Transmetallation and its Applications

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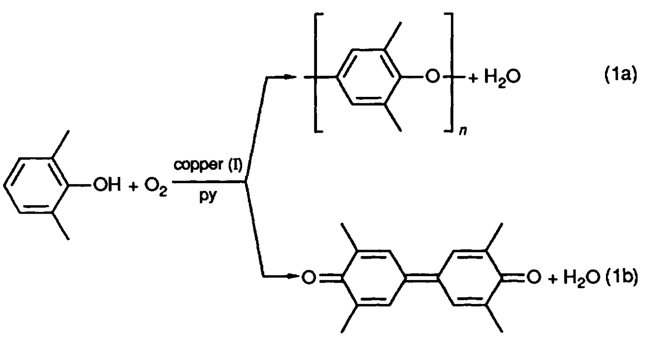
1 Copper–Oxygen Reactions

Copper(I)–O_2 reactions are crucial in Nature[1] and essential components of important industrial reactions that include the Wäcker synthesis of acetaldehyde from ethylene and the production of phenylene oxide polymers from phenols, equation 1a.[2]



In this review we describe how a systematic study of aprotic Cu^I/O_2 chemistry led to the isolation of huge families of new heteropolymetallic molecules through the accidental discovery of transmetallation.[3] Also described are the use of heteropolymetallic transmetallation products for the low-temperature synthesis of metals, alloys, and mixed metal oxides[4] and how the transmetallation phenomenon might be extended to additional elements.

Our story begins in 1976. After much effort we had managed to characterize py_2CuCl_2 and a polymeric, soluble form of copper(II) oxide, $[py_mCuO]_n$, as the products of oxidation of slurried copper(I) chloride by O_2 in neat pyridine (py).[5] This fundamental work was needed before we could investigate the mechanisms of catalytic reactions 1.[6]

Our next goal was to find ligands which give *soluble* halo(amine)copper(I) complexes that react aprotically with O_2 to give simple, isolatable oxocopper(II) products {mixtures CuCl(s)/$py_2CuCl_2/[py_mCuO]_n/py/O_2$ are mechanistically intractable}.[5,7] Hopefully, the oxocopper(II) products would be characterizable catalysts for reaction 1.

Although they are made from common materials, halo(oxo)-copper(II) complexes are uncomfortable species.[7—11] Nevertheless, we found that simple monodentate ligands N = *N,N*-diethylnicotinamide (DENC) and ethylnicotinate (ENCA) and bidentate L = *N,N,N′,N′*-tetraalkyldiamines satisfied our solubility requirements and survive coordination to strongly oxidizing oxocopper(II) centres.[7,8]

Subsequent work[9,10] describes aprotic Cu^I/O_2 chemistry that encouraged substantial new work in this important research area.[1] We learned that oxocopper(II) complexes can deprotonate substrates,[7,10] and that their ability to do so apparently depends on how the oxo groups are disposed in the overall molecular structure (Figure 1).[9—11] The oxo group disposition must depend on the ligand on copper because $[NCuX]_4O_2$ products from equation 2 do not initiate reaction 1 whereas products $py_{3,4}Cu_4X_4O_2$ are initiators.[9—11]

$$[NCuX]_4 + O_2 \rightarrow [NCuX]_4O_2 \qquad (2)$$

The different oxo group dispositions in Figure 1 are due to the oxidation mechanism. The slowest step is insertion of an O_2 molecule through one of the six faces of a $(N,py)_nCu_4X_4$ cubane and not a redox reaction. Transfer of the third electron from Cu^I_4 to O_2 breaks and O–O bond. If O_2 insertion is completed before this third electron is transferred, the result is weakly basic (μ-$O)_2N_4Cu_4X_4$ (Figure 1). On the other hand, if the leading O atom of O_2 only reaches the centre of the $(N,py)_nCu_4X_4$ cubane when the third electron is transferred, then that leading atom becomes the central μ_4-oxo group of $(\mu_4\text{-}O)py_{3,4}Cu_4X_4O$. The other O species created when the O–O bond is broken does not enter the core of $(N,py)_nCu_4X_4$ and ends up coordinated as a very basic terminal oxo group (Figure 1).[9—12]

