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Transmetalation of μ-Carbonatodicopper(II) Complexes with $M(NS)_2$ Reagents

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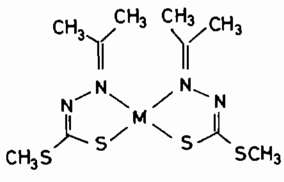
Abstract

Well characterized binuclear μ-carbonatodicopper(II) complexes **III** can be partially and completely transmetalated with $Ni(NS)_2$ reagents **I** or **II** (NS are mononegative anions of S-methyl hydrazinecarbodithioate Schiff bases) to give hetero- and homobinuclear species and $Cu(NS)_2$ coproducts. The neutral ligand HNS stoichiometrically demetalates **III**, showing that a major driving force for transmetalation is the formation of stable $Cu(NS)_2$ coproducts. All nickel-containing products were found to have a strong affinity for water and a tendency to lose their bidentate amine ligands. Products $(H_2O)_6Ni_2Cl_2(CO_3)$ and $(Py)_6Ni_2(OH)Cl(CO_3)\cdot 6H_2O$ have been obtained by direct transmetalation of **III** using different experimental conditions. Nickel(II) complexes, $Ni(NS)_2$, effectively inhibit the oxidation of 2,6-dimethylphenol by dioxygen initiated by complexes **III**.

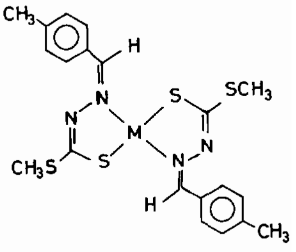
Introduction

Recently, we have found a means of direct aprotic transmetalation of tetranuclear copper complexes $[LCuX]_4Y_2$, $[LCuX]_4X_4$ and $L_4Cu_4X_6O$ (L = N,N-diethylnicotinamide, DENC or ethylnicotinate, ENCA; X = Cl or Br; Y = O or CO_3) by $M(NS)_2$ complexes **I** and **II** (NS is the mononegative anion of an S-methyl hydrazinecarbodithioate Schiff base) [1–3].

The outstanding feature of this chemistry is the direct production of novel transmetalated species with intact tetranuclear cores constructed from monodentate, acid-sensitive ligands.



I



II

The reactions are rapid and quantitative at room temperature and the products typified by eqn. 1 are easily separated by gel permeation chromatography [2, 3].

$$[LCuX]_4X_4 + 4Ni(NS)_2 \xrightarrow{H_2O} [LNi(H_2O)]_4X_4 + 4Cu(NS)_2 \qquad (1)$$

The transmetalation reactions are stepwise, stoichiometric processes up to the point of complete transmetalation [4].

It has been found that transmetalation of such copper complexes by $Ni(NS)_2$ results in the incorporation of one water molecule with each new nickel center during product isolation [2–4].

It is also reported that the presence of μ_2-oxo or μ_2-carbonato groups in reactants controls the extent of substitution of Ni for Cu even in the presence of large excesses of $Ni(NS)_2$ and facilitates the loss of the monodentate ligands L from the new nickel centers [2].

The synthetic potential of direct aprotic transmetalation encouraged us to transmetalate other well-characterized aprotic Cu(II) complexes. These complexes are (sym-μ-carbonato)-dichlorobis(N,N,N′,N′-tetramethyl-1,3-propanediamine)dicopper(II), (μ-CO_3)(tmpd)$_2$$Cu_2Cl_2$, **IIIa**; (asym-$\mu$-carbonato)-dichlorobis(N,N,N′,N′-tetraethylethylenediamine)dicopper(II), (μ-CO_3)(teed)$_2$$Cu_2Cl_2$, **IIIb**; and ($\mu$-carbonato)-dichlorobis(N,N,N′,N′-tetrapropylethylenediamine)dicopper(II), (μ-CO_3)(tped)Cu_2Cl_2, **IIIc** [5, 6].

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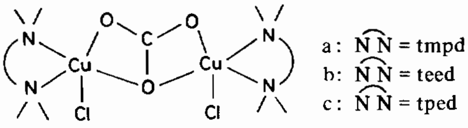
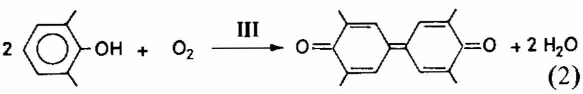


III

The important features of these complexes are: (1) that they effectively initiate the aprotic oxidation of phenols by dioxygen, eqn. 2, and (2) that the physical and chemical properties and stereochemistry of these types of complexes depend on the diamine ligand.



