Inorganica Chimica Acta, *217* (1994) 85–92

Transmetalation of targets (μ-Y)$N_4Cu_2{}^{I}Cu_2{}^{II}Cl_4$ and (μ-Y,μ-O)$N_4Cu_4Cl_4$ (Y=3,4,5,6-tetrachlorocatecholate) with $M(NS)_2$ reagents

Kamal Z. Ismail*,†
Department of Chemistry, University of Qatar, PO Box 2713, Doha (Qatar)

Mohamed A. El-Sayed*,† and Abdel-Mohsen Al-Kouraty
Department of Chemistry, United Arab Emirates University, PO Box 17551, Al-Ain (United Arab Emirates)

Geoffrey Davies*
Department of Chemistry and the Barnett Institute, Northeastern University, Boston, MA 02115 (USA)

(Received August 12, 1993; revised October 21, 1993)

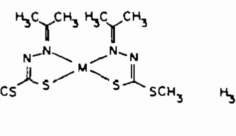
Abstract

The copper(I) molecule $[NCuCl]_4$ (N is monodentate *N,N*-diethylnicotinamide) reacts with one and two moles of 3,4,5,6-tetrachloro-1,2-benzoquinone, Cl_4BQ, in methylene chloride to give (μ-Y)$N_4Cu_2{}^{I}Cu_2{}^{II}Cl_4$ (**C**) and (μ-Y)$_2N_4Cu_4Cl_4$ (**E**), respectively, where Y is 3,4,5,6-tetrachlorocatecholate. **E** is converted to (μ-Y)$N_4Cu_2(Cu(OH))_2Cl_4$ (**F**) by reaction with water. Target **C** reacts with O_2 to give (μ-Y,μ-O)$N_4Cu_4Cl_4$ (**D**), which has distinct copper(II) sites. Reaction of **C** with equimolar *S*-methyl isopropylidenehydrazinecarbodithioate transmetalators $M(NS)_2$ (**A**(M), with M = Co, Ni and Zn in **A**(Co), **A**(Ni) and **A**(Zn), respectively) results in specific copper(I) transmetalation to give (μ-Y)$N_4Cu_2{}^{II}Cu^{I}M(NS)Cl_4$ that react with O_2 to give (μ-Y,μ-O)$N_4Cu_3MCl_4$ (**III**). The same products **III** are obtained by transmetalation of **D** with equimolar **A**(M). Progressive transmetalation of **D** with 2, 3 and 4 moles of **A**(Ni) gives particular isomers of the heteropolymetallic family (μ-Y,μ-O)$N_4Cu_{4-x}(Ni(H_2O))_xCl_4$, x = 0–4, evidently due to the *trans*-directing influence of bridging Y and oxo target groups. Direct transmetalation and isomerization/transmetalation reaction sequences that would give these products are deduced from an 'additive dimer' spectral analysis.

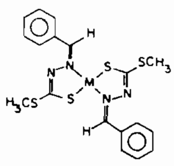
Key words: Transmetalation; Copper complexes; Transition metal complexes

Introduction

Partial or total transmetalation of polymetallic targets with *S*-methyl hydrazinecarbodithioate transmetalators **A**(M) and **B**(M) containing different metals M is a source of large families of heteropolymetallic complexes (HPM) for materials and catalytic application [1–3]. Replacement of the same metal at different target sites is specific [4–6]. *Trans*-effects across groups that bridge metal sites in a target influence the sequence of its progressive transmetalation with a fixed transmetalator [5–7]. For example, isomers **I** and **II**** are obtained from reactions (1) and (2) (N = monodentate *N,N*-diethylnicotinamide) [8, 9]. HPM **I** is the primary product of both reactions but co-product **B**(Cu) of



A(M)



B(M)

$$(\mu\text{-O})_2[NCuCl]_4 + 2\mathbf{A}(Ni) \longrightarrow$$

$$(\mu\text{-O})_2[NCuNi(H_2O)Cl_2]_2 + 2N + 2\mathbf{A}(Cu) \quad (1)$$

I

$$(\mu\text{-O})_2[NCuCl]_4 + 2\mathbf{B}(Ni) \longrightarrow$$

$$(\mu\text{-O})_2[NCuNi(H_2O)Cl_2]_2 + 2N + 2\mathbf{B}(Cu) \quad (2)$$

II

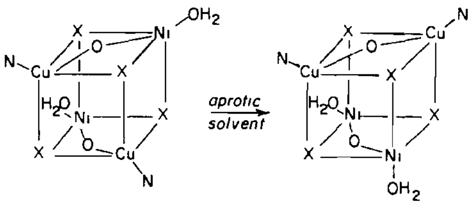
---

*Authors to whom correspondence should be addressed.

†Permanent address: Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt.

Loss of one N ligand and coordination of a water molecule by each Ni center in **I and **II** occurs during their chromatographic isolation [8, 9].

0020-1693/94/$07.00
SSDI 0020-1693(93)03746-W



I **II**

reaction (2) catalyzes isomerization of **I** to **II** [9]. Specific target metal center replacement and catalyzed isomerization are explained by kinetic evidence for transmetalation via site-specific precursor formation between the reactants [10–12]. Metal exchange in precursors gives successor complexes like **I**·**B**(Cu) that isomerize faster than **I**.

A *trans*-effect across μ-oxo groups prevents further replacement of copper(II) in **I** even with large excesses of A(Ni) in reaction (1) and co-product A(Cu) does not catalyze isomerization of **I** to **II**.

