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# Transmetalation of Tetranuclear Copper Complexes. 7. Spectral Evidence for the Substoichiometric Transmetalation of ($\mu_4$-O)[(DENC)Cu]$_4$X$_6$ Complexes (DENC = *N*,*N*-Diethylnicotinamide; X = Cl or Br) by a Ni(NS)$_2$ Reagent[1]

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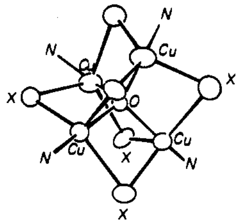
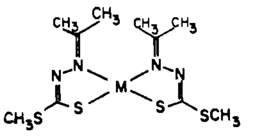
Equation 1 describes the stoichiometric transmetalation[1-6] of tetranulcear ($\mu_4$-oxo)copper(II) complexes (I) by a Ni(NS)$_2$ transmetalating agent A.[3-5] Here, N is monodentate *N*,*N*-diethylnicotinamide (DENC), X is Cl or Br, and NS is a mononanionic *S*-methyl hydrazinecarbodithioate ligand. Reaction 1



I



A

$$I + 4A \rightarrow (\mu_4\text{-O})N_4(Ni(H_2O))_4X_6 + 4Cu(NS)_2 \qquad (1)$$

is rapid[5] in aprotic solvents. The products ($\mu_4$-O)N$_4$(Ni(H$_2$O))$_4$X$_6$ and Cu(NS)$_2$ are easily separated by gel permeation chromatography,[1-5] which results in the coordination of one water molecule at each new 6-coordinate nickel center.[3-5]

Here we present analytical and cryoscopic data and EPR, electronic, and infrared spectral data that indicate that reaction 1 proceeds in distinct, stoichiometric steps (eq 2) to give pure, homologous products with $x$ = 1, 2, 3, or 4 (Table I).

$$I + xA \rightarrow (\mu_4\text{-O})N_4Cu_{4-x}(Ni(H_2O))_xX_6 + xCu(NS)_2 \qquad (2)$$

## Experimental Section

**Syntheses.** We have previously investigated reaction 2 with $x$ = 1 (X = Cl or Br),[5] 2 or 3 (X = Cl),[5] and 4 (X = Cl or Br).[3,4] The same experimental procedures were followed for the reaction of I (X = Br) with $x$ = 2 and 3 in eq 2. Reaction 2 was always allowed to proceed to the point where no further spectrophotometric changes were evident. Gel permeation chromatography (Biobeads SX-12 resin, methylene chloride eluant) cleanly separated the products ($\mu_4$-O)N$_4$Cu$_{4-x}$(Ni(H$_2$O))$_x$X$_6$ from Cu(NS)$_2$ (eq 2) at fixed $x$ and X: in each case vacuum evaporation of the solvent from the first of only two, well-separated colored bands gave ($\mu_4$-O)N$_4$Cu$_{4-x}$(Ni(H$_2$O))$_x$X$_6$ as a pure, dry solid. Unfortunately, many different crystallization procedures gave no single crystals suitable for X-ray structural determinations. Analytical, cryoscopic, and spectral data for transmetalation products ($\mu_4$-O)N$_4$Cu$_{4-x}$(Ni(H$_2$O))$_x$X$_6$ are given in Table I.

**Physical Measurements.** Physical measurements were performed at 25 °C. EPR spectra of methylene chloride solutions of reactants and products (5.0 mM) were obtained with a Varian E-9 instrument at a fixed gain of 5 × 10$^3$. Electronic spectra were measured in methylene chloride or nitrobenzene solution with a Beckman DK-1A spectrophotometer and matched quartz cells. Infrared spectra were obtained in KBr disks with a Perkin-Elmer Model 599B spectrometer.

## Results and Discussion

The analytical data in Table I indicate that one water molecule is coordinated to each new nickel center during chromatographic separation of tetranuclear products IIa–Vb from Cu(NS)$_2$.[1,3-5] These products are all unassociated tetramers at the (3–5) × 10$^{-2}$ *m* level in nitrobenzene near 5 °C (Table I).