(2)

The tmpd complex, **IIIa**, is diamagnetic, ESR inactive and contains a planar symmetrical carbonato bridge with *trans* chlorine atoms [5]. In contrast, the teed complex, **IIIb**, is paramagnetic with a slight antiferromagnetic interaction (μ_{eff} = 1.33 B.M.), and is ESR active. The complex has an asymmetrically bridging carbonato group with stereochemically inequivalent copper atoms and a *cis* arrangement of chlorine atoms [6].

Study of the transmetalation reactions of these binuclear copper(II) complexes with $M(NS)_2$ reagents should answer the following questions:

(1) Is aprotic transmetalation of binuclear copper(II) complexes (with bidentate ligands) by different $M(NS)_2$ reagents possible?

(2) Does complete transmetalation take place or are intermediate heterobimetallic species stable?

(3) How does the presence of a bridging carbonato group affect the extent of transmetalation and, in particular, is the μ-carbonato group of the copper reactants present in the transmetalated products?

(4) Is water incorporated in the transmetalated products and is the bidentate ligand also partially or completely lost on transmetalation?

Experimental Section

Materials and Reagents

The ligands tmpd, teed, and tped (Aldrich) were dried over 4 Å molecular sieves and distillated under reduced pressure immediately before use. The purifications of methylene chloride, pyridine, hexane and nitrogen were carried out as previously described [1]. Copper(I) chloride was prepared and purified by a literature method [7]. Nickel(II) acetate (Alfa) was used as received. The $Ni(NS)_2$ [8] and the binuclear copper(II) reactants were obtained by literature procedures [5, 6].

Preparation of (μ-Carbonato)dichlorodiaquobis(N,N,N′,N′-tetraalkyldiamine)dinickel(II) Complexes, IV

A clear solution of **III(a, b, or c)** (1 mmol) in anhydrous methylene chloride (50 ml) was stirred with **II** (M = Ni, 2 mmol) in methylene chloride (50 ml) for 12 h under dry nitrogen at room temperature. The majority of the $Cu(NS)_2$ coproduct was removed by Shlenk filtration. The chromatographic separation (Biobeads SX-12 resin, 150 cm × 2.5 cm diameter column, anhydrous methylene chloride eluant) of the brownish–green filtrate resulted in poor separation of the mixture into brownish–green (**IV**) and brown (**II** (M = Cu)) bands. A pure green solution of **IV** was isolated after fractional chromatographic separation. Solid **IV** was isolated by evaporating solutions of **IV** under vacuum.

Preparation of (μ-Carbonato)dichlorohexaaquodinickel(II), V

A clear solution of **IIIa** (1 mmol) in methylene chloride (25 ml) was added to **II** (M = Ni, 2 mmol) in methylene chloride (50 ml). The reaction mixture was stirred for 12 h at room temperature. A brown microcrystalline precipitate of **II** (M = Cu) was formed. The separation of this precipitate by filtration using a water pump resulted in the formation of a completely insoluble (in CH_2Cl_2) green precipitate contaminated with some brown complex **II** (M = Cu). Complete separation of the green and the brown precipitates was carried out by Soxhlet extraction using CH_2Cl_2 as a solvent. The green solid residue was identified as **V**.

Preparation of (μ-Carbonato)chlorohydroxohexakis(pyridine)dinickel(II)hexahydrate, VI

A clear solution of **IIIa** (1 mmol) in pyridine (20 ml) was stirred with **II** (M = Ni, 2 mmol) in pyridine (30 ml) for 12 h under dry nitrogen at room temperature. Gel permeation chromatography (Biobeads SX-12 resin, 60 cm × 4 cm diameter column, pyridine eluant) separated the greenish brown product solution into three bands. The first green band (subsequently identified as a solution of **VI**) was followed by an unidentified band and lastly by a brownish-green band characterized as **II**·2Py, (M = Cu). Solid **VI** was isolated by treatment of the first green band with hexane. The precipitated green complex **VI** was filtered and dried in a vacuum desiccator.

