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Transmetallation Reactions of Tetranuclear Copper(II) Complexes. I. Crystal and Molecular Structures of an Intermediate and a Final Product of Reaction of Di-μ-oxo-tetra[chloro(DENC)copper(II)], (DENC = N,N-diethylnicotinamide) with [Zn(N_2S_2)], (N_2S_2 = Diacetyl-bis-hydrazonato-S-methyl-carbodithioate) in Aprotic Solvents

GEOFFREY DAVIES*, AHMED EL-TOUKHY**, KAY D. ONAN* and MIKELIS VEIDIS

Department of Chemistry, Northeastern University, Boston, Mass. 02115, U.S.A.

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Di-μ-oxo-tetra[chloro(DENC)copper(II)], [(DENC)-CuCl]$_4$O$_2$, (DENC = N,N-diethylnicotinamide) reacts with two moles of dimeric [Zn(N_2S_2)]$_2$, (N_2S_2 = diacetyl-bis-hydrazonato-S-methyl-carbodithioate) to give 2 moles of [Cu(N_2S_2)]$_2$ and a variety of zinc-containing products, including zinc(II) oxide. The crystal and molecular structures of the intermediate five-coordinate complex Zn(N_2S_2)(DENC), A, *and a final product, di-μ-(N,N-diethylnicotinamide-O,N)-tetrachlorodizinc(II),* B, *from this interesting metal exchange reaction are reported. Although the ultimate products are the same, no intermediate analog of* A *is detected with monomeric tetrahedral Zn(NS)$_2$ reactants. Complex* A *crystallizes in the triclinic space group* $P\bar{1}$ *with Z = 2 in a cell of dimensions* a = *10.258(1),* b = *10.708(1),* c = *12.548(1)* Å, α = *107.69(1), β = 99.70(1), γ = 106.49(1)°. Complex* B *also crystallizes in space group* $P\bar{1}$ *with Z = 2 but in a cell of dimensions* a = *9.427(4),* b = *14.106(6),* c = *8.589(3)* Å, α = *120.87(3), β = 116.17(3), γ = 106.76(3)°.*

Introduction

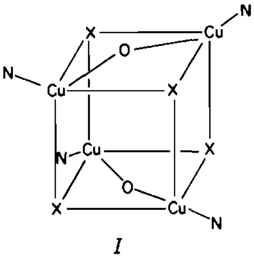
We are exploring the chemistry of tetranuclear dioxocopper(II) products of oxidation of halo(pyridine)copper(I) complexes by dioxygen in aprotic solvents at low pyridine:copper(I) molar ratios [1–3]. The observed rate law for oxidation depends on the molecularity of the copper(I) reactant, eqns. 1 and 2 (L = a monodentate pyridine, m = 4 or 8); however, in all cases the product can be shown to be tetranuclear $L_4Cu_4X_4O_2$ by cryoscopic measurements [2, 3].

$$d[L_4Cu_4X_4O_2]/dt = k_D[L_2Cu_2X_2]^2[O_2] \qquad (1)$$

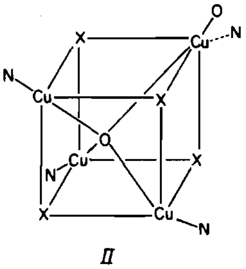
$$d[L_4Cu_4X_4O_2]/dt = k_T[L_mCu_4X_4][O_2] \qquad (2)$$

None of the primary dioxocopper(II) products appear to crystallize in the absence of disproportionation, but the identities of the crystalline disproportionation products themselves and a variety of other observations suggest the formation of one or other of two characteristic product core structures, *I* and *II*, depending on the pyridine ligand coordinated to copper(I) [2, 3].

One of the useful properties of structure *II* is that it initiates (and possibly catalyzes) the oxidative coupling of protic substrates like phenols, eqn. 3; by contrast, structure *I* is inactive, at least in the ligand/solvent systems we have investigated [3]. However, both structures are sensitive to protic substances and it seems likely that substrate deprotonation, presumably by basic oxogroups, is a prerequisite to substrate oxidation by copper(II) [3, 4]. We have argued that the terminal oxogroup in structure



I



II

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*Authors to whom correspondence should be addressed.

**On leave of absence from the Department of Chemistry, Alexandria University, Alexandria, Egypt.

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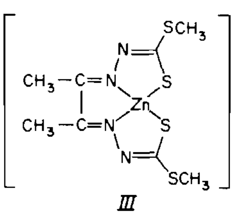
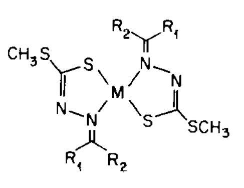


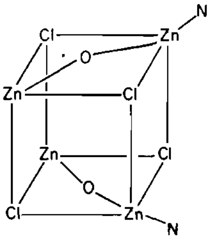
III



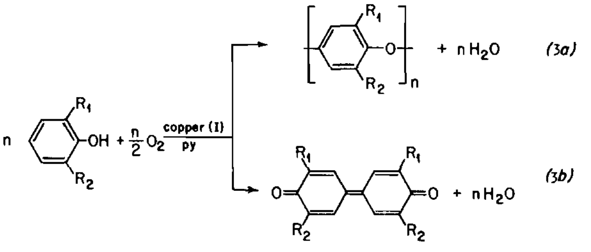
IV

M = Zn(II), Ni(II), Co(II) or Cu(II)

R_1, R_2 = H, Ph; CH_3, CH_3



V



II is the most basic site in this series of complexes [3].