**EPR Spectra.** Figure 1 shows the room-temperature EPR spectra of 5.0 mM solutions of Ia–Vb in methylene chloride at constant instrument gain. EPR silence of fully transmetalated products V (eq 1) confirms that they contain no EPR-active centers or impurities; that is, reaction 1 is complete and gel permeation chromatography cleanly separates V from the coproduct Cu(NS)$_2$. Any Cu(NS)$_2$ impurity would be detectable because of its intense EPR spectrum.[7] The same procedure gives products IIa–IVb, which also are not contaminated with Cu(NS)$_2$. Although reactants I are EPR-inactive at room temperature, products IIa–IVa (Table I) have weak, rhombic spectra with two principal characteristics. First, the EPR parameters (Table II)

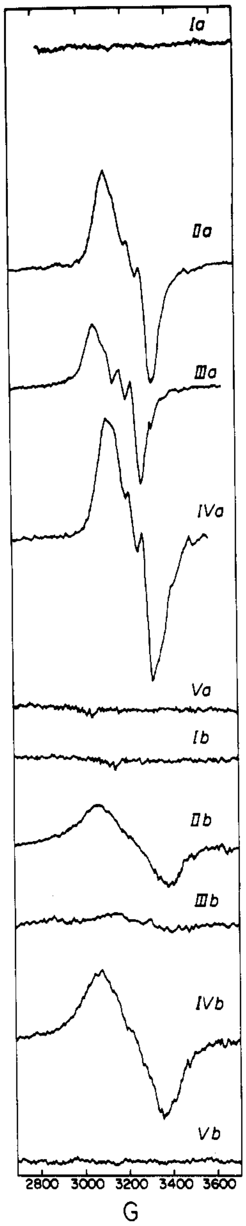


**Figure 1.** EPR spectra of complexes I–V in methylene chloride at 25 °C.

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† On leave of absence from the Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt.

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**Table I.** Analytical and Electronic Spectral Data for $(\mu_4\text{-O})(\text{DENC})_4\text{Cu}_{4-x}(\text{Ni}(\text{H}_2\text{O}))_x\text{X}_6$ Complexes[a,b]

| | | | % anal.[a] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| symbol | X | $x$ | C | H | N | Cu | Ni | $M_r$[a,b] | $\lambda_{max}$, nm ($E_\lambda$, $M^{-1}$ $cm^{-1}$)[c] |
| Ia | Cl | 0 | 40.0 (40.18) | 4.7 (4.72) | 9.2 (9.37) | 21.0 (21.35) | | 1180 ± 20 (1196) | 850 (1630), 775 (1400) |
| IIa | | 1 | 40.0 (39.7) | 4.9 (4.8) | 8.9 (9.3) | 16.3 (15.86) | 4.6 (4.96) | 1240 ± 20 (1208) | 850 (1160), 775 (1030) |
| IIIa | | 2 | 36.6 (39.36) | 4.6 (4.93) | 8.7 (9.18) | 11.0 (10.39) | 10.2 (9.6) | 1250 ± 20 (1223) | 850 (840), 775 (760) |
| IVa | | 3 | 36.5 (38.95) | 4.7 (5.06) | 8.7 (9.08) | 5.5 (5.14) | 15.1 (14.25) | 1260 ± 20 (1236) | 840 (360), 770 (340) |
| Va | | 4 | 37.8 (38.48) | 5.1 (5.17) | 8.7 (8.98) | | 18.5 (18.81) | 1270 ± 20 (1249) | *d* |
| Ib | Br | 0 | 32.8 (32.85) | 3.7 (3.86) | 7.5 (7.66) | 17.6 (17.47) | | 1240 ± 50 (1462) | 850 (3200), 765 (2900) |
| IIb | | 1 | 32.5 (32.5) | 4.0 (3.9) | 7.7 (7.6) | 14.1 (12.9) | 3.9 (4.02) | 1500 ± 20 (1475) | 850 (1700), 775 (1590) |
| IIIb | | 2 | 33.0 (32.25) | 4.11 (4.03) | 7.71 (7.52) | 8.27 (8.53) | 8.01 (7.89) | 1500 ± 20 (1488) | 850 (1330), 775 (1210) |
| IVb | | 3 | 32.0 (31.97) | 4.07 (4.13) | 7.56 (7.46) | 4.17 (4.23) | 11.93 (11.73) | 1500 ± 20 (1502) | 850 (355), 775 (330) |
| Vb | | 4 | 31.9 (31.69) | 4.13 (4.22) | 6.99 (7.39) | | 15.17 (15.50) | 1510 ± 20 (1515) | 850 (71), 775 (75) |

[a] Calculated values in parentheses. [b] Measured cryoscopically in nitrobenzene in the range (3–5) × $10^{-2}$ *m*. [c] In nitrobenzene. [d] Negligible absorptivities at 770–850 nm.

