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# Transmetalation of Tetranuclear Copper Complexes. 6.[1] Transmetalation of $L_4Cu_4O_2$ Complexes (L = 6-Methyl-2-hydroxypyridinate) by $M(NS)_2$ Reagents

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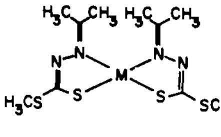
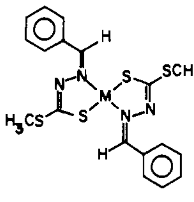
The neutral tetranuclear copper(I) complex $L_4Cu_4$ (L = 6-methyl-2-hydroxypyridinate) is oxidized by excess dioxygen to $(\mu\text{-}O)_2L_4Cu_4$ (IV) in aprotic solvents. The similar ESR and electronic spectra of IV and its dicarbonato derivative $(\mu\text{-}CO_3)_2L_4Cu_4$ (V) are consistent with the presence of trigonal copper(II) centers. Product IV is transmetalated by $M(NS)_2$ reagents I (M = Co, Ni, Zn; NS is a monoanionic *S*-methyl hydrazinecarbodithioate Schiff base) in stoichiometric steps. The reactions are generally slower than transmetalations of oxohalo(pyridine)copper(II) complexes and result in loss of bridging L, particularly when M = Co or Zn. Electronic spectral features at 380 and 600–650 nm in IV and the transmetalation products are assigned to LMCT and d–d transitions, respectively. The presence of $\mu$-oxo groups in IV evidently leads to formation of particular transmetalation product isomers through a kinetic trans effect in decreasing order Co > Cu > Ni > Zn. A tetranuclear complex $(\mu\text{-}O)_2L_4CoNiCuZn\cdot 2H_2O$, which contains four different metals in one molecular unit, has been obtained by consecutive transmetalation of IV with equimolar I (M = Zn, Ni, Co). Its core structure is assigned on the basis of the proposed trans-effect order.

## Introduction

Direct, stoichiometric transmetalation of polynuclear copper(I)[1,2] and copper(II)[3-8] complexes by *S*-methyl hydrazinecarbothioato metal complexes such as I and II is a source of polynuclear, mixed-metal complexes that have not been obtained by other means. The reactions are stoichiometric because of the high stability of $Cu(NS)$[1,2] and $Cu(NS)_2$[3-8] coproducts.



I



II

Recently, we reported the stoichiometry and kinetics of oxidation of tetrakis(6-methyl-2-hydroxypyridinato)tetracopper(I) ($L_4Cu_4$, III) to $L_4Cu_4O_2$ (IV) by dioxygen in aprotic solvents (eq 1).[8] The structures of III (Figure 1)[9] and a number of other

$$\underset{\text{III}}{L_4Cu_4} + O_2 \rightarrow \underset{\text{IV}}{L_4Cu_4O_2} \qquad (1)$$

complexes containing L bridging different metal centers are known.[10-14] We have established the formulation $(\mu\text{-}O)_2L_4Cu_4$ for IV from the stoichiometry of oxidation of III by $O_2$ (eq 1) and from eq 2, which is diagnostic of the presence of $\mu$-oxo

$$\text{IV} + 2CO_2 \rightarrow \underset{\text{V}}{L_4Cu_4(CO_3)_2} \qquad (2)$$

groups.[3,4,8,15,16] The rate-determining step in reaction 1 is insertion of $O_2$ through one of the four unobstructed edges of $L_4Cu_4$[8] (see Figure 1).[9]

In this paper we have used transmetalation chemistry to investigate the likely core structure of IV and to explain its spectral and chemical properties. We report that IV can be completely transmetalated by $M(NS)_2$ reagents I, but not without some core fragmentation.

We found previously that large excesses of I (M = Ni) only transmetalate $(\mu\text{-}O)_2N_4Cu_4X_4$ complexes (N is a monodentate pyridine; X is Cl or Br) to the $Cu_2Ni_2$ stage[3,4] while other polynuclear halocopper complexes are completely transmetalated.[1-7] This difference indicates that metals can influence the rate of replacement of a metal disposed at the opposite end of a shared $\mu$-oxo group through a trans effect. In the present study, a trans-directing influence apparently determines isomeric structures in the transmetalation products. On the basis of transmetalation patterns, we have assigned the core structure of a tetranuclear complex containing four different metals per molecule.

## Experimental Section

**Materials and Measurements.** The syntheses of the reactants I and II (M = Co, Ni, Zn) have been described previously.[3] Ethanol was refluxed with Mg turnings and a few drops of $CCl_4$ until all the Mg had reacted and then distilled.

Literature procedures[1-8] were followed for solvent purification, elemental analysis, cryoscopic molecular weight, conductance and manometric dioxygen uptake measurements, chromatographic product separation, and spectral measurements.

Magnetic susceptibilities of powdered samples were measured at room temperature with a PAR Model FM-1 vibrating-sample magnetometer calibrated with $Hg[Co(SCN)_4]$. EPR spectra of samples in methylene chloride glasses were obtained with a Variant E-9 instrument.

**Synthesis of $L_4Cu_4$ (III).** We found that $L_4Cu_4$ is prone to oxidation by dioxygen, especially when wet, and so the literature synthesis[9] of III was modified as follows. The solid product III from the reaction of NaOEt (9.5 mmol) with equimolar amounts of HL and copper(I) trifluoroacetate in 60 mL of absolute ethanol under dinitrogen was filtered

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(1) Part 5: Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Gilbert, T. R.; Nabih, K. *Inorg. Chem.*, preceding paper in this issue.

