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Transition Metal Chlorides Are Lewis Acids toward Terminal Chloride Attached to Late Transition Metals

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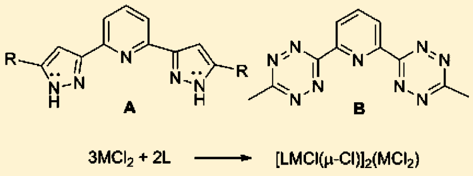
Supporting Information

ABSTRACT: Two different neutral tridentate imine-donor pincer ligands interact with excess MCl_2 (M = Co or Cu) to form compounds of the same stoichiometry, $(LMCl_2)_2{\cdot}MCl_2$, where the assembling force is the electron richness of the terminal *chlorides* on the $LMCl_2$ unit. Finite aggregation occurs for M = Co, but for M = Cu, an infinite polymeric structure is adopted, all because MCl_2 is *bifunctional*, which thus bridges multiple MCl units. The bis-pyrazolylpyridine ligand has two acidic NH protons, and both of these are involved in intramolecular hydrogen bonds. The generality of this Lewis acid aggregation is discussed.



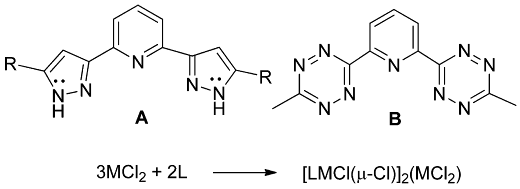
INTRODUCTION

Installation of a *single* neutral polydentate ligand L onto a late transition metal halide, to form $LMCl_n$, is frequently desired, not only to leave an empty metal coordination site in this formula but also to leave manipulable chloride (halide) functionality to be replaced with hydride, alkyl, carbene, etc. It is the purpose of this report to show that for late transition metals, where a terminal chloride ligand can retain considerable nucleophilicity due to the large number of occupied $d\pi$ orbitals,[1] available Lewis acidic MCl_n reagent can become part of the product, yielding "adducts" of composition $(LMCl_n)_x(MCl_n)_y$. While the excess MCl_n is sometimes employed to increase the rate of formation of $LMCl_n$ or to get maximum yield from valuable ligand L, the present report shows that excess MCl_n can interact directly with the primary product $LMCl_n$. This is analogous to "-ate" complex formation, $LMCl_nM'$, where M′ is an alkali metal and is held into the assembly by one or more bridging halides.[2−4]

RESULTS

d^7 Co(II) Case. Bis-pyrazolylpyridine ligand[5] L (**A** in Scheme 1, R = ^{t}Bu) is a pincer ligand with three imine donors.[6−10] Reaction of $CoCl_2$ slurried with L in THF employing a slight (10 mol %) excess of $CoCl_2$ occurs (Scheme 1) with color change within minutes at 25 °C to give a blue solution from which blue solid can be isolated by filtration followed by concentration. The ^1H NMR spectrum of the collected solid, dissolved in CD_2Cl_2, shows resonances consistent with a single product with the ligand **A** in a 2-fold symmetric environment. ^1H NMR chemical shifts range from +70 to −3 ppm, indicative of paramagnetism and thus retention of cobalt oxidation state +2. The NMR spectrum is distinct from that of monomeric $LCoCl_2$, which we characterized and will publish elswwhere. Mass spectrometry (ESI) shows the ions $L_2Co_2Cl_3^+$ and $L_2Co_2Cl_2^+$, which suggests a multimetal identity for the product but also a tendency for the assembly to be reduced in this mass spectrometer injector environment. Aggregation was confirmed by single-crystal X-ray diffraction (Figure 1) of crystals grown from CH_2Cl_2. Figure 1 shows the product to have composition $L_2Co_3Cl_6$, better written as $(LCoCl_2)_2{\cdot}CoCl_2$, to indicate that one triatomic $CoCl_2$ is the glue which links two $LCoCl_2$ into a species that has a crystallographic C_2 axis. The *di*cobalt ions detected by mass spectrometry, $L_2Co_2Cl_3^+$, the product of loss of $CoCl_3^-$, and also $L_2Co_2Cl_2^+$, both illustrate that the pincer-free cobalt acts as a halide-abstracting agent in the ionization chamber. The 2:3 L:Co chemical formula originates from this product being formed under ligand-deficient conditions. Consistent with this, the same product is formed and isolated when the reaction is repeated at the stoichiometric L:Co ratio of 2:3. Cobalt/chloride distances in the structure show a systematic lengthening from terminal on central Co (Co1) to terminal on 5-coordinate cobalt (Co2) to bridging, with distances involving the four-coordinate cobalt center being shorter. Bond lengths and angles in the analogous monomeric $L'CoCl_2$ cobalt complex lacking the ring tBu substituents are very similar, and the Co−Cl distance is the average of the two distances to Co2 here.[11] The Co/N distances and trans N−Co−N angles in $L'CoCl_2$ differ negligibly from those in $(LCoCl_2)_2{\cdot}CoCl_2$. The tau value for the 5-coordinate Co here is 0.597, thus half-way between trigonal bipyramidal and square pyramidal. Each