Structures I and II behave quite differently with aprotic acids, in particular carbon dioxide. Thus, while structure I reacts to form a dicarbonato derivative, structure II is unreactive as a result of the instability of the corresponding monocarbonato complex that might be expected from reaction with its terminal oxogroup [2].

The work reported here was prompted by a desire to develop a basicity scale for these dioxocopper(II) species so that structural and electronic factors could be assessed as contributors to this inherent property. Since protic acids would presumably cause gross structural changes on reaction with $L_nCu_4X_4O_2$ species (n = 3 or 4) because of coordination of the resulting anion, we selected Lewis acids, represented by structure *III*, as standards [5, 6].

This complex is dimeric because of the strong Lewis acidity imposed by the planar ligand geometry at each Zn center. As a result it dissociates to form stable *mono* adducts with simple monodentate Lewis bases B, eqn. 4 [6]. Our expectation was that structure *II* would react with *III* according to eqn. 5, while the corresponding reaction with *I* would have a different stoichiometry, eqn. 6, because it contains *two* accessible oxo sites per molecule.

$$[Zn(N_2S_2)]_2 + 2B \rightleftharpoons 2Zn(N_2S_2){\cdot}B \tag{4}$$

$$[Zn(N_2S_2)]_2 + 2II \rightleftharpoons 2Zn(N_2S_2){\cdot}II \tag{5}$$

$$[Zn(N_2S_2)]_2 + I \rightleftharpoons Zn(N_2S_2){\cdot}I{\cdot}(N_2S_2)Zn \tag{6}$$

We have found instead that exchange of zinc for copper takes place in these systems as a result of the very high thermodynamic stability of $[Cu(N_2S_2)]_2$ [7]. Unfortunately, the zinc analog of structure *I* does not appear to be stable but we have been able to isolate and structurally characterize two of the reaction products, the intermediate $Zn(N_2S_2)$-(DENC), *A*, and a final product di-μ-(N,N-diethylnicotinamide-O,N)-tetrachlorodizinc(II), *B*. The square-pyramidal complex *A* is the first structurally characterized example of the products of reactions 4. The characterized product *B* is one of only two examples of a metal complex in which DENC forms the bridges in a discrete dimer structure [8].

Experimental

Materials and Reagents

DENC (Aldrich) was dried over 4 Å molecular sieves and distilled under reduced pressure immediately before use. Hydrazine-S-methyl carbodithioate and the Schiff bases needed for the preparation of *III* and *IV* were prepared by literature methods [9]. Copper(I) chloride was prepared and purified by literature methods [10]. Zinc(II) acetate dihydrate (Aldrich) was used as received for preparing $Zn(N_2S_2)$ complexes. Nitrobenzene (Aldrich) was distilled over P_4O_{10} at reduced pressure and stored over 4 Å molecular sieves. The purifications of methylene chloride, diethyl ether, hexane and dinitrogen were carried out as previously described [2]. Di-μ-oxotetra[chloro(DENC)copper(II)], *I* [2], dimeric $[Zn(N_2S_2)]_2$, *III* [5], and monomeric $Zn(N_2S_2)$, *IV* [11], were prepared as described previously.

Isolation of $Zn(N_2S_2)(DENC)$, A

A clear greenish brown solution of $[(DENC)CuCl]_4O_2$ (1 mmol) in methylene chloride (30 ml) was added to a suspension of yellow dimeric $[Zn(N_2S_2)]_2$ (2 mmol) in methylene chloride (30 ml). The mixture was stirred at room temperature under a dry nitrogen atmosphere for 10 minutes. During this time a reddish-brown precipitate of dimeric $[Cu(N_2S_2)]_2$ separated and the supernatant solution turned reddish-orange. This supernatant was treated with dry hexane (5 ml) giving a reddish-brown precipitate (which was separated) and an orange solution.

The solvent was then removed in a rotary evaporator, leaving an orange solid. The product *A* crystallized after three days at room temperature from methylene chloride/diethyl ether in a closed system as orange crystals of dimensions suitable for structural characterization. *Anal.* Found [12]: C, 40.21; H, 4.73; N, 15.65; Zn, 12.35%. Calcd. for $Zn(N_2S_2)$(DENC): C, 40.38; H, 4.90; N, 15.70; Zn, 12.21%.

An authentic sample of *A* was obtained as follows. A suspension of dimeric $[Zn(N_2S_2)]_2$ (10 mmol) in methylene chloride (30 ml) was treated with DENC (25 mmol). The mixture was heated on a steam bath for 10 minutes; on cooling, crystals of $Zn(N_2S_2)$(DENC) were deposited. *Anal.* Found [12]: C, 40.18; H, 4.77; N, 15.61; Zn, 12.30%.

Isolation of Di-μ-(N,N-diethylnicotinamide-O,N)tetrachlorodizinc(II), B

This complex was prepared exactly as described for $Zn(N_2S_2)$(DENC) (*A*) except that the reaction mixture was left stirring for three hours at room temperature. The deposited reddish-brown crystals of the $[Cu(N_2S_2)]_2$ (contaminated with white ZnO) were removed by filtration. The filtrate was treated with dry hexane (5 ml) to remove most of the remaining $[Cu(N_2S_2)]_2$. Single crystals of $(DENC)_2Zn_2Cl_4$, *B*, were obtained by slow evaporation of the resulting almost colorless filtrate. *Anal.* Found [12]: C, 38.62; H, 4.74; N, 8.85; Zn, 21.01. Calcd for $(DENC)_2Zn_2Cl_4$: C, 38.23; H, 4.55; N, 8.91; Zn, 20.84.