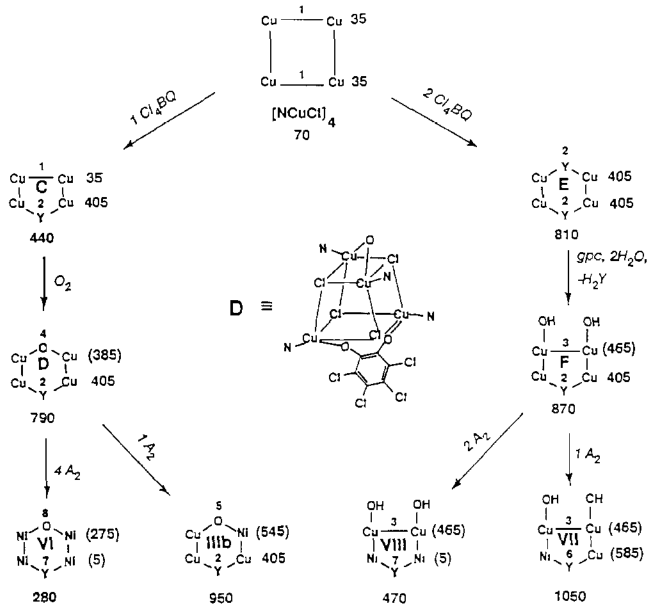
These considerations are pertinent to the transmetalation of newly discovered targets **C** and **D** from reactions (3) and (4) [13, 14]. Mixed valence target **C**

$$[NCuCl]_4 + Cl_4BQ \longrightarrow \underset{\mathbf{C}}{(\mu\text{-Y})[N_4Cu_2{}^{I}Cu_2{}^{II}Cl_4]} \qquad (3)$$

$$(\mu\text{-Y})[N_4Cu_2{}^{I}Cu_2{}^{II}Cl_4] + 1/2O_2 \longrightarrow \underset{\mathbf{D}}{(\mu\text{-Y},\mu\text{-O})N_4Cu_4{}^{II}Cl_4} \qquad (4)$$

results from oxidation of two of the four copper(I) centers in $[NCuCl]_4$ with 3,4,5,6-tetrachlorobenzoquinone, Cl_4BQ. The resulting 3,4,5,6-tetrachlorocatecholate dianion Y bridges the two copper(II) centers in **C**. Oxidation of the remaining two copper(I) centers of **C** with O_2 (eqn. (4)) gives product **D** that contains a μ-oxo group bridging two of the copper(II) centers (Scheme 1*) [13, 14].

This paper answers the following questions. (i) Is mixed valence target **C** transmetalated by reagents A(Co), A(Ni) and A(Zn)? Is copper(I) or copper(II) transmetalated first? How do the monotransmetalated** targets react with O_2? (ii) Is copper(II) in target **D** monotransmetalated by A(M)? Are the same HPM products obtained if monotransmetalated **C** is oxidized with O_2? How do the different bridging groups in **D** (Scheme 1) influence its progressive transmetalation with A(Ni) and what is the transmetalation sequence? Do any of the HPM products isomerize?



Scheme 1.

We show that (i) copper(I) in target **C** is monotransmetalated by A(M) in preference to copper(II), eqn. (5); (ii) the oxidation of a heteropolymetallic complex derived from reaction (5) gives the same HPM product (eqn. (6)) as obtained from monotransmetalation of **D**, eqn. (7); (iii) progressive transmetalation of **D** with A(Ni), eqn. (8), gives particular HPM product isomers, Scheme 2; (iv) the isolated HPM products from reactions (8) do not isomerize at significant rates.

$$\mathbf{C} + A(M) \longrightarrow (\mu\text{-Y})N_3Cu^{I}M(NS)Cu_2{}^{II}Cl_4 + N + Cu(NS)(s) \qquad (5)$$

$$(\mu\text{-Y})N_3Cu^{I}M(NS)Cu_2{}^{II}Cl_4 + N + 1/2O_2 \longrightarrow \underset{\mathbf{III}}{(\mu\text{-Y},\mu\text{-O})N_4Cu_3{}^{II}MCl_4} + 1/2N_2S_2 \qquad (6)$$

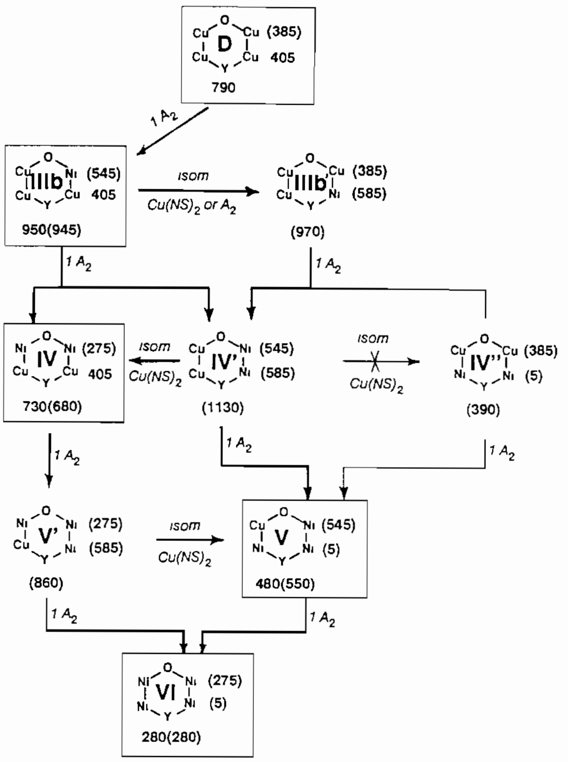
$$\mathbf{D} + A(M) \longrightarrow \mathbf{III} + A(Cu) \qquad (7)$$

$$\mathbf{D} + xA(Ni) \longrightarrow \underset{\mathbf{IIIb–VI}}{(\mu\text{-Y},\mu\text{-O})N_4Cu_{4-x}(Ni(H_2O))_xCl_4} + xA(Cu) \qquad (8)$$

---

*For clarity and later use, Schemes 1 and 2 employ symbolic structures that emphasize specific dimer units **1–8** in targets **C–F** and HPM transmetalation products **III–VIII** in methylene chloride. Each dimer has a fixed molar absorptivity E_n at 850 nm. For example, the measured molar absorptivity of target **D** in methylene chloride at 850 nm ($E_D = 790$ M^{-1} cm^{-1}, Table 2) is equated to $E_2 + E_4 = 405 + 385 = 790$ (see text). A three-dimensional representation of the symbol for **D** is shown at the center of Scheme 1. Vertical structural lines in each symbol designate two Cl bridges. Horizontal lines designate two Cl bridges when bridge units O and Y are absent. References 13 and 14 give proposed molecular structures of **C–F** that enable the symbols of proposed HPM **III–VIII** to be drawn as molecular structures.