Preparation of (μ-Carbonato)dichloroaquobis(N,N,N′,N′-tetraalkyldiamine)copper(II)nickel(II) Complexes, VII

These complexes were obtained in exactly the

TABLE I. Analytical Data for Transmetalation Products.[a]

Symbol	Complex	%C	%H	%N	%Cl	%Ni	%Cu
IVa	$(tmpd)_2Ni_2(H_2O)_2Cl_2(CO_3)$	32.9 (33.1)	7.4 (7.3)	9.9 (10.3)	12.8 (13.0)	21.1 (21.6)	
IVb	$(teed)_2Ni_2(H_2O)_2Cl_2(CO_3)$	39.8 (40.1)	8.4 (8.3)	8.7 (8.9)	11.2 (11.3)	18.3 (18.7)	
IVc	$(tped)_2Ni_2(H_2O)_2Cl_2(CO_3)$	46.8 (47.1)	9.0 (8.9)	7.3 (7.6)	9.5 (9.6)	15.6 (15.9)	
V	$(H_2O)_6Ni_2Cl_2(CO_3)$	3.5 (3.4)	3.1 (3.3)		19.6 (19.8)	23.1 (23.9)	
VI	$(Py)_6Ni_2Cl(OH)(CO_3)\cdot 6H_2O$	45.85 (45.8)	4.9 (5.3)	10.2 (10.3)	4.6 (4.3)	14.1 (14.4)	
VIIa	$(tmpd)_2CuNi(H_2O)Cl_2(CO_3)$	33.7 (33.9)	7.3 (7.15)	10.4 (10.5)	13.1 (13.4)	10.8 (11.1)	12.3 (11.9)
VIIb	$(teed)_2CuNi(H_2O)Cl_2(CO_3)$	40.8 (40.9)	8.3 (8.1)	9.0 (9.1)	11.3 (11.5)	9.0 (9.6)	10.6 (10.3)
VIIc	$(tped)_2CuNi(H_2O)Cl_2(CO_3)$	47.8 (48.0)	8.7 (8.8)	7.6 (7.7)	9.5 (9.8)	7.8 (8.1)	9.2 (8.8)

[a] Calculated values given in parentheses.

same manner as for **IV** except that the reaction molar ratio **III**:**II** (M = Ni) was 1:1.

Analytical data are collected in Table I*.

Physical Measurements

Solution electronic spectral measurements were made with a Beckman DK-1A spectrophotometer in matched quartz cells at room temperature. Infrared spectra, in KBr disks, were obtained with a Perkin–Elmer Model 567 spectrometer calibrated with the 906.5 or 3026.3 cm^{-1} absorptions of polystyrene. Spectrophotometric titrations of **IIIa** with HNS and **I** (M = Ni) were carried out by standard techniques at 25 °C in the thermostatted cell compartment of a Beckman DK-1A spectrophotometer using matched quartz cells. Absorbance was recorded at 575 nm. The solvent methylene chloride was used as reference.

Results and Discussion

Spectrophotometric titrations of **IIIa** (2.0×10^{-3} M) with HNS and **I** (2.0×10^{-3} M) were carried out in methylene chloride at 575 nm. The reaction mixtures were allowed to stand for two hours before measurement. The results (Fig. 1) indicate that complete reaction requires four equivalents of HNS (demetalation, eqn. 3), and two equivalents of **I** (M = Ni) (transmetalation, eqn. 4), and give no evidence for any variation in these stoichiometries.

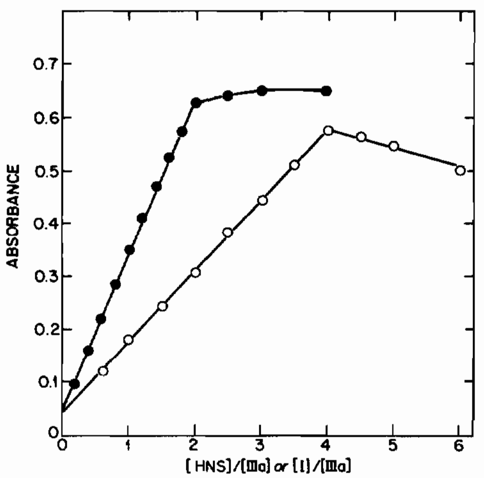


Fig. 1. Spectrophotometric titrations of 2×10^{-3} M CH_2Cl_2 solutions of **IIIa** with HNS (○) and with **I** (M = Ni) (●) at 575 nm.

$$\mathbf{IIIa} + 4HNS \longrightarrow 2Cu(NS)_2 + 2HCl + H_2CO_3 + 2tmpd \qquad (3)$$

$$\mathbf{IIIa} + 2\mathbf{I} \xrightarrow{H_2O} \mathbf{IV} + 2Cu(NS)_2 \qquad (4)$$

These results support the contention that a major driving force for transmetalation of copper(II) complexes by $M(NS)_2$ reagents is the high thermodynamic stability of the $Cu(NS)_2$ coproducts [1–4].