An authentic sample of *B* was obtained as follows: A clear solution of DENC (10 mmol) in methylene chloride (20 ml) was added dropwise with constant stirring to zinc(II) chloride (40 mmol) in methylene chloride (30 ml). The reaction mixture was stirred at room temperature for two hours, filtered and the methylene chloride removed in a rotary evaporator, leaving a white solid, which was recrystallized from methylene chloride/diethyl ether to give white crystals of *B*. *Anal.* Found [12]: C, 38.44; H, 4.60; N, 8.72; Zn, 20.93%.

Physical Measurements

Solution electronic spectral measurements were made with Cary 14 and Beckman DK-1A spectrophotometers in matched quartz cells at room temperature. Infrared spectra, either in KBr disks or in solution, were obtained with a Perkin-Elmer Model 567 spectrometer calibrated with the 906.5- or 3026.3 cm^{-1} absorptions of polystyrene. ^{1}H NMR spectra were observed with a JEOL Model FX60Q spectrometer at 25 °C with TMS as internal reference. Spectrophotometric titrations of oxocopper(II) complex with $[Zn(N_2S_2)]_2$ 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 500 nm. The solvent (methylene chloride) was used as reference.

TABLE I. Crystal data for *A* and *B*.

	A	*B*
formula	$C_{18}H_{26}N_5OS_4Zn$	$C_{10}H_{14}Cl_2N_2OZn$
formula weight	536.0	314.5
system	triclinic	triclinic
a, Å	10.258(1)	9.427(4)
b, Å	10.708(1)	14.106(6)
c, Å	12.548(1)	8.589(3)
α, deg	107.69(1)	120.87(3)
β, deg	99.70(1)	116.17(3)
γ, deg	106.49(1)	106.76(3)
V, Å^3	1212.4(2)	654.7(5)
Z	2	2
d_{calcd}, g/cm^2	1.466	1.595
F(000)	516	844
μ(Cu-Kα), cm^{-1}	46.8	62.8
λ(Cu-Kα), Å	1.5418	1.5418
space group	$P\bar{1}(C_i^1)$	$P\bar{1}(C_i^1)$

Kinetic Measurements

Kinetic measurements of reactions of *I* with *IV* (M = Zn, $R_1 = R_2 = CH_3$) were always conducted with *IV* in sufficient excess to ensure pseudo-first-order conditions. The rates of formation of $Cu(NS)_2$, *IV*, (M = Cu) on mixing homogeneous solutions of *I* and *IV* (M = Zn) were monitored using a computer-assisted stopped-flow spectrophotometer [13] at temperatures controlled to within ±0.05 °C of the desired value.

X-Ray Crystallography: Intensity Data and Structure Analysis

A clear, bright-orange crystal of *A* of dimensions 0.15 × 0.18 × 0.45 mm was attached to a glass fiber and was mounted on a Syntex $P2_1$ automated diffractometer. Crystal data are summarized in Table I. The unit cell dimensions were obtained by a least squares fit of 15 reflections well separated in reciprocal space. One hemisphere of data, 3926 reflections, was collected in the range $4.0 \leqslant 2\theta \leqslant 130.0°$ using $\theta/2\theta$ scans. Two standard reflections, monitored after every 98 reflections, showed no significant variation with time. The data were corrected for Lorentz and polarization effects; an empirical absorption correction, determined from a ψ scan, was also made. The 3642 data remaining with $I > 2.0\sigma(I)$ were used in the structure solution and refinement.

A chunky (0.25 × 0.25 × 0.50 mm), opaque, whitish-yellow crystal of *B* was placed in a capillary

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) for the non-Hydrogen Atoms in Complex *A*, with Estimated Standard Deviations in Parentheses.

Atom	*x/a*	*y/b*	*z/c*
S(1)	3078(1)	4224(1)	2147(1)
C(2)	2567(3)	2653(3)	957(3)
N(3)	1357(2)	1967(3)	152(2)
N(4)	413(2)	2649(3)	343(2)
C(5)	−786(3)	2199(3)	−424(3)
C(51)	−1247(4)	967(4)	−1524(4)
C(6)	−1684(3)	3058(3)	−126(3)
C(61)	−3068(3)	2753(4)	−946(4)
N(7)	−1149(2)	4069(3)	872(3)
N(8)	−1855(2)	4981(3)	1216(3)
C(9)	−1083(3)	6044(3)	2172(3)
S(10)	601(1)	6424(1)	3011(1)
S(11)	3923(1)	1980(1)	867(1)
C(12)	3150(4)	434(4)	−448(4)
S(13)	−1786(1)	7346(1)	2721(1)
C(14)	−3517(4)	6690(4)	1734(3)
N(15)	−120(2)	2872(2)	2799(2)
C(16)	−1419(3)	2666(3)	2931(2)
C(17)	−2043(3)	1785(3)	3451(2)
C(18)	−1257(4)	1085(3)	3863(3)
C(19)	74(4)	1292(3)	3742(3)
C(20)	610(3)	2190(3)	3212(3)
C(21)	−3557(3)	1439(3)	3490(2)
N(22)	−3969(2)	2469(3)	4057(2)
C(23)	−5448(3)	2115(4)	4102(3)
C(24)	−5637(4)	1805(5)	5152(4)
C(25)	−3024(3)	3931(3)	4709(3)
C(26)	−3244(4)	4891(4)	4105(3)
O	−4355(3)	211(3)	3001(2)
Zn	760.1(4)	4252.6(4)	1972.1(3)

TABLE III. Fractional Atomic Coordinates ($\times 10^4$) for the Non-Hydrogen Atoms in Complex *B*, with Estimated Standard Deviations in Parentheses.