Scheme 1



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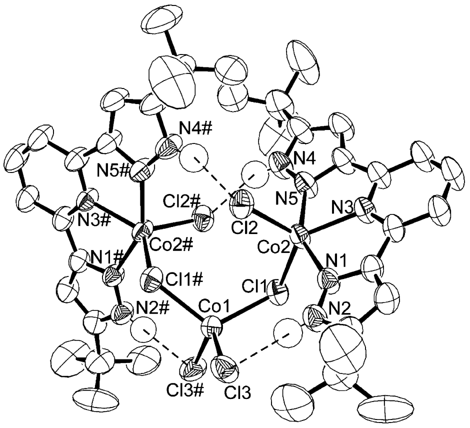

Figure 1. ORTEP view (50% probabilities) of the nonhydrogen atoms of $[(L)CoCl_2]_2(CoCl_2)$. Unlabeled atoms are carbons. Atoms labeled # are derived by a crystallographic C_2 axis of symmetry, and that axis is vertical in this view. Dashed lines are hydrogen bonds to H (open circles) on N. Selected structural parameters: Co1−Cl3, 2.2596(11) Å; Co1−Cl1, 2.3000(10) Å; Co2−N3, 2.056(3) Å; Co2−N5, 2.129(3) Å; Co2−N1, 2.139(3) Å; Co2−Cl2, 2.2706(12) Å; Co2−Cl1, 2.3391(11) Å; Cl3−Co1−Cl3#1, 113.62(7)°; Cl3−Co1−Cl1, 106.16(4)°; Cl3#1−Co1−Cl1, 107.72(4)°; Cl1−Co1−Cl1#1, 115.69(6)°; N5−Co2−N1, 151.61(12)°; N3−Co2−Cl2, 115.40(10)°; N5−Co2−Cl2, 98.65(11)°; N1−Co2−Cl2, 96.87(9)°; N3−Co2−Cl1, 128.82(10)°; N5−Co2−Cl1, 96.11(10)°; N1−Co2−Cl1, 98.33(9)°; Cl2−Co2−Cl1, 115.78(4)°; Co1−Cl1−Co2, 110.89(4)°.

pincer has two NH protons, and the whole molecule has four terminal chlorides. These functionalities are thus highly complementary for hydrogen bonding, and indeed, each NH group is within hydrogen-bonding distance to one terminal chloride. Hydrogen bonding is a general feature of bis-pyrazolylpyridine ligands.[5,12,13] These intramolecular interactions dictate the *conformation* of the terminal $LCoCl_2$ complexes around the central $CoCl_2$ linker unit and contribute to the overall stability of this aggregate. They also further confirm the nucleophilicity of the chloride attached to high d electron count metals. A different form of hydrogen bonding, intermolecular, exists in $L'CuCl_2$.

d^9 Cu(II) Case. The Lewis base bis-2,6-tetrazinyl pyridine, btzp, is a pincer ligand (**B**, Scheme 1) also carrying imine donors but far less electron rich than the bis-pyrazolylpyridine, due to the large complement of imine nitrogens in a tetrazine. Ligand **B** also lacks appropriate hydrogens needed to be a hydrogen-bond donor. Compared to cobalt above, analogous Lewis acid behavior occurs with this pincer ligand and Cu(II), but here the structure is even more complicated than for cobalt, due to an apparent tendency of copper to adopt a higher coordination number than Co(II); this makes copper a linker of higher dimensionality.

Reaction of btzp with anhydrous $CuCl_2$ (mole ratio 1:2) in acetonitrile occurs (Scheme 1) within minutes at 25 °C. Slow evaporation of that solution yields crystals shown by X-ray diffraction to be $[(btzp)CuCl_2]_2(CuCl_2)\cdot 2MeCN$ (Figure 2); hence, all coppers are divalent.