On a preparative scale, the treatment of **IIIa** with **I** in a 1:2 molar ratio resulted in the immediate

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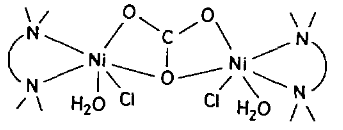
*Elemental Ni and Cu analyses were performed by Dr. T. R. Gilbert with an inductively coupled plasma spectrometer at Northeastern University. All other elemental analyses were made by the Microanalytical Laboratory at the Department of Chemistry, Faculty of Science, Cairo University, Egypt.

formation of a black solution characteristic of the $Cu(NS)_2$ coproduct [9]. At longer reaction times (>3 h) the characteristic black color of **I** (M = Cu) disappeared. The precipitated yellowish product was separated by filtration and identified as Cu^I-(NS). The filtrate was not identified.

This observation, together with the clean spectrophotometric titration data, indicate that the transmetalation reaction is stoichiometric but that the $Cu(NS)_2$ coproduct suffers reduction to virtually insoluble $Cu^I(NS)$. This reduction is catalyzed by the desired nickel(II) product most probably because of the presence of terminal chloride ion in **IV**.

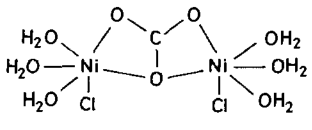


IV

In support of this conclusion no such redox processes were observed in the transmetalation reactions of tetranuclear copper(II) species [2, 3] which contain either chloride ion bridging two metal centers in $L_4Ni_4(H_2O)_4Cl_6O$ [2] or chloride ion bridging three metal centers in $[LCuNi(H_2O)Cl_2]_2Y_2$, (Y = O or CO_3, L = DENC or ENCA) [2, 3].

Because **II**, (M = Cu), is less susceptible to reduction and much less soluble in methylene chloride compared to **I**, (M = Cu) [9], no reduction was observed when using **II** (M = Ni) as a transmetalating agent.

When clear solutions of **IIIa** and **II** (M = Ni) are mixed in 1:2 molar ratio and stirred for 12 h, a brown microcrystalline precipitate of **II**, (M = Cu), is formed. The separation of this precipitate by filtration using a water pump resulted in the formation of **V** (see experimental section).

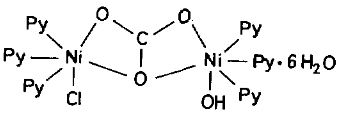


V

The complex **V** is insoluble in all common polar and non-polar solvents. It gives positive carbonate and chloride tests. Its infrared spectrum contains a strong broad absorption centered at 3400 cm^{-1}, due to $\nu(OH)$ of H_2O molecules [10], and the four characteristic bands of the CO_3 group at 1620, 1400, 980 and 670 cm^{-1} [11] with no bands due to the tmpd ligand.

The Nujol mull electronic spectrum exhibited three bands at λ_{max}, 430, 740 and 985 nm, which are typical of distorted octahedral nickel(II) complexes [12], leading to the proposed structure for **V**.

It is known that **II** (M = Cu) is soluble in pyridine giving the bis-pyridine adduct, **II**·2Py [13]. The transmetalation reaction was carried out in pyridine as solvent to avoid precipitation of the coproduct **II** (M = Cu). Products were separated by gel permeation chromatography with pyridine as eluant. The first and third bands were identified as **VI** and **II**·2Py, respectively. The second band gave unreliable analytical results and is likely a mixture of different disproportionation products.



VI

We tried to use the aquo complex **V** as a starting material for preparing some amine complexes through water/amine exchange by adding mono-, bi- or tridentate amine ligands to suspensions of **V** in CH_2Cl_2. However, no reaction was observed even in neat amine ligands. This indicates the high affinity of Ni for H_2O in **V**. When the reaction mixtures were treated with methanol, complex **V** dissolved, giving mixtures of ionic complexes $[L_mNi]Cl_2 \cdot nH_2O$ and $[L_mNi]CO_3 \cdot nH_2O$, (m = 6, 3 or 2 for L = mono-, bi- or tridentate amines, respectively).

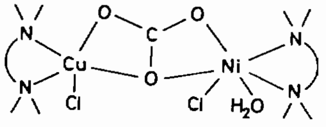
Spectrophotometric titrations of suspensions of **V** with methylimidazole and ethylenediamine in methanol showed that the reaction stoichiometries are $\Delta L/\Delta V \approx 12$ and 6, respectively.