But our work was far from complete: the primary oxocopper(II) products in Figure 1 disproportionate on attempted isolation as single crystals to $(\mu_4\text{-}O)(py,N)_4Cu_4X_6$ molecules that do not initiate reactions 1.[9—11] Excellent initiators $[LCuX]_2O$ from equation 3 are even more reactive and have never been successfully crystallized.[7—9]

$$2[LCuX]_2 + O_2 \rightarrow 2[LCuX]_2O \qquad (3)$$

Then Fortune smiled. One of us had been studying $M(NS)_n$ complexes.[13] Here, NS are monoanionic hydrazinecarbodithioate Schiff base ligands (Figure 2).[13,14] Some $M(NS)_n$ complexes have antitumour activity that can be tuned by choice of metal M and ligand NS. Their efficacy depends on $M(NS)_n$–DNA interactions.[13] DNA is a potential ligand and is basic, so $M(NS)_n$ complexes must be Lewis acids. This was confirmed by

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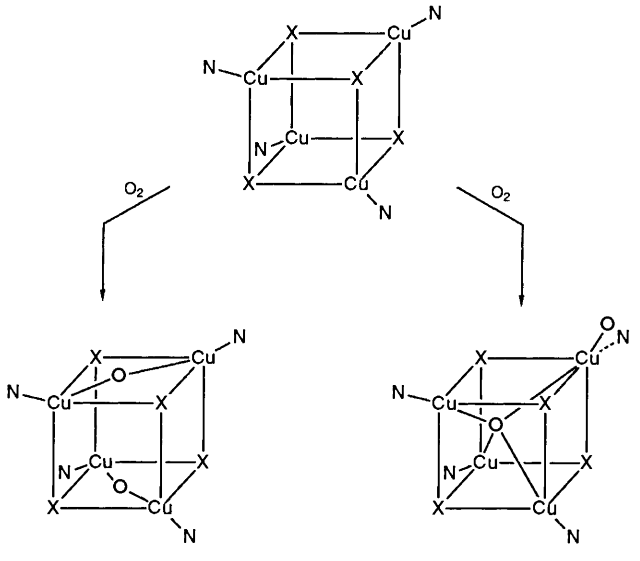

Forms stable dicarbonate
ENCA
DENC

No reaction with CO_2
py

Figure 1 Proposed alternative dioxotetracopper(II) products from the reactions of $(N,py)_mCu_4X_4$ complexes with O_2 in aprotic solvents.[10,11]

their tunable ability to form adducts with Lewis bases like pyridines.[15]

Aprotic Lewis acids $M(NS)_n$ were being studied in Alexandria and Lewis bases like $(\mu_4\text{-O})py_{3,4}Cu_4X_4O$ were being made in Boston. Perhaps these acids and bases would combine to form adducts? Adduct stability would vary with M and NS in $M(NS)_n$ and with the different proposed oxo group dispositions in Figure 1. We carefully planned a basicity scale that would differentiate oxocopper(II) core structures and ran the experiment.

2 Transmetallation

The result was completely unexpected. Instead of just adduct formation, we found stoichiometric exchange of M from $M(NS)_n$ for copper(II) in $(py,N)_mCu_4X_4O_2$[3] and $[LCuX]_2O$.[16] The reactions gave entirely new heteropolymetallic products. We called this new metal exchange phenomenon transmetallation, which is the stoichiometric replacement of the metals in a polymetallic *target* with different metals from reagents called *transmetallators*.[3] Targets are Lewis bases and transmetallators are Lewis acids.[15–17] Acid–base interactions in precursors organize metal exchange between the reactants.[16,17] *Direct* transmetallation gives heteropolymetallic products with the same number of metal centres as the target (for example, equations 4—6, 8, 9) but *fragmentation* reduces it (equation 7). *Monotransmetallation* replaces just one of several metals in a target. Targets can react *selectively* with transmetallator mixtures.[12] When the target contains more than one element, the replacement of a particular element is said to be *specific*.[17] Most importantly, transmetallation gives heteropolymetallic products that otherwise cannot be obtained.

$$(\mu_4\text{-O})N_4Cu_4X_6 + xM(NS)_2 \rightarrow (\mu_4\text{-O})N_4Cu_{4-x}M_xX_6 + xCu(NS)_2 \text{ (refs. 18, 19)} \qquad (4)$$

$$N_4Cu_4X_4 + Co(NS)_3 \rightarrow N_3Cu_3Co(NS)_2X_4 + N + Cu(NS)(s) \text{ (ref. 12)} \qquad (5)$$

$$(\mu_3\text{-O})N_3Ni_3X_4 + 2\,Co(NS)_2 \rightarrow (\mu_3\text{-O})N_3NiCo_2X_4 + 2\,Ni(NS)_2 \text{ (ref. 18)} \qquad (6)$$

$$(\mu_4\text{-O})N_4Cu_4X_6 + Hg(NS)_2 \rightarrow (\mu_3\text{-O})N_3Cu_3X_4 + HgX_2\cdot NCu(NS)_2 \text{ (ref. 18)} \qquad (7)$$

$$[LCuX]_2O + M(NS)_2 \rightarrow [LCu(X,X)ML]O + Cu(NS)_2 \text{ (ref. 16)} \qquad (8)$$

$$(\mu_3\text{-O})N_3Ni_2CoCl_4 + Zn(NS)_2 \rightarrow (\mu_3\text{-O})N_3NiCoZnCl_4 + Ni(NS)_2 \text{ (ref. 18)} \qquad (9)$$