Repeating the synthesis with a 2:3 btzp:Cu ratio gives this same product. The divalent copper character is further established by the range of ^1H NMR chemical shifts, from +50 to +7.9 ppm. The ^1H NMR spectrum of this single product is distinct from that of the simpler 1:1 btzp:Cu(II) complex $(btzp)CuCl_2$, which will be published separately. The ESI mass spectrum of this compound in MeCN shows only $Cu(btzp)_2^+$; this observed ligand redistribution is consistent with aggregation in the fundamental unit of this solid.

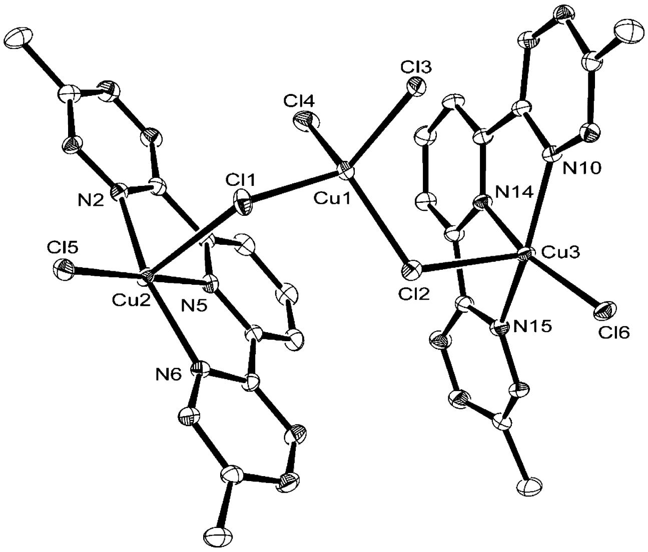

Figure 2. ORTEP view (50% probabilities) of the nonhydrogen atoms in the asymmetric unit of $[(btzp)CuCl_2]_2(CuCl_2)$. Selected structural parameters: Cu1−Cl4, 2.1961(5) Å; Cu1−Cl3, 2.2443(5) Å; Cl3−Cu2#, 2.8445(5) Å; Cu1−Cl1, 2.2637(5) Å; Cu1−Cl2, 2.2772(5) Å; Cu2−N5, 1.9585(15) Å; Cu2−N2, 2.0673(15) Å; Cu2−N6, 2.0793(15) Å; Cu2−Cl5, 2.1765(5) Å; Cu2−Cl1, 2.6416(5) Å; Cu3−N14, 1.9624(15) Å; Cu3−N10, 2.0671(16) Å; Cu3−N15, 2.0840(17) Å; Cu3−Cl6, 2.1728(5) Å; Cu3−Cl2, 2.5486(5) Å. Cl3 links onward to Cu2#, as illustrated in Figure 3 (vide infra).

The asymmetric unit of $[(btzp)CuCl_2]_2(CuCl_2)$ is composed (Figure 2) of three coppers, two pincers, and six chlorides, with metal coordination numbers of 4 (Cu1 approximately tetrahedral), 5 (Cu3), and 6 (Cu2). In general, one can imagine a Lewis acid like $CuCl_2$ binding to terminal chloride on any metal, MCl, to make M−(μ-Cl)-$CuCl_2$, and this functionality serves as a linker in the aggregation/oligomerization (Figure 3). This is also nicely consistent with the fact that the synthesis employed involves a L:Cu ratio less than 1:1, so that free Lewis acid $CuCl_2$ is available. In forming the polymer chain, $CuCl_2$ donates one chloride lone pair to another copper and accepts one chloride from a *different* copper. The polymer chain involves Cu1 and Cu2, while Cu3 donates its apical Cl2 to Cu1 on the chain, allowing Cu1 to become 4 coordinate. In summary, the polymer chain in Figure 3 is decorated by substituent Cu3 hanging outward from the chain, like a Christmas tree string of lights. Terminal CuCl distances are at least 0.04 Å shorter than those to bridging chlorides, and bridging chloride distances to copper vary widely (2.24−2.85 Å). In general, the long distances originate both from bridging functionality and also from the first-order Jahn−Teller effect, which elongates on the axis perpendicular to the Cu/pincer plane. The crystal lattice contains two acetonitrile molecules per asymmetric unit, but these merely fill holes in the lattice; together with the crystallization from acetonitrile, this shows that chloride bridging is favored over nitrile complexation in the solid lattice; *chloride* is the stronger Lewis base here. Copper to nitrogen distances vary negligibly between six-coordinate Cu2 and five-coordinate Cu3, being 1.96 Å to pyridine and 2.07 Å to tetrazine. The structure of $[(btzp)CuCl_2]_2(CuCl_2)$ shows that bridging chloride distances are exceptionally deformable, varying by 0.67 Å for $[(btzp)CuCl_2]_2(CuCl_2)$.