**Table II.** EPR Data for $(\mu_4\text{-O})(\text{DENC})_4\text{Cu}_{4-x}(\text{Ni}(\text{H}_2\text{O}))_x\text{X}_6$ Complexes in Methylene Chloride at 25 °C

| | EPR params | | | | | |
|---|---|---|---|---|---|---|
| complex | $g_1$ | $g_2$ | $g_3$ | $\langle g\rangle$ | $g(\Delta M_s = 2)$ | $\Delta_{pp}$, G |
| IIa | 2.17 | 2.08 | 2.03 | 2.09 | 4.24 | |
| IIIa | 2.20 | 2.12 | 2.07 | 2.13 | 3.70 | |
| IVa | 2.17 | 2.09 | 2.04 | 2.10 | 4.24 | |
| IIb | | | | 2.09 | *a* | 300 |
| IIIb | | | | 2.08 | *a* | 290 |
| IVb | | | | 2.12 | *a* | 280 |

[a] Weak, but discernible, transitions observed.

are remarkably similar and indicate trigonal-bipyramidal geometries for electronically coupled copper(II) centers.[8] On this evidence we conclude that replacement of 5-coordinate (DENC)Cu in Ia with 6-coordinate $(\text{DENC},\text{H}_2\text{O})\text{Ni}$ centers[3-5] has little effect on the molecular environment of the remaining copper(II). Second, the EPR signals of IIa–IVa do not differ greatly despite progressive reduction of the number of EPR active copper(II) centers. Since reactants I are EPR-inactive, this indicates that transmetalation with nickel(II) results in progressive electronic decoupling of the remaining copper(II) centers.

Products IIb–IVb with X = Br are also EPR-active but their EPR spectra are isotropic, as generally observed for bromocopper(II) complexes,[8,9] and thus give no geometrical information. The signal for IIIb (X = Br) is much weaker than that for IIIa (X = Cl) under the same experimental conditions. Both species contain an even number of electrons, but electronic coupling of copper(II) centers is evidently much stronger for X = Br.

**Electronic Spectra.** The electronic spectra of complexes I–V summarized in Table I and illustrated in Figure 2 all exhibit maximum absorption near 850 nm and a distinct shoulder near 760 nm. Negligible solvent effects were observed. Very low absorptivities in products V confirm that these spectral features are due almost entirely to d–d transitions in copper(II).[10] The molar absorptivities, $E_\lambda$ ($M^{-1}$ $cm^{-1}$), at the maxima decrease with increasing $x$ in the general formula $(\mu_4\text{-O})\text{N}_4\text{Cu}_{4-x}(\text{Ni}(\text{H}_2\text{O}))_x\text{X}_6$ (Figure 3), with $E_\lambda$ (at fixed wavelength and $x$) greater for X = Br than for X = Cl. $E_\lambda$ for X = Cl decreases linearly with $x$; however, $E_\lambda$ for $x$ = 1, 2, or 3 and X = Br is lower than expected from the data with $x$ = 0 and $x$ = 4, and the deviations are irregular. The electronic spectral data for X = Cl indicate little, if any, geometrical difference between copper(II) centers in the reactants and transmetalated products IIa–IVa, as concluded from the EPR data. However, the spectra for X = Br indicate that the electronic ligand environment of copper(II) in Ib differs from those in IIb–IVb. These differences seem greatest for $x$ = 1 or 3 (Figure 3). Part of the disparities may be due to the role of X = Br in affecting electronic coupling (see above).

**Infrared Spectra.** All the reactants and transmetalated products of this study exhibit single IR bands at 1630–1635 $cm^{-1}$, which indicate the presence of monodentate DENC bonded to each metal center through its pyridinic nitrogen atom.[2-6,8] Broad bands