**Monotransmetalation replaces a single target metal center with a different metal from a transmetalator [1–3].



Scheme 2.

Experimental

Materials

N,N-Diethylnicotinamide (N, Aldrich) was distilled under reduced pressure immediately before use. Copper(I) chloride was prepared from copper(II) chloride (Aldrich) as described in the literature [15]. Methylene chloride was purified as described previously [3]. High purity dinitrogen was deoxygenated by passage through a freshly activated column of Alfa DE-OX solid catalyst. Oxidant 3,4,5,6-tetrachloro-1,2-benzoquinone (Cl_4BQ, Aldrich) was used as received. Mixed valence target (μ-Y)[$N_4Cu_2^ICu_2^{II}Cl_4$] (**C**) and the product of its oxidation with O_2, (μ-Y,μ-O)$N_4Cu_4Cl_4$ (**D**), were made as previously described [13, 14]. Transmetalators **A**(Co), **A**(Ni) and **A**(Zn) (NS = monoanionic *S*-methyl isopropylidenehydrazinecarbodithioate) were obtained by literature procedures [16].

Synthesis of (μ-Y,μ-O)$N_4Cu_3MCl_4$ (M = Co, Ni and Zn in IIIa, IIIb and IIIc, respectively)

From monotransmetalation/oxidation of (μ-Y)[$N_4Cu_2^ICu_2^{II}Cl_4$] (C)

The title complexes were obtained by reaction of **C** with equimolar **A**(Co), **A**(Ni) or **A**(Zn) in deoxygenated methylene chloride, removal of precipitated co-product Cu(NS)(s), eqn. (5) [4] and oxidation of the filtrate with O_2, eqn. (6). A typical example is as follows. A stirred, clear solution of **C** [13] (5.00 mmol) in anhydrous methylene chloride (30 ml) was treated dropwise with an equimolar solution of **A**(Ni) in anhydrous methylene chloride (30 ml) under N_2. The mixture was then stirred magnetically under N_2 at 25 °C for 12 h. The product mixture was filtered by the Schlenk method to remove precipitated co-product Cu(NS)(s), which was washed with anhydrous hexane, dried at 100 °C and weighed (*Anal.* calc. for 5.00 mmol Cu(NS): 1.225 g; found: 1.180 g). The filtrate was oxidized by flushing it with excess O_2 for 20 min at 25 °C. Product **IIIb** was then purified by gel permeation chromatography on Biobeads SX-12 resin with methylene chloride as the eluant*. Solid product (μ-Y,μ-O)$N_4Cu_3(Ni(H_2O)Cl_4$ (**IIIb**) was isolated by vacuum solvent evaporation from the first eluted band. Analytical and cryoscopic molecular weight data [3] for homologous products **IIIa–IIIc** are collected in Table 1.

From oxidation/monotransmetalation of C

Products that were identical in all respects to **IIIa–IIIc** were obtained by oxidation of **C** with O_2, eqn. (4), followed by monotransmetalation of the product **D** with equimolar **A**(Co), **A**(Ni) and **A**(Zn), respectively, eqn. (7), and gel permeation chromatographic isolation (Table 1).

Synthesis of (μ-Y,μ-O)$N_4Cu_{4-x}(Ni(H_2O)_xCl_4$ (x = 1–4 in IIIb, IV, V and VI, respectively) from D (Scheme 2)

A solution of (μ-Y,μ-O)$N_4Cu_4Cl_4$ (**D**) (10.0 mmol) in anhydrous methylene chloride (25 ml) was mixed with a solution of 1, 2, 3 or 4 equiv. of nickel reagent **A**(Ni) in anhydrous methylene chloride (25 ml). The resulting solutions were stirred magnetically at 25 °C for 6 h to ensure complete reaction and then separated by gel permeation chromatography as described above. Two well-separated bands were eluted in each case. The first band gave the respective transmetalation products **IIIb**, **IV**, **V** and **VI** (Scheme 2, Table 1), which were isolated as solids by vacuum solvent evaporation. The second, black eluted band contained only transmetalation co-product **A**(Cu) from eqn. (8).

Growth of single crystals of targets **C** and **D** and of HPM products **III–VI** for X-ray structural determination was attempted with a variety of techniques. Unfortunately, only decomposition or disproportionation products were obtained from many experiments.

Physical measurements

The molecular weights of targets and transmetalation products were measured cryscopically in anhydrous nitrobenzene [3]. FT-IR spectra of HPM products **III–VI**

---

*This step removes traces of oxidized, soluble Cu(NS) as the second eluted band [4].