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**Table I.** Analytical and Cryoscopic Data for Reactants and Transmetalation Products[a]

| | | anal., % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| symbol | complex | C | H | N | Cu | Ni | Zn | Co | $M_r$[b] |
| III | $L_4Cu_4$[c] | 42.0 | 3.5 | 7.9 | 37.5 | | | | 690 ± 20 |
| | | (42.0) | (3.5) | (8.2) | (37.0) | | | | (686) |
| IV | $L_4Cu_4O_2$ | 37.2 | 3.7 | 7.5 | 35.9 | | | | 720 ± 20 |
| | | (40.1) | (3.3) | (7.8) | (35.4) | | | | (718) |
| V | $L_4Cu_4(CO_3)_2$ | 36.3 | 3.6 | 6.7 | 31.6 | | | | 810 ± 20 |
| | | (35.7) | (3.0) | (6.9) | (31.5) | | | | (807) |
| VI | $L_4Cu_3NiO_2 \cdot H_2O$ | 32.2 | 3.6 | 6.8 | 25.5 | 7.5 | | | 790 ± 20 |
| | | (39.4) | (3.6) | (7.7) | (26.1) | (8.0) | | | (731) |
| VII | $L_4Cu_2Ni_2O_2 \cdot 2H_2O$ | 35.5 | 3.9 | 8.0 | 17.0 | 15.4 | | | 720 ± 20 |
| | | (38.7) | (3.8) | (7.5) | (17.1) | (15.8) | | | (744) |
| VIII | $L_4CuNi_3O_2 \cdot 3H_2O$ | 33.5 | 3.9 | 8.0 | 8.1 | 24.2 | | | 760 ± 20 |
| | | (38.0) | (4.0) | (7.4) | (8.4) | (23.2) | | | (758) |
| IX | $L_3Ni_4O_2(OH) \cdot 5H_2O$ | 32.2 | 3.6 | 6.3 | | 34.8 | | | 740 ± 30 |
| | | (31.0) | (4.0) | (6.0) | | (33.7) | | | (697.8) |
| X | $L_3Cu_3Zn(OH)O_2 \cdot 2H_2O$ | 30.0 | 3.3 | 6.6 | 28.5 | | 10.7 | | 760 ± 20 |
| | | (32.5) | (3.5) | (6.3) | (28.7) | | (9.8) | | (66.49) |
| XI | $L_3Cu_2Zn_2(OH)O_2 \cdot 3H_2O$ | 29.3 | 3.2 | 6.4 | 17.9 | | 17.9 | | 710 ± 20 |
| | | (30.7) | (3.6) | (6.0) | (18.0) | | (18.6) | | (685) |
| XII | $L_2CuZn_2(OH)_2O \cdot 5H_2O$ | 24.4 | 4.0 | 5.3 | 10.6 | | 21.8 | | 630 ± 20 |
| | | (26.2) | (4.4) | (5.1) | (11.5) | | (23.8) | | (550) |
| XIII | $L_3CoCu_3(OH)O_2 \cdot 4H_2O$ | 29.3 | 3.4 | 5.7 | 26.2 | | | 8.8 | 1420 ± 30 |
| | | (31.0) | (3.9) | (6.0) | (27.4) | | | (8.5) | (696) |
| XIV | $L_3Co_2Cu_2(OH)O_2 \cdot 8H_2O$ | 28.2 | 4.3 | 5.8 | 17.9 | | | 15.9 | 780 ± 20 |
| | | (28.4) | (4.7) | (5.5) | (16.7) | | | (15.5) | (762) |
| XV | $L_3Co_3Cu(OH)O_2 \cdot 8H_2O$ | 28.5 | 3.7 | 6.4 | 8.3 | | | 23.3 | 2960 ± 40 |
| | | (28.5) | (4.6) | (5.6) | (8.4) | | | (23.3) | (758) |
| XVI | $L_4CuNi_2ZnO_2 \cdot 2H_2O$ | 40.1 | 3.9 | 7.6 | 9.1 | 16.4 | 9.1 | | 740 ± 20 |
| | | (39.5) | (3.8) | (7.7) | (8.7) | (16.1) | (9.0) | | (728.5) |
| XVII | $L_4CoCuNiZnO_2 \cdot 2H_2O$ | 34.6 | 3.7 | 7.3 | 9.5 | 8.1 | 9.1 | 7.3 | 720 ± 20 |
| | | (38.6) | (3.8) | (7.5) | (8.5) | (8.0) | (8.8) | (7.9) | (747) |

[a] Calculated values given in parentheses. [b] In nitrobenzene; typical concentration $3 \times 10^{-2}$ *m*. [c] Data from ref 9.

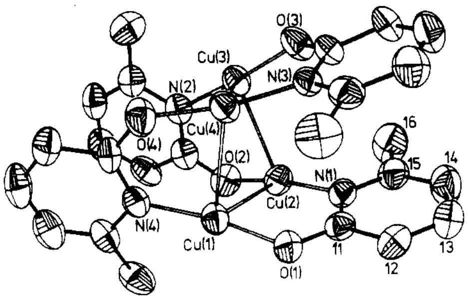

**Figure 1.** Molecular structure of III.[9]

(Schlenk), washed three times with absolute ethanol, and dried under vacuum to give a pale yellow powder. This powder is air-sensitive and becomes progressively less soluble in methylene chloride and nitrobenzene even when stored under vacuum. Analytical data are given in Table I.

**Synthesis of $L_4Cu_4O_2$ (IV) and $L_4Cu_4(CO_3)_2$ (V).** A solution of III in methylene chloride was flushed with dioxygen at room temperature for 20 min. Dark green IV was obtained by vacuum evaporation of the solvent. The dicarbonato derivative V was obtained similarly by oxidation of $L_4Cu_4$ in the presence of excess $CO_2$. Analytical data are given in Table I.