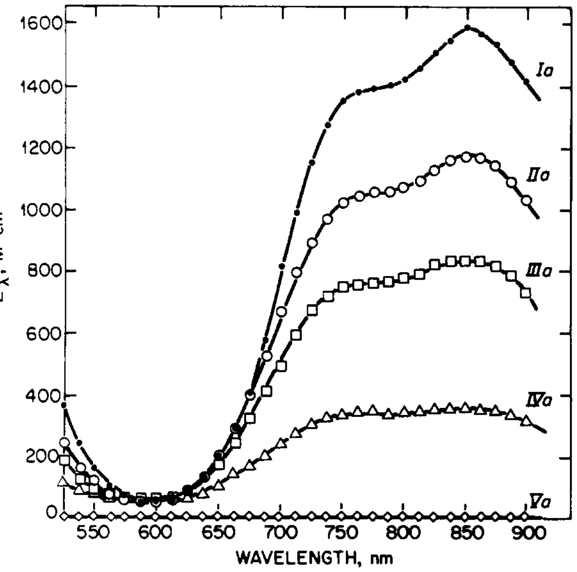

**Figure 2.** Electronic spectra of $(\mu_4\text{-O})(\text{DENC})_4\text{Cu}_{4-x}(\text{Ni}(\text{H}_2\text{O}))_x\text{Cl}_6$ complexes in nitrobenzene at 25 °C.

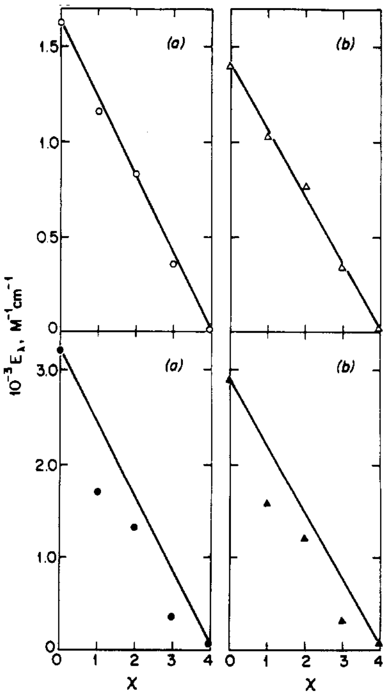

**Figure 3.** Plots of $E_\lambda$ vs. $x$ for $(\mu_4\text{-O})(\text{DENC})_4\text{Cu}_{4-x}(\text{Ni}(\text{H}_2\text{O}))_x\text{X}_6$ complexes (X = Cl or Br) in nitrobenzene at (a) 850 nm and (b) 775 nm. Open points are for X = Cl.

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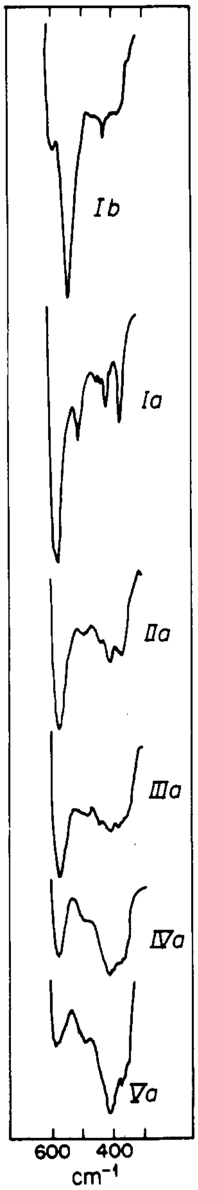

**Figure 4.** KBr disk IR spectra (300–600 cm$^{-1}$) for ($\mu_4$-O)(DENC)$_4$Cu$_{4-x}$(Ni(H$_2$O))$_x$H$_6$ complexes.

centered at 3400 cm$^{-1}$ in the IR spectra of the transmetalated products are due to coordinated water.[1-6]

Dieck[10] has shown that bands in the 300–600-cm$^{-1}$ region are characteristic of the OM$_4$ unit in ($\mu_4$-O)N$_4$Cu$_4$X$_6$ complexes, where N is a monodentate ligand. Figure 4 shows that four such bands are resolved in Ia, while broader bands at lower frequency are exhibited by Ib. The data for products IIa–Va in Figure 4 indicate a change of relative intensities of the bands at 580 cm$^{-1}$ and 500, 460, 410, and 370 cm$^{-1}$ with increasing $x$. The intense bands at 410 and 370 cm$^{-1}$ are clearly due to $\nu_{\mathrm{Ni-OH_2}}$ with high absorptivity relative to those for $\nu_{\mathrm{OM_4}}$. The absorptivities of the latter are sufficient to obscure the band at 460 cm$^{-1}$ in Ia. These spectra confirm the same basic core structures in complexes Ia–Va. The band at 520 cm$^{-1}$ in Ib (X = Br, $x$ = 0; Figure 4) decreases in intensity relative to bands at 410 and 370 cm$^{-1}$ with increasing $x$. This is further confirmation of the assignment of the latter to $\nu_{\mathrm{Ni-OH_2}}$.

