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Influence of catecholate bridges on the transmetalation of tetranuclear copper(II) complexes $[NCuCl]_4Y_2$ and $N_4Cu_4(OH)_2Cl_4Y \cdot 3H_2O$ (N = *N,N*-diethylnicotinamide; Y = 3,4,5,6-tetrachlorocatecholate) with $Ni(NS)_2$ (NS = S-methyl isopropylidenehydrazinecarbodithioate) in methylene chloride*

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Abstract

Tetranuclear copper(I) complex $[NCuCl]_4$ (N is monodentate N,N-diethylnicotinamide) reacts with 2 mol of 3,4,5,6-tetrachloro-1,2-benzoquinone (Cl_4BQ) in deoxygenated methylene chloride at room temperature to give the tetranuclear complex $[NCuCl]_4Y_2$ (VI), where Y is 3,4,5,6-tetrachlorocatecholate. Complex **VI** is converted by hydrolysis to $N_4Cu_4(OH)_2Cl_4Y \cdot 3H_2O$ **(VII)** by gel permeation chromatography on Biobeads SX-12 resin with methylene chloride as the eluent. Targets VI and **VII** are transmetalated by 1, 2, 3 or 4 mol of $Ni(NS)_2$ (NS is monoanionic S-methyl isopropylidenehydrazinecarbodithioate) to give tetranuclear products isolated as the copper-nickel homologues $N_4Cu_{4-x}Ni_x(OH)_2Cl_4Y \cdot 3H_2O$ (x = 1-4; VIII-XI, respectively). Analysis of the electronic spectra of VI-XI indicates that the copper(II)–Y centers of VII are specifically replaced by nickel from $Ni(NS)_2$. The copper(H)-Y center of $N_4Cu_3Ni(OH)_2Cl_4Y \cdot 3H_2O$ **(VIII)** has unusually high atomic absorptivity $\epsilon'_X = 580$ l (mol of copper))' cm-' at 850 nm. Isotropic EPR spectra for VI-X at room temperature indicate a flexible coordination environment for copper(II). Decreased signal intensity suggests increased molecular rigidity and stronger electronic coupling at lower temperatures. Reduction of catecholato complexes VI-X at a platinum electrode in methylene chloride containing 0.1 M tetrabutylammonium perchlorate is quasi-reversible and occurs at E^f = 0.80 and 0.63 ± 0.02 V (versus SCE) with copper(B)-Y units in VI and VII, respectively, and at 0.43 ± 0.01 V with nickel(H)-Y units in IX and X.

Introduction

Copper(I) halides, CuX, form a variety of polynuclear complexes with amines in aprotic solvents [1]. Examples are $[LCuX]_2$ [2] and $[NCuX]_4$ [3], where L and N are bidentate and monodentate amines, respectively. Aprotic oxidation of these species with dioxygen rapidly gives oxocopper(II) complexes. When.ligands N are employed, the products are tetranuclear dioxocopper(II) complexes $[NCuX]_4O_2$, eqn. (1), whose core structures and chemical properties depend on N [3, 4].

$$[NCuX]_4 + O_2 \longrightarrow [NCuX]_4O_2 \qquad (1)$$

$[NCuX]_4$ complexes also react with equimolar transmetalators $M(NS)_2$ (M = Co, Ni, Cu or Zn; NS is a monoanionic S-methyl hydrazinecarbodithioate ligand) in aprotic solvents according to eqn. (2) [5]. The monotransmetalated derivatives $N_3Cu_3M(NS)X_4$ are oxidized by dioxygen in eqn. (3) and the tetranuclear products $N_3Cu_4MX_4O_2$ can be isolated as aquocomplexes by gel permeation chromatography. A variety of evidence indicates that these products contain a third different arrangement **III** and IV of two oxo groups in a tetranuclear oxo(halo)copper(II) core structure [4, 5].

$$[NCuX]_4 + M(NS)_2 \longrightarrow N_3Cu_3M(NS)X_4 + N + Cu(NS)(s) \qquad (2)$$

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*Taken in part from A. A. El-Maradne, *M.S. Thesis,* Alexandria University, 1989.

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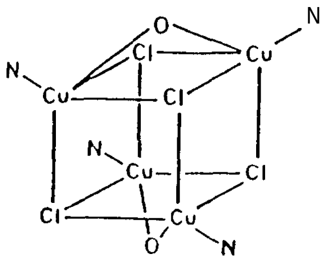

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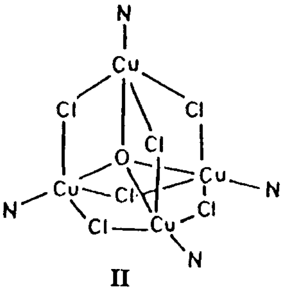

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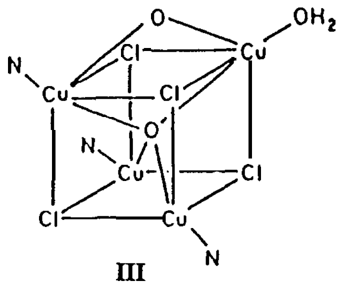