Many different procedures were applied in attempts to crystallize IV and V. Small, single crystals were only obtained by carefully allowing slow air oxidation of the ethanolic supernatant (see above) from the synthesis of III; mp 194 ± 1 °C dec. anal. calcd for $Cu_4C_{28}H_{36}N_4O_8$: C, 41.5; H, 4.4; N, 6.9; Cu, 31.3; wt loss, 11.4%. Found: C, 41.6; H, 4.2; N, 6.8; Cu, 30.7; wt loss (100 °C, vacuum), 10.9. These crystals were freely soluble in methylene chloride, and dry samples were sufficiently stable in capillaries to give basic crystal information (Table II). However, many careful attempts at full X-ray structure determination were thwarted by rapid (1–3 h) peak broadening and loss of reflection intensities.

**Transmetalation of $L_4Cu_4O_2$ by $M(NS)_2$ Reagents I (M = Co, Ni, Zn).** Basic transmetalation stoichiometries and reaction times were established by spectrophotometric titrations of IV with $M(NS)_2$ complexes at room temperature in methylene chloride. The spectra of solutions containing different reactant ratios were measured at regular intervals for at least 6 days. The stoichiometric synthetic reaction 3 was generally run with

$$\mathrm{IV} + x\mathrm{M(NS)_2} \rightarrow \mathrm{L_4Cu_{4-x}M_xO_2} + x\mathrm{Cu(NS)_2} \qquad (3)$$

**Table II.** Crystal Data for $L_4Cu_4O_2 \cdot 2C_2H_5OH$

| | |
|---|---|
| mol formula: $Cu_4C_{28}H_{36}N_4O_8$ | $a$ = 18.613 (5) Å |
| fw: 810 | $b$ = 19.694 (4) Å |
| space group: $Pca2_1$ or $Pbcm$ (orthorhombic) | $c$ = 22.930 (9) Å |
| $Z$ = 8 | $V$ = 8405.3 Å$^3$ |

5 mmol of IV and $x$ equiv of $M(NS)_2$ in 60 mL of anhydrous methylene chloride under dinitrogen. Product separation by gel permeation chromatography (methylene chloride eluant[4]) gave two colored bands. Transmetalation products isolated by evaporation of the first band often contained fewer than four L ligands and had incorporated water (see Results and Discussion).[3,4]

Analytical data for all transmetalation products are collected in Table I. Attempts to grow single crystals of these products suitable for X-ray structure determinations were unsuccessful.

## Results and Discussion

**Properties of $L_4Cu_4$.** The essential feature of the molecular structure of yellow III (Figure 1[9]) is a square of copper(I) centers nearly linearly 2-coordinated by O and N atoms of separate, anionic bridging ligands L. The "butterfly"[9] distortion from almost perfect $Cu_4$ planarity, thought to be due to crystal-packing forces,[9] indicates that the molecule is not rigid. Although the average Cu--Cu distance (2.683 (1) Å) is close to that in elemental copper,[17] the wide range of observed distances (2.656 (1)–2.709 (1) Å) and mass spectroscopic evidence indicate no significant Cu–Cu bonding.[9]

$L_4Cu_4$ must either be freshly prepared or carefully stored under vacuum to obtain reproducible data for its second-order, stoichiometric aprotic oxidation by dioxygen, eq 1.[8]

**Properties of $L_4Cu_4O_2$.** Complexes III–V are all tetranuclear in nitrobenzene (Table I). Room-temperature electronic spectra of HL and III–V in methylene chloride are presented in Figure 2 (see also Table III).[18] Maximma in the 200–310-nm region are clearly due to intraligand transitions attenuated by Cu.

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(17) Sutton, L. E., Ed. *Table of Interatomic Distances and Configurations in Molecules and Ions*; Special Publication No. 18; The Chemical Society: London, 1965; supplement.

(18) Supplementary data.