Atom	*x/a*	*y/b*	*z/c*
N(1)	1555(6)	6352(4)	8735(6)
C(2)	2147(6)	6684(4)	7813(8)
C(3)	3865(7)	6891(4)	8225(8)
C(4)	4954(7)	6702(5)	9621(9)
C(5)	4328(7)	6350(5)	10513(9)
C(6)	2630(8)	6193(5)	10095(9)
C(7)	4358(6)	7218(4)	7072(8)
N(8)	6008(5)	8581(4)	8566(7)
C(9)	6571(7)	8907(5)	7455(8)
C(10)	5673(10)	9486(6)	6711(11)
C(11)	7412(8)	9837(6)	11391(9)
C(12)	9542(9)	10260(7)	13009(10)
O(13)	3189(5)	6189(3)	4648(6)
Zn	1044(1)	3972(1)	2005(1)
Cl(1)	399(2)	3054(2)	−1442(2)
Cl(2)	1867(2)	3192(1)	3623(3)

and was mounted on a Syntex $P2_1$ automated diffractometer. Crystal data are summarized in Table I. The data collection was carried out as described above. Of 2009 reflections collected, 1851 had $I > 2.0\sigma(I)$ and these data were used in the structure solution and refinement.

Both structures were solved via three-dimensional Patterson and Fourier syntheses. Least squares refinement of positional and isotropic (subsequently anisotropic) thermal parameters of non-hydrogen atoms brought *R* to 0.053 for *A* and 0.070 for *B*. Hydrogen atomic positions were calculated, verified in difference maps, and added to the structure factor calculations. Continued refinement of the positional and thermal (anisotropic non-hydrogen, isotropic hydrogen) parameters brought the refinements to convergence at $R = 0.038$ for *A* and $R = 0.062$ for *B* [14].

The atomic scattering factors for the non-hydrogen atoms were taken from ref. [15], with those of Zn and S(*A*) and Zn and Cl(*B*) corrected for anomalous scattering [16]; the scattering factor of ref. [17] was used for hydrogen.

Final atomic positional coordinates for the non-hydrogen atoms of *A* appear in Table II and those for *B* are in Table III. Tables IV and V are of the inter-

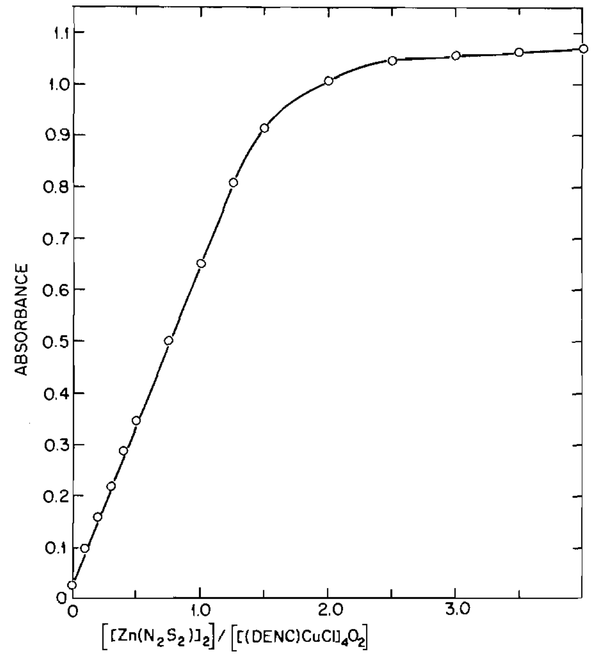


Fig. 1. Spectrophotometric titration of *I* (5.0×10^{-4} *M*) with *III* (5.0×10^{-3} *M*) in methylene chloride at 500 nm. Reaction mixtures were allowed to stand for 3 hours prior to absorbance measurements.

TABLE IV. Interatomic Distances (Å) and Valency Angles (deg.) in Complex *A*, with Estimated Standard Deviations in Parentheses.

Bond lengths

Coordination Sphere

Zn–S(1)	2.360(1)	Zn–S(10)	2.362(1)
Zn–N(4)	2.132(3)	Zn–N(15)	2.139(2)
Zn–N(7)	2.120(3)		

Ligands

S(1)–C(2)	1.746(3)	S(13)–C(14)	1.791(4)
C(2)–N(3)	1.309(4)	N(15)–C(16)	1.335(4)
C(2)–S(11)	1.744(3)	N(15)–C(20)	1.332(4)
N(3)–N(4)	1.379(4)	C(16)–C(17)	1.379(4)
N(4)–C(5)	1.287(4)	C(17)–C(18)	1.385(5)
C(5)–C(6)	1.491(5)	C(17)–C(21)	1.504(5)
C(5)–C(51)	1.481(5)	C(18)–C(19)	1.362(5)
C(6)–N(7)	1.286(4)	C(19)–C(20)	1.373(5)
C(6)–C(61)	1.492(5)	C(21)–N(22)	1.339(4)
N(7)–N(8)	1.384(4)	C(21)–O	1.227(4)
N(8)–C(9)	1.305(4)	N(22)–C(23)	1.470(4)
C(9)–S(10)	1.729(3)	N(22)–C(25)	1.467(5)
C(9)–S(13)	1.760(3)	C(23)–C(24)	1.487(6)
S(11)–C(12)	1.804(4)	C(25)–C(26)	1.495(5)