Reactions 4 proceed in four distinct, stoichiometric steps.[17] For this reason they are sources of new heteropolymetallic molecules containing up to four different metals.[18] The first product of equation 5 is a mixed valence molecule that formally contains two copper(I), one copper(II), and one cobalt(II) centres.[12] These and other partially transmetallated complexes have useful photoemissive properties.[20] Reactions 6 and 9 demonstrate that transmetallation is not restricted to copper targets.[12,21] 'Scissor' transmetallators $M(NS)_2$ (M = Cd, Hg, or Sn) snip one corner from the targets in reactions 7, which are the only known routes to $(\mu_3\text{-O})N_3Cu_3X_4$ molecules. The latter are transmetallated to a host of new heterometallic trimers.[18] Equation 8 demonstrates that we can transmetallate catalytic[2,6,10] targets to alter catalysis mechanisms. Reaction 9 shows that direct transmetallation is specific (nickel is replaced in preference to cobalt): the first product shown contains three different metals.[18]

Subsequent work shows that the most fundamental requirements for efficient transmetallation are labile targets and transmetallators and a strong driving force for metal exchange.[17] A list of other desirable target and transmetallator characteristics has been offered.[16]

3 Major Conclusions

The metal nuclearity of neutral halo(amine)copper(I) complexes in aprotic solvents depends on the denticity of the amine ligand and the experimental conditions.[9,10] Bidentate ligands favour dimeric copper(I) complexes $[LCuX]_2$[7,16] whereas monodentate pyridines allow monomers, dimers, and tetramers to exist at different copper(I) concentrations.[10] DENC spontaneously forms invariant, soluble complexes $[NCuX]_4$ (X = Cl or Br) and has been the ligand in most of our work on tetranuclear target transmetallation.[21] Alternative core structures in Figure 1 can be differentiated by a number of means, including their patterns and products of transmetallation with $M(NS)_n$ reagents.[11,21] Transmetallation can be used to synthesize large families of entirely new heteropolymetallic molecules under mild conditions.[17,18,21] The reactions are quantitative and the products are easily separated by gel permeation chromatography.[3,19] Distinct transmetallation patterns depend on the target and transmetallator structures[11,14] and relative stabilities.[22] Transmetallation is selective[12] because of different transmetallator stabilities[22] and transmetallation rate laws.[16,17] Step-wise, site-specific transmetallation has been demonstrated.[12,13] Nucleophilic centres in the reactants organize and facilitate specific transmetallation.[16,17] The transmetallation phenomenon is not restricted to polynuclear copper targets[18,21] and is very useful for heteropolymetallic product synthesis.[21]

4 The Inherent Interest of Heteropolymetallic Molecules

Heteropolymetallic chemistry is of obvious interest for several reasons.[23] Molecular families containing different metals have inherent specific character and could catalyse specific, 'tunable' thermal or photochemical coordination and redox reactions. Communication between metals is affected by changing the metallic constitution of a molecule.[18] The availability of families with a common core structure but containing different and easily variable metals allows us to find out whether one metal knows that another is at some other molecular site. Lastly, a family of molecules, say $(\mu_4\text{-O})N_4Cu_{4-x}Ni_xX_6$, (from equation 4; $x = 0$—4), can be reduced under very mild conditions to the alloy family $Cu_{4-y}Ni_y$.[4] These alloys might function as heterogeneous catalysts that differ from materials with the same atomic proportions prepared by other methods.[24]