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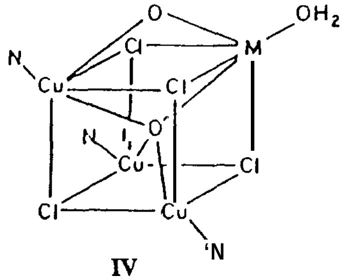

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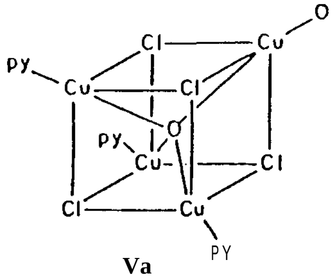

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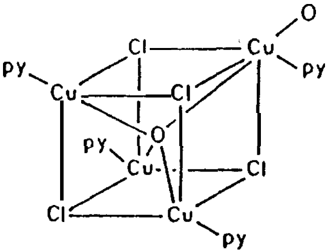


Vb

$$N_3Cu_3M(NS)X_4 + O_2 \longrightarrow N_3Cu_3MX_4O_2 + 0.5N_2S_2 \quad (3)$$

One means of distinguishing the different oxocopper(II) core structures is their behavior on transmetalation with $M(NS)_2$ reagents [4]. For example, reaction of I with excess $Ni(NS)_2$ stops when only two copper centers have been replaced [6], while structures IV (M = Co, Ni, Zn) lose 1 mol of CuO in the first transmetalation step [5, 7]. On the other hand, structures II [8, 9] and III [4] can be completely transmetalated in stoichiometric steps to give the respective tetranickel products.

Recently [10], it was reported that $[NCuX]_4$ complexes (N = *N*,*N*-diethylnicotinamide; X = Cl, Br, I) react stoichiometrically with 2 mol of 3,4,5,6-tetrahalo-1,2-benzoquinones X_4BQ (X= Cl, Br) to give tetranuclear complexes $[NCuX]_4Y_2$ in eqn. (4). Entities Y are the corresponding 3,4,5,6-tetrahalocatecholates when X in [NCuX] is Cl or Br and the corresponding semiquinones when X is I [10].

$$[NCuX]_4 + 2X_4BQ \longrightarrow [NCuX]_4Y_2 \quad (4)$$

This paper reports that the tetranuclear catecholatocopper(II) complex $[NCuCl]_4Y_2$ (VI: Y = 3,4,5,6-tetrachlorocatecholate, Cl_4Cat) reacts stoichiometrically with 1, 2, 3 or 4 mol of $Ni(NS)_2$ (NS is monoanionic S-methyl isopropylidenehydrazinecarbodithioate) to give the tetranuclear family $N_4Cu_{4-x}Ni_xCl_4Y_2$, which is isolated as the copper-nickel family $N_4Cu_{4-x}Ni_x(OH)_2Cl_4Y \cdot 3H_2O$ (VIII-XI) by gel permeation chromatography. The analytical, spectral and electrochemical properties of the new complexes VII-XI are compared and discussed.

Experimental

Materials

N,*N*-Diethylnicotinamide (N, Aldrich) was distilled under reduced pressure immediately before use. Nitrobenzene was distilled under reduced pressure from P_2O_5 and stored over 4 Å molecular sieves. High purity dinitrogen was deoxygenated by passage through a column of Alfa DE-OX solid catalyst. Copper(I) chloride was prepared as described in the literature [11]. Oxidant 3,4,5,6-tetrachloro-1,2-benzoquinone (Cl_4BQ) Aldrich) and the supporting electrolyte tetrabutylammonium perchlorate (Eastman polarographic grade) were used as received. $[NCuCl]_4Y_2$ (VI: Y = 3,4,5,6-tetrachlorocatecholate) was synthesized as described previously [10]. Transmetalator $Ni(NS)_2$ (NS = monoanionic S-methyl isopropylidenehydrazine carbodithioate) was obtained by the literature procedure [6a].

Synthesis of complexes

$N_4Cu_{4-x}Ni_x(OH)_2Cl_4Y \cdot 3H_2O$ (VII-XI: Y= Cl_4Cat; $x = 0$, 1, 2, 3 or 4)

Product $N_4Cu_4(OH)_2Cl_4Y \cdot 3H_2O$ (VII) was obtained by passing $[NCuCl]_4Y_2$ (VI, from eqn. (4)) through a Biobeads SX-12 gel permeation chromatographic column with methylene chloride as the eluent. Solid VII was isolated by evaporation of the solvent from the first, brown eluted band. Analytical and cryoscopic data are given in Table 1. The sole component of the second eluted yellow band was identified as 3,4,5,6-tetrachlorocatechol (YH_2) by microanalysis and comparison with an authentic sample (Aldrich).