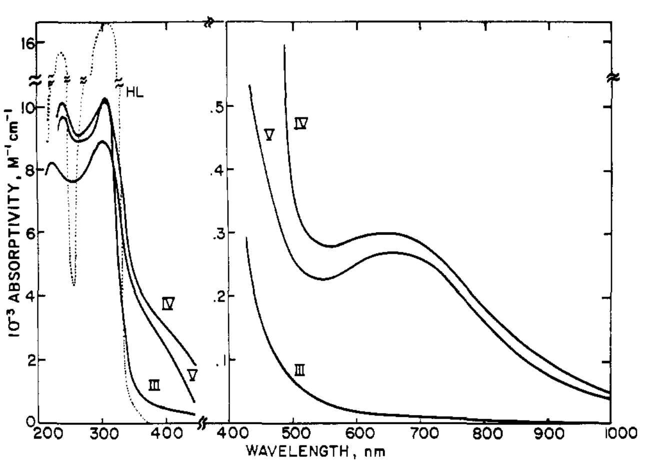

**Figure 2.** Electronic spectra of HL and copper complexes III–V at room temperature in methylene chloride.

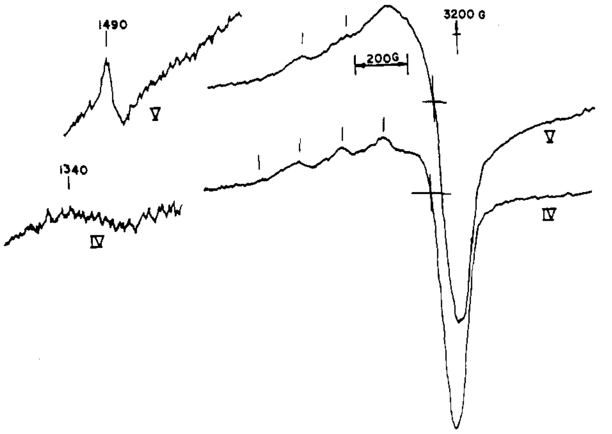

**Figure 3.** ESR spectra of IV and V in methylene chloride glasses at 9–11 K.

**Table IV.** EPR Data

| complex | state | temp, K | EPR params | | | |
|---|---|---|---|---|---|---|
| | | | $g_{\parallel}$ ($A_{\parallel}^{a}$) | $g_{\perp}$ | $g$ ($\Delta M_s = 2$) | $G$ |
| IV | $CH_2Cl_2$ | 9 | 2.44 (150) | 2.11 | 4.85 | 4.0 |
| V | $CH_2Cl_2$ | 11 | 2.45 (170) | 2.12 | 4.40 | 3.75 |

[a] Units are $10^{-4}$ cm$^{-1}$.

Oxidation of III by $O_2$ to IV and V gives new broad spectral features near 380 nm and at 680 nm, which are assigned as charge-transfer and d–d– transitions, respectively (see below).

The magnetic moment of solid IV is $\mu_{300} = 1.42\ \mu_B$, indicating Cu–Cu electronic coupling through $\mu$-oxo bridges.[4] Like (*sym*-$\mu$-$CO_3$)(tmpd)$_2$$Cu_2X_2$ (tmpd = *N,N,N′,N′*-tetramethyl-1,3-propanediamine),[19] IV and V are ESR-silent at room temperature but IV and V have similar axial spectra ($g_{\parallel} > g_{\perp}$) at 9–11 K (Figure 3 and Table IV). Core structures for IV and V in Figure 4 are proposed to account for these properties of IV and V as follows.

Oxidation of III to IV and V by dioxygen (eq 1) is expected to result in an overall stiffening of the core structure of III (Figure 1) and a tendency to $Cu_4O_2$ planarity because of the higher effective nuclear charge on copper and the presence of bridging oxo groups. There is no hard evidence for metal–metal bonding in III,[9] and we are even more reluctant to invoke metal–metal bonding in IV and V. Thus, we should consider the possibility that IV and V are 3-coordinate copper(II) complexes.

The mechanism proposed for reaction 1,[8] the observation of reaction 2, and room-temperature ESR silence suggest that IV contains $\mu$-oxo groups on opposite edges of a symmetrical $Cu_4O_2$ core (Figure 4).[8,20] Bridging ligands L also must be accommodated by these edges. Ligands L have been found to bridge metal centers that are up to 2.829 (1) Å apart in a chromium(III) complex.[21]

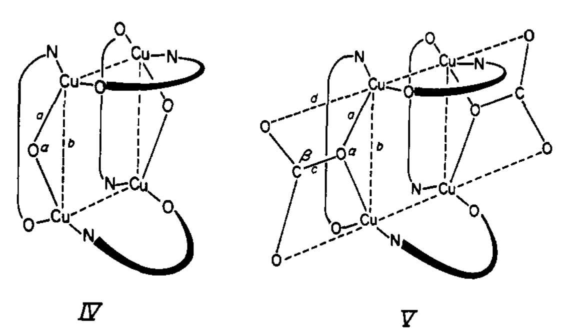

**Figure 4.** Proposed core structures for IV and V.

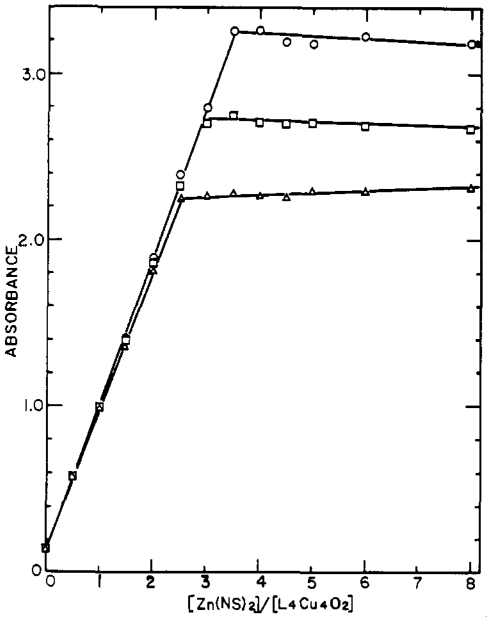

**Figure 5.** Spectrophotometric data at 600 nm for reactions of IV with I (M = Zn) (eq 3; $x$ = 8) in methylene chloride at 25 °C and the following reaction times: (△) 1 day; (□) 2 days; (○) 6 days.

Adoption of a planar $Cu_4O_2$ core for IV with $a$ = 1.95 Å[19] and $b$ = 2.83 Å[21] leads to $\alpha$ = 94° in Figure 4. This calculated Cu–O–Cu angle is much more acute than in those in known ($\mu$-carbonato)dicopper(II) complexes.[19] If we adopt the typical values $c$ = 1.30 Å and $\beta$ = 120° in the latter,[19] then $d$ in Figure 4 for V is predicted to be ca. 3.5 Å. This distance is too long to increase the coordination number from 3 in IV to 4 in V, consistent with the closely similar electronic and ESR spectra of IV and V (Tables III and IV, respectively).

We therefore propose that IV and V contain 3-coordinate copper(II) centers. Further analysis of the spectral properties will depend on detailed structural data for IV and V, since we know of no other low molecular weight structurally characterized, 3-coordinate copper(II) complexes.