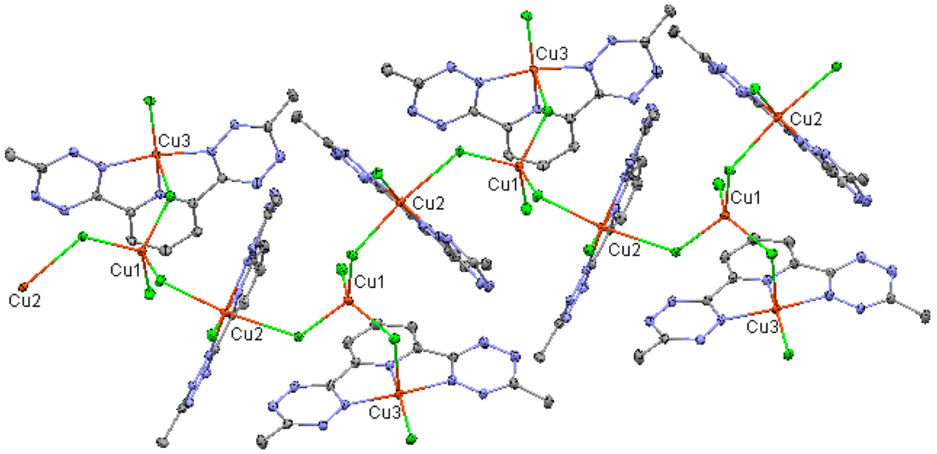

Figure 3. Mercury view of four repeat units of the polymer chain of $[(btzp)CuCl_2]_2(CuCl_2)$, showing five-coordinate Cu3 unit pendant onto the $(Cu1ClCu2Cl)_n$ polymer chain.

■ DISCUSSION

The presence of repulsive interactions between filled d orbitals and halide lone pairs leads to enhanced Lewis basicity/nucleophilicity for terminal halide in higher d electron count complexes, hence for later transition elements.[1] This same filled−filled repulsion is what makes N_2H_4 unusually Brønsted basic and the homolytic bond dissociation energy of H_2N-NH_2 or HO−OH or F_2 unusually small. This M−Cl character contrasts to early transition metal halides, which show π donation from halide lone pairs to the *attached* metal; hence, terminal halides for such d electron counts are less nucleophilic. This effect is manifest in late transition metal reactivity trends, where attempted electrophile-induced chloride removal from later transition metal complexes can fail to go to completion (i.e., fail to deposit AgCl), and instead leads to isolable $M(\mu\text{-}Cl)M'(+)$ species where M′ is Ag or Tl.[14−26] The moiety MCl_2 is a *bifunctional* or an amphoteric reagent (M seeks a coordination number of at least 4), so it does more than simply bind to one chloride, as does $SnCl_2$ toward any M−Cl unit. MCl_2 is thus a linker and one which can be paramagnetic. For comparison, the homometallic adduct formation described here might be useful as a synthetic intermediate for installing a distinct type of ligand, giving $[LMCl_n][L'MCl_n]$, or comprising new materials whose magnetic properties and electrical conductivity might be exploited, including for sensors. Because we demonstrate these concepts here with two very different kinds of ligands, with and without the presence of hydrogen bonds, these principles are likely to be generally applicable.[27−31]

Other examples of his phenomenon also warrant mention. Monatomic nitride, N^{3-}, and oxide, O^{2-}, ligands typically interact with Lewis acidic alkali metal cations, and there is growing evidence that interaction with higher charged cations, e.g., Sc^{3+}, can influence reactivity of these terminal ligands.[32−34] However, the behavior reported here contrasts to reactions of terpyridyl pincer ligands, which react with Lewis acidic CuX (X = halide) to often give $[L_2Cu^+][CuX_2^-]$, where Lewis acid completely *removes* halide from ligated copper.[35,36] On the other hand, reaction of $(terpy)CuCl_2$ with $HgCl_2$ gives a μ-Cl adduct[37] analogous to those reported here.

Finally, the notably different structure for the same stoichiometry observed here can be summarized in the diagrams in Scheme 2. Monomer units are designated by the metal coordination number of the two distinct monomer units *prior to* aggregation, hence “5” and “2.”