Transmetalation products $N_4Cu_{4-x}Ni_x(OH)_2Cl_4Y \cdot 3H_2O$ ($x = 1$–4, complexes VIII–XI, respectively) were obtained as follows. A solution of $[NCuCl]_4Y_2$ (VI; 10 mmol) in methylene chloride (25 ml) was mixed with a solution of 1, 2, 3 or 4 equiv. of $Ni(NS)_2$ in methylene chloride (25 ml). The resulting solutions were stirred for 2 h at room temperature and then separated by gel permeation chromatography as described above. Three well separated bands were eluted in each case. The first band gave brown solid transmetalation products VIII-X or reddish brown XI (Table 1) after solvent evaporation. The second, black band contained only the transmetalation coproduct $Cu(NS)_2$ [6, 8] from eqn. (6). The third, yellow band contained 3,4,5,6-tetrachlorocatechol, YH_2. Identical products VIII-XI were obtained by reacting VII with 1, 2, 3 or 4 equiv. of $Ni(NS)_2$, respectively, using the same procedure.

Physical measurements

The electronic spectra of VI-XI in methylene chloride were measured with Beckman DK-1A and DB-G spectrophotometers in matched quartz cells at room temperature. EPR spectra of these solutions were recorded at 100 kHz and 6.28 G modulation amplitude on a Bruker Electrospin model ESP 300 spectrometer. Incident power was 100 mW. Resonance conditions were found at c. 9.39 GHz (X-band) at room temperature and 130 K. Cyclic voltammograms were recorded with a Bionanalytical Systems CV-1B instrument connected to a Honeywell model 530 X-Y recorder. A platinum working electrode (Beckman) and a platinum wire auxiliary electrode were employed in all measurements. Samples of VII-XI were dissolved in methylene chloride containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. All solutions were deoxygenated with dinitrogen and were kept under an inert atmosphere during electrochemical measurements. All potentials were measured with respect to a saturated calomel electrode, SCE and referenced to the potential of the ferrocenium/ferrocene couple (0.40 V) [12].

Results and discussion

Tetranuclear copper(I) complex $[NCuCl]_4$ reacts stoichiometrically with 2 mol of 3,4,5,6-tetrachloro-1,2-benzoquinone (Cl_4BQ) in dioxygen-free methylene chloride to give the tetranuclear bis-catecholatocopper(II) complex $[NCuCl]_4Y_2$ (VI) according to eqn. (4) [10].

Behavior of $[NCuCl]_4Y_2$ on gel permeation chromatography

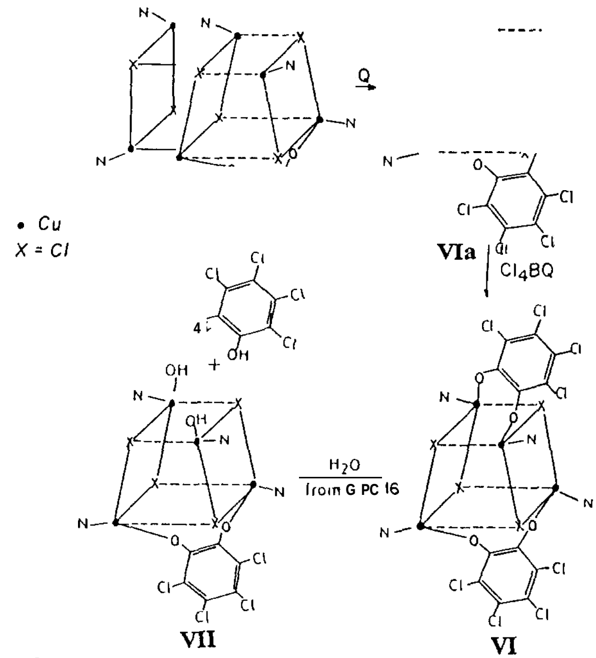
Transmetalation of copper(II) centers results in the stoichiometric exchange of other metals M from a transmetalator $M(NS)_2$ for copper and is driven by the formation of the especially stable co-product $Cu(NS)_2$ (NS = S-methyl isopropylidenehydrazinecarbodithioate). After reaction, the desired heteropolymetallic products are easily separated from $Cu(NS)_2$ by gel permeation chromatography on Bio-beads SX-12 resin with methylene chloride as the eluent [6, 8, 13].