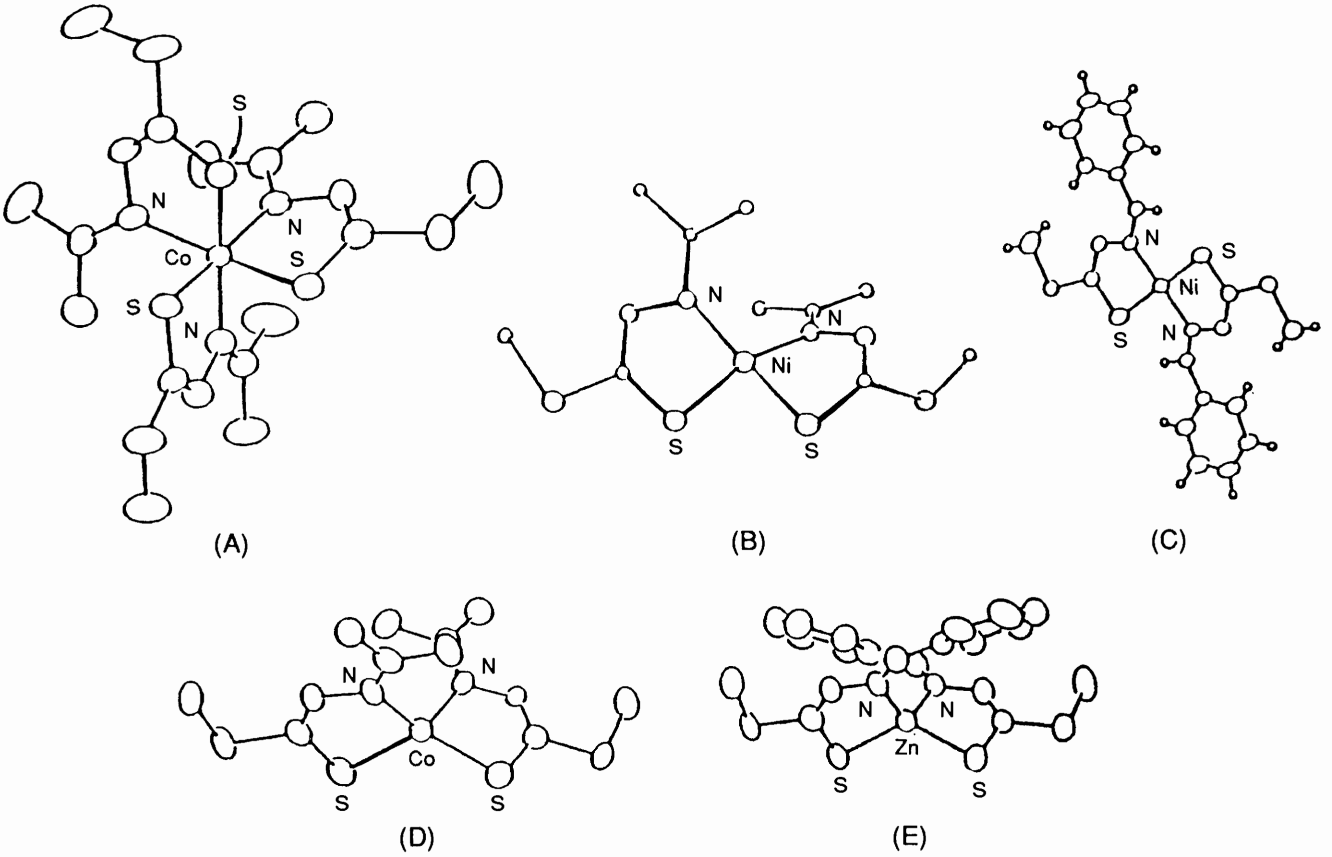

Figure 2 Molecular structures of some $M(NS)_n$ transmetallators.[14] NS is *S*-methyl isopropylidenehydrazinecarbodithioate in molecules A, B, and D and *S*-methyl benzylidenehydrazinecarbodithioate in molecules C and E.

5 Further Development of Transmetallation Chemistry

The limitations of current transmetallation and its application to alloy and mixed metal oxide synthesis are that (a) not all transmetallation reactions are direct:[21] this limits the range of uniform compositions that can be obtained from transmetallation product starting materials; (b) $(\mu_4\text{-O})N_4(M^1,M^2,M^3,M^4)_4X_6$ molecules cannot contain more than two zinc centres;[18] (c) iron–copper transmetallation reactions are slow because transmetallators $Fe(NS)_{2,3}$ and co-products $Cu(NS)_2$ have similar thermodynamic stability;[21] (d) the approach cannot easily be extended to catalytic heavy metals like M = Pd or Pt because transmetallators $M(NS)_2$ are substitution-inert and we have found no easily made, *labile* polymetallic targets containing such heavy metals. However, early indications are that dithiophosphatometal complexes $M(S_2P(OR)_2)_n$ (R = alkyl or aryl) are good alternatives to $M(NS)_n$ as transmetallators.[25] Among their advantages are easy synthesis and availability for most of the metallic elements. There are many obvious uses of heteropolymetallic molecules, alloys, and mixed metals and their oxides that contain catalytic heavy metals.[23,24,26]

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