Scheme 2

As illustrated, $CoCl_2$ is only a Lewis acid, leading to finite aggregation, while $CuCl_2$ is both a Lewis acid and a halide donor (bridge former), leading to a polymer chain from which hangs an $LCuCl_2$ unit which only furnishes a chloride *donor* bridge and hence remains five coordinate in the product. Certainly the hydrogen-bonding ability in the ligand **A** also encourages finite aggregation, due to the complementarity of the number of acidic hydrogens and the number of terminal chlorides.

■ EXPERIMENTAL SECTION

General. All manipulations were carried out under an atmosphere of ultra-high-purity nitrogen using standard Schlenk techniques or in a glovebox. Solvents were purchased from commercial sources, purified using an Innovative Technology SPS-400 PureSolv solvent system or by distilling from conventional drying agents and degassed by the freeze−pump−thaw method twice prior to use. Glassware was oven dried at 150 °C overnight and flame dried prior to use. NMR spectra were recorded in various deuterated solvents at 25 °C on a Varian Inova-400 spectrometer (^{1}H 400.11 MHz). Proton chemical shifts are reported in ppm versus solvent protic impurity but referenced finally to $SiMe_4$. Mass spectrometry analyses were performed in an Agilent 6130 MSD (Agilent Technologies, Santa Clara, CA) quadrupole mass spectrometer equipped with a multimode (ESI and APCI) source. All starting materials have been obtained from commercial sources and used as received without further purification. Synthesis of ligand btzp is reported separately.[38]

$[Co(bis\text{-}pyrazolylpyridine)Cl_2]_2\cdot CoCl_2$. To a stirring slurry of anhydrous $CoCl_2$ (60.3 mg, 0.464 mmol) in 2 mL of THF was added dropwise a solution of ligand **L** (see Supporting Information), *bis*-pyrazolylpyridine (100 mg, 0.309 mmol), in 3 mL of THF. The solution becomes homogeneous within minutes of addition and exhibited a deep blue color. The solution was allowed to stir at room temperature for 2 h with no further color change. The solution was then filtered through Celite to remove any insolubles, and the solvent was removed under reduced pressure. This resulted in an analytically pure blue powder from which single crystals suitable for X-ray diffraction can be grown via slow evaporation of a concentrated solution in CH_2Cl_2; slow solvent removal is effected by coaxial vials, the inner one, 12 mm outer diameter, containing a solution with solute and the outer one, a 20 mL scintillation vial, containing stopcock grease, which slowly absorbs solvent (acting as a "solvent sponge") from the inner tube by vapor transport. Yield: quantitative. ^{1}H NMR (400 MHz, CD_2Cl_2 298 K), δ(ppm) full width at half height (Hz): 70.7(2H, 500 Hz), 32.9(2H, 750 Hz), −2.22(18H, 450 Hz); the remaining two resonances belonging to the ligand could not be located and are assumed to be too paramagnetically broadened to be detected. MS (ESI positive ion, CH_2Cl_2): *m*/*z*, 869.2 $[(L)_2Co_2Cl_3]^+$ ($C_{38}H_{50}{}^{35}Cl_3Co_2N_{10}$), 834 $[(L)Co_2Cl_2]^+$ ($C_{38}H_{50}{}^{35}Cl_2Co_2N_{10}$). Also observed were heavier chlorine isotopomers of the given ion with appropriate relative intensities.

$[Cu(btzp)Cl_2]_2\cdot CuCl_2$. Ligand btzp (6 mg, 22.45 μmol) was dissolved in 5 mL of acetonitrile and added to a stirring mixture of anhydrous $CuCl_2$ (4.53 mg, 33.68 μmol) and 5 mL of acetonitrile. The mixture was stirred for 3 h and filtered with a medium glass frit. The solvent was removed in vacuum to reveal a dark red-orange solid. Yield: quantitative. Dark red-orange crystals were grown by slow evaporation in acetonitrile. ^{1}H NMR (400 MHz, CD_3CN 298 K): 7.89 (b, 6H) 11.90 (b, 2 H, C−H Ar) 50.00 (b, 1H, C−H Ar). MS (ESI positive ion, MeCN) *m*/*z*: obsd, 597.1276, calcd, 597.1258 for $(btzp)_2Cu^+$ ($C_{22}H_{18}N_{18}{}^{63}Cu$).

ASSOCIATED CONTENT

Supporting Information

Full crystallographic and ligand synthesis details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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