Valency angles

Coordination Sphere

S(1)–Zn–N(4)	80.36(7)	N(4)–Zn–S(10)	148.74(8)
S(1)–Zn–N(7)	147.34(7)	N(4)–Zn–N(15)	96.19(10)
S(1)–Zn–S(10)	115.55(3)	N(7)–Zn–S(10)	80.95(8)
S(1)–Zn–N(15)	103.23(7)	N(7)–Zn–N(15)	98.65(9)
N(4)–Zn–N(7)	73.38(10)	S(10)–Zn–N(15)	105.16(7)

Ligands

Zn–S(1)–C(2)	94.5(1)	Zn–S(10)–C(9)	94.7(1)
S(1)–C(2)–N(3)	129.2(2)	C(2)–S(11)–C(12)	103.3(2)
S(1)–C(2)–S(11)	112.5(2)	C(9)–S(13)–C(14)	103.4(2)
N(3)–C(2)–S(11)	118.3(2)	Zn–N(15)–C(16)	121.4(2)
C(2)–N(3)–N(4)	110.8(2)	Zn–N(15)–C(20)	121.4(2)
Zn–N(4)–N(3)	121.6(2)	C(16)–N(15)–C(20)	117.2(3)
Zn–N(4)–C(5)	118.5(2)	N(15)–C(16)–C(17)	124.0(3)
N(3)–N(4)–C(5)	119.4(3)	C(16)–C(17)–C(18)	117.3(3)
N(4)–C(5)–C(51)	124.3(3)	C(16)–C(17)–C(21)	123.9(3)
N(4)–C(5)–C(6)	113.8(3)	C(18)–C(17)–C(21)	118.6(3)
C(51)–C(5)–C(6)	121.9(3)	C(17)–C(18)–C(19)	119.4(3)
C(5)–C(6)–C(61)	121.5(3)	C(18)–C(19)–C(20)	119.3(3)
C(5)–C(6)–N(7)	114.3(3)	N(15)–C(20)–C(19)	122.8(3)
C(61)–C(6)–N(7)	124.2(3)	C(17)–C(21)–N(22)	119.1(3)
Zn–N(7)–C(6)	118.9(2)	C(17)–C(21)–O	117.7(3)
Zn–N(7)–N(8)	121.7(2)	N(22)–C(21)–O	123.1(3)
C(6)–N(7)–N(8)	119.4(3)	C(21)–N(22)–C(23)	118.6(3)
N(7)–N(8)–C(9)	111.2(2)	C(21)–N(22)–C(25)	124.5(3)
N(8)–C(9)–S(10)	129.9(2)	C(23)–N(22)–C(25)	116.8(3)
N(8)–C(9)–S(13)	117.8(2)	N(22)–C(23)–C(24)	112.2(3)
S(10)–C(9)–S(13)	112.3(2)	N(22)–C(25)–C(26)	112.7(3)

TABLE V. Interatomic Distances (Å) and Valency Angles (deg.) in Complex *B*, with Estimated Standard Deviations in Parentheses.

Bond lengths			
N(1)–C(2)	1.333(8)	N(8)–C(9)	1.469(9)
N(1)–C(6)	1.340(9)	N(8)–C(11)	1.477(10)
C(2)–C(3)	1.396(8)	C(9)–C(10)	1.501(11)
C(3)–C(4)	1.401(10)	C(11)–C(12)	1.522(12)
C(3)–C(7)	1.470(9)	O(13)–Zn	2.010(5)
C(4)–C(5)	1.342(10)	Zn–Cl(1)	2.199(2)
C(5)–C(6)	1.395(10)	Zn–Cl(2)	2.203(2)
C(7)–N(8)	1.322(8)	Zn–N(1)[a]	2.073(6)
C(7)–O(13)	1.269(9)		
Valency angles			
C(2)–N(1)–C(6)	119.2(6)	C(9)–N(8)–C(11)	116.3(5)
N(1)–C(2)–C(3)	122.7(6)	N(8)–C(9)–C(10)	113.1(6)
C(2)–C(3)–C(4)	117.4(6)	N(8)–C(11)–C(12)	112.7(6)
C(2)–C(3)–C(7)	118.6(6)	C(7)–O(13)–Zn	130.7(4)
C(4)–C(3)–C(7)	123.9(6)	O(13)–Zn–Cl(1)	105.6(1)
C(3)–C(4)–C(5)	119.3(6)	O(13)–Zn–Cl(2)	113.1(2)
C(4)–C(5)–C(6)	120.7(7)	O(13)–Zn–N(1)[a]	100.8(2)
N(1)–C(6)–C(5)	120.7(6)	Cl(1)–Zn–Cl(2)	120.1(1)
C(3)–C(7)–N(8)	119.8(6)	Cl(1)–Zn–N(1)[a]	109.4(2)
C(3)–C(7)–O(13)	119.6(6)	Cl(2)–Zn–N(1)[a]	106.2(2)
N(8)–C(7)–O(13)	120.6(6)	Zn–N(1)[a]–C(2)[a]	120.5(4)
C(7)–N(8)–C(9)	120.2(6)	Zn–N(1)[a]–C(6)[a]	120.3(5)
C(7)–N(8)–C(11)	123.5(6)		

[a] Coordinates from Table III translated by $-x$, $1-y$, $1-z$.

atomic distances and angles in *A* and *B*, respectively. Tables of anisotropic thermal parameters; hydrogen atomic positions, isotropic thermal parameters, and bond lengths involving hydrogen atoms; torsion angles; interatomic separations less than 3.8 Å; observed and calculated structure factors and packing diagrams for both *A* and *B* may be obtained from the Authors.