Chromatography of VI on a flash column under dinitrogen resulted in two well-separated bands. Analytical and cryoscopic data for the first, brown band indicated the formula $N_4Cu_4(OH)_2Cl_4Y \cdot 3H_2O$ (VII; Table 1). The second band contained 3,4,5,6-tetrachlorocatechol, YH_2, which was identified by mi-

TABLE 1. Analytical **and cryoscopic data for $N_4Cu_{4-x}Ni_x(OH)_2Cl_4Y \cdot 3H_2O$ complexes (Y = Cl_4Cat)**

Label	Complex	Analysis[a] (%)						M_r[b]
		C	H	N	X	cu	Ni	
VII	$N_4Cu_4(OH)_2Cl_4Y \cdot 3H_2O$	39.5	4.2	8.0	20.1	17.7		1400 ± 30
		(38.3)	(4.4)	(7.8)	(19.7)	(17.6)		(1440)
VIII	$N_4Cu_3(OH)_2NiCl_4Y \cdot 3H_2O$	37.5	4.5	8.4	19.4	12.7	4.1	1400 ± 30
		(38.5)	(4.0)	(7.8)	(19.8)	(12.8)	(4.3)	(1440)
IX	$N_4Cu_2(OH)_2Ni_2Cl_4Y \cdot 3H_2O$	37.8	4.2	7.9	19.3	9.4	8.0	1400 ± 30
		(38.5)	(4.5)	(7.8)	(19.8)	(9.3)	(7.8)	(1430)
X	$N_4Cu(OH)Ni_3(OH)Cl_4Y \cdot 3H_2O$	37.6	4.2	7.9	19.4	4.5	12.0	1380 ± 30
		(38.7)	(4.5)	(7.9)	(19.9)	(4.6)	(12.2)	(1430)
XI	$N_4Ni_4(OH)_2Cl_4Y \cdot 3H_2O$	40.6	4.3	7.9	20.7	–	16.8	1350 ± 30
		(39.5)	(4.7)	(8.0)	(20.3)		(16.5)	(1420)

[a] Calculated values in parentheses. [b] Measured in nitrobenzene at the 3–5 × 10^{-2} molal level [3].



Scheme 1.

croanalysis. The reaction on the column is accounted for by eqn. (5)*.

$$\mathrm{VI} + 5H_2O \longrightarrow N_4Cu_4(OH)_2Cl_4Y \cdot 3H_2O\ (\mathrm{VII}) + YH_2 \qquad (5)$$

Our explanation for reaction (5) is as follows. Scheme 1 suggests that attack of the first Cl_4BQ molecule on a face of $[NCuCl]_4$ results in an increased Cu...Cu separation in that face to accommodate the requirements of the newly-created bridging catecholate ligand in mixed-valence structure **VIa**. This bridge formation causes distortion of **VIa** that reduces the Cu(I)...Cu(I) distance of the opposite face [14]. Reaction of a second Cl_4BQ molecule with this distorted face gives a strained situation in VI that can be relieved by formation of VII in hydrolysis reaction (5).

Transmetalation of tetranuclear copper(H) targets VI *and* VII *with transmetalator* $Ni(NS)_2$ *(NS = S-methyl isopropylidenehydrazinecarbodithioate)*

Targets VI and VII and transmetalator $Ni(NS)_2$ are freely soluble in methylene chloride. Reactions of VI and VII with $Ni(NS)_2$ in this solvent result in the rapid production of black co-product $Cu(NS)_2$, as observed in other copper(B) transmetalation reactions [6, 8, 9, 13].

Spectrophotometric titrations of VI and VII (1.0×10^{-4} M) with $Ni(NS)_2$ in methylene chloride at 575 nm*, in which the reactant mixtures were left overnight at room temperature to ensure complete reaction, indicated that total transmetalation of these targets requires 4 mol of $Ni(NS)_2$, eqn. (6), where **XIa** and XI are the tetranickel(II) analogues of VI and VII, respectively.

$$(\mathrm{VI\ or\ VII}) + 4Ni(NS)_2 \longrightarrow (\mathbf{XIa}\ \mathrm{or\ XI}) + 4Cu(NS)_2 \qquad (6)$$

Sequential transmetalation with $Ni(NS)_2$

Equation (7) indicates that eqn. (6) (reactant VII) proceeds in four, separate stoichiometric steps to give pure, homologous products VIII-XI with $x = 1$, 2, 3 or 4, respectively. Products VIII-XI were easily separated from co-product $Cu(NS)_2$ by gel permeation chromatography. Use of target VI in eqn. (6) and subsequent gel permeation chromatography resulted in the loss of 1 mol of 3,4,5,6-tetrachlorocatechol from primary bis-catecholate products $N_4Cu_{4-x}Ni_xCl_4Y_2$, eqn. (8), as found on chromatography of VI (eqn. (5) and Scheme 1). Analytical and cryoscopic data for isolated solid products VIII-XI are given in Table 1.

$$\mathrm{VII} + xNi(NS)_2 \longrightarrow N_4Cu_{4-x}Ni_x(OH)_2Cl_4Y \cdot 3H_2O + xCu(NS)_2 \qquad (7)$$

$$\mathrm{VI} + xNi(NS)_2 + 5H_2O \longrightarrow N_4Cu_{4-x}Ni_x(OH)_2Cl_4Y \cdot 3H_2O + xCu(NS)_2 + YH_2 \qquad (8)$$

Attempted crystallization of VI–XI

Despite many attempts with different procedures, we were unable to obtain single crystals of targets VI and VII or transmetalation products VIII-XI. The only crystals obtained were identified by microanalysis to be $(\mu_4\text{-}O)N_4Cu_4Cl_6$ (II), which is a common product of disproportionation of tetranuclear oxo(chloro)pyridine-copper(II) complexes and their transmetalated derivatives [4, 6, 9].