A tendency toward a linear Cu–O–Cu angle would tend to break the L bridges on two of the four edges in IV and may be responsible, at least in part, for LH loss on transmetalation (see below).

**Transmetalation of IV with M(NS)$_2$ Reagents. General Observations.** Figure 5 shows the results for three spectrophotometric

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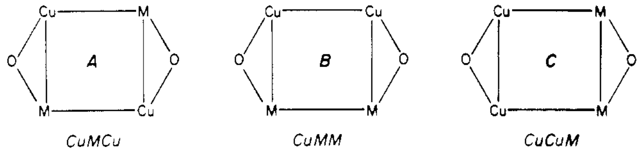
(19) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; Hutchinson, J. P. *Inorg. Chem.* **1982**, *21*, 1002 and references cited therein.

(20) An alternative structure for IV with $\mu$-oxo groups on adjacent edges of an $L_4Cu_4$ core would give formal 4-, 3- and 2-coordinate copper(II) centers in IV. That structure would have complex spectra and be ESR-active at room temperature, contrary to observation. See also ref 8.

(21) Akhter, L.; Clegg, W.; Collison, D.; Garner, C. D. *Inorg. Chem.* **1985**, *24*, 1725.

**Chart I**



titrations of IV and 8 equiv of I (M = Zn) in methylene chloride at room temperature under dinitrogen. The measurements were made at 600 nm, where $Cu(NS)_2$, the coproduct of eq 3, is the predominant absorbing species.[22] Reaction 3 with $x = 3$ was complete in 1 day, but complete transmetalation ($x = 4$) took about 6 days for M = Zn and 2 days for M = Ni. These transmetalation reactions are much slower than those of tetranuclear oxo-halo-pyridine complexes (usually complete in 6 h),[3] presumably due, at least in part, to the absence in IV of core atoms X, which readily form rings $\overline{S-M-X-Cu}$ to facilitate metal exchange in halocopper(II) complexes.[6]

Complex IV and $[NCuX]_4O_2$ (N not pyridine) are all bis($\mu$-oxo)copper(II) species.[3,4,8] However, complex IV can be completely transmetalated by reagents I and II (M = Ni, Co, Zn) whereas only isomeric heterotetranuclear $[NCuNi(H_2O)X_2]_2O_2$ products are obtained from $[NCuX]_4O_2$.[3,4]

Synthetic reaction 4 was allowed to proceed in methylene chloride for 5 h, 12 h, 3 days, and 7 days for $x$ = 1, 2, 3 and 4, respectively. All the product solutions were nonconducting. The transmetalated products VI-XVII were easily isolated by gel permeation chromatography.[3] Analytical and spectral data are collected in Tables I and III,[18] respectively.

**Transmetalation of IV by I (M = Ni).** The data for isolated products VI-IX in Table I indicate that IV can be transmetalated by I in stoichiometric steps (eq 3) to give tetranuclear products that do not associate[3,4] in nitrobenzene. The data for $x$ = 1-3 are consistent with the incorporation of 1 mol of $H_2O$ per new nickel center during isolation (as observed in other systems[3,4]) and with retention of all four original ligands L. One of these ligands is absent in product IX:[23] it presumably was dissociated during chromatographic separation through protonation (reaction 4,

$$L^- + H_2O \rightarrow LH + OH^- \qquad (4)$$

where $L^-$ is coordinated 6-methyl-2-hydroxypyridinate).[24] Products VI-IX all exhibit strong IR spectral bands centered at 3400 $cm^{-1}$ (coordinated water)[3] and a broad, medium-intensity band at 560 $cm^{-1}$ ($\nu_{M-O}$ or $\nu_{M-OH_2}$). Reactant IV has this feature at 510 $cm^{-1}$ (Table III).[18] The IR spectrum of complex IX contains no band attributable to bridging $OH^-$;[25] isolated IX presumably does not contain a cyclic $(\mu-O)_2Ni_4$ core unit because one of the four bridging ligands L in III-VIII is missing.[26]

**Electronic Spectra of VI-IX.** We have previously distinguished pairs of isomeric complexes$[NCuNi(H_2O)X_2]_2Y_2$ (Y = O, $CO_3$).[3,4] These isomers exist because of the presence of bridging Y groups (see structures V-VIII of ref 3). We have concluded from spectral and kinetic data that reactions of $[NCuX]_4Y_2$ complexes with I (M = Ni) give isomers with two Ni-Y-Cu units because of a trans-directing influence Cu > Ni across bridging ligands Y.[3,4]

Possible isomers A-C from reaction 3, $x = 2$, are represented schematically in Chart I.[27] We assign the spectrum of VII (Figure 6) to isomer A and/or B[27] (M = Ni) because the large increase in absorptivity in changing $x$ from 2 to 3 (Figure 6) must be due to the creation of strongly absorbing Ni-O-Ni units with square-planar nickel centers[28] in VIII. The absorptivity of IX is about twice that of VIII at 600 nm because IX contains *two* Ni-O-Ni units. This relationship holds despite one less bridging ligand L in IX.

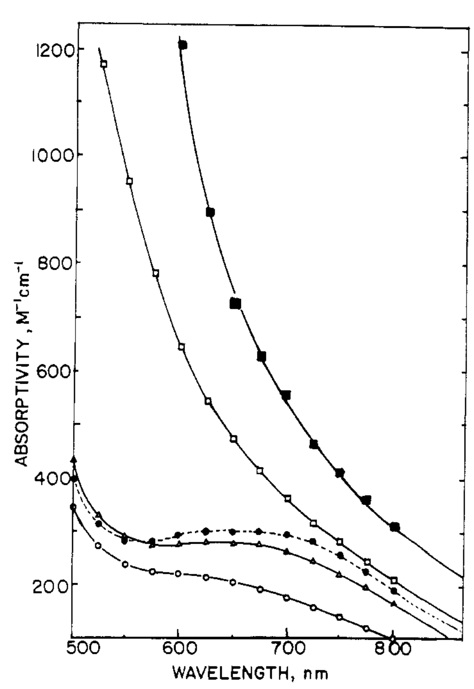


Figure 6. Electronic spectra of IV (●), VI (○), VII (△), VIII (□), and IX (■) at 25 °C in methylene chloride.