Results and Discussion

Spectrophotometric titration of $[(\mathrm{DENC})\mathrm{CuCl}]_4\mathrm{O}_2$, *I*, ($5.0 \times 10^{-4}$ *M*) with $[\mathrm{Zn}(\mathrm{N_2S_2})]_2$, *III*, ($5.0 \times 10^{-3}$ *M*) in methylene chloride at 500 nm, in which the reaction mixtures were allowed to stand for 3 hours, indicated that two equivalents of *III* react with one equivalent of *I*, Fig. 1, consistent with overall reaction 9.

$$I + 2III \longrightarrow$$

$$[\mathrm{Cu(N_2S_2)}]_2 + 2A + (\mathrm{DENC})_2\mathrm{Zn_2Cu_2Cl_4O_2} \qquad (7)$$

$$(\mathrm{DENC})_2\mathrm{Zn_2Cu_2Cl_4O_2} + 2A \longrightarrow$$

$$[\mathrm{Cu(N_2S_2)}]_2 + [(\mathrm{DENC})\mathrm{Zn_2Cl_2}]_2\mathrm{O_2} + 2\mathrm{DENC} \qquad (8)$$

net

$$I + 2III \longrightarrow$$

$$2[\mathrm{Cu(N_2S_2)}]_2 + [(\mathrm{DENC})\mathrm{Zn_2Cl_2}]_2\mathrm{O_2} + 2\mathrm{DENC} \qquad (9)$$

An isosbestic point was observed at 650 nm. Titration of *I* with *IV* (M = Zn, $R_1 = R_2 = CH_3$) showed that 4 equivalents of *IV* are required for reaction in the analog of reaction 9 where the copper-containing product is *IV* (M = Cu).

Evidence for intermediate reaction 7 and for reaction 10 comes from experiments directed at the isolation of $[(\mathrm{DENC})\mathrm{Zn_2Cl_2}]_2\mathrm{O_2}$.

$$[(\mathrm{DENC})\mathrm{Zn_2Cl_2}]_2\mathrm{O_2} \longrightarrow 2\mathrm{ZnO(s)} + B \qquad (10)$$

Under the conditions described in the Experimental section, $[\mathrm{Cu(N_2S_2)}]_2$ is virtually insoluble in methylene chloride and can be easily removed by filtration of the product mixture. This product does not react with DENC, as found in analogous systems [7]. The isolation of product *A* at short reaction times (10 min) is evidence for reaction 7. The rate law for the first observed reaction of excess *IV* (M = Zn, $R_1 = R_2 = CH_3$) with *I* in methylene

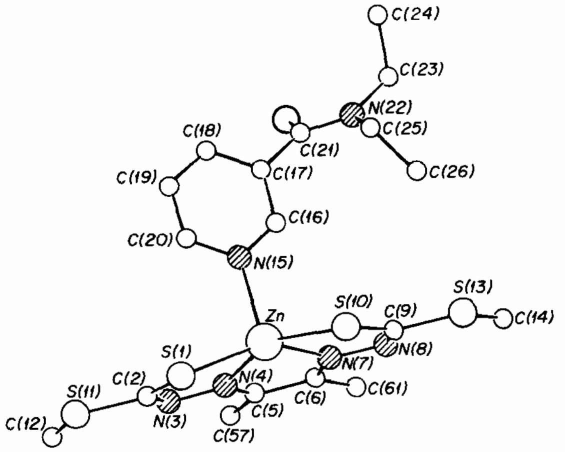


Fig. 2. Perspective view of the non-hydrogen atoms of complex *A* showing the numbering scheme.

chloride is given by eqn. 11, with k = (2.0 ± 0.1) 10^4 M^{-2} sec^{-1} at 25 °C.

$$d[Cu(NS)_2]/dt = k[Zn(NS)_2]^2[I] \qquad (11)$$

These studies were made with *IV* because *III* (M = Zn) has limited solubility in methylene chloride. This result is consistent with the formation of $(DENC)_2Zn_2Cu_2Cl_4O_2$ as a primary product. However, no analog of *A* was detected as an intermediate with *IV* (M = Zn) as a reactant because *IV* has little affinity for Lewis bases like DENC (see below). In fact, the isomeric species $(DENC)_2Cu_2Ni_2Cl_4(OH_2)_2O_2$ are *final* products of the corresponding transmetallation reactions of *IV* (M = Ni; $R_1 = R_2 = CH_3$; R_1 = H, R_2 = p-$CH_3C_6H_4$) with *I* [18]. At longer reaction times the characteristic orange color of *A* disappears and the precipitated $[Cu(N_2S_2)]_2$ product is contaminated with ZnO(s) which was separately identified. Product *B* can be crystallized from the product filtrate.

It is evident from these results that complete transmetallation of Zn for Cu in *I* occurs, but that $[(DENC)Zn_2Cl_2]_2O_2$ undergoes disproportionation reaction 10.

Molecular Structure of A

The intermediate complex, $Zn(N_2S_2)(DENC)$, *A*, exists as isolated units consisting of *cis*-N_2S_2 coordination in the equatorial plane and an axial DENC ligand (Fig. 2). The N(4), N(7), S(1), S(10) plane is nearly orthogonal (83.7°) to the plane of the pyridine ring. The zinc atom is displaced 0.46 Å out of plane 1 toward the pyridine nitrogen but lies in the plane of the pyridine ring (Table VI). Atoms C(2), N(3), S(11) and C(12) are all very slightly displaced from plane 1 in the same direction as is the zinc atom. The remainder of the atoms in the tetradentate ligand are displaced to the opposite side of the plane. Because of these displacements there is only one separation of less than 3.50 Å between the two ligands in the complex [N(7)···C(16) 3.38 Å].

