamine complex–anion systems.

Single crystals of the nitrate and perchlorate adducts could be grown by slow diffusion of hexane into saturated CH_2Cl_2 solutions. The solid state structures were determined by X-ray diffraction, and the results are displayed in Fig. 3.[13] The neutral supramolecular adducts $[Re(CN^tBu)(CO)_3(1,2\text{-}(NH_2)_2C_6H_4)]\cdot NO_3$ and $[Re(CN^tBu)(CO)_3(1,2\text{-}(NH_2)_2C_6H_4)]\cdot ClO_4$ crystallized separately from the salt $[Bu_4N][BAr'_4]$, a fact previously found by us in other instances.[9] In both structures, the benzene ring of the diamine bends towards the CN^tBu ligand; thus, the bulky ^{t}Bu group does not hinder the approach of the anion to the N–H groups.



Scheme 1 Synthesis of $[Re(CN^tBu)(CO)_3(1,2\text{-}(NH_2)_2C_6H_4)]BAr'_4$ (**1**).

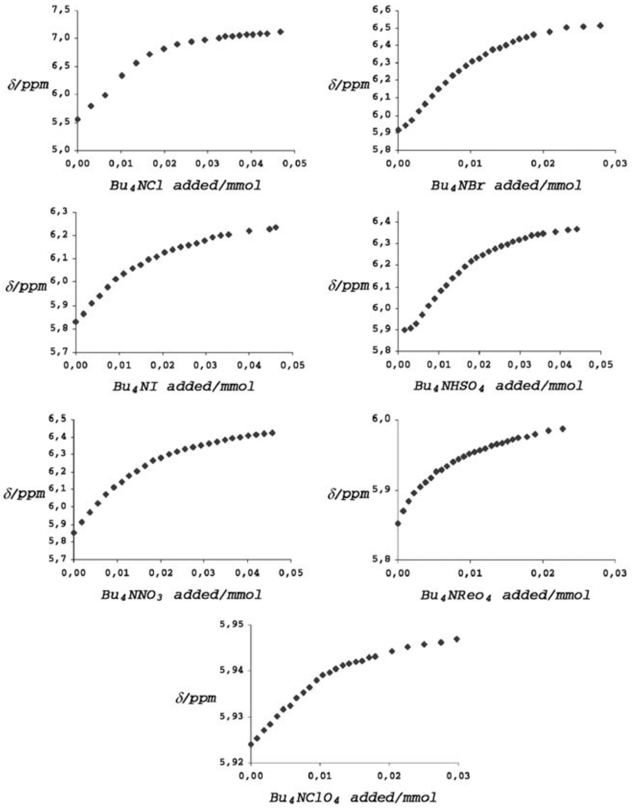


Fig. 2 ^1H NMR titration plots of compound $[Re(CN^tBu)(CO)_3(1,2\text{-}(NH_2)_2C_6H_4)]BAr'_4$ (**1**) in CD_3CN with different anions.

In the structure of the ClO_4^- adduct, each perchlorate oxygen forms hydrogen bonds with one of the N–H groups of a cationic complex, resulting in a tridimensional network (Fig. 3a). In contrast, in the structure of the NO_3^- adduct, two oxygen atoms of a nitrate anion interact each with one of the *exo*-N–H groups of a single cationic complex, forming $R^2_2(8)$ systems. The N(11)–O(11)···H = 122.9(1)°, close to the ideal value of 120°, and the small dihedral angle H···O(11)–N(11)–O(12) = 12.9(1)° suggest hydrogen bonding with the nitrate lone pair electrons.[14] As can be seen in Fig. 3b, the structure of the $[Re(CN^tBu)(CO)_3(1,2\text{-}(NH_2)_2C_6H_4)]\cdot NO_3$ unit has space group imposed mirror symmetry. The resulting $[Re(CN^tBu)(CO)_3(1,2\text{-}(NH_2)_2C_6H_4)]\cdot NO_3$ adducts are linked through hydrogen bonds between the same two oxygens and N–H groups of adjacent similar units, resulting in zigzag chains (Fig. 3b).

In summary, we have synthesized the compound *fac*-$[Re(CN^tBu)(CO)_3(1,2\text{-}(NH_2)_2C_6H_4)]BAr'_4$, designed to interact with anions by a combination of coulombic attraction and hydrogen bonds. Both in solution, where the interactions with the Bu_4N^+ salts of the anions X^- (X^- = NO_3^-, ClO_4^-) are very weak, albeit detectable, and in the solid state, the cationic complex maintains its integrity and forms 1 : 1 adducts with a number of anions. The neutral adducts $[Re(CN^tBu)(CO)_3(1,2\text{-}(NH_2)_2C_6H_4)]\cdot X$ crystallize separately from $[Bu_4N][BAr'_4]$, and their structures are dominated by the X···H–N hydrogen bonds.