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**Registry No.** Ia, 90741-95-0; Ib, 95785-44-7; IIa, 101998-13-4; IIb, 101998-14-5; IIIa, 101998-15-6; IIIb, 101998-16-7; IVa, 102046-56-0; IVb, 101998-17-8; Va, 90742-00-0; Vb, 101998-18-9; Ni(NS)$_2$, 34214-73-8.

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# A Sequential Double Arbuzov-like Demethylation of *cis*-PtX$_2$(P(OMe)$_3$)$_2$ by Added Halide Ion

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The classical Arbuzov rearrangement involves an alkyl-transfer reaction between an alkylated nucleophile and a phosphorus(III) ester to give an organophosphorus(V) compound. An analogous reaction can occur with a phosphite ligand complexed to a transition-metal ion. Now the nucleophile induces dealkylation of the coordinated alkyl phosphite, resulting in its conversion to a complexed phosphonato ligand.[1]

The halide-induced dealkylation of complexed phosphite ligands has been well documented, but double dealkylations using this technique have few precedents.[2] An interesting application of this reaction is the generation of a complexed phosphito ligand having negative charge on oxygen which can be homologated to a diphosphite by reaction with a halophosphine. Such a sequence has been used to prepare $(CO)_5\overline{W((MeO)_2P}OPPh_2)$ and similar complexes.[3] Conceptually, an analogous double sequence could be carried out with a d$^8$ metal phosphite complex to generate a "ligand" that has the potential to form bimetallic complexes.[4] Such a method has general appeal because one can realistically place a wide variety of substituents on the phosphorus ligating atoms and also because one has the potential to synthesize heterobimetallic A-frame complexes with each metal at specific phosphorus ligating sites.

This paper describes our successful conversion of the compound *cis*-PtCl$_2$(P(OMe)$_3$)$_2$ into PtCl$_2$(P(OMe)$_3$)(OP(OMe)$_2$)$^-$ and then into PtCl$_2$((OP(OMe)$_2$)$_2$)H$^-$ using chloride ion as nucleophile. Each anionic complex can be separately identified and isolated, and we then use our spectral data to try to ascertain the charge localization in these complexes.

## Experimental Section

The complexes *cis*-PtCl$_2$(P(OMe)$_3$)$_2$ and *cis*-PtI$_2$(P(OMe)$_3$)$_2$ were prepared by the literature method.[5] Melting points were measured on a Fisher-Johns apparatus and are uncorrected. Conductivity measurements were made on a Model RC 1682 conductivity bridge with platinum black electrodes. Microanalyses were carried out by Galbraith Inc., Knoxville, TN. Nuclear magnetic resonance spectra were measured on a Bruker AC 200 NMR spectrometer. Tetraphenylarsonium iodide was prepared by mixing aqueous solutions of Ph$_4$AsCl and NaI. The precipitated product was washed sequentially with water, acetone, and diethyl ether and was then air-dried. Acetonitrile was dried by continuous distillation from CaH$_2$. CD$_3$CN (Aldrich) was used as supplied.

**Tetraphenylarsonium *cis*-Dichloro(dimethyl phosphonato)(trimethyl phosphite)platinum(II) (1).** A 25-mL round-bottom flask, fitted with a reflux condenser, containing *cis*-PtCl$_2$(P(OMe)$_3$)$_2$ (104 mg, 0.202 mmol) and tetraphenylarsonium chloride (vacuum-dried at 110 °C) (254 mg, 0.606 mmol) was placed in an oil bath at 63 °C. Just sufficient CH$_3$CN (ca. 1 mL) was added to give a solution that was saturated when hot. After 25 min the solvent was removed on a rotary evaporator. To the solid was added CH$_2$Cl$_2$ (5 mL), and the solution was washed with water (3 × 5 mL). The CH$_2$Cl$_2$ solvent was removed under vacuum, and the residue was then vacuum-dried for 5 min and redissolved in acetone. Excess Ph$_4$AsCl was precipitated from the solution by addition of hexane until an oil just began to form (the solution remained cloudy), at which time the mixture was centrifuged. Solvent removal yielded an oil that on stirring in a mixture of hexane and ether (1:1) gave a colorless solid.

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