Electronic spectra of VI and WI

The electronic spectra of VI and VII are shown in Fig. 1. These targets exhibit similar broad maxima

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*Biobeads SX-12 resin extracts and accumulates traces of water from eluting solvents. This water is often stoichiometrically coordinated by nickel, cobalt and zinc centers during the chromatographicisolation of transmetalation products. A good example is isolation of the family $(\mu_4\text{-}O)N_4Cu_{4-x}(Ni(H_2O))_xX_6$ on chromatographic separation of the products of $(\mu_4\text{-}O)N_4Cu_4X_6/Ni(NS)_2$ reactions [8].

*Co-product $Cu(NS)_2$ is the principal absorber at 575 nm [6].

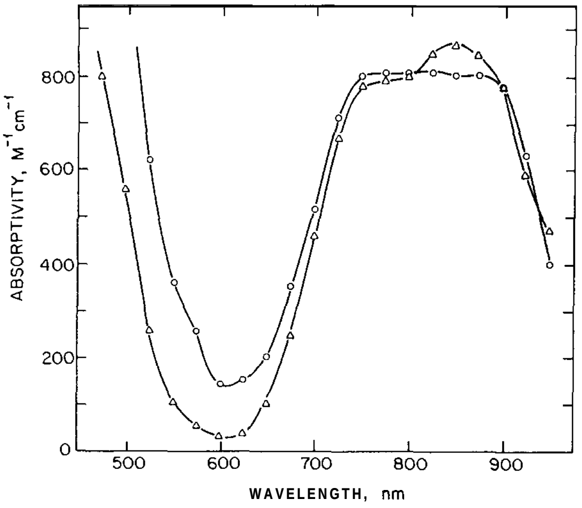


Fig. 1. Electronic spectra of $[NCuCl]_4Y_2$ (0) and $N_4Cu_4(OH)_2Cl_4Y\cdot3H_2O$ (A) in methyiene chloride at 2.5 “C.

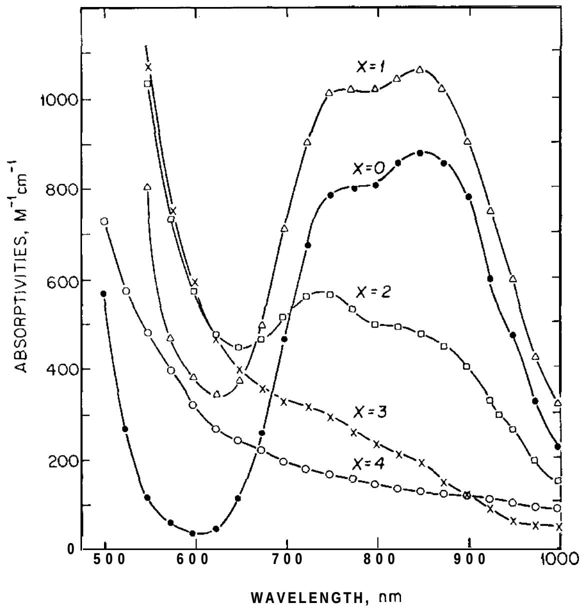


Fig. 2. Electronic spectra of $N_4Cu_{4-x}Ni_x(OH)_2Cl_4Y\cdot3H_2O$ complexes in methylene chloride at 25 “C.

TABLE 2. EPR and electronic spectral data for complexes VI-XI in methylene chloride

Complex	EPR 298 K g_i	EPR 298 K A_i (G)	EPR 130 K g_i	λ_{max} (nm) (a (M^{-1} cm-‘))
VI	2.06	78	2.07	850(810), 785(810)
VII	2.08	63	2.06	850(870), 775(795)
VIII	2.09	73	2.07	850(1050), 780(1010)
IX	2.06	63	2.07	850(470), 740(565)
X	2.08	73	2.06	850(190), 735(315)
XI’				850(120), 775(150)

“Tetranickel complex XI exhibits no absorption maxima in the region 550-900 nm (Fig. 2). Data for XI are given for comparative purposes only.

at 775 and 850 nm. The two maxima for VI have about the same molar absorptivity, while the molar absorptivity of **VII** at 850 nm is about 10% greater than that at 775 nm. These spectra are consistent with the presence of five-coordinate copper(II) coordinated to three chloro ligands [4], which points to terminal OH groups in **VII** (Scheme 1). These **Cu–OH** groups are responsible for a band at 2950 cm^{-1} in the IR spectra of VII-X.