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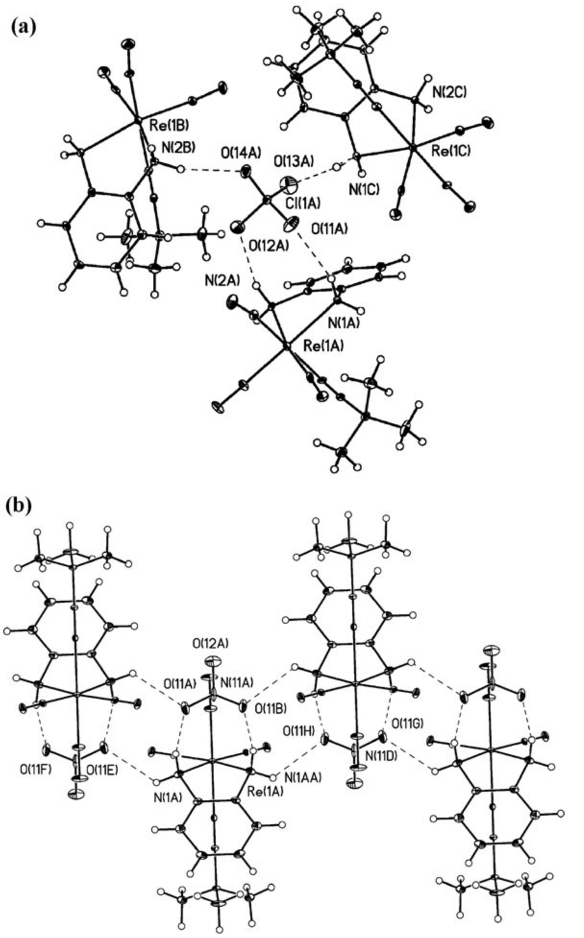

Fig. 3 (a) View of the crystalline structure of the [Re(CN^{t}Bu)(CO)$_3$(1,2-(NH$_2$)$_2$C$_6$H$_4$)] · ClO$_4$ adduct. (b) View of the zig-zag chains formed by the [Re(CN^{t}Bu)(CO)$_3$(1,2-(NH$_2$)$_2$C$_6$H$_4$)] · NO$_3$ adduct. The additional letters A in the atom labels indicate that these atoms are related to the original ones by the operation (x, $1/2 - y$, z). In both figures the probability of the thermal ellipsoids has been kept at 5% for clarity.

Experimental

All manipulations were carried out under a nitrogen atmosphere using Schlenk techniques. Tetrabutylammonium salts were purchased from Fluka or Aldrich. Deuterated acetonitrile (Cambridge Isotope Laboratories, Inc.) was stored under nitrogen in Young tubes. NMR spectra were recorded in Bruker AC-300 and DPX-300 instruments. IR solution spectra were obtained in a Perkin-Elmer FT 1720-X spectrometer using 0.2 mm CaF$_2$ cells. NMR samples were prepared under nitrogen using Kontes manifolds purchased from Aldrich. Oven-dried 5 mm NMR tubes were subjected to several vacuum–nitrogen cycles, filled with the solution of the receptor (prepared separately in a Schlenk tube, typically in a 10^{-2} M concentration in CD$_3$CN) by means of a 1 mL syringe, and stoppered with rubber septa. After the ^{1}H NMR spectrum of the receptor was recorded, successive aliquots of the tetrabutylammonium salt (typically 4×10^{-2} M in CD$_3$CN, separately prepared and kept in a septum-stoppered vial during the titration) were injected through the septum using Hamilton microsyringes (10–100 μL). Data were treated using the WinEQNMR program.[11]

Crystal structure determination

General description. A crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite monochromatized Mo Kα X-radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to $2\theta = 48.6°$. Raw frame data were integrated with the SAINT[15] program. The structures were solved by direct methods with SHELXTL.[16] An empirical absorption correction was applied with the program SADABS.[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter. Calculations were made with SHELXTL and PARST.[18]