It is evident that the nickel centers in completely transmetalated products have a high affinity for water. The transmetalation reactions of **III** with **II** (M = Ni) in CH_2Cl_2 were repeated under dry nitrogen and rigorously anhydrous conditions. The $Cu(NS)_2$ coproduct was removed by Shlenk filtration instead of with a water pump. We thus avoided the deposition of the aquo complex **V**. The chromatographic separation of the brownish green filtrate resulted in poor separation of the brownish green and brown bands. The separation is poor presumably because of the comparable molecular volumes of the products. Although the transmetalation is quantitative, the poor separation in these systems is responsible for very low product yields (*ca.* 20%). The desired compounds **IV** isolated after fractional chromatographic separation were always contaminated with small amounts of copper (0.4–0.8%).

Freshly prepared samples of **IV** were soluble in CH_2Cl_2 and nitrobenzene; the solubility decrease with time may be due to association through intermolecular hydrogen bonding involving water molecules which are present in the transmetalated products. The infrared spectra of **IV** indicate the presence of the characteristic bands of the diamine ligands, with bands for μ-CO_3 little different from those of the copper reactants, **III**. The ν(Ni–Cl) stretching band appears at 380 cm^{-1}; a broad band centered at 3400 cm^{-1} is due to ν(OH) of the incorporated water.

The Nujol mull and methylene chloride solution electronic spectra of **IV** are similar and consistent with an octahedral ligand environment around each nickel(II) center.

The heterobimetallic Cu–Ni complexes **VII** were also prepared using the same procedure for preparation of **IV** except that the reaction molar ratio of **III**:**II** was 1:1.



VII

Attempted crystallization of **VII** from methylene chloride/ether resulted in disproportionation and gave the starting material **III** as one of the disproportionation products in crystalline form.

Inhibition of Copper-Catalyzed Phenolic Oxidative Coupling

The species **III** are effective initiators for the oxidative coupling of 2,6-dimethylphenol to the corresponding diphenoquinone by dioxygen (eqn. 2) [5, 6]. Addition of 2 mol of **I** or **II** to 1 mol of **III** in nitrobenzene gives a solution that no longer initiates phenolic oxidative coupling by dioxygen. Also, 2 mol of $Ni(NS)_2$ abruptly halts dioxygen consumption and diphenoquinone production in an active catalytic system initiated by 1 mol of **III**. These results are consistent with complete transmetalation of μ-carbonatocopper(II) initiators and copper catalysts to produce catalytically inactive nickel(II) species.

Conclusions

(1) Although the transmetalations of **III** by **I** or **II** are quantitative, the separation of the desired products is difficult and always leaves some copper impurities in the desired products.

(2) The new nickel(II) centers have a much higher affinity for water than for diamine ligands.

(3) The transmetalated products become less soluble in aprotic solvents with time, which makes further physical and chemical investigation very difficult.

(4) The oxidation of 2,6-dimethylphenol by dioxygen initiated by **III** was found to be inhibited by addition of $Ni(NS)_2$ complexes.

References

1 G. Davies, A. El-Toukhy, K. D. Onan and M. Veidis, *Inorg. Chim. Acta, 84,* 41 (1984).

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

3 G. Z. Cai, G. Davies, A. El-Toukhy, T. R. Gilbert and M. Henary, *Inorg. Chem.,* in press.

4 G. Z. Cai, G. Davies, M. A. El-Sayed, A. El-Toukhy and T. R. Gilbert, to be published.

5 M. R. Churchill, G. Davies, M. A. El-Sayed, M. F. El-Shazly, J. P. Hutchinson, M. W. Rupich and K. O. Watkins, *Inorg. Chem., 18,* 2296 (1979).

6 M. R. Churchill, G. Davies, M. A. El-Sayed, M. F. El-Shazly, J. P. Hutchinson and M. W. Rupich, *Inorg. Chem., 19,* 201 (1980).

7 R. N. Keller and H. D. Wycoff, *Inorg. Synth., 2,* 1 (1946);
O. Glemser and H. Sauer, in G. Brauer (ed.) 'Handbook of Preparative Inorganic Chemistry, Vol. 2', Academic Press, New York, 1965, p. 1006.

8 M. F. Iskander, M. M. Mishrikey, L. El-Sayed and A. El-Touky, *J. Inorg. Nucl. Chem., 41,* 815 (1979).

9 M. F. Iskander, L. El-Sayed and A. El-Toukhy, *J. Inorg. Nucl. Chem., 42,* 1145 (1980).

10 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd edn.', Wiley, New York, 1978, p. 226.

11 A. R. Davies, F. W. B. Einstein, N. F. Curtis and J. W. L. Martin, *J. Am. Chem. Soc., 100,* 6258 (1978).

12 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, Amsterdam, 1968, p. 333.

13 A. El-Toukhy, *M.Sc. Thesis,* Alexandria University, Egypt, 1973.