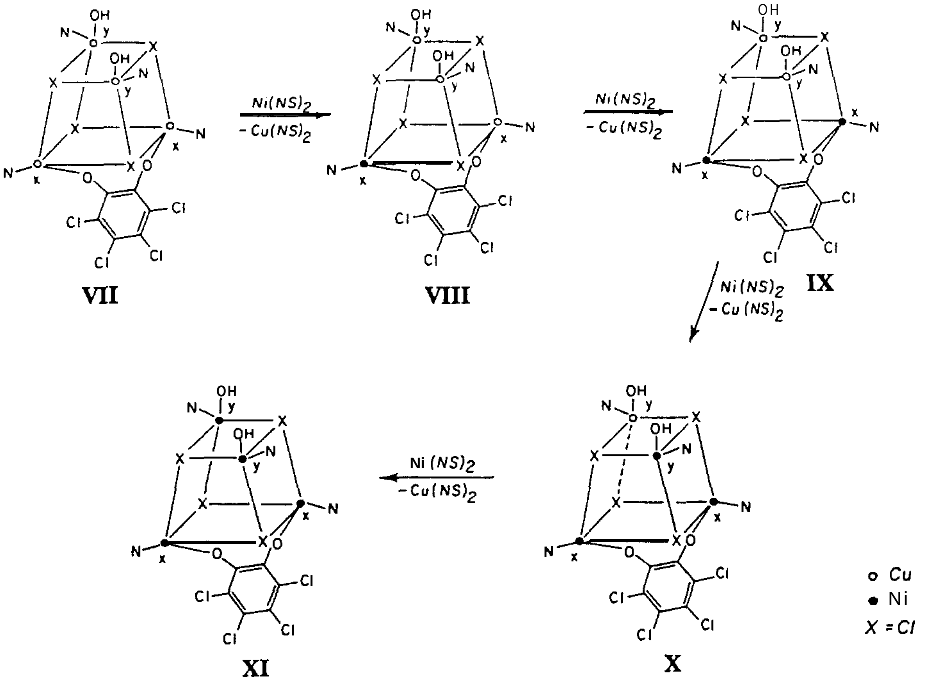
Electronic spectra of copper-nickel products VIII–XI

The electronic spectra of tetranuclear copper-nickel products VIII-XI are summarized in Table 2 and illustrated in Fig. 2. The main features of these spectra are as follows. (i) All except tetranickel(II) complex XI exhibit broad maxima in the region *735-850* nm. This indicates that pronounced absorption in this region is due to the' presence of copper(II). (ii) The spectra were invariant over long periods of time, indicating the absence of isomerization that occurs in other tetranuclear oxo(halo)pyridinecopper-nickel complexes (see below) [4, 6]. (iii) The position of the longer wavelength absorption maxima of VI-X is independent of the nickel occupancy, *x*. (iv) The wavelength of the second absorption maximum decreases with x; it is found at c. 740 nm when $x = 3$, (v) the maximum absorptivity of Cu_3Ni complex **VIII** is 24 ± 3% greater than that of Cu, target VII at 775 and 850 nm.

Spectral assignments

Increase of absorptivity on replacement of the first copper(II) center of **VII** to give **VIII** suggests that nickel(II) increases the absorptivity of a copper(II) center that shares the same catecholato bridge (Scheme 2). By contrast, replacement of a second copper(II) center in VII with nickel to give **IX** results in a 50% absorptivity decrease at 850 nm. We suggest that the two nickel centers of IX share the single catecholato bridge in this complex. This would indicate that the nickel center in **VIII** *trans*-directs replacement of copper(II) with nickel from $Ni(NS)_2$ to give **IX***. The absorptivity of X at 850 nm is 25% of that of target **VII,** indicating that the one remaining copper(OH center in X is electronically isolated (Scheme 2).

‘nuns-directing influence of one metal on replacement of another metal that shares an oxo bridge has been observed in several other transmetalation systems [9].



Scheme 2.

The Appendix contains a quantitative analysis of the observed molar absorptivities E of VI-XI at 850 and 765 nm (Table 2) in terms of atomic absorptivities for nickel and copper at the distinct sites of their proposed core structure (Scheme 2). This analysis supports the proposed transmetalation sequence and product core structures. An important finding is especially high atomic absorptivity $\epsilon_{X'} = 580$ l mol(of copper)-' cm-' at 850 nm for the copper(II)-Y center *trans* to nickel in product VIII*. The observed molar absorptivity $E_X = 190$ $M^{-1}cm^{-1}$ is lower than the calculated value. This suggests that the single copper(OH center in X has some elongated or broken Cu-Cl bonds, as proposed for other tetranuclear oxo(halo)pyridinecopper-nickel complexes with single absorption maxima centered near 700 nm (Fig. 2) [4, 6].

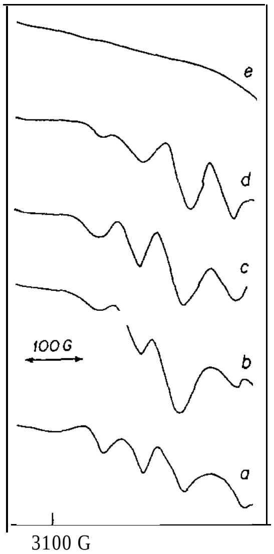


Fig. 3. EPR spectra of $N_4Cu_{4-x}Ni_x(OH)_2Cl_4Y\cdot 3H_2O$ complexes (1.0 mM) in methylene chloride at 25 “C: a, $x=0$ (VII); b, $x=1$ (VIII); c, x=2 (IX); d, x=3 (X); e, x=4 (XI). Sensitivity is 3.20 x10^5.