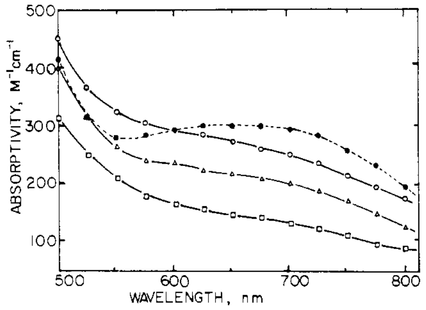


Figure 7. Electronic spectra of IV (●), X (○), XI (△), and XII (□) at 25 °C in methylene chloride.

We conclude that isomer C is not formed because copper directs transmetalation across $\mu$-oxo bridges more efficiently than does nickel, as found in related systems.[3,4] We designate the trans effect as Cu > Ni (see below).

**Transmetalation of IV by I (M = Zn).** Analytical data for products X-XII of the title reactions (Table I) have the following principal features: (a) fewer ligands L are retained after chromatographic isolation (eq 4) even with $x = 1$ in eq 3; (b) complexes X and XI are tetranuclear, but XII, obtained with $x = 3$, is trinuclear and contains only two ligands L; (c) the products contain unpredictable numbers of coordinated water molecules, but they are not intermolecularly associated[3,4] (Table I; see below).

Attempts to prepare fully transmetalated complexes ($x = 4$) gave mixtures of ill-defined products, some with very high zinc contents.

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(22) Experiments at different concentration levels have been scaled to a common ordinate axis; in no case was the measured absorbance >1.000.

(23) Note that complex IX contains a molar ratio of $H_2O$:Ni > 1, consistent with the absence of one of the original four L bridges (Table I).

(24) Isolated products VI-VIII contain four L ligands while most other isolated products do not. This suggests that products of reaction 3 often contain strained or broken L bridges that are subject to reaction 4 during chromatographic isolation.

(25) Karlin, K. D.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. A. *Inorg. Chem.* **1984**, *23*, 519.

(26) From this point planar schematic diagrams without coordinated L are presented for clarity; although III is nearly planar, with a square of copper atoms, we do not know that any complexes of this study contain a planar $M_4O_2$ core. If this is the case, $M_4$ is likely to be oblong (see text).

(27) Note that the distinction between isomers A and B does not exist in $T_d$ symmetry. None of the $L_nCu_2M_2O_2$ products isomerize[3,4] at an appreciable rate in methylene chloride at room temperature. Cyclic isomers A-C are regarded as precursors to isolated, ring-opened species.[24]

(28) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

**Table V.** Magnetic Moment Data

| complex | $\mu_{300}$, $\mu_B$ | complex | $\mu_{300}$, $\mu_B$ |
|---|---|---|---|
| IV | 1.42 | XI | 1.56 |
| X | 1.68 | XII | 2.12 |

Our earlier work[26] established that tetranuclear $(\mu\text{-O})_2[NZnX]_4$ cores are unstable; the data in Table I indicate that bridging L confers some stability on the transmetalation products, but the tendency for LH loss and disproportionation on attempted isolation is much greater for M = Zn than for M = Ni (previous section).[24]

We have assigned square-planar nickel(II) from the spectra of VIII and IX (Figure 6). We feel that IX is more stable than its zinc analogue for three reasons: (a) square-planar nickel is compatible with the proposed structure of IV (no square-planar zinc complexes have been reported); (b) zinc(II) ($d^{10}$) would give products at fixed $x$ that contain more electrons than with nickel(II) ($d^8$);[29] (c) zinc(II) evidently has a greater affinity for oxygen donor atoms (from water and $OH^-$, Table I) than does nickel(II).

**Spectra of Products X–XII.** The IR spectra of complexes VI–XII are similar (see previous section and Table III).[18] There is no evidence for bridging $OH^-$ in X–XII.[25]

The electronic spectra (500–800 nm) shown in Figure 7 illustrate the effect on molar absorptivities of progressive replacement of copper(II) with zinc(II). They are clearly due to d–d transitions.

**Magnetic Moments.** Room-temperature magnetic moments for IV and X–XII are compared in Table V. Complex XII is the only species with the magnetic moment expected for an isolated copper(II) center with ionic or weakly covalent bonds: all the other complexes have $\mu_{300}$ values less than the spin-only value for copper(II),[30] which indicates electronic coupling.

**Trans-Effect Order.** The featureless spectra of X–XII (Figure 7) cannot be identified with isomers A–C in the absence of structural information. However, because X and XI are formed much more rapidly than XII under similar conditions (Figure 5) we tentatively assign XI as isomer A or B: that is, Cu apparently directs transmetalation across $\mu$-oxo bridges more rapidly than does Zn.[31]

**Assignment of the 380-nm Spectral Feature.** The progressive decrease in the molar absorptivities of the spectral shoulder at 380 nm for the series IV, X–XII suggests its assignment to a ligand-to-metal charge transfer transition; LMCT (L → Zn) is not possible.