Synthesis of [Re(CN^{t}Bu)(CO)$_3$(1,2-(NH$_2$)$_2$C$_6$H$_4$)]BAr′$_4$ (1). A mixture of [ReBr(CO)$_5$] (0.050 g, 0.123 mmol) and 1,2-phenylenediamine (0.013 g, 0.123 mmol) was refluxed in toluene (20 mL) for 4 h. The solvent was evaporated to dryness, the residue redissolved in CH$_2$Cl$_2$ (20 mL) and AgOTf (0.032 g, 0.123 mmol) was added. The resulting slurry was stirred at room temperature in the dark for 1 h and then filtered through Celite. To the colorless solution, NaBAr′$_4$ (0.109 g, 0.123 mmol) and CN^{t}Bu (0.014 mL, 0.123 mmol) were added and the mixture was stirred for 30 min. The solution was filtered by cannula, concentrated *in vacuo* and upon addition of hexane, a white microcrystalline solid precipitated. Yield: 0.095 g, 77%. IR(CH$_2$Cl$_2$): ν/cm^{-1}: 2187m (CN); 2044 s, 1962 vs, 1945 vs (CO). ^{1}H NMR (CD$_3$CN, 300 MHz): δ 7.80 [m, 8H, H$_o$ of BAr′$_4$], 7.77 [m, 4H, H$_p$ of BAr′$_4$], 7.39 [m, 4H, C$_6$H$_4$], 5.94, 5.90, 5.79, 5.75 [AA′BB′system, 4H, NH$_2$], 1.34 [s, 9H, ^{t}BuNC]. ^{13}C {^{1}H} NMR (CD$_3$CN, 300 MHz): δ 192.4 [2CO], 191.7 [CO], 161.1 [q ($^1J_{CB}$ = 49.8 Hz), C^i of BAr′$_4$], 140.5 [C$_6$H$_4$], 136.2 [C^o of BAr′$_4$], 130.4 [q ($^2J_{CF}$ = 31.9 Hz), C^m of BAr′$_4$], 129.4, 128.2 [C$_6$H$_4$], 125.9 [q ($^1J_{CF}$ = 273.5 Hz), CF$_3$ of BAr′$_4$], 119.2 [C^p of BAr′$_4$], 72.0 [(CH$_3$)$_3$*C*NC], 32.1 [CH$_3$ of ^{t}BuNC]; the ^{t}BuN*C* signal could not be observed. Anal. Calcd. for C$_{46}$H$_{29}$BF$_{24}$N$_3$O$_3$Re: C, 41.71; H, 2.21; N, 3.17. Found: C, 41.85; H, 2.09; N, 3.14%.

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13 *Crystal data*: for adduct $[\mathrm{Re(CN^{\mathit{t}}Bu)(CO)_3(1,2\text{-}(NH_2)_2C_6H_4)}]\cdot\mathrm{NO_3}$, $\mathrm{C_{14}H_{17}N_4O_6Re}$: crystal dimensions 0.14 × 0.11 × 0.06 mm^3, monoclinic, space group $P2(1)/m$, a = 9.227(4) Å, b = 10.155(4) Å, c = 10.156(4) Å, β = 106.496(7)°, V = 912.4(7) Å^3, Z = 2, T = 296(2) K, D_c = 1.906 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å), 4105 reflections collected, 1404 independent reflections (2.09 ≤ θ ≤ 23.28°), $R1$= 0.0412, w$R2$= 0.1078, GOF on F^2 =1.057. For adduct $[\mathrm{Re(CN^{\mathit{t}}Bu)(CO)_3(1,2\text{-}(NH_2)_2C_6H_4)}]\cdot\mathrm{ClO_4}$, $\mathrm{C_{14}H_{17}ClN_3O_7Re}$: crystal dimensions 0.26 × 0.10 × 0.09 mm^3, orthorhombic, space group $P2(1)2(1)2(1)$, a = 10.160(7) Å, b = 12.354(9) Å, c = 15.993(12) Å, V = 2007(3) Å^3, Z = 4, T = 296(2) K, D_c = 1.856 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å), 17956 reflections collected, 2893 independent reflections (2.08 ≤ θ ≤ 23.31°), $R1$ = 0.0452, w$R2$ = 0.1085, GOF on F^2 =1.053. The XPREP routine of SHELXTL gave R(int) = 0.094 for a monoclinic lattice with β = 90.07° , and slightly higer R(int) = 0.105 for orthorhombic space group $P2(1)2(1)2(1)$, leading to $R1$ = 0.0452, and $wR2$ = 0.1131 (all data) which are lower than those obtained in the alternative choice of monoclinic $P2(1)$ ($R1$ = 0.745, w$R2$ = 0.1839). CCDC reference numbers 292720 and 292721. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602907h.

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