TABLE VI. Distances (Å) of Atoms from Least-Squares Planes through Various Groups of Atoms; Atoms defining the Plane are italicized.

Complex A			
Plane 1			
S(1)	0.01	C(9)	0.11
N(4)	−0.01	S(11)	−0.04
N(7)	0.01	C(12)	−0.01
S(10)	−0.01	C(51)	0.24
C(2)	−0.03	C(61)	0.41
N(3)	−0.04	S(13)	0.28
C(5)	0.12	C(14)	0.34
C(6)	0.17	Zn	−0.46
N(8)	0.11		
Plane 2			
N(15)	0.00	*C(19)*	0.00
C(16)	0.00	*C(20)*	0.00
C(17)	0.00	Zn	0.01
C(18)	0.00		
Complex B			
Plane 3			
N(1)	0.00	*C(5)*	0.01
C(2)	0.01	*C(6)*	−0.01
C(3)	−0.01	Zn[a]	0.06
C(4)	0.00		
Plane 4			
C(3)	0.00	*O(13)*	0.00
C(7)	0.00	Zn	−0.42
N(8)	0.00		

[a] Coordinates from Table III are transformed by −x, 1 − y, 1 − z.

Table IV shows the tetradentate ligand to possess a pseudo-two-fold axis. The interatomic distances within this ligand indicate electron delocalization which is responsible for the stability of this intermediate relative to those formed by monodentate, tetrahedral complexes *IV*. The observed molecular parameters in the ligand are very like those found in related compounds [19–22].

The coordination about the zinc atom is a very distorted square pyramid in which the angles in the

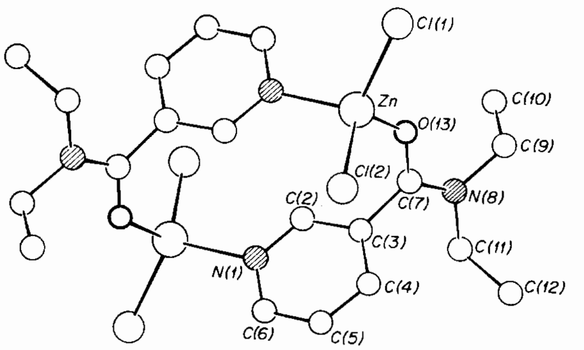


Fig. 3. Perspective view of the non-hydrogen atoms of a dimer of complex *B* showing the numbering scheme.

equatorial plane range from 73.4(1)° (N–Zn–N) to 115.55(3)° (S–Zn–S). These angles vary more than do analogous values for Ni(II) [19] or Cu(II) [20, 21] complexes of a similar nature. This is, in part, a result of the larger ionic radius of Zn(II) which requires that the atom lie further out of the basal plane. The coordination exhibited here is, however, very similar to that observed in aquo [3-ethoxy-2-oxobutyraldehyde-*bis*-(thiosemicarbazonato)]zinc(II) in which the angles in the equatorial plane range from 74.3° to 118.1° [22]. The Zn–S and Zn–N distances are also comparable in these two examples.

The molecules pack along the *x*-direction in such a manner that rows of DENC ligands alternate with rows of $Zn(N_2S_2)$ moieties in the *y*-direction. Van der Waals forces determine the molecular packing in the crystal.

Crystal and Molecular Structure of B

Crystallographic analysis shows di-μ-(N,N-diethylnicotinamide-O,N)-tetrachlorodizinc(II), *B*, to consist of discrete centrosymmetric dimers in which the bridging of the tetrahedrally coordinated zinc centers is via DENC ligands in which both the amide oxygen and the pyridine nitrogen atoms are coordinated (Fig. 3). The fact that *B* is a final product in this reaction sequence is consistent with the stability of tetrahedrally coordinated zinc. A very similar complex, $Zn_2(DENC)_2(NCS)_4$ (*C*), results upon allowing the octahedral complex $Zn(DENC)_2(NCS)_2(H_2O)_2$ to stand in mother liquor [8].

The tetrahedron about the zinc is quite distorted, with an angular range of 100.8(2) to 120.1(1)° (Table V). Of these angles, the O–Zn–N is the smallest and is comparable to the 102.5° angle found for *C* [8]. The slight difference can be attributed to the larger C–O–Zn angle in *C* (132.2° vs. 130.7(4)° in *B*) and the larger modulus of the C(2)–C(3–C(7)–O(13) torsion angle (82.8° *vs.* 74.6(7)° in *B*). These conformational preferences lead to a very small separation (4.35 Å) between the donor atoms in an individual DENC ligand in *B*. In fact, this is the smallest N, O separation in a bridging DENC ligand observed to date (others vary from 4.40 Å to 4.56 Å) [8, 23, 24]. The smaller rotation about the C(3)–C(7) bond in *B* also brings the pyridine rings closer together than they are in *C*: in *B*, the C(2) atoms approach one another at 3.23 Å whereas in *C* the closest approach is a N(1)···C(2) separation of 3.37 Å.