**Transmetalation of IV by I (M = Co).** The title reactions are slower with M = Co than with M = Zn: XIV took roughly twice as long to form as XI under similar experimental conditions, and a fully transmetalated complex was not obtained in 7 days even in the presence of excess I. The stoichiometries and properties of products X–XV are similar, exhibiting the effects of LH loss during isolation (eq 4) and coordination of unpredictable amounts of water; these characteristics are not marked in products VI–IX and again point to incompatibility between the preferred ligands, coordination numbers, and geometries of zinc(II) or cobalt(II) centers and the apparent planar-trigonal $(\mu\text{-O})_2Cu_4$ core of IV (Figure 4).

Products XIII and XV associate, presumably through hydrogen-bonding, at ca. 5 °C in nitrobenzene at the $(3\text{–}5) \times 10^{-2}$ level (Table I). This phenomenon has been observed previously and is reversed by dilution.[3,4]

**Electronic Spectra and Trans-Effect Order.** The large difference between the molar absorptivities at 500 nm of complexes IV and XIII and the similarity of those for XIV and XV (Figure 8) allow the tentative assignment of XIV as isomer C (see above), since XV must contain a strongly absorbing Co–O–Co structural unit. The apparent trans-effect order is thus Co > Cu > Ni, Zn.

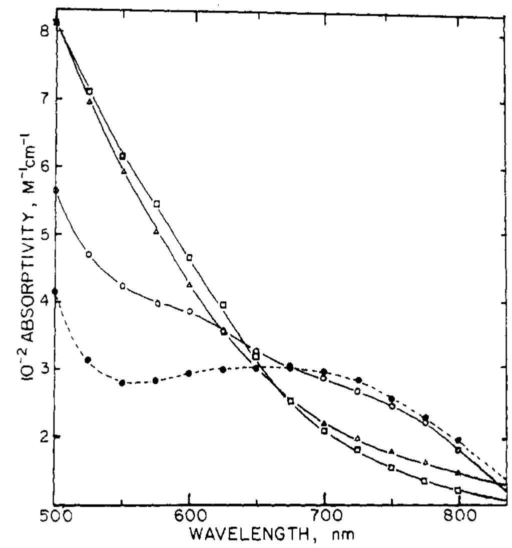


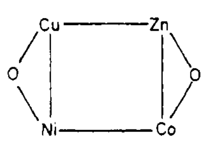
Figure 8. Electronic spectra of IV (●), XIII (○), XIV (△), and XV (□) at 25 °C in methylene chloride.

**Completion of the Trans-Effect Order.** The following data show that the trans-effect order for transmetalation of IV by I is Co > Cu > Zn > Ni. Complex IV was treated consecutively in methylene chloride with 1 equiv each of I in the order M = Ni, Zn, Ni. The product of the second addition was $(\mu\text{-O})_2L_4Cu_2ZnNi$ containing Cu–O–Ni and Cu–O–Zn units on the basis of Cu > Ni, Zn (previous sections). If the trans-effect order were Ni > Zn, the product of the third addition would contain a Ni–O–Ni unit with a large molar absorptivity at 650 nm (Figure 6): the isolated complex XVI only had $\epsilon = 300\ M^{-1}\ cm^{-1}$ at 650 nm (Table III), showing that no Ni–O–Ni unit formed and that the apparent trans-effect order is Co > Cu > Zn > Ni.

**Nature of the Trans Effect.** There is a variety of evidence in the present work and in previous studies[3,4] for the ability of a $\mu$-oxo group to transmit electronic character from a metal coordinated at one end. The *thermodynamic* driving force in all these transmetalation systems is the production of stable $Cu(NS)_2$ products (eq 3).[3,4] The *rate* at which copper(II) in IV is replaced by M is, of course, different from those in tetranuclear oxohalo(pyridine)copper(II) complexes because the core atoms and structures are very different. For this reason there probably is no universal trans-effect order in oxocopper(II) systems.

Exchange of the first copper in IV by cobalt or zinc probably induces a geometric change on the core (compare properties of products VI–IX and X–XVI, particularly with regard to resistance to LH loss when M = Ni). This may well affect the geometries of *all* the metal centers now present. The question is whether the monosubstituted species $L_4Cu_3Co(Zn)O_2$ transmetalates more slowly than IV because of geometric and electronic differences. The point is that transmetalation trans to cobalt(II) in $L_4Cu_3CoO_2$ could still proceed more rapidly (to give isomer C) than transmetalation trans to copper(II) (to give isomers A/B) because exchange of *all* copper(II) centers in $L_4Cu_3CoO_2$ is slower than in IV. There certainly is evidence for a progressive decrease in rate as $x$ increases from 1 to 4 in eq 3.

**Synthesis of $L_4CoNiCuZnO_2\cdot 2H_2O$, a Tetranuclear Complex with Four Different Metals.** The title complex XVII (Table I) was obtained by consecutive additions of 1 equiv each of I in the order M = Zn, Ni, and Co, followed by chromatographic separation. If the trans-effect order Co > Cu > Zn > Ni is maintained in this sequence, we anticipate the following core structure for this product:



Molecule XVII is tetranuclear (Table I), but its electronic

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[29] Davies, G.; El-Toukhy, A.; Onan, K. D.; Veidis, M. *Inorg. Chim. Acta* **1984**, *84*, 41.

[30] Kato, M.; Jonassen, H. B.; Fanning, J. C. *Chem. Rev.* **1963**, *64*, 99.