TABLE 1. Analytical and cryoscopic data for $(\mu\text{-Y},\mu\text{-O})N_4Cu_3MCl_4$ and $(\mu\text{-Y},\mu\text{-O})N_3Cu_{4-x}(Ni(H_2O))_xCl_4$ ($x=0$–4). Y is 3,4,5,6-tetrachlorocatecholate

Label	Complex	Analysis[a] (%)					M_r[b]
		C	H	N	Cu	M	
IIIa	$(\mu\text{-Y},\mu\text{-O})N_4Cu_3Co(H_2O)Cl_4$	39.9 (40.4)	4.0 (4.1)	8.0 (8.2)	13.6 (14.0)	4.4 (4.3)	1320±30 (1365)
IIIc	$(\mu\text{-Y},\mu\text{-O})N_4Cu_3ZnCl_4$	39.8 (40.2)	3.8 (4.1)	8.0 (8.2)	14.3 (13.9)	4.5 (4.8)	1350±30 (1365)
D	$(\mu\text{-Y},\mu\text{-O})N_4Cu_4Cl_4$[c]	39.8 (40.3)	4.2 (4.1)	7.9 (8.2)	18.1 (18.5)		1400±30 (1370)
IIIb	$(\mu\text{-Y},\mu\text{-O})N_4Cu_3(Ni(H_2O))Cl_4$	39.5 (39.9)	4.3 (4.3)	7.9 (8.1)	13.4 (13.8)	4.5 (4.2)	1340±30 (1383)
IV	$(\mu\text{-Y},\mu\text{-O})N_4Cu_2(Ni(H_2O))_2Cl_4$	39.1 (39.5)	4.1 (4.3)	7.7 (8.0)	9.4 (9.1)	8.6 (8.4)	1350±30 (1396)
V	$(\mu\text{-Y},\mu\text{-O})N_4Cu(Ni(H_2O))_3Cl_4$	38.8 (39.2)	4.2 (4.4)	7.7 (7.9)	4.8 (4.8)	12.2 (12.5)	1350±30 (1410)
VI	$(\mu\text{-Y},\mu\text{-O})N_4(Ni(H_2O))_4Cl_4$	38.5 (38.8)	4.2 (4.5)	7.7 (7.9)		16.3 (16.5)	1400±30 (1423)

[a] Calculated values in parentheses [b] Measured cryoscopically in nitrobenzene at the $3\text{–}5\times10^{-2}$ molal level [3]. [c] Data from ref. 13.

in KBr disks were measured with a Shimadzu model 8101 spectrometer at 25 °C. Their electronic spectra were recorded in methylene chloride solution in matched quartz cells with a Perkin-Elmer Lambda 4B spectrophotometer at room temperature. The maximum experimental error in molar absorptivities E is ±3%. The EPR spectra of solid samples **III**–**VI** were recorded at 100 kHz and 6.28 G modulation amplitude with a Bruker Electrospin model ESP300 spectrometer at room temperature. The incident power was 100 mW. Resonance conditions were found at *c.* 9.39 GHz (X-band).

Results and discussion

Tetranuclear copper(I) complex $[NCuCl]_4$ reacts with equimolar two-electron oxidant Cl_4BQ in methylene chloride under N_2 to give mixed valence tetranuclear complex $(\mu\text{-Y})N_4Cu_2{}^{I}Cu_2{}^{II}Cl_4$ (**C**), eqn. (3) [13, 14]. Each of the four copper centers in **C** is bridged by three Cl [13, 14, 17]. The two trigonal-bipyramidal copper(II) centers are bridged by 3,4,5,6-tetrachlorocatecholate (Y), Scheme 1. Oxidation of **C** with excess O_2 has stoichiometry $\Delta[C]/\Delta[O_2]=2.0\pm0.1$ and gives $(\mu\text{-Y},\mu\text{-O})N_4Cu_4Cl_4$ (**D**), eqn. (4). Two of the four copper(II) centers in **D** are bridged by an oxo group and the other two are bridged by Y (Scheme 1) [13, 14].

Monotransmetalation of **C** *with transmetalators* **A**(*M*)

Reactions of target **C** with transmetalators **A**(M) proceed by replacement of one of its copper(I) centers with M(NS) and co-production of 1 mol of Cu(NS)(s), which is virtually insoluble in methylene chloride [4] and can be isolated and weighed to verify the stoichiometry of reactions (5). Thus, copper(I) in mixed valence **C** is transmetalated in preference to copper(II). This preference is observed for target $N_3Cu_2{}^{I}Cu^{II}Co^{II}(NS)_2Cl]_4$ in reactions (9) but *two* copper(I) centers are replaced with **M** in those cases [4].

$$N_3Cu_2{}^{I}Cu^{II}Co^{II}(NS)_2Cl]_4+\mathbf{A}(M)\longrightarrow N_3Cu^{II}Co^{II}(NS)_2MCl_4+2Cu(NS)(s) \quad (9)$$

Dioxygen uptake experiments indicated that the first products in the filtrate from eqns. (5) react with O_2 in reaction (6) to give products $(\mu\text{-Y},\mu\text{-O})N_4Cu_3MCl_4$ (**IIIa**–**IIIc**, Table 1). Here N_2S_2 is the disulfide product of oxidation of coordinated NS [4]. This kind of behavior has been seen previously, eqn. (10) [4, 5].

$$N_3Cu_3{}^{I}M(NS)Cl_4+O_2\longrightarrow (\mu_4\text{-O},\mu\text{-O})N_3Cu_3{}^{II}MCl_4+1/2N_2S_2 \quad (10)$$

Reversing this transmetalation–oxidation sequence results in reactions (4) and (7). The products **III** of reaction (7) are identical to the products of reactions (5) and (6) with the same metal M. The difference is co-products Cu(NS)(s) and N_2S_2 from reactions (5) and (6) and co-product **A**(Cu) from reaction (7).

*Total, stepwise transmetalation of **D** with **A**(Ni)*

Spectrophotometric titration of **D** with **A**(Ni) at 575 nm revealed that the complete transmetalation of **D** requires 4 mol of **A**(Ni), eqn. (11).

$$(\mu\text{-Y},\mu\text{-O})N_4Cu_4Cl_4 + 4\mathbf{A}(Ni) \longrightarrow (\mu\text{-Y},\mu\text{-O})N_4(Ni(H_2O))_4Cl_4 + 4\mathbf{A}(Cu) \quad (11)$$

Linear absorbance increases with increasing mole ratio [**A**(Ni)]/[**D**] suggest reactions (8) (x is 1, 2, 3 or 4). These reactions actually do occur in stoichiometric steps to give tetranuclear HPM $(\mu\text{-Y},\mu\text{-O})N_3Cu_{4-x}(Ni(H_2O))_xCl_4$ ($x=1$–4 in products **IIIb** and **IV–VI**, respectively, Scheme 2 and Table 1). Stepwise, stoichiometric copper replacement is observed in reactions (12) [18] and other copper(II) target transmetalations [1, 2, 4, 5].

$$(\mu_4\text{-O})N_4Cu_4Cl_6 + x\mathbf{A}(Ni) \longrightarrow (\mu_4\text{-O})N_4Cu_{4-x}(Ni(H_2O))_xCl_6 + x\mathbf{A}(Cu) \quad (12)$$

Products **IIIb** and **IV–VI** from eqn. (8) with $x=1$–4, respectively, are easily separated from co-product **A**(Cu) by gel permeation chromatography. This procedure results in the coordination of a water molecule by each nickel center, as found in other transmetalation systems [1–6, 8–10].