EPR spectra

EPR spectra for products VII-XI are summarized in Table 2 and illustrated in Figs. 3 and 4. The room temperature spectra are isotropic ($g_i =$ 2.08 fO.O1, $A_i \simeq$ 71 G (Fig. 3)). They are isotropic but of much lower intensity at 130 K (Fig. 4), as found for VI [10]. This indicates that the EPR activity of VI-X is due to the presence of five-coordinate copper(II) in a flexible coordination environment that becomes more rigid at lower temperatures [10].

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*For comparison, the atomic absorptivities of $(\mu$-$O)_2N_4Cu_4Cl_4$ (I) and $(\mu_4$-$O)N_4Cu_4Cl_6$ (II) are 180 [3] and 410 [8] 1 mol(of copper)-' cm-‘, respectively, at 850 nm.

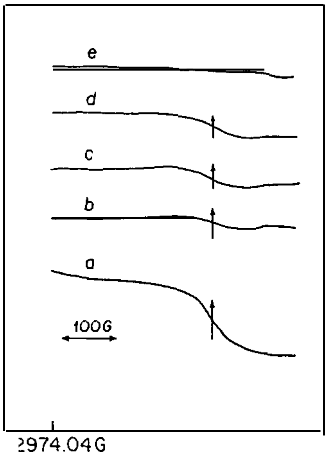

Fig. 4. EPR spectra of $N_4Cu_{4-x}Ni_x(OH)_2Cl_4Y \cdot 3H_2O$ complexes (1.0 mM) in methylene chloride at 25 °C: a, $x=0$ (VII); b, $x=1$ (VIII); c, $x=2$ (IX); d, $x=3$ (X); e, $x=4$ (XI). Sensitivity is 8.00 X 10^4.

No *isomerization of VIII-X*

Isomerization of such tetranuclear complexes as $(\mu\text{-}O)_2[NCuNi(H_2O)Cl_2]_2$ [6] and $(\mu_4\text{-}O,\mu\text{-}O)\text{-}N_3Cu_3Ni(H_2O)Cl_4$ [4] is driven by the formation of new Cu–Cl bonds and is accompanied by large absorbance increases at 850 nm. Lack of evidence for isomerization of VIII-X indicates a strong thermodynamic preference of copper(II) for the Cu–OH sites of these molecules. It is also consistent with selective transmetalation of the copper(II)–Y centers in VII and VIII by $Ni(NS)_2$.

Redox chemistry

Our previous identifications of transmetalation patterns have relied heavily on analytical and spectral data because the products disproportionate on attempted crystallization and they are electrochemically inactive. Electrochemical inactivity is unfortunate because the redox properties of homologous heteropolymetallic families are of considerable interest.

The cyclic voltammetric behavior of complexes VIII-X* ($0.3\text{–}2.1 \times 10^{-3}$ M in methylene chloride) was examined and compared with those of VI, Cl_4BQ and 3,4,5,6-tetrachlorocatecholate Y^{2-} (generated by adding a five-fold excess of pyridine to YH_2) in methylene chloride [10]. The supporting electrolyte was tetrabutylammonium perchlorate (0.1 M). Data were obtained over the scan rate range 50-200 mV s^{-1}. Typical results are shown in Fig. 5.

Voltammograms of all the analytes are quasi-reversible [15] with single anodic and cathodic peaks under our experimental conditions. The derived potentials E^f for Cl_4BQ, Y^{2-} and complexes VI-X are 0.17, 0.42, 0.80, 0.63, 0.72, 0.42 and 0.44 V versus SCE, respectively. The maximum error in these measurements is estimated to be ±0.02 V. Electrochemical irreversibility was observed to increase with increasing nickel content in VIII-X*.