[31] The fact that XI is not a cyclic $(\mu\text{-O})_2Cu_2Zn_2$ unit (because of LH loss, eq 4) does not prevent the assignment of Cu–O–Cu or Cu–O–Zn units in primary product isomers A–C.

spectrum contains no well-defined maxima (Table III).[18]

**Lack of Activity in Initiators for Phenolic Oxidative Coupling.** Like other tetranuclear ($\mu$-oxo) complexes, complexes IV–XVII of this study are not initiators for the oxidative coupling of phenols by dioxygen under standard conditions.[3,4]

**Acknowledgment.** Financial support from the Department of Health and Human Services (Grant RR07143) is gratefully acknowledged. We also thank Professor W. H. Orme-Johnson and co-workers for assistance in obtaining low-temperature spectra at MIT and Professor A. W. Addison for valuable discussions.

**Registry No.** I (M = Co), 54166-06-2; I (M = Ni), 34214-73-8; I (M = Zn), 72871-59-1; III, 80301-55-9; IV, 102109-29-5; IV·$2C_2H_5OH$, 102109-30-8; V, 102132-55-8; XVII, 102132-56-9.

**Supplementary Material Available:** Table III, spectral data (2 pages). Ordering information is given on any current masthead page.

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# Dissociation and Isomerization Kinetics of (*C-meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (Red) Cation in Strongly Acidic, Aqueous Media

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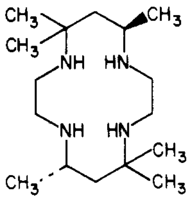
In order to investigate the effect of structure variation upon complex dissociation rate constants, the kinetics of the dissociation and isomerization of (*C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (red) cation has been examined spectrophotometrically at 25 °C in 0.1–5.0 M $HNO_3$. The possible pathways for the cleavages of the copper–nitrogen bonds, the factors influencing the dissociation rates, and the factors affecting the relative importance of each of these possible pathways are considered.

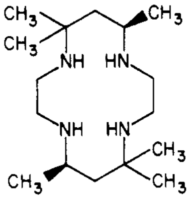
## Introduction

Previously, we have reported the dissociation kinetics of the blue copper(II) complexes of tetraamine macrocyclic ligands, *C-meso*- and *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, tet a (I) and tet b (II), in strongly acidic, aqueous media.[1,2]



I

tet a or *meso*-1,7-CTH



II

tet b or *rac*-1,7-CTH

In the current investigation, we have attempted to gain more detailed understanding of the effect of structure variation on the kinetics of acid-catalyzed dissociation of macrocyclic ligand complexes. To accomplish this, we have extended our studies to the reaction of the red copper(II) complex of tet a in strongly acidic, aqueous media. The crystal structure determinations of $[Cu(tet\ a)\ (blue)]^{2+}$, $[Cu(tet\ a)\ (red)]^{2+}$, and $[Cu(tet\ b)\ (blue)]^{2+}$ have been reported,[3-6] thus providing the opportunity to elaborate the ways in which the different structures of the coordinated macrocyclic tetraaza ligands convey properties on the acid-assisted dissociation kinetics of their metal complexes.

## Experimental Section

**Reagents.** The macrocyclic ligand tet a was prepared by using the procedure described by Hay, Lawrence, and Curtis.[7] The complex $[Cu(tet\ a)\ (red)](ClO_4)_2$ used is the same as that reported earlier.[8-10] All other chemicals used in this work were of GR grade (Merck or Fluka).

**Protonation Constant Determinations.** For pH measurements a Radiometer PHM 64 equipped with a GK 2401B combined electrode was used. The pH was standardized with NBS buffers. The hydrogen ion and hydroxide ion concentrations in 0.1 M $NaNO_3$ were calculated from $-\log [H^+] = pH - 0.11$ and $pK_w = 13.78$.[11] Above pH 12, the readings were corrected by using standard NaOH solutions to give the hydroxide ion concentration.

Appropriate aliquots of standard solutions of acidic ligand were titrated with a standard sodium hydroxide solution. In all titrations the ionic strength was maintained relatively constant by using 0.1 M $NaNO_3$ as supporting electrolyte. The solutions were protected from air by a stream of humidified prepurified nitrogen and were maintained at 25.0 ± 0.1 °C during measurements.

**Kinetic Measurements.** Kinetic runs were initiated by mixing a freshly prepared $[Cu(tet\ a)\ (red)](ClO_4)_2$ solution with a solution that contained the desired quantities of $HNO_3$ and $NaNO_3$. All samples were then well mixed and transferred to a thermostated quartz cell sealed with Teflon. These reactions were followed spectrophotometrically by repetitive scanning through the range 360–700 nm, with particular focus on 504 nm (a maximum for $[Cu(tet\ a)\ (red)]^{2+}$). A Perkin-Elmer Lambda-5 UV–vis spectrophotometer was used for all the solutions studied. The rate constants were obtained by using the CDC Cyber-172 computer.[1]

## Results

The electronic spectrum of $[Cu(tet\ a)\ (red)]^{2+}$ has been reported.[1] The kinetics of the dissociation reactions of this complex were studied spectrophotometrically in 0.1–5.0 M $HNO_3$ (eq 1).

$$[Cu(tet\ a)\ (red)]^{2+} + 4H^+ \rightarrow Cu^{2+} + (H_4tet\ a)^{4+} \qquad (1)$$

This process was not found to occur by a single stage but to take place in consecutive–concurrent steps. The isomerization between the red and the blue species also occurs concurrently with its

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(1) Liang, B.-F.; Chung, C.-S. *Inorg. Chem.* **1981**, *20*, 2152–2155.
(2) Liang, B.-F.; Chung, C.-S. *Inorg. Chem.* **1983**, *22*, 1017–1021.
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(6) Lee, T.-J.; Lee, H. Y. J.; Lee, C.-S.; Chung, C.-S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 641–644.
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(10) Liang, B.-F.; Chung, C.-S. *Inorg. Chem.* **1980**, *19*, 1867–1871.
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