*Infrared and electronic spectra of **IIIa–IIIc** and **IV–VI***

The major features of the KBr disk FT-IR spectrum of 3,4,5,6-tetrachlorobenzoquinone, Cl_4BQ, are a C=O stretching band at 1680 cm^{-1} and C=C stretching vibrations at 1510 and 1560 cm^{-1} [19]. These features are absent in targets **C**, **D** and the HPM products from reactions (3)–(5), (7) and (8), indicating the presence of 3,4,5,6-tetrachlorocatecholate Y [14], Schemes 1 and 2.

The electronic spectra of **III–VI** are listed in Table 2 and illustrated for **IIIa–IIIc** in Fig. 1 and for **D, IIIb** and **IV–VI** in Fig. 2.

Beer's law is obeyed by **C**, **D** and HPM **III–VI** in methylene chloride. Intense broad, split maxima in the 750–850 nm region and minima between 600 and 650 nm are characteristic of molecules in which each copper(II) center is bonded to three chlorine atoms [17]. This indicates 'cubane' [13, 14] structures for **III–VI** with no broken Cu^{II}–Cl bonds. HPM **III–VI** can be thought of as μ-Y and μ-oxo dimers that are bridged by chlorine (M–M means M(Cl,Cl)M when symbolized by vertical structural lines in Schemes 1 and 2, see below).

Strong, structured features are observed for five-coordinate cobalt(II) in HPM $(\mu_4\text{-O})N_4Cu_{4-x}Co_xCl_6$ when x is 2, 3 or 4, but not when x is 1 [6]. It was concluded that cobalt(II) in $(\mu_4\text{-O})N_4Cu_3Co(H_2O)Cl_6$ is six-coordinate. Weak, structureless absorption at 600 nm (Fig. 1) is consistent with the formulation $(\mu\text{-Y},\mu\text{-O})N_4Cu_3Co(H_2O)Cl_4$ for **IIIa**, Table 1.

The first step in reactions (8)

Products **III** from reactions (5)+(6) or (4)+(7) with a fixed transmetalator **A**(M) have the same electronic spectra and other properties. Specific replacement of copper(I) in **C** with M(NS), eqn. (5), leaves one copper(I) center and the M(NS) unit to react with O_2 in eqn. (6). The result of reaction (6) is linkage of the M center in **III** to copper(II) through the resulting oxo group O and not through the existing catecholate bridge Y. We thus know the first step of transmetalation of **D** by **A**(M) in eqn. (8): it results in replacement of one copper(II) in the Cu–O–Cu unit of **D** (Scheme 1) to give a M–O–Cu unit in **III** (Scheme 2, see below).

Molar absorptivities

Figure 3 shows a plot of molar absorptivities E_{III}–E_{VI} at 850 nm versus x for monotransmetalation products **III** and the homologous HPM family $(\mu\text{-Y},\mu\text{-O})N_4Cu_{4-x}(Ni(H_2O))_xCl_4$ ($x=1$–4; **IIIb** and **IV–VI**) from reactions (8). The absorptivities of **III** are in the order $E_{IIIb} > E_{IIIa} > E_{IIIc}$.

The absorptivities E of the family $(\mu_4\text{-O})N_4Cu_{4-x}(Ni(H_2O))_xCl_6$ from reactions (12) decrease linearly with x because the copper(II) centers are equivalent and electronically isolated from nickel [18]. The dashed line in Fig. 3 predicts how E_{850} would vary if this were the case for the HPM family $(\mu\text{-Y},\mu\text{-O})N_4Cu_{4-x}(M(H_2O))_xCl_4$ (M = Co, Ni, Zn). The only datum near this predicted line is for **IIIc** (M = Zn, d^{10}). Since the spectra in Figs. 1 and 2 exhibit no evidence for broken Cu–Cl bonds [8, 17], we conclude that the larger E_{850} for **IIIa** and **IIIb** are either due to slight geometric differences at Cu in the Cu–O–M when M is Co and Ni or to different extents of electronic coupling between M and Cu in the structural unit Cu–O–M. These possibilities exist for all family members $(\mu\text{-Y},\mu\text{-O})N_4Cu_{4-x}(Ni(H_2O))_xCl_4$ with $x>0$ because all their E values are larger than predicted by the dashed line in Fig. 3.

EPR spectra

The room temperature solid-state EPR spectra of **D** and **IIIb–VI** are illustrated in Fig. 4 and summarized in Table 2. These complexes display classical rhombic copper spectra that indicate trigonal–bipyramidal geometry. Solid targets **C** and **D** also have rhombic EPR spectra that become isotropic at 130 K [13, 14]. More than four hyperfine lines are observed because of the different copper(II) centers in **D** and **III** [13, 14]. HPM **V** contains a single copper center with an isotropic EPR spectrum. HPM **VI** that contains no copper is EPR inactive.