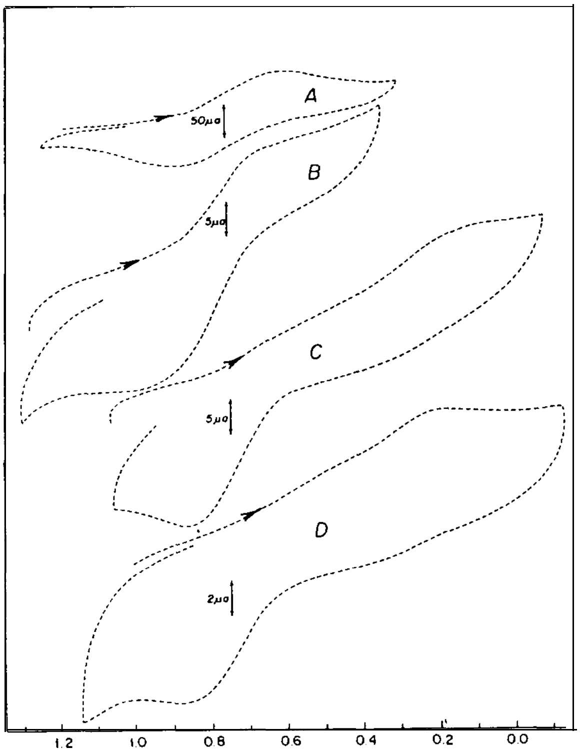

Fig. 5. Typical cyclic voltammetric data for VII (A), VIII (B), IX (C), X (D) in methylene chloride containing 0.1 M tetrabutylammonium perchlorate at 25 °C. The scan rate ν is 200 mV s^{-1} in all cases.

Changes in the forms of the voltammograms in Fig. 5 with x are another indication that the X sites of VI and VII are preferentially transmetalated by $Ni(NS)_2$. The assigned core structures of VI-X (Scheme 2) also are consistent with trends in their formal reduction potentials E^f for the following reasons. Complex $[NCuCl]_4Y_2$ (VI) contains only copper(II)–Y centers that are reduced at 0.80 V. The presence of Cu-OH units lowers E^f of all the tetramers VII-X. Only VIII contains a copper(II)–catecholate–nickel(II) unit, and its E^f is anomalously large. We recall that the copper(II) center of this particular unit also has especially high atomic absorptivity ϵ'_X (Appendix). Transmetalation products IX and X both contain a nickel(II)–catecholate–nickel(II) unit with $E^f = 0.43 \pm 0.01$ v.

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* Tetranickel complex XI exhibits no discernable anodic or cathodic peaks under our experimental conditions.

Conclusions

We have found that catecholatocopper(II) complex VII is electrochemically active and that its redox behavior is altered by substitution of nickel for copper. This implies that transmetalation is a useful means of altering the mechanisms of copper-catalyzed phenol-catechol systems, as indicated by earlier work [6a]. We are continuing to explore this chemistry and will report our findings in subsequent papers.

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Appendix

The distinct copper(II)–Y and copper(OH centers of target VII are labelled X and Y and assigned atomic absorptivities ● X and ● y l (mol of copper)-' cm-', respectively, at 850 nm. The copper(II)–Y center of **VIII** is assigned atomic absorptivity ϵ'_X l (mol of copper)-' cm-'. Nickel(II)–Y and nickel(II)-OH centers of **VIII–XI** are assigned atomic absorptivities ϵ''_X and ϵ''_Y l (mol of nickel)-' cm^{-1}, respectively, at 850 nm.

We assume that transmetalation of VII by $Ni(NS)_2$ occurs in sequence at sites X,X,Y,Y and that the above atomic absorptivities are additive. We can then write eqns. (A-l)-(A-6) for the observed molar absorptivities E $(M^{-1}$ cm-') of VI [IO]-XI at 850 nm, respectively, which are taken from Table 2.

$$E_{VI} = 4\epsilon_X = 810 \tag{A-l}$$

$$E_{VII} = 2\epsilon_X + 2\epsilon_Y = 870 \tag{A-2}$$

$$E_{VIII} = \epsilon'_X + 2\epsilon_Y + \epsilon''_X = 10.50 \tag{A-3}$$

$$E_{IX} = 2\epsilon_Y + 2\epsilon''_X = 470 \tag{A-4}$$

$$E_X = 2\epsilon''_X + \epsilon_Y + \epsilon''_Y = 190 \tag{A-5}$$

$$E_{XI} = 2\epsilon''_X + 2\epsilon'''_Y = 120 \tag{A-6}$$

Linear eqns. (A-l)-(A-6) contain five unknowns and are easily soluble as simultaneous equations to give $\epsilon_X = 203, \epsilon_Y = 232, \epsilon'_X = 580,$ ● ;=3 and $\epsilon''_Y = 57$ l (mol of metal)-' cm-'. The molar absorptivities E of **VI-XI** are then calculated to be 812, 870, 1047, 470, 295 and 120 M^{-1} cm-', respectively, at 8.50 nm. The observed and calculated E are in excellent agreement except for complex X, whose calculated E_X is c. *30%* too large. This particular complex appears to contain a copper(II) center with an atomic absorptivity at 850 nm that is less than ● y in the other complexes. However, the same analysis of molar absorptivities E of **VI-XI** at 765 nm gives a maximum discrepancy between observed and calculated E of ± *12%* with $\epsilon_X = 203, \epsilon_Y =$ 195, $\epsilon'_X = 532, \epsilon''_X = 88$ l (mol of metal)-' cm^{-1} and ϵ''_Y negligible at this wavelength.

We interpret these findings to indicate that copper at site Y in X is geometrically distorted as compared to its local environment in **VI-IX.** This particular copper center actually could be coordinated to fewer than three chloro ligands (see text).