The Zn–Cl bond lengths, 2.199(2) and 2.203(2)° (Table V) are similar to those found in many monomeric $ZnCl_2L_2$ complexes (L is a monodentate ligand), for example in dichlorobis-(4-methylpyridine)zinc(II) [25] and in dichlorobis-(1-methyltetrazole)zinc(II) [26]. However, $ZnCl_2L_2$ complexes most often adopt a Cl–Zn–Cl angle of approximately 110° [27] and in *B* the Cl–Zn–Cl angle is 120.1(1)°. This value is similar to that found in dichlorobis-(1-methyltetrazole)zinc(II) [26], 118.3(2)°, and to that found in dichloro-(N,N,N′,N′-tetramethylethylenediamine)zinc(II), 119.4° [27]. In this latter complex the tetrahedral geometry has been distorted by the restricted angle of bite of the bidentate ligand.

This seems to indicate that the observed distortion of the tetrahedral geometry about Zn in *B* might be attributable to either the constraint due to dimer formation or to an increase in s character of the Zn orbitals used to coordinate Cl. This would be expected to result in an increase in p character for the Zn orbitals directed towards N and O and hence to a lengthening of these bonds.

The Zn–N length (2.073(6) Å) is normal for these types of complexes but much longer than the 2.006(5) Å Zn–N(py) length in *C*. The Zn–O distance of 2.010(5) Å is very similar to that found in *C* though in *C* the C(7)–O(13) bond is shorter and the C(3)–C(7) bond longer than those in *B*.

The DENC ligand is unexceptional with all bond lengths and angles lying within normal ranges. The pyridine ring is rigorously planar with the zinc atom lying only 0.06 Å from the ring. The zinc atom, however, lies 0.42 Å from the C(3), C(7), N(8), O(13) plane (Table VI).

The zinc analog of structure *I* would contain 5-coordinate (20 electron) metal centers. For this reason we formulate the second product of reaction 8 as structure *V*. This formulation consists of two, highly distorted 4-coordinate (18 electron) centers and two 5-coordinate (20 electron) centers. It is easy to visualize the formation of ZnO(s) and *B* as ultimate reaction products from the disproportionation of *V*.

The electronic spectrum of *A* (in methylene chloride; maxima at 330 nm (ϵ = 14000 M^{-1} cm) and 425 nm (ϵ = 4800)) is similar in form to that of solid *III* (maxima at 325 and 475 nm) [5]. In *A* we have an essentially planar N_2S_2 ligand arrangement in a 5-coordinate Zn(II) complex (Fig. 2). The similarity of its spectrum to that of *III* and the fact that the spectra of very similar monomeric (tetrahedral) $M(NS)_2$ complexes *IV* ($M = Zn$, $R_1 = R_2 = CH_3$) [11] do not contain maxima at wavelengths longer than 300 nm indicates that the 425 nm band of *A* is due to intraligand transitions in its conjugated, planar N_2S_2 ligand system. Each half of *III* is a strong Lewis acid [6], which explains why *A* is isolated in the reaction of *I* with *III* but not in the reaction with *IV*.

The IR spectrum of *A* is consistent with the N_2S_2 molecule acting as dianionic tetradentate ligand chelated to the central zinc atom *via* the azomethine nitrogen and the deprotonated thiol sulphur, with the fifth position around the zinc(II) atom occupied by the pyridinic nitrogen of the DENC moiety. This is evident from the disappearance of ν(N–H) and the negative shift in both ν(C=N) and $NCSSCH_3$ bands, as compared to the spectrum of the parent N_2S_2 ligand [5]. The position of the ν(C=O) band of DENC in *A* is almost unchanged relative to that of free DENC, demonstrating that the carbonyl oxygen is not coordinated to the zinc atom.

The large shift ($\Delta\nu = -40$ cm^{-1}) in ν(C=O) (DENC) in the IR spectrum of *B* is due to formation of the bridging structure. The medium intensity band centered at 525 cm^{-1} may be assigned to νZn–O(carbonyl)

The ^1H NMR spectrum of *A* in $CDCl_3$ exhibits singlets at 2.5 and 2.27 ppm attributed to the two magnetically equivalent SCH_3 and CH_3 groups of the diacetyl moiety, respectively. The SCH_3 protons appear as a doublet in the parent dimeric $[Zn(N_2S_2)]_2$ complex [28]. The resonances centered at 3.32 and 1.24 ppm due to the methylene and methyl groups of the coordinated DENC moiety in *A*, respectively, exhibit a small downfield shift as compared to free DENC (3.26, 1.05 ppm, respectively). By contrast, resonances associated with the pyridine ring of DENC centered at 8.4, 7.83 and 7.5 ppm change significantly on coordination [2]. We conclude that DENC is coordinated only through its pyridine nitrogen atom, as established by the IR spectrum and molecular structure, Fig. 2.

We could not measure the ^1H NMR spectrum of *B* due to its insolubility in $CDCl_3$ and its dissociation to give solid $ZnCl_2$ in d_5-nitrobenzene.

Concluding Remarks

We have discovered a means of replacing the copper centers in unusual tetrameric copper(II) complexes with other metals and have established the likely first step of this process (removal of 2 mols of DENC from $[(DENC)CuCl]_4O_2$ by $[Zn(N_2S_2)]_2$ to give *A*), at least with zinc as the transmetallation reagent. The present work shows that $[(DENC)Zn_2Cl_2]_2O_2$ is unstable, but work [18] with other metals indicates that at least two copper(II) centers in halo(DENC)copper(II) tetramers can be replaced with Ni and Co to give stable tetrameric products. This raises the possibility of altering the efficiency and specificity of oxocopper(II) species as catalysts for oxidative coupling reactions by transmetallation. We shall report further progress in this area in subsequent papers.

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