TABLE 2. Room temperature solid-state EPR and electronic spectral data for (μ-Y,μ-O)$N_4Cu_3MCl_4$ and (μ-Y,μ-O)-$N_3Cu_{4-x}(Ni(H_2O))_xCl_4$ (x=0–4). Y is 3,4,5,6-tetrachlorocatecholate

Label	Complex	EPR					λ_{max} (nm)^a (E_λ (M^{-1} cm^{-1}))
		g_1	g_2	g_3	$\langle g \rangle$	g_i	
IIIa	(μ-Y,μ-O)$N_4Cu_3Co(H_2O)Cl_4$	2.30	2.06		1.99	2.27	850 (840) 750 (900)
IIIc	(μ-Y,μ-O)$N_4Cu_3ZnCl_4$	2.48	2.06		2.02	2.19	850 (550) 750 (560)
D	(μ-Y,μ-O)$N_4Cu_4Cl_4$	2.46	2.06	1.99	2.17		850 (790) 750 (790)
IIIb	(μ-Y,μ-O)$N_4Cu_3(Ni(H_2O))Cl_4$	2.30	2.05	2.00	2.12		850 (950) 750 (890)
IV	(μ-Y,μ-O)$N_4Cu_2(Ni(H_2O))_2Cl_4$	2.32	2.06	2.00	2.13		850 (730) 750 (700)
V	(μ-Y,μ-O)$N_4Cu(Ni(H_2O))_3Cl_4$	v. weak signal					850 (480) 750 (450)
VI	(μ-Y,μ-O)$N_4(Ni(H_2O))_4Cl_4$	inactive					850 (280) 750 (250)

^{a}In methylene chloride at 25 °C.

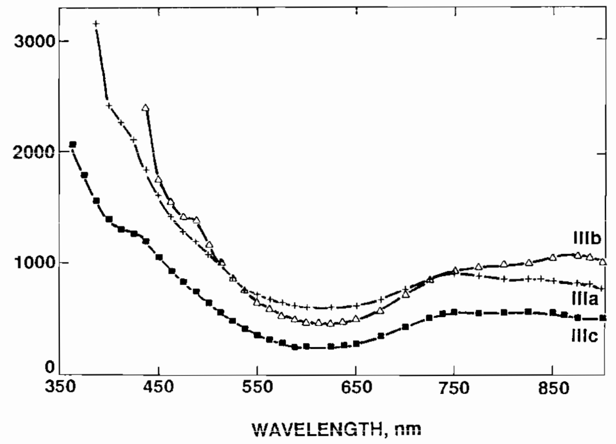


Fig. 1. Electronic spectra of **IIIa** (+), **IIIb** (△) and **IIIc** (■) in methylene chloride at 25 °C.

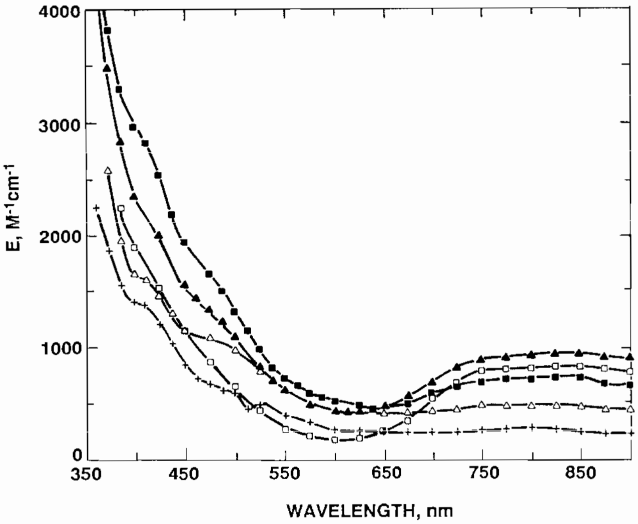


Fig. 2. Electronic spectra of **D** (□), **IIIb** (▲), **IV** (■), **V** (△) and **VI** (+) in methylene chloride at 25 °C.

Lack of EPR evidence for gross geometrical differences at copper in **III**–**VI** favors electronic coupling in M–(O, Y)–Cu structural units as the origin of the molar absorptivity variations in Fig. 3.

Product isomer assignment and pathways for reactions of D with A(Ni)

In this section we use molar absorptivity data E (M^{-1} cm^{-1}) at 850 nm to (i) identify the HPM products and (ii) investigate the sequence of reactions of **D** with 1, 2, 3 and 4 mol of **A**(Ni) (eqns. (7) and (8)).

Products **E** and **F** in Scheme 1 are made from reactions (13) and (14) (H_2Y is 3,4,5,6-tetrachlorocatechol). Products **VII** and **VIII** result from transmetalation of **F** with x=1 or 2 mol of **A**(Ni), respectively, eqn. (15) [13, 14].

$$[NCuCl]_4 + 2Cl_4BQ \longrightarrow \underset{\mathbf{E}}{(\mu\text{-}Y)_2N_4Cu_4Cl_4} \qquad (13)$$

$$\mathbf{E} + 2H_2O \longrightarrow \underset{\mathbf{F}}{(\mu\text{-}Y)N_4Cu_2(Cu(OH))_2Cl_4} + H_2Y \qquad (14)$$

$$\mathbf{F} + x\mathbf{A}(Ni) \longrightarrow (\mu\text{-}Y)N_4Cu_{2-x}(Ni(H_2O))_x\text{-}(Cu(OH))_2Cl_4 + x\mathbf{A}(Cu) \qquad (15)$$

The number under each symbolic structure in Scheme 1 is the measured molar absorptivity E at 850 nm. Our guiding principles are that (i) each tetranuclear molecule in Schemes 1 and 2 behaves as if it were two distinct

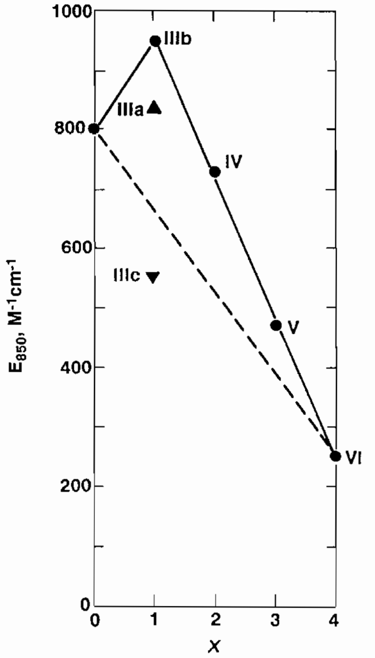


Fig. 3. Plot of E_{850} vs. x for **IIIa–IIIc** and (μ-Y,μ-O)-$N_3Cu_{4-x}(Ni(H_2O))_xCl_4$ (x=0–4: **IIIb–VI**) in methylene chloride at 25 °C. The dashed line assumes no geometrical change at copper and no electronic coupling between copper, cobalt, nickel and zinc in these complexes (see text).

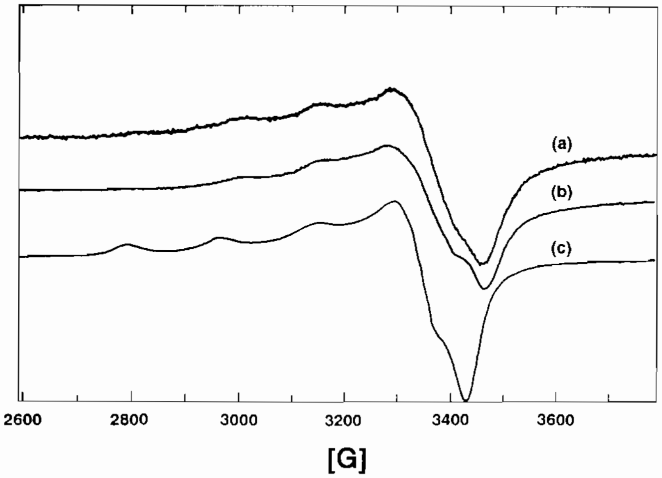


Fig. 4. Room temperature solid state EPR spectra of : (a) **IIIa**; (b) **IIIb**; (c) **IIIc**.

dimer units (e.g. 2 and 4 in molecule **D**, with $E_D = E_2 + E_4$) and (ii) each dimer unit has a fixed absorptivity E_n. $E_2 = 405$ comes from $E_{850} = 2E_2 = 810$ for molecule **E** [13]. $E_3 = E_F - E_2 = 870 - 405 = (465)$; E_3 and E_n calculated in like fashion are put in parentheses. We write eqns. (16)–(20) and use the results to discuss stepwise reactions (8) in the next section.

$$E_4 = E_D - E_2 = 790 - 405 = (385) \tag{16}$$

$$E_5 = E_{IIIb} - E_2 = 950 - 405 = (545) \tag{17}$$

$$E_6 = E_{VII} - E_3 = 1050 - (445) = (585) \tag{18}$$

$$E_7 = E_{VIII} - E_3 = 470 - (465) = (5) \tag{19}$$

$$E_8 = E_{VI} - E_7 = 280 - (5) = (275) \tag{20}$$

There are two kinds of reactions in Scheme 2. One kind is direct* transmetalation and the other is HPM isomerization [5, 8, 9].

We established earlier that monotransmetalation of **D** with A(Ni) gives isomer **IIIb**. The measured and predicted E_{850} of the proposed structure for **IIIb** (Scheme 2) are in excellent agreement.

Isomerization reaction **IIIb**→**IIIb′** could be catalyzed by transmetalation co-product A(Cu) from reactions (8). Isomer **IIIb′** might then be transmetalated by A(Ni) to give isomers **IV′** and/or **IV″** in Scheme 2. The predicted E_{850} of these isomers are much higher (1130) and much lower (390), respectively, than the measured $E_{850} = 730$ for (μ-Y,μ-O)$N_4Cu_2(Ni(H_2O))_2Cl_4$ (Table 2), which is assigned structure **IV** in Scheme 2. The calculated absorptivity of **IV** (680) is 7% less than the measured $E_{850} = 730$. This illustrates the predictive power of our 'additive dimer' approach.

Isomerization **IV″**→**IV′** sacrifices a Cu–O–Cu unit, whose formation is the likely driving force for analogous isomerization **I**→**II** [8, 9]. Isomer **IV″** is eliminated from further consideration on these grounds.

The three possible sequences of transmetalation of **D** by 2 mol of A(Ni) are then represented by reactions (21)–(23) in Scheme 2.

$$\mathbf{D} \longrightarrow \mathbf{IIIb} \longrightarrow \mathbf{IV} \tag{21}$$

$$\mathbf{D} \longrightarrow \mathbf{IIIb} \longrightarrow \mathbf{IV'} \longrightarrow \mathbf{IV} \tag{22}$$

$$\mathbf{D} \longrightarrow \mathbf{IIIb} \longrightarrow \mathbf{IIIb'} \longrightarrow \mathbf{IV'} \longrightarrow \mathbf{IV} \tag{23}$$

The first sequence requires no isomerization and is directed by the oxo group of **IIIb**, as in eqn. (1) [8, 9]. The second route requires isomerization **IV′**→**IV** that could be catalyzed by co-product A(Cu). The third route involves isomerizations **IIIb**→**IIIb′** (to make a Cu–O–Cu unit) and **IV′**→**IV** that could be catalyzed by A(Ni) and A(Cu), respectively. Isomerization **IV′**→**IV** creates a Cu–Y–Cu unit and has precedent **I**→**II** (the latter contains a Cu–O–Cu unit [8, 9]). Thus **IV′** could be an intermediate in the production of **IV**.

Reaction of **D** with 3 mol of A(Ni) gives (μ-Y,μ-O)$N_4Cu(Ni(H_2O))_3Cl_4$, with $E_{850} = 480$. We predict product isomer **V** in Scheme 2. Isomers **IV** and **IV′** are possible reaction intermediates. The three possible reaction sequences are as follows.

---

*Direct transmetalation gives HPM containing the same number of metal atoms as the target [8, 9], as observed in the present work.

$$\mathbf{D} \longrightarrow \mathbf{IIIb} \longrightarrow \mathbf{IV'} \longrightarrow \mathbf{V} \qquad (24)$$

$$\mathbf{D} \longrightarrow \mathbf{IIIb} \longrightarrow \mathbf{IIIb'} \longrightarrow \mathbf{IV'} \longrightarrow \mathbf{V} \qquad (25)$$

$$\mathbf{D} \longrightarrow \mathbf{IIIb} \longrightarrow \mathbf{IV} \longrightarrow \mathbf{V'} \longrightarrow \mathbf{V} \qquad (26)$$

Sequence (24) involves no isomerization and has **IV′** as an intermediate. Sequence (25) has the **IIIb**→**IIIb′** isomerization (see above and Scheme 2) with intermediate **IV′** directly transmetalated by **A**(Ni) to give **V** that is directly converted to final HPM family member **VI** by reaction with 1 mol of **A**(Ni). Sequence (26) involves isomerization **V′**→**V** to create an Ni–Y–Ni unit. This step could be catalyzed by co-product **A**(Cu).

The assigned product structures are given in boxes in Scheme 2 and the possible reaction sequences are heavily lined. We cannot distinguish between the sequences in Scheme 2 because **IIIb′**, **IV′** and **V′** are reaction intermediates. However, it is worth noting that they all (i) contain an Ni–Y–Cu unit and (ii) have large predicted E_{850}. The first product of reaction (15) ($x=1$) contains a Ni–Y–Cu unit with an unusually large atomic absorptivity ϵ_{850} for its copper(II) center and an unusually positive reduction potential [14].

No isomerization of IV and V

Spectrophotometric measurements indicated that **IV** has no measurable tendency to isomerize to **IV′** or **IV″** in methylene chloride. Likewise, **V** appears to be by far the more thermodynamically stable isomer of the pair **V**,**V′**.

Acknowledgements

Financial support from the National Science Foundation Grant INT-9100117 and a Barnett Innovative Research Award are gratefully acknowledged. Thanks are extended to Professor Ahmed El-Toukhy for helpful discussions and to Dr Ralph Weber of Bruker Instruments, Inc., for assistance with the EPR measurements.

This is contribution Number 586 from the Barnett Institute at Northeastern University.

References

1 G. Davies, M.A. El-Sayed and A. El-Toukhy, *Comments Inorg Chem*, *8* (1989) 203

2 G. Davies, M A. El-Sayed and A. El-Touhky, *Chem. Soc Rev.*, *21* (1992) 101; G. Davies, B.C. Giessen and H -L. Shao, *Proc. Mater Res. Soc*, *249* (1992) 87, and refs. therein; S.P. Kounaves, B. Workie, A. Robbat, Jr. and G. Davies, *J. Electrochem Soc*, submitted for publication; T.M. Abdel-Fattah, G. Davies, K.J Balkus, Jr. and J. Leiton, *J. Am Chem. Soc*, submitted for publication.

3 A. Abu-Raqabah, G. Davies, M.A. El-Sayed, A. El-Toukhy and M. Henary, *Inorg Chem*, *28* (1989) 1156.

4 G. Davies, M.A. El-Sayed, A El-Toukhy, M. Henary, T.S. Kasem and C.A. Martin, *Inorg Chem.*, *25* (1986) 3904, and refs. therein.

5 G. Davies, M A El-Sayed, A El-Toukhy, M. Henary and C.A. Martin, *Inorg Chem*, *25* (1986) 4479.

6 M. Henary, G. Davies, A. Abu-Raqabah, M.A. El-Sayed and A. El-Toukhy, *Inorg Chem*, *27* (1988) 1872, and refs. therein

7 G.-Z. Cai, G. Davies, M.A El-Sayed, A. El-Toukhy and K.D. Onan, *Inorg Chem.*, *25* (1986) 1935.

8 A El-Toukhy, G.-Z Cai, G Davies, T.R. Gilbert, K.D. Onan and M. Veidis, *J. Am Chem Soc.*, *106* (1984) 4596.

9 G.-Z. Cai, G Davies, A El-Toukhy, T.R Gilbert and M. Henary, *Inorg Chem*, *24* (1985) 1701.

10 S. Al-Shehri, G. Davies, M.A El-Sayed and A. El-Toukhy, *Inorg Chem.*, *29* (1990) 1198, 1206.

11 A Ali and G. Davies, *Inorg Chim. Acta, 177* (1990) 167; *179* (1991) 245.

12 G Davies, A Ali, S Al-Shehri, N. El-Kady, M.A. El-Sayed and A. El-Toukhy, *Qatar Univ Sci J*, *14* (1993) in press.

13 M.A. El-Sayed and G. Davies, *Inorg Chem*, *29* (1990) 4891; M.A. El-Sayed, A. El-Toukhy, K.Z. Ismail and A.A. El-Maradne, *Inorg. Chim Acta, 177* (1990) 155.

14 M.A. El-Sayed, A. El-Toukhy, K Z. Ismail, A.A. El-Maradne and G. Davies, *Inorg Chim Acta, 182* (1991) 213.

15 R.N. Keller and H.D. Wycoff, *Inorg Synth*, *2* (1946) 1.

16 K.D. Onan, G. Davies, M.A El-Sayed and A. El-Toukhy, *Inorg Chim. Acta, 113* (1986) 109, and refs. therein.

17 G. Davies, A. El-Toukhy, K D. Onan and M. Veidis, *Inorg Chim. Acta, 98* (1985) 85

18 G Davies, M.A. El-Sayed and A El-Toukhy, *Inorg Chem*, *25* (1986) 2269.

19 R.T. Conley, *Infrared Spectroscopy,* Allyn and Bacon, Boston, MA, USA, 2nd edn., 1972, p. 178